Phytochemicals from Sugarcane Bagasse and Maize Residues

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Billions of tons of agro-industrial residues are produced worldwide. This is associated with the risk of pollution as well as management and economic problems. Simultaneously, non-edible portions of many crops are rich in bioactive compounds with valuable properties. For this reason, developing various methods for utilizing agro-industrial residues (such as sugarcane bagasse and maize residues) as a source of high-value by-products is very important.

bioactive compounds antioxidants agricultural residues

1. Introduction

The agricultural industry generates billions of tonnes of waste from the tillage and processing of various crops. The crops with the largest amounts of produced residues are rice, maize, soybean, sugarcane, potato, tomato, and cucumber, as well as some fruits, mainly bananas, oranges, grapes, and apples [1][2]. It has been estimated that European food processing companies generate annually approximately 100 Mt of waste and by-products, mostly during the production of drinks (26%), dairy and ice cream (21.3%), and fruits and vegetables (14.8%) [3].

In **Table 1**, the amounts of particular wastes generated worldwide are presented. Many of them are rich in biologically active compounds and have the potential to become important raw materials for obtaining valuable phytochemicals. Vegetable and fruit processing by-products are promising sources of valuable phytochemicals having antioxidant, antimicrobial, anti-inflammatory, anti-cancer, and cardiovascular protection activities [4]. The applications of these agro-industrial residues and their bioactive compounds in functional food and cosmetics production were presented in many studies [5][6][7]. Moreover, due to the potential health risk of some synthetic antioxidants such as BHA, the identification and isolation of natural antioxidants from waste has become increasingly attractive. Important criteria to decide if a product or by-product can be of interest to recover phytochemicals are the absolute concentration and preconcentration factor, as well as the total amount of product or by-product per batch [8].

Table 1. Amount of residues from some crops produced in the world in 2020.

Crop	Global Crop Production * [Million Ton]	Residue to Crop Ratio	Amount of Residue ** [Million Ton]	References
Sugarcane	1869.7	0.1	189.1	Jiang et al. [9]
Maize	1162.4	2.0	2324.8	Jiang et al. [9]
Wheat	760.9	1.18	897.9	Searle and Malins [10]
Rice	756.7	1.0	756.7	Jiang et al. [9]
Potato	359.1	0.4	143.6	Ben Taher et al. [11]
Soybean	353.5	1.5	530.3	Yanli et al. [12]
Sugar beet	253.0	0.27	68.3	Searle and Malins [10]
Tomato	186.8	3.5	653.8	Oleszek et al. [13]
Barley	157.0	1.18	185.3	Searle and Malins [10]
Banana	119.8	0.6	71.9	Gabhane et al. [14]
Cucumber	91.3	4.5	410.9	Oleszek et al. [13]
Apples	86.4	0.25	21.6	Cruz et al. [15]
Grapes	78.0	0.3	23.4	Muhlack et al. [16]
Oranges	75.5	0.5	37.8	Rezzadori et al. [17]
Olives	23.6	0.12	2.8	Searle and Malins [10]

* based on FAOSTAT 2022, ** calculated based on the global crop production in 2020 and the residue-to-crop ratio according to cited references.

2. Sugarcane Bagasse

Large amounts of waste are generated during the processing of sugarcane. In fact, one metric ton of sugarcane generates 280 kg of bagasse. Sugarcane bagasse is one of the most abundant agro-food by-products and is a very promising raw material available at low cost for recovering bioactive substances [18][19]. Sugarcane bagasse consists mainly of cellulose (35–50%), hemicellulose (26–41%), lignin (11–25%), but also some amount of plant secondary metabolites (PSM), mainly anthocyanins and mineral substances [20][21][22][23][24][25].

Phenolic compounds are a very important group of natural substances identified in sugarcane waste. Nonetheless, steam explosion and ultrasound-assisted extraction (UAE) pretreatment was applied for the production of valuable phenolic compounds from the lignin included in this residue. Chromatographic analysis revealed that sugarcane bagasse is a good feedstock for the generation of phenolic acids. The concentration of total phenolics with the Folin-Ciocalteau method was between 2.8 and 3.2 g/L. Zhao et al. [26] have identified many phenolics, mainly flavonoids and phenolic acids, in sugarcane bagasse extract (**Table 2**). The total polyphenol content was detected as higher than 4 mg/g of dry bagasse, with total flavonoid content of 470 mg quercetin/g of polyphenol. The most abundant phenolic acids identified in the sugarcane bagasse extract were gallic acid (4.36 mg/g extract), ferulic acid (1.87 mg/g extract) and coumaric acid (1.66 mg/g extract). Spectroscopic analysis showed that a predominant amount of *p*-coumaric acid is ester-linked to the cell wall components, mainly to lignin. On the other hand, about half of the ferulic acid is esterified to the cell wall hemicelluloses. The purified sugarcane bagasse hydrolysate consisted mainly of *p*-coumaric acid. Besides, the purified products showed the same antioxidant activity, reducing power and free radical scavenging capacity as the standard *p*-coumaric acid. Al Arni et al. [27] stated that the major natural products contained in the lignin fraction were *p*-coumaric acid, ferulic acid, syringic acid, and vanillin.

Table 2. Phytochemicals derived from sugarcane bagasse.

Name	MW * [g mol^{-1}]	$C_xH_yO_z$	References
Phenolic acids—hydroxybenzoic acids			
p-Hydroxybenzoic acid	138.12	$C_7H_6O_3$	Zheng et al. [19]
Vanillic acid	168.14	$C_8H_8O_4$	Zheng et al. [19]
Benzoic acid	122.12	$C_7H_6O_2$	Zheng et al. [19]
Protocatechuic acid	154.12	$C_7H_6O_4$	Zheng et al. [19]
Gallic acid	170.12	$C_7H_6O_5$	Zhao et al. [26]
Syringic acid	198.17	$C_9H_{10}O_5$	Zhao et al. [26]
Phenolic acids—hydroxycinnamic acids			
p-Coumaric acid	164.04	$C_9H_8O_3$	González–Bautista et al. [28]
Cinnamic acid	148.16	$C_9H_8O_2$	González–Bautista et al. [28]
Ferulic acid	194.18	$C_{10}H_{10}O_4$	González–Bautista et al. [28]
Caffeic acid	180.16	$C_9H_8O_4$	González–Bautista et al. [28]
Chlorogenic acids	354.31	$C_{16}H_{18}O_9$	Zhao et al. [26]
Sinapic acid	224.21	$C_{11}H_{12}O_5$	Zhao et al. [26]
Flavonoids—flavonols			
Quercetin	302.24	$C_{15}H_{10}O_7$	Zheng et al. [19]
Flavonoids—flavones			
Luteolin	286.24	$C_{15}H_{10}O_6$	Zheng et al. [29]

Name	MW * [g mol^{-1}]	$C_xH_yO_z$	References
Tricin	330.29	$C_{17}H_{14}O_7$	Zheng et al. [29]
Flavonoid glycosides			
Diosmetin 6-*C*-glucoside	462.40	$C_{22}H_{22}O_{11}$	Zheng et al. [29]
Tricin 7-*O*-*β*-glucopyranoside	492.43	$C_{23}H_{24}O_{12}$	Zheng et al. [29]
Isoflavone			
Genistin	432.37	$C_{21}H_{20}O_{10}$	Zheng et al. [19]
Genistein	270.24	$C_{15}H_{10}O_5$	Zheng et al. [19]
Others			
Catechol	110.11	$C_6H_6O_2$	Zheng et al. [19]
Phenol	94.11	C_6H_6O	Zheng et al. [19]
Guaiacol	124.14	$C_7H_8O_2$	Zheng et al. [19]
Vanillin	152.15	$C_8H_8O_3$	Zheng et al. [19]
Isovanillin	152.15	$C_8H_8O_3$	Van der Pol et al. [30]
Syringaldehyde	182.17	$C_9H_{10}O_4$	Zheng et al. [19]
Piceol	136.15	$C_8H_8O_2$	Van der Pol et al. [30]
Apocynin	166.17	$C_9H_{10}O_3$	Van der Pol et al. [30]
Acetosyringone	196.19	$C_{10}H_{12}O_4$	Van der Pol et al. [30]
Syringaldehyde	182.17	$C_9H_{10}O_4$	Van der Pol et al. [30]
Creosol	138.16	$C_8H_{10}O_2$	Lv et al. [31]
4-Ethylguaiacol	152.19	$C_9H_{12}O_2$	Lv et al. [31]
Chavicol	134.17	$C_9H_{10}O$	Lv et al. [31]
4-Vinylguaiacol	150.17	$C_9H_{10}O_2$	Lv et al. [31]
4-Allylsyringol	194.23	$C_{11}H_{14}O_3$	Lv et al. [31]

* MW—molecular weight.

from raw ... IPLC) [28]. The aromatic phenolic compounds (*p*-coumaric acid, ferulic acid, *p*-hydroxybenzaldehyde, vanillin, and vanillic acid) were reported in sugarcane bagasse pith. Five phenolic compounds (tricin 4-*O*-guaiacylglyceryl ether-7-*O*-glucopyranoside, genistin, *p*-coumaric acid, quercetin, and genistein) in 30% hydroalcoholic fraction of sugarcane bagasse were identified using ultra-high performance liquid chromatography/high-resolution time of flight mass spectrometry (UHPLC-HR-TOF-MS); (**Table 2**). The total phenolic content was 170.68 mg gallic acid/g dry extract [19].

Phenolic compounds derived from sugarcane bagasse exhibited many biological activities, which were used in various applications. The most important biological activities and the newest and most interesting applications have been summarized in **Table 3**.

Table 3. Biological activities and potential applications of phytochemicals obtained from sugarcane bagasse.

Material	Extract/Compound	Biological Activity/Application	References
Sugarcane bagasse	phenolic compounds	- natural antioxidant - used in pharmacology	Al Arni et al. [27]
		- antibacterial agents against the foodborne pathogens *Escherichia coli*, *Listeria monocytogenes*, *Staphylococcus aureus*, *Salmonella typhimurium*	Zhao et al. [26]
	gallic and tannic acids	- deactivate cellulolytic and hemicellulolytic enzymes	Michelin et al. [32]
	extract	- antioxidant and radical scavenging activity - antimicrobial activity against *Staphylococcus aureus* TISTR029 and *Escherichia coli* O157:H7 - added value for the sugar industry	Juttuporn et al. [33]
		- antihyperglycemic ability - useful therapeutic agents to treat T2D patients	Zheng et al. [19]
		- used for the low-cost bio-oil production	Treedet and Suntivarakorn [34]
		- feedstock for ethanol (bioethanol) production	Krishnan et al. [35] Zhu et al. [36]
		- raw material for the production of industrial enzymes, xylose, glucose, methane	Guilherme et al. [37]
		- raw material for the production of xylitol and organic acids	Chandel et al. [38]
		- used to prepare highly valued succinic acid	Xi et al. [23]
		- used as a reducing agent in synthesizing biogenic platinum nanoparticles	Ishak et al. [20]
		- used as a fuel to power sugar mills	Mohan et al. [22]

3. Maize Residues

Maize (corn *Zea mays* L.) bran, husk, cobs, tassel, pollen, silk, and fiber are residues of corn production. They contain substantial amounts of phytochemicals, such as phenolic compounds, carotenoid pigments and phytosterols [39] (**Table 4**).

Table 4. Phytochemicals identified in corn waste.

Name	MW [g mol^{-1}]	Molecular Formula	References
Phenolic acids—hydroxycinnamic acids			
p-Coumaric acid	164.04	$C_9H_8O_3$	Guo et al. [39]
Ferulic acid	194.18	$C_{10}H_{10}O_4$	Guo et al. [39]
trans-ferulic acid	194.18	$C_{10}H_{10}O_4$	Guo et al. [39]
trans-ferulic acid methyl ester	208.21	$C_{11}H_{12}O_4$	Guo et al. [39]
cis-ferulic acid	194.18	$C_{10}H_{10}O_4$	Guo et al. [39]
cis-ferulic acid methyl ester	208.21	$C_{11}H_{12}O_4$	Guo et al. [39]
Flavonoids—flavonols			
Rutin	610.52	$C_{27}H_{30}O_{16}$	Bujang et al. [40]
Quercetin-3-*O*-glucoside	463.37	$C_{21}H_{19}O_{12}$	Dong et al. [41]
Isorhamnetin-3-*O*-glucoside	478.41	$C_{22}H_{22}O_{12}$	Dong et al. [41]
Kaempferol-3-*O*-glucoside	447.37	$C_{21}H_{19}O_{11}$	Li et al. [42]
Maysin	576.50	$C_{27}H_{28}O_{14}$	Haslina and Eva [43]
Isoorientin-2″-*O*-*α*-l-rhamnoside	594.50	$C_{27}H_{30}O_{15}$	Haslina and Eva [43]
Maysin-3′-methyl ether	590.50	$C_{28}H_{30}O_{15}$	Tian et al. [44]
ax-4″–OH–3′-Methoxymaysin	592.50	$C_{28}H_{32}O_{14}$	Tian et al. [44]
2″-*O*-*α*-l-Rhamnosyl-6-C-fucosylluteolin	578.50	$C_{27}H_{30}O_{14}$	Tian et al. [44]
Flavonoids—anthocyanins			
Pelargonidin-3-*O*-glucoside	433.40	$C_{21}H_{21}O_{10}$	Lao and Giusti [45]
Pelargonidin-3-(6″malonylglucoside)	519.23	$C_{24}H_{23}O_{13}$	Chen et al. [46]
Cyanidin-3-*O*-glucoside	449.39	$C_{21}H_{21}O_{11}$	Barba et al. [47]

Name	MW [g mol^{-1}]	Molecular Formula	References
Cyanidin 3-(6″-malonylglucoside)	535.11	$C_{24}H_{23}O_{14}$	Fernandez-Aulis et al. [48]
Peonidin-3-*O*-glucoside	463.41	$C_{22}H_{23}O_{11}$	Barba et al. [47]
Peonidin-3-(6″malonylglucoside)	549.50	$C_{25}H_{25}O_{14}$	Fernandez-Aulis et al. [48]
	Other compounds		
p-Hydroxybenzaldehyde	122.12	$C_7H_6O_2$	Guo et al. [39]
β-Sitosterol glucoside	576.85	$C_{35}H_{60}O_6$	Guo et al. [39]
Indole-3-acetic acid	175.06	$C_{10}H_9NO_2$	Wille and Berhow [49]
Vanillin	154.05	$C_8H_8O_3$	Guo et al. [39]

…al grains, … source of ferulic acid compared to other cereals, fruits and vegetables. Guo et al. [39] isolated four forms of ferulic acid and its derivates from corn bran. On the other hand, it has been reported that the hexane-derived extract from corn bran contains high levels of ferulate-phytosterol esters, similar in composition and function to oryzanol.

Another corn waste is a husk. It is the outer leafy covering of an ear of *Zea mays* L. The main constituents of the maize husk extracts determined in various phytochemical studies are phenolic compounds, e.g., flavonoids [41][50]. Saponins, glycosides, and alkaloids are present mainly in the aqueous and methanolic extracts, while phenols and tannins are numerous in methanolic ones [51]. Moreover, corn husk has high contents of anthocyanins [48][52]. Simla et al. [53] reported that anthocyanins concentration in corn husks ranges from 0.003 to 4.9 mg/g. The major anthocyanins of corn husk were identified as malonylation products of cyanidin, pelargonidin, and peonidin derivatives [54].

Important by-products of the corn industry are cobs. For every 100 kg of corn grain, approximately 18 kg of corn cobs are produced. Corn cob is one of the food waste-material having a phytochemical component that has a healthy benefit [55]. They contain cyanidin-3-glucoside and cyanidin-3-(6″malonylglucoside) as main anthocyanins, as well as pelargonidin-3-glucoside, peonidin-3-glucoside and their malonyl counterparts [48].

Corn tassel is a by-product from hybrid corn seed production and an excellent source of phytochemicals (the flavonol glycosides of quercetin, isorhamnetin and kaempferol) with beneficial properties [56]. In Thailand, purple waxy corn is considered a special corn type because it is rich in phenolics, anthocyanins, and carotenoids in the tassel [57]. Besides, corn tassels could be considered a great source of valuable products such as volatile oils.

Corn pollen is another corn waste. Significant amounts of phytochemicals, including carotenoids, steroids, terpenes and flavonoids, are present in maize pollen [52]. Bujang et al. (2021) showed that maize pollen contains a high total phenolic content and total flavonoid content of 783.02 mg gallic acid equivalent (GAE)/100 g and 1706.83 mg quercetin equivalent (QE)/100 g, respectively. The flavonoid pattern of maize pollen is characterized by an accumulation of the predominant flavonols, quercetin and traces of isorhamnetin diglycosides and rutin. According to Žilić et al. [58], the quercetin values in maize pollen were 324.16 μg/g and 81.61 to 466.82 μg/g, respectively.

Corn silk, another by-product from corn processing, contains a wide range of bioactive compounds in the form of volatile oils, steroids, saponins, anthocyanins [59], and other natural antioxidants, such as flavonoids [52] and phenolic compounds [41][58][59]. In the corn silk powder, the high phenolic content (94.10 ± 0.26 mg GAE/g) and flavonoid content (163.93 ± 0.83 mg QE/100 g) are responsible for its high antioxidant activity [60]. About 29 flavonoids have been isolated from corn silk. Most of them are C-glycoside compounds and have the same parent nucleus as luteolin [44]. Ren et al. [61] successfully isolated and separated compounds such as 2″-*O*-*α*-l-rhamnosyl-6-C-3″-deoxyglucosyl-3′-methoxyluteolin, ax-5′-methane-3′-methoxymaysin, ax-4″-OH-3′-methoxymaysin, 6,4′-dihydroxy-3′-methoxyflavone-7-*O*-glucoside, and 7,4′-dihydroxy-3′-methoxyflavone-2″-*O*-*α*-l-rhamnosyl-6-C fucoside from corn silk. Moreover, among flavonoids, Haslina and Eva [43] determined in corn silk: apigmaysin, maysin, isoorientin-2″-*O*-*α*-l-rhamnoside, 3-methoxymaysine, and ax-4-OH maysin.

This richness of biologically active compounds results in advantageous properties and applications. The most important properties and the newest studies on the application are listed in **Table 5**.

Table 5. Biological activity and potential applications of phytochemicals obtained from corn wastes.

Material	Extract/Compound	Biological Activity/Application	References
Corn bran	tocopherols and polyphenolic compounds	- antioxidant properties - used as bioactive compounds in cosmetics or natural substitutes (antioxidants, preservatives, stabilizers, emulsifiers, and colorings) in foods to prevent potential adverse effects associated with the consumption of artificial ingredients	Galanakis [62]
Corn husk	extract	- used in the treatment of diabetes because it has shown high: - antidiabetic potential	Brobbey et al. [51]
		- anti-inflammatory effects	Roh et al. [63]
Corn stigma	extract	- antifungal and antibacterial activities against 23 of the studied microorganisms - use as a functional ingredient in the food and pharmaceutical industry	Boeira et al. [64]
Corn tassel	extract	- used as a traditional medicine in China - antioxidant capacity - the high ability to inhibit the proliferation of MGC80-3 gastric cancer cells	Wang et al. [65]
	tasselin A	- inhibition of melanin production - used as an ingredient in skin care whitener	Wille and Berhow [49]
Corn pollen	phenolic compounds	- antiradical activity	Bujang et al. [40]

Material	Extract/Compound	Biological Activity/Application	References
	extract	- the source of functional and bioactive compounds for the nutraceutical and pharmaceutical industries	Bujang et al. [40]
		- the source of antioxidants and is high in nutrients	Žilić et al. [58]

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