Phytochemicals in bioenergy crops

Marta Oleszek · Iwona Kowalska · Wiesław Oleszek

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Abstract The use of natural compounds derived from agricultural crops and other plants as health promoting chemicals gains tremendous growing interest in various industrial sectors as well as among people worldwide. These chemicals have been more and more employed by the food industry as food additives, functional food ingredients, nutraceuticals, by feedstuffs industry, but also by the cosmetic and pharmaceutical industries. The general idea for this interest is to use natural products as potential alternatives to synthetic chemicals. On the other hand, some plants characterized by high yield and being used as energy crops also contained significant amount of bioactive compounds. This review focuses on the wide spectrum of the phytochemicals present in available biomass plants. It is supposed that extraction of bioactive chemicals from energy crops before their energetic use may increase economical effectiveness, providing simultaneously a double benefit in the form of phytochemicals and bioenergy as value added products. This remains in line with bioeconomy, which is defined by European Commission as “the

production of renewable biological resources and the conversion of these resources and waste streams into value added products, such as food, feed, bio-based products and bioenergy”. However, the issue is still a challenging effort due to the high costs, technology readiness and regulatory hurdles.

Keywords Biomass · Biomass phytochemicals · Natural products source · Biorefinery concept

Introduction

Increase in food, feed and energy demands stressed to explore sustainable opportunities for the combined production of fuels, food and phytochemicals (Parajuli et al. 2017). Energy crops and wood were generally used as a feedstock for energy production, due to their high biomass yield, great calorific value, as well as low agronomic input. They find application in the production of biofuels, both by direct combustion and biological fermentation, i.e. biogas and bio-ethanol (Oleszek and Matyka 2017). Nonetheless, available literature data have proven that many of them have a potential to become suitable source of valuable phytochemicals for industrial use, because of substantial concentration of antioxidants and other biologically active compounds (Duynisveld et al. 1990; Veitch et al. 2010; Parveen et al. 2011; Oleszek and

M. Oleszek (✉)
Institute of Agrophysics, Polish Academy of Sciences,
Doświadczalna 4, 20-290 Lublin, Poland
e-mail: m.oleszek@ipan.lublin.pl

I. Kowalska · W. Oleszek
Institute of Soil Science and Plant Cultivation, State
Research Institute, Czartoryskich 8, 24-100 Pulawy,
Poland

Krzemińska 2017). Moreover, some compounds usable in the pharmaceutical, cosmetic and food sectors may be produced and extracted during various pretreatment of lignocellulose, main component of all energy biomasses. Such plants versatility and the wide use of their products indicate that energy crops and woody biomass are suitable for the development of a bio-refinery concept, where the production of bioenergy/biofuels is preceded by recovery of bio-based compounds and coupled with generation of other value-added products. It would allow the comprehensive usage of crops, to maximize the benefits from the unit of arable land area of their cultivation and to improve the profitability of their processing (Montastruc et al. 2011; Corno et al. 2014). Moreover, it has been shown that extraction of valuable compounds may be a good method of biomass pretreatment, enhancing its suitability for subsequent bioenergy production (Attard et al. 2015). Furthermore, some phytochemicals contained in energy crops can influence on the efficiency of bioenergy production in biotechnological processes involved microorganisms, such as methane or ethanol fermentation (Popp et al. 2016). Therefore, removal of phytochemicals from biomass by extraction may improve biomass suitability. Clear advantage of multi-product plants has been revealed, essentially pointing to the fact that single-product plants are not feasible (Tsakalova et al. 2014). The selection of an appropriate process for combined recovery of materials and energy from biomass depends primarily on its properties, the expected forms of bioenergy and bio-products, and the economic feasibility (Wang 2013).

The purpose of this paper is to review the literature of bioactive compounds contained in energy crops and woody biomass, their properties, methods of extraction and analysis, as well as potential application in pharmaceutical, cosmetic and food industry. It was

intended to show other possibilities of use the biomass instead of or in combination with energy production.

Herbaceous energy crops

Maize (*Zea mays* L.)

Maize (*Zea mays* L.) belongs to the family of grasses (*Poaceae*); (Fig. 1). This plant is one of the three the highest output and cultivated crops around the world (Qi et al. 2018). Maize is not only a basic element of human diet, but also an important animal feed and raw material for many manufactories (Nile and Park 2014). Moreover, it is also main feedstock for biogas production, particularly in the Central Europe (Herrmann 2013; Oleszek and Matyka 2018).

Both maize seeds, as well as vegetative parts of plant contain many secondary metabolites, such as phenolics, flavonoids, carotenoids and phytosterols. Selected compounds identified previously in maize were listed in the Table 1. Many of them are classified as strong antioxidants. Interestingly, Dewanto et al. (2002) proved that thermal processing significantly elevated the total antioxidant activity of corn by 44%, although 25% loss of vitamin C. Simultaneously, the concentration of phenolic compounds significantly increased. These findings indicated that most of the antioxidant activity comes from the natural combination of phytochemicals such as ferulic acids and other phenolics, not only from presence of vitamin C. It denies the popular notion that processed fruits and vegetables have lower nutritional value than fresh ones. Vazquez-Olivo et al. (2017) indicated that phenolic acids and lignin from maize stover, remaining after maize production, exhibit high antioxidant properties and should be used for valorization of this biomass. Nile and Park (2014) isolated some phenolic acids and anthocyanins from maize kernel to

Fig. 1 *Zea mays* L., *Sorghum* spp. and *Polygonum sachalinensis*

Table 1 Phytochemicals identified in *Zea mays* L

Part of plants	Metabolites	References
Kernels	Protocatechuic acid, vanillic acid, 2,4,6-trihydroxybenzoic acid, <i>p</i> -hydroxycinnamic acid, ferulic acid, hirsutrin, 3'-methoxyhirsutrin, cyanidin-3-glucoside, pelargonidin-3-glucoside, peonidin-3-glucoside, Quinic acid, 1- <i>O</i> -caffeoylquinic acid, 2- <i>O</i> -caffeoylquinic acid, 3- <i>O</i> -caffeoylquinic acid, 4- <i>O</i> -caffeoylquinic acid, 5- <i>O</i> -caffeoylquinic acid, hydroxychlorogenic acid, 3- <i>O</i> -feruloylquinic acid, 5- <i>O</i> -feruloylquinic acid, 5- <i>p</i> -coumaroylquinic acid	Nile and Park (2014) Atanasova-Penichon et al. (2014)
<i>Stigma maydis</i>	Stigmene A-F	Qi et al. (2018)
Cobs	Phydroxybenzoic, protocatechuic, <i>p</i> -coumaric, and ferulic acids	Dewanto et al. (2002)
Roots	Zealactone, zeapyranolactone, 5-deoxystigol, heliolactone, methyl ester of carlactonoic acid	Charnikhova et al. (2018)
Stovers	Ferulic acid, <i>p</i> -coumaric acid	Vazquez-Olivo et al. (2017)

determine their antioxidant, α -glucosidase and xanthine oxidase inhibitory activity. The authors proved that all the phenolic compounds revealed significant biological activities with all examined parameters.

Many maize phytochemicals are its natural protectants, which enhance the plant resistance to pathogens. Atanasova-Penichon et al. (2014) stated that bioactive compounds contained in maize kernel were able to reduce the contamination of grain with fumonisin mycotoxins secreted by *Fusarium verticillioides*. Chlorogenic acid was identified as the main compounds responsible for antifungal activity. Similar results were obtained by Nesci and Etcheverry (2006), who investigated the effect of natural maize phytochemicals, trans-cinnamic acid (CA) and ferulic acid (FA) on the growth of *Aspergillus flavus* and aflatoxin production. In this work, the authors proved that CA and FA can be considered as effective fungitoxicants for *A. flavus* and *A. parasiticus* in in vitro assay. Wang et al. (2014) evaluated antioxidant and antigenotoxic activities of corn tassel extracts (CTTs). The major bioactive compounds belonged to flavonoids (1.67%), saponins (2.41%) and polysaccharides (4.76%) group. CTTs extract exhibited antioxidant activity and inhibited the proliferation of human gastric cancer cells. Anticancer activity of *Zea mays* leaf extracts was stated by Balasubramanian and Padma (2013). The best effect was exerted by the methanolic extract followed by the aqueous and chloroform extracts. Other valuable compounds from maize are sesquiterpenes. Qi et al. (2018) reported that during industrial processing of maize a vast amount of residues

including *stigma maydis* was generated, which is generally regarded as a waste and discarded. From this material, the authors isolated and identified five new macrocarpene-type sesquiterpenes, named stigmenes A-E, along with a known analogue stigmene F. Furthermore, it has been proven that, these compounds exhibited the inhibitory effect of amyloid- β (A β) aggregation, which may give the chance for their application against Alzheimer's disease (AD), an age-related neurodegenerative disease. The latest study concern the new class of plant hormones included in maize roots, namely the strigolactones, which play important role in the regulation of plant architecture, and are also exuded by plants into the rhizosphere. Ahmed (2018) stated the allelopathic effect of maize crude extract against seed germination and seedling growth of *Phalaris minor*, *Helianthus annuus*, *Triticum aestivum*, *Sorghum halepense* and *Zea mays*. Aqueous shoot and root extract contained tannins, phlobatannins, flavonoids, terpenoids, alkaloids and saponins. It has given hope for potential use as natural herbicides to reduce the adverse effects of using synthetic compounds.

Maize is also potential feedstock for natural waxes. Attard et al. (2015) investigated the biorefinery concept, where supercritical extraction was applied for obtaining of waxes from maize stovers. The extraction was used as initial step in biorefinery plant, before fermentation of biomass. It has been proved that such extraction is not only important way for obtaining of waxes, but also good method of biomass pretreatment for the production of 2nd generation

biofuels. Wax from maize can be used in the production of nutraceuticals, pharmaceuticals, cosmetics and as a natural defoaming agent in washing machine, due to replace environmentally hazardous formulations.

Sorghum (*Sorghum* spp.)

Sorghum (*Sorghum* spp.) is one of the most important crops in the world (Fig. 1). This is gluten-free grain crop ranked as the fifth most produced cereal crop globally. This plant is drought tolerant and has been grown in semiarid regions. Seeds are used as a food source in many areas. It produces a large variety of secondary metabolites, including phenolic acids, flavonoids, and condensed tannins, phytosterols, policosanols and bioactive peptides (Awika and Rooney 2004; Dykes et al. 2009; Duodu and Awika 2019). Their types and quantities are affected by the genotype. It was documented that this species contains number of phenolic acids including *p*-hydroxybenzoic, vanillic, caffeic, syringic, ferulic, *p*-coumaric and gentisic acid as well as some aldehydes: *p*-hydroxybenzaldehyde, syringaldehyde and vanillin (Sène et al. 2001). The total phenol concentration reached 1.1–1.5% of the root dry weight and 1.1–2.2% of the aerial part dry weight.

As for the flavonoids, luteolin and apigenin were the two flavones that were identified and quantified in the sorghum varieties (Dykes et al. 2011). Flavonoid phytoalexins, such as 3-deoxyanthocyanidins, are synthesized by sorghum after treatment with jasmonic acid, as an essential component of active defense mechanisms (Du et al. 2010; Meyer et al. 2016). The 3-deoxyanthocyanins have been identified as orange luteolinidin and the yellow apigeninidin.

Not much information has been available in literature on the chemical composition of sorghum straw, which is major by-product, which can be used as biomass. Some sorghum species may contain cyanogenic compounds, in the form of glycosides (dhurrin) or alkaloids (hordenin) (Funnell-Harris et al. 2008). Dhurrin, a major secondary product of aerial shoot sorghum plant, is located almost exclusively in the epidermis and is recognized as a major insect defense component (D'Mello 2000; Kojima and Conn 1982). Dhurrin on enzyme activity readily yields hydrogen cyanid (HCN) strongly toxic to animals.

Some phytochemicals are recognized as important in allelopathic potential of sorghum. Besides of phenolic acids and aldehydes that can be secreted by the root system, the most important in this respect seem to be hydrophobic sorgoleone {2-hydroxy-5-methoxy-*e*-[(8*Z*,11*Z*-8,11,14-pentadecatriene)]-*p*-benzoquinone} and its analogues (Soltys et al. 2010). There is no information available on its appearance in the sorghum straw. In this respect more research is needed. For using of sorghum by-products as a potential source of bioactive compounds there is a need to develop efficient green extraction methods. Conventional methods using refluxing, hotwater, maceration and soxhlet extraction are tedious, low efficient and not environmentally friendly (Azmir et al. 2013). More recently some other high efficient methods including ultrasonic, pulsed electric field, microwave, pressurized water and ultrasonic assisted extraction has been developed (Pasrija and Anandharamakrishnan 2015; Hou et al. 2016; Luo et al. 2018).

Giant knotweed (*Fallopia sachalinensis*, *Reynoutria sachalinensis*, *Polygonum sachalinense*)

Giant knotweed known as *Fallopia sachalinensis* (syn. *Reynoutria sachalinensis* or *Polygonum sachalinense*) is a perennial polyploid species, which was introduced into Europe in the 20th century, mainly as a garden ornamental (Košťálová et al. 2014); (Fig. 1). Biomass of this plant was investigated previously as feedstock for production of energy and activated carbons (Stražil and Kára 2010; Fałtynowicz et al. 2015). This plant produces many secondary metabolites (Table 2) that are medically valuable, such as and phenylpropanoid glycosides, stilbenes, anthraquinones, flavonols, flavonoids and flavanol gallate dimers (Kumagai et al. 2005; Kawai et al. 2006; Fan et al. 2009). Lachowicz et al. (2019) identified seventy-one potential health-promoting compounds in leaves and rhizomes of *Fallopia sachalinensis*, using the ultra-performance liquid chromatography photodiode detector-quadrupole/time-of-flight mass spectrometry (UPLC-PDA-Q/TOF-MS) method. Among them, there were 15 phenolic acids, 12 flavones and flavonols, 11 flavan-3-ols, 8 stilbenes, 9 carotenoids, 13 chlorophylls and 3 triterpenoids. Moreover, three anthraquinones (emodin, emodin-8-*O*- β -D-glucopyranoside and physcion-

Table 2 Phytochemicals identified in *Fallopia sachalinensis*

Part of plants	Metabolites	References
Roots	Procyanidins, flavanol gallate dimers (resveratrolside, piceid, emodin glucoside, piceatannol glucoside)	Fan et al. (2009)
Leaves	Phenolics	Hromádková et al. (2010)
	Seventy-one secondary metabolites: forty-six polyphenolic compounds (15 phenolic acids, 12 flavones and flavonols, 11 flavan-3-ols and 8 stilbenes); 9 carotenoids, 13 chlorophylls, 3 triterpenoids	Lachowicz et al. (2019)
	Phenylacetone nitrile	Noge and Tamogami (2013)
	Phenylacetone nitrile, terpenes: (E)- β -ocimene, linalool, (E)-4,8-dimethyl-1,3,7-nonatriene (DMNT), (E,E)- α -farnesene	Noge et al. (2011)
Flowers	Anthraquinones (emodin, emodin-8- <i>O</i> - β -D-glucopyranoside and physcion-8- <i>O</i> - β -D-glucopyranoside) and flavonoids (quercetin-3- <i>O</i> - α -L-arabinofuranoside, quercetin-3- <i>O</i> - β -D-galactopyranoside, quercetin-3- <i>O</i> - β -D-glucuronopyranoside)	Zhang et al. (2005)
	Campesterol, 1-decanol, β -amyrin, dammaran-3 β -ol, daucosterol, ergosterol peroxide, emodin 8- <i>O</i> - β -D-glucopyranoside, quercetin, isoquercitrin	
Stems	Flavanol gallate dimers (resveratrolside, piceid, emodin glucoside, piceatannol glucoside)	Fan et al. (2009)
	Campesterol, emodin-8- <i>O</i> - β -D-glucopyranoside, quercetin, and isoquercitrin	Eom et al. (2017)
Rhizomes	Emodin, physcion, glycosides of 9,10-anthraquinone derivatives	Inoue et al. (1992)
	Polydatin (piceid)	Li et al. (2013)
	Polyphenolic compounds (phenolic acids, flavones and flavonols, flavan-3-ols, stilbenes); carotenoids, chlorophylls, triterpenoids	Lachowicz et al. (2019)
	Anthraquinones (emodin and physcion), flavan-3-ols, phenylpropanoid esters, tatariside B, hydropiperoside, vanicoside A, B, C; 3,6- <i>O</i> -di- <i>p</i> -coumaroyl- β -fructofuranosyl-(2 $\rightarrow$ 1)-(2'- <i>O</i> -acetyl-6'- <i>O</i> -feruloyl)- β glucopyranoside, hydroxycinnamic sucrose esters	Nawrot-Hadzik et al. (2018)
Sprouts	Stilbenes (resveratrol, piceid) catechins (catechin, epicatechin)	Vrchotova et al. (2007)
Aerial parts	Emodin, physcion, glycosides of 9,10-anthraquinone derivatives	Inoue et al. (1992)
	Glycosylated derivatives of the flavonols kaempferol, quercetin, myricetin, and of the flavones apigenin and luteolin	Kim et al. (2000)
	Rutin, chrysophanol, 6-OH-emodin, emodin, hyperoside, isoquercetin, trifolin, austragalin, polygonimitin B, chrysophanol, emodin-8- <i>O</i> -glucoside, neomangiferin, mangiferin quercetin, kaempferol I3-II8-biapigenin, apigenin	Yu and Zhang (2011)

8-*O*- β -D-glucopyranoside) and three flavonoids (quercetin-3-*O*- α -L-arabinofuranoside, quercetin-3-*O*- β -D-galactopyranoside and quercetin-3-*O*- β -D-glucuronopyranoside) were identified in the flowers of *P. sachalinensis* (Zhang et al. 2005). The emodin, physcion, and glycosides of 9,10-anthraquinone derivatives have been detected also by Inoue et al. (1992), both in the rhizomes and in the aerial part of *Fallopia sachalinensis*. Due to the presence of natural

bioactive compounds, giant knotweed is traditionally used in Japan and China as herbal medicine (Konstantinidou-Doltsinis et al. 2006). Secondary metabolites from *Fallopia* spp. inhibit denitrification and exhibit antioxidant activity (Bardon et al. 2014). The major denitrification inhibitors are B-type procyanidins from the proanthocyanidin class of flavonoids (Bardon et al. 2016). Kim et al. (2000) isolated and identified twenty-one flavonoid compounds with

Table 3 Phytochemicals identified in *Fallopia japonica*

Part of plants	Metabolites	References
Roots	Resveratrol (trans-3,5,4'-trihydroxystilbene), hydroxyresveratrol, resveratrolside, piceid (polydatin), piceatannol, piceatannol glucoside, transresveratrol derivatives and <i>cis</i> -resveratrol derivatives	Vastano et al. (2000), Xiao et al. (2000) and Jayatilake et al. (1993)
	Phenol glycosides: quercetin and its glycosides, kaempferol-3- <i>O</i> - α -L-rhamnoside, (–)-epicatechin-5- <i>O</i> - β -D-glucopyranoside, quercetin, (+)-catechin, apigenin	Huang et al. (2008)
	2-methoxy-6-acetyl-7-methyljuglone, protocatechuic acid, 2,5-dimethyl-7-hydroxy chromone, torachryson-8- <i>O</i> - β -D-glucoside, 7-hydroxy-4-methoxy-5-methylcoumarine, 1-(3- <i>O</i> - β -D-glucopyranosyl-4,5-dihydroxyphenyl)-ethanone	Kimura et al. (1983)
	Chlorogenic acid, tachioside, isotachioside	Lin et al. (2010)
	Anthraquinones chrysophanol, physcion, emodin, emodin-8- <i>O</i> -D-glucoside; the phenolics physcion-8- <i>O</i> -D-glucoside, fallacinol, citerorosein, questin, questinol, protocatechuic acid, (+)-catechin Catechins: (–)-epicatechin-5- <i>O</i> - β -D-glucopyranoside, (+)-catechin and its glucoside	Bais et al. (2003)
Leaves	(–)-lyoniresinol-2a-sulfate, (+)-isolaricireinol-2a-sulfate, 1-(3',5'-dihydroxyphenyl)-2-(4''-hydroxyphenyl)-ethane-1,2-diol, gallic acid and derivative, tryptophan, 2,6-dihydroxybenzoic acid	Xiao et al. (2000) and Xiao et al. (2003)
	Resveratrol	Chen et al. (2013a, b)
	2-hexenal, n-hexanal, 3-hexen-1-ol, 1-penten-3-ol and 2-penten-1-ol	Kim et al. (2005)
	Seventy-one secondary metabolites: forty-six polyphenolic compounds (15 phenolic acids, 12 flavones and flavonols, 11 flavan-3-ols and 8 stilbenes); carotenoids (9), chlorophylls (13) and triterpenoids (3)	Lachowicz et al. (2019)
Stems	Resveratrol	Chen et al. (2013a, b)
Rhizomes	Emodin and its derivatives, anthraglycosides A and B, chrysophanol, physcion, fallacinol, citreorosein, rhein, questin and questinol	Yang et al. (2001) and Zhang et al. (2007)
	Polyphenolic compounds (phenolic acids, flavones and flavonols, flavan-3-ols, stilbenes); carotenoids, chlorophylls, triterpenoids	Lachowicz et al. (2019)
	Stilbenes (piceid and resveratrol), anthraquinones (emodin and physcion), flavan-3-ols, phenylpropanoid esters, tatariside B, hydropiperoside, vanicoside A, B, C; 3,6- <i>O</i> -di- <i>p</i> -coumaroyl- β -fructofuranosyl-(2 $\rightarrow$ 1)-(2'- <i>O</i> -acetyl-6'- <i>O</i> -feruloyl)- β glucopyranoside, hydroxycinnamic sucrose esters	Nawrot-Hadzik et al. (2018)
Seedling	Anthocyanin	Yamaguchi et al. (2000)

antioxidant properties from five *Fallopia* species. They were glycosylated derivatives of the flavonols: kaempferol, quercetin, myricetin and of the flavones: apigenin and luteolin.

Japanese knotweed (*Fallopia japonica*, *Reynoutria japonica*, *Polygonum cuspidatum*)

Japanese knotweed (*Fallopia japonica*, also known as *Polygonum cuspidatum*) is a rhizomatous, herbaceous perennial, which was introduced to the United States during the late eighteenth century as an ornamental

and as a source of fodder (Barney et al. 2006). Japanese knotweed has high productivity (Aguilera et al. 2010) and high concentrations of secondary metabolites, including stilbens, anthraquinones, tannins, lignans, anthocyanins, sterols and phenethyl alcohols (Table 3); (Fan et al. 2009; Miyagi et al. 2010). Resveratrol (stilben) and emodin (an anthraquinone) are listed as the major active ingredients of this plant (El-Readi et al. 2016). Resveratrol concentrations in Japanese knotweed range from 2.96 to 3.77 mg/g dry weight (Vastano et al. 2000). It has been proven that roots contain its much higher amount than

the stem and leaf (Chen et al. 2013a, b). Weston et al. (2005) stated that the amount of stilbenes, including resveratrol, within the roots of *P. cuspidatum* was even higher than concentrations reported in red grapes and wine. Moreover, the roots of *F. japonica* has been reported to contain a large number of stilbens, showing high antioxidant and health promoting activities, frequently found as glycosides and sulfates (Vastano et al. 2000; Xiao et al. 2000). Additionally, phenol glycosides, kaempferol-3-*O*- α -L-rhamnoside, (–)-epicatechin-5-*O*- β -D-glucopyranoside as well as quercetin, (+)-catechin, apigenin and their derivatives were found in the roots (Kimura et al. 1983; Huang et al. 2008). Anthraquinones, including emodin and its derivatives, anthraglycosides A and B, chrysophanol, physcion, fallacinol, citreorosein, rhein, quuestin and quuestinol, are important chemical constituents also in the rhizomes and aerial part of plant (Yang et al. 2001; Kim et al. 2005; Zhang et al. 2007). A total of 18 volatile compounds were identified in the extract of *F. japonica* leaves. The major phytochemicals were n-hexanal, 2-hexenal, 3-hexen-1-ol, 1-penten-3-ol and 2-penten-1-ol (Kim et al. 2005). Lachowicz et al. (2019) described in *F. japonica* leaves forty-six polyphenolic compounds and 25 new compounds belonging to carotenoids, chlorophylls and triterpenoids using UPLC-PDA-Q/TOF–MS method.

Fallopia japonica has been used in Chinese medicine, where emodin is regarded as a quality-control index. Pharmacological studies have evaluated several aspects of *Fallopia japonica* extract including antioxidant (Pan et al. 2007), antiviral (Lin et al. 2010), anti-inflammatory (Bralley et al. 2008) and anticancer activities (Feng et al. 2006). Japanese knotweed extract has ability to inhibit NF- κ B and neutrophil infiltration animal models of edema (Bralley et al. 2008). Its anticancer activity has different molecular modes of action and mechanisms through their ability to modulate the proliferation, apoptosis,

growth factors, cell cycle, NF-kappa B (NF- κ B), protein kinase C (PKC), and mitogen-activated protein kinase (MAPK) signaling cascades (Aggarwal and Shishodia 2006). Kimura and Okuda (2001) showed that the phytoalexine resveratrol isolated from *P. cuspidatum* roots, has received considerable attention for its anti-cancer properties. Kimura et al. (1995) demonstrated that liver peroxidation in rats was found to be mitigated by several components of *P. cuspidatum* root extracts; namely the stilbenes piceid, resveratrol and 2,3,5,4'-tetrahydroxy stilbene-2-*O*-D-glucoside. Song et al. (2006) stated that crude methanolic extract from roots of *P. cuspidatum*, containing alkaloids, sterol/terpenes, tannins, flavonoids, and carbohydrates, inhibited the bacterial viability and may be useful for the control of dental plaque and subsequent dental caries formation.

Jerusalem artichoke (*Helianthus tuberosus* L.)

Helianthus tuberosus L. (known as Jerusalem artichoke), which belong to the *Asteraceae* family, is a native plant of North America. It has recently been recognized as a promising biomass for bioeconomy development, with a number of advantages over conventional crops (Yang et al. 2015); (Fig. 2). Jerusalem artichoke is valuable crop for its applications as functional food and bioactive ingredient sources (Yang et al. 2015). Besides, its yield potential and low requirements meant that it could be of interest in the energy sector (Kowalczyk-Juśko et al. 2012). Recently, rapidly growing interest is for the use of Jerusalem artichoke tubers, which are rich in inulin, as raw materials for bioethanol production (Celp et al. 2012; Song et al. 2017). Jerusalem artichoke also has potential for generating a variety chemicals, such as citric acid, 2,3-butanediol (Liu et al. 2010), butyric acid (Huang et al. 2011) and sorbitol (Wei et al. 2001).

Fig. 2 *Helianthus tuberosus*, *Miscanthus* $\times$ *giganteus*, *Phalaris arundinacea* L

A number of bioactive compounds of medicinal significance have been isolated from the aerial parts of Jerusalem artichoke, indicating anticancer, antidiabetic, antioxidant, antifungal and antimicrobial activities and other medicinal effects (Ahmed et al. 2005; Baba et al. 2005; Liu et al. 2007; Han et al. 2010; Yuan et al. 2012; Al-Snafi 2018). Two flavone glucosides, kaempferol 3-*O*-glucoside and quercetin 7-*O*-glucoside were isolated from the leaves of *Helianthus tuberosus* by Chae et al. (2002). The results obtained by Chen et al. (2013a, b) imply that Jerusalem artichoke leaves might be a potential source of natural fungicides. The extracts of antifungal compounds and phenolic acids were investigated for their potential use in enhancing preservation of fruits and vegetables during storage. Crude leaf extract or *n*-butanol fraction was active against *Botrytis cinerea*, *Colletotrichum gloeosporioides*, *Phytophthora capsici* and *Rhizoctonia cerealis* (Chen et al. 2013a, b). Six phenolic acids were separated using in vitro activity-guided fractionation. Among them, caffeic acid, 3,4-dicaffeoylquinic acid and 1,5-dicaffeoylquinic acid played a dominant role and were active in bioassays against *Gibberellazeae*. The main constituents are chlorogenic and isochlorogenic acids, which have good antioxidant properties. The total phenolic content and radical scavenging activities of *Jerusalem artichoke* leaves were investigated by Yuan et al. (2012). The authors showed that the leaves of Jerusalem artichoke might be a potential source of natural antioxidants.

Another group of secondary metabolites identified in the leaves were sesquiterpene lactones. The ultra-high performance liquid chromatography coupled with the quadrupole time-of-flight mass spectrometry (UHPLC–Q-TOF–MS method) was used for the simultaneous quantification of eleven sesquiterpene lactones in eleven Jerusalem artichoke leaf samples (Yuan and Yang 2017). The results of the study showed that the contents of lactones in the leaves varied significantly in the Jerusalem artichoke from different areas. Bioassay-directed phytochemical study led to the isolation of a number of sesquiterpene lactone of 3-hydroxy-8 β -tigloyloxy-1,10-dehydroariglovin, and ten known sesquiterpene lactones (Yuan et al. 2013).

Abou Baker et al. (2010) proved that the sesquiterpene lactones exhibited cytotoxicity against 1031 leukemia and HCT 116 cancer cell lines, while

heliangine showed moderate activity against Hep G2 and breast cancer MCF7 cell lines.

Significant amount of phytochemicals was contained also in tubers of Jerusalem artichoke. The ethanol extracts showed antidiabetic effect in streptozotocin induced diabetic rats and it also possessed an inhibitory effect on kidney tissue TBARS levels (Aslan et al. 2010). The hydrodistilled essential oils from fresh tubers of Jerusalem artichoke, characterization by GC-FID, GC/MS, and ¹³C-NMR analyses allowed the identification of 195 compounds in total, mainly β -bisabolene, helianthol A, desmethoxyencecalin, desmethylencecalin, euparin, and dihydroeuparin (Radulovic and Dordevic 2014). Other compounds identified by GC–MS, TLC and HPLC methods, in the tubers of *H. tuberosus* were the coumarins, ayapin and scopoletin (Cabello-Hurtado et al. 1998). Ayapin (6,7-methylenedioxy-coumarin) and scopoletin (6-methoxy-7-hydroxy-coumarin) are phenolic compounds belonging to the family of the simple 7-hydroxylated coumarins. Both compounds were accumulated in response to the treatment with chemical elicitors, for example CuCl₂ or sucrose. Phenolics (such as ferulic acids) from the tubers of *H. tuberosus* were separated and identified by Tchone et al. (2006). Using the ultraperformance liquid chromatography–mass spectrometry with an electrospray ionization, Kapusta et al. (2013) characterized phenolic compounds in *H. tuberosus* tubers of two Polish cultivars, Rubik and Albik. Seven compounds, including the naturally occurring isomers of caffeoylquinic acid namely neo-chlorogenic acid, chlorogenic acid and crypto-chlorogenic acid, four isomeric di-caffeoylquinic acids (3,4-*O*-dicaffeoyl; 3,5-*O*-dicaffeoyl; 1,3-*O*-dicaffeoyl and 4,5-*O*-dicaffeoyl esters), were detected. Yuan et al. (2012) investigated total concentration of phenolic acids in the tubers of two Jerusalem artichoke cultivars. The predominant compound in all the samples was 3,4-*O*-dicaffeoylquinic acid. This compound constituted 38 and 35% of total phenolic content in Rubik and Albik varieties, respectively. Among the caffeoylquinic acids, the 3-caffeoylquinic acid showed the highest concentration in both cultivars, accounting for 28% (Rubik) and 25% (Albik) of the total phenolic content. Phytochemicals identified in Jerusalem artichoke are shown in Table 4.

Table 4 Phytochemicals identified in *Helianthus tuberosus* L

Part of plants	Metabolite	References
Tubers	Coumarin: ayapin (6,7-methylenedioxy-coumarin), scopoletin (6-methoxy-7-hydroxy-coumarin)	Cabello-Hurtado et al. (1998)
	Ferulic acids	Tchone et al. (2006)
Tubers	Isomers of caffeoylquinic acid (neo-chlorogenic acid, chlorogenic acid, crypto-chlorogenic acid), isomeric di-caffeoylquinic acids (3,4- <i>O</i> -dicaffeoyl; 3,5- <i>O</i> -dicaffeoyl; 1,3- <i>O</i> -dicaffeoyl; 4,5- <i>O</i> -dicaffeoyl esters)	Kapusta et al. (2013)
	Cyclopentanol, hexadecanoic acid, 9-octadecenoic acid, 9-octadecenoic acid, 9-octadecenoic acid, octadecenoic acid, 13-octadecenal and 9-octadecenoic acid, uteronoenen-1-ol-3; 2-propen-1-ol; 3-deoxy-d-manneolactone; heyadecanic acid; 1-pyrrolin,3-ethyl; 9-octadecenoic acid; octadecenoic acid; 13-octa decenal; 1,2-epoxy-1-vinylcyclo coene and cyclopentadecanon c, 2-hydroxy, 2-furan carboxaldehyde; 2-furan carboxaldehyde; dodecanol,1,1-oxybis; glycine,n-methyl-n-1-oxadodecyl; hexa-decaneic acid; 9-octadecenoic acid; oleic acid; 9-octadecenal; 9-octadecenal and phthalic acid disooctyl ester	Yaeghoobi-Khanghahi et al. (2014)
Leaves	Flavone glucosides (kaempferol 3- <i>O</i> -glucoside and quercetin 7- <i>O</i> -glucoside)	Chae et al. (2002)
	Chlorogenic acids (feruloylquinic acid, caffeoylquinic acids, dicaffeoylquinic acids)	Yuan et al. (2008)
	Phenolic compounds (caffeic acid, 3- <i>O</i> -caffeoylquinic acid, 3,5-dicaffeoylquinic acid, 1,5-dicaffeoylquinic acid, 4,5-dicaffeoylquinic acid, 3,5-dicaffeoylquinic acid methyl ether)	Yuan et al. (2012)
	Chlorogenic acids (two isomers of caffeoylquinic acid, 3- <i>O</i> -caffeoylquinic acid, caffeic acid, <i>p</i> -coumaroyl-quinic acid, 3,4-dicaffeoylquinic acid, feruloylquinic acid, 3,5-dicaffeoylquinic acid, 1,5-dicaffeoylquinic acid and 4,5-dicaffeoylquinic acid) and other phenolics (isorhamnetin glucoside, caffeoyl glucopyranose, kaempferol glucuronide, kaempferol-3- <i>O</i> -glucoside)	Chen et al. (2014)
	Sesquiterpene lactones (3-hydroxy-8 β -tigloyloxy-1,10-dehydroariglovin; 4,15-iso-atrapiolicolide methylacrylate; 4,15-iso-atrapiolicolide tiglate; 4,15-iso-atrapiolicolide isobutyrate; 4,15-iso-atrapiolicolide angelate, budlein A methylacrylate; budlein A tiglate, desacetylovatifolin, 1a-hydroxypinnatifidin, 1a-acetoxypinnatifidin; melampolide) and flavones (pedunculin; 5,8-diOH-6,7diMeO-2-(3,4-diMeOPh)-4-benzopyrone)	Yuan et al. (2013) and Yuan and Yang (2017)
Callus	Lectins	Nakagawa et al. (1996)
Flowers	Terpenoids:monoterpenoid (loliolide acetate), kauranediterpenoids(ent-kaur-16-en-19-oic acid,15-hydroxykaur-16-en-19-oic acid, 17-hydroxykaur-15-en-19-oic acid, 15 α -tiglinoyloxykaur-16-en-19-oic acid)and triterpenoids (faradiol 3- <i>O</i> -fatty acid ester derivative); coumarins (8-methoxyobliquin, 7- <i>O</i> -prenylscopoletin);flavonoids (isoliquiritigenin 2,4,2',4'-tetrahydroxychalcone, liquiritigenin, acerosin, quercetin 7- <i>O</i> - β -glucoside, sulfuretin, sulfurein glycoside) andchromone derivative (7-hydroxychromone)	Jantaharn et al. (2018)
Whole plants	Ent-17-oxokaur-15(16)-en-19-oic acid; ent-17-hydroxykaur-15(16)-en-19-oic acid; ent-15bhydroxykaur-16(17)-en-19-oic acid methyl ester; ent-15-nor-14-oxolabda-8(17); 12E-dien-18-oic acid; 4,15-isoatrapiolicolide angelate; 4,15-isoatrapiolicolide methylacrylate; (+)-pinioresinol; (-)-loliolide; vanillin	Pan et al. (2009)

Giant Miscanthus (*Miscanthus giganteus*)

Giant Miscanthus (*Miscanthus* $\times$ *giganteus*) is a perennial, warm-season C4 grass (Fig. 2). Giant Miscanthus (*Miscanthus* $\times$ *giganteus*) is a perennial, warm-season C4 grass. This is a naturally occurring hybrid between diploid *Miscanthussinensis* and tetraploid *M. sacchariflorus* (Brosse et al. 2012). A characteristic feature of these plants is the very

efficient photosynthesis process, which ensures a large increase in biomass from the assimilation surface. Miscanthus is a major bioenergy crop in Europe and a potential feedstock for second generation biofuels (Zhu et al. 2015). Its use for energy production has the potential to provide significant fossil energy substitution (Heaton et al. 2008) and greenhouse gas mitigation (Clifton-Brown et al. 2007). The Miscanthus biomass can be used as a replacement for lignite, a raw

material for the production of fuel gas and ethanol. The energy value of *Miscanthus* is comparable to the value of hardwoods (approx. 19 MJ/kg); (Sacała 2011). The studies of Parveen et al. (2011) have been the first report of the hydroxycinnamic acid profile of leaves and stems of *M. giganteus*, wherein more than twenty hydroxycinnamates were identified by UV and LC–ESI-MSⁿ (Table 5). Comparative LC–MS studies on the leaf extract showed the presence of isomers of *O*-caffeoylquinic acid (3-CQA, 4-CQA and 5-CQA), *O*-feruloylquinic acid (3-FQA, 4-FQA and 5-FQA) and *para*-coumaroylquinic acid (3-*p*CoQA and 5-*p*CoQA). The presence of certain classes of hydroxycinnamic esters in *M. giganteus* tissues is very important, in the case of potential application of this plant as a feedstock for platform chemicals and biological conversion to biofuels.

The hexaploid *Miscanthus* × *giganteus* can be induced from triploid *M* × *giganteus*. Induced polyploidy can influence the concentration of secondary metabolites (Kato and Birchler 2006; Omidbaigi et al. 2010). The pyrogallol, catechin, veratric acid, *o*-coumaric acid and myricetin were present at higher concentrations in leaf extracts of hexaploid compared

to triploid plants (Ghimire et al. 2016). On the contrary, ferulic acid, gentisic acid, veratric acid, rutin, hesperidin, and myricetin were present in significantly higher levels in triploid plants. Villaverde et al. (2009) studied the chemical composition of *Miscanthus* × *giganteus* extractives using gas chromatography–mass spectrometry (GC–MS). The lipophilic extracts of bark and core of the *Miscanthus* × *giganteus* stalk contained sterols and fatty acids. The concentration of aromatic compounds was 521 mg/kg of bark, with vanillin, vanillic acid and *p*-hydroxybenzaldehyde as the major constituents. Sterols constituted about 949 mg/kg of dry core with stigmasterol, campesterol, β -sitosterol and 7-*oxo*- β -sitosterol, as the major compounds. The high concentration of valuable compounds in core and bark of *M.* × *giganteus*, which constitute waste in most applications, give an opportunity for the integrated upgrading of this grass within the bio-refinery perspective. The analysis of secondary plant metabolites in *Miscanthus* × *giganteus* root exudates showed the presence of various polyphenolics, some of which may take part in biostimulation processes (Techer et al. 2011). It was confirmed also by the study of Techer

Table 5 Phytochemicals identified in *Miscanthus giganteus*

Part of plants	Metabolite	References
Leaves	Hydroxycinnamic acid (isomers of: <i>O</i> -caffeoylquinic acid (3- <i>O</i> -caffeoylquinic acid, 4- <i>O</i> -caffeoylquinic acid, 5- <i>O</i> -caffeoylquinic acid), <i>O</i> -feruloylquinic acid (3- <i>O</i> -feruloylquinic acid, 4- <i>O</i> -feruloylquinic acid and 5- <i>O</i> -feruloylquinic acid) and <i>para</i> -coumaroylquinic acid (3- <i>para</i> -coumaroylquinic acid and 5- <i>para</i> -coumaroylquinic acid)	Parveen et al. (2011)
	Chlorogenic, ferulic, veratric, <i>o</i> -coumaric, gentisic acids, pyrogallol, catechin, myricetin, rutin, hesperidin	Ghimire et al. (2016)
Stems	Hydroxycinnamic acid (isomers of: <i>O</i> -caffeoylquinic acid (3- <i>O</i> -caffeoylquinic acid, 4- <i>O</i> -caffeoylquinic acid, 5- <i>O</i> -caffeoylquinic acid), <i>O</i> -feruloylquinic acid (3- <i>O</i> -feruloylquinic acid, 4- <i>O</i> -feruloylquinic acid and 5- <i>O</i> -feruloylquinic acid) and 5- <i>para</i> -coumaroylquinic acid)	Parveen et al. (2011)
	Chlorogenic and gentisic acid, pyrogallol, catechin	Ghimire et al. (2016)
Roots	Quercetin, rutin, isovitexin, catechin, apigenin, caffeic, chlorogenic, <i>p</i> -coumaric, cinnamic and gallic acid	Techer et al. (2011), Techer et al. (2012)
Barks	Vanillin, vanillic acid, <i>p</i> -hydroxybenzaldehyde, sterols (stigmasterol, campesterol, β -sitosterol, 7- <i>oxo</i> - β -sitosterol)	Villaverde et al. (2009) and Villaverde et al. (2010)
Bio-oils	Phenol (2-methoxy-4-methylphenol, 1,2-benzenediol, 3-methoxy-1,2-benzenediol, 4-ethyl-2-methoxy-phenol, 2-methoxy-4-vinylphenol, 2,6-dimethoxy-phenol, 2-methoxy-6-(2-propenyl)-phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy-phenol, 2,6-dimethoxy-4-(2-propenyl)-phenol) and phenols (4-ethylphenol, 2/3-methylphenol, 4-methylphenol, 2-methoxy-phenol)	Greenhalf et al. (2013)

et al. (2012). Secondary root metabolites could be involved in the biostimulation of PAH-utilizing soil bacteria. It was shown that the addition of root exudate promoted bacterial growth and the catabolic activity of polycyclic molecules.

Reed canary grass (*Phalaris arundinacea* L.)

Reed canary grass (RCG) is perennial grass, belonging to the *Poaceae* family (Fig. 2). Thanks to the high yield per hectare, it may be cultivated as energy crops for combustion or biogas and bioethanol production (Oleszek et al. 2014). Phytochemicals of RCG are mainly alkaloids, either nitrogen-based or steroidal in nature (Lyman et al. 2012). Two major classes of alkaloids include gramine [1-(1H-indol-3-yl)-*N,N*-dimethylmethanamine] and tryptamine derivatives (Marten et al. 1973, 1981). Plant genotypes of *P. arundinacea* can be classified into three phenotypic groups based on the type of alkaloids present. The MeO phenotype contains the methoxy derivatives of the tryptamines (5-methoxy-*N*-methyltryptamine, 5-methoxy-*N,N*-dimethyltryptamine) and β -carbolines (2-methyl-6-methoxy-1,2,3,4-tetrahydro β -carboline). The T phenotype contains the non-methoxy derivatives of the tryptamines (*N*-methyltryptamine; *N,N*-dimethyltryptamine) and β -carbolines (2-methyl-1,2,~4~tetrahydro- β -carboline). The third phenotype, G, contains gramine and is recessive to the other two phenotypes. Most of the recently developed cultivars of RCG are of the G phenotype, and also contain hordenine. Hordenine is the only alkaloid detected in RCG, which is not an indole in the

structure. Determination of hordenine and gramine in *P. arundinacea* material was reported by e.g. Coulman et al. (1977), Woods et al. (1979), Majak et al. (1979) and Duynisveld et al. (1990) (Table 6). Grzelak et al. (2018) identified six alkaloids, i.e. tryptophol and gramine (indole alkaloids), as well as lupanine and 13-OH lupanine and lupanine esters—13 α -isovalericlupanine and 13 α -tigloyloxylupanine (quinolysidine alkaloids). The authors stated that the concentrations of the compounds depended on the stage of plants maturity, while dominant alkaloids in the growth stage were gramine and lupanine. Alkaloids in RCG are confined largely in the leaf blades, than in the culm, therefore, it decreased in whole plant with a maturity, due to increasing culm/foilage ratio (Otani et al. 1997; Gołębiewska et al. 2017). Their concentration is enhanced by moisture stress, light intensity and high rates of N fertilizer, especially in the NH₄-N form (Frelich and Marten 1972; Grzelak et al. 2018). Cutting of RCG every second week produced a sharp increase in indole alkaloid levels, as compared with levels in free growth tissue (Woods and Clark 1971). Alkaloid concentration is greatly reduced in dried grass (Donker et al. 1976) and in silage (Hovin et al. 1980). Alkaloids are secondary metabolites with diverse biological activities (Steppuhn et al. 2004). Their bioactive properties make alkaloids important players in plant defense responses against insects, microbes, and other herbivores (Grzelak et al. 2018). Alkaloids in *P. arundinacea* negatively influence on grass palatability and sometimes have undesirable effects on ruminant animals (Hovin and Marten 1975; Popp et al. 2016). Thus, the differences in palatability

Table 6 Phytochemicals identified in *Phalaris arundinacea* L

Part of plant	Metabolite	References
Aerial part	Hordenine, gramine	Coulman et al. (1977), Woods et al. (1979), Majak et al. (1979) and Duynisveld et al. (1990)
	Tryptophol, gramine, lupanine and 13-OH lupanine, lupanine esters—13 α -isovalericlupanine, 13 α -tigloyloxylupanine	Grzelak et al. (2018)
	Gramine, ergovaline, condensed tannins, saponins	Lyman et al. (2012)
	Gramine, 5-methoxy- <i>N</i> -methyltryptamine, 5-methoxy- <i>N,N</i> -dimethyltryptamine) and β -carbolines (2-methyl-6-methoxy-1,2,3,4-tetrahydro β -carboline, <i>N</i> -methyltryptamine; <i>N,N</i> -dimethyltryptamine, 2-methyl-1,2,~4~tetrahydro- β -carboline	Marten et al. (1973) and Marten et al. (1981)

Fig. 3 *Panicum virgatum* and *Sylphium perfoliatum*

and alkaloid concentration between *P. arundinaceae* genotypes have a substantial biological significance for grazing steers and lambs (Marten et al. 1976). Alkaloids of RCG are known to have wide biocidal activity. Lovett et al. (1994) stated that hordenine inhibits seedling growth of white mustard, *Sinapis alba*, *Mythimna convecta* and *Dreschlera teres*. Golebiowska et al. (2017) investigated the influence of aqueous extract of reed canary grass leaves and runners on the growth of selected weed such as *Geranium pusillum* L., *Amaranthus retroflexus* L., *Papaver rhoeas* L., *Viola arvensis* Murray and *Stellaria media* (L.) Vill. The authors proved that inhibition depended on the collection period and habitat of the plants. The strongest effect was observed for the extract from the biomass collected in autumn before the winter dormancy. Gramine, an indolic alkaloid, apart from being phytotoxic, it was proven to have antibacterial properties against *Pseudomonas* (Sepulveda and Corcuera 1990). Furthermore, gramine inhibits the growth of *Drechslera teres*, armyworm, *Mythimna convecta* and disrupts the respiratory chain at complex I in rat liver mitochondria and in bovine heart submitochondrial particles (Andreo et al. 1984). Moreover, this compound behaved as a typical uncoupler of photosynthetic phosphorylation in spinach thylakoids. Recent study on the action of gramine from reed canary grass showed its negative influence on the methane fermentation process (Popp et al. 2016). It was stated, that its presence in biomass of reed canary grass caused increase in methane yield. Simultaneously, it has been proven that microorganisms were able to adaptate to such unfavorable conditions and to become resistant to this substance.

Switchgrass (*Panicum virgatum* L.)

Panicum virgatum L. (switchgrass) is a dominant, native, perennial species found in the tall grass prairie,

which can be efficient and environmentally friendly energy crop (Shui et al. 2010); (Fig. 3). Switchgrass could be used as livestock feed, if it was not for the presence of steroidal saponins that has been reported as the reason for hepatogenous photosensitization in sheep, lambs and horses. Saponins, with diosgenin as the main aglycon moiety, were identified in leaves and stems, wherein the leaves have higher concentration than the stems (Lee et al. 2001). Lee et al. (2009) identified three major saponins (saponin A-C) from four switchgrass cultivars (Table 7). Saponin A was dichotomin [(25R)-furost-5-ene-3 β ,22 α ,26-triol 3-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)]- β -D-glucopyranosyl 26-O- β -D-glucopyranoside], saponin B was (25R)-furost-5-ene-3 β ,22 α ,26-triol 3-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-glucopyranosyl 26-O- β -D-glucopyranoside and saponin C was protodioscin (25R)-furost-5-ene-3 β ,22 α ,26-triol 3-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)]- β -D-glucopyranosyl 26-O- β -D-glucopyranoside. The concentration of individual and total saponins differed among cultivars and parts of plant.

Sarath et al. (2007) studied the internode structure and cell wall composition in maturing tillers of switchgrass and showed the presence of soluble phenolics. The concentration and complexity of soluble phenolics analyzed by HPLC decreased with increasing distance of the internodes from the top of the plant. Soluble phenolics concentration and complexity was highest in top internodes. The lower internodes contained higher content of wall-bound phenolic acids, principally as 4-coumarate and ferulate. The results of analyses showed that the soluble fractions obtained from top internodes contained substantial amounts of caffeic, 4-coumaric and ferulic acids, and relatively lower amounts of protocatechuic, syringic, sinapic and vanillic acids. Low temperature alkaline hydrolysis of internode samples predominantly

Table 7 Phytochemicals identified in *Panicum virgatum* L

Part of plants	Metabolites	References
Aerial parts	Saponins (diosgenin and yamogenin)	Lee et al. (2001)
	Monoterpenes	Eller et al. (2011)
	Rutin, quercitrin	Nirmal et al. (2009)
Leaves	Saponin A = dichotomin [(25R)-furost-5-ene-3 β ,22 α ,26-triol 3-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)]- β -D-glucopyranosyl 26-O- β -D-glucopyranoside], saponin B (25R)-furost-5-ene-3 β ,22 α ,26-triol 3-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-glucopyranosyl 26-O- β -D-glucopyranoside, saponin C = protodioscin (25R)-furost-5-ene-3 β ,22 α ,26-triol 3-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)]- β -D-glucopyranosyl 26-O- β -D-glucopyranoside	Lee et al. (2009)
	Trigonelline (alkaloid)	Schwartz et al. (2014)
	Flavonoid quercetin	Martin et al. (2011)
Shoots	Alkaloids, phenols, organic acids	Shui et al. (2010)
Stems	Saponin A, B and C	Lee et al. (2009)
	Flavonoid quercetin	Martin et al. (2011)
	Sterols (cholesterol, campesterol, ergosta-5,7,2, 2-trien-3-ol, stigmasterol, β -sitosterol)	Yan et al. (2010)
Cell wall	Soluble phenolics (caffeic, 4-coumaric, ferulic acids, protocatechuic, syringic, sinapic and vanillic acids, ricin)	Sarath et al. (2007)

released caffeic, 4-coumaric and ferulic acid. Schwartz et al. (2014) reported the biosynthesis and accumulation of alkaloids trigonelline in leaves of *P. virgatum* caused by water-deficit stress. Nonetheless, plant response varied for different cultivars. Trigonelline concentration ranged from 0.5 to 31.8 mg/g of fresh weight depending of the cultivar.

Cup plant (*Silphium perfoliatum*)

Cup plant (*Silphium perfoliatum* L.) is a tall, perennial plant from *Asteraceae* family, native to North America (El-Sayed et al. 2002); (Fig. 3). It is regarded as suitable feedstock for bioenergy production, due to its low maintenance requirements, high biomass yield and efficient methane production in anaerobic digestion process (Gansberger et al. 2015). Nonetheless, many studies were performed on the bioactive compounds included in *S. perfoliatum*, and showed that this plant is rich in phenolic acids, flavonoids, terpenes, saponins, as well as essential oils (El-Sayed

et al. 2002; Kowalski and Wolski 2003, 2005; Kowalski 2005; Kowalski and Kędzia 2007). Kowalski (2005) stated that lipophilic extracts of leaves and inflorescence is similar in composition, while the composition of rhizome extract significantly differed from them. Kowalski and Wolski (2005) studied the content and chemical composition of essential oil of leaves, inflorescences and rhizomes of *S. perfoliatum* L. The highest content of oil was contained in rhizomes (0.41% v/w), with the tricyclic sesquiterpenes 7- β -H-silphiperfol-5-ene, isocomene, modhephene and 7- α -H-silphiperfol-5-ene as dominating compounds, which were not detected in leaves and inflorescences. These authors, in their other work on bioactive compounds in *S. perfoliatum* L. identified seven phenolic acids and found that caffeic acid was the most predominant compound in this plant (from 67.8% of total in the leaves to 94.4% in the rhizomes) (Kowalski and Wolski 2003). El-Sayed et al. (2002) isolated two new kaempferol derivatives and other nine known flavonoids from the leaves of *S.*

Table 8 Phytochemicals identified in *Silphium perfoliatum*

Part of plants	Metabolite	References
Leaves	α -amyrine, β -amyrine, heptacosane, sigma sterol, γ -sitosterol	Kowalski (2005)
	β -caryophyllene, caryophyllene oxide, germacrene D, α -pinene	
	Kaempferol 3-O- β -D-apiofuranoside 7-O- α -L-rhamnosyl-(1'''' $\rightarrow$ 6''')-O- β -D-galactopyranoside, kaempferol 3-O- β -D-apiofuranoside 7-O- α -L-rhamnosyl-(1'''' $\rightarrow$ 6''')-O- β -D-(2'''-O-E-caffeoyl)galactopyranoside)	El-Sayed et al. (2002)
	Tricyclene, α -pinene, camphene, sabinene, β -pinene, limonene, α -pinene oxide, a-campholenal, <i>trans</i> -pinocarveol, <i>trans</i> -verbenol, pinocavone, myrtenal, myrtenol, verbenone,	Kowalski and Kędzia (2007)
	α -copaene, β -bourbonene, α -isocomene, β -caryophyllene, β -Copaene, <i>trans</i> - α -bergamotene, α -humulene, germacrene D, cubebol, spathulenol, caryophyllene oxide, humulene epoxide II, β -oplophenone, epoxy allo-alloaromadendrene, khusinol, 6,10,14-trimethyl-2-pentadecanone, hexadecanoic acid, cis-phytol, (Z,Z,Z)-9,12,15-octadecatrienoic acid methyl ester, pentacosane, docosanoic acid methyl ester, heptacosane, tetracosanic acid methyl ester, octacosane, squalene, nonacosane, hexacosanoic acid methyl ester, hentriacontane, octadecanoic acid methyl ester, vitamin E, stigmaterol, γ -sitosterol, β -amyrine, α -amyrine	
	Caffeic acid, <i>p</i> -coumaric acid, proto-catechuic acid, vanilic acid, chlorogenic acid	Kowalski and Wolski (2003)
Inflorescences	α -amyrine, β -amyrine, heptacosane, sigma sterol, γ -sitosterol, β -caryophyllene, caryophyllene oxide, germacrene D, α -pinene	Kowalski (2005)
	Tricyclene, α -pinene, camphene, sabinene, β -pinene, limonene, α -pinene oxide, α -campholenal, <i>trans</i> -pinocarveol, <i>trans</i> -verbenol, pinocavone, myrtenal, myrtenol, verbenone,	Kowalski and Kędzia (2007)
	α -copaene, β -bourbonene, β -caryophyllene, <i>trans</i> - α -bergamotene, α -humulene, Germacrene D, γ -cadinene, cubebol, myristicin, (E)-nerolidol, spathulenol, caryophyllene oxide, humulene epoxide II, β -oplophenone, epoxy allo-alloaromadendrene, khusinol, oplopanone, 6,10,14-trimethyl-2-pentadecanone, hexadecanoic acid, cis-phytol, (Z,Z,Z)-9,12,15-Octadecatrienoic acid methyl ester, pentacosane, docosanoic acid methyl ester, heptacosane, tetracosanic acid methyl ester, octacosane, squalene, nonacosane, hexacosanoic acid methyl ester, hentriacontane, octadecanoic acid methyl ester, vitamin E, stigmaterol, γ -sitosterol, β -amyrine, α -amyrine	
	Caffeic acid, ferulic acid, <i>p</i> -coumaric acid, proto-catechuic, <i>p</i> -hydroxybenzoic acid, vanilic acid	Kowalski and Wolski (2003)
Rhizomes	16-acetocarcterochaetol, 7- β -H-silphiperfol-5-ene, 7- α -H-silphiperfol-5-ene, δ -elemene, isocomene, germacrene D, modhephene	Kowalski (2005)
	7- α -H-silphiperfol-5-ene, δ -elemene, 7- β -H-silphiperfol-5-ene, α -longipinene, silphiperfol-5,7(14)-diene, silphiperfol-6-ene, modhephene, β -elemene, β -isocomene, α -humulene, Germacrene D, β -bisabolene, cubebol, myristicin, spathulenol, caryophyllene oxide, presilphiperfolan-8-ol, humulene epoxide II, β -oplophenone, oplopanone, ambroxide, 16-acetoxycarterochaetol, stigmaterol, γ -sitosterol, β -amyrine, α -amyrine	Kowalski and Kędzia (2007)
	Caffeic acid, ferulic acid, <i>p</i> -coumaric acid, proto-catechuic, <i>p</i> -hydroxybenzoic acid	Kowalski and Wolski (2003)

perfoliatum L. The phytochemicals identified in cup plant was listed in Table 8.

Kowalski and Kędzia (2007) mentioned that the root of *S. perfoliatum* exhibit antiemetic, antirheumatic, analgesic, tonic and diaphoretic activities.

Moreover, it was helpful in liver diseases, spleen maladies, internal bruises, ulcers, as well as fever and debility. Syrov et al. (1992) studied anticholesterololemic effect of saponins isolated from *S. perfoliatum* leaves and found that concentration of cholesterol

Fig. 4 *Robinia pseudoacacia* and *Salix* sp

in rat blood decreased by 12% and 19% depending on a dose and time.

Phytochemicals of cup plant exhibited also antimicrobial activity. Kowalski and Kędzia (2007) demonstrated significant antibacterial activity of hexane and methanol extract from leaves, inflorescences and rhizomes of cup plant toward *Staphylococcus aureus* FDA 209P strains. The highest activity was exhibited by alcoholic extracts from *S. perfoliatum* rhizomes compared to extracts from leaves and inflorescences. Davidjanc et al. (1997) found that saponins isolated from cup plant leaves inhibited the development of phytopathogenic fungi such as *Drechslera graminea* Rabh, *Rhizopus nodosus* Namysl, and *Rhizopus nigricans* Ehr. Antifungal activity was confirmed also by Zabka et al. (2011), who tested the influence of crude extract of *S. perfoliatum* leaves on the mycelial growth of *Fusarium oxysporum*, *Fusarium verticillioides*,

Penicillium expansum, *Penicillium brevicompactum*, *Aspergillus flavus* and *Aspergillus fumigatus*.

Woody energy crops

Willow (*Salix viminalis* L.)

Willow (*Salix viminalis*) is of great interest in European countries as energy crop (Fig. 4). This can be cultivated in set-aside fields. The chain for the production of willow stems has the lowest energy input but willow chips are expensive, because of drying costs. On the other hand, they contain high amounts of fiber, polysaccharides and lignin, as well as some extractables that include interesting phytochemicals showing biological activity (Dou et al. 2016); (Table 9). In the bark of *S. viminalis*, the main

Table 9 Phytochemicals identified in *Salix viminalis* L

Part of plants	Metabolites	References
Barks	Salicin (2-hydroxymethyl-phenyl-β-D-glucopyranoside)	Highfield and Kemper (1999)
	Salicylate compounds (saligenin, salicylic acid, isosalicin, salidroside, picein, triandrin, salicoylsalicin, salicortin, isosalipurposide, salipurposid)	Kammerer et al. (2005)
	Triandrin, salicortin, vimatin, salicin	Palo (1984)
	Polyphenolic compounds (flavonoids, catechin, amelopsin, taxifolin, 7-O-methyltaxifolin-3'-O-glucoside, 7-O-methyltaxifolin)	Shara and Stohs (2015)
	Phenolic acids (salicylic, vanillic, <i>p</i> -hydroxybenzoic, <i>p</i> -coumaric, ferulic, caffeic, syringic)	Skrgan and Vinokurov (1970) and Poblócka-Olech et al. (2010)
Leaves	Flavonoids (isorhamnetin 3-O-6-acetylglucoside, isoquercitrin, apigenin 7-O-glucoside, isorhamnetin 3-O-glucoside)	Karl et al. (1977)
	Absciscic acid	Alvim (1978)
Aerial parts	Monoterpenes and sesquiterpenes (β-caryophyllene, α-farnesene, (E)-nerolidol, (E)-4,8-dimethyl-1,3,7-nonatriene, (E)-β-ocimene)	Fernandez et al. (2007)
	Phenol	Ucisik and Trapp (2006)

substances are salicin, triandrin, salicortin and vimalin. Leaves generally show lower phenolic concentration and less glycoside diversity than bark. *S. viminalis* do not have any phenolic glycosides in the leaves. Leaves of *S. viminalis* contain flavonoids: isorhamnetin 3-*O*-6-acetylglucoside, isoquercitrin, apigenin 7-*O*-glucoside and isorhamnetin 3-*O*-glucoside (Karl et al. 1977). The bark of this plant contain several phenolic acids including salicylic, vanillic, *p*-hydroxybenzoic, *p*-coumaric, ferulic, caffeic and syringic (Skrgan and Vinokurov 1970; Pobłocka-Olech et al. 2010). Palo (1984) gives a summary of phenolic glycosides in the bark and leaves of different *Salix* species.

Willow bark contains active substances known for anti-inflammatory properties. It has been used for over 2000 years in different areas of the world to treat pain and fever e.g. joint, knee or back pain, osteoarthritis, headache, menstrual cramps, tendonitis and flu symptoms (Highfield and Kemper 1999). Therapeutic effectiveness is associated with salicin (2-(hydroxymethyl) phenyl- β -D-glucopyranoside), which is chemotaxonomic markers of the genus *Salix* (Pobłocka-Olech et al. 2007; Kenstavičienė et al. 2009).

Salicin is known as “nature’s aspirin” and is metabolized upon ingestion via hydrolysis to salicyl alcohol (saligenin) followed by the formation of salicylic acid. However, salicin is not the only natural metabolite found in willow’s bark. Chromatographic analysis with mass spectrometry detection revealed number of salicylate compounds including saligenin, salicylic acid, isosalicin, salidroside, picein, triandrin, salicoylsalicin, salicortin, isosalipurposide, and salipurposide (Kammerer et al. 2005). More comprehensive studies of willow bark extracts showed additionally the presence of some polyphenolic compounds and flavonoids such as catechin, amelopsin, taxifolin, 7-*O*-methyltaxifolin-3'-*O*-glucoside and 7-*O*-methyltaxifolin, with high antioxidant and radical scavenging activities. The presence of the latest group may explain discrepancies in clinical efficacy of salicin and related compounds. Numbers of clinical human and animal trials with willow bark extracts provide some confusing results. Some prove its effectiveness while the others not, but general conclusion is rather supporting the view that willow bark extract is effective as an analgesic and anti-inflammatory agent (Shara and Stohs 2015).

Recently, there is much interest in willow bark extracts as antitumor agent inhibiting angiogenesis, the process, which supplies oxygen and nutrients to tumor cells. This was reported that willow bark extract may suppress the growth and induce apoptosis in human colon and lung cancer cells in vitro (Hostanska et al. 2007). Other studies reported the extract to kill 75–80% of acute lymphoblastic leukemia and acute myeloid leukemia cells harvested from human patients, in vitro (El-Shemy et al. 2007).

Bark extracts are components of number of market preparations. They show some advantages over the aspirin (acetylsalicylic acid) as they do not show such side effects and are less stomach irritating than aspirin (Highfield and Kemper 1999). Besides, due to the presence of other phenolics in the extract the effective doses range between 120 and 240 mg salicin while for the same effect 500 mg of aspirin is recommended. But, for the safety reason individuals allergic to aspirin should avoid willow bark extracts as well.

For the application of salicin in medicine, health promoting products and nutraceuticals the industrial protocols for its isolation and purification have been developed and patented (Wang et al. 2016). The extracts performed with “green solvents” (ethanol–water mixtures) are purified by filtration on resin column to obtain product of about 70% purity. The process is low cost, high efficiency and environmentally friendly. Other proposed methods include hot water treatment for the extraction of non-cell-wall components. The aqueous treatment of the bark at 80 °C liberated the extract in > 20% yield under unpressurized conditions (Dou 2018; Dou et al. 2018). The major components of this extract were picein, triandrin and catechin with an overall yield of up to 14%.

Taking under consideration species chemical discrepancies, future prospects for breeding new lines should consider three aspects: a high content of phenolic substances; a high bioethanol yield; and a high resistance to rust (Dou 2018). For phytochemicals, new technics for up scaled purification of desired substances need to be developed. Willow biomass holds much potential for creating greater value from willow biomass by utilizing the phenolic substances and sclerenchyma fibers of the bark and converting the debarked biomass e.g. into bioethanol, bio-char and energy (Dou 2018).

Black locust (*Robinia pseudoacacia*)

The black locust is the leguminous woody species, very effective at colonizing an area, because it freely branches and in Europe is recognized as most dangerous invasive species, as a third species after poplars and eucalyptus for wood production. It shows a higher yield and a faster harvest time than any other woody plant species. Thus, it is very attractive biomass plant (Fig. 4).

The wood of black locust belongs to species noted for their natural decay resistance similar to oak or cherry wood. Due to the decay resistance and high natural durability, black locust hardwood has been used for outdoor fence posts as well as for timber (e.g., beam, railroad sleepers). The heartwood of robinia is highly demanded by users, especially for long, lasting outdoor applications. *R. pseudoacacia* wood has also long been used to age vinegars and, more recently, wine (Sanz et al. 2012). The air transfer efficiency through the pores of this wood favours efficient acidification rates and affects the phenolic composition and sensory quality of vinegar.

The biomass of robinia can be used as a substrate in an integrated biorefinery, including in the production of second-generation biofuels (Stolarski et al. 2015). A biorefinery uses the concept of separation and utilization of all the organic fractions obtained from lignocellulose. Processing the fractions, which are not used in the ethanol production helps to improve the economic balance of the installation. Thus, the residues and waste generated by wood industry can play important role for the implementation of more

cleaner and sustainable economy, as wooden biomasses represents an important source of chemicals useful for different industrial sectors (Di Maria et al. 2018).

The available data on the content of natural products show that *Robinia pseudoacacia* is rich in secondary metabolites (Table 10). The trunk, which consists of the bark and hardwood contains different classes of natural products. The bark has been rich with triterpene saponins, while the hardwood contains wide range of natural products of phenolic, stilbenic or terpenoid structures.

In the *n*-hexane and ethanoic extracts of robinia hardwood, twenty-eight volatile compounds such as acids, fatty acids, aliphatic hydrocarbons, aromatic hydrocarbons, esters, fatty acids ester, pure hydrocarbon oils or mineral oils were identified with GC–MS analysis. The dominant compound was resorcinol (1,3-benzendiol); (52% of total), buthexadecanoic acid, trimethylsilyl ester, 9,12-octadecadienoic acid, (Z,Z)-, tetradecane, bis(2-ethylhexyl) phthalate, hexadecane, 9,12,15-octadecatrien-1-ol, (Z,Z,Z)-, hexadecanoic acid and 9,12-octadecadienoic acid (Z,Z)- were also quite abundant (Hosseinihashemi et al. 2013). Very comprehensive analysis of volatiles in acacia bark grown in Turkey was performed using SPME and GC-FID/MS methods (Özgenç et al. 2017).

Sanz et al. (2012), analysing wines aged in the barrels made of oak and acacia hardwood, identified 43 nonanthocyanic phenolic compounds in both wines by LC–DAD-ESI/MS. Furthermore, wines aged in acacia barrels contained additionally 15 compounds of acacia origin. They included dihydrorobinetin,

Table 10 Phytochemicals identified in *Robinia pseudoacacia*

Part of plant	Metabolite	References
Hard wood	Dihydrorobinetin, dobinetin 2,4-dihydroxybenzaldehyde	Sanz et al. (2012)
	tetrahydroxydihydroflavonol, fustin, butin, trihydroxymethoxydihydroflavonol, 2,4-dihydroxybenzoic acid	Latorraca et al. (2011)
	Resveratrol, piceatannol	Sergent et al. (2014)
	Norathyriol, urolithin C, urolithin M6, catechin lactone A, bis(2-ethylhexyl)phthalate	Sergent et al. (2014)
	Secundiflorol, mucronulatol, isomucronulatol, isovestitol	Hong et al. (2017)
Bark	Robinlin, robiniosides A–D, kaikasaponin III, 3 β ,22 β -dihydroxyolean-12-en-29-oic acid	Tian and Mac Laughlin (2000)
	Robiniosides E–J, catechins, (E)-coniferyl alcohol, phenolic acids	Tian et al. (2001) and Cui et al. (1992)
		Cui et al. (1993) and Di Maria et al. (2018)

robinetin, 2,4-dihydroxybenzaldehyde, a tetrahydroxydihydroflavonol, fustin, butin, a trihydroxymethoxydihydroflavonol and 2,4-dihydroxybenzoic acid, with dihydrorobinetin being most abundant. Another comprehensive metabolic profiling of hardwood natural products allowed identification over 60 compounds, based on their spectroscopic characteristics (Sanz et al. 2011).

Two stilbenic compounds, resveratrol and piceatanol, together with dihydrorobinetin were identified in hardwood (Sergeant et al. 2014). These stilbens are known as highly antioxidant compounds present in number of plants, but predominantly in grapes.

Five triterpene glycosides, robiniosides A–D, were identified in the robinia bark. These included as 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-glucopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranosyl 3 β ,22 β -dihydroxyolean-12-en-29-oic acid, 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-galactopyranosyl(1 $\rightarrow$ 2) β -D-glucuronopyranosyl 3 β ,22 β ,24-trihydroxyolean-12-en-29-oic acid (oxytrogenin), 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-glucopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranosyloxytrogen, 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-galactopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranosyloxytrogenin 22-*O*- α -L-rhamnopyranoside, 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-glucopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranosyloxytrogenin 22-*O*- α -L-rhamnopyranoside, kaikasaponin III and 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-galactopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranosyl 3- β -22- β -dihydroxyolean-12-en-29-oic acid (Cui et al. 1992). The same group of authors later on identified additionally six triterpene glycosides, Robiniosides E–J, including abrisapogenol B 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-galactopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranoside, abrisapogenol B 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-glucopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranoside, 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-galactopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranosylabrisapogenol B 22-*O*- α -L-rhamnopyranoside, 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-glucopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranosylabrisapogenol B 22-*O*- α -L-rhamnopyranoside, 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-galactopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranosylabrisapogenol E 30-*O*- β -D-apiofuranosyl(1 $\rightarrow$ 6)- β -D-glucopyranoside and 3-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 2)- β -D-glucopyranosyl(1 $\rightarrow$ 2)- β -D-glucuronopyranosylabrisapogenol E 30-*O*- β -D-apiofuranosyl(1 $\rightarrow$ 6)- β -D-glucopyranoside (Cui et al. 1993). Other identified compounds include robinin

(kaempferol-3-*O*-ramnosyl-galactosyl-7-ramnoside) and acacetin-7-*O*-rutoside, diosmetin, luteolin, apigenin but also isomucronulatol, mucronulatol, secundiflorol and isovestitol glycosides (Ebel et al. 1970; Kaneta et al. 1980; Veitch et al. 2010).

Dutu and Dinu (2006) showed that the vegetal product of acacia flowers contains polyphenol carboxylic acids, flavones, proanthocyanidins, tannins and triterpenic saponins. The polyphenols (expressed in caffeic acid) were detected at the level of 363.5–395.5 mg%, flavones (expressed in rutin)—92.7–102.5 mg%. The comparison of the flavonoid chemistry of leaves and flowers of *R. pseudoacacia* using LC–UV and LC–MS showed that flavone 7-*O*-glycosides, particularly acacetin, predominated in the leaves, whereas flavonol 3,7-di-*O*-glycosides mainly in the flowers (Veitch et al. 2010). Phenolic compounds available within the leaves and flowers have been proven to have a strong antiradical activity (Ji et al. 2012; Marinas et al. 2014).

In the roots of black locust, the apigenin, naringenin, dihydroxyflavone, 4',7-isoliquiritigenin and an unusual tetrahydrochromeno[4,3- β]indole (type analog of medicarpin), have been isolated (Dejon et al. 2013). The dried, unripe fruits of *R. pseudoacacia* contained bioquercetin (quercetin 3-*O*- β -D-galactopyranosyl-L-rhamnopyranoside); (Maksyutina 1967).

The hardwood of acacia can be a good source of biologically active phytochemicals for different industries as extracts or individual compounds, which show inhibitory activities against number of microorganisms. The method for isolation of different fractions of natural products was optimized. It was documented that optimal extraction solvent for dihydrorobinetin was EtOH/H₂O (50/50). The dihydrorobinetin was purified over 95% using centrifugal partition chromatography (CPC); (Destandau et al. 2016). The method was simple, not expensive and environmentally friendly.

Water soluble extract showed protective effect against *Sphaerotheca fuliginea*, the powdery mildew fungus, which is one of the most destructive foliar diseases of cucurbits. Effectivity of the extract was higher than 80% and can be recognized as very effective natural fungicide, especially interesting for organic and indoor farming (Zhang et al. 2008).

The antibacterial activity of the crude extract and the solvent fractions (hexane, chloroform, ethyl acetate and butanol) were evaluated against

Fig. 5 General approach in extraction, isolation and characterization of woody plant phytochemicals

Streptococcus mutans and *Porphyromonas gingivalis* (Patra et al. 2015). The most active were hexane and chloroform fraction containing hydrophobic compounds giving over 90% inhibition. This indicated that acacia hydrophobic compounds can find clinical application as disinfectants for the treatment of dental plaque and periodontal inflammatory diseases.

The wood decay resistance of acacia is being assigned to the content of two active principles dihydrorobitenin and robinetin. Thus, the extracts of hardwood of acacia can be applied as natural, ecologically green product for outdoor woody furniture, construction and wooden crafts preservation. It was shown that saw dust from *Eucalyptus regnans*, a normally nondurable wood, was no more durable after impregnation with up to 1% robinetin or dihydrorobinetin than were unimpregnated controls (Rudman 1963). As for optimal biofuel production it is recommended to treat hardwood with hot water to remove some interfering components, this wastewater can be used for separation of biologically active principles (Kačík et al. 2016).

Some toxicity to mammals were reported when chewing acacia wood. The toxic principle was not proven but it is believed that glycoproteins (lectins-robin, robinetin, phasin) and/or triterpene saponins are responsible factor (Horejsi et al. 1978).

Extraction, isolation, analysis and application of phytochemicals from bioenergy crops

The subsequent stages of the use of phytochemicals from plants are extraction, isolation and chemical characterization of bioactive compounds, as well as evaluation of their properties and application potential (Sasidharan et al. 2011). For energy crops, the biggest problem in extraction is the scale and the process of biomass preparation. As to the scale, specialized machinery is necessary with high throughput. They are needed for preparation of plant material, which must be meshed before extraction. Several methods has been developed for the extraction of high-value bioactive compounds from plants, such as organic solvent extraction, maceration, hydrodistillation, low-pressure solvent extraction, hydrothermal processing and supercritical extraction. Proper selection of extraction solvents is essential for isolation of wide range phytochemicals having different polarities. The composition of the final extract may influence extract efficacy when used in therapy or as active food ingredient (Shara and Stohs 2015). Recently, significant emphasis on developing “green” technologies of extraction is more often observed (Attard et al. 2015). Non-toxic, cheap and environmentally friendly solvents and their lower amounts are very desirable in the case of clean technology of extraction. The extraction results in the mixture of compounds so called crude extract. The isolation of individual compounds or purified fraction is a long and often arduous process and need individual development for different plant

Table 11 Methods of obtaining and chemical analysis of phytochemicals from energy crops

Plant species/raw material	Extract/compound	Obtaining method (extraction/isolation)	Analysis method	References
Maize stem, husk, grain, root, cob and leaf	Free phenolics	80% aqueous ethanol, 2 h, 25 °C	UPLC-PDA	Vazquez-Olivo et al. (2017)
	Bound phenolics	2 N NaOH, 30 min., 95 °C + HCl, 1 h, room temp. + hexane 10 min. + ethyl acetate (5 × 10 mL)	UPLC-PDA	Vazquez-Olivo et al. (2017)
	Waxes	Supercritical extraction	Silylation (200 µL <i>N,O</i> -bis-(trimethylsilyl)-trifluoroacetamide + 100 µL toluene) HT-GC	Attard et al. (2015)
Maize kernel	Phenolics:	Extraction with 80% ethanol under reflux + chromatography over a silica gel column, elution with petroleum ether (PE, 60–90 °C), CHCl ₃ , EtOAc, CH ₃ COCH ₃ , and CH ₃ OH	LC-MS, NMR, IR	Nile and Park (2014)
	protocatechuic acid, vanillic acid, 2,4,6-trihydroxybenzoic acid, p-hydroxycinnamic acid, ferulic acid, hirsutrin, 3'-methoxyhirsutrin, cyanidin-3-glucoside, pelargonidin-3-glucoside, peonidin-3-glucoside, 5-CQA, CA, PA, benzoxazolin-2-one (BOA)			
Maize kernels		Defatting: Hexane 30 min. Extraction: 70% MeOH in 0.1% acetic acid, 12 h	LC/DAD	Atanasova-Penichon et al. (2014)
Corn tassel	Flavonoids	Fractionation: Toyopearl Fractogel HW-40S column (26 by 320 mm), sequential elution with H ₂ O and MeOH		
	Saponins	75% ethanol, 50 °C water bath for 2.5 h	Aluminum nitrate chromogenic method	Wang et al. (2014)
	Polysaccharides	80% ethanol, 70 °C, water bath for 3 h + defatting in petroleum ether + extraction with n-butanol Water at 50 °C for 1 h + washed by ethanol, acetone and ether successively, and then were dried at 50 °C for 4 h Extraction: 70% aqueous ethanol, n-BuOH	HClO ₄ -Vanillin staining method	Wang et al. (2014)
<i>stigma maydis</i>	Macrocarpene-type sesquiterpenes stigmenes A-F	Fractionation and isolation: vacuum-liquid chromatography of silica gel or ODS column and preparative and semi-preparative HPLC C18 column 1% HCl/methanol, 2 h	Phenol-sulfuric acid method	Wang et al. (2014)
Sorghum grains	Flavonoids: 3-deoxyanthocyanidins, flavones, flavanones		NMR, HRESIMS on qTOF	Qi et al. (2018)
flowering sorghum plants	Phenolic acids	2 M HCl (at 100 °C, under O ₂ for 40 min.) + diethyl ether	HPLC-PDA, LC-MS-ESI	Dykes et al. (2009), Dykes et al. (2011)
flowering sorghum plants	Phenolics	70% (v/v) boiling ethanol for 20 min	HPLC	Sène et al. (2001)
Sorghum	Flavones	100% MeOH	Folin-Ciocalteu method LC-MS	Sène et al. (2001) Du et al. (2010)

Table 11 continued

Plant species/raw material	Extract/compound	Obtaining method (extraction/isolation)	Analysis method	References
Giant knotweed	Crude extract	CH ₂ Cl ₂ (3 × 24 h) followed by MeOH (3 × 24 h)	HPLC/UV/ESI-MS	Fan et al. (2009)
Japanese knotweed	Phenolics	Extraction by the mixture of methanol (30 mL/100 mL), ascorbic acid (2.0 g/100 mL) and acetic acid 2 × 20 min, under sonication	UPLC-PDA-Q/TOF-MS	Lachowicz et al. (2019)
Giant knotweed and Japanese knotweed leaves and rhizomes	Proanthocyanidins	Methanolic solution of phloroglucinol (75 g/L) and ascorbic acid (15 g/L) + HCl (0.3 M), 30 min, 50 °C	UPLC-PDA-Q/TOF-MS	Lachowicz et al. (2019)
Giant knotweed and Japanese knotweed leaves and rhizomes	Triterpenoids	Ethyl acetate and 5 mL of hexane, 20 min., under sonication	UPLC-PDA-Q/TOF-MS	Lachowicz et al. (2019)
Giant knotweed flowers	Emodin, emodin-8-O-β-D-glucopyranoside, physcion-8, O-β-D-glucopyranoside, Avicularin, hyperin, Quercetin-3-O-β-D-glucuronopyranoside	Extraction: methanol Fractionation: hexane, ethyl acetate (EtOAc) and butanol (BuOH) Isolation: silica gel column, elution by CH ₂ Cl ₂ -MeOH and Sephadex LH-20 column, elution by MeOH-H ₂ O 50% acetone, two months, room temperature Fractionation: ether, water Isolation: silica gel, elution by hexane-CHCl ₃ -MeOH 60% ethanol	TLC, LC-MS, 1H-NMR and 13C-NMR TLC, IR, UV, HPLC, GC-MS, NMR	Zhang et al. (2005) Inoue et al. (1992)
Giant knotweed rhizomes with roots, aerial parts and fallen leaves	Emodin, physcion		HPLC	Kovářová et al. (2010)
Japanese knotweed rhizomes	Crude extract containing resveratrol, piceatannol and its glycosides (piceid, resveratrolid, astragines)	50% MeOH	CE-MS	Miyagi et al. (2010)
Japanese knotweed	Crude extract	MeOH in Soxhlet + acidified ethyl acetate (3% HCl) 95% ethanol 50% EtOH	HPLC	Vastano et al. (2000)
Japanese knotweed roots	Stilbene analogues	Immersion in boiling water, 4 min, with acetic acid as antioxidant Extraction: hot water 80–100 °C, 20–30 min. Extraction with 95% ethanol by percolation, 50 °C + petroleum (60–80°), chloroform and finally ethyl acetate Fractionation by hexane	Folin-Ciocalteu methods HPLC	Pan et al. (2016) Bralley et al. (2008) Abou Baker et al. (2010)
Japanese knotweed	Total phenols in crude Extract			
Japanese knotweed root	Crude extract			
Jerusalem artichoke tubers	Inulin			
Jerusalem artichoke leaves	SESQUITERPENE lactones		TLC, IR (KBr) E/MS, 1-H-NMR	Abou Baker et al. (2010)
Jerusalem artichoke leaves	sesquiterpene lactones	Ultrasonical extraction with ethyl acetate (3x30 min.)	UPLC-Q-TOF-MS	Yuan and Yang (2017)

Table 11 continued

Plant species/raw material	Extract/compound	Obtaining method (extraction/isolation)	Analysis method	References
Jerusalem artichoke leaves	Sesquiterpene lactones	Extraction by maceration overnight with ethyl acetate 3 x at room temperature	UPLC-MS, IR, ¹ H and ¹³ C-NMR	Yuan et al. (2013)
Jerusalem artichoke tubers		Fractionation: silicagel kolumn chromatography elution by with petroleum ether/ethyl acetate Purification by preparative HPLC(MeOH-H ₂ O = 45:55) hydrodistillation	GC-FID, GC/MS, and ¹³ C-NMR	Radulovic and Dordevic (2014)
Jerusalem artichoke tubers	Cumarins	Extraction with 2% (v/v) EtOAc and purification by TLC and HPLC	GC-MS, TLC and HPLC	Cabello-Hurtado et al. (1998)
Jerusalem artichoke tubers	Neo-chlorogenic acid, chlorogenic acid and crypto-chlorogenic acid, four isomeric di-caffeoylquinic acids (3,4- <i>O</i> -dicaffeoyl; 3,5- <i>O</i> -dicaffeoyl; 1,3- <i>O</i> -dicaffeoyl and 4,5- <i>O</i> -dicaffeoyl esters)	Methanolic extraction	UPLC-MS-ESI	Kapusta et al. (2013)
Jerusalem artichoke tubers	3- <i>O</i> -caffeoylquinic acid and 1,5-dicaffeoylquinic, 3,5-dicaffeoylquinic acid, 1,5-dicaffeoylquinic acid, 4,5-dicaffeoylquinic acid, 3,5-dicaffeoylquinic acid methyl ether	Extraction: 60% ethanol under reflux, 2 x 2 h Fractionation: petroleum ether (PE), ethyl acetate (EA) and <i>n</i> -butanol (NB) Purification: 60–100 mesh polyamide resin column, eluting with a series of ethanol/water from 30:70 (v/v) to 100:0 (v/v) Extraction: boiling water, 10 min. + methanol) the extracts Purification: SPE, C18 cartridges, using a step-elution with a acidified water/methanol CH ₂ Cl ₂ in Soxhlet, 8 h	HPLC, MS, Folin-Ciocalteu method	Yuan et al. (2012)
Miscanthus giganteus	Hydroxycinnamates	Extraction by CH ₂ Cl ₂	UV and LC-ESI-MS ⁿ	Parveen et al. (2011)
Miscanthus giganteus bark and core of the stalks	Sterols, fatty acids, long-chain fatty alcohols, vanillic acid, vanillin, and p-hydroxybenzaldehyde	Extraction with a mixture of acetone/acidified water/diethyl ether (4:7:2:0: 3:3 v/v)	GC-MS	Villaverde et al. (2009)
Reed canary grass	Alkaloids	Extraction: 70% EtOH (3x3 h), CHCl ₃ , <i>n</i> -butanol	GC-MS	Grzelak et al. (2018)
Reed canary grass	Condensed tannins	Extraction: hydrochloric acid, 3 days in room temp. Purification: SPE aromatic sulphonic acid cation Exchange, elution using ammoniated ethanol	Spectrophotometrically, 550 nm	Lyman et al. (2012)
Reed canary grass	Saponin	Extraction: 70% EtOH (3x3 h), CHCl ₃ , <i>n</i> -butanol	LC-MS, GC-MS	Lyman et al. (2012)
Reed canary grass	Gramine	Extraction: 70% EtOH (3x3 h), CHCl ₃ , <i>n</i> -butanol	TLC, HPLC, GC/MS	Lyman et al. (2012)
Switchgrass	Saponins	Extraction: 70% EtOH (3x3 h), CHCl ₃ , <i>n</i> -butanol	LC-MS	Lee et al. (2001)
Switchgrass	Saponins	Extraction: 70% EtOH (3x3 h), CHCl ₃ , <i>n</i> -butanol Purification: 30 cm x 1.8 cm silica gel kolumn, elution by CHCl ₃ -MeOH-H ₂ O	HPLC-ESI-MS	Lee et al. (2009)
Switchgrass	Phenolics	Extraction: 1.5% acetic acid in 50% methanol, 1 h, 22 °C	HPLC	Sarath et al. (2007)

Table 11 continued

Plant species/raw material	Extract/compound	Obtaining method (extraction/isolation)	Analysis method	References
Cup plant	Kaempferol derivatives and other nine flavonoids	Deflating in petroleum ether (40–60 °C) for 2 h Extraction: MeOH Fractionation: CCl ₄ , CHCl ₃ and EtOAc Purification: polyamide column, elution by using H ₂ O and Sephadex LH-20 column, elution by MeOH–H ₂ O (1:1) Extraction with MeOH, H ₂ O, Deflating with petroleum ether, Second extraction with diethyl ether and NaHCO ₃ , acidification with 36% HCl	UV, LSI MS, FAB MS, CIMS, ¹ H, ¹³ C and 2D-NMR, DEPT, HMQC and HMBC	El-Sayed et al. (2002)
Cup plant	Phenolics		HPLC	Kowalski and Wolski (2003)
Cup plant	Essential oils	Steam distillation in a Deryng's apparatus in the presence of m-xylene.	GC–MS	Kowalski and Wolski (2005)
Cup plant	Lipophilic fraction	Extraction with petroleum ether in Soxhlet, 12 h, 60 °C	GC–MS	Kowalski (2005)
Cup plant	Extract	Extraction with hexane	GC–MS	Kowalski and Kędzia (2007)
Willow	Salicylate compounds	MeOH, 2 h	LC–MS	Kammerer et al. (2005)
Willow bark	Purified extract	Extraction: EtOH Purification on risin column	LC–MS	Dou (2018)
Willow bark	Extract	hot water extraction, 80 °C	HPAEC, HPLC, GC–MS, NMR	Dou et al. (2019)
Black locust hardwood	Extract	Extraction with ethanol, before and after extraction with n-hexane	GC–MS	Hosseinihashemi et al. (2013)
Black locust bark	Volatile organic compounds (VOCs)	SPME	GC-FID/MS	Özgenç et al. (2017)
Black locust hardwood	Polyphenolics	Extraction with diethyl ether and ethyl acetate	HPLC–DAD, LC–DAD-ESI/MS	Sanz et al. (2011), Sanz et al. (2012)
Black locust hardwood	Resveratrol, piceatannol, dihydroresveratrol	Maceration with EtOH–H ₂ O (1:1), 50 °C, 4 h	UPLC–DAD–MS/MS	Sergent et al. (2014)
Black locust leaves and flowers	Flavone triglycosides	Extraction: 50% aq. MeOH Fractionation: C-18 flash chromatography, elution by 10–80% MeOH and Sephadex LH-20, elution by 10% MeOH Semi-prep. HPLC	LC–ESI–MS	Veitch et al. (2010)
Black locust	Dihydroresveratrol	Extraction: EtOH/H ₂ O (50/50) Purification: centrifugal partition chromatography (CPC), EtOH > 95%	HPLC–MS	Destandau et al. (2016)

Table 12 Biological activity and potential applications of phytochemicals obtained from energy crops

Plant species/raw material	Extract/compound	Biological activity/Application	References
Maize cobs	Free and bound phytochemical extract	Antioxidant activity	Dewanto et al. (2002)
Maize stover	Phenolic acids and lignin	Antioxidant activity (DPPH radical scavenging activity and oxygen radical absorbance capacity (ORAC))	Vazquez-Olivo et al. (2017)
Maize kernels	Phenolics: protocatechuic acid, vanillic acid, 2,4,6-trihydroxybenzoic acid, p-hydroxycinnamic acid, ferulic acid, hirsutrin, 3'-methoxyhirsutrin, cyanidin-3-glucoside, pelargonidin-3-glucoside, peonidin-3-glucoside,	Antioxidant activity (DPPH radical scavenging activity OH radical scavenging activity reducing ability α-glucosidase and xanthine oxidase (XO) inhibition)	Nile and Park (2014)
Maize kernels	Chlorogenic acid	Increasing resistance to <i>Fusarium</i> Sp. inhibition of fumonisin production	Atanasova-Penichon et al. (2014)
Maize	<i>Trans</i> -cinnamic acid (CA) and ferulic acid (FA)	Inhibition of growth and aflatoxin B1 production by <i>Aspergillus flavus Aspergillus parasiticus</i>	Nesci and Eicheverry (2006)
Corn tassel	Flavonoids, saponins, polysaccharides	Antioxidant activity antigenotoxic activity inhibition the proliferation of human gastric cancer cells	Wang et al. (2014)
Maize leaves	Extract	Anticancer activity	Balasubramanian and Padma (2013)
<i>stigma maydis</i>	Macrocarpene-type sesquiterpenes stigmene A-F	The inhibitory effect of amyloid-β (Aβ) aggregation against Alzheimer's disease	Qi et al. (2018)
Maize shoot and root	Extract	Potential use as natural herbicides	Ahmed (2018)
Sorghum	Sorgoleone	Allelopathic properties suppression of weed growth	Soltys et al. (2010)
Sorghum	Luteolin, apigenin	Antifungal activity	Du et al. (2010)
<i>Fallopia</i> spp. roots	B-type procyanidins	Denitrification inhibition antioxidant activity	Bardon et al. (2014) Bardon et al. (2016)
<i>Fallopia</i> spp. leaves	Glycosylated derivatives of kaempferol, quercetin, and myricetin, and of apigenin and luteolin	Antioxidant activity	Kim et al. (2000)

Table 12 continued

Plant species/raw material	Extract/compound	Biological activity/Application	References
Giant knotweed	Flavan-3-ols derivatives, trans-piceid and trans resveratrol, phenolic acids	Antioxidant activity	Lachowicz et al. (2019)
Japanese knotweed			
Giant knotweed flowers	Emodin, emodin-8-O- β -D-glucopyranoside, physcion-8, O- β -D-glucopyranoside, Avicularin, hyperin, Quercetin-3-O- β -D-glucuronopyranoside	Antioxidant activity	Zhang et al. (2005)
Giant knotweed rhizomes and roots	Emodin, physcion	Allelopathic properties, potential use as natural herbicides	Inoue et al. (1992)
Japanese knotweed	Resveratrol, emodin	Anticancer activity	El-Readi et al. (2016)
Japanese knotweed	Crude extract	Antioxidant activity application as antioxidant for prevention lipid peroxidation in peanut oil	Pan et al. (2007)
Japanese knotweed	Resveratrol	Antiviral activity against HIV	Lin et al. (2010)
Japanese knotweed roots	Trans-and cis-resveratrol	Anticancer activity	Feng et al. (2006)
Japanese knotweed	Crude ethanolic extract	Anti-inflammatory	Bralley et al. (2008)
Japanese knotweed	resveratrol	anticancer activity	Aggarwal and Shishodia (2006), and Kimura and Okuda (2001)
Japanese knotweed	Piceid, resveratrol and 2,3,5,4'-tetrahydroxy stilbene-2-O-D-glucoside	Mitigation of liver peroxidation in rats	Kimura et al. (1995)
Japanese knotweed roots	Crude methanolic extract containing alkaloids, sterol/terpenes, tannins, flavonoids, and carbohydrates	Inhibition of <i>Streptococcus mutans</i> and <i>Streptococcus sobrinus</i> viability, potential application for the control of dental plaque formation and subsequent dental caries formation	Song et al. (2006)
Jerusalem artichoke	Inulin	Bioethanol and D-psicose production	Song et al. (2017)
Jerusalem artichoke	Inulin	Citric acid production	Liu et al. (2010)
Jerusalem artichoke juice	Inulin	Sorbitol production	Wei et al. (2001)
Jerusalem artichoke	Crude leaf extract or <i>n</i> -butanol fraction	Antifungal activity against <i>Botrytis cinerea</i> , <i>Colletotrichum gloeosporioides</i> , <i>Phytophthora capsici</i> and <i>Rhizoctonia cerealis</i> Application in preservation of fruits and vegetables during storage	Chen et al. (2013a, b)

Table 12 continued

Plant species/raw material	Extract/compound	Biological activity/Application	References
Jerusalem artichoke leaves	Phenolics	Natural antioxidants	Yuan et al. (2012)
Jerusalem artichoke leaves	Sesquiterpene lactones	Anticancer activity	Abou Baker et al. (2010)
Jerusalem artichoke tubers	Ethanol extracts	Antidiabetic effect	Aslan et al. (2010)
Miscanthus giganteus roots	Polyphenolics	inhibitory effect on kidney tissue TBARS levels	
Reed canary grass	Aqueous extract	Biostimulation of PAH-utilizing soil bacteria	Techer et al. (2011), Techer et al. (2012)
Reed canary grass	Alkaloids	Herbicidal activity	Gołębiewska et al. (2017)
Reed canary grass	Alkaloids	Important players in plant defense responses against insects, microbes, and other herbivores	Grzelak et al. (2018)
Reed canary grass	Alkaloids	Herbicidal activity	Lovett et al. (1994)
Reed canary grass	Alkaloids	Antibacterial activity against <i>Pseudomonas</i>	Sepulveda and Corcuera (1990)
Reed canary grass	Gramine	Inhibition of methane fermentation	Popp et al. (2016)
Switchgrass	Saponins	Hepatotoxic properties	Lee et al. (2001)
Cup plant	Extract	Antiemetic, antirheumatic, analgesic, tonic, and diaphoretic activities	Kowalski and Kędzia (2007)
Cup plant leaves	Saponins	Anticholesterolemic properties	Syrov et al. (1992)
Cup plant leaves, inflorescences and rhizomes	methanolic extract	Antibacterial activity	Kowalski and Kędzia (2007)
Cup plant leaves	saponins	Antifungal activity against <i>Drechslera graminea</i> Rabh, <i>Rhizopus nodosus</i> Namysl, and <i>Rhizopus nigricans</i> Ehr	Davidjanc et al. (1997)
Cup plant leaves	Crude extract	Antifungal activity against <i>Fusarium oxysporum</i> , <i>Fusarium verticillioides</i> , <i>Penicillium expansum</i> , <i>Penicillium brevicompactum</i> , <i>Aspergillus flavus</i> and <i>Aspergillus fumigatus</i>	Zabka et al. (2011)
Willow bark	Salicin (2-(hydroxymethyl) phenyl)- β -D-glucopyranoside)	Anti-inflammatory properties as a phytotherapeutic precursor of aspirin	Dou et al. (2016)

Table 12 continued

Plant species/raw material	Extract/compound	Biological activity/Application	References
Willow bark	Salicin (2-(hydroxymethyl) phenyl)- β -D-glucopyranoside)	SUBSTITUTE of aspirin to treat pain and fever e.g. joint, knee or back pain, osteoarthritis, headache, menstrual cramps, tendonitis and flu symptoms	Highfield and Kemper (1999)
Willow bark	Flavonoids: catechin,amelopsin, taxifolin, 7-O-methyltaxifolin-3'-O-glucoside,	Antioxidant activity	Shara and Stohs (2015)
Willow bark	7-O-methyltaxifolin Extract	Antitumor agent inhibiting angiogenesis anticancer activity against human colon and lung cancer	Hostanska et al. (2007)
Willow bark	Extract	Activity against acute lymphoblastic leukemia andacute myeloid leukemia cells	El-Shemy et al. (2007)
Black locust leaves and flowers	Phenolics	Antiradical activity	Ji et al. (2012) and Marinas et al. (2014)
Black locust	Crude extract	Antifungal effect against <i>Sphaerothecafuliginea</i> potential application in organic farming	Zhang et al. (2008)
Black locust	Hexane, chloroform fraction of crude extract	Antibacterial activity	Patra et al. (2015)
Black locust	Crude extract, robinetin, dihydrorobinetin	potential clinical application as disinfectants for dental plaque and periodontal inflammatory diseases Application as ecologically green product for outdoor woody furniture, construction and wooden crafts preservation	Rudman (1963)
Black locust	Crude extract	Antimicrobial activity against <i>Plasmodiaraviticola</i>	Chen et al. (2002)
Black locust	Crude extract	Antimicrobial activity against <i>Coli bacillus</i> and <i>Staphylococcus</i>	Yuan (1981)
Black locust	Acacetin	Antibacterial activity against <i>Stenotrophomonasmaltophilia</i>	Sun and Sheng (1998)
Black locust	Lectins	Activity against <i>Lymantriadispar</i> larvae	Liu et al. (2004)
Black locust	Cationic peptide	Antimicrobial activity against <i>Staphylococcus aureus</i>	Talas-Ogras, et al. (2005)
Black locust	Ethanol extract	Antimicrobial activity against <i>Staphylococcus ureus</i> , <i>Bacillus subtilis</i> , <i>Pseudomonas aeruginosa</i> , <i>Klebsiella pneumonia</i>	Marinas et al. (2014)
Black locust	Crude extract	<i>Escherichia coli</i> <i>Trametes versicolor</i>	Hosseinhashemi et al. (2016)

Table 12 continued

Plant species/raw material	Extract/compound	Biological activity/Application	References
Black locust	Alcoholic extract	<i>Proteus</i> , <i>Salmonella choleraesuis</i>	Rosu et al. (2012)
Black locust	Aerial parts extracts	<i>Streptococcus mutans</i> , <i>Porphyromonas gingivalis</i> <i>Gloeophyllum trabeum</i>	Patra et al. (2015)

species and different phytochemicals of interest. The general approach in extraction, isolation and characterization of plant bioactive compound followed by their application is presented on the graph (Fig. 5).

Plant bioactive compounds are usually analyzed by spectroscopic and chromatographic methods, as well as by immunoassay (Sasidharan et al. 2011). New approaches in high resolution mass spectrometry combined with liquid or gas chromatography are methods of choice for extract standardization (Rathahao-Paris et al. 2016). The methods of extraction, isolation and analysis, as well as the application of phytochemicals for bioenergy crops described in this paper were presented in Tables 11 and 12.

Conclusions

Interest in biomass power generation is due to the existing potential for immediate reduction of greenhouse gas emissions and technology development. However, high costs of biomass production and necessity to use agriculture lands cropped with food species, slow down the processes of full application of this technology. In order to capture the benefits available today from energy crops and to accelerate the development of energy production from their biomass, policy measures and new technologies of biomass processing are necessary to incentivize biomass power generation. Analysis of costs of the biomass production and utilization is necessary and new technological measures of its utilization are highly required to increase economical effectiveness. One of the possibilities can be development of new technologies for the recovery of biologically active phytochemicals prior to the energetic use of biomass. The bioactive compounds, when extracted from biomass, can find an application in food, feedstuffs, agriculture, cosmetic and pharmaceutical industry. In this review, the authors attempted to point the potential the herbaceous and woody biomass plant species may have in this respect. As results from the in-depth review of the literature, the extraction and recovery of valuable phytochemicals from biomass may lead not only to increase in profitability of its energetic use, but also to improve its properties and suitability for biological conversion to energy sources, such as biogas or bioethanol.

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