

Flavonoids and phenolic acids from sugarcane: Distribution in the plant, changes during processing, and potential benefits to industry and health

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Funding information

Monash University; The Product Makers (Australia) Pty LTD

Abstract

Sugarcane (*Saccharum* sp.) plants are grown in warmer climates throughout the world and processed to produce sugar as well as other useful byproducts such as molasses and bagasse. Sugarcane is rich in (poly)phenols, but there has been no attempt to critically evaluate the published information based on the use of suitable methodologies. The objective of this review is to evaluate the quantitative and qualitative (poly)phenolic profiles of individual parts of the sugarcane plant and its multiple industrial products, which will help develop new processes and uses for sugarcane (poly)phenols. The quantitative analysis involves the examination of extraction, concentration, and analytical techniques used in each study for each plant part and product. The qualitative analysis indicates the identification of various (poly)phenols throughout the sugarcane processing chain, using only compounds elucidated through robust analytical methodologies such as mass spectrometry or nuclear magnetic resonance. In conclusion, sugarcane (poly)phenols are predominantly flavonoids and phenolic acids. The main flavonoids, derivatives of apigenin, luteolin, and tricin, with a substantial proportion of C-glycosides, are consistently found across all phases of sugarcane processing. The principal phenolic acids reported throughout the process include chlorogenic acids, as well as ferulic and caffeic acids mostly observed after hydrolysis. The derivation of precise quantitative information across publications is impeded by inconsistencies in analytical methodologies. The presence of multiple (poly)phenols with potential benefits for industrial applications and for health suggests sugarcane could be a useful provider of valuable compounds for future use in research and industrial processes.

KEY WORDS

apigenin, chlorogenic acid, luteolin, molasses, (poly)phenols

1 | INTRODUCTION

Sugarcane is grown across the world to produce “cane sugar” (sucrose) as the major product, a natural sweetener added to many foods, in addition to sugarcane juice, cane wax, and jaggery (Ali et al., 2019), with colored and flavorful byproducts such as molasses and bagasse. Among other components, the sugarcane plant is extremely rich in (poly)phenols. This has driven research on optimizing the extraction of (poly)phenolic fractions from sugarcane and assessment of their putative properties (Carvalho et al., 2021; Jamir et al., 2021; Singh et al., 2015).

The word (poly)phenol refers to compounds with multiple phenolic rings, and compounds with a single-phenol ring are commonly classified as phenolic acids. Here, the word (poly)phenol is used to encompass both classes (Frank et al., 2020). (Poly)phenols have been proposed to have health benefits, including cardioprotective, antidiabetic, and neuroprotective effects (Rana et al., 2022).

This review will assess the macronutrient and micronutrient profiles, products, byproducts, and processing methods of sugarcane, with the major focus on a detailed assessment of the (poly)phenolic profile of sugarcane. The purpose of this review is to provide a cross-sectional snapshot of the (poly)phenols that exist in each part of the sugarcane plant and its products. The sugarcane plant and its products and byproducts are a sustainable source of (poly)phenols that should be further exploited. This will clarify and confirm the existence of each (poly)phenol in each part/product of sugarcane to help researchers or

potential industries gain an understanding of future possibilities to produce phenolic-rich products and byproducts with potential benefits to human health. This review supports the sustainability of sugarcane industry by repurposing the waste products as valuable (poly)phenol sources.

2 | SUGARCANE PLANT

2.1 | Origin of sugarcane

The sugarcane plant is a perennial grass belonging to the Poaceae family (Singh et al., 2015). Records of sugarcane go back to 326 BC, and modern-day varieties of sugarcane include *Saccharum officinarum*, *Saccharum spontaneum*, *Saccharum robustum*, *Saccharum barberi*, and *Saccharum sinense*. This review will cover hybrids of *S. officinarum*, the most common of the sugarcane cultivars, which originated from New Guinea (Altpeter & Oraby, 2010). It is predominantly produced in Brazil, followed by Asia (Arias & Bhatia, 2015). It prefers tropical, hot, humid climates and grows in well-drained, organically rich soil with a slightly basic pH (Singh et al., 2015). Traditional medicine supports that sugarcane juice has some diuretic, aphrodisiac, laxative, cooling, demulcent, anti-septic, and tonic properties. Modern research supports its anti-inflammatory, antihyperglycemic, and diuretic properties. Sugarcane is cheap, abundantly available, and rich in multiple bioactives (Singh et al., 2015).

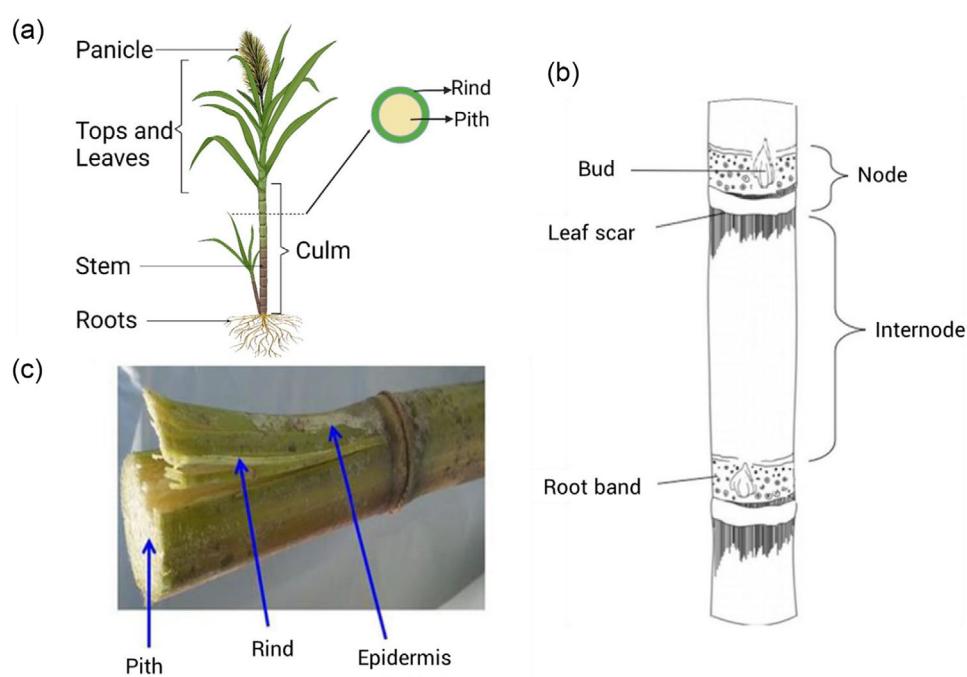


FIGURE 1 Morphological structure of (a) the sugarcane plant, (b) the structure of the node and internode (Meng et al., 2019), and (c) parts of the sugarcane stem (Takahashi et al., 2016). Source: (a) Created with BioRender.com.

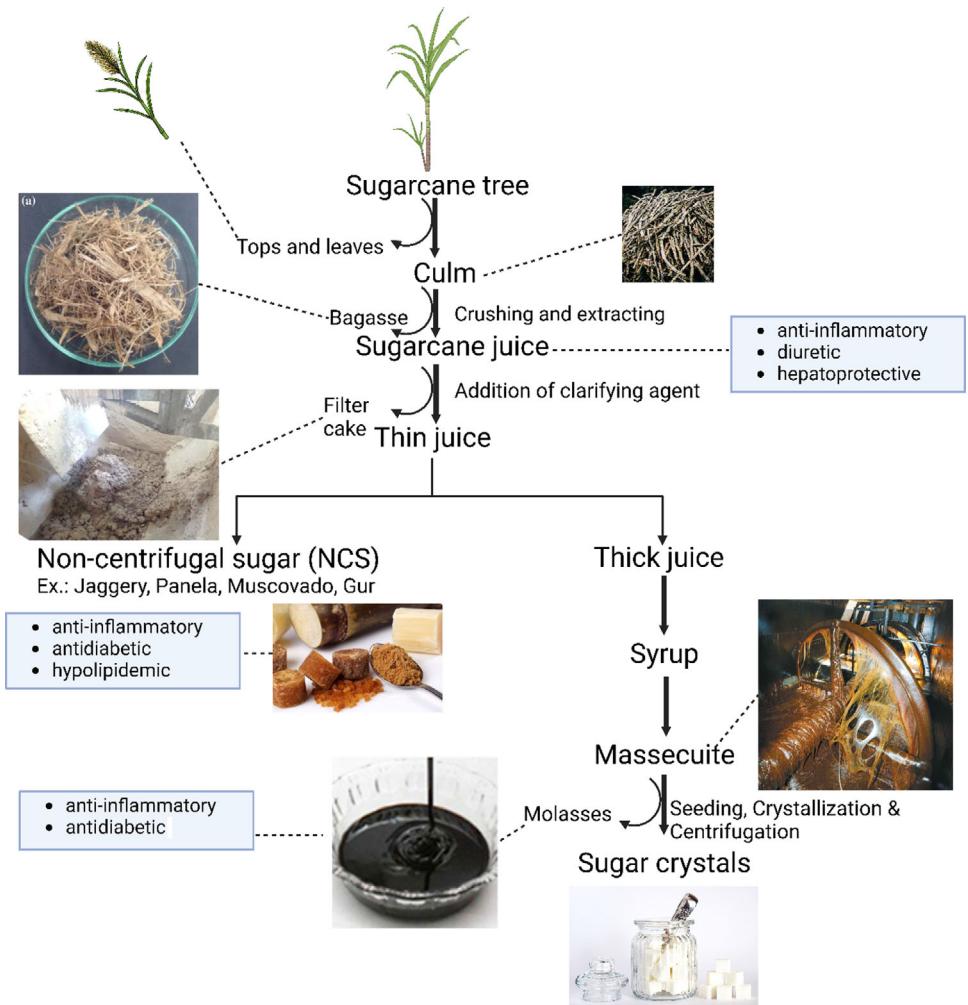


FIGURE 2 Sugarcane processing, products, and byproducts. Only the stems/culms are used, and the rest of the plant, including tops and leaves, are removed (Khaire et al., 2021). Stems are crushed to obtain raw juice, which is then sterilized and subjected to clarification to remove insoluble impurities and gases. The remaining fibrous stem parts after juice extraction are bagasse. During the clarifying process, sludge is separated physically as filter cake due to the addition of clarifying agents, and a thin juice is produced. This juice is sent to evaporators and vacuum pans to remove excess water and bring up the concentration to facilitate the crystallization process. This produces thick juice, syrup, and massecuite. At the massecuite stage, the addition of seed crystals boosts the crystallization process, and sugar crystals are separated from molasses by centrifugation. Sugar crystals are further dried and refined depending on the end product, for example, refined sugar and raw sugar (Payet et al., 2006; East et al., 2015; Santos et al., 2020). Non-centrifugal sugar (NCS) are manufactured by a similar method but are different in texture and composition. NCSs are clarified and evaporated similarly but are concentrated in open pans, with crystals obtained by heating and continuous agitation (Velásquez et al., 2019). As these crystals are not centrifuged, NCSs are not completely separated from molasses (Zidan & Azlan, 2022b). Source: Figure produced using BioRender.com with images from external resources (culm [Photo by A. Andersen from Pexels: <https://www.pexels.com/photo/sugar-canapes-2254097/>], bagasse (Torgbo et al., 2021), filter cake (Makul & Sua-iam, 2016), NCS [Panela] (Gómez-Narváez et al., 2019), massecuite [Photo by M. Thayer <https://www.mauinews.com/the-last-harvest/2017/01/one-final-push/>], molasses (Cheng et al., 2021), and sugar crystals [Photo by S. Hazelwood from Pexels: <https://www.pexels.com/photo/close-up-photo-of-sugar-cubes-in-glass-jar-2523659/>]). Created using BioRender.com. Health benefits of sugarcane juice (Arif et al., 2019; Singh et al., 2015), NCS (Zidan & Azlan, 2022), molasses (Kubota et al., 2023).

2.2 | Sugarcane plant anatomy and utilization

Sugarcane propagates asexually and morphologically resembles a typical grass family plant. As a shoot with seg-

mented culm, each segment has a node and an internode with an attached leaf, a fibrous root system, and a panicle (Figure 1). It is a C₄ plant, efficient in capturing carbon and sunlight (Moore et al., 2014), and can store sucrose for 2 years or more (Burr et al., 1957). The fibrous root system

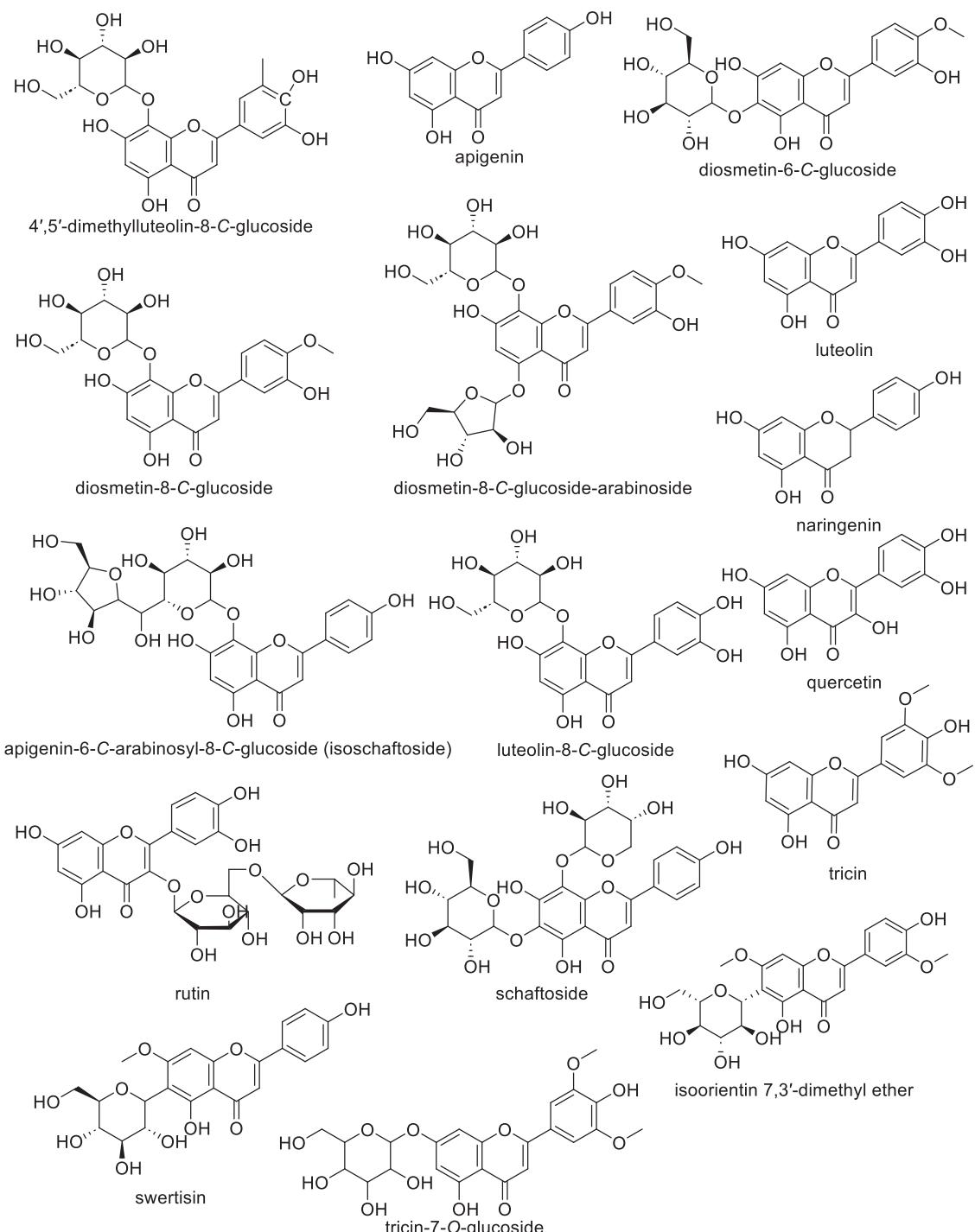
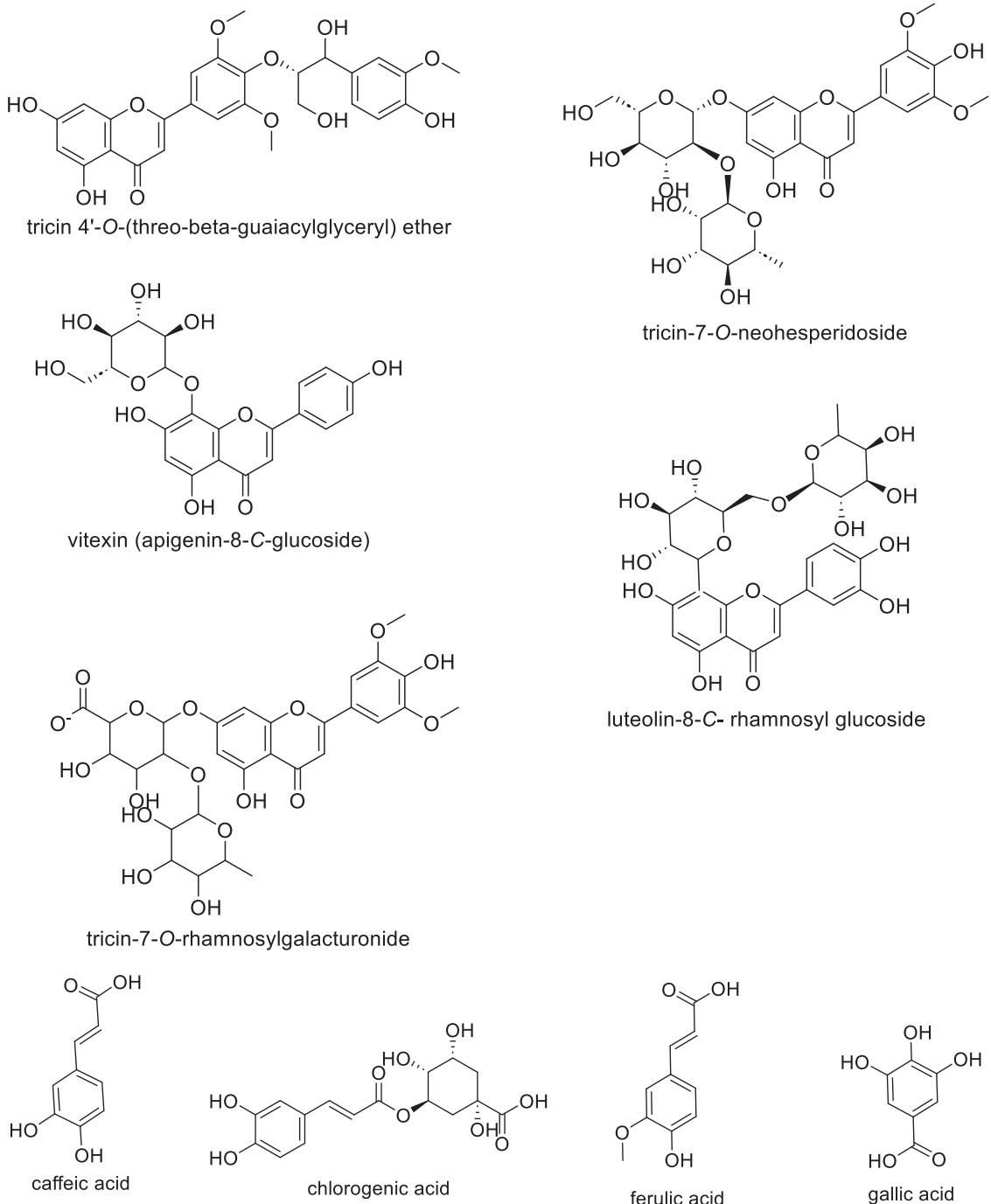


FIGURE 3 Chemical structures of the most abundant (poly)phenols in sugarcane. *Source:* Created using Chemdraw 22.2.0.3300.

absorbs nutrients and water from the soil, whereas the culm stores food for the plant as an energy source (Moore et al., 2014). Sugarcane culm is crushed to extract juice, which undergoes further processing to obtain raw sugar, leaving behind the inedible fibrous remains known as bagasse.

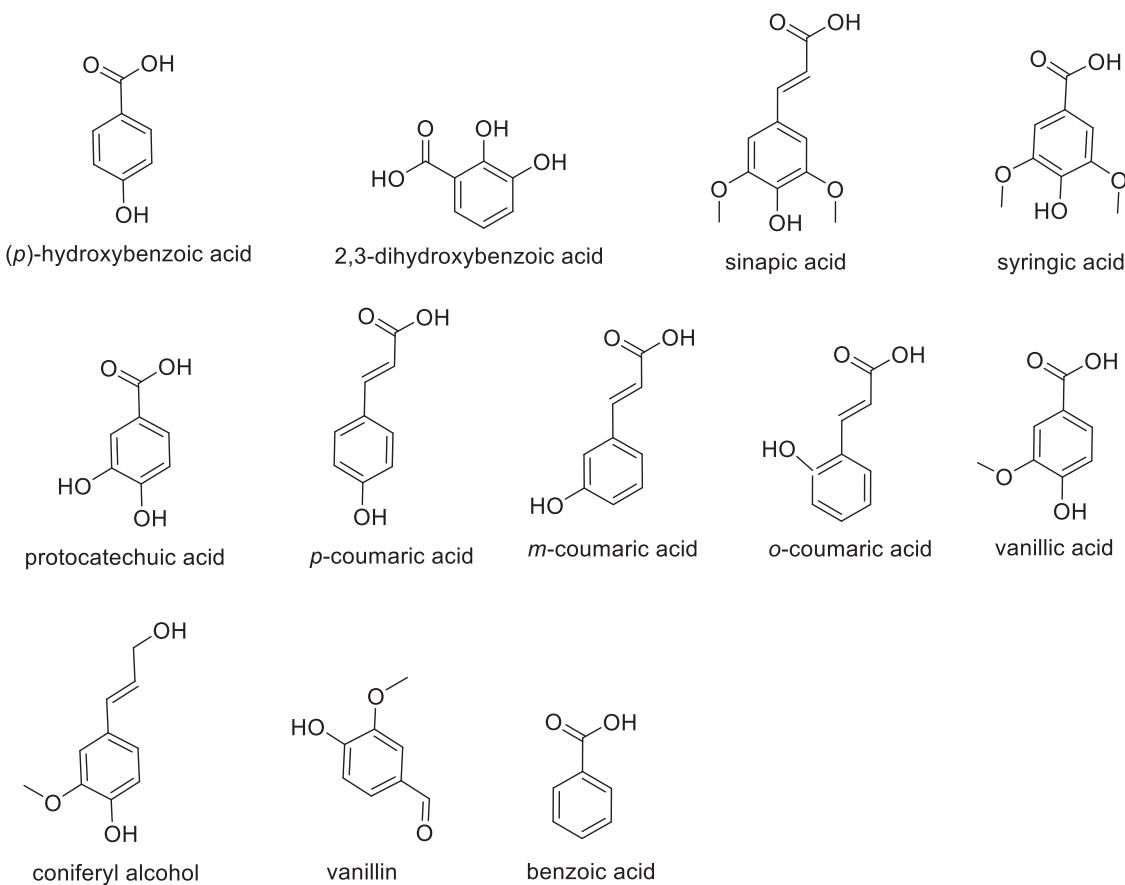
3 | SUGARCANE PROCESSING

Basic steps in sugarcane processing have remained similar for decades, although many new techniques have been incorporated into the process at certain points to enhance production. Sugarcane crop processing involves

**FIGURE 3** Continued

centrifugation and refining steps, leading to the production of various useful end products and dark-colored byproducts (Figure 2). Some products have similar properties but are named differently in various parts of the world. For example, all non-centrifugal sugars (NCSs) have similar production processes but are known as “jaggery” (India, Nigeria, Kenya, and South Africa), “gur” (India and Pakistan), “panela” (Colombia, Ecuador, Guatemala, Panama, and Venezuela), “kokuto” (Japan), “rapadura” (Brazil and Guatemala), and “muscovado” (Philippines)

(Ebadi & Azlan, 2021). NCS are dark and flavorful, and exist in different crystal sizes, believed to be due to the high content of Maillard reaction products (melanoidins). Sugarcane wax and filter cake are products that are rich in policosanols and fatty acids, rather than (poly)phenols (Santos et al., 2020; Singh et al., 2015) and are therefore not discussed here. Filter cake, tops, and leaves are usually returned to the field as fertilizer due to their rich content of minerals, organic matter, and other nonmetallic elements (Santos et al., 2020). The byproduct molasses is the richest


FIGURE 3 Continued

in (poly)phenols (Singh et al., 2015) and therefore has been explored for valuable bioactive compounds.

4 | SUGARCANE NUTRIENT COMPOSITION

4.1 | Macronutrient composition

Fresh sugarcane juice contains approximately 82% water, 17% carbohydrates (mostly sugars) and <1% ash/mineral, proteins, and lipids (Nur Sudraj et al., 2020). Refined sugar contains only carbohydrates (>99.9% disaccharide, sucrose). NCS contains a mixture of monosaccharides (glucose and fructose [3.7%–10.5%]), sucrose, proteins (0.4%–1.7%), and a small amount of fat (<0.1%). NCSs also contain some moisture (1.5–15.8 g) (Ebadi & Azlan, 2021).

4.2 | Micronutrient composition

The micronutrient composition data of sugarcane products have been widely reported. Various NCS products are rich

in water-soluble vitamins, such as thiamine, riboflavin, pyridoxine, pantothenic acid, nicotinic acid, and ascorbic acid. Among all the products tested, food grade molasses have demonstrated a comparatively high vitamin content (Sangster & Righelato, 1989). The mineral profile was also comparatively higher in food grade molasses, which included Na, K, Mg, Ca, Fe, V, Cr, Mb, Co, Ni, Cu, and Zn, with the highest being K and Mn.

Sugarcane juice has also been reported to contain minerals, such as Na, Ca, Cu, Fe, Mg, Zn, P, K, and Mn (de Souza et al., 2015; Takahashi et al., 2016). Apart from (poly)phenols, a study reported small amounts of amino acids (i.e., valine, alanine, and aspartate), organic acids (i.e., lactic, malic, and formic acids), and fatty acids. Gas chromatography/mass spectrometry (MS) analysis detected additional organic acids, including acetic, glyceric and its isomer acetoacetic, itaconic, trans-aconitic, and citric acids (Ali et al., 2019). High-performance liquid chromatography/MS (HPLC/MS) revealed the presence of many fatty acids, including oleic, palmitic, linoleic, octadecatetraenoic, and octadecatrienoic acids, but no quantitative data were available (Ali et al., 2019). All the aforementioned fatty acids were present in sugarcane juice, whereas molasses lacked

oleic, octadecatetraenoic, and octadecatrienoic acids (Ali et al., 2019).

5 | (POLY)PHENOLIC COMPOSITION OF SUGARCANE

The (poly)phenolic composition of sugarcane varies depending on variety, climate, soil type, crop handling method, and variations in processing (Azlan et al., 2023). The variety of sugarcane is the primary influencer of the phenolic content, even under similar cultivation conditions. The color of the outer stem of the sugarcane plant depends on the type and content of anthocyanins among varieties (Manohar et al., 2014). Climatic variations in rainfall and temperature can also result in different (poly)phenolic content for the same location and cultivar (Rodrigues et al., 2021). This review focuses on the variation in (poly)phenolic composition due to processing conditions and extraction and analysis techniques reported previously. The chemical structures of the most abundant (poly)phenols identified in sugarcane and its products are shown in Figure 3.

5.1 | (Poly)phenols reported in the plant

5.1.1 | (Poly)phenols in the rind

Sugarcane rind is the outermost part of the sugarcane plant and is often wasted, even though it has been identified as one of the most phytochemical-rich components (Fang et al., 2017). Sugarcane rind waste accounts for 20% of total sugarcane weight (Feng et al., 2015). Current data on the phytochemical profile of rind are quite limited, but identifying the composition of (poly)phenols and other important phytochemicals in sugarcane rind could improve the usage of this wasted byproduct. Some studies have focused on the methodologies to enhance the purification of certain phenolic acids in the rind, but the complete phytochemical profile has not been reported (Fang et al., 2017; Feng et al., 2015; Geng et al., 2017). After hydrolysis to release bound phenolics and to hydrolyze ester and glycosidic linkages, the most commonly reported phenolics are gallic acid, *p*-coumaric acid, ferulic acid, and catechin, although these are tentative as only absorption spectra data were used to identify the compounds against standards (Table 1). One study identified very high levels of quercetin, catechin, and resveratrol, but the identification was only tentative as it was by absorption spectra data, and a substantial amount of free ferulic acid, for example, was reported even when samples were not hydrolyzed (Kerdchan et al., 2020).

Anthocyanins are a group of colored, water-soluble phenolic compounds. The anthocyanin profile of sugarcane rind was analyzed by ultra-performance LC (UPLC)–electrospray ionization–quadrupole time-of-flight tandem MS (Zhao et al., 2018). The data indicated the presence of 13 anthocyanins in red sugarcane rinds, with a higher total anthocyanin content compared to green varieties. Cyanidin-3,5-diglucoside was found in all three cultivars analyzed. Although the identification of individual compounds is of high certainty, the total anthocyanin content of sugarcane was reported to be lower than berries by at least 25-fold (Zhao et al., 2018). Two studies have reported the purification of phenolic acids from sugarcane rind after sodium hydroxide hydrolysis using ultrasonic-assisted extraction (UAE) (Feng et al., 2015) and pH-zone-refining counter-current chromatography (pZRCCC) (Fang et al., 2017). pZRCCC revealed the presence of caffeic acid, *p*-coumaric acid, and ferulic acid, whereas UAE indicated the presence of gallic acid, chlorogenic acid, and ferulic acid. Using online solid-phase extraction (SPE) with high-speed counter-current chromatography, gallic acid, 4-hydroxyphenylacetic acid, vanillic acid, chlorogenic acid, caffeic acid, syringic acid, *p*-coumaric acid, and ferulic acid were detected (Geng et al., 2017). The assignment of compounds is tentative because all of these studies used absorption spectra data to identify compounds.

5.1.2 | (Poly)phenols in sugarcane leaves

Sugarcane leaves contain multiple phenolics. Compounds identified without hydrolysis with a high level of certainty by LC/MS include various chlorogenic acids, including caffeoyl- and feruloyl-quinic acid isomers with a lower level of free phenolic acids. Orientin and iso-orientin, C-glycosides of luteolin, and vitexin, a C-glycoside of apigenin, are predominant flavonoids in sugarcane leaves (Castro-Moretti et al., 2021). The other publications shown in Table 2 identified (poly)phenols only by absorption spectra against standards and so have a lower degree of confidence in identification. The identification of tricin and diosmetin derivatives is therefore only tentative. Two studies identified free phenolic acids and multiple flavonoids, reporting values much higher than other publications, but they do not have MS identification and therefore are not definitive (Abbas et al., 2014; Lee et al., 2012).

5.1.3 | (Poly)phenols in sugarcane culm and node

Sugarcane culm is the stem-like aerial part of the sugarcane plant that is harvested for the extraction of sugarcane

TABLE 1 Identification of (poly)phenols in the rind of the sugarcane plant.

Method	(Poly)phenols identified	Concentration	Unit	Ref.
Hydrolysis: none				
Extraction: acetone/methanol/acidified water				
Concentration: rotary evaporator at 40°C under vacuum	Cyanidin-3-glucoside	0.0946 ± 0.0039	mg/g DW	Zhao et al. (2018)
Purification: AB-8 adsorptive resin	Malvidin-3,5-diglucoside	0.0798 ± 0.0020		
Analysis and quantification:	Malvidin-3-caffeooyl-glucoside	0.0271 ± 0.0017		
UPLC-ESI-QTOF-MS/MS in positive ion mode. Standards: cyanidin-3-glucoside, peonidin-3-glucoside, and malvidin-3-glucoside (other derivatives are calculated from these). High certainty of correct identification	Cyanidin-3-caffeooyl-glucoside-5-glucoside	0.0168 ± 0.0016		
	Peonidin-3-feruloyl-arabinoside-5-rhamnoside	0.0048 ± 0.0006		
	Pelargonidin-3-diglucoside	0.0046 ± 0.0006		
	Peonidin-3-glucoside	0.0036 ± 0.0003		
	Malvidin-3-caffeooyl-rutinoside	0.0031 ± 0.0000		
	Cyanidin-3-malonyl-glucoside	0.0013 ± 0.0000		
	Cyanidin-3-cinnamoyl-glucoside	0.0004 ± 0.0000		
	Cyanidin-3-succinyl-glucoside	0.0001 ± 0.0000		
	Peonidin-3,5-diglucoside	<5.00 × 10 ⁻⁵		
Hydrolysis: none	Gallic acid	El: 74.5 ± 9.5	mg/g DW	Feng et al. (2015)
Extraction: ultrasonic-assisted solvent extraction using ethanol/water		E2: 91.5 ± 11.2		
Concentration: rotary evaporator at 40°C		E3: 125 ± 14.1		
Purification: El: crude/unpurified sugarcane rind extract; E2: E1 purified by microporous adsorption resins; E3: E1 purified by ethyl acetate extraction	Chlorogenic acid	El: 1.49 ± 0.28		
Analysis and quantification:	high-performance liquid chromatography (HPLC)/UV-visible; retention times and standards. Low/medium certainty of correct identification	E2: 3.16 ± 1.20		
	Ferulic acid	E3: 11.1 ± 2.4		
		El: 2.10 ± 0.38		
		E2: 1.62 ± 0.18		
		E3: 9.13 ± 2.50		

(Continues)

TABLE 1 (Continued)

Method	(Poly)phenols identified	Concentration	Unit	Ref.
Hydrolysis: NaOH Extraction: separation by pZRC(4C), acidification, and extraction by ethyl acetate.	<i>p</i> -Coumaric acid	65.2	mg/g of crude/unpurified sample	Fang et al. (2017)
Analysis and quantification: HPLC/UV-visible; retention times and standards. Low/medium certainty of correct identification	Ferulic acid Caffeic acid	12.9 4.80		
Hydrolysis: NaOH Extraction: separation by SPE with high-speed counter-current chromatography, acidification, and extraction by ethyl acetate	<i>p</i> -Coumaric acid	0.0723	mg/g of crude/unpurified sample	Geng et al. (2017)
Concentration: rotary evaporator Analysis and quantification: HPLC with diode array detector (HPLC/DAD); retention times and standards. Low/medium certainty of correct identification	Gallic acid Ferulic acid	0.0449 0.0185		
Hydrolysis: none Extraction: acidified solvent extraction using ethanol with sonication	Catechin	40.5 ± 34.3	mg/g DW	Kerdchan et al. (2020)
Analysis and quantification: Reverse-phase HPLC (RP-HPLC) with DAD; retention times and standards. Low/medium certainty of correct identification	Quercetin Ferulic acid Resveratrol Epicatechin Gallic acid Myricetin Caffeic acid Rutin <i>p</i> -Coumaric acid	18.7 ± 7.2 7.10 ± 1.96 6.54 ± 1.50 2.05 ± 0.46 1.69 ± 0.60 0.672 ± 0.330 0.350 ± 0.021 0.345 ± 0.151 0.145 ± 0.046	mg/g DW	

Abbreviations: DW, dry weight; ESI, electrospray ionization; pZRC(4C), pH-zone-refining counter-current chromatography; QTOF-MS/MS, quadrupole time-of-flight tandem; SPE, solid-phase extraction; UPLC, ultra-performance liquid chromatograph.

TABLE 2 Identification of (poly)phenols in the leaves of the sugarcane plant.

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Diosmetin-8-C-glycoside	0.0870 ± 0.0010	mg/g fresh sample (wet wt)	Colombo et al. (2006)
Extraction: methanol/water extraction with ultrasonic maceration		0.0500 ± 0.0000		
Concentration: rotary evaporator	Tricin-4-O-(erythro- or threo-guaiacylglyceryl) ether [$n = 3$; data expressed as mg diosmin/g fresh sample]	0.0330 ± 0.0010		
Purification: SPE	Tricin-4-O-(erythro- or threo-guaiacylglyceryl) ether-7-O-glucopyranoside [value obtained by the sum of all flavonoids' chromatographic peaks]	0.0220 ± 0.0000		
Analysis and quantification: thin-layer chromatography (TLC) and HPLC/DAD; retention times and standards (diosmin standard used for quantification). Low/medium certainty of correct identification	Tricin-4-O-(erythro- or threo-guaiacylglyceryl) ether-7-O-glucopyranoside [$n = 3$; data expressed as mg diosmin/g fresh sample]	0.0100 ± 0.0000		
	Tricin-4-O-(erythro- or threo-guaiacylglyceryl) ether [value obtained by the sum of all flavonoids' chromatographic peaks]			(Continues)

TABLE 2 (Continued)

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Maysin	0.0398 ± 0.0172	mg/g DW	Castro-Moretti et al. (2021)
Extraction: water/methanol/chloroform	Isoorientin	0.0373 ± 0.0017		
Concentration: speed vacuum	3-O-Caffeoylquinic acid	0.0288 ± 0.0083		
Purification: 3 kDa Amicon filtering device	Coniferyl alcohol	0.0282 ± 0.0118		
Analysis and quantification:	5-O-Caffeoylquinic acid	0.0208 ± 0.0023		
Untargeted metabolomics: GC/MS	Orientin	0.0112 ± 0.0059		
Targeted metabolomics: LC/MS, using standards for quantification	Isovitexin/vitexin	0.0107 ± 0.0013		
(S 30-Susceptible variety after 30 days of inoculation of the bacteria). High certainty of correct identification.	Rhamnosylisorientin	0.0073 ± 0.0009		
	4-O-Caffeoylquinic acid	0.0059 ± 0.0007		
	<i>p</i> -Coumaroylquinic acid 2	0.0037 ± 0.0011		
	Feruloylquinic acid isomer 3	0.0030 ± 0.0003		
	Feruloylquinic acid isomer 2	0.0026 ± 0.0007		
	Feruloylquinic acid isomer 4	0.0018 ± 0.0008		
	<i>p</i> -Coumaroylquinic acid 1	0.0015 ± 0.0003		
	Coumaric acid	0.0011 ± 0.0008		
	Caffeic acid	0.0009 ± 0.0007		
	Feruloylquinic acid isomer 1	0.0009 ± 0.0002		
	3,4-Caffeoylquinic acid	0.0009 ± 0.0004		
	Vanillin	0.0005 ± 0.0002		
	Benzoic acid	0.0003 ± 0.0001		
	Vanillic acid	0.0003 ± 0.0003		
	Salicylic acid	0.0003 ± 0.0003		
	Syringic acid	0.0002 ± 0.0002		
	Apigenin	0.0002 ± 0.0001		
	Sinapic acid	0.0002 ± 0.0001		
	Ferulic acid	0.0002 ± 0.0001		
	4-Hydroxybenzoic acid	0.0002 ± 0.0001		
	Luteolin-7-O-glucoside	0.0001 ± 0.0000		

(Continues)

TABLE 2 (Continued)

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Isoorientin	0.0993 ± 0.0203	mg/g DW	Castro- Moretti et al. (2021)
Extraction: water/methanol/chloroform	5-O-Caffeoylquinic acid	0.0858 ± 0.0216		
Concentration: speed vacuum	3-O-Caffeoylquinic acid	0.0795 ± 0.0176		
Purification: 3 kDa Amicon filtering device	Maysin	0.0388 ± 0.0239		
Analysis and quantification:	Coniferyl alcohol	0.0342 ± 0.0070		
Untargeted metabolomics: GC/MS	Rhamnosylisoorientin	0.0156 ± 0.0054		
Targeted metabolomics: (LC/MS, using standards for quantification) (R 30-Resistant variety after 30 days of inoculation of the bacteria). High certainty of correct identification	<i>p</i> -Coumaroylquinic acid 2	0.0155 ± 0.0054		
	4-O-Caffeoylquinic acid	0.0148 ± 0.0024		
	Orientin	0.0144 ± 0.0066		
	Isovitexin/Vitexin	0.0116 ± 0.0021		
	<i>p</i> -Coumaroylquinic acid 1	0.0080 ± 0.0035		
	Feruloylquinic acid isomer 3	0.0074 ± 0.0020		
	Feruloylquinic acid isomer 4	0.0027 ± 0.0005		
	Feruloylquinic acid isomer 2	0.0023 ± 0.0004		
	Coumaric acid	0.0021 ± 0.0007		
	Caffeic acid	0.0020 ± 0.0007		
	4-Hydroxybenzoic acid	0.0019 ± 0.0010		
	Salicylic acid	0.0014 ± 0.0007		
	Feruloylquinic acid isomer 1	0.0011 ± 0.0002		
	Luteolin-7- <i>O</i> -glucoside	0.0009 ± 0.0004		
	Syringic acid	0.0006 ± 0.0002		
	Vanillin	0.0006 ± 0.0001		
	3,4-Caffeoylquinic acid	0.0006 ± 0.0002		
	Vanillic acid	0.0005 ± 0.0002		
	Benzoic acid	0.0005 ± 0.0001		
	Ferulic acid	0.0004 ± 0.0002		
	Sinapic acid	0.0003 ± 0.0002		
	Apigenin	0.0001 ± 0.0000		
	Sinapaldehyde	0.0001 ± 0.0001		

(Continues)

TABLE 2 (Continued)

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Ferulic acid	14.6 ± 0.0	mg/g	Abbas et al. (2014)
Extraction: air-dried, ground, and soaked in boiling water (residue further extracted twice and concentrated)	Coumaric acid	11.7 ± 0.0		
	Quercitrin	11.0 ± 0.0		
	Caffeic acid	9.16 ± 0.01		
	Ellagic acid	9.03 ± 0.02		
	Quercetin	5.81 ± 0.01		
	Epicatechin	5.78 ± 0.01		
	Catechin	4.51 ± 0.01		
	Gallic acid	4.38 ± 0.02		
	Isoquercitrin	3.98 ± 0.01		
	Rutin	3.34 ± 0.01		
	Chlorogenic acid	3.27 ± 0.02		
	Caffeic acid	43.1 ± 4.1 (<i>n</i> = 1)	mg/g	Lee et al. (2012)
Hydrolysis: none				
Extraction: boiling				
Concentration: freeze-drying				
Analysis and quantification: RP-HPLC/UV-visible; retention times and standards. Low/medium certainty of correct identification	Chlorogenic acid	3.23 ± 1.46 [1.68–4.58] (<i>n</i> = 3)		
	Vitexin	2.55 ± 0.46 (<i>n</i> = 1)		
	Hydroxybenzoic acid	0.622 ± 0.718 [0.114–1.13] (<i>n</i> = 2)		
	<i>p</i> -Coumaric acid	1.13 ± 0.28 (<i>n</i> = 1)		
Hydrolysis: none				
Extraction: solvent extraction with 70% ethanol, acidified, and then ethyl acetate extraction.	Ferulic acid	0.0373 ± 0.0010	mg/g	Zhao et al. (2008)
	Coumaric acid	0.0284 ± 0.0010		
	Caffeic acid	0.0103 ± 0.0000		
	Chlorogenic acid	0.0104 ± 0.0000		
	<i>p</i> -Hydroxybenzoic acid	0.0081 ± 0.0000		
	Sinapic acid	0.0077 ± 0.0000		
	Gallic acid	0.0073 ± 0.0000		
	Syringic acid	0.0063 ± 0.0000		
	Vanillic acid	0.0058 ± 0.0000		
	Protocatechuic acid	0.0044 ± 0.0000		

Abbreviations: DAD, diode array detection; DW, dry weight; GC, gas chromatography; HPLC, high-performance liquid chromatography; LC, liquid chromatography; MS, mass spectrometry; RP-HPLC, reverse-phase high-performance liquid chromatography; SPE, solid-phase extraction. Multiple values reported for the same compound are represented as mean plus/minus SD [range] (*n* of samples).

TABLE 3 Identification of (poly)phenols in the culm of the sugarcane plant.

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Chlorogenic acid	0.0141 ± 0.0026 [0.0111–0.0160] (n = 3)	mg/g	Duarte-Almeida et al. (2011)
Extraction: methanol/water extraction	Coumaric acid	0.0107 ± 0.0043 [0.0059–0.0141] (n = 3)		
Purification: SPE	Luteolin	0.0060 ± 0.0008 [0.0051–0.0067] (n = 3)		
Concentration: evaporated under reduced pressure	Apigenin	0.0047 ± 0.0019 [0.0026–0.0060] (n = 3)		
Analysis and quantification: RP-HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Tricin	0.0033 ± 0.0003 [0.0029–0.0035] (n = 3)		
	Caffeic acid	0.0014 ± 0.0005 [0.0010–0.0020] (n = 3)		
Hydrolysis: none	Orientin	0.132 (n = 1)	mg/g	McGhie (1993)
Extraction: 80% acetonitrile in milli-Q water	Swertiajaponin	0.109 ± 0.078 [0.0530–0.164] (n = 2)		
Clarification/Purification: centrifuge	Apigenin	0.0625 ± 0.0021 [0.0610–0.0640] (n = 2)		
Analysis and quantification: capillary zone electrophoresis (quantified as apigenin equivalents). Medium certainty of correct identification	Tricin-7-glucoside sulphate	0.0430 (n = 1)		
	Tricin-7-rhamnosylgalacturonide	0.0260 (n = 1)		
	Isoschaftoside	0.0170 ± 0.0028 [0.0150–0.0190] (n = 2)		
	Schaftoside	0.0165 ± 0.0021 [0.0150–0.0180] (n = 2)		

Abbreviations: DAD, diode array detection; RP-HPLC, reverse-phase high-performance liquid chromatography; SPE, solid-phase extraction. Multiple values reported for the same compound are represented as mean plus/minus SD [range] (no. of samples).

juice to manufacture cane sugar and other related products (Driemeier et al., 2012). There are no definitive qualitative or quantitative analyses on the phenolic composition of the culm, as all publications have only reported high-performance LC with diode array detection (HPLC/DAD) with no studies using LC/MS. Apart from apigenin in culm, none of the compounds tentatively detected have been reported in more than one publication. No studies have conducted any hydrolysis steps, and therefore there could be some undiscovered bound (poly)phenolics. According to one study (Kerdchan et al., 2020), the most abundant (poly)phenols in sugarcane culm were identified as orientin, swertiajaponin, and apigenin (Table 3). When writing this literature review, we found only one publication on (poly)phenols in sugarcane node (Kerdchan et al., 2020). This study did not conduct a hydrolysis step, and the identification was done by HPLC/DAD using retention times and standards, giving only a tentative identification. According to this publication, the most abundant (poly)phenols in sugarcane node are catechin, quercetin, and resveratrol, but these are very tentative identifications as resveratrol is unlikely to be present, and quercetin aglycone is unlikely to be present without hydrolysis (Table 4).

In summary, the sugarcane plant consists of various phenolic acids and flavonoids. The amount of (poly)phenols reported varies with the extraction technique, implying that optimizing extraction can lead to higher amounts of (poly)phenols.

5.2 | (Poly)phenols in products and byproducts

5.2.1 | Sugarcane juice

Sugarcane juice is a widely studied product of the sugarcane industry because cold-pressed sugarcane juice is a popular drink in many countries. According to the compiled literature in this review, many researchers have used HPLC coupled with UV/DAD techniques to analyze the (poly)phenolic profile of sugarcane juice, and so most compounds are only tentatively identified. Analyses using nuclear magnetic resonance (NMR) (Ali et al., 2019) and LC/MS (Rodrigues et al., 2021) techniques provide more certainty in identification. Apigenin, tricin, and luteolin derivatives were the most abundant types of flavonoids,

TABLE 4 Identification of (poly)phenols in the node of the sugarcane plant.

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Catechin	21.4 ± 16.4 [7.54–43.8] (n = 4)	mg/g DW	Kerdchan et al. (2020)
Extraction: acidified solvent extraction (ethanol) with sonication	Quercetin	13.3 ± 11.8 [5.02–30.5] (n = 4)		
Analysis and quantification: RP-HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Resveratrol	7.30 ± 0.82 [6.59–8.39] (n = 4)		
	Ferulic acid	5.30 ± 3.54 [3.40–10.6] (n = 4)		
	Gallic acid	1.89 ± 0.92 [1.27–3.23] (n = 4)		
	Epicatechin	1.36 ± 0.47 [0.820–1.93] (n = 4)		
	Myricetin	0.400 ± 0.486 [0.0400–1.11] (n = 4)		
	Caffeic acid	0.373 ± 0.029 [0.340–0.410] (n = 4)		
	Rutin	0.235 ± 0.182 [0.100–0.490] (n = 4)		
	p-Coumaric acid	0.140 ± 0.050 [0.0900–0.210] (n = 4)		

Abbreviations: DAD, diode array detection; DW, dry weight; RP-HPLC, reverse-phase high-performance liquid chromatography. Multiple values reported for the same compound are represented as mean plus/minus SD [range] (no. of samples).

with *C*-glycosides being a common substitution (Table 5). In addition, after alkaline hydrolysis (Payet et al., 2006), several free phenolic acids were identified by LC/MS, with *p*-coumaric and ferulic acids being the most abundant. The extraction technique plays a key role in quantifying individual (poly)phenols, with studies that used a resin-based extraction technique often reporting higher values, suggesting this could be a high-yielding technique.

5.2.2 | Sugarcane syrup

Sugarcane syrup is less studied compared to juice, probably because it is an intermediate product that often does not come out of the production process of making sugar. Only one study reported the abundance of ferulic, *p*-coumaric, and caffeic acids using LC/MS analysis after alkaline hydrolysis (Payet et al., 2006) (Table 6).

5.2.3 | Massecuite

Massecuite is a very thick mixture of mill syrup and molasses. During industrial processing, seed crystals are added to massecuite to encourage the sugar crystallization process (Payet et al., 2006). Only one study has reported the (poly)phenolic profile of massecuite (Payet et al., 2006), using LC/MS after alkaline hydrolysis. The most abundant phenolics reported in sugarcane massecuite after hydrolysis were *p*-coumaric acid, ferulic acid, and *p*-hydroxybenzoic acid (Table 7).

5.2.4 | Sugar

Sugar crystals are the main product of the sugarcane industry; however, processed sugar generally has fewer

(poly)phenols than other products or sugarcane plant parts as most are retained in molasses. On the other hand, brown sugar or minimally refined brown sugar has slightly higher (poly)phenolic contents compared to refined white sugar. The majority of studies used LC/MS to analyze the different types of sugars with good-quality reliable data (Table 8). In general, unhydrolyzed samples contain syringic acid, vanillic acid, and vanillin, whereas ferulic acid and *p*-coumaric acid are extremely low in quantity. After alkaline hydrolysis or ultrasonication, both ferulic acid and *p*-coumaric acid were detected in significant amounts (Azlan et al., 2020; Payet et al., 2005, 2006).

5.2.5 | NCS

NCS are quite popular in many countries and are produced via a traditional method of making sugar, where the molasses fractions, otherwise usually removed in sugar manufacturing, remain intact with the sugar crystals. The brown color of NCS is gained from the presence of molasses, melanoidins, and phytochemical pigments (Zidan & Azlan, 2022). Two studies conducted by the same research group have used NMR to identify the (poly)phenolic profile of kokuto (Takara et al., 2002, 2003), delivering reliable (poly)phenolic profile identification. When acid hydrolysis was used in one study (Takara et al., 2003), bound glycosides were removed, making it easier to analyze the (poly)phenolic profile (Rommel & Wrolstad, 1993). However, acid hydrolysis was used to isolate only one compound (2-[4-(3-hydroxy-1-propenyl)-2,6-dimethoxyphenoxy]-3-hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)propyl-β-D-glucopyranoside [compound 13]) (Takara et al., 2003). The use of an alkaline hydrolysis followed by MS coupled with HPLC delivers a more reliable and simplified (poly)phenolic profile (Shang et al., 2022). The most

TABLE 5 Identification of (poly)phenols in sugarcane juice.

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none		0.0535 ± 0.0332 [0.0300–0.0770] (<i>n</i> = 2)	mg/g fresh sample	Colombo et al. (2006)
Extraction: methanol/water extraction with sonication	Isoschafitoseide	0.0500 ± 0.0396 [0.0220–0.0780] (<i>n</i> = 2)		
Concentration/Purification: SPE	Schafitoseide			
Analysis and quantification: HPLC/DAD; retention times and standards (Diosmin standard used for quantification).	4'-5'-dimethyl-luteolin-8-C-glycoside	0.0215 ± 0.0092 [0.0150–0.0280] (<i>n</i> = 2)		
Low/medium certainty of correct identification	Vitexin	0.0135 ± 0.0007 [0.0130–0.0140] (<i>n</i> = 2)		
Hydrolysis: none		0.0173 ± 0.0020	mg/g	Duarte-Almeida et al. (2011)
Extraction: methanol/water extraction				
Purification: SPE	Apigenin			
Concentration: evaporated under reduced pressure using a rotary evaporator	Coumaric acid	0.0090 ± 0.0060	mg/L	Duarte-Almeida et al. (2006)
Analysis and quantification: RP-HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Tricin	0.0059 ± 0.0060		
Hydrolysis: none	Ferulic acid	0.0028 ± 0.0010		
Extraction/Purification: using Amberlite XAD2 and elution by methanol/ammonia	Luteolin	0.0027 ± 0.0050		
Concentration: rotary evaporator				
Analysis and quantification: RP-HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Hydroxycinnamic acids	14084 ± 213		
Hydrolysis: none	Tricin	11791 ± 363		
Extraction/Purification: using Amberlite XAD2 and elution by methanol/ammonia	Apigenin	7508 ± 216		
Concentration: rotary evaporator	Sinapic acid	5695 ± 45		
Analysis and quantification: RP-HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Luteolin	2633 ± 229		
Hydrolysis: none	Caffeic acid	739 ± 18		
Extraction/Purification: fresh sugarcane juice obtained by mechanical juicer; no further extraction	Gentisic acid	6.50	mg/g	Ali et al. (2019)
Concentration: lyophilized to remove water	Luteolin	6.20		
Analysis and quantification: NMR and quantified by integrating the peak areas with the internal standard trimethylsilyl propionate (TSP) peak areas (and using the equation). High certainty of correct identification				(Continues)

TABLE 5 (Continued)

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Apigenin-6-C-glucoside-8-C-arabinoside (schaffatoside) (C)	18.9 ± 2.1 [16.8–21.0] (n = 3)	mg/L	Rodrigues et al. (2021)
Extraction: none (fresh sugarcane juice obtained by grinding in a mechanical mill)	Tricin-7-O-rhamnosylglucuronide (C)	12.8 ± 3.0 [10.0–16.0] (n = 3)		
Purification: SPE quantification by HPLC/DAD; retention times and standards	Diosmetin-6-C-hexosyl-7-O-methyl (C)	7.68 ± 1.52 [5.95–8.80] (n = 3)		
A: Quantified as gallic acid	Glucosyringic acid (A)	4.90 ± 2.10 [2.80–7.00] (n = 3)		
B: Quantified as p-coumaric acid	1-O-trimethylgallyloyl-6-O-gallyloyl-D-glucoside (malaysin A) (C)	4.11 ± 0.42 [3.84–4.60] (n = 3)		
C: Quantified as diosmin	Luteolin-6-C-hexosyl-8-C-pentosyl (C)	2.22 ± 0.16 [2.10–2.40] (n = 3)		
High certainty of correct identification	2-O-caffeooylglucarate (A)	1.93 ± 0.35 [1.55–2.23] (n = 3)		
Hydrolysis: NaOH	Diosmetin-8-C-glucoside (B)	0.90 ± 0.115 [0.800–1.03] (n = 3)		
Extraction: solvent extraction using NaOH and ethyl acetate, then acidifying, and again extraction with ethyl acetate.	(Ortho or meta) coumaric acid (B)	0.647 ± 0.025 [0.620–0.670] (n = 3)		
Organic layer dried over anhydrous sodium sulfate	p-Coumaric acid	0.136	mg/g DW	Payet et al. (2006)
Concentration: rotary evaporator	Ferulic acid	0.0698		
Analysis and quantification: HPLC/DAD/MS; retention times, standards, and electrospray mass spectra. High certainty of correct identification	p-Hydroxybenzoic acid	0.0158		
Hydrolysis: none	Caffeic acid	0.0083		
Extraction: HPLC-micro-fractionation	Vanillin	0.0081		
Concentration: SPE and rotary evaporator	Protocatechic acid	0.0063		
Analysis and quantification: HPLC/UV/DAD and TLC; retention times and standards (expressed as Diosmin equivalents). Low/medium certainty of correct identification	Syringic acid	0.0050		
	Ioschaffatoside	43.0 ± 1.0	mg flavonoid/L	Vila et al. (2008)
	Schaftoside	17.0 ± 1.0		
	Vitexin	8.00 ± 1.00		
	4',5'-Di-O-methyl-luteolin-8-C-glucoside	8.00 ± 1.00		
	Diosmetin-8-C-glucoside	7.00 ± 1.00		

(Continues)

TABLE 5 (Continued)

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Caffeic acid	2.26 ± 0.06	mg/L	Zhao et al. (2008)
Extraction: acidified and extracted 4 times with ethyl acetate, dried over anhydrous sodium sulfate	Gallic acid	1.15 ± 0.02		
Concentration: rotary evaporator	Ferulic acid	1.13 ± 0.02		
Analysis and quantification: HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Vanillic acid	0.970 ± 0.030		
	Coumaric acid	0.930 ± 0.020		
	Protocatechuic acid	0.896 ± 0.020		
	<i>p</i> -Hydroxybenzoic acid	0.860 ± 0.020		
	Chlorogenic acid	0.810 ± 0.030		
	Syringic acid	0.470 ± 0.020		
	Sinapic acid	0.420 ± 0.010		
Hydrolysis: none	<i>p</i> -Coumaric acid	0.01655	mg/g dry wt	Marasinghe et al. (2022)
Extraction: using ethyl acetate (3 times)				
Concentration: vacuum drying	5-Hydroxymethylfurfural	0.01269		
Analysis and quantification: HPLC/DAD; retention times and standards (quantified as quercetin equivalents).	protocatechuic acid			
Low/medium certainty of correct identification	Ferulic acid	0.01148		
	Vanillic acid	0.00703		
	Syringic acid	0.00459		
	Vanillin	0.00254		
	4-Hydroxybenzoic acid	0.00253		
	Gallic acid	0.00161		
	Protocatechuic acid	0.00105		
	Coumarin	0.00091		
	(+)-Catechin	0.00037		
	Sinapic acid	0.00009		

Abbreviations: DAD, diode array detection; DW, dry weight; HPLC, high-performance liquid chromatography; LC, liquid chromatography; MS, mass spectrometry; NMR, nuclear magnetic resonance; RP-HPLC, reverse-phase high-performance liquid chromatography; SPE, solid-phase extraction. Multiple values reported for the same compound are represented as mean plus/minus SD [range] (no. of samples).

TABLE 6 Identification of (poly)phenols in sugarcane syrup.

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Coumaric acid	0.0555 ± 0.0107	mg/g	Duarte-Almeida et al. (2011)
Extraction: methanol/water extraction	Chlorogenic acid	0.0293 ± 0.0013		
Purification: SPE	Apigenin	0.0231 ± 0.0010		
Concentration: evaporated under reduced pressure using a rotary evaporator	Tricin	0.0215 ± 0.0014		
Analysis and quantification: RP-HPLC/DAD; retention times and standards. Low/medium	Ferulic acid	0.0141 ± 0.0060		
	Luteolin	0.0105 ± 0.0012		
Hydrolysis: NaOH	<i>p</i> -Coumaric acid	0.141	mg/g DW	Payet et al. (2006)
Extraction: solvent extraction using NaOH and ethyl acetate, then acidifying, and again extraction with ethyl acetate. Organic layer dried and concentrated	Ferulic acid	0.114		
Analysis and quantification: HPLC/DAD/MS; retention times, standards, and electrospray mass spectra. High certainty of correct identification	Caffeic acid	0.0570		
	<i>p</i> -Hydroxybenzoic acid	0.0164		
	Syringic acid	0.0111		
	Vanillin	0.0103		
	Protocatechuic acid	0.0085		
	Vanillic acid	0.0022		

Abbreviations: DAD, diode array detection; DW, dry weight; MS, mass spectrometry; RP-HPLC, reverse-phase high-performance liquid chromatography; SPE, solid-phase extraction.

TABLE 7 Identification of (poly)phenols in sugarcane massecuite.

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: NaOH	<i>p</i> -Coumaric acid	0.144	mg/g DW	Payet et al. (2006)
Extraction: solvent extraction using NaOH and ethyl acetate, then acidifying, and again extraction with ethyl acetate. Organic layer dried and concentrated	Ferulic acid	0.0713		
Analysis and quantification: HPLC/DAD/MS; retention times, standards, and electrospray mass spectra. High certainty of correct identification	<i>p</i> -Hydroxybenzoic acid	0.0276		
	Caffeic acid	0.0252		
	Protocatechuic acid	0.0194		
	Vanillin	0.0145		
	Syringic acid	0.0135		
	Vanillic acid	0.0075		
	Benzoinic acid	0.0021		

Abbreviations: DAD, diode array detection; DW, dry weight; HPLC, high-performance liquid chromatography; MS, mass spectrometry.

abundant (poly)phenols recorded in NCS were gallic acid, syringic acid, and vanillic acid, with the most recorded (poly)phenols being chlorogenic acid, *p*-coumaric acid, caffeic acid, ferulic acid, protocatechuic acid, syringic acid, and vanillic acid (Table 9).

5.2.6 | Bagasse

Bagasse is a major waste and byproduct of the sugarcane industry but has the potential to be exploited due to the presence of phytochemicals such as (poly)phenols. Some studies have reported the (poly)phenolic profile of bagasse

(Table 10). One study used LC/MS to quantify three (poly)phenols (Zheng, Su, Zhou, et al., 2017), whereas a tentative identification was reported by others using HPLC with detection by absorption spectra (Colombo et al., 2006; Juttuporn et al., 2018; Zhao et al., 2008, 2015). None of these studies reported using any hydrolysis steps during extraction. One study reported the presence of tricin derivatives, but only based on HPLC/DAD. Despite the lack of hydrolysis, several studies have reported the presence of free ferulic acid, gallic acid, *p*-coumaric acid, protocatechuic acid, sinapic acid, and vanillic acid. It appears that processing steps could be enough to release some free phenolic acids.

TABLE 8 Identification of (poly)phenols in sugar products from sugarcane.

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none				
Extraction: methanol/water extraction	Apigenin	0.0071 ± 0.0010	mg/g	Duarte-Almeida et al. (2011)
Purification: SPE	Chlorogenic acid	0.0057 ± 0.0010		
Concentration: rotary evaporator	Luteolin	0.0042 ± 0.0010		
Analysis and quantification: RP-HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Coumaric acid	0.0038 ± 0.0020		
	Tricin	0.0031 ± 0.0010		
	Ferulic acid	0.0013 ± 0.0010		
Hydrolysis: none				
Extraction: solvent extraction using dichloromethane by a Soxhlet	Syringic acid	0.0060 ± 0.0050 [0.0010–0.0016] (n = 7)	mg/g	Payette et al. (2005)
Concentration: rotary evaporator	Vanillic acid	0.0030 ± 0.0030 [0.0000–0.0080] (n = 7)		
Analysis and quantification: GC/MS for volatiles, LC/MS for non-volatiles and HPLC/DAD for further confirmation; retention times, standards, and electrospray mass spectra. High certainty of correct identification	Vanillin	0.0030 ± 0.0010 [0.002–0.005] (n = 7)		
	Homovanillic acid	0.0010 (n = 1)		
	<i>p</i> -Coumaric acid	0.0010 ± 0.0010 [0.000–0.0030] (n = 7)		
	Benzoic acid	0.0010 ± 0.0000 [0.0010–0.0020] (n = 7)		
	Ferulic acid	0.0000 ± 0.0000 [0.0000–0.0020] (n = 7)		
	Acetosyringone	0.0010 (n = 1)		
	<i>p</i> -Hydroxybenzoic acid	0.0000 ± 0.0000 [0.0000–0.0020] (n = 7)		
	Coniferyl alcohol	0.0000 (n = 1)		
Hydrolysis: NaOH				
Extraction: solvent extraction using NaOH and ethyl acetate, then acidifying, and again extraction with ethyl acetate. Organic layer dried and concentrated	Ferulic acid	0.0112	mg/g dry content	Payette et al. (2006)
Concentration: rotary evaporator	<i>p</i> -Coumaric acid	0.0102		
Analysis and quantification: HPLC/DAD/MS; retention times, standards, and electrospray mass spectra. High certainty of correct identification	Caffeic acid	0.006		
Sample: Refined sugar	Protocatechuic acid	0.004		
Hydrolysis: none				
Extraction: acidified ethanolic solution followed by ultrasonication	<i>p</i> -Coumaric acid	0.0176 ± 0.0051	mg/g sample	Azlan et al. (2020)
Concentration: rotary evaporator	Syringic acid	0.0094 ± 0.0022		
Analysis and quantification: UHPLC/UV-visible/MS; retention times and standards. High certainty of correct identification	Benzoic acid	0.0072 ± 0.0013		
Sample: Refined sugar	Vanillic acid	0.0071 ± 0.0022		

(Continues)

TABLE 8 (Continued)

Method	(Poly)phenols present	Concentration	Unit	Reference
Sample: Brown sugar				
<i>p</i> -Coumaric acid	0.0199 ± 0.0031			
Benzoic acid	0.0084 ± 0.0031			
Vanillic acid	0.0063 ± 0.0036			
Syringic acid	0.0021 ± 0.0080			
Caffeic acid	0.0019 ± 0.0018			
Trans-ferulic acid	0.0012 ± 0.0080			
Syringic acid	0.0073 ± 0.0067			
Caffeic acid	0.0078 ± 0.0037			
<i>p</i> -Coumaric acid	0.0065 ± 0.0035			
Vanillic acid	0.0048 ± 0.0021			
Benzoic acid	0.0048 ± 0.0013			

Abbreviations: DAD, diode array detection; GC, gas chromatography; HPLC, high-performance liquid chromatography; LC, liquid chromatography; MS, mass spectrometry; RP-HPLC, reverse-phase high-performance liquid chromatography; SPE, solid-phase extraction; UHPLC, ultra-high-performance liquid chromatography.

5.2.7 | Molasses

Molasses is a widely studied byproduct of the sugarcane industry. Several studies have reported (poly)phenolic profiles of molasses using NMR or MS coupled with HPLC (Ali et al., 2019; Asikin et al., 2016; Deseo et al., 2020; Payet et al., 2006). One of these studies used alkaline hydrolysis (Payet et al., 2006), and another used acid hydrolysis, followed by HPLC/DAD, and so only a tentative identification of the compounds (Yu et al., 2017). The most abundant (poly)phenols in molasses are caffeic acid, apigenin, and gentisic acid. In addition, the most recorded (poly)phenols were swertisin, chlorogenic acid, caffeic acid, ferulic acid, apigenin, and syringic acid (Table 11).

6 | QUALITATIVE (POLY)PHENOLIC PROFILE IN SUGARCANE

6.1 | Flavonoid profile

Several flavonoids have been reported multiple times in sugarcane plant parts and processed products, and this strengthens the evidence for their presence. The most reported flavonoids across the entire plant and its derivatives are apigenin (14 times), luteolin (12 times), and tricin (11 times) (Table 12). Apigenin derivatives include vitexin (apigenin-8-C-glucoside), swertisin (7-O-methylapigenin 6-C-glucoside), schaftoside (apigenin 6-C-glucoside-8-C-arabinoside), and isoschaftoside (apigenin 6-C-arabinoside 8-C-glucoside), whereas luteolin derivatives include orientin (luteolin-8-C-glucoside), luteolin-7-O-glucoside, 4'-5'-dimethyl-luteolin-8-C-glycoside and luteolin-6-C-hexosyl-8-C-pentosyl, and a single tricin derivative was reported as tricin-7-O-neohesperidoside (4',5,7-trihydroxy-3',5'-dimethoxyflavone-7-O-neohesperidoside). Other flavonoids reported in multiple papers include catechin, diosmetin-8-C-glucoside (3',5,7-trihydroxy-4'-methoxyflavone-8-C-glucoside), and quercetin. Although four derivatives of diosmetin (3',5,7-trihydroxy-4'-methoxyflavone) have been reported, diosmetin aglycone has not. Derivatives of diosmetin are frequently found in leaves, but in processed products, they are only reported in juice.

Apigenin and derivatives have been reported in many products (juice, syrup, sugar, molasses, NCS) as well as in plant parts (leaves, culm), and so they seem to survive processing quite well. Many derivatives are C-glycosides, and this substitution adds stability to the molecule. C-glycosides are not removed by endogenous hydrolyzing enzymes such as glucosidases, but apigenin C-glycosides are possibly broken down by gut microbiota

TABLE 9 Identification of (poly)phenols in non-centrifugal sugar (NCS).

Product	Method	(Poly)phenols present	Concentration	Unit	Reference
Kokuto (NCS)	Hydrolysis: none Extraction: XAD-2 amberlite resin extraction eluted by different concentrations of methanol. Series of solvent extractions to isolate each compound Concentration: vacuum drying Analysis and quantification: IR, NMR, and HPLC/UV-visible; retention times and standards. High certainty of correct identification	4-[Ethane-2-[3-(4-hydroxy-3-methoxyphenyl)-2-propen]oxy]-2,6-dimethoxyphenyl- β -D-glucopyranoside 3-Hydroxy-4,5-dimethoxyphenyl- β -D-glucopyranoside 3-Hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-[4-(3-hydroxy-1-(E)-propenyl)-2,6-dimethoxyphenoxy]propyl- β -D-glucopyranoside β -D-fructofuranosyl- α -D-(6-vanillyl)-glucopyranoside 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-[4-(3-hydroxy-1-(E)-propenyl)-2-methoxyphenoxy]propyl- β -D-glucopyranoside Dehydrodiconiferyl alcohol-9'- β -D-glucopyranoside β -D-Fructofuranosyl- α -D-(6-syringyl)-glucopyranoside 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-[4-(3-hydroxy-1-(E)-propenyl)-2,6-dimethoxyphenoxy] 4-[Ethane-2-[3-(4-hydroxy-3-methoxyphenyl)-2-propen]oxy]-2-methoxyphenyl- β -D-glucopyranoside	0.0041 0.0034 0.0033 0.0020 0.0017 0.0016 0.0014 0.0012 0.0008	mg/g	Takara et al. (2002)
	Hydrolysis: acid hydrolysis only for fraction isolated for compound 13 Extraction: XAD-2 amberlite resin extraction eluted by different concentrations of methanol. Series of extractions and Sephadex gel column to isolate each compound fraction isolated for compound 13 Analysis and quantification: IR, NMR, and HPLC/UV-visible; retention times and standards. High certainty of correct identification	9-O- β -D-xylopyranoside of icariol a2 2-[4-(3-Hydroxy-1-propenyl)-2,6-dimethoxyphenoxy]-3-hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)propyl- β -D-glucopyranoside (compound 13) 4-(β -D-glucopyranosyloxy)-3,5-dimethoxyphenyl-propanone	0.0088 0.0035 0.0028	mg/g	Takara et al. (2003)
		4-[Erythro]2,3-dihydro-3(hydroxymethyl)-5-(3-hydropropyl)-7-methoxy-2-benzofuranyl]-2,6-dimethoxyphenyl- β -D-glucopyranoside 3-[5-[Threo]2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl]-7-methoxybenzofuran]]-propanoic acid	0.0014 0.0013		

(Continues)

TABLE 9 (Continued)

Product	Method	(Poly)phenols present	Concentration	Unit	Reference
NCS	Hydrolysis: NaOH Extraction: sample dissolved in water and centrifuged to separate supernatant and sediments. Supernatant acidified and solvent extraction with ethyl acetate	Gallic acid Syringic acid Vanilllic acid <i>p</i> -Coumaric acid Fumalic acid/Ferulic acid	2101 ± 700 [1197–3561] (n = 9) 202 ± 93 [88.8–353] (n = 9) 103 ± 66 [38.9–256] (n = 9) 44.3 ± 19.0 [19.5–68.6] (n = 9) 38.6 ± 14.0 [18.2–58.9] (n = 9) 38.4 ± 22.1 [10.5–85.6] (n = 9) 19.2 ± 20.6 [1.02–62.0] (n = 9) 15.7 ± 6.6 [5.57–26.5] (n = 9) 7.91 ± 3.02 [2.86–13.2] (n = 9) 7.36 ± 4.12 [1.91–16.7] (n = 9) 6.45 ± 5.04 [1.41–15.1] (n = 9) 3.01 ± 1.17 [1.47–4.87] (n = 9) 3.00 ± 2.21 [0.360–7.01] (n = 9) 1.83 ± 0.99 [0.0600–3.26] (n = 9) 1.19 ± 0.71 [0.110–2.48] (n = 9) 0.333 ± 0.200 [0.0000–0.640] (n = 9) 0.257 ± 0.052 [0.220–0.390] (n = 9) 0.0367 ± 0.0738 [0.0000–0.190] (n = 9) 4.39 ± 292 [30.2–924] (n = 9) 12.4 ± 0.9 [11.0–13.7] (n = 9) 5.73 ± 1.55 [3.45–8.06] (n = 9) 2.96 ± 0.41 [2.49–3.71] (n = 9) 2.94 ± 0.98 [1.34–4.56] (n = 9) 1.89 ± 0.27 [1.47–2.32] (n = 9) 1.42 ± 0.79 [0.650–3.27] (n = 9) 1.22 ± 0.50 [0.420–1.94] (n = 9) 0.2689 ± 0.1744 [0.0000–0.540] (n = 9) 0.257 ± 0.063 [0.220–0.420] (n = 9) 0.123 ± 0.072 [0.0000–0.190] (n = 9) 0.0433 ± 0.0180 [0.0000–0.0600] (n = 9) 0.0211 ± 0.0501 [0.0000–0.150] (n = 9) 0.0022 ± 0.0067 [0.0000–0.0200] (n = 9)	mg/L	Shang et al. (2021)
	Concentration: vacuum drying Analysis and quantification: ultraperformance liquid chromatography–mass spectrometry (UPLC/MS) with standards. High certainty of correct identification	Hydroxybenzoic acid Chlorogenic acid Sinapic acid Syringaldehyde Protocatechuic acid Caffeic acid Vanillin Luteolin Naringenin Apigenin Gentisic acid Rutin Catechin			
	Hydrolysis: NaOH Extraction: sample dissolved in water and centrifuged to separate supernatant and sediments. Sediment acidified and solvent extraction with ethyl acetate	Gallic acid Syringic acid Vanilllic acid Hydroxybenzoic acid Fumalic acid <i>p</i> -Coumaric acid Sinapic acid Syringaldehyde Caffeic acid Vanillin Luteolin Protocatechuic acid Rutin Chlorogenic acid Naringenin Gentisic acid Apigenin			

(Continues)

TABLE 9 (Continued)

Product	Method	(Poly)phenols present	Concentration	Unit	Reference
Granulated non-NCS (NCS-G)	Hydrolysis: none	Chlorogenic acid	0.0026 ± 0.0014 [0.0025–0.0028] (n = 5)	mg phenolic compound/g of product (DW)	Alarcón et al. (2021)
	Extraction: sample diluted with deionized water, acidified to pH 2 with HCl, and extracted using diethyl ether	Syringic acid	0.0025 ± 0.0015 [0.0023–0.0026] (n = 5)		
		p-Coumaric acid	0.0011 ± 0.0034 [0.0069–0.0014] (n = 5)		
		Vanillic acid	0.0009 ± 0.0001 [0.0008–0.0010] (n = 5)		
		Ferulic acid	0.0007 ± 0.0002 [0.0005–0.0009] (n = 5)		
	Concentration: vacuum drying	Protocatechuic acid	0.0005 ± 0.0000 [0.0004–0.0005] (n = 5)		
	Analysis and quantification: UHPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Chlorogenic acid	0.0030 ± 0.0010 [0.0028–0.0031] (n = 4)		
		Syringic acid	0.0018 ± 0.0000 [0.0017–0.0018] (n = 4)		
		p-Coumaric acid	0.0010 ± 0.0000 [0.0090–0.0011] (n = 4)		
		Ferulic acid	0.0009 ± 0.0001 [0.0008–0.0009] (n = 4)		
		Vanillic acid	0.0008 ± 0.0000 [0.0008–0.0008] (n = 4)		
		Protocatechuic acid	0.0004 ± 0.0000 [0.0004–0.0004] (n = 4)		
		Chlorogenic acid	0.0026 ± 0.0000 [0.0025–0.0027] (n = 4)		
		Syringic acid	0.0015 ± 0.0030 [0.0011–0.0016] (n = 4)		
		p-Coumaric acid	0.0010 ± 0.0000 [0.0010–0.0010] (n = 4)		
		Ferulic acid	0.0008 ± 0.0001 [0.0007–0.0009] (n = 4)		
		Vanillic acid	0.0008 ± 0.0000 [0.0007–0.0008] (n = 4)		
		Protocatechuic acid	0.0004 ± 0.0000 [0.0004–0.0005] (n = 4)		
		Syringic acid	0.0028 ± 0.0000		
		Chlorogenic acid	0.0021 ± 0.0010		
		p-Coumaric acid	0.0009 ± 0.0001		
		Vanillic acid	0.0009 ± 0.0000		
		Ferulic acid	0.0006 ± 0.0000		
		Protocatechuic acid	0.0005 ± 0.0000		
		Chlorogenic acid	0.0038 ± 0.0010		
		Syringic acid	0.0015 ± 0.0010		
		p-Coumaric acid	0.0014 ± 0.0010		
		Protocatechuic acid	0.0010 ± 0.0000		
		Ferulic acid	0.0010 ± 0.0020		
	NCS block sample		0.0009 ± 0.0000		
	Non-centrifugal cane sugar syrup at brix 50° (NCS-S50)		0.0010 ± 0.0000		

(Continues)

TABLE 9 (Continued)

Product	Method	(Poly)phenols present	Concentration	Unit	Reference
Non-centrifugal cane sugar syrup at brix 70° (NCS-S70)		Chlorogenic acid Syringic acid Ferulic acid Vanillic acid <i>p</i> -Coumaric acid Protocatechuic acid	0.0028 ± 0.0000 0.0018 ± 0.0000 0.0015 ± 0.0010 0.0011 ± 0.0010 0.0010 ± 0.0000 0.0008 ± 0.0020	mg/g	Zhu et al. (2020)
M-NCS (50 nm ceramic membrane clarified NCS)	Hydrolysis: none Extraction: extraction using ethyl acetate/HCl	Gallic acid Caffeic acid Syringic acid <i>p</i> -Coumaric acid Chlorogenic acid Vanillic acid Ferulic acid Protocatechuic acid Gallic acid Caffeic acid Syringic acid <i>p</i> -Hydroxybenzoic acid	0.0053 ± 0.0004 0.0031 ± 0.0000 0.0018 ± 0.0002 0.0012 ± 0.0002 0.0009 ± 0.0001 0.0009 ± 0.0001 0.0008 ± 0.0001 0.0004 ± 0.0000 0.0001 ± 0.0000 0.0050 ± 0.0001 0.00177 ± 0.0001 0.0006 ± 0.0000 0.0055 ± 0.0003 0.0044 ± 0.0004 0.0021 ± 0.0001 0.0018 ± 0.0002 0.0017 ± 0.0001 0.0011 ± 0.0000 0.0008 ± 0.0001 0.0007 ± 0.0000 0.0014 ± 0.0002 0.0008 ± 0.0001 0.0006 ± 0.0000 0.0003 ± 0.0001 0.0002 ± 0.0000 0.0002 ± 0.0000	mg/g	Zhu et al. (2020)
NCS1 (commercially produced NCS)					
NCS2 (secondary processed products on NCS1)					
NCS3 (secondary processed products on NCS1)					

(Continues)

TABLE 9 (Continued)

Product	Method	(Poly)phenols present	Concentration	Unit	Reference
GBS1 (colored sugar, using molasses and sucrose powder as source)		Gallic acid Caffeic acid Vanillic acid	0.0143 ± 0.0005 0.0007 ± 0.0001 0.0005 ± 0.0001		
GBS2 (colored sugar, using molasses and sucrose powder as source)		Gallic acid Vanillic acid Caffeic acid Protocatechuic acid <i>p</i> -Hydroxybenzoic acid Ferulic acid	0.0101 ± 0.0004 0.0014 ± 0.0001 0.0010 ± 0.0002 0.0009 ± 0.0000 0.0008 ± 0.0001 0.0001 ± 0.0000		
GBS3 (colored sugar, using raw sugar and camel color as source)		Gallic acid Caffeic acid Protocatechuic acid Vanillic acid <i>p</i> -Coumaric acid	0.0033 ± 0.0002 0.0016 ± 0.0003 0.0006 ± 0.0001 0.0004 ± 0.0001 0.0002 ± 0.0000		
Granulated jagger (GJ)	Hydrolysis: none Extraction: extraction using distilled water	Cinnamic acids	0.380 ± 0.0300	mg/g	Barrera et al. (2020)
Muscovado sugar (MS)	Concentration: SPE, rotary evaporation under vacuum Analysis and quantification: RP-HPLC/DAD; retention times and standards, Low/medium certainty of correct identification	Chlorogenic acid Apigenin Tricin Caffeic acid Luteolin Coumaric acid Ferulic acid Cinnamic acids Apigenin Chlorogenic acid Tricin Caffeic acid Luteolin Coumaric acid Ferulic acid	0.280 ± 0.0200 0.190 ± 0.0300 0.113 ± 0.0100 0.0760 ± 0.0050 0.0250 ± 0.0070 0.0181 ± 0.0019 0.0079 ± 0.0005 0.200 ± 0.040 0.174 ± 0.030 0.128 ± 0.040 0.108 ± 0.007 0.0490 ± 0.0030 0.0210 ± 0.0030 0.0150 ± 0.0020 0.0039 ± 0.0008		

(Continues)

TABLE 9 (Continued)

Product	Method	(Poly)phenols present	Concentration	Unit	Reference
Light jaggery block (LJB)	Apigenin		0.0970 ± 0.0130		
	Tricin		0.0960 ± 0.0170		
	Cinnamic acids		0.0950 ± 0.0040		
	Ferulic acid		0.0430 ± 0.0040		
	Caffeic acid		0.0260 ± 0.0020		
	Luteolin		0.0200 ± 0.0040		
	Chlorogenic acid		0.0180 ± 0.0030		
	Coumaric acid		0.0083 ± 0.0018		
	Tricin		0.130 ± 0.012		
	Apigenin		0.119 ± 0.019		
Regular jaggery block (RJB)	Cinnamic acids		0.117 ± 0.007		
	Ferulic acid		0.0560 ± 0.0030		
	Caffeic acid		0.0315 ± 0.0019		
	Luteolin		0.0220 ± 0.0060		
	Chlorogenic acid		0.0200 ± 0.0011		
	Coumaric acid		0.0100 ± 0.0011		
	Apigenin		0.0170 ± 0.0030		
	Tricin		0.0071 ± 0.0007		
	Cinnamic acids		0.0049 ± 0.0003		
	Caffeic acid		0.0027 ± 0.0002		
Brown sugar (BS)	Chlorogenic acid		0.0014 ± 0.0001		
	Coumaric acid		0.0008 ± 0.0001		
	Cinnamic acids		0.133 ± 0.003		
	Apigenin		0.116 ± 0.018		
	Tricin		0.0950 ± 0.0090		
	Chlorogenic acid		0.0780 ± 0.0040		
	Ferulic acid		0.0320 ± 0.0021		
	Coumaric acid		0.0114 ± 0.0012		
	Caffeic acid		0.0113 ± 0.0008		
	Cane honey (CH)				
Abbreviations: DAD, diode array detection; DW, dry weight; HPLC, high-performance liquid chromatography; NCS, non-centrifugal sugar; NMR, nuclear magnetic resonance; SPE, solid-phase extraction. Multiple value reported for the same compound are represented as mean plus/minus SD [range] (no. of samples).					

Abbreviations: DAD, diode array detection; DW, dry weight; HPLC, high-performance liquid chromatography; NCS, non-centrifugal sugar; NMR, nuclear magnetic resonance; SPE, solid-phase extraction. Multiple value reported for the same compound are represented as mean plus/minus SD [range] (no. of samples).

TABLE 10 Identification of (poly)phenols in bagasse.

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Tricin-4-O-(erythro- or threo-guaiaacylglyceryl) ether [$n = 3$; data expressed as mg diosmin/g fresh sample]	0.0670 ± 0.0010	mg/g fresh sample	Colombo et al. (2006)
Extraction: methanol/water extraction with ultrasonic maceration				
Concentration: rotary evaporation				
Purification: SPE	Tricin-4-O-(erythro- or threo-guaiaacylglyceryl) ether [value obtained by the sum of all flavonoids' chromatographic peaks]	0.0120 ± 0.0000		
Analysis and quantification: HPLC/DAD; retention times and standards (Diosmin standard used for quantification). Low/medium certainty of correct identification	Tricin-4-O-(erythro- or threo-guaiaacylglyceryl) ether-7-O-glucopyranoside [$n = 3$; data expressed as mg diosmin/g fresh sample]	0.0100 ± 0.0000		
	Tricin-4-O-(erythro- or threo-guaiaacylglyceryl) ether-7-O-glucopyranoside [value obtained by the sum of all flavonoids' chromatographic peaks]	0.0040 ± 0.0000		
Hydrolysis: none	<i>p</i> -Coumaric acid	3.11 ± 0.16	mg/g DW	Juttuporn et al. (2018)
Extraction: steam explosion, solvent extraction (ethanol) with UAE	Ferulic acid	0.521 ± 0.028		
Concentration: rotary evaporator	Syringic acid	0.403 ± 0.021		
Analysis and quantification: RP-HPLC/UV-visible; retention times and standards. Low/medium certainty of correct identification	Sinapic acid	0.201 ± 0.011		
	Hydroxybenzoic acid	0.0259 ± 0.0010		
	Vanillic acid	0.0227 ± 0.0010		
	Gallic acid	0.0085 ± 0.0000		
Hydrolysis: none	Gallic acid	4.36 ± 0.12	mg/g DW	Zhao et al. (2015)
Extraction: solvent extraction using ethanol and methanol in two different stages	Ferulic acid	1.87 ± 0.13		
Concentration: dried under vacuum and stream of nitrogen at two different stages	Coumaric acid	1.66 ± 0.14		
Analysis and quantification: RP-HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Chlorogenic acid	1.63 ± 0.12		
	<i>p</i> -Hydroxybenzoic acid	1.42 ± 0.16		
	Sinapic acid	1.12 ± 0.09		
	Vanillic acid	0.620 ± 0.090		
	Protocatechuic acid	0.230 ± 0.150		
Hydrolysis: none	<i>p</i> -Coumaric acid	12.6 ± 0.3	mg/g DW of 30% hydroalcoholic fraction	Zheng, Su, Zhou et al. (2017)
Extraction: dry powder extracted with ethanol/water assisted with ultrasonication. Further extracted with ethyl acetate and sent through polyamide resin column for purification	Genistein	15.2 ± 1.3		
Concentration: vacuum drying	Quercetin	9.98 ± 0.40		
Analysis and quantification: ultra-high-performance liquid chromatography/high-resolution time of flight mass spectrometry (UHPLC-HR-TOFMS) and quantified using standards. High certainty of correct identification				

(Continues)

TABLE 10 (Continued)

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none	Ferulic acid	0.120 ± 0.004	mg/g	Zhao et al.
Extraction: solvent extraction with 70% ethanol, acidified and then ethyl acetate extraction	Coumaric acid	0.0679 ± 0.0030		(2008)
Concentration: rotary evaporator	Protocatechuic acid	0.0423 ± 0.0020		
Analysis and quantification: HPLC/UV-visible; retention times and standards. Low/medium certainty of correct identification	Gallic acid	0.0386 ± 0.0010		
	p-Hydroxybenzoic acid	0.0349 ± 0.0010		
	Caffeic acid	0.0299 ± 0.0010		
	Vanillic acid	0.0277 ± 0.0010		
	Chlorogenic acid	0.0275 ± 0.0010		
	Syringic acid	0.0212 ± 0.0010		
	Sinapic acid	0.0081 ± 0.0000		

Abbreviations: DAD, diode array detection; DW, dry weight; HPLC, high-performance liquid chromatography; RP-HPLC, reverse-phase high-performance liquid chromatography; SPE, solid-phase extraction; UAE, ultrasonic-assisted extraction.

into lower molecular weight products (Mori et al., 2021). Catechin has been found in both plant parts and products, including juice, molasses, and NCS, indicating that it also appears to survive the production process. However, catechin was identified by LC/MS only in NCS and at very low levels; thus, the presence of catechin in sugarcane cannot be classed as definitive. Luteolin and its derivatives have been found in numerous products (juice, syrup, sugar, bagasse, molasses, NCS) as well as plant components (leaves, culm). Most derivatives seem to survive processing but luteolin aglycone will not be produced from C-glycosides during processing. In addition to juice, luteolin-8-C-(rhamnosylglucoside) has been found in leaves.

The only place diosmetin-8-C-glucoside has been found in the plant is in the leaves, but it is present in products such as molasses and juice. There are a few plant components that contain epicatechin, including leaves, rinds, and nodes. It has not been identified in edible goods but was noted in bagasse and so may be eliminated with the bagasse during processing. It has been shown that leaves contain isoschaftoside (apigenin-6-C-arabinosyl-8-C-glucoside). Although it has not been documented in other plant components, it has been reported a few times in juice. In addition, it appears to survive the concentrating process, so it has ended up in both syrup and NCS.

Rutin, quercetin, and orientin were largely identified in plant components but less frequently in products. As they have been found in molasses and NCS, orientin and rutin might survive processing. Most plant components were found to contain schaftoside, found in juice several times as well as in syrup, molasses, and NCS. Although plant parts do not contain swertisin, it has been found in juice and other products, including syrup, molasses, and juice. Its presence in molasses and syrup suggests that it is concentrated during processing. Tricin was found in all

plant parts and appears to survive processing. There is no evidence for tricin-7-O-glucoside in plant tissues, but it has been reported in molasses and juice. Tricin-7-O-neohesperidoside has been observed in leaves, molasses, bagasse, and juice. Vitexin has been found in leaves, and in juice and molasses.

6.2 | Phenolic acid profiles of sugarcane

Most plant tissues contain very low concentrations of free phenolic acids. Mostly, phenolic acids are ester-linked to either quinic acid, as in chlorogenic acids, or to plant cell wall structures, such as arabinoxylans. Upon hydrolysis, ester linkages are broken, and the free phenolic acid is released. This can occur during processing or by intentional hydrolysis before analysis. The most commonly reported free phenolic acids across the entire sugarcane plant and its products are ferulic acid (30 times) and caffeic acid (27 times). Ester-linked phenolic acids, often grouped together as chlorogenic acids (23 times), have also been commonly reported (Table 12). Other often reported phenolic acids are protocatechuic acid, coumaric acid (including p-coumaric acid), sinapic acid, (p)-hydroxybenzoic acid, syringic acid, vanillic acid, and gallic acid. Numerous plant parts and products included caffeic acid, coumaric acid, chlorogenic acid, ferulic acid, and gallic acid. Analyzed both before and after hydrolysis, they appear to be quite stable during the procedure.

Many of the phenolic acids reported here are cinnamic acid derivatives. Cinnamic acid is one of the precursors of the mevalonate–shikimate biosynthesis pathway, leading to phenolic acids such as p-coumaric, ferulic, caffeic, and sinapic acids (Muronetz et al., 2020). Protocatechuic, sinapic, ferulic, and p-hydroxybenzoic acids have not been reported widely in plant components but have been exten-

TABLE 11 Identification of (poly)phenols in molasses.

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none			mg/g	Duarte-Almeida et al. (2011)
Extraction: methanol/water extraction	Chlorogenic acid	0.243 ± 0.018		
Purification: SPE	Coumaric acid	0.234 ± 0.004		
Concentration: evaporated under reduced pressure using a rotary evaporator	Apigenin	0.168 ± 0.010		
	Tricin	0.132 ± 0.016		
Analysis and quantification: RP-HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Ferulic acid	0.0788 ± 0.0130		
	Luteolin	0.0635 ± 0.0050		
Hydrolysis: none			mg/g	Ali et al. (2019)
Extraction: fresh sugarcane juice obtained by mechanical juicer; no further extraction	Apigenin	11.2		
	Gentisic acid	10.6		
	Luteolin	8.5		
Concentration: lyophilized to remove water				
Analysis and quantification: NMR and quantified by integrating the peak areas with the internal standard TSP peak areas (and using the equation). High certainty of correct identification				
Hydrolysis: none	Diosmin	ME: 0.0195 ± 0.0011 SPE: 0.0376 ± 0.0090 RBF: 0.227	mg/g DW	Deseo et al. (2020)
Extraction/Purification: solvent extraction using ethanol (ME: molasses ethanol extract), ME further purified using SPE. ME further fractionated using amberlite resin (RBF: resin base fraction)	Syringic acid	ME: 0.0110 ± 0.0020 SPE: 0.182 ± 0.0183 RBF: 0.108		
	Chlorogenic acid	ME: 0.0065 ± 0.0000 SPE: 0.0378 ± 0.0022 RBF: 0.0743		
	Caffeic acid	ME: 0.0010 ± 0.0000 SPE: 0.0091 ± 0.0020 RBF: 0.0075		
Concentration: vacuum drying (ME)	Swertisin	ME: 0.0070 ± 0.0000 SPE: 0.0095 ± 0.0000 RBF: 0.0053		
	Orientin	ME: 0.0030 ± 0.0000 SPE: 0.0085 ± 0.0000 RBF: 0.0045		
	Vanillin	ME: 0.0020 ± 0.0010 SPE: 0.0118 ± 0.0080 RBF: 0.0021		
	Sinapic acid	ME: 0.0020 ± 0.0000 SPE: 0.0050 ± 0.0010 RBF: 0.0017		
	Vitexin	ME: 0.0010 ± 0.0000 SPE: 0.0019 ± 0.0000 RBF: 0.0016		
	Homo-orientin	ME: 0.0000 ± 0.0000 SPE: 0.0070 ± 0.0000 RBF: 0.0060		
	Tricin	ME: 0.0000 ± 0.0000 SPE: 0.0060 ± 0.0000 RBF: 0.0040		
	Diosmetin	ME: 0.0020 ± 0.0000 SPE: 0.0026 ± 0.0010 RBF: 0.0020		
Hydrolysis: none	Caffeic acid	11.6	mg/g	Kong et al. (2016)
Extraction: macroporous ion-exchange resin	Ferulic acid	10.5		
Analysis and quantification: HPLC/UV-visible; retention times and standards. Low/medium certainty of correct identification	Chlorogenic acid	1.77		
	Gallic acid	0.870		

(Continues)

TABLE 11 (Continued)

Method	(Poly)phenols present	Concentration	Unit	Reference
Hydrolysis: none			mg/g	Asikin et al. (2016)
Extraction: suspended in water and sent through Amberlite XAD-2 resin. Eluted by methanol	(7R,8S)-Dehydridocinneryl alcohol-4-O- β -D-glucoside	0.0073	mg/g DW	Payet et al. (2006)
Analysis and quantification: HPLC/DAD; retention times and standards; proton and Carbon NMR (neolignan compounds). High certainty of correct identification	(7S,8R)-simulanol-9'-O- β -D-glucoside	0.0045	mg/g DW	Payet et al. (2006)
Hydrolysis: NaOH			mg/g DW	Payet et al. (2006)
Extraction: solvent extraction using NaOH and ethyl acetate, then acidifying, and again extraction with ethyl acetate. Organic layer dried and concentrated	p-Coumaric acid Ferulic acid Caffeic acid	0.379 ± 0.078 [0.289–0.425] (n = 3) 0.198 ± 0.050 [0.168–0.255] (n = 3) 0.106 ± 0.036 [0.0821–0.148] (n = 3)	mg/g DW	Payet et al. (2006)
Analysis and quantification: HPLC/DAD/MS; retention times, standards, and electrospray mass spectra. High certainty of correct identification	Benzoic acid p-Hydrobenzoic acid Protocatechuic acid Syringic acid Vanillin	0.0824 ± 0.0415 [0.0478–0.128] (n = 3) 0.0738 ± 0.0318 [0.0451–0.108] (n = 3) 0.0721 ± 0.0297 [0.0429–0.102] (n = 3) 0.0544 ± 0.0166 [0.0377–0.0708] (n = 3) 0.0412 ± 0.0071 [0.0331–0.0463] (n = 3)	mg/g DW	Payet et al. (2006)
Hydrolysis: acid hydrolysis	Vanillic acid p-Coumaric acid Syringic acid Tricin 7-O-glucoside	0.0250 ± 0.0174 [0.0071–0.0418] (n = 3) 0.0118 ± 0.0033 [0.0081–0.0143] (n = 3) 0.0116 ± 0.0031	mg/g of sugarcane molasses extract	Yu et al. (2017)
Extraction: solvent extraction with ethanol accompanied by sonication, further extraction by D101 macroporous resin	Catechin Vanillic acid	0.0108 ± 0.0023	mg/g of sugarcane molasses extract	Yu et al. (2017)
Concentration: rotary evaporator	p-Coumaric acid	0.0081 ± 0.0024		
Analysis and quantification: HPLC/DAD; retention times and standards. Low/medium certainty of correct identification	Syringic acid	0.0030 ± 0.0011		
	Tricin 7-O-glucoside	0.0087 ± 0.0044		

Abbreviations: DAD, diode array detection; DW, dry weight; HPLC, high-performance liquid chromatography; MS, mass spectrometry; NMR, nuclear magnetic resonance; RP-HPLC, reverse-phase high-performance liquid chromatography; SPE, solid-phase extraction; UHPLC, ultra-high-performance liquid chromatography. Multiple values reported for the same compound are represented as mean plus/minus SD [range] (no. of samples).

TABLE 12 Sugarcane (poly)phenols identified in at least two studies with a minimum of one study by mass spectrometry (MS) or nuclear magnetic resonance (NMR).^a

Compound	Leaves	Rind	Culm	Node	Juice	Syrup	Sugar	Bagasse	Molasses/Cane honey	NCS	
4',5'-Dimethylilluteolin-8-C-glucoside/glycoside					(1), NMR (2) MS (3), (4)	(7), (9)	(7)	(7), (10)	(10), (7), NMR (2)	MS hyd (11), (10)	
Apigenin	MS (5), MS (6)		(7), (8)								
Benzoic acid	MS (5)							MS hyd (14)			
Caffeic acid	MS (5), (15), (16), MS (6), (17)	hyd (18), hyd (19), (20)		(20)	(9), MS hyd (14), (21), (17), (22)	MS hyd (14) MS (13), (10)	(17)	(10), MS (23), (24), MS hyd (14)	MS hyd (11), (10), (25)		
Catechin	(15)	(20)		(20)	(22)			hyd (26)		MS hyd (11)	
Chlorogenic acid	(15), (16), (17)	(27), hyd (19)	(7)		(21), (17)	(7)	(7), MS (13), (10)	(10), (7), MS (23), (24), MS hyd (14)	MS hyd (11), (29), (10), (25)		
Coniferyl alcohol	MS (5)						MS (12)				
(p)-Coumaric acid	MS (5), (15), (17) (16)	hyd (18), hyd (19), (20)	(7)	(20)	(7), (17), MS hyd (14), (21), (22)	(7) MS hyd (14)	(7), (10) MS (12), MS hyd (14), MS (13)	(17), (28) (30), MS (31), MS (32)	(10), (7) MS hyd (14), hyd (26)	(10), (33), MS hyd (11), (29), (25)	
Dihydroxybenzoic acid							NMR (2)			MS hyd (11)	
Diosmetin 6-C-glucoside							MS (34)			MS (31)	
Diosmetin-8-C-glucoside/glycoside	MS (35), (1), MS (3), (4)						NMR (2), (1), MS (34), MS (3)			NMR (2)	
Diosmetin-8-C-glycoside-arabinoside			MS (3)				MS (36)				
Ferulic acid	MS (5), (15), (17)	(27), hyd (18), hyd (19), (20)		(20)	(7), MS hyd (14), (21), (17), (22)	(7), MS (12), MS hyd (14) (10)	(30), (37), (28), (17)	(10), (7), (38), MS hyd (14)	(29), (10), (25)		
Gallic acid	(15) (17)	(27), hyd (19) (20)		(20)	(17), (22)		(30), (37), (28), (17)	(24)	MS hyd (11), (25)	(Continues)	

TABLE 12 (Continued)

Compound	Leaves	Rind	Culm	Node	Juice	Syrup	Sugar	Bagasse	Molasses/Cane honey	NCS
(<i>p</i> -Fydrioxybenzoic acid	(16) MS (5) (17)				(22) MS hyd (14) (14), (21), (17)	MS hyd (14) MS (13) MS (12)	(30) (28), (17)		MS hyd (11), (25)	
Ioschafftosside (apigenin-6-C-arabinosyl-8-C-glucoside)	(8), NMR (39)				(4), MS (40), hyd (41) (1), MS (36), MS (3)				(33)	
Luteolin	MS (5)		(7)		(7), (9), NMR (2)	(7)	MS (31)	(7), NMR (2)	MS hyd (11), (10)	
Luteolin-8-C-(rhamnosylglucoside)		MS (40), (1)			MS (40), MS (36)					
Naringenin	MS (5)								MS hyd (11)	
Orientin (luteolin-8-C-glucoside)	MS (5), MS (35)		(8)		MS (40)					
Protocatechuic acid		(17)			MS hyd (14), (21), (17), (22)	MS hyd (14), MS (13) (17)	(28), MS (31), MS hyd (14) (17)	MS hyd (14)	MS hyd (11), (29), (25)	
Quercetin	(15), MS (6)	(20)		(20)			(37), MS (32)			
Rutin	(15)	(20)		(20)					MS hyd (11)	
Schaftosside (apigenin-6-C-glucosyl-8-C-ribenoside)	NMR (39)		(8)		(4), MS (40), hyd (41) (1), MS (36), MS (3), NMR (2)		NMR (2)		(33)	
Sinapic acid	MS (5), (17)				(9), (17), (22)		(30), (28), (17)	MS (23)	MS hyd (11)	
Swertisin					NMR (2), MS (36), MS (3)	hyd (41)		NMR (2), MS (23),		
Syringic acid	MS (5), (17)		hyd (19)		MS hyd (14), (21), (17), (22)	MS hyd (14) (13)	(30), (17)	MS (23), MS hyd (14), hyd (26)	MS hyd (11), (29), (25)	
Tricin					(7), (9)	(7)	(7), (10)	MS (31)	(10), (7), MS (23)	
									(Continues)	

TABLE 12 (Continued)

Compound	Leaves	Rind	Culm	Node	Juice	Syrup	Sugar	Bagasse	Molasses/Cane honey	NCS
Tricin-7-O-glucoside/glycoside	MS (40)				MS (34), MS (40), (1) MS (36), MS (3)				hyd (26)	
Tricin-7-O-rhamnosylgalacturonide ^b	MS (42)		(8)		MS (3), (1)					
Tricin-4-O-(threo or erythro guiaacylglyceril) ether	MS (3), (4)									
Tricin-4-O-(threo or erythro guiaacylglyceril) ether-7-O-glucopyranoside	MS (3), (4)									
Tricin-7-O-neohesperidioside	MS (40), (1)				NMR (2), MS (40), (1), MS (36)		MS (40)		NMR (2)	
Vanillic acid	MS (5), (17)	hyd (19)			(17), (22)	MS hyd (14)	MS (12), MS (13)	(28), (17)	MS hyd (14), hyd (26)	MS hyd (11), (29), (25)
Vanillin	MS (5)				MS hyd (14), (22)	MS hyd (14)	MS (12)		MS (23), MS hyd (14)	MS hyd (11)
Vitexin (apigenin-8-C-glucoside)	MS (40), (16), (1)				(4), NMR (2), MS (40), (1), MS (3)				NMR (2), MS (23)	

^aWhere a study has used MS, NMR, and/or hydrolysis in the identification of the compound, this has been specified as follows: MS, mass spectrometry; NMR, nuclear magnetic resonance; hyd, with hydrolysis.

^bTricin-7-O-rhamnosylgalacturonide has been corrected to tricin-7-O-rhamnosylgalacturonide.

^cReferences numbered as follows: (1) Vila et al. (2008); (2) Ali et al. (2019); (3) Colombo et al. (2005, 2006, 2008) (4) Castro-Moretti et al. (2021); (5) Sun et al. (2014); (6) Duarte-Almeida et al. (2006, 2011); (7) McGhie (1993); (8) Barrera et al. (2020); (9) Shang et al. (2021); (10) Payet et al. (2005, 2006); (11) Azlan et al. (2020); (12) Abbas et al. (2014); (13) Lee et al. (2012); (14) Zhao et al. (2008, 2013, 2015); (15) Fang et al. (2017); (16) Geng et al. (2017); (17) Kerdchan et al. (2020); (18) de Armas et al. (1999); (19) Marasinghe et al. (2022); (20) Deseo et al. (2020); (21) Kong et al., (2015, 2016); (22) Zhu et al. (2020); (23) Yu et al. (2017); (24) Feng et al. (2015); (25) Alarcón et al. (2021); (26) Juttuporn et al. (2018); (27) Zheng, Su, Li et al. (2017) and Zheng, Su, Zhou et al. (2019); (28) Kinjo et al. (2019); (29) Rodrigues et al. (2021); (30) Leme et al. (2014); (31) Vijayalaxmi et al. (2015); (32) Coutinho et al. (2016); (33) Mabry et al. (1984).

sively documented in products. Only the leaves and rind of sugarcane have been found to contain syringic acid and vanillic acid, although they are widely recorded in sugarcane products. Benzoic acid, 4-hydroxybenzoic acid, cinnamic acid, gentisic acid, and hydroxybenzoic acid are other phenolic acids that are less frequently reported.

6.3 | Other phenolics in sugarcane

In the qualitative table (Table 12), vanillin is recorded in leaves and in many products and may impart some flavor. Vanillic acid has been reported in leaf and rind but not recorded in all the products. It is possible that vanillin (the aldehyde) is produced from vanillic acid during processing. Tables 13 and 14 include standardized names of (poly)phenols according to the International Union of Pure and Applied Chemistry (IUPAC). The names from recommendations for standardizing nomenclature (Kay et al., 2020) have also been indicated (Tables 13 and 14).

7 | ASSESSMENT OF THE AMOUNTS OF (POLY)PHENOLS IN SUGARCANE

The extraction of (poly)phenols from plants and products is very dependent on the technique used, and certain techniques appear to yield comparatively large amounts. However, when interpreting quantitative compositional data, it is necessary to carefully assess the techniques used. Here, we report techniques that have resulted in a (poly)phenol content (PC) of >1 mg/g or 1 mg/L for at least one reported compound.

For leaves, “boiling” resulted in comparatively larger amounts of (poly)phenols. This was surprising, as (poly)phenols are often extracted using organic solvents, but the effectiveness of this depends on the chemical structure and the polarity (Kim & Lee, 2002). According to the compiled data tables, there are a limited number of studies on sugarcane nodes. The extraction method used in the one study on nodes was solvent extraction with ethanol, acid hydrolysis, and sonication, and the values appear high (Kerdchan et al., 2020). However, additional research on sugarcane nodes would be helpful to understand whether this is due to the analytical approach or whether the sugarcane node naturally accumulates a higher quantity of (poly)phenols.

There are more publications reporting the (poly)phenolic composition and quantification data of sugarcane products compared to sugarcane plant parts. Sugarcane juice has been analyzed numerous times, and some of the studies have reported higher values without any extraction. These studies have obtained fresh juice directly from a mechanical juicer or the grinding mill

itself, with a concentration step followed by, for example, lyophilization or SPE. In addition, resin-based extraction (e.g., using Amberlite XAD 2 resin) combined with methanol/ammonia elution resulted in comparatively larger values (Maurício Duarte-Almeida et al., 2006). NCS are a group of sugarcane products that are often rich in (poly)phenols because of the molasses fraction that is retained in the product compared to refined white sugar. However, the extraction technique seems to play a significant role when determining the (poly)phenolic profile and quantities. One study combined multiple techniques to achieve a high PC compared to other studies on sugarcane NCS (Shang et al., 2021). They dissolved the sample in water, centrifuged it, and analyzed both the sediment and supernatant. Supernatants had larger amounts than sediment, and a combination of techniques such as acidification, solvent extraction using ethyl acetate, and vacuum concentration might be the reason for reporting very high values. Bagasse is a byproduct of the sugarcane industry and is often sustainably used as fuel to generate heat and electricity (Xu et al., 2018) or further processed to make paper (Rainey & Covey, 2016). However, studies have indicated that it could be a valuable source of (poly)phenols. Extraction techniques, such as steam explosion combined with solvent extraction using ethanol and ultrasonication or stepwise solvent extraction using ethanol and methanol, have resulted in comparatively large recoveries of (poly)phenols. One study used a combination of several techniques, yielding a higher PC than other methods (Zheng, Su, Zhou, et al., 2017). This included extraction with ethanol/water with ultrasonication, followed by vacuum drying and further extraction using ethyl acetate and polyamide resin purification. Molasses is another valuable byproduct of the sugarcane industry. One study recorded values higher than 1 mg/g after only lyophilization to remove water without any other extraction method (Ali et al., 2019). Another study used microporous resin-based extraction, which also resulted in comparatively larger values (Feng et al., 2015). Each of the aforementioned concentration, extraction, and analytical methods has its advantages and disadvantages, and often trial and error is required to extract the maximum amount of (poly)phenols.

Unfortunately, most researchers have only used HPLC/DAD systems to analyze the (poly)phenolic profile, using standards matched to retention time and absorption spectra. Although it provides a tentative identification, the confidence is increased when a mass spectrometric technique is employed, as in LC/MS. In addition, a few studies have employed NMR methods, which are very useful for establishing the chemical identity. Many standards are available for purchase nowadays, but they are expensive, and simple matching by absorption spectra is insufficient for positive identification. MS or NMR can

TABLE 13 International Union of Pure and Applied Chemistry (IUPAC) names of flavonoids in sugarcane.

Flavonoid	IUPAC name
Apigenin	5,7-Dihydroxy-2-(4-hydroxyphenyl)chromen-4-one
Catechin	(2R,3S)-2-(3,4-Dihydroxyphenyl)-3,4-dihydro-2H-chromene-3,5,7-triol
Cyanidin-3,5-diglucoside	(2S,4S,5S)-2-[2-(3,4-Dihydroxyphenyl)-7-hydroxy-3-[(2S,5S)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]oxychromenylium-5-yl]oxy-6-(hydroxymethyl)oxane-3,4,5-triol
Cyanidin-3-glucoside	2-[2-(3,4-Dihydroxyphenyl)-5,7-dihydroxychromenylium-3-yl]oxy-6-(hydroxymethyl)oxane-3,4,5-triol;chloride
Cyanidin-3-malonyl-glucoside	3-[[6-[2-(3,4-Dihydroxyphenyl)-5,7-dihydroxychromenylium-3-yl]oxy-3,4,5-trihydroxyoxan-2-yl]methoxy]-3-oxopropanoic acid
Diosmetin	5,7-Dihydroxy-2-(3-hydroxy-4-methoxyphenyl)chromen-4-one
Diosmetin-6-C-glucoside	5,7-Dihydroxy-2-(3-hydroxy-4-methoxyphenyl)-6-[(2S,3R,4R,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]chromen-4-one
Diosmin (diosmetin-7-O-rhamnoglucoside)	5-Hydroxy-2-(3-hydroxy-4-methoxyphenyl)-7-[(2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-[(2R,3R,4R,5R,6S)-3,4,5-trihydroxy-6-methoxyan-2-yl]oxymethyl]oxan-2-yl]oxychromen-4-one
Genistein	5,7-Dihydroxy-3-(4-hydroxyphenyl)chromen-4-one
Homo-orientin/isoorientin (luteolin-8-C-glucoside)	2-(3,4-Dihydroxyphenyl)-5,7-dihydroxy-6-[(2S,3R,4R,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]chromen-4-one
Isoorientin 7,3'-dimethyl ether	5-Hydroxy-2-(4-hydroxy-3-methoxyphenyl)-7-methoxy-6-[3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]chromen-4-one
Isoschaftoside (apigenin-6-C-arabinosyl-8-C-glucoside)	5,7-Dihydroxy-2-(4-hydroxyphenyl)-8-[(2S,3R,4R,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]-6-[(2S,3R,4S,5S)-3,4,5-trihydroxyoxan-2-yl]chromen-4-one
Isovitexin (apigenin-6-C-glucoside)	5,7-Dihydroxy-2-(4-hydroxyphenyl)-6-[(2S,3R,4R,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]chromen-4-one
Luteolin	2-(3,4-Dihydroxyphenyl)-5,7-dihydroxychromen-4-one
Luteolin-7-O-glucoside	2-(3,4-Dihydroxyphenyl)-5-hydroxy-7-[(2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]oxychromen-4-one
Malvidin-3-caffeooyl-glucoside	[(2R,3S,4S,5R,6S)-6-[2-(3-Ethenyl-5-methoxy-4-methylphenyl)-5,7-dihydroxychromenylium-3-yl]oxy-3,4,5-trihydroxyoxan-2-yl]methyl (E)-3-(3,4-dihydroxyphenyl)prop-2-enoate
Maysin (luteolin-6-C-diglycoside)	2-(3,4-Dihydroxyphenyl)-5,7-dihydroxy-6-[4-hydroxy-6-methyl-5-oxo-3-(3,4,5-trihydroxy-6-methoxyan-2-yl)oxyoxan-2-yl]chromen-4-one
Naringenin	5,7-Dihydroxy-2-(4-hydroxyphenyl)-2,3-dihydrochromen-4-one
Orientin (luteolin-8-C-glucoside)	2-(3,4-Dihydroxyphenyl)-5,7-dihydroxy-8-[(2S,3R,4R,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]chromen-4-one
Peonidin-3,5-diglucoside	(2S,4S,5S)-2-[7-Hydroxy-2-(4-hydroxy-3-methoxyphenyl)-3-[(2S,5S)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]oxychromenylium-5-yl]oxy-6-(hydroxymethyl)oxane-3,4,5-triol
Quercetin	2-(3,4-Dihydroxyphenyl)-3,5,7-trihydroxychromen-4-one
Isoorientin 2''-C-rhamnoside	6-[(2S,3R,4S,5S,6R)-4,5-Dihydroxy-6-(hydroxymethyl)-3-[(3R,4R,5R,6S)-3,4,5-trihydroxy-6-methoxyan-2-yl]oxyoxan-2-yl]-2-(3,4-dihydroxyphenyl)-5,7-dihydroxychromen-4-one
Rutin (quercetin-3-O-rhamnoglucoside)	2-(3,4-Dihydroxyphenyl)-5,7-dihydroxy-3-[(2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-[(2R,3R,4R,5R,6S)-3,4,5-trihydroxy-6-methoxyan-2-yl]oxymethyl]oxan-2-yl]oxychromen-4-one
Schaftoside (apigenin-6-C-glucoside-8-C-arabinoside)	5,7-Dihydroxy-2-(4-hydroxyphenyl)-6-[3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]-8-(3,4,5-trihydroxyoxan-2-yl)chromen-4-one
Swertiajaponin	2-(3,4-Dihydroxyphenyl)-5-hydroxy-7-methoxy-6-[(2S,3R,4R,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]chromen-4-one
Swertisin (7-O-methylapigenin 6-C-glucoside)	5-Hydroxy-2-(4-hydroxyphenyl)-7-methoxy-6-[(2S,3R,4R,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]chromen-4-one
Tricin	5,7-Dihydroxy-2-(4-hydroxy-3,5-dimethoxyphenyl)chromen-4-one
Tricin-7-O-glucoside	5-Hydroxy-2-(4-hydroxy-3,5-dimethoxyphenyl)-7-[(3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]oxychromen-4-one

(Continues)

TABLE 13 (Continued)

Flavonoid	IUPAC name
Tricin-7-O-neohesperidoside	7-[(2S,3R,4S,5S,6R)-4,5-Dihydroxy-6-(hydroxymethyl)-3-[(2S,3R,4R,5R,6S)-3,4,5-trihydroxy-6-methyloxan-2-yl]oxyoxan-2-yl]oxy-5-hydroxy-2-(4-hydroxy-3,5-dimethoxyphenyl)chromen-4-one
Vitexin (apigenin-8-C-glucoside)	5,7-Dihydroxy-2-(4-hydroxyphenyl)-8-[(2S,3R,4R,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]chromen-4-one

help with positive identification, especially when the MSⁿ fragmentation pattern is compared to an authentic standard. Conjugates such as glycosides or glucuronides can present a further element of difficulty, as many standards are not easily available. This is why techniques such as enzyme, acid, or alkaline hydrolysis, which removes the sugar moiety, allow identification of the aglycone. However, C-glycosides cannot be easily hydrolyzed to the aglycone. In addition, using hydrolysis can result in (poly)phenol instability (Pimpão et al., 2013). Alkaline hydrolysis has been utilized by many researchers, but it is well recognized that it can destroy hydroxycinnamic acids (Pimpão et al., 2013). None of the researchers used enzyme hydrolysis during the extraction process, which could potentially be a superior technique to unravel complex (poly)phenols and retrieve aglycones, although enzymic hydrolysis does not usually lead to 100% hydrolysis, which is important for quantification.

Two recent publications highlighted over 30 (poly)phenols identified in non-edible sugarcane straw using resin-based extraction technique that were quantified accurately using MS. The purified extract has the potential to be utilized as a food preservative and anti-inflammatory agent (Carvalho et al., 2023; Oliveira et al., 2022). One research study examined the antidiabetic potential of (poly)phenols found in sugarcane straw by measuring their inhibition of α -glucosidase activity using the enzyme from *Saccharomyces cerevisiae* (Oliveira et al., 2022). However, it is important to note that these findings may not be directly applicable to human digestion because human α -glucosidases were not used in the study. Future investigations are required to determine if these (poly)phenols have any inhibitory effects on human α -glucosidases. Further, almost 40 compounds were identified in sugarcane syrup using MS, highlighting the abundance of natural products in most sugarcane products (Carvalho et al., 2022).

7.1 | Measurement of total (poly)phenol contents (TPCs) using general assays such as Folin–Ciocalteu

Instead of running specific analyses using HPLC, many publications have reported the total PC (TPC) and/or

antioxidant capacities of sugarcane samples. There are various forms of antioxidant assay based on chemical redox reactions, but all are much simpler and cheaper than the preferred LC/MS analysis. TPC is an adequate technique for extracts, which consist mostly of (poly)phenols. However, the Folin–Ciocalteu assay, the most used method to analyze TPC, has severe limitations when measuring more complex samples. The reagent reacts with many interfering compounds that exist in plant extracts, including sugarcane, thus delivering an overestimation of TPC (Rodrigues et al., 2021). Maillard reactive products (such as melanoidins) that are formed during sugarcane processing are strongly positive in the Folin–Ciocalteu method. A thorough study conducted to analyze the reactivity of various compounds toward the Folin–Ciocalteu reagent has suggested that the Folin–Ciocalteu assay is more suitable as an antioxidant assay rather than a measurement of TPC due to its significant reactivity toward non-phenolic compounds (Everette et al., 2010). TPC has often been correlated with antioxidant capacities due to similar chemistry between the assays (Huang et al., 2005). Therefore, in this review, we will not be addressing TPC or antioxidant assays as methods to estimate (poly)phenolics in sugarcane.

8 | (POLY)PHENOLIC PROFILE VARIATIONS ACCORDING TO PROCESSING METHODS

One study reported the variation between the phenolic profiles of sugarcane products and byproducts at each stage of processing (Payet et al., 2006). The clear juices start with lower concentrations (total: 249 mg/kg), which increase in syrup (total: 361 mg/kg) and molasses (total: 761–1233 mg/kg). Most of the individual compounds also follow the above trend. Molasses has the highest concentration, whereas the raw sugar separated from molasses has very low concentrations (total: 22.4 mg/kg), with the removal of (poly)phenols and other impurities during centrifugal crystallization to obtain pure sucrose crystals. Certain (poly)phenols, such as chlorogenic acid, vanillic acid, and benzoic acid, seem to have not been detected in sugarcane juice. As chlorogenic and vanillic acids are detected in lesser amounts in other products as well, they

TABLE 14 International Union of Pure and Applied Chemistry (IUPAC) and standardized names of phenolic acids and other (poly)phenols in sugarcane.

Common phenolic acid name	IUPAC name	Standardized nomenclature
Acetosyringone	1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone	
Caffeic acid	(2E)-3-(3,4-dihydroxyphenyl)prop-2-enoic acid	3',4'-dihydroxycinnamic acid
2-O-caffeoyleglucarate	(2R,3S,4S,5S)-2-[(E)-3-(3,4-dihydroxyphenyl)prop-2-enoyl]oxy-3,4,5-trihydroxyhexanedioic acid	
Chlorogenic acid	(1S,3R,4R,5R)-3-[(E)-3-(3,4-dihydroxyphenyl)prop-2-enoyl]oxy-1,4,5-trihydroxycyclohexane-1-carboxylic acid	
Feruloylquinic acid isomer 1	Feruloyl quinic acid: 1,3,5-trihydroxy-4-[(E)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoyl]oxycyclohexane-1-carboxylic acid	
Feruloylquinic acid isomer 2		
Feruloylquinic acid isomer 3		
Feruloylquinic acid isomer 4		
Gallic acid	3,4,5-Trihydroxybenzoic acid	3,4,5-trihydroxybenzoic acid
Gentisic acid	2,5-Dihydroxybenzoic acid	2,5-dihydroxybenzoic acid
Glucosyringic acid	3,5-Dimethoxy-4-[(2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]oxybenzoic acid	
Homovanillic acid	2-(4-Hydroxy-3-methoxyphenyl)acetic acid	4'-hydroxy-3'-methoxyphenylacetic acid
p-Coumaroylquinic acid 1	p-Coumaroylquinic acid: (1R,3S,4S,5S)-1,3,4-trihydroxy-5-[(E)-3-(4-hydroxyphenyl)prop-2-enoyl]oxycyclohexane-1-carboxylic acid	
p-Coumaroylquinic acid 2		
Protocatechuic acid	3,4-Dihydroxybenzoic acid	3',4'-dihydroxycinnamic acid
Salicylic acid	2-Hydroxybenzoic acid	
Sinapic acid	(E)-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoic acid	
Syringic acid	4-Hydroxy-3,5-dimethoxybenzoic acid	3,5-Dimethoxy-4-hydroxybenzoic acid
Vanillic acid	4-Hydroxy-3-methoxybenzoic acid	3-hydroxy-4-methoxybenzoic acid
Sinapaldehyde	(E)-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enal	
Ferulic acid/fumalic acid/ <i>trans</i> -ferulic acid	(E)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid	4'-hydroxy-3'-methoxycinnamic acid
<i>o</i> -Coumaric acid	(2E)-3-(2-hydroxyphenyl)prop-2-enoic acid	2'-hydroxycinnamic acid
<i>m</i> -Coumaric acid	(2E)-3-(3-hydroxyphenyl)prop-2-enoic acid	3'-hydroxycinnamic acid
<i>p</i> -Coumaric acid	(2E)-3-(4-hydroxyphenyl)prop-2-enoic acid	4'-hydroxycinnamic acid
Hydroxybenzoic acid/ <i>p</i> -hydroxybenzoic acid	4-Hydroxybenzoic acid	
3-O-caffeoylelquinic acid	Chlorogenic acid/(1S,3R,4R,5R)-3-[(E)-3-(3,4-dihydroxyphenyl)prop-2-enoyl]oxy-1,4,5-trihydroxycyclohexane-1-carboxylic acid	
4-O-caffeoylelquinic acid	Cryptochlorogenic acid/(3R,5R)-4-[(E)-3-(3,4-dihydroxyphenyl)prop-2-enoyl]oxy-1,3,5-trihydroxycyclohexane-1-carboxylic acid	
5-O-caffeoylelquinic acid	Neochlorogenic acid/(1R,3R,4S,5R)-3-[(E)-3-(3,4-dihydroxyphenyl)prop-2-enoyl]oxy-1,4,5-trihydroxycyclohexane-1-carboxylic acid	

could have been below the limit of detection in the juice analysis due to extremely low concentrations. However, benzoic acid has been detected in higher concentrations in later products, which could otherwise be due to the dissociation of other (poly)phenols, such as hydroxycinnamic acids, into benzoic acid and *p*-hydroxybenzoic acid, during processing (Payet et al., 2006).

Even though the (poly)phenolic profiles have been explored in detail in many studies, comparisons of the data are quite challenging due to the various analytical techniques used, and the use of differing sources of sugarcane for each product will introduce further variation. Therefore, a detailed analysis of the phenolic profiles, from the starting material of sugarcane up to all byproducts and products, would be helpful to identify the effects of production processes. It would further help researchers to fine-tune the production processes to achieve desired phenolic profiles in products.

Most colored compounds formed during sugarcane processing include melanoidins, byproducts of caramelization, alkaline degradation of reducing sugars, and oxidative reactive phenolic compounds. Other enzymatic reactions of phenolic compounds are catalyzed by polyphenol oxidase (PPO) and peroxidase (Bucheli & Robinson, 1994), which can induce changes in appearance and organoleptic properties of sugarcane juice (Kaavya et al., 2019). PPO (identified as catechol oxidase, tyrosinase, phenolase, catecholase, and *o*-diphenol oxidase) facilitates the conversion of monophenols to *o*-diphenols and further oxidation to *o*-quinones that react with other (poly)phenols, amino acids, and other cellular constituents to produce melanoidins (Marques Silva & Sulaiman, 2019). (Poly)phenol oxidase is active when the juice is released from the sugarcane culms and produces *o*-diphenols that impact the quality, taste, and color of sugarcane byproducts. The subsequent color that is produced, particularly increased by chlorogenic acid, increases the cost of the sugar refining step (Cabral et al., 2022).

Heat used during sugarcane processing can lead to the destruction of certain (poly)phenols in sugarcane juice and promote the formation of Maillard reaction products that interfere with the Folin-Ciocalteu assay, providing an overestimation of TPC, as mentioned above. Thus, the initial PC of raw juice will be changed by industrial processing. However, if attempts are made to retain the PC of the initial raw juice during processing in sugar mills, it might increase costs and decrease production efficiencies. Instead, utilizing the waste products of the sugarcane industry may be more sustainable and economical in obtaining (poly)phenols from sugarcane.

9 | APPLICATIONS IN THE FOOD INDUSTRY AND POTENTIAL HEALTH BENEFITS

Numerous studies have established (poly)phenols as possible agents to lower the risk of chronic diseases, including when taken as supplements (Rana et al., 2022). There are only a few studies, however, which have explored the potential of sugarcane extracts and products to promote health benefits. There are several *in vivo* preclinical and *in vitro* studies, but currently no human trials, that have demonstrated therapeutic outcomes related to sugarcane (poly)phenolic extracts.

(Poly)phenol-rich sugarcane extract (PRSE) is a resin-based extraction of sugarcane molasses. PRSE has demonstrated the ability to mitigate the detrimental effects of feeding mice a diet high in fat and carbohydrates (Flavel et al., 2021). Furthermore, preclinical *in vivo* investigations on different sugarcane extracts (i.e., ethanolic extracts of leaves and stems) have indicated antihepatotoxic, antihyperglycemic, and diuretic properties (Singh et al., 2015). *In vitro*, PRSE inhibited glucose and fructose uptake and the expression of GLUT2, while increasing the expression of GLUT5 in Caco-2 cells. It also demonstrated the capacity to restore insulin production in dysfunctional β -cells (Ji et al., 2019), inhibited pro-inflammatory cytokine formation, and reduced DNA damage (Ji et al., 2020). PRSE has also exhibited a proposed anti-cancer activity on certain cell lines, such as human (LIM2045) and mouse (MC38, CT26) colon cancer cell lines, human lung cancer (A549), human ovarian cancer (SKOV-3), human promonocytic leukemia (U937), and mouse melanoma (B16) cell lines (Prakash et al., 2021). The (poly)phenol tricin-7-O- β -(6"-methoxycinnamic)-glucoside has been prepared from sugarcane juice and demonstrated antiproliferative activity against several human cancer cell lines (Duarte-Almeida et al., 2007). If the activities described from *in vitro* studies are proven to work in human intervention studies, then the relevant (poly)phenols could have increased value, and sugarcane could be a sustainable source of (poly)phenols.

Apigenin, luteolin, and tricin are the three flavonoids that are most abundant and recorded in sugarcane. Although *in vitro* and *in vivo* studies have demonstrated the ability of apigenin, luteolin, and tricin to exhibit biological activities relevant to health (Salehi et al., 2019), many remain to be proven clinically in humans. Some of the compounds reported here, such as some of the C-glycosides of particular flavonoids (Table 12), have not been extensively studied for their biological activities.

There are a few human studies on apigenin. It has been shown to improve cognitive function in people with Alzheimer's, reduce the demand of analgesics in knee osteoarthritis patients, and reduce body weight and arterial blood pressure in people who suffer from anxiety and depression (Salehi et al., 2019). Luteolin and tricin, however, have not been extensively tested in clinical trials, although many in vitro and preclinical in vivo data exist to support potential health benefits. In vivo preclinical studies of luteolin have indicated anti-inflammatory, neuroprotective, cardiovascular protective, and antidiabetic properties (Taheri et al., 2021). Similarly, in vivo preclinical studies of tricin have demonstrated anti-tumor and anti-inflammatory properties (Jiang et al., 2020).

Ferulic acid, caffeic acid, and the parent compound chlorogenic acid are the three major phenolic acids recorded in sugarcane. Numerous properties have been reported for these phenolic acids. For example, when hyperlipidemic subjects were given ferulic acid, there was a reduction in oxidative stress and inflammatory status and an improvement in lipid profile, potentially lowering the risk of cardiovascular disease (Bumrungpert et al., 2018). Here we show ferulic acid contents up to ~10–14 mg/g in waste parts of sugarcane plants such as rind, leaves, and molasses. (Tables 1, 2, and 11). Bumrungpert et al. used an extract containing 500 mg of ferulic acid. This amount might be feasibly extracted from approximately 50 g of sugarcane leaves, which otherwise would just be fed to a boiler to generate heat energy. There are some patented ferulic acid-containing products, including a neuroprotective drug and an anti-hypertensive drug (Raj & Singh, 2022). Apart from this, there are some in vitro and preclinical in vivo data indicating antidiabetic and anti-cancer properties (Raj & Singh, 2022). Caffeic acid has been the subject of considerable research in vitro and in animal models. However, more clinical research is needed to fully understand the mechanisms and pathways underlying the action of caffeic acid, even though the data have confirmed a promising role in anti-inflammatory, antioxidant, and anticancer properties (Espíndola et al., 2019). Chlorogenic acid at a dose of 140 mg/day for 12 weeks reduced blood pressure in mildly hypertensive patients and healthy adults (Tajik et al., 2017) and is present in sugarcane leaves at up to 3 mg/g (Table 2), suggesting that ~50 g of leaves could provide the necessary quantity of chlorogenic acid. It may also reduce fasting blood glucose, serum insulin, body weight, body mass index, waist circumference, and cholesterol levels in randomized controlled trials conducted in humans (Yu et al., 2022). In addition, there are many animal model studies indicating positive effects on cardiovascular-related health benefits (Tajik et al., 2017).

Uses in industrial processes are also possible, as PRSE inhibits enzymatic browning and is an effective food preservative (Ahtesh et al., 2020; Oliveira et al., 2022), two major problems in the food industry. Apigenin has applications in industry, such as an ingredient in sports drinks as an aid to reduce inflammation, as a natural food colorant, and in cosmetics (Chen et al., 2023). Luteolin has received attention due to its anti-bacterial properties against common bacteria, thus leading to applications in hand sanitizers (Xi et al., 2022), and also as a preservation agent, an anti-browning agent, and in active packaging (Punia Bangar et al., 2023). Ferulic acid acts as an inhibitor of food discoloration, a precursor of vanillin and a food preservative, a photoprotective agent in the cosmetic industry, and a growth enhancer in animal husbandry (Kumar & Pruthi, 2014). Caffeic acid can act as a formulation stabilizer and is currently used extensively as an additive in the food, cosmetic, and pharmaceutical industries due to its antioxidant activity. It also inhibits tyrosinase, preventing enzymatic browning in food (Silva et al., 2014). In the food industry, chlorogenic acid has been used as an emulsifier and a preservative (Wang et al., 2022).

10 | CHALLENGES AND FUTURE RESEARCH DIRECTIONS

This paper has identified the (poly)phenolic compounds that exist in sugarcane plant parts and products. There are many factors that affect the content of (poly)phenols present in an extract, such as origin, variety, extraction technique, and method of analysis. The certainty of individual (poly)phenol identification relies upon the use of a suitable analytical technique. It is important to use techniques such as MS (e.g., LC/MS) and NMR with authentic standards to identify and accurately measure (poly)phenols, whereas techniques such as HPLC/DAD only provide a tentative identification. Acid or base hydrolysis techniques could potentially simplify the composition of (poly)phenols and facilitate the identification of compounds that may otherwise remain otherwise unnoticed. It may be beneficial to quantify the variation of (poly)phenols between each step of sugarcane processing under standardized laboratory conditions, using the appropriate techniques to identify the crucial steps that remove or concentrate the valuable (poly)phenols in sugarcane.

11 | SUMMARY AND CONCLUSIONS

Sugarcane (poly)phenols mainly consist of flavonoids and phenolic acids. The three major flavonoids that survive

through all the steps of sugarcane processing are apigenin, luteolin, and tricin, many of which are C-glycosides. The two major phenolic acids are ferulic and caffeic acids, as well as the parent chlorogenic acid, found throughout the plant and processing steps. It is essential to use high-quality suitable analytical methods to assess (poly)phenols in the sugarcane plant and derived products. The applications of the constituent (poly)phenols to health and industrial processes highlight the potential to improve processing sustainability and exploit novel uses of sugarcane (poly)phenols in multiple settings.

AUTHOR CONTRIBUTIONS

Ulluwis H. A. J. Hewawansa: Conceptualization; writing—original draft; methodology; validation; visualization; writing—review and editing; formal analysis; data curation; investigation. **Michael J. Houghton and Elizabeth Barber:** Conceptualization; investigation; writing—review and editing; supervision. **Ricardo J. S. Costa:** Conceptualization; writing—review and editing; supervision. **Barry Kitchen:** Conceptualization; writing—review and editing; investigation. **Gary Williamson:** Conceptualization; investigation; funding acquisition; writing—original draft; methodology; validation; writing—review and editing; project administration; supervision; resources.

ACKNOWLEDGMENTS

We thank The Product Makers (Australia) Pty LTD for a contribution to the PhD fellowship of UHAJH.

CONFLICT OF INTEREST STATEMENT

UHAJH was partially funded by a fellowship from The Product Makers (Australia) Pty LTD.

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How to cite this article: Hewawansa, U. H. A. J., Houghton, M. J., Barber, E., Costa, R. J. S., Kitchen, B., & Williamson, G. (2024). Flavonoids and phenolic acids from sugarcane: Distribution in the plant, changes during processing, and potential benefits to industry and health. *Comprehensive Reviews in Food Science and Food Safety*, 23, e13307. <https://doi.org/10.1111/1541-4337.13307>