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Edulcorantes Naturales en Alimentos y Bebidas, Una Alternativa a la Sacarosa

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1. INTRODUCCIÓN

Los carbohidratos son macronutrientes que proporcionan del 40 al 60% de la ingesta total de energía de la dieta humana. En los alimentos, los carbohidratos se pueden encontrar como azúcares libres y no libres; los azúcares no libres están naturalmente presentes dentro de la estructura celular, por ejemplo, azúcar en frutas y verduras, carbohidratos con almidón en granos, lactosa en productos lácteos, etc. Por el contrario, los azúcares libres no se presentan de forma natural, sino que a menudo se añaden a los alimentos, como los monosacáridos (glucosa, fructosa) y los disacáridos. Sin embargo, el consumo excesivo de energía está asociado con la acumulación de grasa corporal (Onaolapo *et al.*, 2020). Más específicamente, el consumo excesivo de azúcares libres no solo da como resultado la acumulación de grasa, sino que también compromete la densidad de micronutrientes y aumenta el riesgo de otras condiciones de salud adversas, como diabetes y enfermedades cardiovasculares (Hagger *et al.*, 2017).

La sacarosa (azúcar común), compuesta por fructosa y glucosa a partes iguales, es fundamental en nuestra dieta ya que el metabolismo de la glucosa es necesario para producir adenosín trifosfato (ATP), la síntesis de diferentes biomoléculas y, lo que es más importante, para la función de respiración celular (Archer, 2018). Desafortunadamente, la fructosa provoca una desregulación del metabolismo de los carbohidratos y de los lípidos. Esto se debe a que el metabolismo de la fructosa no está regulado por los requerimientos de energía hepática, lo que resulta en una absorción excesiva de fructosa por parte del hígado y un aumento en la *lipogénesis de novo* (DNL) (Stanhope, 2016). En consecuencia, aunque el azúcar es una fuente de energía importante en la dieta humana, también puede promover condiciones dismetabólicas (Lee *et al.*, 2018).

La principal desventaja del azúcar común elaborado con jugo de caña de azúcar, es que el producto refinado carece de compuestos beneficiosos adicionales (por ejemplo, moléculas bioactivas), que podrían mejorar su valor nutricional. En el proceso de refinación del jugo de caña de azúcar se obtienen como subproductos azúcares de caña no centrífugos, azúcar moreno y melaza. Se demostró que estos subproductos contienen varias moléculas bioactivas, incluidos los glucósidos flavonoides y los ácidos fenólicos (Singh *et al.*, 2015), lo que luego llevó a varios otros autores a recomendar los azúcares

no centrífugos para sustituir los azúcares refinados debido a los efectos dietéticos favorables de los fenoles y flavonoides (Cervera-Chiner, *et al.*, 2021). Por la misma razón, las alternativas de edulcorantes naturales son cada vez más atractivas para los consumidores.

Cabe señalar que los edulcorantes son todas aquellas sustancias o aditivos, distintos de los monosacáridos, disacáridos, oligosacáridos o azúcares, que pueden dar un sabor dulce característico a los productos de diferentes industrias, especialmente en la industria alimentaria (Wakida-Kuzunoki, 2017). Lo anterior permite generar una sensación agradable en el paladar del consumidor y despertar la preferencia por estos productos industrializados, haciéndolos los más consumidos desde las primeras etapas de la vida (Gil-Campos *et al.*, 2015; Manzur-Jattin *et al.*, 2020; Padrón-Martínez *et al.*, 2013; Wakida-Kuzunoki, 2017). En cuanto a su clasificación, si bien no está estrictamente regulada, en la mayoría de los casos se consideran dos factores: el contenido calórico (calórico y no calórico) y el origen del edulcorante (natural y artificial), como se muestra en la Tabla 1.

Tabla 1. Clasificación de edulcorantes (Adaptado de Briones-Avila *et al.*, 2021; García-Almeida *et al.*, 2013).

Edulcorantes calóricos		
Natural	Azúcares	Sacarosa, glucosa, fructosa, dextrosa, lactosa, maltosa, galactosa, trehalosa, tagatosa
	Edulcorantes calóricos	Miel, sirope de arce, sirope de agave, azúcar de palma, azúcar de coco, jarabe de sorgo
Artificial	Azúcares modificados	Jarabe de maíz con alta fructuosa, caramelo, azúcar invertido
	Alcoholes de azúcar	Sorbitol, xilitol*, manitol, eritritol, maltitol, isomaltulosa, lactitol, glicerol
Edulcorantes no calóricos		
Natural	No calóricos	Estevia, taumatina, pentadina, monelina, brazzeína
Artificial	No calóricos	Aspartamo, sucralosa, sacarina, acesulfamo K, ciclamato, neotamo

* El xilitol también se clasifica a veces como un edulcorante natural; sin embargo, se clasifica aquí como edulcorante artificial debido a cómo se obtiene para su uso como edulcorante.

Aunque la demanda mundial de azúcar ha disminuido en general debido a las crecientes preocupaciones sobre los posibles efectos en la salud causados por el consumo elevado de azúcar, los datos de la Organización para la Agricultura y la Alimentación (FAO) sugieren que el crecimiento del consumo de azúcar seguirá siendo fuerte en los países en desarrollo. Para el 2028, se estima que aumente en 32 Mt, en comparación con el valor aproximado de 203 Mt en 2008 (OCDE/FAO, 2019).

Actualmente, los alimentos procesados juegan un papel importante en el consumo excesivo de azúcar. Steele *et al.* (2016) informaron que ~ 90 % de la ingesta promedio total de azúcar proviene de alimentos ultraprocesados (p. ej., jugos de frutas), jarabes concentrados, refrescos y bebidas deportivas, productos de panadería, entre otros, que a menudo consisten en índices de sacarosa elevados que oscilan entre 50 a 1000 g/L

(Raganati *et al.*, 2015). Además, las bebidas más populares (por ejemplo, bebidas energéticas, gaseosas, jugos de frutas), según el tipo de bebida, poseen contenidos de azúcar entre 100 y 135 g/L (Health, 2014). Estudios anteriores han señalado que una mayor ingesta de bebidas azucaradas (SSB, por sus siglas en inglés) está relacionada con un aumento del 30 % en el desarrollo de diabetes tipo 2 (Wang *et al.*, 2015), y un consumo de unos 250 ml/día de SSB, aumenta la incidencia de diabetes tipo 2 en un 18% (Imamura *et al.*, 2015).

La creciente demanda ha llevado a los investigadores a explorar nuevos edulcorantes naturales y sintéticos como alternativas a la sacarosa (Castro-Muñoz *et al.*, 2022; Saraiva *et al.*, 2020). Cuando se extraen con los compuestos beneficiosos de sus fuentes, los edulcorantes naturales (glucosa, fructosa y sacarosa) se clasifican como opciones nutricionales. Se han propuesto y estudiado nuevas posibilidades para atender la demanda, incluyendo miel, xilitol, eritritol, maltosa, maltodextrina, estevia, melaza, sirope de arce, azúcar de coco, sirope de agave y azúcar de dátiles (Valle *et al.*, 2020).

En cuanto a los edulcorantes artificiales, en general, tienen un contenido calórico muy bajo y un dulzor intenso, lo que los hace atractivos tanto para los consumidores como para los fabricantes de alimentos. Sin embargo, estos edulcorantes no calóricos tienen un valor nutricional mínimo. También pueden dar como resultado una activación incompleta de las vías de recompensa de los alimentos, lo que lleva a antojos de dulces y búsqueda de alimentos, lo que puede causar una ingesta calórica excesiva y un aumento de peso (Mooradian *et al.*, 2017). Además, algunos experimentos en animales han demostrado que estos edulcorantes artificiales influyen en síndromes metabólicos específicos. Por ejemplo, la tolerancia a la glucosa puede reducirse en respuesta a los cambios en el microbioma después de un consumo moderadamente prolongado de edulcorantes artificiales (Green y Syn, 2019). Aunque las principales autoridades relacionadas con esta materia, incluidas la *Food and Drug Administration* (FDA) y la *European Food Safety Authority* (EFSA), han aprobado algunos edulcorantes artificiales, la evidencia disponible para respaldar su uso y consumo industrial aún no es concluyente. Además, se informaron muchos hallazgos contradictorios sobre las implicaciones para la seguridad y la salud, lo que hace que su uso sea controvertido.

Actualmente, tanto la sacarosa como los edulcorantes artificiales pueden ser reemplazados por edulcorantes naturales. Las tendencias predominantes en el mercado sugieren que los productos alimenticios naturales son más atractivos para los consumidores, quienes identifican los productos naturales como opciones más saludables. La tendencia actual indica que los consumidores están dispuestos a probar alternativas naturales a la sacarosa (Mora y Dando, 2021). Por ejemplo, las bebidas endulzadas con estevia tienen percepciones de los consumidores más positivas que las SSB comunes (Olivo, 2019). Por lo tanto, el uso de edulcorantes naturales puede representar una oportunidad comercial nueva y sustancial para muchas empresas. Los edulcorantes naturales también presentan efectos positivos de consumo, como mejorar la salud metabólica, prevenir el aumento de peso y disminuir la glucosa en sangre. Otras ventajas son; (1) la baja potencia glucémica, como se presenta en la miel y el sirope de agave, podría ser ventajosa para las personas con dietas de bajo índice glucémico, (2) el bajo contenido de fructosa, como se encuentra en el sirope de arce (Edwards *et al.*, 2016), y (3) que contienen biomoléculas con beneficios nutricionales y para la salud (por ejemplo, vitaminas, fitohormonas y minerales) (Valle *et al.*, 2020). Se informó que la composición general de la miel, el arce y el sirope de agave consta de al menos un 3 % de fibra dietética, un 1,4 % de proteínas, <2 % de minerales (potasio, calcio y magnesio) y polifenoles con potencial actividad antioxidante (Edwards *et al.*, 2016). De manera similar, la melaza oscura y la melaza negra contienen actividades antioxidantes altas, a 4,89 y 4,56 mmol/100 g, respectivamente. La sustitución de 130 g de azúcar refinada por 337 g de melaza negra en productos viables aumentaría su contenido de antioxidantes en ~ 10,7 mmol (Eggleston, 2019).

En el siglo XX, los países desarrollados resolvieron la falta de seguridad alimentaria con un importante aporte de la industrialización agroalimentaria (Asioli *et al.*, 2017; Lusk, 2016; Meneses *et al.*, 2014). El procesado de los alimentos ha jugado un papel vital en la prolongación de la vida útil de los productos alimenticios, la mitigación de las pérdidas de alimentos y la reducción del desperdicio y en la mejora de la producción de nutrientes y su disponibilidad (Augustin *et al.*, 2016; Weaver *et al.*, 2014). Sin embargo, las percepciones diarias de los consumidores dependen de otros factores además de estos logros. En las sociedades modernas, los mercados más globalizados y los que se esfuerzan más en la fabricación de alimentos han dado lugar a brechas de conocimiento y una separación percibida entre los fabricantes locales y los ciudadanos (por ejemplo,

cómo se producen los alimentos, dónde se producen, etc.) (Princen, 1997; Weis, 2007). Los consumidores se están volviendo cada vez más conscientes de los ingredientes naturales, mientras que la creciente importancia de la naturalidad entre los consumidores ha tenido implicaciones clave para la industria alimentaria (Román *et al.*, 2017). Esto bien podría tener implicaciones no solo para el desarrollo y la venta de alimentos, sino también para el aumento de las tecnologías alimentarias emergentes. Es posible que aquellos alimentos que no se perciben como naturales no sean aceptados por muchos consumidores en la mayoría de los países.

La demanda de edulcorantes sin calorías y de origen natural ha crecido drásticamente en la última década porque los consumidores son más conscientes de su salud (Philippe *et al.*, 2014). Durante décadas, los edulcorantes se han utilizado para hacer que los alimentos tengan más sabor y atraer a los consumidores. Fueron adoptados por primera vez debido a la alta proporción de azúcar en calorías en la dieta, y esto favoreció la obesidad en la población general, que se generalizó en bebés y niños (Mooradian *et al.*, 2017). Debido a ello, un edulcorante bajo en calorías, la sacarina, se lanzó al mercado en la década de 1980. A la popularidad de este edulcorante le siguieron otros como los ciclamatos, el aspartamo y el acesulfamo K, que son los más habitualmente empleados. Los edulcorantes han sido durante mucho tiempo objeto de controversias y conflictos a lo largo de los años, que han incluido acusaciones de toxicidad en el hígado y la vejiga, carcinogenicidad, malformaciones del feto, junto con otros riesgos (Carocho *et al.*, 2015). Si bien se investigaron todos estos puntos, los edulcorantes se consideraron seguros (Anwar *et al.*, 2023; Kumar *et al.*, 2021; Serra-Majem *et al.*, 2018), aunque persiste cierta pérdida de confianza del consumidor, ya que algunos no están permitidos en los Estados Unidos pero sí lo están en la Unión Europea (por ejemplo, ciclamato y ácido ciclámico). Por lo tanto, la necesidad de sustitutos naturales es crucial (Carocho *et al.*, 2014).

Sirope de Agave

El sirope de agave, también conocido como néctar de agave, es un producto alimenticio desarrollado recientemente (posterior a 1990) elaborado a partir de la savia de la planta de agave, en particular *Agave salmiana* y *Agave tequilana*, es decir, salmiana y agave azul, respectivamente. Dado su bajo índice glicémico y su condición de vegano,

este producto se ha vuelto popular como sustituto de los edulcorantes tradicionales como el azúcar de mesa (sacarosa) y la miel (Wolever, 2012; Foster-Powell *et al.*, 2002; Thalheimer, 2015).

La hidrólisis de fructanos produce este edulcorante natural. El néctar, que proviene de los corazones de agave (piñas) en forma de fructanos, es una de las principales reservas de carbohidratos de las plantas de agave. Cultivado en ambientes áridos y semiáridos, el género Agave aplica la adaptación fotosintética y un metabolismo ácido de las crasuláceas al suministro periódico de agua. Estas plantas son comunes en América Central y del Norte, pero una gran proporción de las especies (alrededor del 55 %) se encuentran en México, que se cree que es el centro de la diversidad y el origen del agave (Castro-Muñoz *et al.*, 2022). Tanto el consumo como los impactos socioeconómicos del agave se remontan a la época precolombina, dado su alto contenido de azúcar (Pérez-López y Simpson, 2020).

Sirope de Arce

El sirope de arce es un manjar que se prepara hirviendo la savia de diferentes especies de Acer, principalmente árboles de arce de azúcar (*Acer saccharum* Marsh.) (Nimalaratne *et al.*, 2020). Agriculture and Agri-Food Canada (2017) informa que Canadá es el mayor productor mundial de productos de arce y es responsable de casi el 71% de la producción de sirope de arce en el mundo. En 2017, Quebec produjo aproximadamente el 92 % de todo el jarabe de arce en Canadá y alberga a más de 13 300 productores de sirope de arce (RMSPSCNUSA, 2022).

Entre la variedad de edulcorantes naturales existentes, el sirope de arce es reconocido como una alternativa muy superior a la del azúcar refinado no solo por su contenido mineral, sino también por su alta concentración de compuestos fenólicos con propiedades bioactivas, es decir, antimutagénico, antiradicalario, antioxidante, y anticancerígeno (Mellado-Mojica *et al.*, 2016; González-Sarrías *et al.*, 2012; Phillips *et al.*, 2009). En comparación con la dextrosa, el sirope de maíz y el sirope de arroz integral, el sirope de arce genera respuestas más bajas de glucosa e insulina, lo que lo convierte en

un sustituto más saludable de los azúcares refinados en nuestra dieta (Mellado-Mojica *et al.*, 2016; St-Pierre *et al.*, 2014).

La extracción de arce a menudo comienza a fines del invierno o principios de la primavera. Solo dura unas pocas semanas debido al clima. Para hacer sirope de arce, se recolecta y concentra la savia de xilema dulce y acuosa. Como resultado de la acumulación de presión causada por el ciclo de congelación y descongelación, esta savia sale de los troncos de los árboles de arce. Para hacer un litro de sirope de arce, se requieren alrededor de 40 litros de savia (que contiene 2-3% de azúcar) (66% de azúcar). Aparte de la sacarosa, que es el azúcar principal del sirope de arce, su sabor es el resultado de una mezcla compleja no solo de minerales, aminoácidos, oligosacáridos, ácidos orgánicos y compuestos aromáticos volátiles y fenólicos, sino también de microorganismos presentes en la savia de arce (Ball, 2007; Filteau *et al.*, 2009). Según Filteau *et al.* (2009). Así como su microbiota asociada, el contenido de savia puede cambiar durante las estaciones y el color del sirope generalmente se oscurece a medida que avanza la temporada.

Como se indicó anteriormente, la composición química de la savia y el sirope puede diferir significativamente según el origen geográfico (Stuckel y Low, 1996; Perkins y van den Berg, 2009). Los pueblos indígenas de América del Norte introdujeron el sirope de arce a los europeos colonizadores. Desde entonces, el sirope de arce y los productos de arce se han vendido comercialmente (Koelling *et al.*, 1996). Se ha mostrado más interés en estudiar la composición elemental del sirope de arce a medida que se expanden los mercados comerciales y mejoran las tecnologías analíticas. Como resultado, se han realizado varios trabajos de investigación científica en el último siglo para determinar los componentes químicos y la constitución mineral del sirope de arce (Mohammed *et al.*, 2022).

Sirope/Azúcar de Coco

En la cocina del sur/sureste de Asia, el azúcar de coco es un edulcorante popular (Levang, 1988) y está hecho de la savia del floema de las flores de la palmera de coco (*Cocos nucifera* L.) (BAFPS 76:2010, 2022). Los trabajadores recolectan savia escalando palmeras y usan hoces para cortar las inflorescencias sin abrir. Durante 8 a 12 h, la savia

que rezuma se recolecta con bambú o recipientes de plástico. Ocasionalmente se agrega cal a la savia para evitar que fermente (Hebbar *et al.*, 2015; Dalibard, 1999). A continuación, la savia se calienta sobre llamas abiertas y se agita regularmente para que se espese y cristalice (Levang, 1988). Durante el método de producción, el color del azúcar puede variar de marrón claro a marrón oscuro. Finalmente, el azúcar se selecciona a mano y se tamiza para producir productos de grano fino (PCA, 2015).

Cada palmera de coco produce típicamente una inflorescencia una vez al mes. Se recolectan aproximadamente 1,5 L de savia dos veces al día (mañana y tarde) de todas las inflorescencias. Basado en aproximadamente 15 g de azúcar por cada 100 g de contenido de azúcar de savia de coco fresca, la savia hirviendo permite que se produzcan diariamente 200 g de azúcar por inflorescencia (Hebbar *et al.*, 2015; Dalibard, 1999).

Incluso en edades tempranas, las palmeras de coco se pueden utilizar para recolectar savia. Cada vez que se extrae y extrae la savia del floema, se deben cortar 1–2 mm de espádice. El espádice se puede reducir a un muñón repitiendo esta técnica. Siguiendo este procedimiento, se puede tocar un solo espádice durante 40 a 45 días. Las palmeras de coco se pueden explotar durante un período de 20 años (Levang, 1988; Hebbar *et al.*, 2015).

Debido al creciente interés que muestra el público en una dieta saludable y la percepción negativa del público sobre el uso excesivo de azúcar, los consumidores frecuentemente intentan sustituir los azúcares refinados por edulcorantes alternativos como el azúcar de coco (Wrage *et al.*, 2019). Los comerciantes destacan los pequeños productores tradicionales de azúcar de coco, el crecimiento orgánico de la palmera en la agricultura mixta con otros cultivos, el índice glicémico (IG) más bajo y el bajo contenido de fructosa que el azúcar de remolacha refinada normal o la caña (EPSE, 2016). El azúcar de coco tiene un precio superior que los consumidores están dispuestos a pagar. Un kilogramo (kg) puede costar entre 15 y 46 €. Por el contrario, el precio de un kg de azúcar tradicionalmente refinado fue de solo 0,88 € en 2021 (Meliany *et al.*, 2022).

2. OBJETIVOS

Los edulcorantes naturales tradicionales discutidos en esta tesis, los siropes de arce y de agave, y el azúcar/sirope de coco, son las alternativas nutritivas comunes y poseen potenciales comerciales prometedores. La mayoría de estos edulcorantes se introducen fácilmente en varios productos comerciales, frecuentemente comercializados como opciones más saludables y aceptados por los consumidores en general por sus atributos positivos. Esta Tesis Doctoral también recopila la información sobre las principales vías de extracción, sostenibilidad en el medio ambiente donde son producidos, producción y purificación de los edulcorantes naturales. Igualmente importante, se presentan sus propiedades fisicoquímicas, donde se plantean los métodos más adecuados para su análisis, como se lleva a cabo el control de calidad y seguridad alimentaria, y prácticas de sostenibilidad. Finalmente, se proporciona una descripción general de los usos y aplicaciones actuales en la industria alimentaria, bien como sus beneficios nutricionales e impactos en la salud del consumidor.

Partiendo de estas premisas, esta Tesis Doctoral tiene como objetivo estudiar el perfil nutricional y los impactos en la salud del consumo de sirope de agave, de sirope de arce y de sirope/azúcar de coco, sus posibles aplicaciones en la industria alimentaria y cuestiones de sostenibilidad, así como sus parámetros centrales de seguridad y calidad, incluido el análisis químico de sus principales componentes.

3. PRESENTACIÓN DE ARTÍCULOS



3.1 ARTÍCULO Nº 1

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Review

Agave Syrup: Chemical Analysis and Nutritional Profile, Applications in the Food Industry and Health Impacts

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Abstract: Agave syrup (AS), a food product made from agave plant sap, is a vegan sweetener that has become popular for replacing conventional sweeteners such as sucrose. As the demand for naturally derived sweeteners has grown in the last decade, this review paper addresses and discusses, in detail, the most relevant aspects of the chemical AS analysis, applications in the food industry, sustainability issues, safety and quality control and, finally, nutritional profile and health impacts. According to our main research outcome, we can assume that the mid-infrared-principal components analysis, high-performance anion exchange chromatography equipped with a pulsed amperometric detector, and thin-layer chromatography can be used to identify and distinguish syrups from natural sources. The main agave–derived products are juice, leaves, bagasse, and fiber. In sustainability terms, it can be stated that certified organic and free trade agave products are the most sustainable options available on the market because they guarantee products being created without pesticides and according to specific labor standards. The Mexican government and AS producers have also established Mexican guidelines which prohibit using any ingredient, sugar or food additive that derives from sources, apart from agave plants, to produce any commercial AS. Due to its nutritional value, AS is a good source of minerals, vitamins and polyphenols compared to other traditional sweeteners. However, further research into the effects of AS on human metabolism is necessary to back its health claims as a natural sugar substitute.

Keywords: agave syrup; chemical analysis; food industry; health impacts; nutrition

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1. Introduction

Agave syrup (AS), also referred to as agave nectar, is a recently developed (post-1990) food product made from agave plant sap, particularly *Agave salmiana* and *Agave tequilana*, that is, salmiana and blue agave, respectively. Given its low glycemic index and vegan status, this product has become popular as a substitute for traditional sweeteners such as table sugar (sucrose) and honey [1–3].

Fructan hydrolysis produces this natural sweetener. Nectar, which comes as fructans from agave cores (*piñas* in Spanish), is a principal carbohydrate reserve of agave plants. Grown in arid and semi-arid environments, the Agave genus applies photosynthetic adaptation and a crassulacean acid metabolism to periodic water supply. Such plants prevail in Central and Northern America, but a large proportion of the species (about 55%) are located in Mexico, believed to be the centre of agave's diversity and origin [4]. Both the

consumption and socio-economic impacts of agave originate from pre-Columbian times, given its high sugar content [5].

Nowadays, consumers are increasingly becoming familiar with natural ingredients, and the growing prominence of naturalness for consumers has had significant repercussions for the food industry [6,7]. It is feasible that consumers in most countries may reject food products that are not perceived as natural. In recent decades, demand for naturally derived sweeteners has exploded [8].

Based on these premises, this review aims to study the nutritional profile and health impacts of AS consumption, its possible applications in the food industry and sustainability issues, as well as its central safety and quality parameters, including the chemical analysis of its main components.

2. Chemical Analysis

Fructose is a sugar present in high contents (approximately 80%) in AS sugars (ASs). The food industry frequently employs it as a sweetener. However, extracting fructose from agave involves fractionation methods, mainly chromatographic techniques, followed by qualitative and quantitative analysis methods [9] NMR (Nuclear Magnetic Resonance), HPLC (High-Performance Liquid Chromatography) and GC-MS (Gas Chromatography Coupled with Mass Spectrometry) are the most widespread analytical methods [9]. Table 1 summarizes the most widespread analytical techniques to characterize ASs, where HPLC is the most followed method. However, these methods are expensive and time-consuming [9].

Several authors have developed analytical methods for sugar analysis that are faster, cheaper, and easier than those previously referred to.

Ja et al. (2018) [9] successfully developed a polarimetric method for the fructose-glucose ratio analysis. The obtained results were evaluated and validated by HPLC using fructose and glucose standards. HPLC and the polarimetric method are statistically equivalents in accuracy and reproducibility terms and prove the technical feasibility of the polarimetric method. This method reduces the equipment required for the fructose-glucose ratio analysis and makes fructose-glucose ratio quantification easier and faster [9]. Thermally untreated and treated *Agave salmiana* syrups have been analyzed by HPLC associated with a refractive index detector, and later by Liquid Chromatography Coupled with Electrospray Ionisation Mass Spectrometry (LC-ESI-MS). The chromatogram profile obtained by HPLC shows the presence of glucose, sucrose, fructose and kestose in the two samples. However, sucrose concentration significantly rises in the thermally treated sample. In both the treated and untreated samples analyzed by LC-ESI-MS, the presence of sucrose, kestose and oligomeric fructans is confirmed. However, fructose and glucose are not detected under the tested conditions. Therefore, authors conclude that, compared to GC-MS, this technique reduces sample preparation times and allows for the analysis of tri- and tetra-saccharides [10].

In an attempt to discriminate ASs from other natural sugars, *Agave tequilana*, *Agave salmiana*, honey, corn and cane syrups have been analyzed by methods of the vibrational spectroscopic type, namely MIR (mid-infrared) and NIR (near-infrared) combined with chemometrics (for example, multivariate data analyses) [11]. Oligosaccharide content and monosaccharide ratios have been evaluated by HPAEC-PAD (High-Performance Anion Exchange Chromatography with a Pulsed Amperometric Detector). This technique is used for sugar analysis thanks to its low detection limits, as is Thin Layer Chromatography (TLC). All the samples show high glucose, fructose and sucrose contents. However, the fructose-glucose ratio can be used to discriminate ASs. The AS analysis by HPAEC-PAD and TLC shows specific sugar profiles, mainly composed of fructose and fructo-oligosaccharides (FOS) compared to other tested syrups. *Agave salmiana* has high sucrose content and *Agave tequilana* exhibits a large quantity of fructose. Hence these techniques can confirm the authenticity of ASs. As vibrational methods, NIR is unable to distinguish the assayed syrups. The combination of MIR spectroscopy and a PCA (Principal Components Analysis) shows significant differences between 1185 and 950 cm^{-1} in the sugar region. Given its high

fructose content, in the fructose region *Agave tequilana* syrups display a marked absorption, from 1061 to 1063 cm^{-1}, and *Agave salmiana* syrups present high sucrose contents with marked absorption from 997 to 1054 cm^{-1}. The other tested syrups also show specific characteristic absorption bands in the carbohydrate's region. Therefore, MIR-PCA, HPAEC-PAD and TLC can be used to identify and discriminate syrups from natural sources. These methods are fast, nondestructive, simple and economic compared to other techniques (for example, HPLC, GC-MS and NMR) [11].

As a tool to prevent adulteration in ASs and to control their authenticity, Portaluri et al., (2021) [12] developed an approach to detect C4 plants called the 13C site-specific natural isotopic fractionation (SNIF)-NMR approach. After obtaining ethanol from the sugar fermentation of several ASs, it is analyzed via the optimization of a method based on an insensitive nucleus enhanced by a polarization transfer (INEPT) pulse sequence for 13C SNIF-NMR to reduce the acquisition time; it produces reproducible and reliable results. Of 11 commercial ASs, only 1 is authentic. The results also show that maize and cane are converted into sugar syrups, masked by the glucose-fructose ratio. This suggests the probability of using ASs for adulteration [12].

Table 1. Analytical methods for the characterization of agave syrup sugars.

Plant	Analytical Method	Detector	Standards	Analysis Conditions	Results	References
Agave salmiana	HPLC	Refractive-index	Fructose, arabinose, glucose, lactose, maltose, ribose, galactose, mannose, xylose sucrose and chicory inulin	Stationary phase: column ion exchange; mobile phase: HPLC grade water (flow rate of 0.6 mL/min) Column temperature: 75 °C Run time: 20 min Injection volume: 50 µL	Sugars were well separated with good resolution. Sucrose, glucose and fructose were identified and quantified (85.6 ± 2.52%, 4.67 ± 0.22% and 3.99 ± 0.14% (6.36 ± 0.54%, dry matter), respectively).	[13]
			Arabinose, fructose, galactose, glucose, lactose, maltose, mannose, ribose, sucrose, and xylose	Stationary phase: Zorbax column specific for carbohydrates from the Agilent Mobile phase: 75:25 acetonitrile:water at a flow rate of 1.4 mL/min Column temperature: 30 °C Run time: 15 min Injection volume: 20 µL	Identified sugars: xylose, fructose, glucose, sucrose, maltose. Use of plants in the quiotilla maturity state, including the stem up to its neck, whose fructose concentration was even higher than that presented at its base	[14]

Table 1. *Cont.*

Plant	Analytical Method	Detector	Standards	Analysis Conditions	Results	References
			Fructose, glucose, sucrose, fructo-oligosaccharides standards 1-nystose, 1-β-fructofuranosyl and nystose 1-kestose	Stationary phase: Prevail Carbohydrate ES column Mobile phase: acetonitrile:water (70:30) (1.0 mL/min flow rate) Run time: 18 min Injection volume: 20 µL	Fructose, glucose, sucrose and kestose were identified in thermally untreated agave syrups The sucrose concentration increased in the thermally treated agave syrups The quantity of fructose, glucose and kestose in the agave syrup was similar before/after heat treatment (1.2 and 0.7, 15.21 and 16.12 and 10.89 and 12.71 g L^{-1}, respectively)	[10]
	LC	ESI-MS		MS analyses were performed in the $[M-H]^{-1}$ negative mode The nebulizing gas was nitrogen and the damping gas was helium. 3.0 kV spray voltage, 90.0 V capillary voltage Temperature was 250 °C, 10 µL/min flow rate Run time: 7 min Injection volume: 20 µL m/z range acquisition spectra: 50–2000	For the thermally untreated/treated syrups, under the employed conditions the masses that corresponded to glucose and fructose were not identified. The kestose, sucrose and oligomeric fructans were confirmed unambiguously in the untreated/treated agave syrups	
Agave tequilana	Total reducing sugars (TRS) and direct reducing sugars (DRS)	-	Fructose corn syrup, fructose and glucose standards.	-	4.4 kg of a fresh head of *A. tequilana* were needed to obtain 1 kg of syrup with 70% TRS and a fructose content of 87.92 ± 1.28%	[15]

Table 1. *Cont.*

Plant	Analytical Method	Detector	Standards	Analysis Conditions	Results	References
Agave tequilana e A. salmiana	HPAE	PAD	Fructose, glucose, inositol and mannitol. Fructo-oligosaccharide standard	Monosaccharides analysis: stationary phase: a Dionex CarboPac PA1 column in series was used with a CarboPac PA1 guard column. The mobile phase: isocratic of 80 mM NaOH (1.0 mL/min flow rate) Oligosaccharide analysis: stationary phase: a Dionex CarboPac PA100 column in series was used with a CarboPac PA100 guard column. Mobile phase: solvent A = 160 mM NaOH; solvent B = 160 mM NaOH/1.0 M NaOAc. solvent C = 1.0 M NaOH (0.0 mL/min flow rate)	The main identified monosaccharide was fructose (71.86–92.13% concentration range), followed by glucose (4.73–15.06% concentration range) Fructose-glucose ratio 10:1 Two polyols were detected: one was mannitol (concentration in the ASs went from 0.02% to 2.54%). The other was inositol (0.31–0.43% concentration range) Inulobiose was the main identified oligosaccharide	[16]
	CGC	FID		Oligosaccharide analysis: stationary phase: an Agilent J&W DB-5 (30 m × 0.25 mm, 0.25 µm film thickness; 95% dimethyl–5% diphenyl polysiloxane) open tubular fused-silica capillary column Carrier gas: ultrapure hydrogen (flow rate = 1.2 mL/min) Makeup gas: ultrapure nitrogen (flow rate = 30 mL/min) Injection port temp.: 250 °C Detector temp.: 300 °C		

Table 1. *Cont.*

Plant	Analytical Method	Detector	Standards	Analysis Conditions	Results	References
	^{1}H-NMR spectroscopy-PCA	-	-	NMR spectra of syrup samples acquired by the Varian/Agilent 600 MHz AR Premium COMPACTTM spectrophotometer. ^{1}H-NMR spectra were measured at 300 K and frequency 599.77 MHz with D_2O as the solvent, plus an internal reference. The residual HOD signal was employed at 4.9 ppm. The used $\pi/2$ pulse was 8.7 µs. The relaxation time was 15 s. There were 16 repetitions.	The *A. salmiana* syrup had an identical profile and another signal at 5.4 ppm, which corresponded to sucrose. The *A. tequilana* syrups showed a greater intensity signal emitted by peaks at 4.0 ppm for fructose, and peaks at 3.8 and 3.7 ppm for sucrose. This method allowed agave syrups to be identified and classified, and was able to differentiate for other natural sweeteners	[17]

3. Food Industry Applications and Sustainability Issues

Juice, leaves, bagasse, and fibers are the main products that are derived from agave. The agave industry produces other residue types, such as stalks cuticles and spines with relevant cellulose and bioactive compounds. This section contemplates the utilization and sustainability of ASs as a main product in the food industry.

Industrial (nonalcoholic) AS production is similar to that of the tequila procedure (40–50% alcohol or 80–100 US proof). The exceptions are additional fermentation processes and distillation/purification steps. Variability of production methods, type of agave, agave-growing region and the plant part employed in production processes (leaves, pine, sap) produce wide-ranging products sold as ASs.

Since the 17th century, ASs have been used to produce distilled alcohol drinks in Mexico, such as tequila, mezcal, sotol, pulque and henequen, of which Mezcal and tequila are the 2 most popular. The global tequila market is projected to reach $6.36 billion by the end of 2025 [18]. According to the Consejo Regulador del Mezcal, global shipments of mezcal rose by 26% in 2019 [19] (Pattillo, 2021). AS, or nectar, fetched 156 million US$ in 2021 and is projected to fetch 272 million US$ by 2026 [18].

The commonest agave species used for AS production are *A. tequilana*, *A. americana*, *A. potatorum*, *A. salmiana* and *A. atrovirens* [20,21]. Several products can be obtained from agave plants (see Figure 1), and these by-products are important sources of income that drive this crop's cultivation. The agave plant is also utilized in foods such as sugars and syrups, and in Mexican stews [22]. Non-food and non-beverage by-products, such as biofuel and other biomaterials, are presently being questioned in environmental sustainability terms.

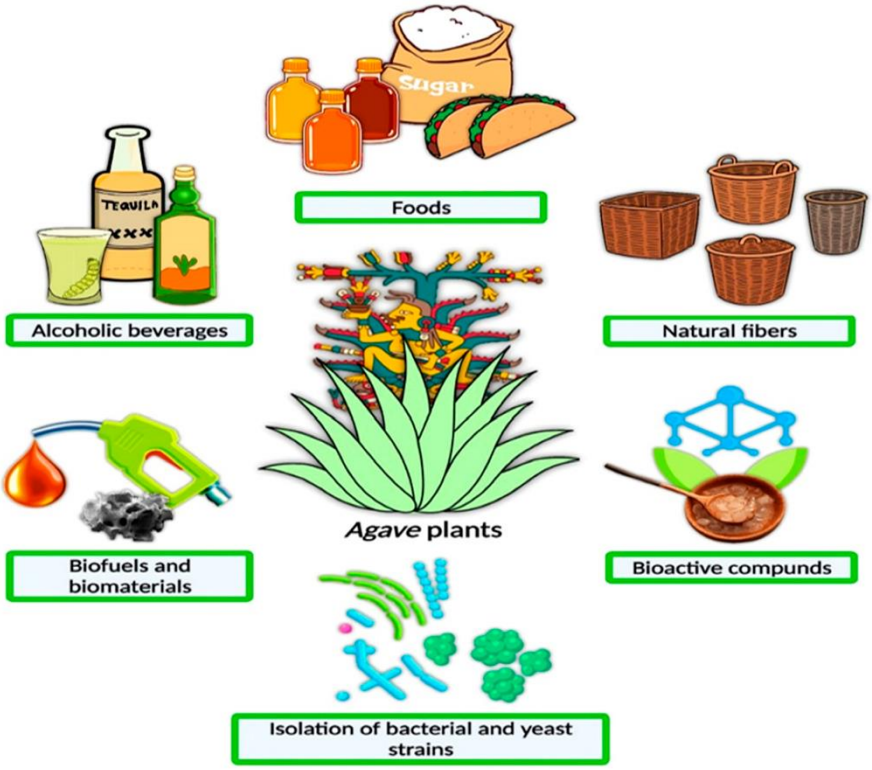

Figure 1. Produce acquired from agave plants [22] (Reprinted with permission from Ref. [22]. Copyright 2021 Elsevier).

The process followed to generate ASs begins by harvesting mature 5–7-year-old blue agave plants. From them, the high carbohydrate contents in plant *piñas* (pine) can be stored. A *piña* looks similar to a pineapple once leaves have been removed. A high-quality piña (weighing up to 68 kg) contains approximately 25–30% *w*/*w* sugars [4]. The next phase consists in milling and crushing piñas for juicy fibers to be obtained. Juice is obtained by hot water washing in a diffuser and discarding fibers, followed by filtration to eliminate solid particle residue from raw agave juices. Filtered juice is thermally hydrolyzed by heating (80 °C) for 8–12 h before refiltering. A second filtration lowers water content. Then, juice is vacuum-evaporated (90 °C) for glycosidic activity denaturation. This results in the end syrup product [23].

Natural aguamiel (juices obtained from fresh or cooked agave "piñas" or cores) can be employed for obtaining high fructose syrup, agave fructans, polysaccharides, biofuel and Maillard compounds [24]. Recent research into the extraction and generation of novel bioactive compounds (for example, saponins and antioxidants) indicates more opportunities for the agave value chain industry [22]. More and more attention has been paid to fructose-rich syrups in recent times, which have become the most demanded sweeteners by the global pharmaceutical and food industries thanks to their technological and functional advantages over sucrose, and their beneficial health effects [11,25] in relation to the bioac-

tive compounds present (fructanes amino and acids) [26]. All of this confers antibacterial properties and antioxidant capacity.

Traditional processing to exploit agave as a source of bioactive compounds and carbohydrate-rich syrups can be performed for direct use or as substrates to yield spirits and hydrolyzed fermented products [21,26].

In recent times, the food industry has paid attention to extract fructopolysaccharides from agave species, which are known as agave fructans (or agavins), because agavins promote human health [27]. ASs can be generated by acid hydrolysis, thermal hydrolysis or glycosidic enzymes from agave fructans [23]. Fructans are the main water-soluble carbohydrate in agave species; they represent > 60% of total soluble carbohydrates [28]. Fructan content in the heads of some agave species falls within the 35–70% dry matter range [29].

The demand for agave fructans in the food industry is increasing because of the technological and prebiotic effects proven by native agave fructans and a considerable degree of polymerization fractions. Agave fructans comprise simple sugars, a complex fructo-oligosaccharides (FOS) and fructans mixture, and linkages β-(2-1) and β-(2-6), including an external (graminans fructans) and internal (neoseries fructans) glucose unit, which varies depending on plant age [30]. Agave fructans are classified as FOS according to the degree of polymerization (DP) (DPs range between 2 and 10) or high DPs (DPs between 2 and 60) [11]. The extraction of agave fructans gives a frequently discarded insoluble dietary fiber-rich by-product [31]. The discarded by-product can be used for developing food ingredients, for example, adding agave ingredients modifies short-chain fatty acid production in granola bars [30].

The use of agave fructans as healthy additives continue to gain interest in the food industry due to their nutritional and technological characteristics, their prebiotic benefits such as soluble dietary fiber, as well as stabilizers and sweeteners, among other applications [32]. The presence of these low molecular carbohydrates makes it possible to obtain prebiotics, fermented products and/or syrups [32].

ASs can be regarded as vegan. As such, manufacturers use them to achieve the same sweet results in their vegan recipes. ASs can also be utilized as a natural sweetener in a wide variety of end products, including prepared beverages, pharmaceuticals, sport drinks, pastry, confection, energy bars, dairy products, sauces, and dressings [33].

The percentage of sucrose replacement with ASs affects both the microstructural rheological and properties of batters, and the physical parameters of baked products. The sensory evaluation of muffins substituted for AS and partially hydrolyzed AS (PHAS) can serve as excellent alternatives for as much as 75% sucrose replacement. Cohesiveness also significantly increases as sucrose substitution levels escalate [34]. Muffin formulations with PHAS present better flavor, color, and texture in particular, and acceptability in general, compared to those formulated with ASs when substituting 100% sucrose [34].

ASs have a different carbohydrate profile with a higher phytochemical potential compared to other sweeteners because more natural compounds are present that display antioxidant activity [35]. A difference in chemical composition is also noted in the same *A. tequilana* syrup samples. This difference lies in the distinct times applied to agave cooking. The color of sweeteners is associated with the content of pigments that possess antioxidant activity. Those with greater antioxidant activity, a higher phenols content and containing pro-anthocyanidins tend to be darker sweeteners [35].

Agave leaves contain non-structural sugars at much lower levels. These levels diminish from the base up to the tip. In *A. tequilana* leaves (fresh weight), the total reducing sugars range lies between 9.4% at the base and 3.3% at the tip. Conventionally, neither plant leaves nor bagasse have been utilized [29], which make them candidates to be employed as fuel. It is possible to use the fibrous waste from agave as several sources, such as straw, paper-making fiber, fertilizers, and baskets [24].

Sustainability issues need to be considered against this backdrop on agave plant versatility. In the food industry, the functional-technical properties of certain food products

can be improved by adding bagasse extracts and leaves. By way of example, *A. americana* leaves are employed as powder in steamed yoghurt formulations because a product's color, texture and viscosity can significantly improve [36]. Calorie and fat content are significantly lower and soluble fiber increases when employing fructans isolated from *A. angustifolia* to replace fat in cookies [37]. Oil- and water-holding capacity are enhanced, which helps to control cookies and can avoid having to add fructans, which means higher yields, meaning larger cookies. Cooky sensory-texture properties also increase, for example, their hardness and color. A sensory analysis shows no differences in the general preference of the formulations that include 10% and 20% fructans as fat substitutes in yoghurts [37].

Bagasse, fibers, and leaves (from stems and leaves) are the principal by-products/residue that the agave industry generates. However, stalks, cuticles and spines are being studied for their high cellulose contents and some bioactive compounds. For the textile industry, although spines and stalks are less commonly employed, they are a relevant source of biocolorants, fibers and bioactive compounds, which can serve as substrates for saccharification. Traditionally, cuticles have been utilized to wrap meat preparations of lots of Mexican dishes and to manufacture paper [38]. Varieties such as *Agave salmiana*, *Agave sisalana* (sisal) and *Agave mapisaga* yield hard fibers, which are highly appreciated because they can be employed to make string and ethnic clothing, and their durability stands out [39].

Bagasse is obtained as fibrous waste after employing stems to produce tequila and mescal, or for agave sap extraction. Bagasse represents approximately 40% of the original stem weight. It comprises both lignin and cellulose. Stems are scrapped to yield fibers and sap (bagasse). They are extracted, considered to be waste and discarded. Some 7,710,520 tons of residual bagasse were produced between 1995 and 2019 [40]. Otherwise, bagasse is an excellent source of bioactive compounds (phenolic compounds, fructans and saponins), sugars, fibers, and other valuable biomolecules [38].

It is noteworthy that the booming agave product market imposes grave environmental consequences. For example, those making mezcal respond to this drink's meteoric rise from ramping up their wild agave collection. This alarms some environmentalists because they fear that slow-growing populations might not recover. Nevertheless, this issue does not apply to tequila or most commercial agave nectars. This is because only cultivated blue agaves are employed, and growers have to keep up with the increased chemical use on farms [41].

Agave plants' economic sustainability can extend if expended biomass is converted into useful produce and applied for forage, food, agriculture, ensilage, energy, medicine, environment, cosmetic, aesthetic and textile purposes. The demand for the three principal agave industries (bioethanol, tequila, and fructose syrup) is growing. Moreover, a non-quantified blue agave inventory is expected to result in newly established relationships between agave producers and industry. For example, it is possible to mechanically harvest and employ the whole blue agave plant for biofuel production purposes by employing lignocellulosic materials and sugars without separation [42].

Similarly to plenty of other industrially employed crops, agave is internationally associated with global markets. *Agave tequilana* can deteriorate local agro-ecosystems for being mono-cropped and requiring huge investments being made in agricultural inputs to obtain high yields. It has been estimated that emissions in the order of 700,000 tons of CO_2eq were emitted in 2014 by the agave tequila chain. Of these greenhouse gas emissions, 44% were directly emitted in agricultural and industrial phases, and the remaining 56% while producing inputs, and transporting and distributing the product. In the agricultural phase, the largest contribution stemmed from using nitrogen fertilizers [43].

It can be argued that the most sustainable agave market options are certified as being free-trade organic products. This guarantees that products are manufactured without pesticides and some occupational standards are followed.

4. Quality and Safety Control

Agave tequilana Weber var. azul is the blue AS. It is a natural sweet substance obtained through the hydrolysis of the fructans stored in agave plants [44], whose use had led to its wide consumption on the world market, which has also increased the fraudulent use of other syrups. Agave has become a popular sweetener thanks to its low glycemic index and prebiotic effect compared to other honeys and natural syrups [44]. Nevertheless, *Agave tequilana* plants are more popular because they are the sugar source employed to produce tequila. The genus Agave includes more than 210 species, and 159 of the species are ubiquitous in Mexico [40]. Maximum AS production is reached when plants are at least 6 years old, which is the agave plant's maturity age [44].

The carbohydrate content of ASs is high. They comprise mostly fructose (≥60% total soluble solids), followed by glucose and sucrose traces [11]. Such a carbohydrate composition provides ASs with a low glycemic index. This means that they are sweeter than other syrups with quite high glucose and/or sucrose levels such as sugarcane and maize [4]. Apart from glucose and fructose, some FOS are present in certain ASs in smaller amounts because agavin hydrolysis is incomplete [45]. They are decisive for calculating carbohydrate composition to avoid adulterations from other sugars being added.

Regarding identification, a very useful molecular marker of the adulterant detection, authenticity, origin, and quality of natural sweeteners is carbohydrate fingerprinting. Both the determination of glucose-fructose-sucrose contents and oligosaccharide profiles are methods that establish quality in syrup and honey [46–48]. During ASs production, the main agronomic species are the *Agave salmiana* and *Agave tequilana* Weber Blue varieties, with differences in their composition and carbohydrate content [44,49]. The Government of Mexico and agave manufacturers have set Mexican standard rules that do not allow any food additives, ingredients or sugars from other sources that are not agave plants to be used to manufacture commercial ASs [50] and other derivative products, such as tequila and mezcal. The specifications and test methods for products made with the blue AS (*Agave tequilana* Weber var. azul and *Agave Salmiana* spp.) are mentioned in this document, which include the definition of fructans (inulina and FOS), and FOS from 2 to 11 degrees of polymerization, hydrolysis type (chemical, thermal or enzymatic, or their combination). It only accepts a unique degree of quality for AS and it is compulsory to produce AS wholly from agave. The microbiological parameters are the usual ones for this food type: fungi and yeasts (<10 CFU/g), coliforms and *E. coli* (negative), total count bacteria (<100 CFU/g) and *Salmonella* spp. (negative at 25 g).

A different compound in AS is agavins, which are reserve carbohydrates in the agave plant, are formed by fructose polymers and one unique glucose. Nowadays, they are considered to be prebiotic substances and offer several applications (wall material and encapsulating bioactive compounds) [51]. As a result of of their special phytochemical and chemical composition, agavins do not undergo degradation by oral microbiome in either the oral cavity or the small intestine by digestive enzymes. Nonetheless, agavins arrive at the large intestine and are fermented by intestinal microbiota to promote the growth of *Bifidobacterium* sp., *Lactobacillus* sp. and *Saccharomyces Boulardii*, considered the main probiotics [52].

Some authors [52] have explored how agavins affect mice. They have observed that their consumption accelerates body weight loss by microbiota modification and the presence of short-chain fatty acids (SCFA) as determining factors [52]. It is known that agavins favor the host's health by bringing about certain changes in the activity and/or composition of the intestinal microbiome, considered to be prebiotics [53].

Their structural complexity lies behind this action on the microbiome. Agavins cannot be degraded by endogenous gastrointestinal enzymes when they pass through the stomach and small intestine. They arrive at the caecum and colon. Here, the saccharolytic microbiotas present at these sites ferment them to produce SCFA, mainly propionate, acetate and butyrate. SCFA are extremely relevant for reducing body weight gain by G-protein-coupled receptors (GPRs). This impacts the secretion of the hormones that are implicated

in controlling appetite [54]. Figure 2 shows the mechanism by which agavine consumption can pose beneficial health effects through agave fermentation in the colon. A change in the intestinal microbiome can be brought about by agavins fermentation (SCFA) in the caecum and gut due to a lower pH [15,55].

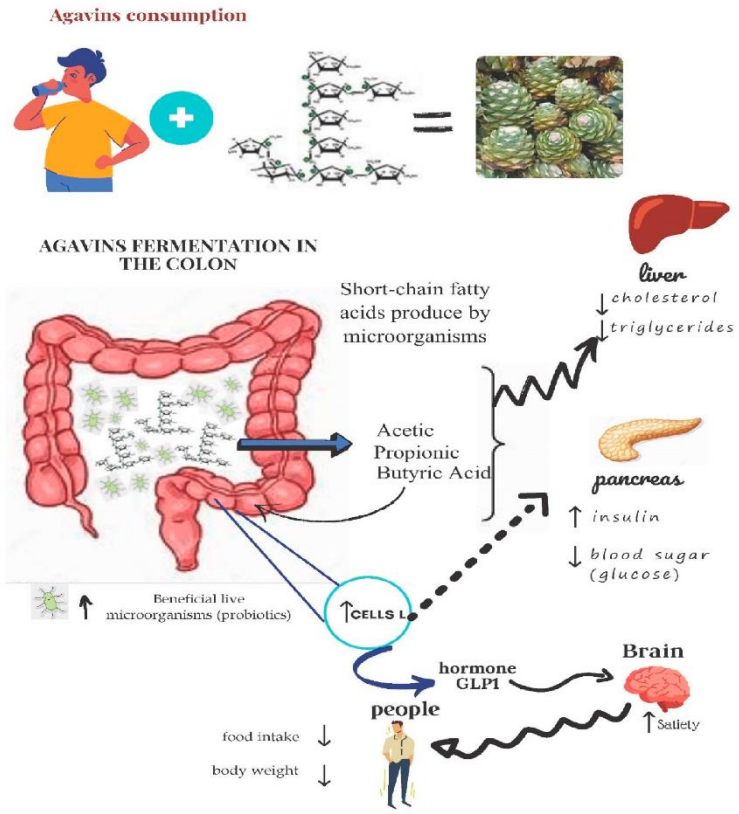

Figure 2. Mechanism by which agavine consumption can generate beneficial effects on health (adapted from [56]).

Gut microbiome growth is not the same for all bacteria [12]. There are three Firmicutes, Proteobacteria and Bacteroidetes phyla, along with five other minor phyla (Tenericutes, Actinobacteria, Cyanobacteria, Defferribacteres, Verrucomicrobia) that dominate the caecal microbiota of mice.

Agavins or oligofructose supplementation is related to distinct communities: with the agavins group, it enhances two genera (*Klebsiella*, *Citrobacter*) and diminishes four (*Ruminococcus*, *Coprococcus*, *Lactobacillus*, *Prevotella*). Oligofructose enhances three (*Faecalibacterium*, *Allobaculum*, *Prevotella*) and diminishes six (Ruminococcus, Enterococcus, *Odoribacter*, *Lactobacillus*, *Desulfovibrio*, *Adlercreutzia*) [52].

Diet supplementation modifies both microbiota activity and caecal microbiota composition. However, the concentration of butyric, acetic, and propionic acids significantly rise by supplementation with oligofructose or agavins, and the pH of caecal content considerably lowers in relation to non-supplemented controls [52].

In short, the agave sweetener can be used in lots of food applications as an alternative to sucrose; for instance: muffins [34], cheese [57], cookies [58,59], gummy bear [20,60], ice cream [61], yoghurt [22,62].

5. Nutritional Profile and Health Impacts

ASs typically have high soluble solids (>70° Brix) and are primarily made up of fructose and glucose, with small nystose, kestose and sucrose contents [10,63]. The prebiotic action of nystose and kestose in ASs increases its functional value [10,44]. Distinct from other traditional sweeteners, ASs are a source of polyphenols, vitamins and minerals, as shown in Table 2 [64].

Table 2. The typical total phenolic and nutrient composition of traditional common sweeteners (adapted with permission from Edwards et al., 2016, Elsevier) [64] [1].

Component	Agave Syrup	Honey	Molasses	Maple Syrup	Carob Syrup	HFCS	Sucrose
Energy (kcal/100 g)	310	304	290	260	248 [a]	281	387
Water (g/100 g)	23	17	22	32	35 [a]	24	0
Protein (g/100 g)	0.1	0.3	0.0	0.0	1.4 [a]	0.0	0.0
Total lipids (g/100 g)	0.5	0.0	0.1	0.1	0.0 [a]	0.0	0.0
Carbohydrate per difference (g/100 g)	76.4	82.4	74.7	67.0	-	76.0	100.0
Total dietary fibre (g/100 g)	0.2	0.2	0.0	0.0	3.3 [a]	0.0	0.0
Total sugars (g/100 g)	68.0	82.1	74.7	60.5	63.9 [a]	75.7	99.8
Minerals (mg/100 g)							
Calcium (Ca)	1	6	205	102	86 [a]	0	1
Iron (Fe)	0.09	0.42	4.72	0.11	1.10 [a]	0.03	0.05
Magnesium (Mg)	1	2	242	21	54 [a]	0	0
Phosphorus (P)	1	4	31	2	239 [a]	0	0
Potassium (K)	4	52	1464	212	1608 [a]	0	2
Sodium (Na)	4	4	37	12	113 [a]	2	1
Zinc (Zn)	0.01	0.22	0.29	1.47	-	0.02	0.01
Vitamins							
Vitamin C (ascorbic acid; mg/100 g)	17	0.5	0	0	-	0	0
Vitamin B_1 (thiamin; mg/100 g)	0.122	0	0.041	0.066	-	0	0
Vitamin B_2 (riboflavin; mg/100 g)	0.165	0.038	0.002	1.27	-	0.019	0.019
Vitamin B_3 (niacin, mg/100 g)	0.689	0.121	0.93	0.081	-	0	0
Vitamin B_6 (pyridoxine, mg/100 g)	0.234	0.024	0.67	0.002	-	0	0
Folate (µg/100 g)	30	2	0	0	-	0	0
Vitamin A (RAE µg/100 g)	8	0	0	0	-	0	0
Vitamin E 'α-Tocopherol' (mg/100 g)	0.98	0	0	0	-	0	0
Vitamin K (phylloquinone, µg/100 g)	22.5	0	0	0	-	0	0
Total polyphenolics (mg GAE/100 mL)	1.292 [b]	1.935 [b]	9.195 [b]	1.494 [b]	-	0.268 [b]	-

[1] Unless otherwise specified, data were taken from the USDA database (2019) [65]. [a] Data came from Özcan et al., 2007 [66] and [b] St-Pierre et al., 2014 [67]. The enzymatic gravimetric methods 985.29 or 991.43 of the AOAC were applied to determine total dietary fibre content. Abbreviations: HFCS; RAE; retinol activity equivalents, high fructose corn syrup and GAE; gallic acid equivalents.

In some areas, AS is popular for its low glycemic index (10–27), which is much lower than honey and sucrose [2,16,68], and partially for its carbohydrate pool that contains up to 90% fructose [69]. As AS has a high fructose concentration, it can be used as a sweeter which is better than other many commercially available syrups mostly made up of glucose or sucrose [16]. As a result, not as much AS is required to reach a comparable level of sweetness. This promotes it as a calorie-reduced sweetener. However, such an approach is not without criticism [70].

AS can be controversial if we wish to know if it is a healthier option to sweeteners and table sugar. Syrup proponents argue that it is a better sweetener for diabetics than honey or table sugar thanks to its low glycemic index, and because it creates a smaller blood sugar

spike [34,71]. There are, however, additional aspects to bear in mind. According to Jones (2012) [72], the types and content of sugars, macronutrients and ingredients that differ in food products lead to vastly varied glycemic index values. Furthermore, the glycemic index does not correctly reflect food processing and/or cooking methods, individuals' diet or quantities consumed [1,72]. Nor should the glycemic index be employed as the only criterion to establish a given food or diet's health effects [1], but ought to be combined with different nutritional factors. Consumers can be misled and end up believing that a low glycemic index allows them to consume more than with conventional sweeteners.

Recent research reports that fructose overconsumption is connected to the liver accumulating fat. This is associated with cardiovascular disease, insulin resistance [73], among other harmful problems [74]. Stanhope et al. (2011) [75] report that those who eat 25% of their daily calories in the form of high-fructose corn syrup (55% fructose, 45% glucose) can present higher triglyceride and cholesterol levels than those who eat pure fructose. However, this is more than what most people eat on a daily basis. It is also noteworthy that fructose is not ingested alone in a typical diet but is often combined with glucose [76].

The way that AS is advertised and how much is consumed may be the most important concerns. There is very little knowledge about the long-term effects of ingesting fructose-high foods or beverages on human health [77]. Given these uncertainties, consumers ought to endeavor to consume energy-dense foods in moderation, including AS. Regardless of the source of sugar, one calorie is one calorie for body fatness alterations [78] The sugars in ASs apparently have the same effect on human weight loss as other sugars do [78]. This means that AS is no more natural than either fruit juice concentrate or high-fructose maize syrup. While enterprises are entitled to sell AS as a sweetener, they ought not to claim that this alternative is more natural or healthier than other widely used sweeteners or sucrose. Making strong claims that favor AS intake should be avoided simply because additional research into fructose and its effects on human nutrition and metabolism is necessary.

6. Conclusions

This review explores the potentials of AS as a natural sweetener for human consumption. As consumers show considerable interest in demanding a more natural ingredient in their food, it critically examines the quality characteristics, and nutritional and health impacts of AS. We herein examine the analytical methods that are currently available to characterize sugars in agave to help to confirm its quality and to avoid adulteration. Lucrative industrial agave production raises concerns about ethical considerations that hinder sustainability, especially the environment. Finally, we expect more research to be conducted into AG intake on human metabolism to justify its health claims as a natural alternative to other sugars. In addition, research to improve the industrial process for obtaining AS from agave juice via enzymatic or acid hydrolysis, with the goal of preserving beneficial components (for example, polyphenols, saponins, dietary fiber), while lowering the content of potentially harmful components (for example, fructose), is crucial.

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3.2 ARTÍCULO Nº 2

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Review

Maple Syrup: Chemical Analysis and Nutritional Profile, Health Impacts, Safety and Quality Control, and Food Industry Applications

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Abstract: Maple syrup is a delicacy prepared by boiling the sap taken from numerous Acer species, primarily sugar maple trees. Compared to other natural sweeteners, maple syrup is believed to be preferable to refined sugar for its high concentration of phenolic compounds and mineral content. The presence of organic acids (malic acid), amino acids and relevant amounts of minerals, such as potassium, calcium, zinc and manganese, make maple syrup unique. Given the growing demand for naturally derived sweeteners over the past decade, this review paper deals with and discusses in detail the most important aspects of chemical maple syrup analyses, with a particular emphasis on the advantages and disadvantages of the different analytical approaches. A successful utilization on the application of maple syrup in the food industry, will rely on a better understanding of its safety, quality control, nutritional profile, and health impacts, including its sustainability issues.

Keywords: maple syrup; food industry; nutrition; chemical analysis; health impacts

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1. Introduction

Maple syrup is a delicacy prepared by boiling the sap taken from different Acer species, mainly sugar maple (*Acer saccharum* Marsh.) trees [1]. Agriculture and Agri-Food Canada [2] reports Canada as the world's largest producer of maple products and it is responsible for nearly 71% of the maple syrup production in the world. In 2017, Quebec produced approximately 92% of all the maple syrup in Canada and is home to more than 13,300 maple syrup producers [3].

Of the many natural sweeteners, maple syrup is recognized as a much superior alternative to refined sugar for not only its mineral content, but also for its high concentration of phenolic compounds with bioactivity properties, i.e., anti-mutagenic, anti-radical, antioxidant, and anti-cancer [4–6]. Compared to dextrose, corn syrup and brown rice syrup, maple syrup brings about lower glucose and insulin responses, which make it a healthier substitute for refined sugars in our diet [4,7].

Maple tapping often begins late in winter or early in spring. It only lasts a few weeks because of the weather. To make maple syrup, sweet watery xylem sap is collected and concentrated. As a result of the pressure build-up caused by the freeze-thaw cycle, this sap pours out of maple tree trunks. To make one liter of maple syrup, around 40 liters of sap (containing 2–3% sugar) are required (66% sugar). Other than sucrose, which is

maple syrup's principal sugar, its flavor is a complex mix of not only minerals, amino acids, oligosaccharides, organic acids, and phenolic and volatile aromatic compounds, but also microbial contaminants from maple sap [8,9]. According to Filteau et al. [9], as well as its associated microflora, sap content can change during seasons and syrup color usually darkens as the season progresses.

As previously stated, the chemical composition of sap and syrup can significantly differ depending on geographical origin [10,11]. Indigenous peoples in North America introduced maple syrup to colonizing Europeans. Since then, maple syrup and maple products have been commercially sold [12]. More interest has been shown in studying the elemental composition of maple syrup as commercial markets expand and analytical technologies improve. As a result, several scientific research works have been conducted in the last century to determine the chemical components and mineral constitution of maple syrup [13].

According to these premises, the present review intends to examine the nutritional profile and health impacts of maple syrup consumption, some of its possible food industry applications and its sustainability issues, along with its main safety and quality parameters, and the chemical analysis of its principal components.

2. Chemical Analysis—Advantages and Disadvantages of the Different Analytical Methods

Maple syrup has a long-standing history of consumption, particularly in North America, where it is very much appreciated. More recently, interest in this product has spread to other areas of the globe like Europe and Japan, owing to the demand for natural sweeteners [14,15]. Maple syrup is regarded as a high-value product for its unique flavor [16]. Accordingly, diverse tools have been proposed to assess its quality and authenticity, protect consumers, and ensure fair competition among producers [17].

Maple syrup quality is assessed according to classification schedules in the USA and Canada, with typical standards applied to judge this product's price, including the product's color intensity (light-colored products tend to be more expensive). This means that syrup darkening can be used as an indicator of the irregularities that might arise during processing or microbial contamination [18]. Lighter maple syrups tend to be typically sweet and contain no further prominent flavors, while darker ones possess burned caramel flavors and are apt to be blended with light syrups for a more classic "maple flavor" [11]. Past consumer studies report a preference for darker maple syrups over lighter ones [19]. These darker syrups contain more beneficial bioactive compounds, such as polyphenols [20,21]. That being said, the Canadian Food Inspection Agency (CFIA) monitors Canadian maple syrup safety and quality [22] so that producers meet high federal standards. The CFIA is also responsible for the federal classification of Canadian maple syrup color descriptors and grades by ensuring that they align with standard international grading systems. Canadian regulation defines two grades (Grade A and Processing Grade) and four color classes (Gold, Amber, Dark, Very dark) for maple syrup.

Grade A Maple Syrup: according to the definitions dictated by the product specification, maple syrup can be classified as grade A, but only if it meets these requirements:

- With no undesired uniform fermentation color;
- Sediment-free. No turbidity;
- Characteristic natural maple flavor for all four color classes;
- No uncharacteristic odors or flavors.

Processing Grade Maple syrup: the maple syrup called processing grade is also obtained from maple sap concentration, but does not respect at least one of the quality parameters defined for Grade A or more.

To ensure its stability, maple sugar must not contain more than 10% moisture.

Grade A maple syrup can differ in the four color classes, defined by either a transmittance value or the ratio between the intensity of the light passing through samples and that of the light emerging from them [23]. The higher the transmittance value, the clearer and

more transparent maple syrup is. The lower the transmittance value, the darker and denser maple syrup is.

It is nature itself that characterizes maple syrup nuances. When harvest begins, syrup tends to be clear, and its sweetness is slight. As the season progresses, syrup becomes darker in color and displays distinct aromatic connotations. Indeed, this natural sweetener presents a range of differing aromatic components, including flavors such as vanilla, hazelnut, floral, coffee and spicy aromas.

All the color classes are characterized by a denomination and accompanied by a note about taste [23]:

- Gold (delicate taste);
- Amber (rich taste);
- Dark (strong taste);
- Very dark (robust taste).

All in all, maple syrup quality is driven mainly by its physico-chemical and microbial features. Thus, in order to verify that maple syrup has the appropriate characteristics, namely in terms of color, density and flavor, simple physico-chemical tests are routinely performed. For instance, maple syrup color has been set by measuring the percentage of light transmittance at 560 nm, while sucrose content is determined using a refractometer [24]. These methods are convenient because they provide immediate results [24]. Yet analyses involving more complex techniques that lead to more data, and greater sensitivity, accuracy, and precision in the results are essential to develop processes that allow maple syrup's functional profile to improve and adulterations and contaminants to be detected. Several studies were conducted to deal with the analysis of the physico-chemical and microbiological parameters of maple syrup. Table 1 presents an overview of the followed analytical techniques and the obtained results.

Maple syrup xylem sap contains naturally occurring molecules and process-derived compounds that are generated during sap evaporation [20]. This means that it contains more than 250 compounds other than sucrose, which is the major maple syrup component [13]. Its minor components include minerals and trace elements, amino acids, other carbohydrates, organic acids, phenolic compounds, sulfur compounds, and pyrazines. Table 2 summarizes the research works carried out as part of a study of maple syrup's inorganic and organic constituents. Regarding its mineral profile, maple syrup contains considerable amounts of Ca, K and Mg, along with other minerals and trace elements like Zn, P, Mn, Na and Fe [10,25–28]. Several techniques have been used to determine minerals in maple syrup, including flame and furnace atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Regarding amino acids, maple syrup is remarkably rich and particular emphasis is placed on D-alanine and other D-amino acids, which have been shown to be generated during the Maillard reaction [29]. By means of a sap samples analysis by metabolomics, the noteworthy work by Garcia et al. [30] reports that amino acid composition varies with season, which is the case of glutamic acid and histidine, whose content is liable to lower as the season progresses, while that of methionine and asparagine tends to grow. The last two have been reported as precursors of the compounds responsible for off-flavors developing in syrup [30]. High-performance liquid chromatography (HPLC) is the gold standard for determining many types of compounds present in maple syrup, namely non-volatile ones, because HPLC allows swift, sensitive, specific, and accurate measurements to be taken, but other equally sound techniques can be used. For example, Pätzold and Brückner [29] employed gas chromatography (GC) coupled with mass detection (MS) to study the amino acids profile of maple syrup. In this case, the polar nature of amino acids required a derivatization step prior to the analysis to make them more volatile and to improve their chromatographic performance. Applying MS is advantageous for its sensitivity and ability to provide structural data [31].

Concerning carbohydrates, in addition to sucrose, monosaccharides fructose, and glucose, different oligosaccharides and polysaccharides are found. For instance, Sato

et al. [32] developed a method based on hydrophilic interaction chromatography coupled with charged aerosol detection (HILIC-CAD). It allows analyses of up to hepta-saccharides in only 30 min. It enabled the separation and quantification of fructosyl oligosaccharides in maple syrup for the first time. Refractive index (RI) and pulsed amperometric detectors (PAD) are widely used in sugar analyses, and although the RI type is often utilized to analyze known substances, it does not exhibit high sensitivity [32]. PAD yields a high-resolution analysis of multiple sugars [32], but this entails employing an anion exchange column and sodium hydroxide solution as the mobile phase (e.g., [10,33]). Desalting is necessary, which makes identifying new compounds more difficult. So CAD has become increasingly popular [32]. An alternative to chromatographic methods to separate sugars is capillary electrophoresis (CE), which requires a derivatization step to make them electrically charged. This was shown by Taga and Kodama [34]. CE is an appealing option as it incurs moderate operating costs compared to HPLC, employs less solvent and is easily automatable. However, its robustness still raises doubts [35]. To determine organic acids, phenolics and vitamins in maple syrup, HPLC coupled with UV-Vis or diode-array detection (DAD) are some analytical approaches of choice. Compared to UV-Vis detectors, the speed, sensitivity and resolution of DAD are superior despite it being more susceptible to noise interferences [31]. Phenolics are one of the maple syrup constituents to which the most attention has been paid for their numerous health benefits [36,37]. To date, more than 100 phenolics have been identified [13,20,38,39] thanks to the application of techniques such as nuclear magnetic resonance (NMR), which enables the swift analysis of complex mixtures without having to perform separation and/or purification steps, which makes it ideal to analyze maple syrup (e.g., [20]).

One aspect that deserves our attention is that, as the frequency of fraud resulting from admixing inexpensive sugars in maple syrup increases, the development of detection methods is more pressing [40]. Table 3 summarizes the studies performed in this field. Some tools, such as infrared (IR) spectroscopy, are noteworthy. It requires minimal sample pretreatment, is non-destructive [40] and provides reliable results, as shown in the work by Paradkar et al. [41] which successfully reported the addition of beet and cane sugars to maple syrup. Isotope ratio mass spectrometry (IRMS) is another technique with a huge potential for detecting the same type of adulteration, as proved by Tremblay and Paquin [16]. This technique exhibits high precision and the required sample is smaller than that in NMR [40].

As a final remark, along with developing analytical tools, the possibility of employing elemental maple syrup content as a strong marker for fingerprinting maple syrup against other syrups must be actively investigated. A literature analysis backs the possibility of identifying percentages by allowing the detection of adulterations to maple syrup with inexpensive syrups employing contents of element. Nevertheless, wide fluctuations in metal contents are reported, which hinders making consistent comparisons, while the possible release of metals from instruments can interfere with acquiring accurate data. These techniques has been used in other foods, such as honey and coffee [42,43]

Jointly, the progress made with new analytical techniques can help with the detection of elemental maple syrup content as a solid marker for fingerprinting this appreciated product, unlike other syrups with lower quality compositions, which should be more exhaustively studied.

Table 1. Physico-chemical and microbiological analyses of maple syrup.

Physico-Chemical and Microbiological Parameters	Studies					
	Samples		Technique	Analysis Details	Main Results	Refs.
	No.	Origin				
Color	33	Canada (Nova Scotia, Quebec, Ontario, New Brunswick) and the United States (New York, Massachusetts, Vermont, New Hampshire)	UV–Vis spectrophotometry	Color intensity was assessed by reading the % light transmittance (%T) at 560 nm.	Color differed markedly depending on the sample origin, with %T ranging from 88.9 to 14.8%. Syrup color darkened near the end of the production season.	[1]
	18 (A) + 7 (NA)	United States (Vermont and New Hampshire)	UV–Vis spectrophotometry	Color measurement was performed using a colorimeter.	The color parameter has not been proved an appropriate tool to distinguish between authentic (A) and non-authentic (NA) maple syrups.	[44]
	233	Canada (Quebec)	UV–Vis spectrophotometry Fluorescence spectroscopy	UV–Vis spectrophotometry: Color intensity was assessed by reading %T at 560 nm. Fluorescence spectroscopy Sample preparation: Syrup samples were diluted with distilled (1:25) prior to analysis.	Intrinsic fluorescence allowed syrup color to be determined with good accuracy (r^2 = 0.88–0.91).	[45]
	35	Canada (Ontario)	UV–Vis spectrophotometry	Color intensity was assessed by reading %T at 560 nm.	No significant correlation was observed among %T and glucose, fructose or total reducing sugars.	[26]
	20	Canada (Quebec)	UV–Vis spectrophotometry	Color intensity was assessed by reading %T at 560 nm.	Protocatechuic acid and 3-hydroxybenzoic acid concentrations increased with color intensity.	[46]
	32	Canada (state not specified)	UV–Vis spectrophotometry	Sample preparation: Maple syrup samples were diluted 10-fold with water.	Darker-colored syrups displayed stronger antioxidant activity and appeared to contain a higher content of reducing sugars than lighter grades.	[47]
	101	Canada (Quebec)	UV–Vis spectrophotometry Plate count Adenosine triphosphate (ATP) bioluminescence	UV–Vis spectrophotometry: Color intensity was assessed by reading %T at 560 nm. Plate count: Sap samples were diluted in peptone water before being plated on plate count (PC) agar to estimate the total aerobic counts and on acidified potato dextrose (PD) agar to determine fungi. ATP bioluminescence: An assay based on exposing sap samples to the luciferase enzyme and its substrate luciferin was performed.	The ATP bioluminescence measurement of sap allowed a good maple syrup color assessment. In general, lighter syrups were produced from the saps with a low level of microbial contamination, while those with darker colors came from the saps with a high contamination level.	[48]

Table 1. *Cont.*

Physico-Chemical and Microbiological Parameters	Studies					
	Samples		Technique	Analysis Details	Main Results	Refs.
	No.	Origin				
Density	35	Canada (Ontario)	Gravimetric procedure	Maple syrups were incubated in a water bath at 25 °C, and 1 mL was weighed on an analytical balance.	No significant differences were found in density across the maple syrup grades.	[26]
	124	Canada (Quebec)	Refractometry	Total soluble solids–Brix values–were determined using a refractometer.	The total soluble solids values were higher close to the mid-production season.	[49]
	81	Canada (Nova Scotia, New Brunswick, Quebec)	Total solids content	Total solids were determined by evaporating moisture and weighing the dry residue.	No significant differences were found between the different regions of origin of the matrix under study concerning total solids content. This parameter decreased as the production season advanced.	[27]
pH	81	Canada (Nova Scotia, New Brunswick, Quebec)	pH meter		Upon the early production season, maple sap obtained its highest pH value.	[27]
	233	Canada (Quebec)	pH meter Fluorescence spectroscopy		Intrinsic fluorescence provided semi-quantitative information on pH (r^2 = 0.51–0.75)	[45]
	124	Canada (Quebec)	pH meter		At the beginning of the flow season, maple sap obtained its highest pH value.	[49]
Rheological behaviour	5	Canada (Quebec)	Rheology	The impact of variation in both temperature (5–55 °C) and the soluble sugar concentration (66–75 °Brix) in terms of rheological properties was evaluated.	Maple syrup primarily exhibits Newtonian behavior. Yet, both syrup grade and temperature can impact apparent viscosity within a range from 0.035 to 0.651 Pa s. Furthermore, increasing the maple syrup concentration enhanced its non Newtonian behavior. Overall, the darkest syrups exhibited the greatest viscosity, while very clear ones had the least viscosity.	[50]
	18 (A) + 7 (NA)	Canada (Quebec)	Rheology	A stepped ramp equilibrium flow assay was performed.	Viscosity values ranged between 0.128 and 0.247 Pa s at 25 °C. No relation between maple syrup grade and viscosity was found.	[44]
Microbiological parameters						
Bacteria and fungi	233	Canada (Quebec)	Plate count Fluorescence spectroscopy	Plate count: Sap samples were diluted in peptone water before being plated on PC agar to estimate the total bacterial counts and on acidified PD agar to determine fungi. Fluorescence spectroscopy Sample preparation: Syrup samples were diluted using water (1:23) prior to analysis.	Intrinsic fluorescence provided semi-quantitative information on the microbial count (bacterial count: r^2 = 0.80–0.85; yeasts and moulds count: r^2 = 0.62–0.73). Fungi and bacteria can be major contributors to maple syrup typicity.	[45]

A—Authentic; NA—Non-authentic (fraudulent or adulterated).

Table 2. Chemical analysis of inorganic and organic constituents of maple syrup.

Inorganic Constituents	Studies					
	Samples		Technique	Analysis Details	Main Results	Refs.
	No.	Origin				
Macrominerals and trace elements	2	Canada (Quebec)	Inductively coupled plasma-mass spectrometry (ICP-MS)	Sample preparation: 10 mg of each sample were mixed with nitric acid (1 mL) and digested in a microwave oven. Subsequently, the digested solutions were centrifuged, and an aliquot (200 µL) was further diluted (to 10 mL) with water and analyzed.	The predominant minerals were Ca (212.78–380.48 mg/100 g), K (70.50–128.35 mg/100 g), Mg (18.79–124.51 mg/100 g) and Zn (2.3–80.86 mg/100 g). Determinations were made of the Na (3.32–4.86 mg/100 g), Mn (53.19–58.45 mg/100 g) and Fe (0.44–0.70 mg/100 g) levels.	[25]
	80	Canada (Quebec, Ontario) and the USA (Vermont, Massachusetts, Wisconsin, New Hampshire, Michigan)	Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)	Sample preparation: 0.25 g of sample were diluted with water (25 mL) and directly aspirated into the spectrometer.	The Ca, K and Mg levels respectively ranged between 266 and 1702 mg/L, 1005 and 2990 mg/L, 10 and 380 mg/L. O. The authors indicate that knowledge of maple syrup's mineral profile might be useful for determining its geographic origin.	[11]
	35	Canada (Ontario)	Inductively coupled plasma-mass spectrometry (ICP-MS)	Sample preparation: 10 mL of nitric acid were added to 5 mL of maple syrup. Then the solution was filtered and placed inside a volumetric flask (50 mL). The final volume was made up with water.	The total mineral content varied between 2988.296–4106.729 mg/L. The Mg, Mn, P, Zn, Ca and K levels ranged between 193.32–238.540 mg/L, 3.107–4.640 mg/L, 2.804–7.731 mg/L, 5.134–6.747 mg/L, 687.310–1354.757 mg/L and 2157.499–2327.860 mg/L, respectively.	[26]
	81	Canada (Nova Scotia, New Brunswick, Quebec)	Flame and furnace atomic absorption spectrophotometry (AAS)	Sample preparation: Syrup samples were diluted (1:50), filtered, and further analyzed.	The Cu, Fe and Zn levels detected in maple syrup samples ranged between 0.09–8.28 µg/mL, 0.41–44.01 µg/mL and 2.81–129.03 µg/mL, respectively.	[27]
	8	Canada (state not specified) and the United States (Vermont, Massachusetts, Maine, New York)	Inductively coupled plasma-mass spectrometry (ICP-MS)	Sample preparation: Digestion using closed-vessel microwave heating.	The Co, Cu, Mn and Zn levels varied between <89 ng/g, <56–2795 ng/g, 1.8–101 µg/g and 5.2–44.2 µg/g, respectively.	[28]
Organic constituents						
Non-volatiles						
Amino acids	2	Canada (state not specified)	Gas chromatography-mass spectrometry (GC-MS)	Sample preparation: 1 g of sample was diluted with water (5 mL). pH was adjusted to 2.3. Ion exchange solid-phase extraction was applied, followed by drying, redissolving and redrying. Pentafluoropropionic acid anhydride was used as the derivatizing agent. Column: Varian Fused silica capillary column with N-propionyl-L-valine tert-butylamide polysiloxane (Chirasil-Val; 25 m × 0.25 mm; 0.12 µm)	Large amounts of D-amino acids were detected, with D-alanine accounting for 33–34%. D-valine (~0–1.3%), D-proline (3.8–8.9%), D-serine (~0–11.3%). D ass, i.e., a combination of D-aspartate and D-asparagine (3.4–8.0%), D-phenylalanine (6.4–7.0%), D-glx, i.e., combination of D-glutamic acid and D-glutamine (~0–11.8%) and D-isoleucine (12.7–16.8%), were also detected.	[29]

Table 2. *Cont.*

Inorganic Constituents	Studies					
	Samples		Technique	Analysis Details	Main Results	Refs.
	No.	Origin				
Carbohydrates	80	Canada (Quebec, Ontario). The USA (Vermont, Massachusetts, Wisconsin, New Hampshire, Michigan)	High-performance anion exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD)	Sample preparation: For the sucrose analysis, 0.154 g of maple syrup was diluted to 1 L. For the fructose and glucose analysis, 0.875 g of sample were diluted to 250 mL. Column: A Dionex CarboPac PA1 analytical column (250 × 4 mm) Mobile phase: 80 mM sodium hydroxide	The main carbohydrates found were fructose (0.00–3.95%), glucose (0.00–9.59%) and sucrose (51.7–75.6%).	[11]
	1	Canada (state not specified)	High-performance anion exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD). Gas chromatography-mass detection (GC-MS) Nuclear magnetic resonance (NMR)	Polysaccharides extraction: Performed by ethanol precipitation and dialysis. Polysaccharides purification: Column: A Hiprep Q Sepharose anion exchange column (GE Healthcare Life Sciences; 100 × 16 mm) Mobile phase: Water; sodium chloride Glycosyl composition analysis: Column: Metrohm Hamilton RCX-30 column (250 × 4.6 mm) Mobile phase: Sodium hydroxide Glycosyl linkage analysis: Column: An SP-2331 capillary column (Sigma-Aldrich Supelco; 30 × 0.25 mm)	Isolation of a prebiotic carbohydrate: inulin. Two acidic polysaccharides were identified as arabinogalactans were isolated.	[33]
	4	USA (New Hampshire)	Hydrophilic interaction liquid chromatography coupled with charged aerosol detection (HILIC-CAD)	Sample preparation: Maple syrup was dried, dissolved in water and centrifuged. Then the supernatant was filtered, and acetonitrile was added to adjust the solvent concentration to 75% acetonitrile. Column: Showa Denko Asahipak NH2P-50 4E (4.6 × 250 mm; 5 µm) Mobile phase: Water–acetonitrile	Maple syrup contained not only sucrose, glucose and fructose, but also fructo-oligosaccharides like 1-kestose, blastose, nystose and nenkestose, among other unidentified saccharides.	[32]
	1	Canada (Quebec)	Capillary electrophoresis coupled with UV detection (CE-UV)	Sample preparation: Samples were pretreated by enzymatic digestion followed by precolumn derivatisation with 1-phenyl-3-methyl-5-pyrazolone. Column: GL Sciences Fused silica capillary (62 cm; 50 µm) Background electrolyte: 200 mM borate buffer at pH 10.5	9 monosaccharides and 5 disaccharides were detected. Glucose was the major reducing sugar. Mannose was detected at quite high concentrations compared to the other sugars. Arabinose, galactose, N-acetyl-glucosamine, ribose and xylose were also found. Melibiose was detected when samples were treated with invertase, which suggests the presence of raffinose in maple syrup.	[34]
	35	Canada (Ontario)	Enzymatic method	Sample preparation: Samples were diluted (1:25).	Across all the grade syrup samples, no significant differences were observed in glucose (0.670–0.810 g/L), fructose (0.088–0.255 g/L) or in the total reducing sugars (0.870–0.878 g/L).	[26]

Table 2. *Cont.*

Inorganic Constituents	Studies					
	Samples		Technique	Analysis Details	Main Results	Refs.
	No.	Origin				
Organic acids	80	Canada (Quebec, Ontario). The USA (Vermont, Massachusetts, Wisconsin, New Hampshire, Michigan)	High-performance ion exchange liquid chromatography with UV detection (HPIEC-UV)	Sample preparation: 0.63 g of sample were diluted in 25 mL of water and then filtered. Column: Anion exchange Phenomenex Rezex organic acid column (300 × 7.8 mm) Mobile phase: 0.005 N sulfuric acid	Malic acid (0.1–0.7%) was the main organic acid in maple syrups. Trace levels of citric fumaric and succinic acids were also detected.	[11]
	2	Canada (Quebec)	High-performance liquid chromatography coupled with diode-array detection (HPLC-DAD)	Column: Restek Allure organic acid column (150 × 4.6 mm) Mobile phase: 100 mM potassium dihydrogen phosphate	Malic acid and fumaric acid levels ranged between 241.85–780.99 mg/100 g and 7.51–15.92 mg/100 g, respectively.	[25]
Phenolics	33	Canada (Ontario)	Modified Fast Blue BB salt method	Experiment procedure: 20 µL of 0.1% Fast Blue BB salt were added to 200 µL of sample. The mix was homogenized and 20 µL of 5% sodium hydroxide were added to each microplate well. Finally, absorbance was measured at 420 nm.	The darker syrups exhibited higher total phenolic contents than the lighter ones; that is, 872.147 µg/mL, 654.780 µg/mL and 415.111 µg/mL for the very dark, dark and amber ones, respectively.	[26]
	5	Canada (Quebec)	High-performance liquid chromatography with UV/Vis spectrophotometric detection (HPLC-UV/Vis)	Sample/extract preparation: Syrup samples (300 mL) were adjusted to pH 7. Three sequential extractions with ethyl acetate were performed. The organic phase that contained phenolics was recovered after all the extractions to be mixed with 100 mL of water to remove residual sugars. The organic phase was dried with anhydrous sodium sulfate and filtered. Finally, the extract was evaporated, dissolved in methanol and dried in nitrogen. Column: Varian analytic column C_{18} (7.8 × 300 mm; 5 µm) Mobile phase: Water/acetonitrile/formic acid (91/5/1, *v*/*v*/*v*)–water/acetonitrile/formic acid (69/30/1, *v*/*v*/*v*)	At the beginning of the season (0%), the total phenolics content in maple syrup was 63.81 g of the gallic acid equivalent (GAE) per 100 g of extract (g GAE/100 g). A significant decline occurred with a value of 17.81 g GAE/100 g up to 75% of the season. At the end of the season (100%), a marked increase took place with 59.41 g GEA/100 g.	[22]
	1	Canada (Ontario)	High-performance liquid chromatography coupled with diode-array detection (HPLC-DAD)	Sample preparation: Maple syrup samples (10 mL) were extracted by liquid-liquid extraction using ethyl acetate 3 times. The combined extracts were evaporated. The residue was dissolved in methanol/water (85:15) and filtered before the HPLC analysis. Column: Agilent Technology Eclipse Plus C_{18} (4.6 × 150 mm; 5 µm) Mobile phase: Methanol/acetonitrile (95:5)–0.05% aqueous formic acid.	The following phenolics were detected and identified from a medium-grade maple syrup: (1) Phenolic acids: (1.1) Benzoic acid and derivatives: (a) gallic acid; (b) 1-O-galloyl-β-D-glucose; (c) protocatechuic acid; (d) gentisic acid; (e) syringic acid; (f) vanillic acid; (g) γ-resorcylic acid); (1.2) Cinnamic acid derivatives: (a) p-coumaric acid; (b) 4-methoxycinnamic acid; (c) caffeic acid; (d) chlorogenic acid; (e) ferulic acid; (f) sinapic acid (2) Flavonoids: (a) catechin and (b) epicatechin; (c) kaempferol and its 3-O-β-D-glucoside (d); (e) 3-O-β-D-galactoside; (f) quercetin and its 3-O-β-(1)-glucoside (g); (h) 3-O-β-1-rhamnoside; (i) 3-O-rhamnoglucoside.	[31]

Table 2. *Cont.*

Inorganic Constituents	Studies					
	Samples		Technique	Analysis Details	Main Results	Refs.
	No.	Origin				
	1	Canada (Quebec)	High-performance liquid chromatography coupled with UV detection (HPLC-UV) Liquid chromatography coupled with mass spectrometry (LC-MS) Nuclear magnetic resonance (NMR)	Sample/extract preparation: Maple syrup was subjected to liquid-liquid partition with ethyl acetate. It was followed by n-butanol to obtain ethyl acetate and n-butanol extracts, respectively, after solvent evaporation. The butanol extract was further extracted with methanol to yield soluble and insoluble methanol fractions. (1) EtOAc extract: Analytical HPLC: Column: Phenomenex Luna C_{18} column (250 × 4.6 mm; 5 µm) Mobile phase: 0.1% aqueous trifluoroacetic acid–methanol (2) BuOH extract: Analytical HPLC: Column: Phenomenex LunaC$_{18}$ column (250 × 4.6 mm; 5 µm) Mobile phase: 0.1% aqueous trifluoroacetic acid–methanol (2.1) MeOH soluble fraction: Analytical HPLC: Column: Waters Sunfire C_{18} column (250 × 10 mm; 5 µm) Mobile phase: Different methanol/0.1% aqueous trifluoroacetic acid systems	The following phenolics were detected and identified from a very dark-grade maple syrup. (1) Lignans: (a) lyoniresinol [a]; (b) secoisolariciresinol [a]; (c) dehydroconiferyl alcohol [a]; (d) 5′-methoxy-dehydroconiferyl alcohol [a]; (e) *erythro* guaiacylglycerol-β-O-4′-coniferyl alcohol [a]; (f) *erythro*-guaiacylglycerol-β-O-4′-dihydroconiferyl alcohol [a]; (g) threo-guaiacylglycerol-β-O-4′-dihydroconiferyl alcohol [b]; (h) *erythro,erythro*)-1-[1-[2-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-1-[(5-hydroxymethyl)ethoxy]-3,5-dimethoxyphenyl]- 1,2,3-propanetriol [b]; (i) (*erythro,threo*)-1-[4-[2-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-1-(hydroxymethyl)ethoxy]-3-methoxyphenyl]-1,2,3-propanetriol [b]; (k) (*threo,threo*)-1-[4-[(2-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-1-(hydroxymethyl)ethoxy]-3-methoxyphenyl]-1,2,3-propanetriol [b]; (l) *erythro*-1-(4-hydroxy-3-methoxyphenyl)-2-[4-(3-hydroxypropyl)-2,6-dimethoxyphenoxy]-1,3-propanediol [b]; (m) 2-[4-[2,3-dihydro-3-(hydroxymethyl)-5-(3-hydroxypropyl)-7-methoxy-2-benzofuranyl]-2,6-dimethoxyphenoxy]-1-(4-hydroxy-3-methoxyphenyl)-1,3-propanediol [b]; (n) acernikol [a]; (o) leptolepisol D [b]; (p) buddleenol F [b]; (q) (1S,2R)-2-[2,6-dimethoxy-4-[(1S,3aR,4S,6aR)-tetrahydro-4-(4 hydroxy 3,5 dimethoxyphenyl) 1H,3H furo [3,4 c]furan-1-yl]phenoxy]-1-(4-hydroxy-3-methoxyphenyl)-1,3-propanediol [b]; (r) syringaresinol [b]; (s) isolariciresinol [b]; (t) icariside [a]; (u) sakuraresinol [b]; (v) [3-[4-[(6-deoxy-α-l-mannopyranosyl)oxy]-3-methoxyphenyl]methyl]-5-(3,4 dimethoxyphenyl)dihydro-3-hydroxy-4-(hydroxymethyl)-2(3H)-furanone [a]; (w) 5-(3′′,4′′ dimethoxyphenyl)-3-hydroxy-3-(4′-hydroxy-3′-methoxybenzyl)-4-(hydroxymethyl)dihydrofuran-2-one [a]. (2) Phenylpropanoids: (a) 1,2-dignaiacyl-1,3-propanediol [b]; (b) 2,3-dihydroxy-1-(3,4-dihydroxyphenyl)-1-propanone [b]; (c) 2,3-dihydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone [b]; (d) 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-one [a]; (e) dihydroconiferyl alcohol [b]. (3) Coumarins: (a) scopoletin [c]; (b) fraxetin [a]; (c) isofraxidin [b]. (4) Stilbene: (a) (E)-3,3′-dimethoxy-4,4′ dihydroxystilbene [a]. (5) Simple phenolics: (a) 2-hydroxy-3′,4′-dihydroxyacetophenone [c]; (b) 1-(2,3,4-trihydroxy-5-methylphenyl)ethanone [c]; (c) 2,4,5-trihydroxyacetophenone [c]; (d) 3′,4′,5′-trihydroxyacetophenone [a]; (e) 3,4-dihydroxy-2-methylbenzaldehyde [b]; (f) catechaldehyde [a]; (g) vanillin [a]; (h) syringaldehyde [a]; (i) gallic acid [a]; (j) trimethyl gallic acid methyl ester [a]; (k) protocatechuic acid [b]; (l) syringic acid [a]; (m) syringenin [a]; (n) (E) coniferol [a]; (o) tyrosol [b]; (p) C-veratroylglycol [a]; (q) catechol [a]; (r) 4-acetylcatechol [b]; (s) 4-hydroxycatechol [b]; (t) 4-(dimethoxymethyl)-pyrocatechol [b]. (6) Sesquiterpene: (a) phaseic acid [b]. (7) Non natural phenolic compound: 2,3,3-tri-(3-methoxy-4-hydroxyphenyl)-1-propanol [w] (not originally present in maple sap).	[20,38,39]

Table 2. *Cont.*

Inorganic Constituents	Samples		Studies			
	No.	Origin	Technique	Analysis Details	Main Results	Refs.
Vitamins	2	Canada (Quebec)	High-performance liquid chromatography coupled with diode-array detection (HPLC-DAD)	Column: Phenomenex Luna (250 × 4.6 mm; 5 µm) Mobile phase: 0.1% aqueous trifluoroacetic acid–acetonitrile	The riboflavin and niacin levels fell within the 290.45–410.26 mg/100 g range and the 7.13–9.83 mg/100 g range, respectively.	[29]
Volatiles						
Sulphur compounds	4 (Free of BF) + 3 (with BF)	Canada (Quebec)	Headspace solid-phase microextraction combined with gas chromatography–mass spectrometry (HS-SPME-GC-MS)	Sample preparation: A 1 g sample of maple syrup was weighed inside a 10 mL headspace amber vial. 1 mL of sodium chloride 6 M was added. Then the vial was sealed using a screw cap containing a septum. Chromatographic separation: Column: An agilent INNOWax capillary column (30 m × 0.25 mm; 0.25 µm)	Two new volatile sulfur compounds were detected: dimethyl disulfide and dimethyl trisulfide. The first molecule was related to an unpleasant taste in maple syrups.	[52]
Pyrazines	3	Canada (Quebec)	Gas–liquid chromatography (GLC)	Sample preparation: 100 g of sample were diluted with water (100 mL). pH was adjusted to 3. Then 30 mg of sodium chloride were added. The mixture was extracted with diethyl ether. This was subsequently followed by separating the aqueous phase, adjusting to pH 11 and extracting with dichloromethane. Finally, the extract was concentrated. Column: Supelcowax 10^{TM} fused silica (30 m × 0.32 mm; 0.1 µm)	The total pyrazine content in different maple syrup classes differed markedly, with "medium" grade maple syrups exhibiting the highest contents (68 ng/g), whilst "amber" grade syrups showed the lowest levels (48.89 ng/g).	[53]
	4	Canada (Quebec)	Headspace solid-phase microextraction combined with gas chromatography–mass spectrometry (HS-SPME-GC-MS)	Sample preparation: A 1 g maple syrup sample was weighed inside a 10 mL headspace vial. 1 mL of sodium chloride 6 M was added. The vial was sealed using a screw cap containing a septum. Chromatographic separation: Columns: Supelco Supelcowax 10 and Varian VF-5ms (both with 30 m × 0.25 mm; 0.25 µm).	27 pyrazines were identified, of which 15 were reported as flavor components. All the molecules were alkylpyrazines (except 2-methoxy-3-(1-methylethyl) pyrazine and tetramethylpyrazine).	[54]

BF—Buddy off-flavor; [a]—Compounds detected in the BuOH extract; [b]—Additional compounds detected in the EtOAc extract; [c]—Additional compound detected in the MeOH soluble faction of the BuOH extract.

Table 3. Detection of adulterants in maple syrups.

Adulterants	Samples		Studies			
	No.	Origin	Technique	Analysis Details	Main Results	Refs.
Beet and cane sugar	4 (A) – 10 (NA)	Canada (Quebec). The USA (Vermont)	Site-specific deuterium nuclear magnetic resonance (SNIF-NMR)	Sample preparation: Maple syrup samples were diluted with water and underwent a fermentation process. Ethanol was distilled and its extractive yield was calculated. Analysis: The ethanol analysis was performed by a high-field NMR spectrometer.	The $(D/H)_I$ value of the exogenous sugars-adulterated samples considerably differed from that of the pure maple syrups. More specifically, the $(D/H)_I$ parameter decreased when adding beet sugar to maple syrup at 1 mg/g for every 10% added sugar. It grew when cane sugar was added, specifically at 1 mg/g per 10% added sugar. One disadvantage of this method is that when it is applied to specific sugar beet, cane or corn mixtures, its sensitivity decreases, but this may be useful for combining it with the ^{13}C ratio measurement.	[55]
Beet and cane invert syrups Beet and cane sugar solutions	1 (A) + 4 (NA)	Canada (state not specified)	Fourier transform infrared (FTIR) and near-infrared (NIR) spectroscopy conjugated with a discriminant analysis, i.e., a canonical variate analysis (CVA), a linear discriminant analysis (LDA) and a quantitative analysis, i.e., partial least squares (PLS) and principal component regression analysis (PCRA)	Sample preparation: Pure maple syrup was adulterated with varying amounts of cane and beet invert syrups, and also with 60% beet and cane sugar solutions.	All in all, it is possible to detect adulterants like pure beet and cane sugar solutions by both NIR and FTIR, but FTIR outperforms NIR in detecting invert syrups.	[41]
Beet and cane sugar	231 (A) + 112 (NA)	Canada (Quebec). The USA (Vermont, Maine, New Hampshire, New York)	Stable carbon isotope ratio mass spectrometry ($\delta^{13}C$ IRMS)	Malic acid, an organic acid that is naturally present in maple syrups, was suggested to act as an internal isotopic standard to improve the adulteration LoDs. Sample preparation/malic acid isolation: Organic acids were isolated from maple syrup by lead precipitation. Malic acid was separated by means of preparative reversed-phase liquid chromatography. Column: Phenomenex Maxil C_{18} analytical column (250 × 21.21 mm; 5 µm); Mobile phase: Potassium dihydrogen phosphate adjusted to pH 2.4	The mean $\delta^{13}C$ of the maple syrup sample sugars was −24.07‰, while that of malic acid was −26.71‰, which agree with the stable carbon isotopic ratios characteristic of C_3 plants. The correlation between sugars and malic acid was good, i.e., $r = 0.34$. This proves that malic acid is an appropriate internal standard. A new calculation method was developed and applied to improve the decision limit of maple syrup adulteration according to the correlation between the $\delta^{13}C_{malic\ acid}$ and the $\delta^{13}C_{sugars}$-$\delta^{13}C_{malic\ acid}$ ($r = 0.704$). The theoretical LoD markedly lowered when this technique was applied compared to the usual two standard deviation (SD) method, particularly for the beet sugar-adulterated maple syrup (24 ± 12% vs. 48 ± 20%).	[16]

Table 3. *Cont.*

Adulterants	Studies					
	Samples		Technique	Analysis Details	Main Results	Refs.
	No.	Origin				
Cellulose gum	18 (A) + 7 (NA)	The USA (Vermont, New Hampshire)	Rheology	Viscosity analysis: A stepped ramp equilibrium flow test was performed. Studying the impact of cellulose gum on syrup rheological behavior: An oscillatory frequency sweep test was run.	The dynamic rheological method applied detected, with adequate sensitivity, changes in viscosity caused by the addition of polymers such as cellulose gum, wherefore this technique can be successfully employed to detect this type of adulteration.	[44]

A—Authentic; NA—Non-authentic (fraudulent or adulterated); LoD—Limit of detection.

3. Nutritional Profile and Health Impacts

Boiling maple sap concentrates carbohydrates and other elements, which is how maple syrup is made. The timing of collection affects the amounts of micronutrients, macronutrients and phenolics in maple sap, which result in variations in maple syrup [56]. Maple syrup is high in phytochemicals, macronutrients (sucrose) and micronutrients [7,11,57], and sucrose is its main component (96%), with a small amount of hexoses. Much lower concentrations of minerals, trace elements, organic acids, phytochemicals (lignan, stilbene, coumarin, phenolic compounds) and vitamins are found than in sugars [8,11,18,20,38,39,51,58]. St Pierre et al. [7] compared chemical maple syrup components to those of other natural sweeteners, including honey, molasses, blue agave syrup, brown rice syrup and golden corn syrup (abscisic acid [ABA], carbohydrates and phenolics). This research concluded that when compared to brown rice syrup, corn syrup, and pure dextrose, maple syrup significantly reduced the peak and total responses of glucose, insulin, amylin, and gastric inhibitory polypeptide (GIP). Molasses and agave syrup both had similar metabolic effects to maple syrup, however, honey increased the peak responses of insulin, amylin, and GIP. The elemental composition of maple syrup and the metabolic reactions to it in rats suggest that it is a healthy natural substitute for refined sugar.

Multiple bioactive compounds appear to be involved in the distinct flavor of maple syrup, such as carbonyl compounds [59,60], phenolics [61–63], pyrazines, alcohols, acids, and furan derivatives [53,54,59,60,64–66].

Apart from process-generated components, maple syrup often contains phytonutrients obtained from sap [8,11,20]. Maple syrup has been found to include vanillin, coniferyl alcohol, protocatechuic acid and syringic aldehyde [1]. Syrup extracts contain coniferaldehyde, vanillin, syringaldehyde, benzoic acid derivatives, cinnamic acid and flavonoids (flavonols) [63].

Thériault et al. [21], Legault et al. [67], Kamei et al. [68], Maisuria et al. [69] and Liu et al. [70] have found that maple sap and the phenolic-rich extracts of maple syrup perform antiproliferative, antiradical, antimicrobial, antimutagenic and antioxidant activities. From maple sap and syrup, Thériault et al. [21] identified aglycone phenolic and glycosylated molecules. Glycosylated sap/syrup components have stronger antioxidant and antiradical properties than aglycones. SOS induction suppression in *Salmonella typhimurium* TA1535/pSK1002 that contained fusion gene umuC-lacZ was used to investigate each chemical's antimutagenic activity. Glycosylated phenolic compounds' antimutagenic properties are optimal for 25% of the season for syrup and for 75% of the season for sap at different times of the year. Aglycones in sap present the greatest antimutagenic feature for 75% of the season, whereas aglycones in syrup do so for 25–100% of the season.

Li and Seeram [20] applied the DPPH (2,2-diphenyl-1-picrylhydrazyl) experiment to separate phenolics from MS-BuOH and to compare their antioxidant activities to a positive antioxidant control (butylated hydroxytoluene). Coumarins have stronger antioxidant capacity than stilbenes and lignans among isolated phenolics. Zhang et al. [25] investigated the biological activity and safety characteristics of maple syrup extract. In vitro, the extract demonstrated anti-inflammatory and antioxidant (DPPH test) properties, and inhibited glucose intake (by HepG2 cells). The study by Liu et al. [70] found that phenolics-enriched maple syrup extract (61.7 g/mL) scavenged ∼50% DPPH and decreased free radical production by 20% throughout the glycation process.

The biological effects of an organic phenolics-rich, sugar-reduced maple syrup extract employed as a new dietary component high in phenolics were studied by Nahar et al. [58]. With a lipopolysaccharide-stimulated RAW 264.7 murine macrophage cell model, anti-inflammatory MS-EtOAc activity and its purified isolates were investigated. MS-EtOAc reduced nitric oxide (NO) and prostaglandin E2 (PGE2) generation by lowering NO synthase (iNOS) levels, while upregulating the protein expression of cyclooxygenase 2 (COX-2) mRNA. The most effective inhibitor of PGE2 and NO was (E)-3,3′- Dimethoxy-4,4′- dihydroxystilbene. In a mouse model of Alzheimer's disease, a phenolics-enriched maple syrup extract presented anti-neuroinflammatory actions [71]. The expression of

several inflammatory proteins, including Alzheimer's disease risk-associated proteins, was reduced by maple syrup extract. The impact that maple syrup extract had on hepatic gene expression in mice on a high-fat diet has been reported by Kamei et al. [68] and Kamei et al. [72]. According to changes in the expression of the genes associated with lipid metabolism and immune response, maple syrup extract can help to attenuate hepatic inflammation in mice.

The antiproliferative effects of botj MS-EtOAc (Grades C and D) extracts and purified phenolics against non-tumorigenic (CCD-18Co) and human tumorigenic (HCT-116, HT-29, CaCo-2) colon cells have been investigated by González-Sarrías et al. [5]. Extracts MS-EtOAc, MS-BuOH and MS-MeOH proved more effective against tumorigenic colon cells than non-tumorigenic colon cells. The most active compounds were gallic acid, syringaldehyde, catechaldehyde and catechol, whose presence in Grade D MS-BuOH extract could explain its anticancer properties. Cancer apoptosis was not caused by extracts, but they did cause cell cycle arrest. The synergistic action of various phenolics might explain the high activity of MS-BuOH extract. González-Sarrías et al. [73] studied the anti-proliferative effects of ginnalins A-C on tumorigenic and non-tumorigenic colon (HCT-116) and breast (MCF-7) cells. Ginnalins A-C were twice as active against tumorigenic vs. non tumorigenic cells. This finding indicates that their selectivity for cancer cells is stronger. Ginnalin A was more active than ginnalins B and C. Maple phenolics may have a cancer chemopreventive effect via cell cycle arrest, as well as their direct cytotoxic effect. Yamamoto et al. [74] investigated the effects of dark-colored maple as a drug for gastrointestinal cancer therapy. It suppressed protein kinase B phosphorylation and further decreased cell proliferation by limiting protein kinase B activation. According to Yamamoto et al. [75], MS-EtOAc reduced cell proliferation, migration, and invasion in pancreatic cancer cells.

St-Pierre et al. [7] found several maple syrup components with health-promoting effects on glucose homeostasis. α-glucosidase inhibitory activity has been found in maple syrup phenolics [7,20,76]. ABA is a phytohormone in maple with promising anti-diabetic properties [7,77–80]. Furthermore, ABA has been shown to protect against Type-2 diabetes [78,80,81]. The impact of MS-EtOAc and MS-BuOH extracts on inhibiting carbohydrates by hydrolyzing enzymes (i.e., α-glucosidase) has been studied by Apostolidis et al. [82], where MS-BuOH exhibited more marked inhibitory action than EtOAc and was posed as a potential adjuvant with antihyperglycemics for Type-2 diabetes management. How phenolics-rich maple syrup extract affects Type-2 diabetes model mice has been evaluated by Toyoda et al. [81]. In Type-2 diabetic mice livers, treating rats with maple syrup extract inhibited fat accumulation by down and upregulating lipolysis hepatic enzymes and lipogenesis. The same research group [83] revealed how maple syrup extract can help with some dyslipidemia symptoms by another experiment.

In healthy rats, St-Pierre et al. [7] examined maple syrup metabolic reactions against other sweeteners. Dextrose corn syrup and brown rice syrup resulted in lower peak responses insulin, glucose, amylin, and gastric inhibitory polypeptide than maple syrup. Maple syrup's unique properties, plus metabolic reactions to its consumption in animals, indicate that it might be a healthy alternative to other sugars.

Dupuy and Tremblay [84] examined the effects that maple-sweetened beverages (sap or syrup) have on cognitive flexibility while practicing high-intensity exercise using a commercial sports drink, water, and glucose. The glycemic index of maple products was lower than the glycemic index of glucose alone.

Antimicrobial potential and a significant synergistic effect with various antibiotics were found in a phenolics-rich maple syrup extract against Gram-negative microorganisms (*Escherichia coli*, *Proteus mirabilis* and *Pseudomonas aeruginosa*). Catechol was effectively combined with antibiotics and other phenolics in a phenolics-rich maple syrup extract to inhibit microbial growth [70].

In summary, we would like to remark that, in addition to the main constituent sucrose, maple products also include phenolics, pyrazines, vitamins, minerals, organic acids, and

phytohormones. These bioactive substances have the potential to be valuable due to their positive impacts on health, such as their antioxidant, antiproliferative, and antimutagenic properties. It is proposed that quebecol, lariciresinol, and secoisolariciresinol serve as distinctive markers for maple products and are uncommon in syrups made from other plants [56].

4. Safety and Quality Control

4.1. Food Safety

Food safety is a key determinant in the quality of maple syrup, wherefore aspects related to it should be seriously considered. In particular, the risk of contamination with metals and toxic microorganisms, namely fungi [49,85] given the potential for occurrence of mycotoxins even at low water activity levels (aw) [86], which still needs to be investigated. Table 4 summarizes the main findings in terms of the occurrence of contaminants in maple syrup.

Table 4. Detection of contaminants in maple syrups.

Contaminants	Studies					
	Samples		Technique	Analysis Details	Main Results	Refs.
	No.	Origin				
Toxic metals	81	Canada (Nova Scotia, New Brunswick, Quebec)	Furnace atomic absorption spectrophotometry (FAAS)	Sample preparation: Syrup samples were diluted (1:50) and filtered prior to the analysis.	The Pb levels detected in the maple syrup samples ranged between 0.33 and 2.68 µg/mL.	[27]
	2	Canada (Quebec)	Inductively coupled plasma-mass spectrometry (ICP-MS)	Sample preparation: 10 mg of each sample were mixed with nitric acid, and digested in a microwave oven. Subsequently, the digested solutions were centrifuged. A 200 µL aliquot was further diluted to 10 mL with deionized water and analyzed.	Al levels were between 0.32 and 0.46 mg/100 g.	[25]
	8	Canada (state not specified). The USA (Vermont, Massachusetts, Maine, New York)	Inductively coupled plasma-mass spectrometry (ICP-MS)	Sample preparation: Digestion by closed-vessel microwave heating.	As, Cd, Pb and V levels varied between 1.3–7.1 ng/g, 1.5–49 ng/g, 18–367 ng/g and <1.1 [a]–187 ng/g, respectively.	[28]
Microorganisms	101	Canada (Quebec)	Plate count Adenosine triphosphate (ATP) bioluminescence	ATP bioluminescence: An assay based on exposing maple samples to the luciferase enzyme and its substrate luciferin was performed.	The maple syrups produced from the sap with higher ATP bioluminescence values were darker and had unpleasant flavors.	[48]
	183	Canada (Ontario)	Plate count Polymerase chain reaction (PCR)	Microbiological analysis: Syrup samples were inoculated in two media: Yeast Extract Sucrose (YES) agar and Dichloran Glycerol (DG18) agar. Distinct colonies were placed on 2% Malt Extract (ME) agar for further DNA extraction, and on ME and Czapek Yeast Extract (CYE) agars for identification purposes.	*Eurotium herbariorum* was the most prevalent fungus found in the maple syrup samples. It was followed by *Penicillium chrysogenum*, three *Aspergillus* species (*A. penicillioides*, *A. restrictus*, *A. versicolor*) and two *Wallemia* species (*W. muriae* and *W. sebi*). *Cladosporium cladosporioides* was also isolated.	[85]

[a]—LoD for V = 1.1 ng/g, LoD—Limit of detection.

4.2. Quality Control

As in other natural sweeteners obtained from vegetables, maple syrup is collected from maple sap trees in some regions of eastern Canada and northwestern USA (Figure 1). It being a seasonal product with given harvest dates means that it can be collected in about 35 days. Its characteristics depend on the production region where it is harvested, and it is affected by both the weather and its extraction process (boiling), performed to obtain the final syrup. For these reasons, Canadian and US maple syrup production can fluctuate yearly due to changes in the weather. The principal Canadian maple syrup production concentrates in the eastern province of Quebec. Therefore, Quebec is the leading maple

syrup producer in Canada, and has by far the most maple farms, taps and, as a result, the most maple syrup [87].

Quebec is the province with the highest maple syrup production levels in Canada, which leaves the second highest producing province, New Brunswick, far behind (Table 5). New Brunswick's production levels are the same as that of Vermont in the USA, which is by far the nation's biggest maple syrup producer, followed by New York (Table 5).

Although there are only four species of maple trees used to collect maple sap and to obtain maple syrup, there are actually over 150 maple tree species worldwide [88]. The more important producing species are *Acer saccharum* (70%) and *Acer rubrum* (29%). Nevertheless, other silver species, such as silver maple *Acer saccharinum* and black maple *Acer nigrum* (1%), can be considered as maple sap-producing species.

We briefly summarize the maple sap-producing description. Maple sap is normally collected in February-March when weather conditions make it easy to collect sap. This is done by boring holes in maple tree trunks. The encrusted tap permits sap to flow by pipelines to buckets. Sap is then concentrated by boiling it down into maple syrup [89]. For Canada, maple sup products (sugar and maple butter, maple syrup and taffy) are very interesting in economic and cultural terms because maple product exports have constantly increased and exported maple products now amount to more than 385 million Canadian dollars.

On the other hand, factors such as processing procedures, geographical and seasonal fluctuations, and microbiological contamination can impact maple syrup composition. The seasonal compositional changes in Nova Scotia syrup minerals are reported by Nimalaratne et al. [1], with K (2431–2547 mg/L), Ca (568–900 mg/L) and Mg (120–158 mg/L) being the main minerals, followed by Mn (15–20 mg/L), P (7–13.5 mg/L) and Zn (2.8–3.8 mg/L). Brix (61.6–70.2°) pH, color, and mineral content (2.6–4.8 g/L) vary depending on origin, but pH, sugars and Brix do not alter across seasons.

4.2.1. The Maple Syrup Quality Standard

Maple trees accumulate starch as they grow, which is converted into sugar during spring thaws and mixes with water absorbed by tree roots to create maple sap, which generally flows between February and April every year [90]. Producers employ tubing systems, RO, and high-performance evaporators to collect sap before boiling it down to obtain maple syrup. Canadian maple syrup products range from traditional maple syrup to maple butter, maple candy and maple sugar, plus a wide range of maple syrup-containing products.

Canadian maple syrup takes two grade names: "Canada Grade A" (further graded into four color classes– "Golden, Delicate Taste", "Amber, Rich Taste", "Dark, Robust Taste" and "Very Dark, Strong Taste"–that typically reach consumers and commercial markets); and "Canada Processing Grade", which has no color classes and is frequently applied to large-scale commercial applications [22]. In 2020, they harvested 13.2 million gallons. Thanks to favorable spring weather and more taps, higher yields account for more production. Prices in other maple-producing provinces are set by producers. As a result, they can substantially vary. Prices in Quebec are controlled by the Régie des Marchés Agricoles et Agroalimentaires du Québec. This organization helps to stabilize prices from year to year. In 2020, the price in Quebec remained at $38.55/gallon, and the total maple products value was $509.2 million [90]. Maintaining final product quality is most important. Thus, for economic performance to improve, the increase in maple farmers and maple taps denotes the profitability of such activities [68]. There are several quality guidelines for the production and commercialization of maple syrup from Canada and the US [91,92], but they are all generic guidelines for food safety without a focus on specific hazards.

4.2.2. Factors That Can Influence Final Maple Syrup Composition

Unlike other sugar sources, maple syrup has a unique characteristic flavor that depends on its composition, e.g., organic compounds (sugars, alcohols, ketones, aldehydes), micronutrients and phytochemicals, of which more than 200 compounds appear in maple

syrup that are either natural or are transformed during processing [13]. Hence this unique composition can be used for either detecting possible fraud and adulteration with other syrups of lesser quality, such as cane sugar, beet, and corn [13], or for confirming those classified according to strict Canadian and US regulations.

Thus, many essential and non-essential metals are present in maple sap, and their numbers may rise during maple sap concentration done by boiling [13]. Several studies have shown the utility of determining some essential elements, such as salt content, to be used in maple syrup characterization and for differentiating it from other syrups depending on the relation of these compounds.

Several authors, such as Lagacé et al. [49], have studied maple sap during different harvest periods to show variations in its organic composition: sugar (sucrose, fructose, and glucose), organics acid, and phenolic compounds. This means having to change some intrinsic factors, such as maple tree sap flowing in trunks. Moreover, other changes could modify its composition given the microbial maple sap population (fungi and total aerobics), which progressively increase during the season [9,93]. After maple sap is collected, it is contaminated by microorganisms, which are responsible for sucrose hydrolysis and the final presence of fructose and glucose in maple syrup [50].

Figure 1. Regions of maple syrup production in Canada and the USA according to the Maple Syrup Producers' Association of Ontario [94].

Table 5. Maple syrup production [95] per province (in thousands of gallons).

	Maple Sap Production							
Country	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**	**2021**	**2022**
Canada	8908	12,160	12,512	9796	13,204	14,294	11,311	
Quebec	8090	11,185	11,493	8914	12,033	13,210	10,027	15,949
New Brunswick	430	528	551	361	598	561	786	
Ontario	369	398	425	465	502	467	462	
USA	3204	4207	4271	4159	4240	4111	3721	5028
Vermont	1410	1990	1980	1940	2070	1950	1750	2550
New York	601	707	760	806	820	804	647	845

(1) Conversion factors: 1 gallon of syrup equals 10.0 pounds of maple sugar. One gallon of syrup weighs 13.24760 pounds. (2) 1 gallon US: 3.785 L.

5. Applications in the Food Industry and Sustainability Issues

Maple syrup comprises sugar, trace amounts of organic acids, free amino acids, protein, minerals, and phenolic compounds [11]. These trace components allow maple syrup's taste profile to be distinguished from that of sucrose. They are what contributes to its potential health benefits when compared to sucrose [96]. Maple syrup can be manufactured from a combination of corn syrup, maple coloring and flavoring. However, maple syrup in its natural state contains minerals like calcium and potassium, which may not be at the same levels when it is manufactured [97]. Pure maple syrup possesses specific standards for clarity, density, flavor, and color properties, along with descriptors that typically include woody, vanilla, caramel, floral, fruit and herbaceous [11,19].

When considering maple syrup applications as an ingredient in the food industry, the chemical analysis and nutritional profile of maple syrup are essential, as discussed in the previous Sections 2 and 3. A better understanding of the physico-chemical and microbiological analyses, organic and inorganic constituents, adulterants, and contaminants of maple syrup will help to ensure its uniformity and quality standards in the food industry.

According to the International Maple Syrup Institute, pure maple syrup has a small market share in the USA, Canada and elsewhere overseas. For example, in the USA, maple syrup, along with honey, represents 1% of all the sweeteners delivered for food and beverage uses [98]. Maple syrup is not only employed as a pancake topping, but its unique characteristics are mediated by bioactive compounds, which makes its suitable for several culinary and industrial applications.

Several other maple syrup applications are found in the food and beverages industry and have been paid some attention as part of the culinary education guide compiled by Kimball [99]. They include the following:

- Maple butter: It is thick, but spreadable, and is also called maple cream or spread. It is a whipped version of pure maple syrup;
- Clear maple: It begins as maple syrup. It is then altered by adding a processing aid, which is removed later to create higher invert sugar content. The resulting product is a product with a honey-like consistency made from pure maple syrup;
- Pure maple syrup concentrate: It is produced after removing almost 50% of the sucrose content in pure maple syrup;
- (Medium or coarse) maple flakes: They are made with pure maple syrup that has been dehydrated by means of a unique exclusive process;
- Maple jelly: It is made from pure maple syrup with a jelly-like structure and can be used for culinary purposes.
- Maple sugar: It is made from pure maple syrup by dehydration into granulated sugar crystals. It can be replaced at 1:1 with regular granulated sugar in the majority of formulae and recipes;
- Maple vinegar: It is produced from pure maple syrup by alcoholic fermentation and acetic fermentation processes. Adding maple vinegar creates a signature salad dressing.

Maple syrup can be employed in diverse menu items to sweeten tea, lemonade, regular coffee, and café lattes. Acorn squash or sweet potatoes can be glazed with maple syrup. Maple can be used to create a sweet and savory barbecue sauce, and drizzled on pears, walnuts, and gorgonzola pizzas. Baked maple-kissed goods, ice-cream and desserts can be prepared to gain a better taste. For a wider application, there is a need to utilize maple syrup on an industrial scale that will ensure that more consumers gain from its naturalness and health benefits.

Maple syrup processing mainly involves water removal to increase its viscosity. The main industrial processing techniques are based on conventional evaporation and reverse osmosis (RO), as described by Ramadan et al. [56].

The two processing methods shown in Figure 2 will have impacts on the quality characteristics of the obtained maple syrup. When comparing the two processes, evaporation can result in varying sensory attributes, such as color and flavor, while RO performed at room temperature does not change maple syrup's chemical properties [56]. The heating and

evaporation steps of maple sap are critical maple syrup processing stages. Flavor and color are essential factors that affect the maple syrup grade, which range from very dark-colored strong-flavored syrup to very light-colored delicate-flavored syrup [11]. Maple syrup flavor is also influenced by the regions where sugar maple trees grow. The amount of nitrogen compounds, phenolic compounds, flavonoids, and organic acids in maple sap may vary throughout the maple syrup season, and also from one season to the next, according to the region, and even from one maple tree to the next [99].

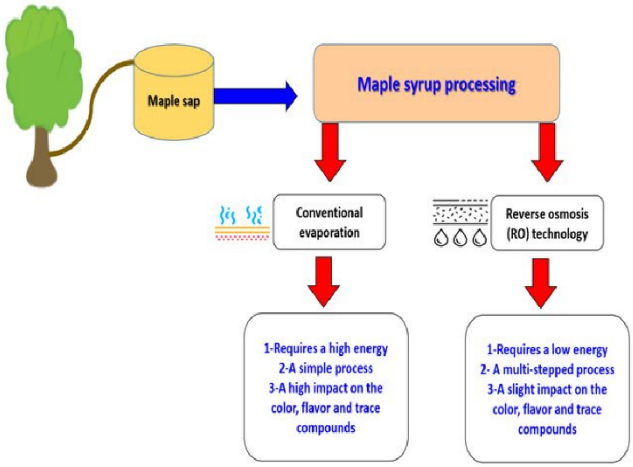

Figure 2. A comparison of the two processing methods to produce maple syrup (Adapted from Ramadan et al. [56]).

When comparing RO to conventional evaporation, which requires high energy use, RO can be used to concentrate maple sap to cut energy costs [100]. In industry, most RO techniques are extensive processes involving many steps [101]. To obtain 1 kg of maple syrup (68% sugar), 34 kg of maple sap (2% sugar) are required, plus conventional evaporation. Conversely, when RO concentrates maple saps up to 20%, only 3.5 kg of sap are necessary to obtain 1 kg of maple syrup [102].

It is crucially important to note that quality standards of the obtained maple syrup products are affected by the processing parameters; the phytochemical profile of these products will also influence flavor and color when they are considered for applications in the food industry. Recently, it was suggested that quebecol, lariciresinol, and secoisolariciresinol are distinct markers for maple products since they are not common in other plant-derived syrups [56]. Another significant limitation in the quest for further industrial application of maple syrup is microbial contamination of the maple sap which will affect maple product quality. The application of a continuous heat treatment on buddy syrups for 2 h at 104.5 °C was able to remove the buddy off-flavor by reducing the volatile dimethyl disulfide content in maple syrup which is responsible for this off flavor [52]. Henceforth, it is important to conduct further research on how processing techniques and environmental conditions affect the phytochemicals profile and biological effects of industrially produced maple food products.

With increasing climate change awareness, there is contention about evidence for a climate optimum for syrup production based on a standardized protocol for collecting sap from individual trees under natural conditions. There are indications that there will be shorter sap flow with warming winter temperatures if traditional tapping schedules are maintained [103]. Modeling the relations among climate, sap flow and sugar concentration

is necessary to gain an understanding of the basic eco-physiological responses underlying climate effects on syrup production [104]. As Duchesne and Houle [105], Collins et al. [106], and Bal et al. [107] misrepresented this, further research is necessary [104]. In Canada, producers must adhere to the strict standards and guidelines set by Canadian Law and the Federation throughout the maple syrup production process. It is important that the maple syrup value chain is sustainable. The role of maple syrup as a non-timber forest product, an alternative to extractive forest timber activities within the community will contribute to subsistence needs and help diversify and supplement rural incomes [108]. Generally, harvesting is carried out in such a way that sugar maple trees are tapped in a different area from that of the year before to preserve tree health. For instance, the Canadian "Preservation of Agricultural Land and Agriculture Activities Act" forbids felling a whole maple tree in an agricultural area [57]. While maple syrup demand as a natural and healthy sweetener alternative in the food industry increases, the entire value chain's sustainability is an important criterion from production to consumption.

6. Conclusions

This review explores the potential of maple syrup as a natural sweetener to be used in human diet. As consumers are showing considerable interest in demanding more natural ingredients in their food items, it critically examines maple syrup, along with its quality characteristics, and nutritional and health impacts. In fact, current scientific evidence indicates that phenolic compounds play a key role in the body's defense, protecting it from damage caused by reactive oxygen species known to be involved in the genesis of various pathologies, cardiovascular, oncological, autoimmune, degenerative, etc. That said, the potential of maple syrup, derived from *Acer saccharum* Marsh., as a source of nutrients and bioactive compounds is immense and deserves to be highlighted.

Therefore, the objective of this paper was to perform a global review on maple syrup as an interesting sweetener with application in the food sector. Furthermore, this review also aims to contribute to the improvement of food availability in a sustainable way and to provide also economic welfare. Finally, this sweetener can offer an important contribution for the development of new food products in the future and can contribute to decisive improvements in public health.

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3.3 ARTÍCULO Nº 3

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Review

Coconut Sugar: Chemical Analysis and Nutritional Profile; Health Impacts; Safety and Quality Control; Food Industry Applications

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Abstract: Consumers often wish to substitute refined sugar with alternative sweeteners, such as coconut sugar, given growing interest in healthy eating and the public's negative perception of excess sugar intake. Coconut sugar is a healthier, sweetener option than the majority of other sugars that are commercially available. Sap is collected from trees to be transported, stored, and evaporated during processing, which are labor- and resource-intensive operations. Consequently, the cost of production is higher than it is for cane sugar. Given its high nutritional value and low glycemic index, people are willing to pay higher prices for it. However, one barrier is ignorance of its health benefits. This review examines and deals in-depth with the most significant features of coconut sugar chemical analyses to focus on several analytical methodologies given the increasing demand for naturally derived sweeteners in the last 10 years. A deeper understanding of the quality control, safety, health effects, nutritional profile, and sustainability issues corresponding to coconut sugar is necessary to effectively implement them in the food industry.

Keywords: alternative sweeteners; coconut sugar; chemical analysis; health impacts; nutrition; food industry

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1. Introduction

In south/south-eastern Asian cuisine, coconut sugar is a popular sweetener [1] and is made of phloem sap from coconut palm tree (*Cocos nucifera* L.) blossoms [2]. Workers collect sap by scaling palm trees and use sickles to chop off unopened inflorescences. For 8–12 h, oozing sap is collected with bamboo or plastic containers. Lime is occasionally added to the sap to stop it from fermenting [3,4]. Next, the sap is heated on open flames and regularly shaken for it to thicken and crystallize [1]. During the production method, sugar color can range from light to dark brown. Finally, sugar is hand-selected and sieved to produce fine-grained produce [5].

One inflorescence is typically produced by each coconut palm tree once a month. Approximately 1.5 L of sap is harvested twice a day (morning and evening) from all the inflorescences. Based on the approximate 15 g of sugar per 100 g sugar content of fresh coconut sap, boiling sap allows 200 g of sugar per inflorescence to be produced daily [3,4].

Even at early ages, coconut palm trees can be utilized for sap collection purposes. Every time phloem sap is tapped and harvested, 1–2 mm of spadix must be cut away.

Spadix can be diminished to a stump by repeating this technique. Following this procedure, a single spadix can be tapped for 40–45 days. Coconut palm trees can be tapped for a 20-year period [1,3].

Due to the growing interest that the public is showing in healthy diet and the negative public perception of excess sugar use, consumers frequently attempt to substitute refined sugars for alternative sweeteners like coconut sugar [6]. Traders highlight coconut sugar's traditional small-farmer producers, organic palm tree growth in mixed farming with other crops, lower glycemic index (GI), and low fructose content than regular refined beet sugar or cane [7]. Coconut sugar has a premium price that consumers are willing to pay. One kilogram (kg) might cost something between €15 and €46. In contrast, the price of a kg of traditionally refined sugar was only €0.88 in 2021 [8].

Customers today are increasingly more aware of natural ingredients. Consumers' growing emphasis on naturalness has had a significant impact on the food industry [9,10]. Consumers in most nations often reject the food products that they do not perceive as natural. The demand for sweeteners made from natural sources has skyrocketed in recent decades [11].

In light of the above, the present review investigates the health effects and nutritional profile linked with consuming coconut sugar, its potential food industry applications and sustainability issues, and its primary safety–quality parameters, plus a chemical analysis of its major components.

2. Chemical Analysis

Food attributes like color, consistency, texture, flavor, and smell are extremely relevant for consumers and, consequently, for industry. In coconut sugar and syrup, these characteristics derive from the quality of the sap from which they are produced and the chemical reactions that occur during the heating process, namely non-enzymatic browning via caramelization and Maillard reactions (MR) [12]. The latter involves a highly complex reaction between reducing sugars and amino acids, and has major effects on coconut sugar and syrup properties, including their nutritional and functional value, color, aroma, and flavor [12–15]. Regarding flavor, the characteristics of MR products may vary from a pleasant flowery aroma to a burnt aroma in accordance with the sugar and amino acid compositions of the food matrix and the involved reaction pathways [13–16]. MR products, such as acrylamide and 5-hydroxymethylfurfural, have been directly linked with the degree of coconut sugar browning, and high levels of these products can lead to toxic health effects [13–17]. In this context, it is worth noting the study by Phaenon et al. [18] in which the level of acrylamide was determined in both coconut sap and coconut syrup, and, while in the first case this compound was not detected, the reported levels in the latter were of 867 µg/kg. Many MR products exhibit beneficial biological functions, such as potent antioxidant activity [13]. As a matter of fact, the coconut sugar and syrup production process generates hundreds of distinct MR products that are more or less desirable [19]. Bearing this in mind, it is easy to understand that coconut sugar and syrup are much more than merely a concentrated sugar solution, and the study of their chemical composition, which is fundamental to improve their nutritional and functional properties and to guarantee consumer safety, is a complex and demanding task.

Several research works have been conducted to evaluate the physico-chemical, microbiological, and antioxidant characteristics of coconut sap, sugar, and syrup. Some of the most important ones are presented in Table 1 and focus on the analytical techniques used and the main outcomes. Color determination, pH, and total soluble solids are some of the analyses routinely performed in coconut sap, sugar, and syrup. However, despite being fundamental for the quality control of these products, they provide limited means for more specific quality profile analyses and, hence, the need for more advanced analytical techniques arises.

Coconut sugar and syrup contain well over 100 different types of compounds, including carbohydrates, free amino acids, proteins, minerals, vitamins, aromatic compounds,

and phenolics. Table 2 provides an overview of some of the most recent studies carried out to assess the inorganic and organic compositions of coconut sap, sugar, and syrup. Atomic absorption spectroscopy (AAS) is the most commonly followed technique reported for mineral analyses. The main issue in determining mineral composition is the accurate quantification of these elements in a complex matrix, like that of coconut sugar or syrup, which has other components and at much higher levels (e.g., sugars), while dealing with the problem of interferences from mineral elements other than that being measured [20]. AAS is a technique with good detection limits. It is relatively simple to perform and incurs low to moderate acquisition and operation costs. It allows only a limited number of elements to be analyzed [19]. Other techniques like ICP-MS (inductively coupled plasma mass spectrometry) require costlier equipment and greater proficiency to operate, but stand out for having better detection limits and allow the quantification of many elements at ultra-trace concentrations in large numbers of samples. Therefore, they should be increasingly used [20]. For studying organic constituents, the non-volatile ones are analyzed mainly by high-performance and ultrahigh liquid chromatography (HPLC/UHPLC) coupled to different detectors (e.g., refractive index (RI), mass spectrometry (MS), UV-Vis), while volatile ones are determined mostly by GC–MS (gas chromatography coupled to mass spectroscopy) (e.g., [21–23]). Indeed, coupling a chromatography system (e.g., UHPLC/HPLC or GC) to a mass spectrometer is one of the most powerful ways to identify and quantify compounds because this analytical strategy provides two different types of data per run analysis: (i) retention time and (ii) mass spectral pattern (molecular ion and fragmentation), for each separated compound. This information can be used to make comparisons to appropriate reference standards or literature data [24].

As part of quality control, another critical aspect is the need to develop swift and accurate analytical methods for fraud detection. Like honey, agave syrup, and maple syrup, coconut sugar and syrup are prone to adulteration via the addition of less expensive exogenous sugars, such as cane sugar, beet sugar and corn sugar. In fact, the addition of a minor quantity of cane sugar, i.e., less than 5% w/v, to coconut sugar for "seed" purposes and to accelerate its crystallization is common and well-accepted in the industry [25]. The risk of fraud is a major issue given the important economic advantage of adding an extra amount of cane sugar or another inexpensive sugar [25]. Some of the most relevant analytical approaches recently proposed to combat this problem are presented in Table 3. Technologies like NMR (nuclear magnetic resonance) and IRMS (isotope ratio mass spectrometry) are noteworthy, as shown by the results obtained with the studies of Bachmann et al. [26] or Rogers et al. [25], respectively. NMR is a non-destructive technique that provides fast results and requires easy sample preparation. However, it implies using a large amount of sample to obtain an adequate signal [27]. IRMS, however, requires a considerably smaller amount of sample than in NMR analyses and displays 0.2‰ precision on the δ-scale [28]. One important limitation of IRMS is the fact that it only provides the global $\delta^{13}C$ values of the analyte [28]. Specifically, in the coconut sugar and syrup adulteration context, applying the IRMS tool involves a significant disadvantage because, although it is highly successful for detecting the addition of cane and corn sugar to coconut sugar and syrup, it does not allow the detection of beet sugar addition [18,29]. This is because coconut is a C3 plant-like beet, while cane and corn are C4 plants. The $^{13}C/^{12}C$ ratio of C3 plants is lower than that of C4 plants, and it is on this difference that the IRMS technique is based because it is impossible to detect admixtures of beet sugar with coconut sugar [29] Notwithstanding, both IRMS and NMR have a high potential, and their combined approach could shed considerable light on the food fraud and adulteration issue. Energy-dispersive X-Ray fluorescence (ED-XRF) is an alternative tool with a very high potential for detecting coconut sugar adulterations with both cane and beet sugars, as evidenced by Zdiniakova and Calle [29]. ED-XRF offers the excellent advantage of requiring almost no sample preparation and can be performed with portable devices, but has relatively high quantification limits [29,30]. That said, from an analytical point of view and despite important advances, there is still a lot of work to be done to gain fast

and eco-friendly methods that can be performed with portable devices and used by both consumers and producers quickly to easily detect adulterations.

In addition to food fraud, another aspect that cannot be neglected is food safety. Coconut sugar and syrup undoubtedly provide consumers with important nutritional and functional benefits when produced from high-quality sap that is properly collected, preserved, and processed, i.e., following good manufacturing practices (GMP). However, employing sap of inferior quality and its processing under unhygienic conditions are real problems that deserve our utmost attention because they pose the risk of contamination by insects and microorganisms (see Table 4). In this context, the dire need to carry out studies to determine the risk of other contaminants occurring is noteworthy. Research work on contaminants from food processing (acrylamide), agrochemicals (e.g., pesticide residues), heavy metals (e.g., mercury, lead, arsenic, cadmium, etc.), microorganism toxins (e.g., mycotoxins), and cleaning agents (e.g., detergents) or disinfectants (quaternary ammonium, detergents) has been increasingly performed in other natural sweeteners and sugar products, but is still almost nonexistent for coconut sugar and syrup.

Table 1. Physico-chemical, microbiological, and antioxidant characteristics of coconut sap, sugar, and syrup.

	Studies						
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Physico-Chemical Parameters							
Color	2 *	Coconut sap (collected by two different methods)	India (Kasaragod)	Sensory analysis	A panel of 50 evaluators used a 5-point hedonic scale.	The authors assessed the color attributes of the sap collected by (1) the traditional approach using a lime-coated clay pot; (2) a novel "coconut-sap chiller method". It was designed to collect fresh non-fermented sap free of foreign matter. The coconut sap collected by the traditional method was found to be oyster white, while that collected by the new method was golden brown.	[21]
	3 *	Coconut syrup (produced by three different methods)	Malaysia (Jelai)	Colorimetry	Outcomes were included in the CIELAB system: L* (lightness/darkness); a* (redness/greenness); b* (yellowness/blueness).	The authors investigated processing coconut sap in syrup by alternative processes compared to the conventional open heat evaporation technique. The L* parameter ranged from 23.84 to 35.61, a* from 2.31 to 3.746, and b* from 17.71 to 23.30.	[22]
	107 *	Coconut sugar	Indonesia, Philippines, and unknown origin	Sensory analysis	A descriptive test was carried out according to the official German methodology. For this purpose, a panel made up of 18 trained evaluators was selected.	The most expensive coconut sugars were light brown.	[17]
	6 *	Coconut sugar and coconut syrup	Philippines (Makati)	Colorimetry	Outcomes were included in the CIELAB system: L* (lightness/darkness); a* (redness/greenness); b* (yellowness/blueness).	The color of both coconut sugar and coconut syrup was evaluated for 6 months. For coconut sugar, the L* parameter ranged from 53.38 to 63.50, a* from 7.50 to 9.08, and b* from 24.02 to 28.28. For coconut syrup, L* ranged from 17.87 to 19.96, a* from 7.72 to 8.26, and b* from 1.44 to 1.67.	[31]

Table 1. *Cont.*

	Studies						
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Physico-Chemical Parameters							
Consistency and texture	107 *	Coconut sugar	Indonesia, Philippines, and unknown origin	Sensory analysis	A descriptive test was carried out according to the official German methodology. To do so, a panel made up of 18 trained evaluators was selected.	The more expensive products, i.e., those that were light brown, were characterized as fine powders, while the cheaper ones were described as being coarse-grained.	[6]
Smell	2 *	Coconut sap (collected by two different methods)	India (Kasaragod)	Sensory analysis	A panel made up of 50 evaluators used a 5-point hedonic scale.	The sap collected by the traditional method had a fetid smell, which was not detected in the sap collected by a novel "coconut-sap chiller method" that the authors put forward. It is noteworthy in the traditional method that the collection system is open. This allows the emission of volatile molecules by sap to attract insects like bees, which leads to sap contamination. As the method developed by the authors is a closed system, this contamination does not occur.	[21]
	107 *	Coconut sugar	Indonesia, Philippines, and unknown origin	Sensory analysis	A descriptive test was applied in accordance with the official German methodology. For this purpose, a panel made up of 18 trained evaluators was selected.	In cheaper coconut sugars, i.e., those with a darker color, the sweet aroma predominated, while the caramel aroma was particularly dominant in the expensive products.	[6]

Table 1. *Cont.*

	Studies						
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Physico-Chemical Parameters							
Flavor	2 *	Coconut sap (collected by two different methods)	India (Kasaragod)	Sensory analysis	A panel was made up of 50 evaluators who used a 5-point hedonic scale.	The flavor of the sap obtained by a novel "coconut-sap chiller method" was sweet and delicious, but that traditionally collected had a foul astringent aftertaste.	[21]
	107 *	Coconut sugar	Indonesia, Philippines, and unknown origin	Sensory analysis	A descriptive test was carried out according to the official German methodology. A panel made up of 18 trained evaluators was selected.	The coconut sugar flavor was described as mainly sweet. For the expensive products, i.e., those lighter in color, malty and caramel attributes were added.	[6]
pH	2 *	Coconut sap (collected by two different methods)	India (Kasaragod)	pH meter	NR **	The pH of the coconut sap collected by the traditional method was <6, whereas the sap collected by a new "coconut-sap chiller method" had a pH of 7–8. The sap collected by the novel method was fresh and non-fermented, but the traditionally collected sap was partially fermented.	[21]
	2 *	Coconut sap (with and without preservative, i.e., limestone solution)	Kemloko (Indonesia)	NR **	NR **	The pH levels of the fresh coconut sap, both with and without added preservative/s, were 4.26 and 4.68, respectively.	[32]
	6 *	Coconut sugar and coconut syrup	Philippines (Makati)	pH meter	NR **	The pH levels in coconut sugar and coconut syrup were evaluated over 6 months and ranged from 5.11 to 5.79 for the former, and from 4.28 to 4.45 for the latter. It should be noted that pH levels lowered in both products over time, which may be related to microbiological contamination.	[31]

Table 1. *Cont.*

	Studies						
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Physico-Chemical Parameters							
Density	2 *	Coconut sap (collected by two different methods)	India (Kasaragod)	Refractometry	A refractometer measured both total soluble solids and Brix values.	The soluble solids content was higher in the sap collected by a new "coconut-sap chiller method" proposed by the authors (15.5–18 [a]) compared to that determined in the sap collected by the conventional procedure (13–14 [a]). This might be owing to the metabolization of sugars in sap by the microorganisms found in it, which were detected in much larger numbers in the conventionally collected sap. [a]—Values expressed as °Brix.	[21]
	6 *	Coconut sugar and coconut syrup	Philippines (Makati)	Refractometry	A refractometer measured both total soluble solids and Brix values.	Brix was evaluated over 6 months for coconut sugar and syrup, and ranged from 97.6 to 98.9 for the former and from 79.6 to 80.3 for the latter.	[31]
Microbiological parameters	2 *	Coconut sap (fresh and 12-h fermented)	India (Kasaragod)	Metagenomic analysis	A culture-independent metagenomic methodology suitable for bacterial and fungal microbiome determinations with 16S rRNA and ITS amplicon sequencing, respectively, was used to perform the analysis of the fresh and fermented coconut sap.	The analysis of the microbiome of the fresh and fermented coconut sap revealed that the former presented a considerably larger number of bacterial species than the latter. In contrast, the fresh sap showed lower fungi and yeast diversity than the fermented sap. The fresh coconut sap displayed an abundance of *Leuconostoc* spp., followed by akin proportions of *Acetobacter* sp., *Fructobacillus* sp., and *Gluconobacter* sp. The fermented coconut sap exhibited a substantial increase in *Gluconobacter* sp. with a marked reduction in *Leuconostoc* spp. Regarding fungi and yeast occurrence, the fresh sap showed a predominance of species of the *Saccharomyces* genera and of *Hanseniaspora*. The fermented sap showed abundance for *Cortinarius saturnus* and *Hanseniaspora guilliermondii*.	[33]

Table 1. *Cont.*

	Studies						
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Physico-Chemical Parameters							
Antioxidant potential	3 *	Coconut sap (collected by two different methods) and coconut sugar	India (Kasaragod)	Colorimetry	FRAP (ferric-reducing antioxidant power) assay.	According to the FRAP assay, the values of the conventionally collected coconut sap, the coconut sap obtained by a novel "coconut-sap chiller method" and the coconut sugar generated from the latter were respectively 8.34 [a], 14.8 [a], and 22.9 [a] [a]—Values are expressed as mg of AEAC (ascorbic acid equivalent antioxidant capacity)	[21]
	2 *	Coconut sugar	Thailand (Samut Songkhram and Phetchaburi)	Colorimetry	The DPPH (2,2-Diphenyl-1-picrylhydrazyl) radical scavenging activity assay. The ORAC (oxygen radical antioxidant capacity) assay.	The DPPH free radical inhibition percentage and ORAC values ranged between 25.7–87.37 [a] and 740.7–3815.6 [b], respectively. [a]—Values shown as %; [b]—Values shown as mg of trolox equivalents (TE)/100 g.	[34]

* Total number of samples analyzed in the study; ** NR—Not reported.

Table 2. Chemical analyses of the organic and inorganic constituents of coconut sap, sugar, and syrup.

	Studies						
	Samples			Methodology	Analyiical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Inorganic constituents	9 *	Coconut sugar	Ivory Coast	Spectrometry	Sample preparation: Coconut sugar was incinerated until ash was obtained. Sample processing: The coconut sugar ash analysis was performed by (SEM).	The mineral levels in coconut sugar samples fell within the ranges of 101.77–128.95 [c] (K), 85.32–94.66 [c] (Cl), 7.96–16.28 [c] (Mg), 12.68–15.87 [c] (Si), 8.33–14.57 [c] (P), 5.58–13.17 [c] (S), 8.05–11.65 [a] (Na), 1.23–2.19 [c] (Cu), and 1.73–2.09 [c] (Fe). Traces—1.04 [c] (Br) and 0.17 [b] (Zn). [c]—Values expressed as mg/100 g.	[35]
	1 *	Coconut sap	Malaysia (Jelai)	FAAS (flame atomic absorption spectrophotometry)	Sample preparation: Coconut sap was first diluted (10×), then filtered and further analyzed.	The predominant minerals were K (960.87 [a]), Na (183.21 [a]) and Mg (22.91 [a]). The levels of Fe (1.36 [a]), Ca (0.42 [a]), Zn (0.338 [a]), Mn (0.105 [a]) and Cu (0.065 [a]) were also determined. [a]—Values expressed as mg/L.	[36]
	6 *	Coconut sugar and coconut syrup	Philippines (Makati)	Atomic absorption spectrophotometry (AAS)	NR **	The mineral composition of both coconut sugar and coconut syrup was evaluated for 6 months. For coconut sugar, the K, Na, and Fe ranges were 954–1075 [a], 99–112 [a], and 0.5–0.6 [a], respectively. The Ca and Zn levels remained constant over time and were 8 and 0.1 [a], respectively. For coconut syrup, the levels of K varied between 609–632 [a], Na between 110–126 [a], Ca between 1–2 [a], and Zn between 0.1–0.2 [a]. The Fe levels were 0.4 [a] at the three different measurement times. [a]—Values expressed as mg/100 g.	[31]
Organic constituents							
Non volatiles							

Table 2. *Cont.*

	Studies							
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Amino acids	3 *	Coconut sap (collected by two different methods) and coconut sugar	India (Kasaragod)	Ninhydrin method (for free amino acids quantification) UHPLC-TQD-MS/MS (ultrahigh performance liquid chromatography coupled to tandem quadrupole mass spectrometry) for the amino acids profile analysis	Amino acids profile: Sample preparation: Samples were hydrolyzed in a vacuum using hydrochloric acid, 6 M. Then, hydrolysates were dried (also in a vacuum) after neutralization. They were dissolved in a known volume of the mobile phase, filtered (0.2 um), and finally injected into the analytical system. Column: Waters UPLC BEH-C18 column (2.1 × 50 mm; 1.7 µm), protected by a Waters Vanguard BEH C-18 guard column (1.7 µm). Mobile phase: 0.1% formic acid in water-methanol: water (1:1) with 0.1% formic acid.	The total free amino acids content of the sap attained conventionally, the sap obtained from a "new coconut-sap chiller method", and the sugar produced from the latter was, respectively 0.413 [a], 1.03 [a], and 3.05 [b]. The following amino acids were quantified in the coconut sap obtained by the traditional method: (i) glutamic acid (39.9 [c]); (ii) aspartic acid (83.7 [c]); (iii) serine (64.5 [c]); (iv) alanine (16.2 [c]); (v) threonine (17.7 [c]); (vi) proline (13.1 [c]; (vii) arginine (11.9 [c]); (viii) lysine (7.81 [c]); (ix) valine (6.48 [c]); (x) citrulline (6.38 [c]); (xi) methionine (5.90 [c]); (xii) phenylalanine (2.14 [c]); (xiii) asparagine (0.86 [c]); (xiv) leucine (0.61 [c]); (xv) histidine (0.42 [c]); (xvi) tyrosine (0.29 [c]); (xvii) tryptophan (0.01 [c]). For the sap acquired by the novel method, amino acids and respective levels were as follows: (i) glutamic acid (6.26 [c]); (ii) aspartic acid (1.18 [c]); (iii) serine (58.1 [c]); (iv) arginine (17.3 [c]); (v) alanine (15.1 [c]); (vi) proline (14.6 [c]); (vii) threonine (12.2 [c]); (viii) methionine (6.28 [c]); (ix) valine (6.10 [c]); (x) citrulline (6.07 [c]); (xi) lysine (5.93 [c]); (xii) phenylalanine (2.56 [c]); (xiii) asparagine (2.41 [c]); (xiv) histidine (0.65 [c]); (xv) leucine (0.56 [c]); (xvi) tyrosine (0.16 [c]); (xvii) tryptophan (0.01 [c]). In turn, sugar contained (i) glutamic acid (39.4 [d]); (ii) aspartic acid (131 [d]); (iii) proline (112 [d]); (iv) alanine (84.5 [d]); (v) serine (78.0 [d]); (vi) lysine (64.5 [d]); (vii) threonine (59.1 [d]); (viii) arginine (33.7 [d]); (ix) valine (30.9 [d]); (x) phenylalanine (30.7 [d]); (xi) tyrosine (26.0 [d]); (xii) leucine (21.8 [d]); xiii) methionine (19.6 [d]); (xiv) histidine (5.83 [d]); (xv) citrulline (5.79 [d]); (xvi) asparagine (4.25 [d]); (xvii) 3,4-dihydroxy-phenylalanine (0.76 [c]); (xviii) tryptophan (0.18 [d]). [a]—Values appear as g/100 mL; [b]—Values appear as g/100 g; [c]—Values appear as mg/100 mL; [d]—Values appear as mg/100 g	[21]

Table 2. *Cont.*

	Studies						
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Carbohydrates	3 *	Coconut syrup (produced by three different methods)	Malaysia (Jelai)	HPLC-RID (high-performance liquid chromatography coupled with refractive index detection)	Sample preparation: Coconut syrup samples were diluted (10×), filtered (0.45 µm), and further analyzed. Column: Merck LiChroCART® Single bond NH_2 column (250 × 4.6 mm; 5 µm). Mobile phase: Acetonitrile-water (80:20, v/v).	The authors investigated the processing of coconut sap in syrup by alternative process techniques compared to the conventional open heat evaporation technique. The fructose, glucose, and sucrose levels respectively ranged between 18.27–35.07 [a], 21.38–23.71 [a], and 7.33–25.67 [a]. The coconut syrup obtained by the rotary evaporation technique displayed larger quantities of glucose and fructose, but a smaller quantity of sucrose, than that produced by the other techniques. The total sugar content for all the analyzed samples was between 64.89–65.66 [a]. [z]—Values expressed as %.	[22]
	1 *	Coconut sap	Malaysia (Jelai)	HPLC-RID (high-performance liquid chromatography coupled with refractive index detection)	Sample preparation: Coconut sap was diluted, (10×), filtered (0.45 µm), and further analyzed. Column: Merck LiChroCART® Single bond NH_2 column (250 × 4.6 mm; 5 µm). Mobile phase: Acetonitrile-water (80:20, v/v).	Three sugars (sucrose, fructose, glucose) were detected in coconut sap. Their respective values were 6.91 [z], 3.48 [z], and 2.33 [z]. [a]—Values expressed as %.	[36]
	3 *	Coconut sap (collected by two different methods) and coconut sugar	India (Kasaragod)	Phenol–sulphuric acid method (for total sugars content determination) Nelson-Somogyi's method (for reducing sugars content quantification)	NR **	The total sugars content of the sap acquired traditionally, the sap obtained following a new "coconut-sap chiller method", and the sugar produced from the latter was 9.20 [a], 16.2 [a], and 91.8 [b], respectively. For the reducing sugars content, the reported values were 1.24 [a] for the sap obtained conventionally, 0.68 [a] for the sap collected by the novel approach, and 4.69 [b] for sugar. [z]—Values shown as g/100 mL; [b] Values shown as g/100 g.	[37]

Table 2. *Cont.*

Studies							
Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
No.	Kind	Origin				
6 *	Coconut sugar and coconut syrup	Philippines (Makati)	GC–MS (gas chromatography-mass spectrometry)	NR **	The sugar composition of both coconut sugar and coconut syrup was evaluated for 6 months. For coconut sugar, the sucrose, glucose, fructose, and mannose levels ranged between 83.18–90.50 [a], 9.40–11.45 [a], 2.89–3.69 [a], and 0.51–3.90 [a], respectively. For coconut syrup, they varied between 35.85–38.96 [b], 10.74–14.03 [b], 15.39–15.57 [b], and 3.91–5.35 [b], respectively. [a]—Values expressed in mg/100 g.	[38]
4 *	Coconut sap (with and without preservative, i.e., limestone solution) and coconut sugar (with and without preservative)	Kemloko (Indonesia)	HPLC-RID (high-performance liquid chromatography coupled with refractive index detection)	Sample preparation: For each sample, 1 g was weighed, and then dissolved in 100 mL of distilled water. The mixture was filtered, and the solution was injected into the HPLC. system. Column: Amines HPX-87C. Mobile phase: Water.	For the fresh sap to which no preservative was added, lower sucrose content (1.76 [a]) and higher fructose (5.76 [a]) and glucose (4.46 [a]) contents were found compared to the sap with the preservative whose sucrose, fructose and glucose levels were 5.76 [a], 3.23 [a], and 2.25 [a], respectively. For coconut sugar, the sucrose content of that prepared with fresh coconut sap, but without adding a preservative, was lower (49.41 [a]) than that of coconut sugar produced with the fresh coconut sap to which a preservative was added (49.41 vs. 57.05 [a]). Their glucose (15.90 [a]) and fructose (14.15 [a]) levels were higher than those of the coconut sugar prepared from the fresh coconut sap to which a preservative was added; that is, glucose 6.97 [a] and fructose 5.45 [a]. [a] Values expressed in %.	[32]

Table 2. *Cont.*

Studies							
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Phenolics	3 *	Coconut sap (collected by two different methods) and coconut sugar	India (Kasaragod)	Folin's Ciocalteu method (for total phenolic content determination purposes) Ultrahigh performance liquid chromatography coupled with UHPLC-TQD-MS/MS (tandem quadrupole mass spectrometry) for the phenolic profile analysis	Phenolic profile: Sample preparation: The extraction of the individual phenolics was performed with 80% aqueous methanol (*v*/*v*). Thereafter, filtering the extracted sample was performed (0.2 µm). This sample was injected into the analytical system. Column: Waters UPLC BEH C18 column (2.1 × 50 mm; 1.7 µm) protected by a Waters Vanguard BEH C-18 guard column (1.7 µm). Mobile phase: 0.1% formic acid in water 0.2% formic acid in methanol	The total phenolics content of the sap acquired traditionally, the sap obtained by a novel "coconut-sap chiller method", and the sugar produced from the latter was 14.8 [a], 21.7 [a], and 47.2 [b], respectively. The following phenolic compounds were quantified in the coconut sap obtained by the traditional method: (i) vanillic acid (2.92 [c]); (ii) syringic acid (1.80 [c]); (iii) *trans*-cinnamic acid (0.636 [c]); (iv) *p*-hydroxy benzoic acid (0.308 [c]); (v) ferulic acid (0.502 [c]); (vi) protocatechuic acid (0.182 [c]); (vii) 2,4-dihydroxy benzoic acid (0.126 [c]); (viii) gentisic acid (0.104 [c]); (ix) gallic acid (0.073 [c]); (x) *o*-coumaric acid (0.064 [c]); (xi) rutin (0.043 [c]); (xii) caffeic acid (0.042 [c]); (xiii) salicylic acid (0.010 [c]); (xiv) umbelliferone (0.030 [c]); (xv) *p*-coumaric acid (0.008 [c]). Regarding the sap collected by the new method, the identified phenolics were as follows: (i) vanillic acid (3.54 [c]); (ii) *trans*-cinnamic acid (2.40 [c]); (iii) *p*-hydroxy benzoic acid (0.963 [c]); (iv) syringic acid (0.707 [c]); (v) salicylic acid (0.477 [c]); (vi) ferulic acid (0.246 [c]); (vii) catechin (0.157 [c]); (viii) quercetin (0.156 [c]); (ix) hesperetin (0.116 [c]); (x) myricetin (0.105 [c]); (xi) caffeic acid (0.103 [c]); (xii) rutin (0.078 [c]); (xiii) protocatechuic acid (0.065 [c]); (xiv) *o*-coumaric acid (0.062 [c]); (xv) umbelliferone (0.036 [c]); (xvi) gallic acid (0.044 [c]); (xvii) *p*-coumaric acid (0.030 [c]); (xviii) gentisic acid (0.026 [c]); (xix) 2,4-dihydroxy benzoic acid (0.015 [c]). In sugar: (i) vanillic acid (12.8 [d]); (ii) benzoic acid (9.41 [d]); (iii) *trans*-cinnamic acid (4.25 [d]); (iv) catechin (2.37 [d]); (v) *p*-hydroxy syringic acid (1.96 [d]); (vi) *p*-coumaric acid (1.27 [d]); (vii) ferulic acid (0.908 [d]); (viii) *o*-coumaric acid (0.706 [d]); (ix) salicylic acid (0.653 [d]); (x) myricetin (0.390 [d]); (xi) hesperetin (0.327 [d]); (xii) quercetin (0.313 [d]); (xiii) apigenin (0.230 [d]); (xiv) protocatechuic acid (0.224 [d]); (xv) gallic acid (0.203 [d]); (xvi) rutin (0.192 [d]); (xvii) gentisic acid (0.111 [d]); (xviii) caffeic acid (0.109 [d]); (xix) umbelliferone (0.078 [d]); (xx) 2,4-dihydroxy benzoic acid (0.037 [d]). [a]—Values are mg of gallic acid equivalents (GAE)/100 mL; [b] Values are mg of GAE/100 g; [c]—Values are mg/100 mL; [d]—Values are mg/100 g.	[21]

Table 2. *Cont.*

	Studies						
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
Vitamins	1 *	Coconut sap	Malaysia (Jelai)	HPLC/UV-Vis (high-performance liquid chromatography coupled with ultraviolet-visible detection)	Sample preparation: Coconut sap was diluted (10x), filtered, and further analyzed. Column: Agilent Poroshell 120 EC column (100 × 4.6 mm; 4 µm). Mobile phase: Potassium dihydrogen phosphate buffer (pH 3.4, 50 mM).	Vitamins C, B1, B2, B3, B4, and B10 were all detected in coconut sap. Their levels were 116.19 [a], 4.33 [a], 0.084 [a], 1.88 [a], 0.53 [a], and 0.53 [a], respectively. [a]—Values expressed as µg/mL.	[36]
	3 *	Coconut sap (collected by two different methods) and coconut sugar	India (Kasaragod)	6-Dichlorophenol-indophenol (DCPIP) method for vitamin C level measurements (ultrahigh performance liquid chromatography coupled to tandem quadrupole mass spectrometry) for the quantification of other vitamins	Sample preparation: Water-soluble vitamins: Samples were extracted with 10 mM ammonium acetate:methanol 50:50 (*v*/*v*) that contained 0.1% butylhydroxytoluene and centrifuged. Next, the supernatant was (0.2 µm) filtered and injected into the analytical system. Fat-soluble vitamins: The residue from the previously described extraction (please refer to "water-soluble vitamins") was re-extracted with ethyl acetate that contained 0.1% butylhydroxytoluene, centrifuged and filtered (0.2 µm) before being injected into the analytical system. Column: Waters UPLC BEH-C18 column (2.1 × 50 mm; 1.7 µm) protected by a Waters Vanguard BEH C-18 guard column (1.7 µm). Mobile phase: Water-soluble vitamins: 0.1% formic acid in water-acetonitrile. Fat-soluble vitamins: Acetonitrile—0.2% formic acid in methanol.	The following vitamins were detected and quantified in the coconut sap obtained by the traditional method: (i) vitamin C—16.3 [a]; (ii) B1—0.021 [c]; (iii) B3—11.4 [c]; (iv) B5—1.64 [c]; (v) B6—1.32 [c]; (vi) B7—0.095 [c]; (vii) B9—0.031 [c]; (viii) D2—0.028 [c]; (ix) D3—0.062 [c]; (x) E—2.94 [c]; (xi) K1—0.601 [c]; (xii) K2—0.428 [c]. For the sap collected by a new "coconut-sap chiller method", the vitamins and their respective levels were as follows: (i) vitamin C—19.6 [a]; (ii) B1—0.068 [c]; (iii) B3—14.9 [c]; (iv) B5—3.99 [c]; (v) B6—2.33 [c]; (vi) B7—0.073 [c]; (vii) B9—0.036 [c]; (viii) D2—0.074 [c]; (ix) D3—0.056 [c]; (x) E—7.20 [c]; (xi) K1—1.73 [c]; (xii) K2—0.771 [c]. Sugar contained (i) vitamin C—3.98 [b]; (ii) B1—14.3 [d]; (iii) B2—0.248 [d]; (iv) B3—34.7 [d]; (v) B5—2.53 [d]; (vi) B6—1.01 [d]; (vii) B7—2.51 [d]; (viii) B9—0.260 [d]; (ix) D2—0.171 [d]; (x) D3—0.256 [d]; (xi) E—19.6 [d]; (xii) K1—7.35 [d]; (xiii) K2—5.37 [d]. [a]—Values are given as mg/100 mL; [b]—Values are given as mg/100 g; [c]—Values are given as ng/100 mL; [d]—Values are given as µg/100 g.	[21]

Table 2. *Cont.*

	Studies						
	Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
	No.	Kind	Origin				
	6 *	Coconut sugar and coconut syrup	Philippines (Makati)	2,6-Dichloroindophenol titrimetric method	NR **	Vitamin C levels in both coconut sugar and coconut syrup were evaluated over 6 months and ranged from 16 to 44 [a] for the former, and from 19 to 30 [a] for the latter. [a]—Values expressed as mg/100 g.	[31]
Volatiles							
Aliphatic/aromatic hydrocarbons, ketones, aldehydes, alcohols, esters, fatty acids, furans, pyrazines, pyrans and sulfur-containing compounds.	3 *	Coconut sap (fresh, clarified, and fermented)	India (Mandakalli)	GC–MS (gas chromatography-mass spectrometry)	Isolated volatiles: Volatile compounds were isolated by the SDE (simultaneous distillation-extraction) method with a Likens-Nikerson apparatus. The extractive solvent was dichloromethane. GC–MS: Column: Supelco-fused silica column SPB-1 (30 m × 0.32 mm; 0.25 µm) coated with polydimethyl siloxane. Gas carrier: Helium.	The following 21 compounds were identified in the fresh coconut sap: (i) palmitic acid (2024 [a]); (ii) palmitoleic acid (1042 [a]); (iii) ethyl lactate (560 [a]); (iv) phenyl ethyl alcohol (337 [a]); (v) 3-hydroxy-2-pentanone (236 [a]); (vi) tetradecane (167 [a]); (vii) farnesol (125.3 [a]); (viii) 2-methyl tetrahydrofuran (115 [a]); (ix) tetradecanone (104.5 [a]); (x) tetradecanoic acid (94.0 [a]); (xi) nonanoic acid (84.8 [a]); (xii) dodecane (74.3 [a]); (xiii) dodecanoic acid (52.6 [a]); (xiv) hexanoic acid (49.8 [a]); (xv) pentadecane (48.4 [a]); (xvi) 2-hydroxy-3-pentanone (45.6 [a]); xvii) nerolidol (44.9 [a]); (xviii) hexadecane (37.2 [a]); (xix) 1-hexanol (27.3 [a]); (xx) hexadecanone (25.9 [a]); (xxi) tridecanone (24.5 [a]). For the clarified coconut sap, 13 compounds were identified, which were as follows: (i) palmitic acid (342 [a]); (ii) ethyl lactate (300 [a]); (iii) phenyl ethyl alcohol (195 [a]); (iv) palmitoleic acid (141 [a]); (v) 3-hydroxy-2-pentanone (75.9 [a]); (vi) hexanoic acid (54.7 [a]); (vii) tetradecane (46.9 [a]); (viii) 2-methyl tetrahydrofuran (45.4 [a]); (ix) dodecane (30.5 [a]); (x) 1-hexanol (24.8 [a]); (xi) pentadecane (21.8 [a]); (xii) hexadecane (16.4 [a]); (xiii) 2-hydroxy-3-pentanone (14.0 [a]). In the fermented coconut sap, 11 compounds were identified, namely as follows: (i) palmitoleic acid (14,603 [a]); (ii) isoamylalcohol (7467 [a]); (iii) ethyl lactate (4636 [a]); (iv) phenyl ethyl alcohol (1189 [a]); (v) palmitic acid (2421 [a]); (vi) dodecanoic acid (1084 [a]); (vii) ethyl caprate (797 [a]); (viii) ethyldodecanoate (709 [a]); (ix) tetradecanoic acid (597 [a]); (x) ethyl caprylate (503 [a]); (xi) farnesol (224 [a]). [a]—Values expressed as µg/L.	[12]

Table 2. *Cont.*

Studies						
Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
No.	Kind	Origin				
6 *	Coconut sap, coconut syrup and coconut sugar	Indonesia (Blitar)	Gas chromatography—mass spectrometry (GC–MS)	Isolated volatiles: Volatile compounds were isolated by a simultaneous distillation–extraction (SDE) method using a Likens–Nikerson apparatus. The extractive solvent was diethylether. GC–MS: Column: CBP-5 column (50 m). Gas carrier: Helium.	Five volatiles were isolated in the fresh coconut sap: (i) 2-butanol (60.26–68.37 [a]); (ii) acetic acid (25.83–30.43 [a]); (iii) 2-methylcyclohexane (0.66–6.39 [a]); (iv) cyclohexyloctane (1.81–4.23 [a]); (v) 1,4 dimethyl-6,1-butyl acetate (0.91–1.11 [a]). For coconut syrup, the following occurred: (i) 2-butanol (45.35–51.02 [a]); (ii) acetic acid (24.56–6.47 [a]); (iii) dodecanoic acid (0.34–21.59 [a]); (iv) 2-furan (1.97–6.73 [a]); (v) cyclohexane (3.56–4.41 [a]); (vi) 1,4 dimethyl-6,1-butyl acetate (0.40 10.26 [a]); (vii) 4,6 dimethyl-5-cyclo-hexo pyrimidine (0–2.25 [a]); (viii) 2,3 dimethylpirazine (0–0.77 [a]). Finally for coconut sugar, the following compounds were identified: (i) acetic acid (21.54–35.05 [a]); (ii) 2-butanol (29.98 31.23 [a]); (iii) 1,4 dimethyl-6,1-butyl acetate (1.7–13.50 [a]); (iv) N,N dimethyl 2-(diphenylmetoxi)-ethylamine (9.31–13.26 [a]); (v) cyclohexyloctane (0.0–17.01 [a]); (vi) dodecanoic acid (0.0–12.41 [a]); (vii) methylpyrazine (1.46–1.81 [a]). [a]—Values expressed as %.	[37]
1 *	Coconut sugar	Thailand (Samutsongkhram)	GC–MS (gas chromatography-mass spectrometry) GCO (gas chromatography-olfactometry)	Isolated volatiles: Volatile compounds were extracted three times with diethyl ether. The combined extract was left to concentrate in a Vigreux column. Then, the concentrated extract was subjected to high vacuum distillation and then concentrated, first in a Vigreux column and finally in a nitrogen flow. GC–MS: Column: Restek Stabilwax column (30 m × 0.25 mm; 0.25 µm) and an Agilent DB-5MS column (30 m × 0.25 mm; 0.25 um). Gas carrier: Helium. Descriptive sensory analysis: The sensory evaluation panel included nine properly trained evaluators.	The following volatile compounds were identified in coconut sugar: (i) acetic acid [a]; (ii) 2,3-pentanedione; (iii) acetoin; (iv) 2,3-dimethyl pyrazine; (v) 2,3-butanedione; (vi) methional; (vii) furfural; (viii) 5-methyl furfural; (ix) 2-furanmethanol; (x) 4-methyl-5H-furan-2-one; (xi) 5-methyl-2-furan methanol; (xii) benzylalcohol; (xiii) maltol [3-Hydroxy-2-methyl- 4H-pyran-4-one]; (xiv) Furaneol® [2,5-dimethyl-4-hydroxy-3(2H)-furanone]; (xv) vanillin [4-Hydroxy-3-methoxybenzaldehyde]. The sweet, roasted, burnt, nutty, smoky, and caramel notes of coconut sugar were attributed mostly to pyrazine, furan, and pyran derivatives being present. Benzyl alcohol and vanillin also introduce sweet notes. In addition, acetoin, 2,3-pentanedione and 2,3-butanedione were found to be responsible for the buttery, cheesy, and creamy aromas. [a]—Major component identified; values not reported.	[38]

Table 2. *Cont.*

Studies						
Samples			Methodology	Analytical Details	Principal Outcomes	Ref.
No.	Kind	Origin				
2 *	Coconut sugar	Thailand (Ampawa)	GC–MS (gas chromatography–mass spectrometry)	Isolated volatiles: Volatile compounds were extracted by SPME (solid-phase microextraction). GC–MS: Column: An Agilent DB-624 capillary column (30 m × 0.25 mm). Gas carrier: Helium.	The identified volatile compounds were as follows: (i) 2,3-diethyl-5-methyl pyrazine; (ii) 2,3-dimethyl pyrazine; (iii) 2,5- dimethyl pyrazine; (iv) 2-ethyl-3,5-dimethyl pyrazine; (v) 2-methyl pyrazine; (vi) ethyl pyrazine; (vii) 5-methyl furfural; (viii) furfural.	[12]
2 *	Coconut sugar	Thailand (Samut Songkhram and Phetchaburi)	GC–MS (gas chromatography–mass spectrometry)	Isolated volatiles: Volatile compounds were isolated by means of headspace gas chromatography. GC–MS: Column: An Agilent DB wax-fused silica capillary column (60 m × 0.25 mm; 0.25 um). Gas carrier: Helium.	The detected volatile components comprised the following: (i) ethanol (9.48–52.21 [a]); (ii) 4-methanol (19.58–27.85 [a]); (iii) acetaldehyde (<0.01–16.33 [a]); (iv) 2-furanmethanol (<0.01–13.54 [a]); (v) acetic acid (<0.01–11.98 [a]); (vi) 1-hydroxy-2-propanone (<0.01–10.24 [a]); (vii) acetone (2.63–9.98 [a]); (viii) 2-ethyl-3,6-dimethyl pyrazine (<0.01–6.46 [a]); (ix) 2-propanol (2.29–4.37 [a]); (x) hexanoic acid (<0.01–2.93 [a]); (xi) 3-methyl hexanal (<0.01–2.35 [a]); (xii) 2-furaldehyde (<0.01–1.48 [a]); (xiii) hydroxy-2-butanone (0.01–1.10 [a]); (xiv) butanoic acid (<0.01–1.01 [a]); (xv) 2-methyl propanal (0–0.91 [a]); (xvi) 3-(methylthio)-propanal (<0.01 [a]); (xvii) 2,3-butanedione (<0.01 [a]); (xviii) 2-methyl-3-buten-2-ol (<0.01 [a]); (xix) 2-methyl-1-propanol (<0.01 [a]); (xx) 2-ethyl-5-methyl pyrazine (<0.01 [a]); (xxi) 3-methyl-butanol (<0.01 [a]); (xxii) 2-acetylfuran (<0.01 [a]). [a]—Values expressed as %.	[34]

* Total number of samples analyzed in the study; ** NR—Not reported.

Table 3. Detecting adulterants in coconut sap, sugar, and syrup.

Adulterants	Works						
	Samples			Methodology	Analytical Details	Principal Outcomes	Refs.
	No.	Kind	Origin				
Cane and beet sugar	21 *	Coconut sugar	NR **	^{1}H NMR (proton nuclear magnetic resonance). ULPC-Q-TOF-MS (ultraperformance liquid chromatography quadrupole time-of-flight mass spectrometry). MRA (multivariate regression analysis).	^{1}H NMR: Sample preparation: To identify polar minor metabolites, 500 mg of every sugar sample were dissolved in 1 mL of deuterium oxide to be vortexed. Then, a 600 µL aliquot was placed inside an NMR tube to be analyzed. To study the non-polar extracts, 1 mL of chloroform-*d* was added to 500 mg of all the coconut sugars. Then, suspensions were vortexed and centrifuged. Finally, a 600-µL aliquot of the supernatant was placed inside an NMR tube. Analysis: Spectra were recorded at 300 K. UPLC-Q-TOF-MS: Sample preparation: Of each sample, 1 g was dissolved in 20 mL of water and the solution was filtered (0.20 µm). A 2-µL aliquot of this filtrate was diluted (10x) to be then injected into the analytical system. Column: Waters HSS T3 C-18 column. Mobile phase: 15 mM acetic acid, 10 mM tributylamine, 5% (*v*/*v*) methanol-2-propanol.	Pyroglutamic acid has been identified as a unique marker for coconut sugar. Additionally, coconut sugars exhibited substantially higher levels of acetic, formic, lactic, and succinic acids than both cane and beet sugars. *Trans*-aconitic acid was shown to be a marker for cane sugar, as was betaine for beet sugar.	[26]
	11 *	Coconut sugar	Indonesia and unknown origin	Energy-dispersive X-ray fluorescence Soft independent modeling of class analogies (SIMCA)	Sample preparation: First, samples were ground, and pellets were prepared. To do so, 5 g of sugar needed to be mixed with 1 g of wax. Energy-dispersive X-ray fluorescence: The irradiation time (s) was 200 for Ca, Cl, Cu, Fe, K, P, and S, and 500 for Br, Rb, and Sr. Analytical parameters: LOQ *** (mg/Kg): 1.7 Br; 118.4 Ca; 78 Cl; 1.2 Cu; 4.6 Fe; 566 K; 171 P; 4.2 Rb; 1.19 Sr. Precision (%): 22 Br; 3.5 Ca; 2 Cl; 10.5 Cu; 6.5 Fe; 3 K; 6 P; 5 Rb; 8 Sr.	This research work established the mass fractions of Br, Ca, Cl, Cu, Fe, K, P, Rb, S, and Sr in the coconut, cane, and beet sugar samples. On average, all the aforementioned elements had significantly bigger mass fractions in coconut sugars than in cane and beet sugars.	[13,20,30]

Table 3. *Cont.*

Adulterants	Works						
	Samples			Methodology	Analytical Details	Principal Outcomes	Refs.
	No.	Kind	Origin				
Cane and corn sugar	109 *	Coconut sugar	Indonesia (Central Java)	δ^{13}C IRMS (stable carbon isotope ratio mass spectrometry).	Sample preparation: First, 300 mg of all the coconut sugar samples were dissolved in 5 mL of deionized water in centrifuge tubes. Tubes were then immersed in warm water inside an ultrasonic bath (15 min). Then, solutions were (0.45 µm) filtered and a 10-uL aliquot was transferred to tin capsules, which were dried at 40 °C. Finally, capsules were crimped and subjected to double encapsulation prior to the analysis. Carbon isotope analysis: An isotope ratio mass spectrometer interfaced with an elemental analyzer (EA-IRMS) in the continuous flow mode for δ^{13}C measured isotopes.	The genuine coconut sugar exhibited an average δ^{13}C value of −25.6‰ ± 0.4‰. More positive δ^{13}C values (> −24.8‰) indicate the addition of C4 sugar, i.e., cane or corn sugar/syrup. More negative δ^{13}C values (<−26.4‰) should be related to the use of additives. On the whole, the authors propose a maximum acceptable δ^{13}C value of −24.1‰ for authentic coconut sugars.	[25]

* Total number of samples analyzed in the study; ** NR—Not reported; *** LOQ—Limit of quantification.

Table 4. Detecting contaminants in coconut sap, sugar, and syrup.

Contaminants	Works						
	Samples			Methodology	Analytical Details	Principal Outcomes	Refs.
	No.	Kind	Origin				
Insects	NR **	Coconut sugar	NR **	NR **	NR **	The United Kingdom food safety authorities have reported the occurrence of insect fragments (500–800) in coconut sugar commercialized in the country.	[39]
Microorganisms	2 *	Coconut sap (collected by two different methods)	India (Kasaragod)	Serial dilution, plus, the spread plating method	Microbial analysis: The employed culture media were Nutrient agar, Martin Rose Bengal agar, Sabouraud Dextrose agar, and KenKnight & Munaiers agar, respectively, for bacteria, fungi, yeasts, and actinomycetes. Differing sample dilutions were plated in the respective medium and incubated at 28 °C. Bacteria and yeast colonies were scored as colony-forming units (CFU)/mL of sap after a 24-h incubation period, fungi/yeasts after 48–72 h, and those of actinomycetes after 1 week.	The conventionally collected coconut sap exhibited an extremely large number of bacteria and yeasts. In contrast, the sap collected by a new "coconut-sap chiller method" had a significantly lower level of microorganisms. The predominant populations were bacteria, namely those of the genus *Bacillus*. No actinomycetes growth was observed in either sample.	[21]
	4 *	Coconut sap (with and without preservative, i.e., limestone solution) and coconut sugar (with and without preservative)	Kemloko (Indonesia)	Total plate count	Microbial analysis: The procedure was performed in accordance with the "Indonesian National Standard for Microbe Contamination Test (Method 01-2897-1992)". The employed culture medium was Nutrient agar.	The microbial counts of sap with and without a preservative were, respectively, "not countable/g" and 1.2×10^2 colony-forming units (CFU)/g. The microbial counts of coconut sugar both with and without a preservative were, respectively, 1.2×10^2 CFU/g and 3.6×10^2 CFU/g.	[32]
	6 *	Coconut sugar and coconut syrup	Philippines (Makati)	Counts of: Aerobic plates. Coliforms. Moulds/yeasts. *Salmonella* sp.	Microbial analysis: An aerobic plate count was performed based on FDA-BAM-3; the coliform count was conducted based on FDA-BAM-4; the mould and yeast count was performed in accordance with FDA-BAM-18; the *Salmonella* sp. count was carried out following the FDA-BAM-5 procedure.	Coconut sugar exceeded the allowable limits for *Salmonella* sp. (/25 g; microorganism should not be detected) and coliform counts (should be <10 colony-forming units (CFU)/g). The values of the aerobic plate count, and the fungal and yeast counts, complied with legislation, i.e., they were below 10 CFU/g. With coconut syrup, the *Salmonella* sp. and coliform count values were in accordance with the stipulated criteria. The aerobic plate count exceeded the defined limit (<10–< 250 CFU/g).	[31]

* Total number of samples analyzed in the study; ** NR—Not reported.

3. Food Industry Applications and Sustainability Issues

For the application of coconut sugar in food and beverage industries, it is important to gain an understanding of the sap from which the sugar is processed. Coconut sap is a nutritious fluid enriched with sugars, calcium, phosphorous, iron minerals, and vitamins such as B complex and C [39,40]. It contains important phenolic compounds such as antioxidants and can be categorized as a low glycemic index (GI 35) food [40]. The nutritional composition of coconut sap is further described in Section 5.

Coconut sugar is made from the watery coconut sap found inside palm trees. It is prepared by concentrating inflorescence sap, which is popularly known as 'neera' in Kerala, India [23], and it is obtained by tapping the unopened coconut spadix. Coconut sugar is brown and contains 2–3% moisture. As this sugar is plant-based, natural, and minimally processed, it can be readily applied in many vegan diets as a healthier option [14,41].

The variation in coconut sugar manufacturing processes is extremely varied according to local, traditional, and indigenous knowledge [4]. These factors account for the vast variations in the appearance, taste, and flavor of the different coconut sugar types that can be found on the market [42].

Coconut sap is produced from palm trees all year-round and there is no specific season for tapping the spathe, however, the amount of sap produced from the trees changes with the season [40]. In the traditional method, the sap trickling from the cut surface is collected in an open earthen pot or bamboo sac, which is placed at the top of the palm for at least 8–12 h. Lime is then coated on the inner surface of the pot to prevent fermentation [43]. The sap collected by this method is oyster white in colour and emanates a strong odour with contamination from insects, ants, pollen, and dust particles [3]. The coco-sap chiller developed by Central Plantation Crops Research Institute (CPCRI) in India has helped to improve the quality of unfermented coconut sap, reduced the processing time, eliminated contaminants like ants, other insects, pollen, and dust particles, and enabled better product diversification and market perspectives [3]. A comparison of total sugars, reducing sugar, free amino acid, total flavonoids, and ferric reducing antioxidant power from coconut sap collected traditionally and those from coco-sap chillers are presented in Section 5. Similarly, a comparison of the water-soluble vitamins and fat-soluble vitamins is presented in table for the employed processing methods.

The Asian and Pacific Coconut Community describes how local operations are performed by small-scale cottage industries with coconut sap to yield molded coconut sugar. The traditional operation starts by collecting coconut sap from palms, which this is normally carried out twice a day, morning and evening [44]. The obtained coconut sap is then filtered through muslin cloth to remove ants, insects, and any other polluting elements. The filtered sap is placed inside cooking vessels. Sap concentrates by evaporating water to increase the sap concentration. This is achieved by boiling the filtered sap in cooking vessels for 3 h at 100–110 °C [44]. The resulting material then turns into a thick liquid. Upon boiling, foam forms that should be eliminated from vessels [44]. The usual procedure is to add a few drops of cooking oil or grated coconut to the resulting mash to prevent foam from excessively forming.

This mash is heated for another hour and is occasionally stirred. To prevent sugars from caramelizing, the must be heated slowly [7]. When the mash is very thick and suitable for molding, cooking vessels are lifted from stoves and cooled to 60 °C. The cooled mash is poured inside clean half coconut shells or bamboo vessels to be cooled and to set [45].

The processing technique influences nutritional and health benefits, as described in the previous section. To ensure product quality, the collected sap is tested for its acidity. This is crucial because, if sap is fermented, it is not suitable for brown coconut sugar manufacturing purposes.

Given its high sucrose content, during its storage, coconut sugar displays caking properties. So, it is essential to add an anticaking agent like tricalcium phosphate (TCP) for it to remain stable during food applications. TCP covers the coconut sugar powder surface and its hygroscopicity significantly diminishes, which improves its flowability [45].

Processing coconut sap into sugar syrup has been investigated following several alternative processing techniques. The coconut sugar syrup obtained from the rotary evaporation method has a better nutritional value than the microwave heating and open heating methods [22]. The non-enzymatic browning that results from Maillard reactions (MR) is enhanced when cooking sap at higher temperatures for a long period, which gives the preferred dark-colored coconut sugar as an ingredient, but only for traditional dishes [46]. Rotary evaporation is fast and gentle and performed at a lower temperature. All this results in evaporation with less thermal decomposition [47–49]. The rotary evaporation method is the alternative processing method that the sugar processing industry applies to produce coconut sugar. It operates in a 250-mbar vacuum at 60°C. It results in improved physico-chemical qualities, minimum input energy, and shorter processing times [43].

The employed processing method influences the antioxidant properties and vitamin contents of coconut sugar syrup. It allows coconut sugar production in a minimum time period, but with high vitamin and antioxidant contents [50]. The coconut sugar syrup produced by at 60 °C rotary evaporator (RE-60) shows significantly lower antioxidant activities (DPPPH, ABTS, FRAP, and TPC) values ($p \leq 0.05$) than that generated by other techniques (open-heat evaporation, microwave, etc.). What this suggests is that the coconut sugar syrup that is produced at a lower temperature (60 °C) in vacuum exhibits significantly different and lesser antioxidant activities than all the other samples generated by distinct evaporation techniques [11,45].

Employing coconut sugar syrup with vast amounts of antioxidants is a promising food production ingredient. Former research works have observed how coconut sugar with larger quantities of vitamins and minerals and that perform more antioxidant activities can be used as an alternative natural sugar with improved chemical properties [3,51].

The work by Saputro [52] reveals the use of low-glycaemic-index (GI) sugar, such as (coconut sugar), to produce plain chocolate. They demonstrated that it was more nutritious as a sugar containing more anti-carcinogenic compounds, antioxidants, and minerals than commercial chocolates made with sugarcane sugar or sugar palm. Moreover, if coconut sugar can be employed as an ingredient, it is able to generate more antioxidant activity if food is processed at high temperatures. Very important compounds such as pyroglutamic acid or hydroxymethylfurfural (HMF) form when heated [53].

Coconut blossom sugar is organic with a caramel aroma and has been the target of adulteration and fraud [6,26]. A recent study identified minor metabolites, such as chemical markers for coconut blossom sugar, by profiling these metabolites, which helped to detect adulterations in products. Bachmann et al. [26] were unable to detect HMF in all the samples. However, pyroglutamic acid was employed at a comparatively high concentration, which exceeded other unambiguous metabolites in coconut sugar like inositol or shikimic acid in coconut sugar [26]. Henceforth, HMF is an apparently suitable marker metabolite for coconut sugar. The distinct metabolic profiles of coconut blossom sugar can be better investigated and identified by combining LC-MS and NMR [54].

Coconut sap as a natural non-alcoholic beverage has high demand as an instant thirst quencher. In India, tapping coconut sap has improved the income of farmers and generated employment. Export of the sap is extensively carried out to countries like Canada, South Korea, USA, Norway, France, Japan, Australia, and the Middle East [55]. Coconut water and juice from coconut sap are commercially canned as beverages in Thailand and exported as 'functional food' with health benefits (see Figure 1). These beverages are flavoured with tropical fruits such as watermelon and pineapple. Globally, the beverages industry was forecasted to reach $1.9 trillion in 2021 and continue to grow at a compounded annual growth rate (CAGR) of 3% [56].

Figure 1. Coconut sap as beverages, bought from a local ethnic shop in Rovaniemi, Finland. (Photo credit: ©Dele Raheem, July 2022).

Numerous organic food and drink firms increasingly employ natural alternative sweeteners such as coconut sugar to substitute refined sugars. Coconut sugar is employed thanks to its ecological credentials and nutritional properties. It has many widespread applications in food and beverage industries to prepare bakery products like chocolate (plain chocolate and drinking chocolate), cake, cookies, and brownies. It can be added to juice, tea, or any beverage as a sweetener, and can be employed as a seasoning agent. Adding coconut sugar to several food applications as a healthy option is well justified because it contains important nutrients like vitamins E and C, minerals like zinc, iron, potassium, and phosphorus, and phytonutrients like anthocyanidins, flavonoids, polyphenols, and antioxidants [3,20,35]. This kind of sugar also contains a significant amount of inulin (4.7 g 100 g^{-1}), required for generating short-chain fatty acids like acetate, butyrate, and propionate [15].

The sugar obtained from the sap of palm trees, which includes coconut sap, is utilized mainly in desserts, sweet soy sauce, and beverages, and also in many other traditional foods. This is especially due to its appreciated and accepted taste, color, and flavor when producing drinks and foods [57–60]. Apriyantono [61] indicated that using palm sugar as a soybean sauce sweetener strongly impacts soy sauce flavor because over 70 volatile compounds are present. Employing palm sugar as a potential natural sweetener also impacts cookies' color, textural properties, and flavor [62], which lends this sugar to being a potential natural sweetener.

Pure sucrose is the most widely used sugar as food sweetener. However, coconut sugar is reported to offer health benefits thanks to its lower GI value. The GI values previously obtained from coconut sugar [63,64] are below the GI values for pure sucrose, i.e., refined cane sugar [65]. Pure sucrose is the most commonly employed sugar as food sweetener. During baking operations, and as another research work reveals, palm sap sugar-sweetened bread has a lower GI value than cane sugar-sweetened bread [66]. Moreover, Ref. [66] report that the palm sugars–corn starch mixture brings about a slow digestion rate and, consequently, lower GI values than those made with refined cane sugars. Coconut sugar displays good quality and possesses a high nutritive value if it is processed from hygienic non-fermented sap; however, if poor-quality neera is employed, its crystallization involves having to add several additives and chemicals (e.g., starch and gluten, and adding sugars from C4 plants, palm, or coconut oil). During the manufacturing process, coconut quarters are added to avoid overboiling sap [1].

Regarding sustainability and traceability issues, organic certification comes over as a quality standard that helps to increase coconut sugar's credibility in the European market. In most cases, coconut sugar exporters are from developing countries. They should consider not only certification, but also natural and organic trends [7]. Consumers will also show

an interest in the story behind sustainable production. Export traders can advertise that small farmers traditionally produce coconut blossom sugar, palm trees organically grow mixed with other crops, and sugar has very low fructose contents and lower GI values than traditional refined beet or cane sugar [7].

As the interest in climate change is growing, individual and planetary healthy coconut-based ecosystems offer excellent possibilities to enhance carbon sequestration with crop combinations that involve a range of plants, which include vine, food crops, tubers, and tree crops. For climate-change adaptation intentions, annual intercrops planted under coconuts can be managed to achieve optimum benefits for the whole system. A holistic approach that focuses on the whole system's overall productivity and sustainability, and not on palms alone, is necessary to make coconut-based agroecosystems resilient to climate change [67]. The demand for natural products is expected to grow, and employing alternative sweeteners, such as coconut syrup and sugar, will increase.

4. Safety and Quality Conditions for Control of Palm Sap Sugar Products

Both palm sap sugar (PSS) and sweet sap are alternative sweeteners prepared from the sap and nectar tapped from the flowers of several palm tree species. For example, palmyra palm (*Borassus flabellifer*), nipa palm (*Nypa fruticans* Wurmb), sugar palm (*Arenga pinnata*) and coconut palm (*Cocos nucifera*). They have the potential to be incorporated into food products as substitutes for sucrose [67]. This sweet sap can be consumed fresh, processed as sugar or syrup, or be fermented as vinegar or an alcohol beverage [68]. This sugar is commonly used in many traditional foods in southeast and southern Asia, and plays a vital role in the color-flavor development of distinct food products [57–59]. One major palm sugar exporting country is Indonesia. Based on the most recent data, the exports of products made with palm sugar or coconut sap came to 36.5 thousand tons, valued at US$49.3 million in 2019 [69]. These products destined for export must comply with the food legislation of the country of destination, such as, the European countries (EFSA) or United States (FDA).

The world's PSS business is expected to reach a total of 1.7 billion dollars in 2027, and is currently 630 million dollars [70]. This increase might be due to its potential to be incorporated into food products as a substitute for sucrose [71]. This product is often employed in many traditional foods in Asia, where it plays an important role in the color–flavor development of different food products [57–59]. Unlike other natural sweeteners, its production is located in a limited number of countries or in a certain geographical area; for example, agave is produced mainly in Mexico and maple syrup in Canada and the USA. However, PSS is produced in southeast and southern Asia, and the mainly producing countries are the Philippines, Thailand, and Indonesia.

Around the world, there are more than 3000 different types of palm trees, but only five are economically important. They offer good sugar palm production yields for any of its different products. They are as follows: date palm (*Phoenix dactylifera*), betel nut palm (*Areca catechu*), African oil palm (*Elaeis guineensis*), coconut (*Cocos nucifera*), and pejibaye (*Bactris gasipaes*) [72]. Other authors include more palm species [73], such as the following:

- Coconut palm sugar (*Cocos nucifera*). It grows in coastal tropical regions of the Indian and Pacific oceans. This sugar is generated from blossoms and is often known as coconut blossom sugar.
- Date palm has two varieties (*Phoenix sylvestris* and *Phoenix dactylifera*). They can be found in Asia and the Middle East, respectively. Date palms are grown mostly for their fruit: dates.
- Palmyra palm (*Borassus genus*). It grows in the African continent and in Asia and New Guinea. It is used for making hats, hatching, writing materials, and some food products. Obviously, its wood is employed. Palm sugar is generated from the sap (called 'toddy') of tree flowers.
- Nipa palm (*Nypa fruticans*). It is found in tropical and coastal regions of the Pacific and Indian Oceans. It lies particularity in its favored biome: mangroves. It is the only

palm tree that partially grows underwater. Its tap is rich in sugar, and it is employed to produce palm sugar.

- Sugar palm (*Arenga pinnata*) is native to tropical and coastal regions in Asia. It is grown mostly in Indonesia and China. The sap used to generate palm sugar is called 'gur' and 'gula aren' in India and Indonesia, respectively.

Nevertheless, other authors acknowledge 40 palm species, the tapping of which is either destructive or non-destructive. Non-destructive exploitation with, for instance, *Phoenix canariensis* on the Canary Islands (Spain) results in sustainable harvests during palms' lifetime [68].

Special attention is paid to harvest the sap tapping of *Phoenix canariensis* for its sugary sap on the La Gomera Isle (Canary Islands). It is one of the most relevant cases of sustainable native flora use. It supplies one of the best-known ethnobotany examples on the Canary Islands and is not only a major tourist attraction for visitors, but also an important local farming activity [68].

PSS is produced with the sap/nectar that is tapped from the flowers of several palm tree species. Knowledge about the physico-chemical properties of this sugar should be known if a high-quality product is to be obtained. PSS' physico-chemical characteristics are affected by its raw materials (sap/nectar) and processing techniques [37,52,73]. Further, the form that sugars come in (syrup, coarse/powder, solid) also determines its properties. Coconut sap, the natural and sweet exudate from tapped unopened coconut spathes or inflorescences (*Cocos nucifera* Lin.), is one of the major primary coconut pro- ducts used for many food uses. It can be processed as natural and nutritious food products, such as coconut granulated brown sugar, concentrate, juice, and vinegar. Processes involve easy-to-follow procedures that require a few simple tools and equipment.

Coconut sap juice is a healthy pasteurized beverage, and coconut sap concentrate is a thick, free-flowing syrup. Both can be considered functional foods for consumers and the food industry.

The inflorescence in good stands of coconut trees can produce an average of 2 L of sap per tree a day [74]. An average yield of 1 kg of sugar can be obtained from four coconut trees every day.

Under adequate production conditions, coconut trees' inflorescence can produce a mean yield of 2 L of sap per tree every day. So, the yield of four coconut trees per day can produce 1 kg of sugar. However, as both the sugar content and production of sap depend on trees' location and their variety, nutrition, the season, tapping time, and the system, these conditioning factors also can impact organoleptic and microbiological characteristics.

Some authors have followed different preservation techniques for bottling palm sap; although all probes failed, these authors consider it crucial to understand the biochemical composition, fermentation chemistry, and existing preservation methods [75].

Transforming coconut sap into sugar granules is simple and requires basic equipment, hence, it is appropriate for and best adapted to farms or medium-sized enterprises. It is a good source of immediate income for coconut farmers, and demand is growing on both local and international markets [76].

Engineering the palm sugar production process poses several problems if sap is not immediately cooked after it is removed from palm trees, which results in a lower pH. A drop in pH impacts the produced palm sugar's quality. To obtain a higher product conversion factor value, engineering the production process by adding plant extracts to prevent "gait" is feasible [74], and the palm sugar packaging design is more appealing and varied. Packaging is designed by prioritizing practical, economical, and hygienic aspects, without burdening producers in production terms and consumers in price terms. One alternative for PSS with a high quality (soluble solids content 16 degrees brix and pH 4.7) has been presented with the addition of some preservatives such as citric acid (0.09%) and nisin (10 ppm) [76]. The quality standard in the Philippines includes quality norms to not only produce PSS, but also to obtain a product of standardized quality and well-defined organoleptic and microbiological parameters.

Coconut Sap Sugar Production in the Philippines

General considerations: farm-level technology to produce a high-value production product from coconut inflorescence sap (see Table 5). It is simple, farm-level technology that involves a natural heat evaporation process that converts liquid sap into a solid form of sugar granules without having to resort to complicated and costly machinery or equipment (Figure 2).

Table 5. Reference values for palm sap sugar products. Adapted from Ref. [74].

Physico-Chemical Properties	Reference Values
Color	light yellow to dark brown
Odor	free of burnt odor
Taste	free of burnt taste
Moisture Content (%)	<4.0
Glucose Content	2.8–3
Fructose Content	1.0–4.0
Sucrose	78.0–89.0
Ash	<2.4
Microbiological properties	
Salmonella	Negative
E. coli	Negative
Coliform count	<10 ufc/g
Total Plate Count	<10 ufc/g
Molds and Yeasts	<10 ufc/g

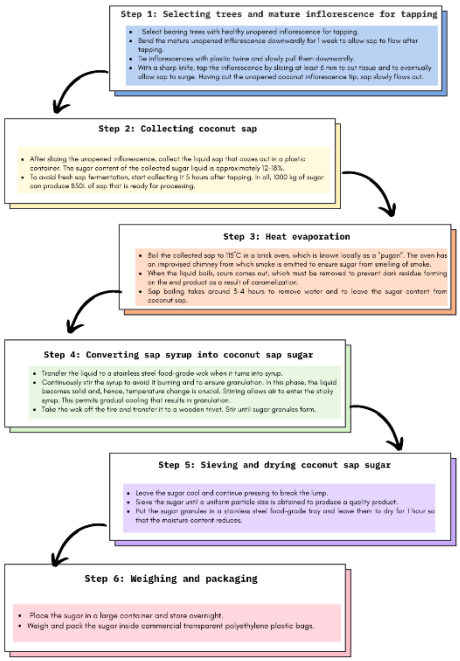

Figure 2. Recommendations for coconut sap sugar production in the Philippines. Adapted from Refs. [17,70,74,77].

5. Nutritional Profile and Health Impacts

Despite its expensive price, coconut sugar is considered by several authors to be one of the greatest natural sweeteners as it offers a number of health advantages [14]. Tables 6–8 list the biochemical properties, vitamins, and other nutritional components of the sugar obtained from coconut inflorescence sap.

Vitamins C and E, minerals including zinc, iron, potassium, and phosphorus, and phytonutrients like antioxidants, flavonoids, anthocyanidins, and polyphenols, are all present in coconut sugar [21]. Additionally, inulin comes in a substantial quantity (4.7 g, 100 g^{-1}) in coconut sap sugar. It is necessary for the synthesis of short-chain fatty acids acetate, butyrate, and propionate [31]. Coconut sugar and syrup (the latter contains dietary fiber and fermentable inulin) are truly promising functional foods and are converted into short-chain fatty acids [31]. As coconut sugar has a sweetening potential that is comparable to saccharose, it is utilized as an alternative sweetener for making confections, drinks, pastries, and other gastronomic delicacies [78]. According to Trinidad et al. [63], coconut sugar has a low GI that falls within the 35–54 range per serving. Low GI diets lower the likelihood of developing certain chronic diseases like type II diabetes. Compared to other sugars, coconut sugar has nutritional superiority. When cane, palm, and coconut sugars, sorbitol, and other sweeteners are blended with wheat flour, sorbitol possesses the best starch digestibility—with an almost identical digestibility for palm or coconut sugars [66]

Compared to the majority of other commercially available sugars, coconut sugar is certainly a healthy sweetener. It is processed by evaporating sap—which requires considerable labor and resources when collected from trees—that is then transported, stored, and processed. Therefore, the manufacture cost is higher than for cane sugar. People are willing to pay high prices for it given its nutritional value and low GI. However, one bottleneck is the lack of knowledge about its health advantages. Natural coconut sugar and other biproducts are produced hygienically as a result of scientific developments in sap collecting and processing, which have occurred in some major producing nations, including India, in the last few years [14].

Table 6. Coconut inflorescence sap obtained with a Cocosap chiller (conventional method) and coconut sugar were studied for their biochemical components and ferric-reducing antioxidant power [14].

Biochemical Characteristics	Coconut Inflorescence Sap Obtained by the Cocosap Chiller Method (100 mL)	Traditionally Collected Sap (100 mL)	Coconut Inflorescence Sap Sugar (100 g)
Total sugars (g)	16.20 ± 0.33	9.20 ± 0.97	91.8 ± 1.01
Reducing sugars (g)	0.68 ± 0.01	1.24 ± 0.87	4.69 ± 4.60
Free amino acids (g)	1.03 ± 0.10	0.413 ± 0.09	3.05 ± 0.07
Total phenolic content (mg gallic acid equivalent)	21.7 ± 0.48	14.8 ± 1.03	3.05 ± 0.07
Total flavonoids (mg catechin equivalent)	0.817 ± 0.19	0.177 ± 0.02	4.76 ± 1.21
Ferric-reducing antioxidant power (mg of ascorbic acid equivalent)	14.8 ± 0.21	8.34 ± 0.83	22.9 ± 4.12

Table 7. Vitamin composition of coconut inflorescence sap obtained with a Cocosap chiller (conventional method) and coconut sugar [14].

Biochemical Characteristics	Coconut Inflorescence Sap Obtained by the Cocosap Chiller Method (100 mL)	Traditionally Collected Sap (100 mL)	Coconut Inflorescence Sap Sugar (100 g)
Water-soluble vitamins			
Vitamin C (mg)	19.6 ± 0.95	16.3 ± 0.76	3.98 ± 1.12
Thiamine (µg)	0.07 ± 0.02	0.02 ± 0.00	14.3 ± 1.16
Niacin (µg)	14.9 ± 2.80	11.4 ± 0.7	34.7 ± 2.1
Pyridoxine (µg)	2.35 ± 0.01	1.32 ± 0.12	101 ± 0.3
Pantothenic acid (µg)	3.99 ± 0.08	1.64 ± 0.11	2.53 ± 0.2
Biotin (µg)	0.07 ± 0.01	0.09 ± 0.01	2.51 ± 0.7
Folic acid (µg)	0.036 ± 0.01	0.031 ± 0.00	0.26 ± 0.07
Riboflavin (µg)	-	-	0.25 ± 0.02
Fat-soluble vitamins			
Cholecalciferol (µg)	0.056 ± 0.00	0.062 ± 0.00	0.256 ± 0.02
Ergocalciferol (µg)	0.074 ± 0.01	0.028 ± 0.00	0.171 ± 0.02
Tocopherol (µg)	7.20 ± 0.93	2.94 ± 0.46	19.6 ± 3.5
Vitamin K1 (µg)	1.73 ± 0.19	0.601 ± 0.09	7.35 ± 0.95
Vitamin K2 (µg)	0.771 ± 0.12	0.428 ± 0.12	5.57 ± 0.61

Table 8. Nutritional profile of coconut sugar made from inflorescence sap on a double-jacketed cooker and a modified conventional processing technique. (The results should be interpreted in light of the biochemical characteristics of coconut sugar, as listed in Tables 6 and 7).

Biochemical Components	Content
Protein (g/100 g)	2.6
Dietary fiber (g/100 g)	3.1
Electrolytes (mg/100 g)	
Sodium	568
Potassium	1002
Microminerals (mg/100 g)	
Iron	2.2
Zinc	2.1
Essential amino acids (mg/100 g)	
Valine	40.68
Threonine	45.81
Leucine	16.01
Lysine	136.5
Methionine	54.55
Histidine	3.48
Phenylalanine	57.66
Tyrosine	5.68

6. Conclusions

The global drive toward better individual and environmental health warrants the need for better knowledge about what we produce and consume. Sweeteners are important food ingredients to formulate edible food products, and for health and sustainability. This review summarizes the micro- and macrocomponents isolated from coconut sugar, sap, and syrup, the chemical components of these natural sugars, and their physicochemical, microbiological, and antioxidant characteristics. A better understanding of these components reveals the health-giving properties of coconut as a plant-based sugar, despite the associated costs of taking coconut-based foods to consumers. Hence, it is important that food industries respond to the demand of health-conscious consumers by incorporating coconut sugar, sap, and syrup into food products. Some shortcomings in this review, which can be addressed in the future, are the need to consider personal dietary preference of coconut sugar in food products, sustainability issues by more rigorous studies, and to study the role of coconut trees and carbon sinks, including life cycle assessments (LCAs).

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4. CONCLUSIONES

La sociedad es cada vez más consciente de la enorme importancia de llevar una dieta equilibrada para mantener y promover la salud. El consumo excesivo de azúcar es ahora una preocupación transversal, pero este hábito no es fácil de romper, por lo que los alimentos y bebidas sin azúcar o bajos en azúcar tienen una gran demanda y los agentes edulcorantes que los hacen factibles son ingredientes de alto valor. Hoy en día, la industria alimentaria utiliza edulcorantes intensos y polioles, principalmente de origen sintético, en sustitución del azúcar (sacarosa). Los consumidores desean cada vez más incorporar a su dieta diaria productos con ingredientes naturales y respetuosos con el medio ambiente y a su vez sostenibles, también tienen preferencias por consumir alimentos con propiedades funcionales y que no comprometan el sabor. Para satisfacer estas demandas, actualmente la industria alimentaria tiene a su disposición edulcorantes naturales alternativos. La producción de estos productos naturales dinamiza las microeconomías de origen y ayudan a un comercio más justo y solidario, así en el caso del Agave se produce en las regiones Jalisco, Guanajuato, Michoacán, Nayarit o Tamaulipas. Algo similar ocurre con el sirope de coco, el cual es producido principalmente en el Sureste Asiático (Filipinas, Indonesia, etc.) y el Subcontinente Indio, su extracción se realiza tal y como lo hacían las poblaciones indígenas desde tiempos inmemoriales, por esta razón su producción a nivel de microcentros de extracción como se realiza actualmente, ayuda a generar una economía de supervivencia de estas zonas subdesarrolladas económicamente.

Cuando hablamos del sirope de arce, producido únicamente en el sureste de Canadá (Ontario principalmente) y en el noreste de Estados Unidos, son regiones en países desarrollados, que no van a depender de esta producción para mejorar su economía estatal, pero si favorece la economía rural y permite el aprovechamiento de un recurso que ya utilizaban las tribus indígenas antes de la colonización europea y que de otra forma no se podrían explotar los bosques de “maple”.

La naturaleza es una fuente increíble de compuestos valiosos, incluidos aquellos con sabor dulce, muchos de los cuales aún no se han explorado. Sin embargo, hay que recalcar que el hecho de ser un alimento natural no asegura su éxito en el mercado. También se debe tener en cuenta que un uso tradicional prolongado en algunas sociedades

restringidas y áreas alrededor del mundo, y esto, a pesar de brindar cierta tranquilidad, no puede descartar la necesidad de realizar estudios científicos detallados para demostrar la seguridad de los compuestos naturales que se utilizarán como alimento, aditivos y, por ejemplo, como edulcorantes. La industria alimentaria necesita afrontar el reto de desarrollar nuevos productos con edulcorantes funcionales naturales para seguir innovando y satisfaciendo a los consumidores.

Con relación al sirope de agave, esperamos que se realicen más investigaciones sobre la ingesta de jarabe de agave en el metabolismo humano para justificar sus declaraciones de propiedades saludables, como una alternativa natural a otros azúcares. Además, la investigación para mejorar el proceso industrial para la obtención del sirope de agave a partir del jugo de agave por hidrólisis enzimática o ácida, con el objetivo de preservar los componentes beneficiosos (por ejemplo, polifenoles, saponinas, fibra dietética), mientras se reduce el contenido de componentes potencialmente dañinos (por ejemplo, fructosa), es crucial.

En cuanto al sirope de arce, de hecho, la evidencia científica actual indica que los compuestos fenólicos juegan un papel clave en la defensa del organismo, protegiéndolo del daño causado por las especies reactivas del oxígeno que se sabe que están involucradas en la génesis de diversas patologías, cardiovasculares, oncológicas, autoinmunes, degenerativas, etc. Dicho esto, el potencial del sirope de arce, derivado de *Acer saccharum* Marsh., como fuente de nutrientes y compuestos bioactivos es muy elevado y merece ser destacado. Este edulcorante puede ofrecer una contribución importante para el desarrollo de nuevos productos alimenticios en el futuro y puede contribuir a mejoras decisivas en la salud pública.

Finalmente, se han resumido los micro y macrocomponentes aislados del azúcar, la savia y el sirope de coco, los componentes químicos de estos azúcares naturales y sus características fisicoquímicas, microbiológicas y antioxidantes. Una mejor comprensión de estos componentes revela las propiedades saludables del coco como azúcar de origen vegetal, a pesar de los costes asociados de llevar los alimentos a base de coco a los consumidores. Por lo tanto, es importante que la industria alimentaria responda a la demanda de los consumidores conscientes de la salud mediante la incorporación de azúcar, savia y sirope de coco en los productos alimenticios. Algunas limitaciones de esta

revisión, que se pueden abordar en el futuro, son la necesidad de considerar la preferencia dietética personal de azúcar de coco en los productos alimenticios, los problemas de sostenibilidad mediante estudios más rigurosos y estudiar el papel de los cocoteros y los sumideros de carbono, incluidas evaluaciones de ciclo de vida.

5. RESUMEN

En un momento en el que la población es cada vez más consciente e implicada en lo que come, tanto los consumidores como el sector alimentario están mostrando un mayor interés por los alimentos naturales. Esta Tesis Doctoral aborda, detalla y discute, los aspectos más importantes relacionados con el análisis químico y el perfil nutricional, las aplicaciones en la industria alimentaria y los impactos en la salud del sirope de agave, el sirope de arce y el azúcar/sirope de coco.

El sirope de agave (AS), un producto alimenticio elaborado a partir de la savia de la planta de agave, es un edulcorante vegano que se ha vuelto popular para reemplazar a los edulcorantes convencionales como la sacarosa. Dado que la demanda de edulcorantes de origen natural ha crecido en la última década, esta Tesis Doctoral aborda y analiza en detalle los aspectos más relevantes del análisis químico del AS, aplicaciones en la industria alimentaria, cuestiones de sostenibilidad, seguridad y control de calidad y, finalmente, perfil nutricional e impactos en la salud. De acuerdo con el principal resultado de nuestra investigación, podemos suponer que el análisis de los componentes principales del infrarrojo medio, la cromatografía de intercambio aniónico de alto rendimiento equipada con un detector amperométrico pulsado y la cromatografía de capa fina se pueden utilizar para identificar y distinguir los siropes de fuentes naturales. Los principales productos derivados del agave son jugo, hojas, bagazo y fibra. En términos de sostenibilidad, se puede afirmar que los productos de agave orgánicos certificados y de libre comercio son las opciones más sostenibles disponibles en el mercado porque garantizan que los productos se elaboran sin pesticidas y de acuerdo con normas laborales específicas. El gobierno mexicano y los productores de AS también han establecido pautas mexicanas que prohíben el uso de cualquier ingrediente, azúcar o aditivo alimentario que se derive de otras fuentes, además de las plantas de agave, para producir cualquier AS comercial. Debido a su valor nutricional, AS es una buena fuente de minerales, vitaminas y polifenoles en comparación con otros edulcorantes tradicionales. Sin embargo, se necesita más investigación sobre los efectos de AS en el metabolismo humano para respaldar sus declaraciones de propiedades saludables como sustituto natural del azúcar.

El sirope de arce es un manjar que se prepara hirviendo la savia de numerosas especies de Acer, principalmente arces azucareros. En comparación con otros edulcorantes naturales, se cree que el sirope de arce es preferible al azúcar refinado por su alta concentración de compuestos fenólicos y contenido mineral. La presencia de ácidos orgánicos (ácido málico), aminoácidos y cantidades relevantes de minerales, como potasio, calcio, zinc y manganeso, hacen que el sirope de arce sea único. Dada la creciente demanda de edulcorantes de origen natural durante la última década, este documento de revisión trata y analiza en detalle los aspectos más importantes de los análisis químicos del jarabe de arce, con especial énfasis en las ventajas y desventajas de los diferentes enfoques analíticos. Una utilización exitosa de la aplicación del jarabe de arce en la industria alimentaria dependerá de una mejor comprensión de su seguridad, control de calidad, perfil nutricional e impactos en la salud, incluidos los problemas de sostenibilidad.

El azúcar de coco es una opción edulcorante más saludable que la mayoría de los otros azúcares disponibles comercialmente. La savia se recolecta de los árboles para ser transportada, almacenada y evaporada durante el procesamiento, que son operaciones que requieren mucha mano de obra y recursos. En consecuencia, el costo de producción es más alto que el del azúcar de caña. Dado su alto valor nutricional y su bajo índice glicémico, la gente está dispuesta a pagar precios más altos por él. Sin embargo, una barrera es la ignorancia de sus beneficios para la salud. Esta Tesis Doctoral examina y trata en profundidad las características más significativas de los análisis químicos del azúcar de coco para centrarse en varias metodologías analíticas dada la creciente demanda de edulcorantes de origen natural en los últimos 10 años. Es necesaria una comprensión más profunda del control de calidad, la seguridad, los efectos en la salud, el perfil nutricional y los problemas de sostenibilidad correspondientes al azúcar de coco para implementarlos de manera efectiva en la industria alimentaria.

PALABRAS-CLAVE: análisis químico; control de calidad; edulcorantes naturales; impactos en la salud; industria alimentaria; nutrición; seguridad alimentaria; sirope de agave; sirope de arce; sirope/azúcar de coco; sostenibilidad alimentaria.

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7. APORTES CIENTÍFICOS

Aportaciones científicas relevantes vinculadas a las investigaciones desarrolladas durante el periodo doctoral

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Topic Editor for the Research Topic: "Traditionally Produced Fermented Foods and Innovative Technological Processes" in "Frontiers in Food Science and Technology" – Frontiers. https://www.frontiersin.org/research-topics/31587/traditionally-produced-fermented-foods-and-innovative-technological-processes#overview

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