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Review

Acylated polyphenolics of family Fabaceae: distribution, chemodiversity, and bioactivity, a comprehensive review

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Summary Polyphenolics are the most common class of plant-derived natural products. They play an important role in the protection of both plants and humans. Acylated polyphenolics, *i.e.*, polyphenolics esterified with either phenolic or organic acids, are abundant in several plant families including Fabaceae. This review article is intended to shed light on the distribution, isolation, chemodiversity, and bioactivity of acylated polyphenolics obtained from selected fabaceous plants mentioned herein. Isolation of these metabolites was mostly performed *via* successive column chromatography, including preparative and semi-preparative HPLC. Structure elucidation was achieved through interpretation of spectral data. Meanwhile, detection was chiefly accomplished *via* diverse liquid chromatography/mass spectrometric analyses. Compared to usual polyphenolics, these unique acylated compounds were found of higher stability and bioactivity. The current survey targets to provide a comprehensive overview of the medicinal role of acylated polyphenolics that may encourage the incorporation of fabaceous plants in pharmaceuticals.

Keywords Acylated polyphenolics, bioactivity, distribution, Fabaceae, isolation, LC/MS techniques, tentative identification.

Introduction

Polyphenolics are widely spread in the plant kingdom. Structurally, these compounds have at least one aromatic ring to which phenolic hydroxyl group(s) is (are) attached (Dai & Mumper, 2010). They are involved in plant protection from abiotic stresses exemplified in harmful environmental conditions such as extreme temperatures, drought, and ultraviolet radiations (Dai & Mumper, 2010; Šamec *et al.*, 2021). Polyphenolics are, as well, synthesised by plants as a part of defence mechanisms against pathogenic, parasitic, and predator invasions; they are also responsible for certain organoleptic characteristics of many plants (Dai & Mumper, 2010). For example, anthocyanins, which vary in colour between red, magenta, purple and blue, are the reason behind the colour of many plants or plant parts including apples, berries, beets, and onions (Dai & Mumper, 2010; Šamec *et al.*, 2021). Besides, the interaction between salivary glycoproteins and certain polyphenolics results in bitterness or astringency of some fruits and juices such as grapes, tea, and wine (Dai & Mumper, 2010).

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Polyphenolics play an important role as protective of human health against several ailments. For example, they alleviate cardiovascular diseases (Li *et al.*, 2012), ameliorate several neurodegenerative conditions (Renaud & Martinoli, 2019), exert a significant antidiabetic effect (Sarian *et al.*, 2017), demonstrate a remarkable cytotoxic activity against different cancer cell lines (Abdelhady *et al.*, 2015), and exhibit a potent anti-inflammatory effect (Liang & Kitts, 2015).

Public awareness of polyphenolics efficiency is continuously increasing due to their presence in many plant-derived foods and beverages and their wide application in various food and pharmaceutical industries (Okumura, 2020). Several methods and technologies have been recently developed for proper extraction of polyphenolics from plant materials, including supercritical fluid, subcritical water, pressurised fluid, microwave-assisted, ultrasound-assisted, and accelerated solvent-extraction techniques (Dai & Mumper, 2010) to avoid hydrolysis or oxidation of some polyphenolics due to the long extraction time of conventional methods (Okumura, 2020). Other factors that can enhance the stability and promote the solubility of plant polyphenolics are glycosylation and malonylation (Šamec *et al.*, 2021). Likewise, acylation improves their physicochemical properties including stability and solubility, together with bioavailability,

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and hence biological activity creating promising targets for pharmaceutical purposes (Oliani *et al.*, 2021; Vazhappilly *et al.*, 2021). Acylated polyphenolics can be of natural occurrence (plant-synthesised) (Fei *et al.*, 2021; Oliani *et al.*, 2021) as found in certain plant families including Lauraceae (Lee *et al.*, 2012), Myrtaceae (Saldanha *et al.*, 2013), Apiaceae (Eftekhari *et al.*, 2021), and Fabaceae, whose members contain a wide range of acylated polyphenolics (Benayad *et al.*, 2014b; Llorent-Martínez *et al.*, 2017). Besides, these compounds could be semi-synthesised through chemical or enzymatic esterification of the parent polyphenolics to enhance their bioactivity. Indeed, the majority of beneficial health attributes referred to family Fabaceae are ascribed to the abundance of certain metabolites as acylated polyphenolics (Hussein *et al.*, 2016; Rolnik *et al.*, 2020). The current review article is intended to shed light on published data concerning this type of bioactive metabolites in a number of fabaceous members in view to develop safer extraction techniques that might improve recovery, chemical characterisation, and biological evaluation of the targeted samples. Special emphasis was done on those reported in *Clitoria ternatea, Inga umbellifera, Pisum sativum, Ceratonia siliqua, Caesalpinia ferrea, Trigonella foenum-graecum*, *Lens culinaris*, and *Vicia faba*.

Classes of polyphenolics reported in family Fabaceae

The Fabaceae or Leguminosae, is a large and economically important family. It is considered the third largest family of flowering plants, after Orchidaceae and Asteraceae (Zhu *et al.*, 2005). Fabaceae members, also called legumes, have been subjected to numerous studies concerning the isolation and chromatographic identification of several bioactive polyphenolics. These polyphenolics can be classified into non acylated (regular) and acylated. The non acetylated are represented by flavonoids, tannins, phenolic acids, stilbenoids, and lignans (Dai & Mumper, 2010; Šamec *et al.*, 2021). Meanwhile, the acylated compounds usually result from esterification of the hydroxyl group(s) in anthocyanin or flavonoid glycoside molecules mostly with hydroxybenzoic, hydroxycinnamic (for example; caffeic, sinapic, ferulic, hydroxyferulic or *p*-coumaric), or organic acids (such as acetic, malonic or 3-hydroxy-3-methyl glutaric acids) (Hachibamba *et al.*, 2013; Nderitu *et al.*, 2013).

Non-acylated polyphenolic constituents

Reported data confirmed that family Fabaceae is particularly rich in flavonoids (Hegnauer & Gpayer-Barkmeijer, 1993) where about 28% and 95% of all known flavonoid and isoflavonoid aglycones, respectively, are produced by legumes. The seeds, seed coats, fruits, flowers, and leaves of legumes were found usually rich in anthocyanins; whereas, different flavonoid aglycones and O-glycosides predominate in the leaves and other organs (Hegnauer & Gpayer-Barkmeijer, 1993). Moreover, phenolic acids, including *p*-coumaric acid, *p*-hydroxybenzoic acid, ferulic acid, and vanillic acid, were stated to be common in fabaceous plants (Yarlagadda, 2014).

Acylated polyphenolic constituents

Earlier reports on acylated polyphenolics occurrence in family Fabaceae revealed that they are mainly acyl derivatives of flavonoid glycosides, predominantly of flavone, isoflavone, flavonol, and anthocyanin (Wojakowska *et al.*, 2013; Benayad *et al.*, 2014b). Structures of the most common esterifying acids in acylated polyphenolics reported in family Fabaceae are represented in Figure S1.

Advantages of acylated polyphenolics over regular non-acylated ones

The acylated polyphenolics were found more stable and biologically active than the corresponding non acylated compounds. (Fei *et al.*, 2021; Vazhappilly *et al.*, 2021; Zeng *et al.*, 2021). Concerning the family Fabaceae, the advantages of acylated fabaceous polyphenolics over non-acylated ones are summarised in Table 1.

In fact, acylated polyphenolics were proven to exert a free-radical scavenging effect (Haggag *et al.*, 2011; Singh *et al.*, 2017), as well as anti-inflammatory activity through inhibition of 5-lipooxygenase (Sen *et al.*, 2019) and cyclooxygenase (Amen *et al.*, 2015) enzymes. Their efficient antimicrobial activity against MRSA (methicillin-resistant *Staphylococcus aureus*) and VRE (vancomycin-resistant *enterococci*), *Staphylococcus aureus*, *Bacillus subtilis*, and *Pseudomonas pikettii* was also recorded (Otsuka *et al.*, 2008; Shahzadi & Shah, 2015). In addition, they exhibited effective cytotoxicity against hepatocellular larynx, colon, breast, and prostate carcinoma cell lines (Haggag *et al.*, 2011; Hussein *et al.*, 2016). Therefore, this specific highly active class of polyphenolics, namely the acylated polyphenolics (either anthocyanins, catechins or flavonoids), constituted the major concern of the current review article.

Isolation, identification, and biological activities of acylated polyphenolics from Fabaceous plants

Naturally occurring acylated polyphenolics were isolated from plant extracts using various column chromatographic techniques; silica gel (normal or reversed phase) or Sephadex LH-20 or through preparative or

Table 1 Advantages of acylated polyphenolics isolated from fabaceae members over non-acylated ones

Acylated polyphenolic compound(s)	Plant name	Plant part	The advantage over non-acylated polyphenolic compound(s)	Reference
Acylated kaempferol tetraglycoside	*Tipuana tipu*	Leaves	Stronger anti-inflammatory activity than that exerted by the three non-acylated flavonoid glycosides isolated concurrently	(Amen *et al.*, 2015)
Galloyl myricetin glycoside	*Leucenia leucocephala*	Leaves	Higher antioxidant activity exceeded that of ascorbic acid and the other non-acylated isolated compounds	(Haggag *et al.*, 2011)
Acylated kaempferol and quercetin rhamnosides	*Sophora japonica*	Root barks	Significant antibacterial activity against *Staphylococcus aureus* and moderate antibacterial activity against *Klebsiella pneumonia*, whereas the concurrently isolated non-acylated flavonol glycoside, exhibited no antimicrobial activity against the tested bacterial species	(Si *et al.*, 2016)

semi-preparative HPLC, or a combination of these. In addition, their structures were identified through interpretation of their MS, NMR, and UV spectral data. Acylated polyphenolics isolated from family Fabaceae along with their reported biological activities and methods of their isolation and structure elucidation are summarised in Table S2.

Acylated anthocyanins

Several blue coloured acylated delphinidin-based anthocyanins (1)–(15) were isolated from *Clitoria ternatea* flowers (Terahara *et al.*, 1989, 1990a, 1990b, 1990c, 1990d, 1996, 1998). Their structures are represented in Fig. 1 (Mukherjee *et al.*, 2008) and they were reported to exert potent antiproliferative activity (Jeyaraj *et al.*, 2021).

Acylated catechins

Two dimeric procyanidins; (16) and (17), along with three monomeric acylated catechins (18)–(20), were isolated as novel compounds from *Inga umbellifera* young leaves (Lokvam *et al.*, 2004). Their structures are represented in Fig. 2.

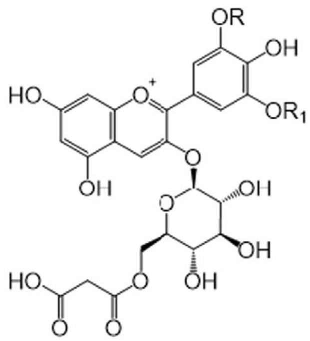
Acylated flavonoid glycosides

The isolation of a large number of acylated flavonoid derivatives has been reported from other fabaceous members, especially flavonols having either kaempferol or quercetin nuclei to which a sugar moiety (consisting of one or more sugar units) is attached at position 3. Besides, others were stated to be isorhamnetin and myricetin derivatives mostly having another sugar moiety at position 7 as represented in Fig. 3. Examples of acylated flavonoids isolated from *Pisum sativum* shoots (21)–(24) (Ferreres *et al.*, 1995), *Onobrychis viciifolia* aerial parts (25)–(34) (Veitch *et al.*, 2011), *Vicia angustifolia* leaves and stems (35)–(36) (Takemura *et al.*, 2002), *Astragalus caprinus* leaves (37) and (38) (Semmar *et al.*, 2005), *Baphia nitida* leaves (39) and (40) (Chaabi *et al.*, 2010), *Astragalus gombiformis* aerial parts (41)–(43) (Montoro *et al.*, 2013), *Tipuana tipu* leaves (44) (Amen *et al.*, 2015), *Lens culinaris* aerial parts (45)–(50) (Rolnik *et al.*, 2020), *Ceratonia siliqua* seeds (51) (Gohar *et al.*, 2009), *Leucenia leucocephala* leaves (52) (Haggag *et al.*, 2011), *Mimosa pigra* leaves (53)–(54) (Okonkwo *et al.*, 2016; Phuong *et al.*, 2017), *Pterogyne nitens* fruits (55) (Regasini *et al.*, 2008), *Sophora japonica* root barks (56)–(58) (Si *et al.*, 2016), and *Caesalpinia ferrea* leaves (59) and (60) (Hussein *et al.*, 2016), are presented in Table S2.

Acylated polyphenolics tentatively identified *via* LC/MS metabolite profiling of Fabaceous extracts

Besides the previously mentioned compounds (Table S2 and Figs 1–3), LC/MS metabolite profiling of different legume extracts allowed the tentative identification of many acylated and non-acylated anthocyanins and flavonoids (Picariello *et al.*, 2017; Farag *et al.*, 2020). Acylated polyphenolics tentatively identified in legumes through LC/MS investigation are recorded in Table S3.

Fenugreek (*Trigonella foenum-graecum*) was found to be a treasure house of acylated flavonoid glycosides. Two reports were traced dealing with investigation of the phenolic composition of fenugreek crude (Benayad *et al.*, 2014a) and germinated (Benayad *et al.*, 2014a, 2014b) seeds by LC–DAD–ESI-MS analysis. These studies revealed the presence of several acylated derivatives of apigenin, luteolin and kaempferol glycosides, esterified with ferulic, gallic, quinic, malonic and acetic acids, in both seed samples. Moreover, the acylated derivatives of flavone glycosides represented about 30% of the total composition of the germinated seeds (Benayad *et al.*, 2014b).



Compound No.	Name	R	R_1
(1)	Ternatin A1	GCGCG	GCGCG
(2)	Ternatin A2	GCGCG	GCG
(3)	Ternatin A3	GCG	GCG
(4)	Ternatin B1	GCGCG	GCGC
(5)	Ternatin B2	GCGC	GCG
(6)	Ternatin B3	GCGCG	GC
(7)	Ternatin B4	GCG	GC
(8)	Ternatin C1	GCGC	G
(9)	Ternatin C2	GCGCG	G
(10)	Ternatin C3	GC	G
(11)	Ternatin C4	GCG	G
(12)	Ternatin C5	G	G
(13)	Ternatin D1	GCGC	GCGC
(14)	Ternatin D2	GCGC	GC
(15)	Ternatin D3	GC	GC

G: glucose, C: *p*-coumaric acid

Figure 1 Structures of Ternatins isolated from *Clitoria ternatea* flowers.

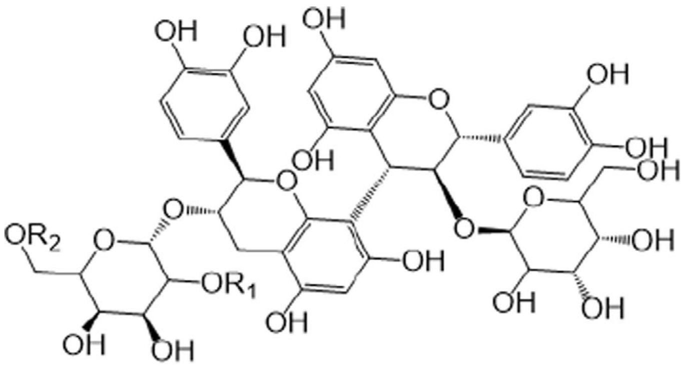
Medicago truncatula proved itself as a wellspring of acylated flavonoid glycosides. Actually, several apigenin, chrysoeriol, tricin and formononetin derivatives esterified with ferulic, coumaric, sinapic and malonic acids, were identified in the leaves through HPLC–MS/MS analysis (Jasiński *et al*., 2009; Marczak *et al*., 2010).

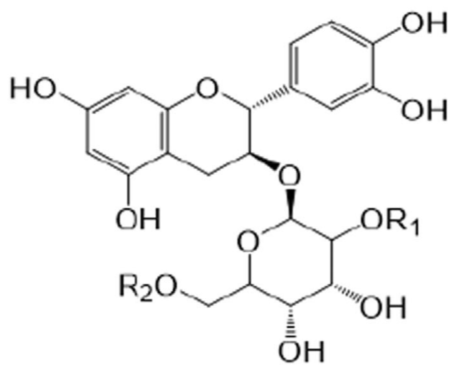
Upon investigation of the metabolic composition of *Anthyllis vulneraria* aerial parts using HPLC-ESI-MS^n, several phenolic compounds were tentatively identified, among these were eleven flavonoid glycosides acylated with meglutol (3-hydroxy-3-methyl glutaric acid), ferulic, and acetic acids. They were found to have kaempferol, methyl kaempferol, methyl, and dimethyl quercetin nuclei (Lorenz *et al*., 2020).

Vigna unguiculata seeds are as well considered a promising source of acylated quercetin glycosides; in fact different quercetin glycosides acylated with ferulic, sinapic, succinic, malonic and acetic acids were identified by LC–MS analysis (Ojwang *et al*., 2012; Hachibamba *et al*., 2013; Nderitu *et al*., 2013).

In addition, *Lathyrus cicera* was found to be very rich in acylated flavonol glycosides. Indeed, cinnamoyl, feruloyl, *p*-coumaroyl, dihydrophaseoyl and malonyl derivatives of kaempferol glycosides were tentatively identified in the seeds (Ferreres *et al*., 2017), whereas acylated quercetin and kaempferol tri- and tetraglycosides were traced and tentatively identified in the aerial parts, by HPLC-ESI-MS^n analysis (Llorent-Martínez *et al*., 2017).

HPLC-DAD-MS^n investigation of *Pisum sativum* leaves led to the detection of several acylated derivatives of kaempferol and quercetin sophorotriosides;





(16) R_1=H R_2= cinnamoyl

(17) R_1= cinnamoyl R_2=H

(18) R_1=H R_2= cinnamoyl

(19) R_1= cinnamoyl R_2=H

(20) R_1= R_2= cinnamoyl

Figure 2 Structures of acylated catechins isolated from *Inga umbellifera* young leaves.

including caffeoyl, coumaroyl, sinapoyl and feruloyl derivatives (Neugart *et al*., 2015).

Concerning *Lens culinaris*, galloyl derivatives of procyanidin and prodelphinidin monomers and dimers were identified in the seeds by HPLC-ESI-MS analysis (Amarowicz *et al*., 2009); whereas, *p*-coumaroyl derivatives of kaempferol glycosides alongside gallate and digallate procyanidin dimers, and catechin gallate were detected in the sprouts through HPLC-DAD-MS (Troszyńska *et al*., 2011).

UHPLC–PDA–qTOF-MS analysis was performed on leaves and shoots of eight *Bauhinia* species for elucidation of their metabolic profiles. Several acylated and non-acylated polyphenolics were detected in the investigated samples. Among the identified acylated polyphenolics galloyl- and cinnamoyl-derivatives of catechin, quercetin, and kaempferol were mentioned (Farag *et al*., 2015).

Concerning lupine, malonylated derivatives of glycosylated isoflavones (genistein, hydroxygenistein, luteone, and wighteone), flavonols (kaempferol, isorhamnetin, and quercetin), flavanone (naringenin), and flavones (luteolin, chrysoeriol, apigenin, and acacetin) were identified in leaves and roots of four lupine species (*Lupinus albus*, *L. angustifolius*, *L. luteus* and *L. mutabilis*) by LC-ion trap and UPLC-qToF-MS analyses (Wojakowska *et al*., 2013). In addition, UPLC-PDA-ESI–qTOF-MS analysis of the seeds of four *Lupinus* species; *L. polyphyllus, L.s angustifolius, L. luteus* and *L.s hispanicus*, led to the tentative identification of genistein malonyl and feruloyl derivatives (Farag *et al*., 2019).

Furthermore, *Vicia faba* is claimed to be a rich source of acylated polyphenolics including acylated flavonoids, procyanidins, and catechins. Acetylated kaempferol glycosides were detected in the leaves of the cited plant by HPLC-DAD-ESI-MS^n (Neugart *et al*., 2015). Meanwhile, gallate and digallate procyanidin dimers were identified in the beans through HPLC-DAD-MS analysis along with catechin gallate and two procyanidin gallates (Amarowicz & Shahidi, 2017). In addition, two dihydro ferulic acid derivatives of vicin were detected in *Vicia faba* var. *minor* beans by high-resolution LC–MS/MS analysis (Kowalczyk *et al*., 2021).

Other Fabaceae members were reported to contain lesser numbers of acylated polyphenolic compounds either as major or minor constituents. For example, Rp-HPLC-DAD-ESI-MS/MS analysis of *Periandra dulcis* roots revealed the presence of three minor acylated quercetin, myricetin, and rhamnetin glycosides (detected as malonyl galloyl, galloyl and acetyl derivatives, respectively), beside one major acetylated myricetin glycoside (Negri & Tabach, 2013). Likewise, two cinnamoyl derivatives of kaempferol; hydroxy and methoxy cinnamoyl kaempferol, were detected as minor constituents in *Astragalus caprinus* leaves by HPLC–MS analysis (Semmar *et al*., 2001). In addition, a malonyl pelargonidin glucoside was reported as a minor constituent in black soybean (*Glycine max*)

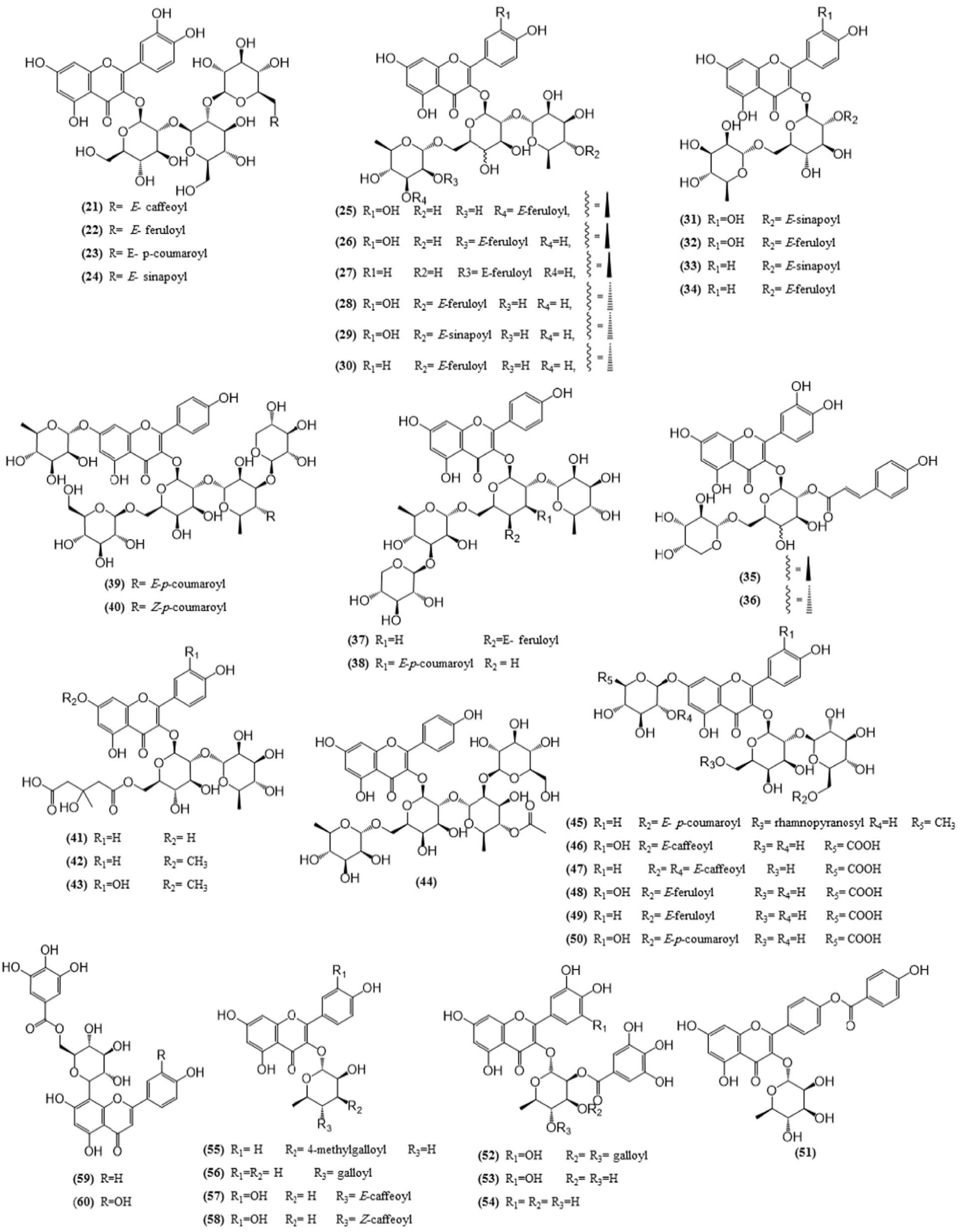


Figure 3 Structures of acylated flavonoid glycosides isolated from Fabaceous plants.

upon HPLC-ESI-MS analysis (Koh *et al.*, 2014). Besides, an acylated quercetin glucoside was detected in *Phaseolus vulgaris* var. *Pinta* by HPLC-PAD and LC-MS-ESI analysis. The study also investigated the effect of soaking, cooking and dehydration of the beans on their phenolic composition and results revealed that many phenolic compounds, including the acylated quercetin glucoside, were not detected in the cooked and dehydrated samples (Aguilera *et al.*, 2011). Finally, anthocyanins in *Pachyrhizus ahipa* root were identified through HPLC-MS analysis, that displayed the presence of six different anthocyanins, two of these were confirmed to be acylated based on their absorbance spectra (Dini *et al.*, 2020).

A comparative Rp-HPLC-DAD and nanoflow-HPLC MS/MS analysis of three South American algarrobo species (*Prosopis alba*, *P. nigra* and *P. ruscifolia*) and European carob (*Ceratonia siliqua*) seed germs revealed the presence of two feruloylated derivatives of apigenin diglycoside as major constituents in *Ceratonia siliqua* seed germ extract and as trace constituents in those of *Prosopis* species (Picariello *et al.*, 2017).

Additionally, UPLC-MS investigation of the sprouts of *Cicer arietinum*, *Lens esculenta*, *Vicia faba*, and *Trigonella foenum-graecum*, respectively was carried out. The analysis revealed the presence of sinapoyl, malonyl and acetyl derivatives of kaempferol hexoside alongside acetyl derivatives of naringenin, pentahydroxy flavone and formononetin hexosides in *Cicer arietinum* sprouts, while only acetylated and feruloylated kaempferol glycosides were detected in those of *Vicia faba* (Farag *et al.*, 2020).

Conclusion

Plant polyphenolics, especially those acylated, display potential bioactivities in a wide variety of pathological conditions including cancer, inflammation and diseases resulting from oxidative stress and bacterial infections. This article aimed to overview and summarise the previous studies concerned with the distribution, isolation, chemodiversity, and bioactivity of acylated polyphenolics derived from several fabaceous plants. These acylated polyphenolics proved to be more stable and biologically active than the non-acylated ones. Biological studies of the isolated acylated polyphenolics confirmed their numerous health benefits including antioxidant, cytotoxic, anti-inflammatory, antibacterial, and platelet modulating activities. In this respect, these secondary metabolites are considered important targets for further exploitation in drug industry. Consequently, extensive trials for their isolation from plants belonging to family Fabaceae are recommended. In addition, intensive biological investigation and clinical trials ought to be carried out to confirm both the safety and efficacy of these secondary metabolites aiming to facilitate implementation of these natural products in pharmaceuticals for skincare, weight loss regulation products, and for treatment of other ailments.

Conflict of interest

The authors confirm that they have no conflicts of interest.

Ethical approval

Ethics approval was not required for this research.

Author contributions

Asmaa Khalil: Conceptualization (equal); methodology (equal); writing – original draft (equal); writing – review and editing (equal). **Omar Sabry:** Conceptualization (equal); methodology (equal); writing – review and editing (equal). **Hesham Askary:** Conceptualization (equal); methodology (equal); supervision (equal); writing – review and editing (equal). **Soheir Elzalabani:** Conceptualization (equal); methodology (equal); writing – review and editing (equal). **Nesrin Fayek:** Conceptualization (equal); methodology (equal); supervision (equal); writing – original draft (equal); writing – review and editing (equal).

Data availability statement

Data availability is not applicable to this article as new data were neither created nor analysed in this study.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Figure S1. Structures of the Most Common Esterifying Acids in Acylated Polyphenolics Reported in Family Fabaceae.

Table S2. Acylated Polyphenolics Isolated from Fabaceous Plants and Their Biological Activities.

Table S3. Acylated Polyphenolics Detected and Tentatively Identified in Fabaceous Plants Extracts Via LC/MS Analysis.