Tannins and Flavonoids from the *Erodium cicutarium* Herb

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A new depside, erodiol, was isolated and identified from the aerial parts of *Erodium cicutarium* (Geraniaceae), together with essential compounds such as: geraniin, didehydrogeraniin, corilagin, (–) 3-*O*-galloylshikimic acid, methyl gallate 3-*O*-β-D-glucopyranoside, rutin, hyperin, quercetin 3-*O*-(6"-*O*-galloyl)-β-D-galactopyranoside, isoquercitrin and simple phenolic acids. Their chemical structures were elucidated by means of spectroscopic (ESI MS, HRESI MS, 1D and 2D NMR) evidence.

Key words: Didehydrogeraniin, *Erodium cicutarium*, Erodiol, Geraniin, Hyperin 6"-Gallate

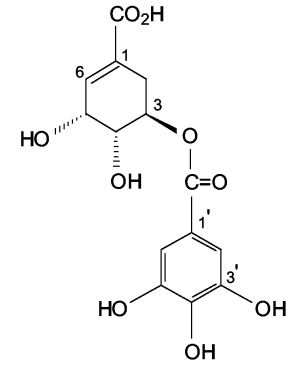
Introduction

E. cicutarium (common stork's bill) is an annual or biannual herb native to Europe, Asia and North America. Extracts from common stork's bill herb were used in traditional medicine as antidiarrheic, diuretic, hemostatic, stomachic and antihemorrhageic drugs [1, 2]. Previous studies revealed the presence of geraniin as the main constituent, and two flavonol glycosides, rutin and isoquercitrin [3, 4]. Gallic acid, gallic acid methyl ester, protocatechuic acid, ellagic acid, brevifolin and brevifolin carboxylic acid, were found in the hot methanol extract [5].

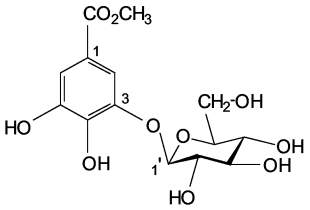
In this paper, we report the isolation and the structure elucidation of tannins, flavonol glycosides and a new depside which are present in the aqueous and aqueous acetone extracts of *Erodium cicutarium* herb.

Results and Discussion

The aqueous acetone extract of the dried aerial parts of *Erodium cicutarium* was subjected to a combination of column chromatography over octadecyl and Sephadex LH-20 to afford the new compound, erodiol (**7**) along with two gallotannins (**2, 4**), three ellagitannins (**5, 6, 8**), four flavonoid glycosides (**9 – 12**) and two phenolcarboxylic acids (**1, 3**). The presence of gallic acid and protocatechuic acid in erodiol was preliminary indicated by acid hydrolysis (2 M aqueous HCl, 60 min, 100 °C), and alkaline hydrolysis (2 M NaOH, 30 min, r.t.). The HRESI MS (MeOH, NH_4OAc) of compound **7** showed the $[M\text{-}NH_4]^-$ ion peak at *m/z* 305.2281 which corresponds to the molecular formula $C_{14}H_8O_7$. Its ^{13}C NMR spectrum revealed the presence of twelve carbon signals in which we observed two ester bonds (δ = 165.29, 164.20) and five methines (DEPT 90: δ = 124.31, 117.83, 115.92, 104.66, 101.48) together with other five carbons (δ = 154.80, 151.27, 145.62, 122.39, 100.42). These results suggested the compound to be an ester of gallic acid and protocatechuic acids, most probably a depside with

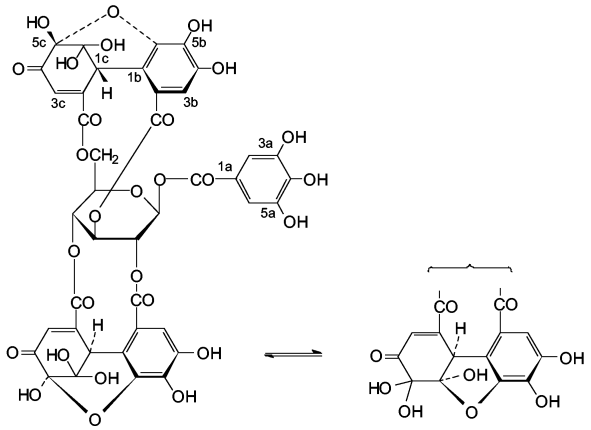


(–) 3-*O*-Galloylshikimic acid (**2**).

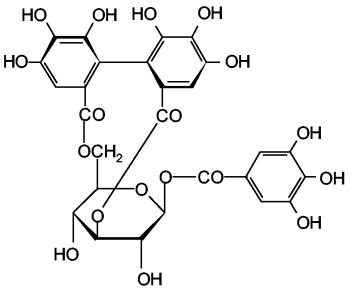


Methyl gallate 3-*O*-β-D-glucopyranoside (**4**).

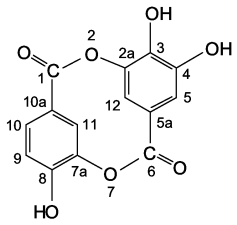
DHHDP



Didehydrogeraniin (**5**).



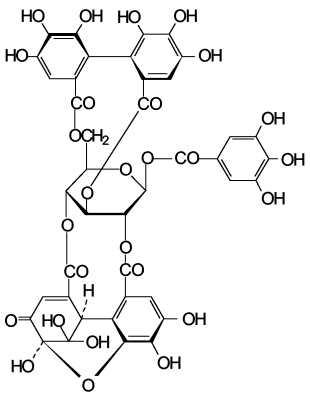
Corilagin (**6**).



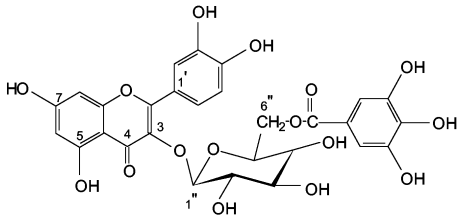
Erodiol (**7**).

two internal esterified carbonyl functions. To find out how both acids are incorporated in the molecule of **7**, the resonance in the ^{1}H NMR spectrum was assigned on the basis of splitting and chemical shift values (Table 1). The assignments were then confirmed by a ^{1}H-^{1}H COSY experiment. Only five aromatic protons as four doublets at $\delta = 7.48$ ($^4J = 2.0$ Hz, H-11), 6.81 ($^3J = 8.2$ Hz, H-9), 6.19 ($^4J = 2.3$ Hz, H-12), 6.13 ($^4J = 2.3$ Hz, H-5), and a single double doublet at $\delta = 7.43$ ($^3J_1 = 8.2$, $^4J_2 = 2.0$ Hz, H-10) were detected in the ^{1}H spectrum. The ^{1}H-^{1}H COSY spectrum (Fig. 1) exhibited two correlation signals in the aromatic region. The first intensive one, between protocatechuic acid moiety protons due to the three-bond coupling at positions H-9 and H-10 and the second one, between gallic acid moiety protons due to the four-bound coupling at H-5 and H-12 of the analyzed compound. The chemical structure of erodiol (**7**) was finally confirmed by comparison of detected carbon signals with analogous data of protocatechuic acid, methyl gallate and ellagic acid (Table 2). On basis of the above evidence, the structure of erodiol is represented by **7**. This natural depside has been isolated for the first time.

HHDP



Geraniin (**8**).



Quercetin 3-*O*-(6”-O-galloyl)-β-D-galactopyranoside (**9**).

Compounds **1** and **3** have been identified with authentic samples as gallic acid and protocatechuic acid using chromatographic techniques (HPLC, TLC). The structures of following compounds have been determined by comparison of their UV, ^{1}H NMR, ^{13}C NMR and MS data with literature values as: **2** (–) 3-*O*-galloylshikimic acid [6], **4** methyl gallate 3-*O*-β-D-glucopyranoside [7], **5** didehydrogeraniin (dehydrogeraniin) [8, 9], **6** corilagin [10], **8** geraniin [1, 10 – 13], **9** 3-*O*-(6”-*O*-galloyl)-β-D-galactopyranoside [14 – 16], **10** rutin, **11** hyperin and **12** isoquercitrin [14, 16]. The assignments of the ^{1}H and ^{13}C NMR chemical shift values on the galactose moiety of **9** were also confirmed by a ^{1}H-^{13}C HMQC correlation.

Table 1. ^{1}H NMR (300 MHz) data of methyl gallate (**1a**), protocatechuic acid (**3**), methyl gallate 3-*O*-β-D-glucopyranoside (**4**), erodiol (**7**) and ellagic acid (**13**).

Proton	1a[a]	3[a]	4[a]	7[a]	13[b]
Gallic moiety					
2	7.42 s		7.45 d (1.7)	6.19 d (2.3)	7.39 s
6	7.42 s		7.60 d (1.7)	6.13 d (2.3)	7.39 s
Protocatechuic moiety					
2’		7.48 d (2.0)		7.48 d (2.0)	
5’		6.82 d (8.2)		6.81 d (8.2)	
6’		7.42 dd (8.2, 2.0)		7.43 dd (8.2, 2.0)	
OMe	3.82 s		3.99 s		
Glucose					
1			5.14 d (6.9)		
2			3.94 dd (12.3, 4.6)		
3			3.79 d (3.3)		
4			4.07 d (12.1)		
5			3.76 m		
$6_1, 6_2$			3.71 m		

[a] CD_3COCD_3-D_2O (3+2); [b] DMSO-d_6; *J* values are given in parentheses as Hz.

Table 2. ^{13}C NMR (75 MHz) data of methyl gallate (**1a**), protocatechuic acid (**3**), methyl gallate 3-*O*-β-D-glucopyranoside (**4**), erodiol (**7**) and ellagic acid (**13**).

Carbon	1a[a]	3[a]	4[a]	7[a]	13[b]
Gallic moiety					
1	120.64		120.39	100.42	106.05
2	111.89		112.15	115.84	112.61
3	145.30		145.18	122.39	136.26
4	140.57		140.14	145.62	141.38
5	145.30		145.34	151.27	148.42
6	111.89		110.06	101.42	109.49
CO_2R	167.77		167.92	164.20	159.37
Protocatechuic moiety					
1’		121.27		100.42	
2’		116.58		117.75	
3’		144.96		122.39	
4’		150.06		154.80	
5’		115.78		104.56	
6’		122.43		124.20	
CO_2R		167.68		165.29	
OMe	52.54		52.30		
Glucose					
1			101.89		
2			73.08		
3			75.68		
4			69.54		
5			76.46		
6			60.72		

[a] CD_3COCD_3-D_2O (3+2); [b] DMSO-d_6.

The total yield (HPLC, Fig. 2) of analyzed compounds from a dried herb was as follows: gallic acid 0.19% (**1**), methyl gallate 0.26% (**1a**), (–) 3-*O*-galloylshikimic acid 1.02% (**2**), protocatechuic acid 0.14% (**3**), methyl gallate 3-*O*-β-D-glucoside 0.24% (**4**), didehydrogeraniin 1.50% (**5**), corilagin 0.65% (**6**), erodiol below 0.01% (**7**), geraniin 3.06% (**8**), 3-*O*-(6”-*O*-galloyl)-β-D-galactoside 0.28% (**9**), rutin 0.33% (**10**), hyperin (**11**) and isoquercitrin (**12**) as a sum 0.16%, ellagic acid 0.46% (**13**).

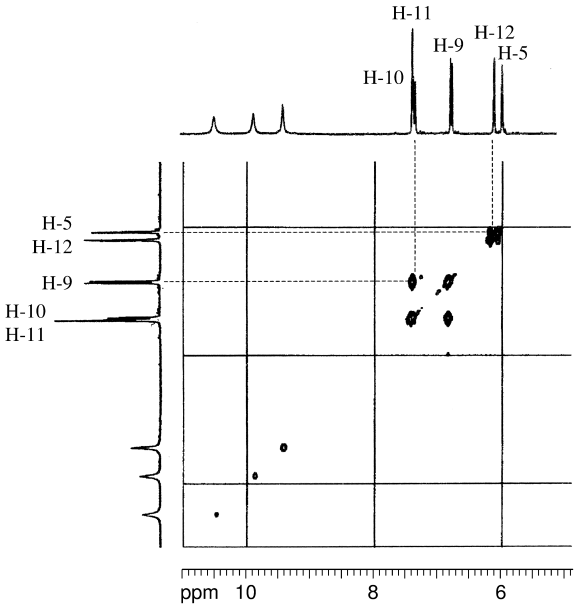


Fig. 1. ^{1}H-^{1}H-COSY spectrum of compound **7** in CD_3COCD_3.

Methyl gallate 3-*O*-β-D-glucoside, (–) 3-*O*-galloylshikimic acid and corilagin were early reported by Lin and Lin [7] in *Erodium moschatum*. Didehydrogeraniin and 3-*O*-(6”-*O*-galloyl)-β-D-galactoside isolated here for the first time from the *E. cicutarium* herb had been previously isolated from *Geranium thunbergii* [8] and *Euphorbium platiphyllos* [15].

Among the genera belonging to the Geraniaceae, *Erodium* L’Hérit. and *Geranium* L. are known to be rich in ellagitannins and gallotannins. The main ellagitannin of all investigated species from both genera has been shown to be geraniin [1, 3, 7, 13, 17]. The differences of a chemical composition are observed between gallotannins and flavonoid glycosides. The species from *Erodium* contain galloylshikimic acids and methyl gallate 3-*O*-β-D-glucoside among gallotannins and rutin or isoquercitrin as the major flavonoid [4, 7]. However, the genus *Geranium* shows a presence of galloylquinic acids, 1,6-di-*O*-galloyl-β-D-glucose and hyperin [7, 17, 18]. Thus, 3-*O*-(6”-*O*-galloyl)-β-D-galactoside (hyperin 6’-gallate) separated from *E. cicutarium* could be considered as a significant chemosystematic agent.

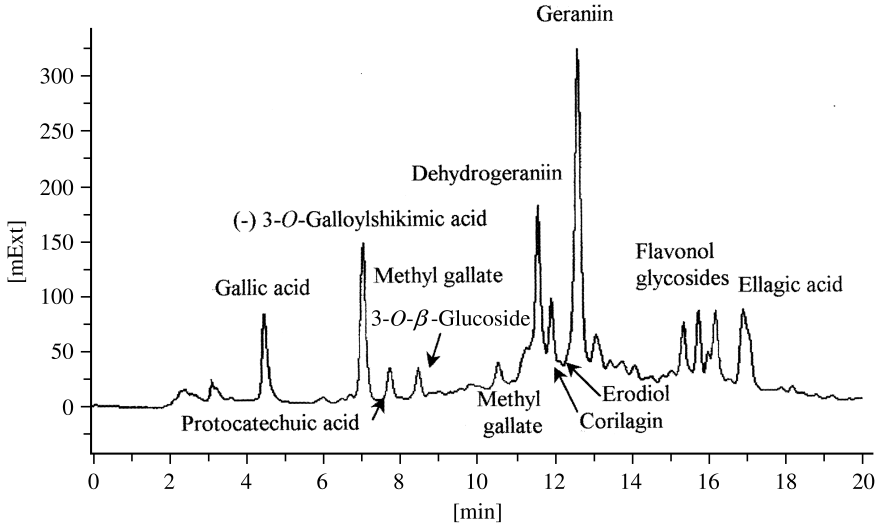


Fig. 2. HPLC chromatogram of aqueous extract from *Erodium cicutarium* herb.

Experimental Section

General

UV spectra were recorded on a Perkin Elmer UV/VIS Lambda 20 spectrometer (MeOH) and IR spectra on a Unicam SP 1000 spectrometer (KBr disc). Optical rotation was measured in MeOH or acetone-water (8 : 2) on an Autopol IV digital polarimeter. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), DEPT 90, COSY, HMQC experiments were recorded on a Bruker WM 52 spectrometer using the residual solvent peaks as internal standard. ESI MS were recorded in MeOH with addition of NaOAc or NH_4OAc on a Finningan Mat TSQ 700 and LSI MS on a AMD 604 using glycerol as a matrix. Column chromatography was performed using Bakerbond Octadecyl (C18, 40 μm) and Pharmacia Sephadex LH-20. HPLC was conducted with a Knauer system (Germany), equipped with two pumps (type 64), a sample injector, a variable wave length UV detector (type 87.00) and a LiChroCART® 100 RP-18 (5 μm; Merck, Germany) column (250-4) with a pre-column (4-4). Detection was carried out at 280 nm. The flow rate was set to 1.0 ml/min. Analyzed compounds were separated using an acetonitrile-water gradient with formic acid addition according to the solvent program: solvent A, 5% formic acid in acetonitrile; solvent B, 5% formic acid in water; starting from 10% A in B in 2 min, up to 30% A in 17 min and to 70% A in 20 min. A 20 μl volume of analyzed samples was injected. For the HPLC analysis gradient grade acetonitrile was used (Merck, Germany). Water was glass-distilled and deionized. Solvent solutions were vacuum degassed with sonication prior to usage. For TLC separations cellulose plates (Merck, Germany) and solvents A, B, C or silica gel precoated plates (Merck, Germany) and solvents D, E, F were used. The composition of the applied solvent system was as follows: (A) 7% acetic acid [8,12]; (B) FSW: sodium formate – formic acid – water (10 : 1 : 200); (C) forestal: glacial acetic acid – chloric acid – water (15 : 3 : 82); (D) ethyl formate – acetone – formic acid (7 : 2 : 1); (E) toluene – acetone – formic acid (7 : 2 : 1); (F) ethyl acetate – glacial acetic acid – formic acid – water (100 : 11 : 11 : 26) [19]. Chromatograms were developed in a horizontal teflon DS-chamber (Chromdes, Poland) at a distance of 9 cm from the origin. Coloured compounds were detected under UV light (254, 365 nm) and by spraying with 1% methanolic $FeCl_3$, *bis*-diazotized sulphanilamide (tannins), $NaNO_2$-AcOH reagent (ellagitannins) [20] or with 1% methanolic $AlCl_3$ (flavonoids). All experiments were performed at room temperature (20 °C). Methyl gallate (1a) was purchased from Fluka (Germany), gallic acid (1), protocatechuic acid (3) and ellagic acid (13) from Extrasynthése (France).

Plant material

The aerial parts of *Erodium cicutarium* (L.) L'Hérit. (Geraniaceae) at the flowering stage were collected in September [17] from a natural habitat (Poland). The fresh plant material was dried at room temperature with forced ventilation. A voucher specimen was deposited in the Herbal Collection of our Department.

Extraction and isolation

The powdered plant material (200 g) was three times extracted with a water and acetone mixture (1 : 1, 2500 ml) at room temperature [17, 21]. The filtrate was evaporated to yield a dark brown aqueous residue (200 ml) which was acidified with 1 ml of 98% formic acid and adsorbed on the octadecyl column (5 × 45; J. T. Baker, USA). Phenolic

compounds were fractionated using a water-methanol solvent gradient (9 + 1, 8 + 2, 7 + 3, 6 + 4, 5 + 5, 0 + 10; v/v). Elutes with a similar chromatographic profile were combined and concentrated to afford ten fractions (Frs. I – X). Frs. I – III were eluted with (9 + 1), Frs. IV – VI with (8 + 2), Frs. VII – VIII with (7 + 3) and Frs. IX – X with (6 + 4). After evaporation of solvents and recrystallization, Frs. I and III yielded compound **1** (214 mg) and **3** (135 mg). Final purification of the other fractions was carried out on Sephadex LH-20 (5 × 50; Pharmacia, Sweden) with acetone, methanol or acetone-methanol mixtures (v/v). Compounds **2** (132 mg), **4** (67 mg) and **5** (90 mg) were achieved from Frs. II, IV and V using acetone-methanol (8 + 2). Fr. VI was purified using acetone-methanol (7 + 3) and yielded compound **6** (76 mg). Fr. VII was first eluted with pure acetone to give compound **7** (20 mg) and next with acetone-methanol (8 + 2) to yield compound **8** (150 mg). Frs. VIII, IX and X were eluted with pure methanol to produce compounds **9** (93 mg), **10** (220 mg) and **11** (38 mg), **12** (20 mg) respectively.

To obtain an aqueous extract, boiling distilled water (100 ml) was poured over the powdered herb (0.625 g) and, after 15 min, passed through filters (Whatman No 1, Millipore 0.22 μm). Aqueous extracts were analyzed by HPLC (Fig. 2).

(–) 3-O-Galloylshikimic acid (**2**)

Colourless needles (acetone). – M. p. 256-257 °C. – $[\alpha]_D^{20}$ – 111.5° ($c = 0.5$, acetone-water). – UV/vis (MeOH): λ_{max} = 215, 277 nm. – IR (KBr): ν_{max} = 3340 (O-H), 1700 (C=O), 1610, 1450 (C=C), 1360 (C-H), 1230, 1100, 1040 (C-O), 780 cm^{-1}. – ^{1}H NMR (300 MHz, CD_3COCD_3+D_2O): δ = 7.36 (s, 2 H, H-2',6'), 6.98 (d, J = 1.6 Hz, 1 H, H-6), 5.51 (m, 1 H, H-3), 4.75 (br s, 1 H, H-5), 4.26 (dd, J = 7.2, 4.2 Hz , 1 H, H-4), 3.07 (dd, J = 18.5, 4.2 Hz, 1 H, H-2), 2.60 (dd, J = 18.5, 4.2 Hz, 1 H, H-2). – ^{13}C NMR (75 MHz, CD_3COCD_3+D_2O): δ = 171.52 (CO_2H), 166.85 (CO_2R), 145.07 (2 C, C-3',5'), 138.58 (C-6), 134.23 (C-4'), 132.27 (C-1), 120.33 (C-1'), 109.48 (2 C, C-2',6'), 70.90 (C-3), 68.60 (C-4), 66.21 (C-5), 31.58 (C-2). – ESI MS (4.5 kV, MeOH): *m/z* (%) = 325.4 (56) [M]$^-$ for $C_{14}H_{14}O_9$ (calcd. 326.2556).

Methyl gallate 3-O-β-D-glucopyranoside (**4**)

Off-white powder (acetone). – $[\alpha]_D^{20}$ – 59.5° ($c = 0.5$, acetone-water). – UV/vis (MeOH): λ_{max} = 220, 268 nm. – IR(KBr): ν_{max} = 3360 (O-H), 1710 (C=O), 1600, 1530, 1460 (C=C), 1375 (C-H, OMe), 1250, 1162, 1080, 1040 (C-O), 780 cm^{-1}. – ^{1}H NMR (Table 1). – ^{13}C NMR (Table 2). – ESI MS (4.5 kV, MeOH+NaOAc): *m/z* (%) = 368.8 (44) [M-Na]$^-$, 714.7 (100) [2M-Na]$^-$ for $C_{14}H_{18}O_{10}$ (calcd. 346.2862).

Didehydrogeraniin (dehydrogeraniin) (**5**)

Yellow powder (acetone). – $[\alpha]_D^{20}$ – 136.0° ($c = 0.5$, MeOH). – UV/vis (MeOH): λ_{max} = 221, 280 nm; IR (KBr): ν_{max} = 3400 (O-H), 1700 (C=O), 1610, 1510, 1440 (C=C), 1430 (C-H), 1330, 1210, 1080, 1030 (C-O), 755 cm^{-1}. – ^{1}H NMR (300 MHz, CD_3COCD_3+D_2O): δ = 7.48 (s, 2 H, galloyl), 7.47, 7.44 (2xs, 2 H, ArH DHHDP), 7.19, 7.06 (2 × s, 2 H, vinyl DHHDP), 6.57 (d, J = 3.0 Hz, 1 H, H-1 β-D-glucose), 5.90 (d, J = 1.5 Hz, 1 H, H-3 glucose), 5.83, 5.63 (2 × s, 2 H, methine DHHDP), 5.21 (d, J = 1.0 Hz, 1 H, H-2 glucose), 4.91 (m, 2 H, H-6$_1$,4 glucose), 4.56 (m, 1 H, H-5 glucose), 3.67 (br s, 1 H, H-6$_2$ glucose). – ^{13}C NMR (75 MHz, CD_3COCD_3+D_2O): δ = 168.58, 166.63, 165.90, 165.65, 164.89 (all CO_2R), galloyl: 145.03 (2 C, C-3a,5a), 139.26 (C-4a), 119.18 (C-1a), 110.11 (2 C, C-2a,6a), DHHDP: 195.77, 194. 32 (2 × C-4c DHHDP), 145,21, 144.63 (2 × C-2c), 144.21, 144.07 (2 × C-4b), 143.97, 143.02 (2 × C-6b), 139.35, 136.68 (2 × C-5b), 135.93, 134.07 (2 × C-3c), 124.29, 123.88 (2 × C-2b), 116.25, 115.75 (2 × C-1b), 115.28, 114.69 (2 × C-3b), 109.50, 108.51 (2 × C-6c), 107.59, 78.41 (2 × C-5c), 54.77, 34.77 (2 × C-1c), glucose: 94.04 (C-1), 72.55 (C-5), 69.41 (C-2), 67.80 (C-4), 63.74 (C-3), 63.54 (C-6). – ESI MS (4.5 kV, MeOH+NH_4OAc) *m/z* (%) = 987.6 (54) [M-NH_4]$^+$ for $C_{41}H_{28}O_{28}$ (calcd. 968.6442).

Corilagin (**6**)

White amorphous powder (acetone). – $[\alpha]_D^{20}$ – 190.0° (c = 1.0, acetone-water). – UV/vis (MeOH): λ_{max} = 217, 270 nm. – IR (KBr): ν_{max} = 3350 (O-H), 1720 (C=O), 1620, 1520, 1450 (C=C), 1340 (C-H), 1210, 1040 (C-O), 760 cm^{-1}. – ^{1}H NMR (300 MHz, CD_3COCD_3+D_2O): δ = 7.41 (s, 2 H, galloyl), 7.06, 6.85 (2 × s, 2 H, ArH HHDP), 6.63 (br s, 1 H, H-1 β-D-glucose), 6.06 (m, 1 H, H-6$_1$ glucose), 5.10 (m, 1 H, H-3 glucose), 4.81 (t, 1 H, H-5 glucose), 4.39 (br s, 1 H, H-4 glucose), 4.12 (t, 1 H, H-6$_2$ glucose), 4.05 (br s, 1 H, H-2 glucose). – LSI MS (20 eV, glycerol + DMSO): *m/z* (%) = 632.9 (37) [M]$^-$, 656.9 (10) [M-Na]$^+$ for $C_{27}H_{22}O_{18}$ (calcd. 634.4528).

Erodiol (**7**)

White powder (acetone). – $[\alpha]_D^{20}$ + 25.2° ($c = 0.5$, acetone-water). – M. p. 167 °C. – UV/vis (MeOH): λ_{max} = 210, 261, 299 nm. – IR (KBr): ν_{max} = 3310 (O-H), 1720 (C=O), 1616, 1525, 1460 (C=C), 1230, 1042 (C-O), 790. – ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 7.48 (d, ^4J = 2.0 Hz, 1 H, H-11), 7.43 (dd, ^3J = 8.2, ^4J = 2.0 Hz, 2 H, H-10), 6.81 (d, ^3J = 8.2, 1 H, H-9), 6.19 (d, ^4J = 2.3 Hz, 1 H, H-12), 6.13 (d, ^4J = 2.3 Hz, 1 H, H-5); – ^{13}C NMR (75 MHz, CD_3COCD_3): δ = 165.29 (C-1), 164.20 (C-6), 154.80 (C-8), 151.27 (C-4), 145.62 (C-3), 124.20 (C-10),

122.39 (2C-2a,7a), 117.75 (C-11), 115.84 (C-2), 104.56 (C-9), 101.42 (C-5), 100.42 (2C-5a,10a); – ESI MS (4.5 kV, MeOH+NH_4OAc) *m/z* (%) = 305.2(100) [M-NH_4] $C_{14}H_{14}O_9$ (calcd. 326.2556)$^-$; - HRESI MS *m/z* (%) = 305.2281 (100) [M-NH_4]$^-$ for $C_{14}H_8O_7$ (calcd. 288.2102).

Geraniin (**8**)

Yellow crystals (acetone). – $[\alpha]_D^{20}$ – 142.0° (c = 0.5, MeOH). – UV/vis (MeOH): λ_{max} = 220, 280 nm. – IR (KBr): ν_{max} = 3400 (O-H), 1720 (C=O), 1620, 1515, 1450 (C=C), 1355 (C-H), 1215, 1070 (C-O), 785 cm^{-1}. – ^{1}H NMR (300 MHz, CD_3COCD_3+D_2O): δ = 7.47 (s, 1 H, DHHDP), 7.45 (s, 2 H, galloyl), 7.19 (s, 1 H, vinyl DHHDP), 7.07, 6.88 (2 × s, 2 H, ArH HHDP), 6.61 (br s, 1 H, H-1 β-D-glucose), 5.85 (m, 3 H, H-2,4,6_1 glucose), 5.73 (s, 1 H, methine DHHDP), 4.85 (m, 2 H, H-3,6_2 glucose), 4.36 (m, 1 H, H-5 glucose). – ESI MS (4.5 kV, MeOH+NH_4OAc) *m/z* (%) = 969.9 (56) [M-NH_4]$^-$ for $C_{41}H_{28}O_{27}$ (calcd. 952.6452).

Quercetin 3-O-(6”-O-galloyl)-β-D-galactopyranoside (hyperin 6”-gallate) (**9**)

Yellow needles (methanol). – M. p. 202-205 °C. – UV/vis (MeOH): λ_{max} = 259, 270 sh, 360 nm; (MeOH+MeONa): λ_{max} = 273, 326, 411 nm; (MeOH+$AlCl_3$): 275, 308 sh, 420, 440; (MeOH+$AlCl_3$+HCl): λ_{max} = 270, 300 sh, 385, 415 nm; (MeOH+NaOAc): λ_{max} = 273, 370 nm; (MeOH+NaOAc+H_3BO_3): λ_{max} = 264, 297 sh, 380 nm; – IR (KBr): ν_{max} = 3352 (O-H), 1710, 1680 (C=O) 1640, 1632, 1542, 1480 (C=C), 1428 (C-H), 1326, 1256, 1182, 1140 (C-O), 864 cm^{-1}. – ^{1}H NMR (300 MHz, CD_3COCD_3+D_2O): δ = 8.24 (d, J = 2.1 Hz, 1 H, H-2’), 7.93 (dd, J = 8.5, 2.2 Hz, 1 H, H-6’), 7.28 (dd, J = 11.1, 2.6 Hz, 1 H, H-5’), 7.28 (s, 2 H, galloyl), 6.83 (d, J = 2.1, 1 H, H-8), 6.61 (d, J = 2.0 Hz, 1 H, H-6,), 5.52 (d, J = 7.8 Hz, 1 H, H-1” β-D-galactose), 4.56 (dd, J = 11.4, 5.4 Hz, 2 H, H-6”), 4.37 (d, J = 3.0 Hz, 1 H, H-4”), 4.29 (m, 1 H, H-5”), 4.22 (t, 1 H, H-2”), 3.97 (dd, J = 9.6, 3.3 Hz, 1 H, H-3”). – ^{13}C NMR (75 MHz, CD_3COCD_3+D_2O): δ = 178.20 (C-4), 166.71 (CO_2R galloyl), 164.40 (C-7), 161.10 (C-5), 157.52 (C-2), 156.94 (C-9), 148.60 (C-4’), 145.07 (2 C, C-3,5 galloyl), 144.44 (C-3’), 138.38 (C-4 galloyl), 134.26 (C-3), 122.06 (C-1’), 121.61 (C-6’), 120.12 (C-1 galloyl), 116.91 (C-5’), 116.44 (C-2’), 109.22 (2 C, C-2,4 galloyl), 104.34 (C-10), 103.38 (C-1”), 99.10 (C-6), 94.23 (C-8), 73.45 (C-3”), 73.25 (C-5”), 71.66 (C-2”), 68.72 (C-4”), 63.18 (C-6”); – ESI MS (4.5 kV, MeOH+NaOAc) *m/z* (%) = 639.0 (100) [M-Na]$^-$ for $C_{28}H_{24}O_{16}$ (calcd. 616.4816).

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