Chapter

Antioxidant Compounds from Agro-Industrial Residue

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Abstract

Agro-industrial residues are a potential source of antioxidant compounds, which in general are phenolic compounds with a large chemical variability. The structure and the complexity of the phenolic compounds (polyphenols) determine their antioxidant capacity, pretreatments, and extraction methods. This chapter gives an overview of the chemical complexity of the phenolic compounds found in extractable and non-extractable fractions of agro-industrial residues, and representative compounds that are present in such residues are shown. Moreover, extraction methods described in this review showed the use of nonconventional technologies and chemical, enzymatic, or thermic treatments, useful to transform non-extractable polyphenols (NEP) to extractable polyphenol (EP) and then apply the EP extraction methods and recover antioxidants.

Keywords: agro-industrial residues, total phenol content, extractable and non-extractable polyphenols

1. Introduction

The agro-industry produces a huge amount of waste, such as peels and seeds from fruits (juice industry), coffee husks, coffee pulp, spent coffee grounds, cocoa husks, cocoa bean shells, acerola bagasse, soybean expeller, rice straw, wheat straw, and sugar bagasse. Most of these wastes contain value-added substances such as phenol-type compounds, which are important for their antioxidant activity. Phenolic compounds possess an aromatic ring, bearing one or more hydroxyl substituents, and whether they have low or high molecular weights (from one to several aromatic rings), all of them are generally referred to as polyphenols. The chemical complexity of polyphenols and the ease of extraction from vegetal tissues divide them into two main groups. The first group is comprised of low-molecular-weight phenols (LMWP) such as flavonoids, hydroxycinnamic acids, stilbenes, and benzoic acids, which are found in free form or as glycosides (**Figure 1**) [1–3]. They are easily extracted by aqueous-organic solvents which is why they are named extractable polyphenols (EP). The second group of compounds are low- or high-molecular-weight polyphenols that include (i) lignans which are phenolic acids or flavonoids associated with the cell wall, such as highly condensed phenylpropanoids [4] and (ii) tannins of high-molecular-weight polyphenols, which can be polymers

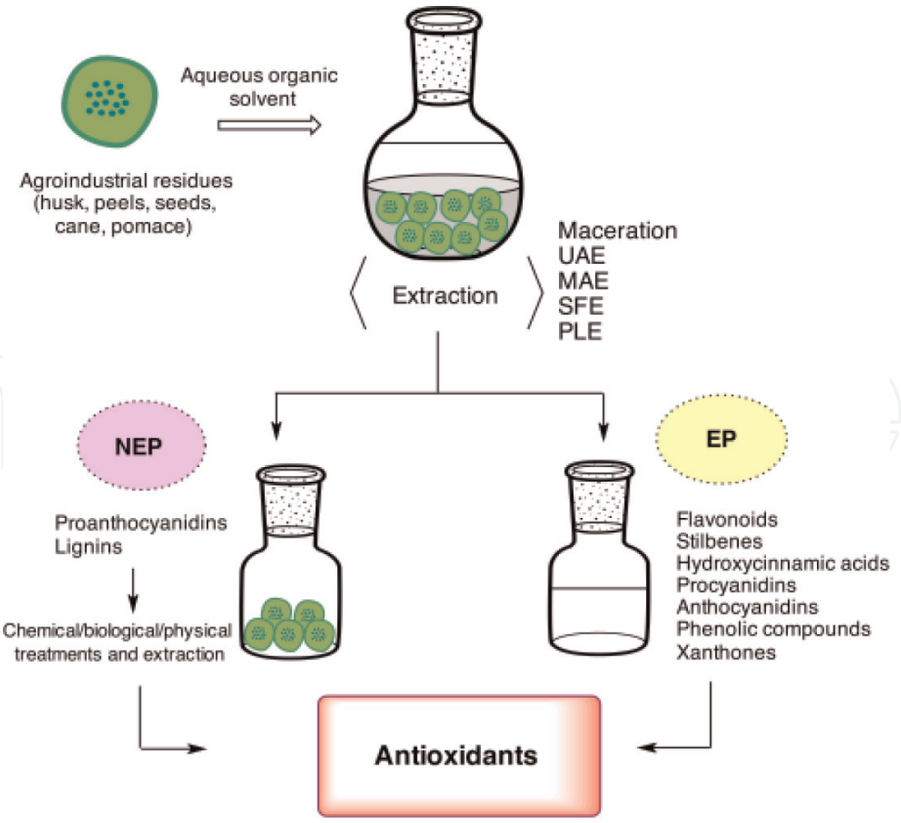


Figure 1.
Extractable (EP) and non-extractable polyphenols (NEP) from ARs.

of phenolic acids and sugars (hydrolysable tannins) or polymers of polyhydroxyflavan-3-ol (condensed tannins or proanthocyanidins) [5]. Due to structural complexity, low solubility, and matrix or vegetal tissue availability, these polyphenols are not easy to extract and therefore are considered non-extractable polyphenols (NEP).

EP and NEP from agro-industrial residues (ARs) represent sources of value-added compounds with potential uses as ingredients in functional foods [6] or dietary supplements due to their health benefits, including antioxidant activity [7–10].

Some problems associated with the recovery of antioxidant phenols or polyphenols are the low availability from matrix (NEP), chemical complexity (NEP), low extraction yields (NEP and EP), and the reduction of antioxidant activity during the extraction process (NEP and EP). All of them present challenges to be overcome for the best use of ARs and economic feasibility. In this review, chemical complexity, extraction methods, and antioxidant activity described in the most recent bibliography are presented. Research in the use of agro-industrial waste involves applying nonconventional extraction methods and establishing conditions that prevent the degradation of polyphenols and, consequently, the loss of antioxidant activity.

Phenolic compounds with antioxidant potential in ARs described to date can be grouped into five classes according to the number of carbon atoms in the basic skeleton: C_6C_1, C_6C_3, $C_6C_1C_6$, $C_6C_2C_6$, and $C_6C_3C_6$ [11]. There are benzoic acids **1–6** (C_6C_1), hydroxycinnamic acids **7–14** (C_6C_3), benzophenones **15–16** and xanthones **17–18** ($C_6C_1C_6$), stilbenes **19–26** ($C_6C_2C_6$), flavan-3-ols **27–30**, anthocyanidins **31–35**, flavonols **36–40**, flavanones **41–45**, flavones **46–49**, isoflavones **50–55** and dihydrochalcone **56** ($C_6C_3C_6$) **Figure 2**. **Table 1** shows low-molecular-weight phenolic compounds and their occurrence in ARs,

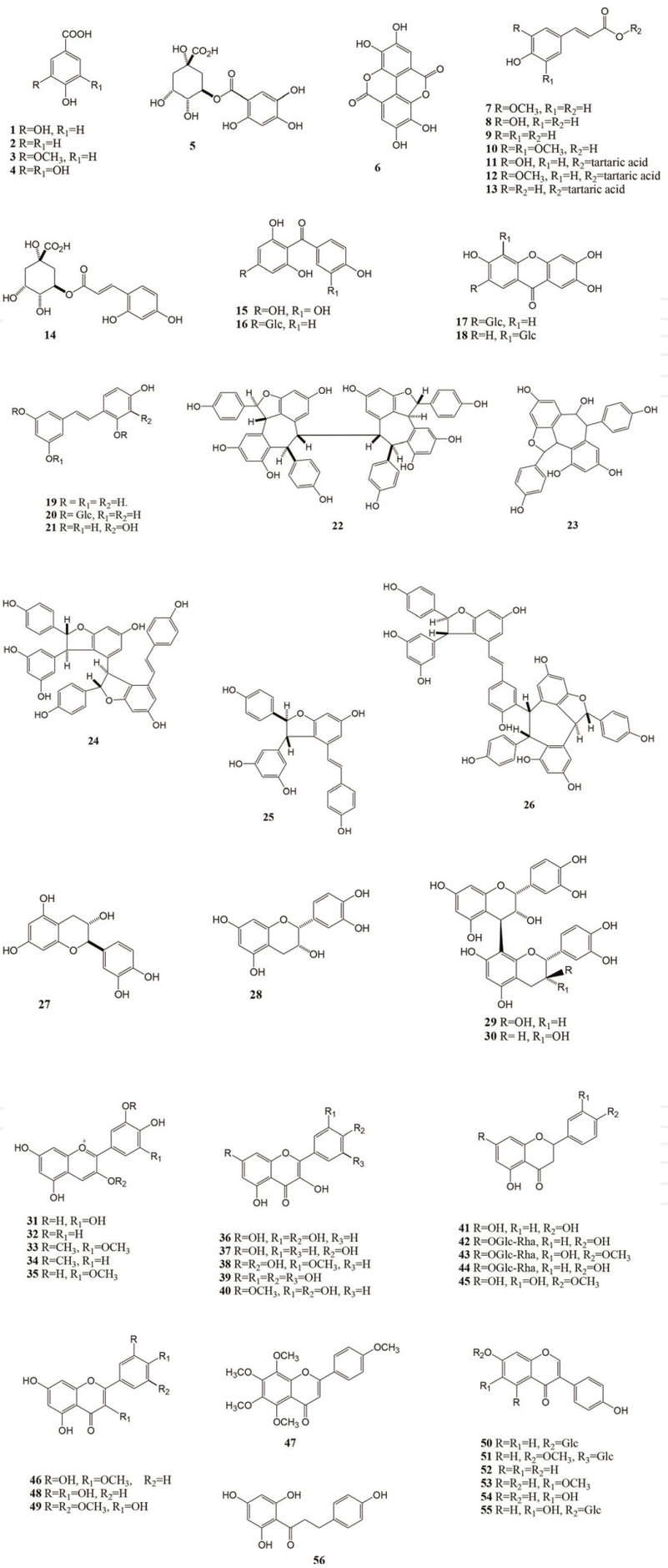


Figure 2.
Structures of low-molecular-weight polyphenols obtained from Ars [14, 31, 50–53].

Polyphenol	Example of ARs
Benzoic acids	
Protocatechuic acid **1**	Mandarin peels [14], grape bagasse [22], spent ground coffee grounds [23], grape pomace [24], sugarcane bagasse [25, 26]
p-Hydroxybenzoic acid **2**	Mandarin peels [14]
Vanillic acid **3**	Mandarin peels [14]
Gallic acid **4**	Mango peels and seeds [17]
Gallic acid derivates theogallin **5** and ellagic acid **6**	Orange peel [18], acerola bagasse [12], Vidal grape pomace [27], jocote [19], grape pomace [24]
Hydroxycinnamic acids and derivates	
Ferulic acid **7**	Coffee pulp [13], grape seed oil press residues [28], Vidal grape pomace [27], pomegranate seeds [29]
Caffeic acid **8**	Grape seed oil press residues [28], grape pomace [24]
p-Coumaric acid **9**	Grape seed oil press residues [28], mandarin peels [14], acerola bagasse [12], Vidal grape pomace [27]
Sinapic acid **10**	Mandarin peels [14], grape pomace [24]
Caftaric acid **11**	Grape seed oil press residues [28], grape pomace [24]
Fertaric acid **12**	Vidal grape pomace [27], seed oil press residues [28], grape pomace [24]
Coutaric acid **13**	Seed oil press residues [28], grape pomace [24]
Caffeoylquinic **14**, coumaroylquinic, and feruloylquinic acids	Coffee pulp [13], apple fiber [3], Saskatoon berry pomace [15], mandarin peels [14], acerola bagasse [12], green coffee seed residue [30], pear fiber [3], jocote [19]
Benzophenones	
Maclurin **15**, riflophenone **16**	Mango peels [17]
Xanthone	
Mangiferin **17**, isomangiferin **18**	Mango peels [17, 31]
Stilbenes	
Trans-resveratrol **19**	Grape pomace [24], grape skin [21], grape cane [32]
Trans-piceid **20**, *cis*-piceid and piceatannol **21**	Grape skin [21], grape cane [32]
Hopeaphenol **22** and isohopeaphenol, ampelopsin **23**, miyabenol C **24**, *trans*-ε-viniferin **25**, r-2-viniferin **26,** and ω-viniferin	Grape cane [32]
Flavan-3-ols	
(+)-Catechin **27**	Vidal grape pomace [27], cocoa husk [20], pomegranate seeds [29]
(−)-Epicatechin **28**	Vidal grape pomace [27], cocoa husk [20], acerola bagasse [12]
Procyanidins B1 **29**, procyanidins B2 **30**	Grape skins [21], grape pomace [24], Vidal grape pomace [27], pomegranate seeds [29]
Anthocyanidin	
Delphinidin **31**	Saskatoon berry pomace [15], blueberry waste [34], grape pomace [24]

Polyphenol	**Example of ARs**
Cyanidin **32**	Saskatoon berry pomace [15], grape skin [21], blueberry waste [33]
Malvidin **33**	Grape skin [21], blueberry waste [33]
Peonidin **34**	Grape skin [21], grape pomace [24], blueberry waste [33]
Petunidin **35**	Grape pomace [24], blueberry waste [33]
Flavonol	
Quercetin **36** and glycosides	Saskatoon berry pomace [15], Vidal grape pomace [27], pear fiber [3], grape skin [21], mango peels [31], jocote peels [19], grape pomace [24], lemon pomace [34]
Kaempferol **37** and glycosides	Vidal grape pomace [27], grape skin [21], mango peels [31], jocote [19], lemon pomace [35], pomegranate seeds [29]
Isorhamnetin **38**, glycosides	Apple fiber [3], grape skin [21]
Myricetin **39** glycosides	Grape skin [21]
Rhamnetin **40** glycosides	Mango peels [27], jocote peels [19]
Flavanone	
Naringenin **41**	Orange peels [18], lemon pomace [34]
Naringin **42**	Orange peels [18], lemon pomace [34], yuzu peels (*Citrus junos*) [16]
Hesperidin **43**	Orange peels [18], lemon pomace [34], yuzu peels (*Citrus junos*) [16]
Narirutin **44**	Orange peels [18]
Hesperetin **45**	Orange peels [18], lemon pomace [34]
Flavone	
Diosmetin **46**	Orange peels [18], sugarcane bagasse [25, 26]
Tangeritin **47**	Orange peels [18]
Luteolin **48**	Cocoa bean shells [35]
Tricin **49**	Milled rice straw extract [36], sugarcane bagasse [25, 26]
Isoflavones	
Daidzin **50**, glycitin **51**, daidzein **52**, glycitein **53**, genistein **54**	Soybean okara [37]
Genistin **55**	Soybean okara [37], cherry pomace [38], sugarcane bagasse [26]
Dihydrochalcone	
Phloretin **56** and glycosides	Apple fiber [3], yuzu peels (*Citrus junos*) [16]

Table 1.
Polyphenols described in agro-industrial residues.

mainly pomace, peels, seeds, and fibers from fruits such as acerola (*Malpighia*) [12], coffee [13], mandarin oranges (*Citrus*) [14], berries [15], yuzu (*Citrus*) [16], mangoes [17], apples [3], pears [3], oranges [18], jocote (*Spondias purpurea* L.) [19], cocoa husks [20], and grapes [21].

2. Extractable polyphenols (EP)

The applied methodologies in the use of ARs to obtain EP depend on residue type and polyphenol stability. For example, acerola bagasse contains water [39], and if the extraction procedure is not done quickly, the residue will need to be dried to avoid microbiological contamination without affecting polyphenol stability. On the other hand, the probable water content of cocoa husk is low, and therefore, the polyphenols' extraction procedures are direct because it is a solid residue. Therefore, drying and extraction technologies or methodologies are necessary to obtain suitable yields of EP with proven antioxidant activity. The description of the drying and extraction methodologies of the EP will focus on the work with anthocyanidins because they are unstable compounds and the conditions of drying or extraction for anthocyanins are important to avoid their decomposition.

2.1 Waste drying

Valorization studies showed acerola bagasse (*Malpighia emarginata* DC) is a good source of antioxidants due to total phenol content (TPC), which ranges from 0.44 to 10.82 g gallic eq/100 g dm (dry matter) [39–41], while the contents of anthocyanins ascorbic acid and proanthocyanidins are 1.002 ± 0.014, 1.002 ± 0.014, and 0.7985 ± 0.0213 g/100 g dw, respectively, and the antioxidant activity evaluation by DPPH• method showed 113.7 ± 0.4 μmol trolox/g dw. However, this residue contains water and therefore must be dried for efficient handling. The drying of the residue has been carried out by hot air (60–80 °C, 4–6 m/s). This procedure showed moderate retention of phenolic (26–31%), anthocyanins (23–36%), and proanthocyanidins (21%) compounds [41]. Better results were obtained using a roto-aerated dryer (115 °C, 2.25 m/s) with a pretreatment of the sample (sprayed with ethanol), and total phenol compounds (TPC) increased 104.6% with respect to fresh residue [42]. A more recent drying method for acerola bagasse is dehydration in a thick-layer dryer, where drying was done at low temperatures (31.7 °C, 230 min, 0.4 m/s or 60 °C, 159.3 min, 0.4 m/s), which were enough to obtain a dry residue with TPC values similar to those obtained in fresh residue (2352.4 ± 57.23 mg gallic acid/100 g dm) [42]. Drying studies of other ARs are described for grape and olive waste using thin-layer drying (air temperature 20–110 °C) [43, 44], and sustainable drying strategies such as the use of solar dryers have been described [45].

2.2 ARs extraction

Generally, EP extraction procedures are done using mixtures of water-organic solvents and assisted by microwave (MAE), heating, and ultrasound (UAE). In recent years, pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE) have been applied, which could be better options because polyphenols are not exposed to severe conditions that promote degradation reactions. In addition, temperature control is a common method to assist the extraction procedures. For example, anthocyanidins, procyanidins, and flavonols were obtained from grape skins using MAE and UAE at 50 ± 5 °C. This work also demonstrated that the yields obtained by MAE with UAE were improved up to 40% (86.39–121.18 mg/100 g dm) [21]. Acid conditions have also been tested to improve the extraction of anthocyanins (anthocyanidin glycosides) from grape peels separated from red grape pomace from vintages 2001 to 2002. The extraction was made in two steps. First, the residue was macerated (2 h) with methanol/HCl 0.1 (v/v) with oxygen reduced in the

mixture to dissolve polar polyphenols. Then extraction with an organic solvent was done to recover less polar polyphenols. Anthocyanin yields found were better (5967–131, 868 mg/kg dm) [24] than those obtained from grape skins from fresh fruits (1211.8 mg/kg dm) [21] due to previous thermic and enzymatic treatments during wine production, which helped release anthocyanins.

Effects of temperature, time, and solvent concentration on polyphenol extraction from grape marc showed better extraction yields with the increase of water (30–50%) in the ethanol-water mixtures, maintaining the temperature at 60 °C for shorter periods (<8 h) to avoid polyphenol degradation [46]. Similar ethanol-water mixtures (40.4 and 55.4%) were used to extract the major components of grape cane: *trans*-resveratrol **19**, *trans*-ε-viniferin **25,** and ferulic acid 7 (**Figure 2**). However, a higher temperature (84 °C) was necessary to obtain the highest antioxidant activities (260.8 and 1378.7 μmol TE/g TEAC and ORAC methods) [47]. Anthocyanins extraction from grape skins, stems, and seeds was effective at 70 °C with ethanol-water mixtures, (1:1) and assisted with pulsed electric fields (PEF) (9 kV, 15 s), ultrasound (35 kHz, 70 °C, 1 h), and high hydrostatic pressurization (600 MPa, 70°C, 1 h). The extraction yields for PEF were 81 and 25% higher than those obtained by ultrasound and hydrostatic pressurization [48]. A combination of methods has also been used, such as the consecutive application of UAE (4 min, 80 °C, 20 kHz, 80 W) and SFE (8 MPa, 40 °C, CO_2/ethanol) for polyphenols extraction from grape marc. The ultrasound treatment increased mass transfer and accelerated access of solvent (CO_2/ethanol) to vegetal tissues, and TPC was increased 27% (2736 ± 11 mg to 3493 ± 61 GAE/100 g dw) [49]. SFE with different conditions (90% CO_2, 5% ethanol, 5% water, 20 MPa, 40 °C) was more efficient than pressurized liquid extraction (PLE) in experiments with blueberry waste. Anthocyanidin yields were 808 ± 0.1 mg/100 g and 248 ± 0.2 mg/100 g for SFE and PLE (20 MPa, 50% water, pH 2, 40 °C) extractions, respectively [33]. PLE with increase of pressure and temperature and change of solvent (65 °C, 10 MPa, 75% ethanol) was shown to be more useful in the extraction of gallic acid **4** together with flavanones **41**–**45** from orange peels. The TPC obtained was 14.9 ± 0.7 mg GAE/g dm [18].

Polyphenols different from anthocyanins, such as phenolic acids (147.4–492.7 g/kg), gallic acid **4** (93.1–353.7 mg/kg), and flavonoids (2.52–13.5 mg/kg), were obtained with acidified methanol from residues of grape (*Vitis vinifera* L.) seed oil production [28], while protocatechuic acid **1** and chlorogenic acid **14** were extracted with hot water (92 ± 3 °C, 2 min) [13]. Other solvents used for EP extraction are acetone/water mixtures (80%, 3 h stirring) to obtain flavonol **37**, **40** glycosides and xanthones **17**–**18** from lyophilized mango peels (**Table 1** and **Figure 2**) [31]. In general, EP extraction is made with water-organic solvents and assisted by conventional and nonconventional methods. However, when extraction conditions are severe as when heating above 70 °C, acid extraction or ultrasound exposure for long periods of time, then these conditions are also useful for obtaining NEP, where the objective is promoting the breakdown of chemical bonds.

3. Non-extractable polyphenols (NEP)

Non-extractable polyphenols (tannins and lignins) are low- or high-molecular-weight compounds associated with vegetal tissue macromolecules; therefore, they are retained in the residue matrix during the extraction process. Depending on the monomeric structures and chemical reactivity of tannins, these are grouped in condensed and hydrolysable tannins. Condensed tannins are polyhydroxyflavan-3-ols oligomers and polymers linked by carbon-carbon bonds between flavanol

units. These are also known as proanthocyanidins because the butanol/HCl/heat treatment produces a red anthocyanidin [54]. Hydrolysable tannins are multiple esters of gallic acid with glucose and products of oxidative reactions, and they can be soluble (EP) or non-soluble (NEP) (**Figure 3**) [55]. Lignin is a phenylpropanoid (C_6C_3) polyphenol where the monomeric units are *p*-coumaryl **71**, coniferyl, and sinapyl. Occurrence of monomeric units in lignin varies according to the taxonomic origin of the ARs, e.g., gymnosperms or angiosperms [56].

Non-extractable polyphenols are common in almost all ARs and represent significant polyphenol percentages of total phenol content (TPC) in vegetal tissues. For example, NEP quantification in peels from apple, banana, kiwi, mandarin, mango, nectarine, orange, pear, and watermelon showed that, of the total phenols found, 7–82% correspond to NEP [58]. Currently research in appropriate methodologies for the extraction of NEP is a priority topic because of the economic advantages of the use of ARs. Some examples of research on the best conditions for the extraction of NEP from ARs are those for the use of cocoa by-products, which involve extractions assisted by ultrasound [20, 35], thermic treatment [59, 60], hydrodynamic cavitation [35], pressurized liquids [50], pulsed electric field [61], subcritical water hydrolysis [62], and solid fermentation [63]. There are also reports on detailed chemical studies of the NEP structure thanks to modern analytical instrumentation, such as liquid chromatography (LC) coupled to matrix-assisted

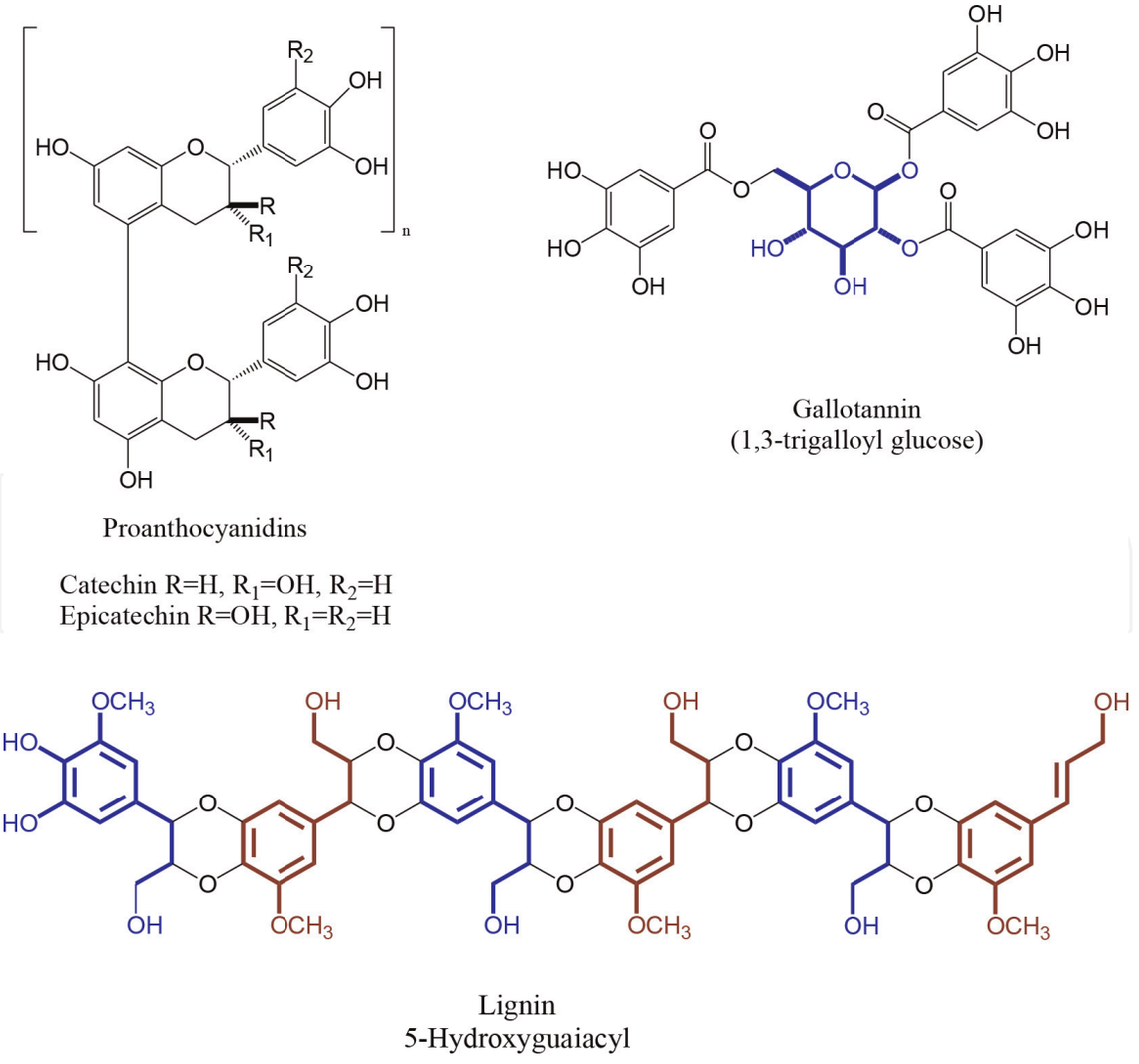


Figure 3.
Structures of condensed tannins (proanthocyanidins), hydrolysable tannins (gallotannins), and lignin (5-hydroxyguaiacyl residue) [55, 57].

laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), electrospray/ionization time-of-flight mass spectrometry (ESI-TOF-MS), LC × LC coupled to tandem mass spectrometry, pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS), and nuclear magnetic resonance (NMR), which has been key to making detailed chemical studies of high-molecular-weight polyphenols [36, 64–66]. In the following paragraphs, some examples of chemical studies of NEP are presented to give an overview of the structural complexity that exists in them.

3.1 Tannins

Studies in pomegranate by-products led to the identification of several polyphenols. EP was extracted with acetone 70% (ultrasound-assisted 20 min, 30 °C), and NEP was previously subjected to basic hydrolysis of insoluble residues before extraction under the same conditions. Ellagic acid **6** and monogalloyl-hexoside **57** were the main compounds, in addition to ellagic acid derivates, valoneic acid bilactone I and II **58**, punicalagin **59** and isomers, trigalloylglucopiranose I and II, and granatin, among 34 hydrolysable tannins described in **Figure 4**. Moreover, condensed tannins such as procyanidin dimers **30** and gallocatechin (or catechin) hexoside were described. Antioxidant activity for polyphenol (EP and NEP) fractions was 0.12–3.58 mmol TE/g dm (DPPH) and 5.34–208.73 μmol TE/g dm (ABTS radical-scavenging activity) [66]. Oligomeric proanthocyanidins such as dimer, trimer, tetramer, pentamer, and hexamer units (MW 600, 889, 1177, 1465, and 1753 amu) were identified in coffee pulp by MALDI-TOF-MS analysis. Extraction of these tannins was made with acid aqueous acetone [67]. Acetone/water also was used to extract anthocyanidins from litchi pericarp (*Litchi chinensis*), after its incubation with *Aspergillus awamori*. Total extractable tannin recovery was increased up to 59%, and ESI-TOF-MS analysis revealed *A. awamori* degraded B-type condensed tannin and showed low capacity to degrade the condensed tannin A-type.

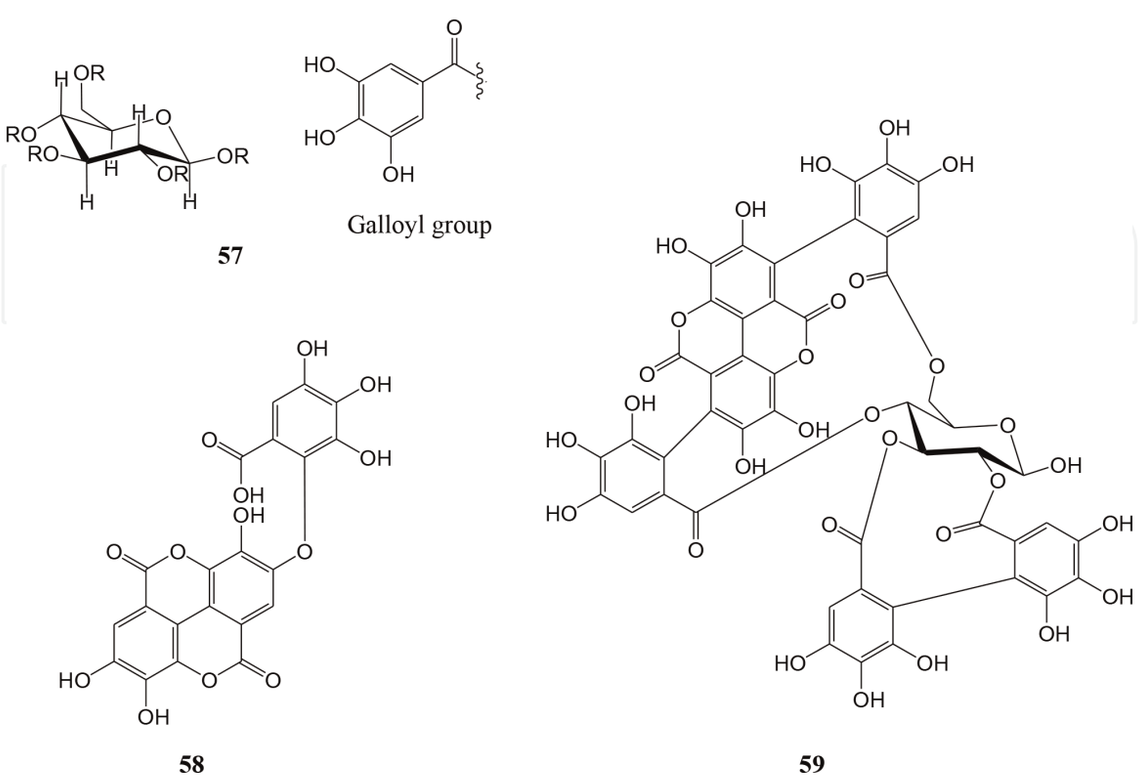


Figure 4.
Hydrolysable tannins identified in pomegranate by-products [55, 69].

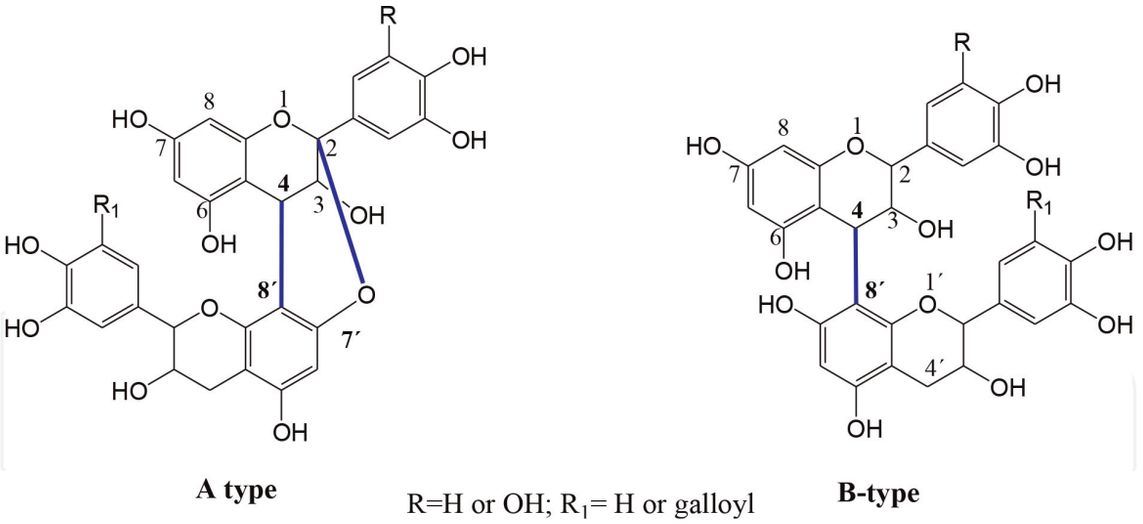


Figure 5.
Condensed A- and B-type condensed tannins. A-type C4-C8 couple C2-O-C7 linkage and B-type C4-C8 linkage [68].

Differences between both compound types are C4-C8 couple C2-O-C7′ linkages for A-type tannin, while C4-C8 linkages are found in B-type tannin (**Figure 5**) [68].

3.2 Lignin

Studies of chemical composition of NEP corresponding to lignin were made for that recovered from black liquor (BL) and milled rice straw extract (RSE). BL is produced from basic hydrolysis/heat of rice straw (straw alkali oxygen cooking). Lignin and phenolics from rice straw were obtained by Soxhlet extraction (ethanol/benzene 1:2, v/v, 8 h). Detailed studies by infrared and nuclear magnetic resonance spectroscopy showed a number of residues from rice straw lignin, including β-O-4'ethers **60**, β-O-4'ethers with acylated γ-OH **61**, phenylcoumarans **62**, resinols **63**, dibenzodioxocyns **64**, α,β-diaryl ethers **65**, tricin units **66**, Cα-oxidized guaiacyl unit **67**, syringyl units **68**, Cα-oxidized syringyl **69**, *p*-hydroxyphenyl units **70**, *p*-coumaroyl **71**, guaiacyl units **72**, feruloyl **73**, cinnamyl alcohol end-groups **74,** and cinnamyl aldehyde end-groups **75** (**Figure 6**). Antioxidant evaluation (DPPH• and ABTS• methods) showed lignin from BL had a better radical-scavenging ability than RSE, which was due to the release of *p*-hydroxyphenyl units by rice straw alkali oxygen cooking. This process caused the destruction of tricin [70]. Lignin and phenolics could also be extracted from milled rice straw by hydrothermal treatment (210 °C) to release cellulosic components, delignification (ethanol/water 60.5%, 130 °C) to fractionate the lignocellulosic biomass and separation (nanofiltration cutoff 280 Da) to isolate the polyphenols [71].

Extraction of NEP from residues that come from industrial processes has been done using methodologies applied to EP because they were released by the industrial process involved. For example, polyphenolics from sugarcane bagasse were extracted with 95% ethanol (maceration 7d) and *p*-coumaric acid; tricin **66**, luteolin, tricin 7-*O*-β-glucopiranoside, diosmetin **46**, 6-*C*-glucoside, and protocatehuic acid **1** (**Figure 2**) were isolated from ethanol extracts (ethanol 95%, 7d, maceration). TPC from extract was 3.0 mg GAE/100 mg dm [25]. Antioxidant activities (ORAC assay) of tricin **49**, *p*-coumaric **9,** and protocatechuic **1** acids were 9.76 ± 1.01, 7.22 ± 0.73, and 6.40 ± 0.62 μmol TE/μmol, respectively. Phenols yields were from <0.2 to 2.12 mg/kg dm. Other compounds reported in this residue were genistein **52** (15.22 ± 1.28 mg/g), genistein **53** (trace), and

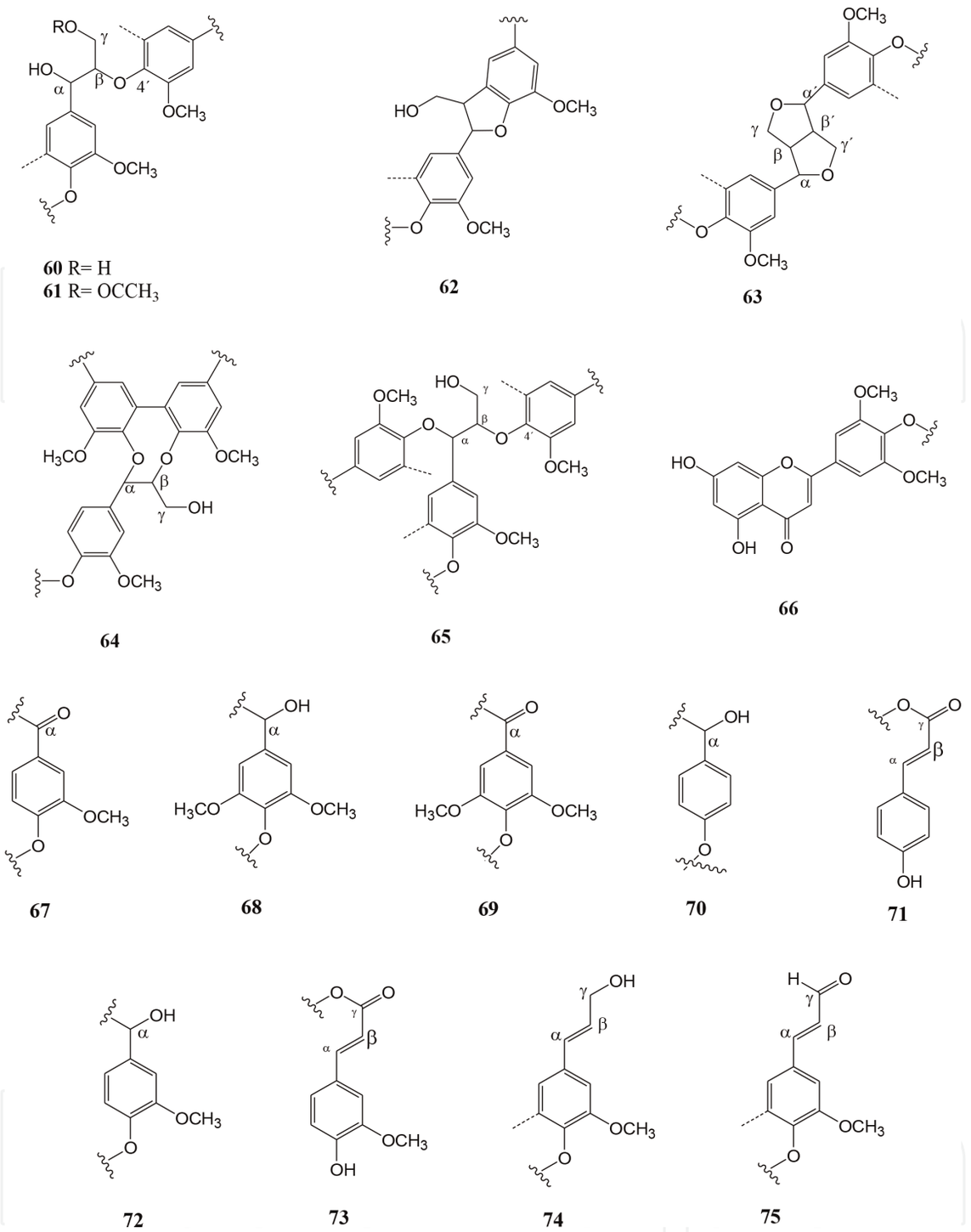


Figure 6.
Residues identified in lignin from rice straw [70].

quercetin **36** (9.98 0.40 mg/g DW) [26]. Polyphenol recovery was improved (117.1%) when residue was treated with glacial acetic acid and hydrogen peroxide at 60 °C for 7 h and later subjected to hydrolysis with xylanase (*Clostridium thermocellum* ATCC 27405). The antioxidant activity was increased 73% (695.8 ± 105.3 μmol trolox eq./L) [72].

Other residue that has undergone industrial processes enough to release polyphenols is the lignin from the ozone, soaking aqueous ammonia pretreatment of wheat. Py/GC/MS analysis showed the presence of 17 phenolic compounds derived from guaiacyl **72**, syringyl **68,** and *p*-hydroxyphenyl **70** units in ratios of 65.09, 23.36, and 11.5%, respectively, the main compounds being Phenol 2-methoxy (guaiacol) **76**, phenol 2-methoxy-4-vinyl (4-vinylguaiacol) **77**, and 2,6-dimethoxy

phenol (syringol) **78**. The residue was identified as a potential source of antioxidants because it showed 86.9 ± 0.34% of inhibition of DPPH radicals similar to that of commercial BHT 103.3 ± 1% [36].

4. Antioxidant activity (AA) and extraction methods

Antioxidant activity (AA) obtained from AR's extracts varies according to the residue type and the extraction method. In case of cocoa residues, UAE (methanol/water 1:1 and acetone water 7:3) showed better method than maceration because AA was improved 8.8% (EC_{50} 0.0486 ± 0.0018 mg/mL) in comparison with that obtained from maceration with the same solvents (EC_{50} 0.0533 ± 0.0022 mg/mL), while total phenol content (TPC) was 41.96% higher (**Table 2**) [20]. Extracts with high TPC (55 mg GAE/g) but low AA values (EC_{50} 8.18 mg/mL) were obtained by hydrothermal treatment (170 °C, 30 min) [60], in comparison with those values for extracts obtained by UAE and maceration. Thermic treatment

Residue/ref.	Extraction method	Antioxidant activity	TPC/(dry matter)
Cocoa husk [20]	UAE 25 kHz, 30 min, MeOH/H_2O 1:1, and acetone/water 7:3	EC_{50} 0.0486 ± 0.0018 mg/mL (DPPH)	25.34 ± 1.82 mg GAE/g
	Maceration MeOH/H_2O 1:1, 2 h stir, acetone/water 7:3	EC_{50} 0.0533 ± 0.0022 mg/mL (DPPH) Ascorbic acid 0.0243 ± 0.0009 mg/mL	17.85 ± 1.33 mg GAE/g
Cocoa husk [60]	Hydrothermal, 170 °C, 30 min	EC_{50} 8.18 mg/mL (DPPH)	55 mg GAE/g
Cocoa bean shells [61]	Extraction EtOH/water rotatory agitation 25 °C with a pretreatment time of 11.99 μs, number of pulses of 991.28, PEF strength of 1.74 kV cm^{-1}, ethanol 39.15%, 118.54 min	101.1–321.97 μM TE/g (DPPH)	17.88–55.16 mg GAE/g
Cocoa bean shells [35]	UAE EtOH/water (70:30), 15 min, 150 W, 19.9 kHz, 40 °C	EC_{50} 66.9 ± 2.4 μg/mL and 235.3 ± 8.4 μM TE/g (DPPH)	125 mg GAE/g
Cocoa bean shells [50]	PLE EtOH, 10.35 MPa, 90 °C, 30 min	65 ± 2 μM TE/g (DPPH) 84 ± 4 μM TE/g (FRAP)	10 ± 0.3 mg ECE/g
Cocoa bean shells [35]	Hydrodynamic cavitation and Hex/EtOH/H_2O mixtures (30:49:21) scale-up reactor	EC_{50} 62.0 ± 3.1 μg/mL (DPPH) and 256.7 ± 9.9 μM TE/g (DPPH)	197.4 mg GAE/g
Cocoa bean shells [63]	Solid state fermentation with *Penicillium roqueforti* and EtOH/water extraction	81.3% inhibition (DPPH) 23.2 μM ferrous sulfate/g (FRAP)	926.6 ± 61 mg GAE/100 g
Acerola bagasse [12]	MeOH 50%, 80 °C, 15 min	405.11 ± 1.83 μM TE/Lg (Rutin 1473.07 ± 21.39 μM TE/Lg) (ABTS)	nd
Acerola bagasse [41]	Water and stirring 30 min	21.7–24.0 μM TE/g (DPPH)	2710.2–3171.9 mg GAE/100 g

Residue/ref.	Extraction method	Antioxidant activity	TPC/(dry matter)
Coffee pulp [13]	Water, 92 ± 3 °C, 2 min	EC_{50} 18–27 μg/mL (ABTS) 82–153 μg/mL (DPPH)	7.61–17.40 mg GAE/L
Coffee husk [23]	SFE 200 bar/323.15 K, CO_2 + 8% EtOH	EC_{50} 630 μg/mL (DPPH) 141 ± 1 μM TE/g (ABTS)	36 ± 1 mg CAE/g
	UAE, EtOH	EC_{50} 235.1 μg/mL (DPPH) 161 ± 3 μM TE/g (ABTS)	133.3 ± 0.6 mg CAE/g
Spent coffee grounds [23]	SFE 200 bar/323.15 K, CO_2 + 4% EtOH	EC_{50} 516.2 μg/mL (DPPH) 169 ± 3 μM TE/g (ABTS)	57 ± 3 mg CAE/g
	Soxhlet extraction, EtOAc	EC_{50} 202.23 μg/mL (DPPH) 160.13 ± 13 μM TE/g (ABTS)	182.6 ± 28.2 mg CAE/g
Coffee silver skin [1]	Hydroalcoholic solvent (50%) at 40°C, 60 min	326.0 ± 5.7 mg TE/L (DPPH) 1791.9 ± 126.3 mg FSE/L (FRAP)	302.5 ± 7.1 mg GAE/L
Spent coffee grounds [73]	Solid state fermentation with *Bacillus clausii* (37 °C, 39 h), defatted (hexane) and EtOH/water (80:20) extraction (orbital shaker, 30 °C, 50 rpm, 3 h)	17.894 μM TE/100 g (ABTS)	1051 mg GAE/100 g Increased 36%
Blueberry waste [33]	SFE 90% CO_2, 5% H_2O, 5% EtOH, 20 MPa	1658 ± 160 μM TE/g (DPPH) 199 ± 20 μM TE/g (ABTS)	134 ± 11 mg GAE/g Wet matter
	PLE 40 °C, 20 MPa, 15 min, 5 mL cell, EtOH/water 1:1	1746 ± 71 μM TE/g (DPPH) 66 ± 1 μM TEAC/g (ABTS)	90 ± 2 mg GAE/g Wet matter
Grape cane [47]	Water/EtOH 40.4 and 55.4%, 84 °C	238.6 μM TE/g (ABTS) 1259.6 μM TE/g (ORAC)	8.93 mg resveratrol eq./g
Grape cane [32]	Acetone/water 6:4, room temperature	1700–5300 μM TE/g (ORAC)	Stilbene total content 2.62–3.30 mg/g
Grape skins [21]	MAE, 600 W, 2450 MHz, 50 ± 5 °C, water/EtOH/phosphoric acid 50:50:1	nd	Stilbenes 1.5 mg/100 g
	UAE, 130 W, 40 kHz, 50 ± 5°C, water/EtOH/phosphoric acid 50:50:1	nd	Stilbenes 0.71 mg/100 g
Soybean okara [37]	Solid state fermentation with *Saccharomyces cerevisiae* r. f. *bayanus* 72 h. Water/MeOH (80%) extraction	24.04 mM TE/g (DPPH) 20.65 mM TE/g (ABTS) Increase 15%	116 mg GAE/10 g

*UAE, ultrasound-assisted extraction; EC_{50}, effective concentration at 50%; PLE, pressurized liquid extraction; PEF, pulsed electric field; SFE, supercritical fluid extraction; TPC, total phenol content; MeOH, methanol; EtOH, ethanol; AcOEt, ethyl acetate; CAE, chlorogenic acid equivalent; GAE, gallic acid equivalent; ABTS, 2,2′-azino-*bis*(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt; DPPH, 2,2-diphenyl-1-picrylhydrazyl; ORAC, oxygen radical absorbance capacity; MAE, microwave-assisted extraction; TE, trolox equivalent; FRAP, ferric-reducing antioxidant power; FSE, ferrous sulfate equivalent; nd, not described*

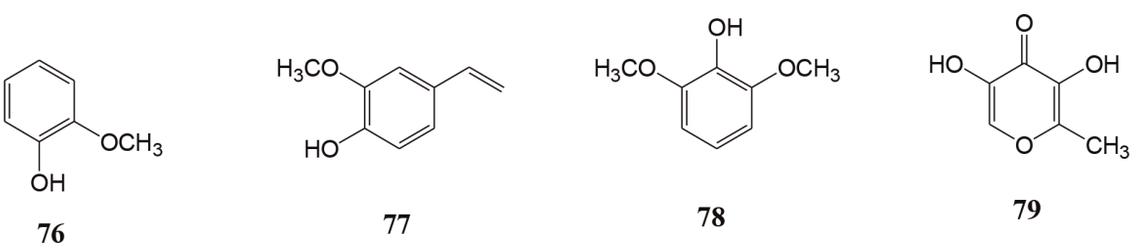
Table 2.
Antioxidant activity and extraction methods in agro-industrial residues.

improves yields of polyphenols because it promotes release of NEP, but polyphenols can loss their antioxidant capacity. A method that significantly improved the TPC without reducing the AA of the extracts is the hydrodynamic cavitation (HC), which was used to assist polyphenols extraction from cocoa bean shells with hexane/ethanol/water mixtures [35]. The authors compared the efficiency of this method with UAE (ethanol/water); AA were similar (EC_{50} 62 ± 3.2 and 66.9 ± 2.4 μg/mL), while TPC was 125 and 197.4 mg GAE/g for extracts obtained by UAE and HC, respectively.

In general, SFE (with the optimal conditions) is an extraction method more convenient in order to avoid degradation reactions and therefore reduces the AA of extracts. Blueberry waste extracts were obtained by SFE (90% CO_2, 5% H_2O, 5% ethanol, 20 MPa) and PLE (40 °C, 20 MPa, 15 min). Both methods showed extracts with similar AA (1658 ± 160 and 1746 ± 71 μM TE/g), but SFE yields extracts with TPC 48% more higher (134 ± 11 mg GAE/g) than those from PLE (90.2 ± 2 mg GAE/g) (**Table 2**) [33]. However, extracts obtained by UAE (ethanol) and Soxhlet (ethyl acetate) from coffee residues showed better AA values (EC_{50} 235.1 and 202.23 μg/mL) than those observed in the extracts obtained by SFE (200 bar/323.15 K, CO_2 + 8 or 4% ethanol) (EC_{50} 630 and 516.2 μg/mL) [23].

Pretreatments as solid-state fermentation before polyphenolic extraction have shown effects on TPC and AA, for example, in spent coffee grounds, an increase in TPC and AA of 36%, and 15% were observed in fermented extracts by *Bacillus clausii* followed by ethanol/water extraction [73]. The same increase in AA was observed when soybean residues were subjected to solid-state fermentation using *Saccharomyces cerevisiae* (20.39–24.04 mM TE/g) [37]. However, the use of *Penicillium roqueforti* in this fermentation type with cocoa shells showed a weak increase of AA from 79.2 to 81.3% (2.6%) and the reduction of TPC from 2120 ± 20 mg GA/100 g to 926.6 ± 61 mg/100 g (56%) [63].

Grape cane residues are rich in stilbene compounds, which can be extracted with mixtures of water/ethanol or acetone/water, and their antioxidant activities depend on stilbene type present in extracts, e.g., quantitative structure-antioxidant activity relationship studies showed structural facts as planar geometry of *trans*-isomers has direct relation with the AA because polyphenols increase their free radical-stabilizing properties [74]. This may explain why AA is lower in extracts with higher stilbene contents; water/ethanol extracts with 8.93 mg resveratrol eq./g showed an AA of 1259.6 μM TE/g (ORAC), while acetone/water extracts with stilbene total content of 2.62–3.30 mg/g showed from 1700 to 5300 μM TE/g. Therefore, stilbene extraction accelerated by temperature can have consequences on stereoisomer content and therefore on the AA. Extraction of grape skins at 50 °C assisted by MAE and UAE showed better stilbenes contents for MAE (1.5 mg/100 g), but authors did not describe the AA [21]. Heat resistance phenol compounds and with significant AA are those found in residues previously treated to release NEP such as **56**, **76-79** [36, 75] (**Figures 2** and **7**). For example, apple pulp was subjected to reflux with water for 2 h, and the EtOAc extract showed an AA of IC_{50}



76 **77** **78** **79**

Figure 7.
Heat resistance phenol compounds identified in ARs [36, 75].

10.59 ± 2.77 μg/mL (DPPH), while 5-hydroxymaltol **79**, isolated from AcOEt extract, showed an IC_{50} value of 8.22 ± 1.83 μg/mL, which was 48 times higher than α-tocopherol (IC_{50} 0.17 ± 0.04 μg/mL) [75].

5. Conclusions

Most of the bibliography related to the study of waste is focused on the search for conditions for the greater extraction of polyphenols from ARs and evaluating the feasibility of using these residues as a source of antioxidants. To evaluate the extraction efficiency of the proposed methods, the content of total phenols (TCP), the quantification and/or identification of specific polyphenols and determination of AA have been described. Antioxidant activity of polyphenols varies mainly by the temperature, which could promote the compound degradation or only small structural changes, mainly with anthocyanidins and stilbenes. Extraction methods applied to ARs described in this review showed the use of nonconventional technologies such as SFE and LPE for EP extraction while chemical, enzymatic, or thermic hydrolysis has been used to transform NEP to EP to apply the EP extraction methods and recover antioxidants. Moreover, significant contributions to the knowledge of the chemistry of ARs are summarized and representative compounds are shown that cover most types of phenols that exist in the plant kingdom and that are present in such residues. The chemical structures of 79 low-molecular-weight compounds, mainly EP and some examples of tannin and lignin residues, are described. Therefore, the use of ARs to recover polyphenols is growing due to the knowledge of ARs chemistry and to the development of nonconventional extraction methods and more efficient dry methods.

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Conflict of interest

The authors declare that there are no conflicts of interests regarding the publication of this chapter.

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