

Iridoids, Flavonoids and Monoterpene Glycosides from *Galium verum* subsp. *verum*

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Received 19.04.2005

From the aerial parts of *Galium verum* subsp. *verum* L. were isolated 7 iridoid glycosides, asperuloside (1), asperulosidic acid (2), deacetyl-asperulosidic acid (3), monotropein (4), 6-*O*-*epi*-acetylscandoside (5), daphylloside (6) and deacetyl-daphylloside (7); 2 flavonol glycosides, astragalín [= kaempferol 3-*O*- β -glucopyranoside] (8) and rutin [= quercetin 3-*O*-rutinoside] (9); and 2 monoterpene glycosides, betulalbuside A (10) and (2E)-2,6-dimethyl-2,7-octadien-1,6-diol-6-*O*- β -glucopyranoside (11). The structures of the isolates were established by 1D and 2D NMR spectroscopy in combination with IR, UV and ESI-MS analysis.

Key Words: *Galium verum* subsp. *verum*, Rubiaceae, iridoid glycosides, asperuloside, asperulosidic acid, deacetyl-asperulosidic acid, monotropein, 6-*O*-*epi*-acetylscandoside, daphylloside, deacetyl-daphylloside, flavonol glycosides, astragalín, rutin, monoterpene glycosides, betulalbuside A, (2E)-2,6-dimethyl-2,7-octadien-1,6-diol-6-*O*- β -glucopyranoside.

Introduction

Galium L. (Rubiaceae) is represented in Turkey by 101 species gathered in 10 sections^{1–3}. *G. verum* is used as a diuretic, choleric, antidiarrheal and sedative in folk medicine⁴. It was found that the methanolic extract of the aerial parts of *Galium verum* subsp. *verum* exhibits antioxidant effects⁵. The chemical composition of *Galium* species was determined as iridoids^{6–20}, anthraquinones^{21–27}, triterpenic saponins^{12,13}, naphthalene derivatives²⁸, flavonoids¹⁹, lignan bis-glucosides²⁹ and alkaloids³⁰. In the present study, we report on the isolation and structure elucidation of 7 iridoid glycosides, asperuloside (1), asperulosidic acid (2), deacetyl-asperulosidic acid (3), monotropein (4), 6-*O*-*epi*-acetylscandoside (5), daphylloside (6), deacetyl-daphylloside

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(7); 2 flavonol glycosides, astragalgin (8) and rutin (9); and 2 monoterpene glycosides, betulalbuside A (10) and (2E)-2,6-dimethyl-2,7-octadien-1,6-diol-6-O- β -glucopyranoside (11), from the aerial parts of *Galium verum* subsp. *verum* L.

Experimental

General Experimental Procedures: The UV (MeOH) spectra were recorded on a Shimadzu UV-160 A spectrophotometer. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker AMX 300 operating at 300 and 500 MHz for proton and 75.5 MHz for carbon using TMS as internal standard. The solvents used were CD_3OD . ESI-MS was performed on a Varian MAT 731 (EL, 70 eV) and Finnigan MAT 311 A (DCI MS, 200 EV, NH_3) spectrometer. Silica gel 60 (0.063-0.200 mm, Merck) and Sephadex LH-20 (Fluka) were used for open column chromatographic separations. MPLC was performed on Labomatic (1.8 x 35.2 cm and 1.3 x 38 cm) and Büchi (2.5 x 46 cm) glass columns packed with LiChroprep RP-18 (Merck), using Lewa M5 (peristaltic) and Büchi B-684 pumps. TLC analyses were carried out on pre-coated silica gel 60 F₂₅₄ aluminum sheets (Merck). Compounds were detected by UV fluorescence and spraying with 1% vanillin- H_2SO_4 reagent, followed by heating at 105 °C for 1-2 min.

Plant Material: *Galium verum* subsp. *verum* L. (Rubiaceae) was collected from Altınyayla, which is located between Fethiye and Burdur, in June 2001. A voucher specimen has been deposited in the Herbarium of the Pharmacognosy Department, Faculty of Pharmacy, Hacettepe University, Ankara, Turkey (HUEF 01032).

Extraction and Purification: Air-dried aerial parts of the plant (750 g) were extracted 3 times with MeOH at 40 °C (3 x 2.5 L). After filtration, the combined extracts were evaporated under vacuum to dryness (147 g). The residue was suspended in H_2O (200 mL) and the water-soluble portion was partitioned between CHCl_3 (5 x 2.5 L) and n-BuOH (3 x 1.5 L). The n-BuOH phase was evaporated under vacuum to near dryness and n-BuOH extract was obtained (56 g). The n-BuOH extract of the plant was chosen for further phytochemical studies as given below:

Isolation of the Compounds: An aliquot of the n-BuOH extract (32 g) was fractionated by silica gel CC, employing CHCl_3 -MeOH mixtures (90:10, 80:20,, 0:100) to yield 12 main fractions (Frs. A-M, Fr. A: 26 mg, Fr. B: 100 mg, Fr. C: 109 mg, Fr. D: 93 mg, Fr. E: 313 mg, Fr. F: 3.514 g, Fr. G: 4.750 g, Fr. H: 472 mg, Fr. I: 12.596 g, Fr. K: 5.295 g, Fr. L: 764 mg, Fr. M: 0.948 g). Fr. I (1.412 g) was subjected to C_{18} medium pressure liquid chromatography (MPLC) using gradient MeOH: H_2O (0%-100%) mixtures to yield Fr_a (243 mg) and Fr_b (58 mg). Silica gel chromatography of Fr_a (243 mg), eluting with CHCl_3 -MeOH mixtures (80:20, 70:30. 40:60), gave a mixture **3** and **4** (Fr. 55-57, 7 mg). Silica gel chromatography of Fr_b (58 mg), eluting with CHCl_3 -MeOH mixtures (95:5, 90:10. 60:40), gave compounds **1** (Fr. 25-31, 7 mg) and **2** (Fr. 45-53, 34 mg). Fr. G (3.700 g) was subjected to a silica gel column using EtOAc:MeOH: H_2O mixtures (100:10:5) to yield Fr_c (13 mg), Fr_d (195 mg) and Fr_e (1.72 g). Fr_c was eluted with MeOH from the Sephadex LH 20 column to give compound **10** (Fr. 25-26, 12 mg). Fr_d was subjected to C_{18} medium pressure liquid chromatography (MPLC) using gradient MeOH: H_2O (0%-100%) mixtures to give a mixture of **8** and **9** (Fr. 122-130, 7.5 mg). Fr_e was subjected to C_{18} medium pressure liquid chromatography (MPLC) using gradient MeOH: H_2O (0%-100%) mixtures to yield Fr. 58-63 (55 mg). Silica gel chromatography of Fr. 58-63, eluting with CHCl_3 -MeOH mixtures (90:10. 70:30), gave compounds **6** (Fr. 5-6, 6 mg) and

7 (Fr. 17-23, 5 mg). Fr. K was subjected to a silica gel column using CHCl₃-MeOH-H₂O mixtures (80:20:2, 80:25:2 and 70:30:3) to yield Fr. 50-76 (578 mg). Fr. 50-76 were subjected to C₁₈ medium pressure liquid chromatography (MPLC) using gradient MeOH:H₂O (0%-100%) mixtures to yield compound **1** (Fr. 2-9, 17 mg), Fr_f (Fr. 11-40, 31 mg) and Fr_g (Fr. 117-132, 160 mg). Silica gel chromatography of Fr_f (31 mg) eluting with CHCl₃-MeOH mixtures (80:20, 70:30) gave compound **5** (Fr. 19-25, 5 mg). Fr_g (160 mg) was applied to repeated Sephadex LH 20 (MeOH) column chromatography to give compound **11** (29 mg).

Results

Asperuloside (1): UV (MeOH) λ_{max} 242.8 nm, IR (KBr) ν_{max} 3405 (OH), 1743 (C=O), 1657 (C=C), 1699 (C=O) cm⁻¹, ESI-MS m/z 414 [M]⁺, 437 [M+Na]⁺, 851 [2M+Na]⁺ (calc. for C₁₈H₂₂O₁₁), ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data (Table 1).

Asperulosidic acid (2): UV (MeOH) λ_{max} 235 nm, IR (KBr) ν_{max} 3384.7 (OH), 1730 (C=O), 1635 (C=C), 1718 (C=O) cm⁻¹, ESI-MS m/z 432 [M]⁺, 455 [M+Na]⁺, 887 [2M+Na]⁺ (calc. for C₁₈H₂₄O₁₂), ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data (Table 1).

Deacetyl-asperulosidic acid (3): UV (MeOH) λ_{max} 234 nm, IR (KBr) ν_{max} 3550 (OH), 1700 (C=O), 1650 (C=C) cm⁻¹, ESI-MS m/z 390 [M]⁺ (calc. for C₁₈H₂₂O₁₁), ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data (Table 1).

Table 1. ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data of compounds **1-3**.

Position	DEPT	1			2			3		
		δ_C (ppm)	δ_H (ppm)	<i>J</i> (Hz)	δ_C (ppm)	δ_H (ppm)	<i>J</i> (Hz)	δ_C (ppm)	δ_H (ppm)	<i>J</i> (Hz)
Aglycone										
1	CH	93.3	5.95dd	1.5/0.5	101.1	5.05d	9.0	101.3	5.03d	9.0
3	CH	150.3	7.29d	2.0	154.9	7.62d	1.0	154.2	7.58s	
4	C	106.2			109.0			110.3		
5	CH	37.5	3.64		42.6	3.02t	6.5	43.2	3.01t	6.5
6	CH	86.3	5.56	6.5/1.5	75.4	4.90s		75.6	4.82	
7	CH	128.9	5.72m		131.8	6.01d	1.0	129.8	6.0d	1.5
8	C	144.3			145.9			151.5		
9	CH	45.3	3.29m		46.3	2.62t		46.1	2.54t	8.0
10	CH ₂	61.9	4.66dd	14.0/1.0	63.8	4.85d	15.0	61.8	4.21d	15.5
			4.77dd	14.0/1.0		4.94d	15.0		4.45dd	15.5/1.0
11	C	172.2			172.5			172.5		
<u>CO</u> CH ₃	C	172.6			172.5					
CO <u>CH</u> ₃	<u>CH</u> ₃	20.6	2.07s		20.8	2.09s				
Glucose										
1'	CH	100	4.67d	8.0	100.5	4.72d	8.0	100.4	4.71d	8.0
2'	CH	74.7	3.17dd	9.0/8.0	74.9	3.25m		75.0	3.21m	
3'	CH	78.4	3.26m		78.5	3.35m		78.5	3.26m	
4'	CH	71.6	3.24m		71.5	3.25m		71.7	3.26m	
5'	CH	77.9	3.36m		77.8	3.31m		77.8	3.37m	
6a'	CH ₂	62.8	3.99dd	12.0/6.5	63.0	3.61dd	12.0/6.0	62.8	3.61dd	12.0/5.5
6b'			3.91dd	12.0/1.8		3.85dd	12.0/2.0		3.84dd	12.0/1.5

Monotropein (4): UV (MeOH) λ_{max} 234 nm, IR (KBr) ν_{max} 3550 (OH), 1700 (C=O), 1650 (C=C) cm^{-1} , ESI-MS m/z 390[M]⁺ (calc. for C₁₆H₂₂O₁₁), ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data (Table 2).

Table 2. ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data of compounds 4-5.

Position	DEPT	4			5		
		δ_C (ppm)	δ_H (ppm)	J J	δ_C (ppm)	δ_H (ppm)	J (Hz)
Aglycone							
1	CH	95.2	5.54d	3.0	97.4	5.29d	6.0
3	CH	150.7	7.31d	1.0	153.3	7.42d	
4	C	113.4			110.9		
5	CH	40.0	3.56d	2.5	42.1	3.27m	
6	CH	138.5	6.21dd	5.5/2.5	83.7	5.58m	
7	CH	133.2	5.60dd	5.5/2.0	126.9	5.78m	
8	C	86.4			150.5		
9	CH	45.8	2.67dd	8.3/3.0	46.9	3.05t	6.5
10	CH ₂	68.5	3.56m		60.9	4.19d	15.5
						4.35d	15.5
11	C	172.5			172.7		
<u>CO</u> CH ₃	C				172.7		
CO <u>CH</u> ₃	<u>CH</u> ₃				21.2	2.01s	
Glucose							
1'	CH	100.1	4.67d	8.0	100.1	4.66d	8.0
2'	CH	74.7	3.21m		74.8	3.20dd	9.0/8.0
3'	CH	78.5	3.26m		77.9	3.36t	9.0
4'	CH	71.4	3.26m		71.5	3.27m	
5'	CH	77.9	3.37m		78.4	3.27m	
6a'	CH ₂	62.6	3.61dd	12.0/5.5	62.7	3.64dd	12.0/6.0
6b'			3.84dd	12.0/1.5		3.87dd	12.0/2.0

6-O-*epi*-acetylscandoside (5): UV (MeOH) λ_{max} 238.8 nm, IR (KBr) ν_{max} 3443 (OH), 1730 (C=O), 1638 (C=C), 1718 (C=O) cm^{-1} , ESI-MS m/z 432 [M]⁺, 455 [M+Na]⁺, 887 [2M+Na]⁺ (calc. for C₁₈H₂₄O₁₂), ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data (Table 2).

Daphylloside (6): UV (MeOH) λ_{max} 235.8 nm, IR (KBr) ν_{max} 3404.3 (OH), 1733.3 (C=O), 1635.1 (C=C), 1706 (C=O) cm^{-1} , ESI-MS m/z 446 [M]⁺, 469 [M+Na]⁺ (calc. for C₁₉H₂₆O₁₂), ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data (Table 3).

Table 3. ^1H NMR (300 MHz, CD_3OD) and ^{13}C NMR (75.4 MHz, CD_3OD) data of compounds **6-7**.

Position	DEPT	6			7	
		δ_C (ppm)	δ_H (ppm)	J (Hz)	δ_H (ppm)	J (Hz)
Aglycone						
1	CH	101.2	5.06 d	8.5	5.05 d	9.0
3	CH	155.4	7.65 d	1.0	7.62 d	1.0
4	C	108.1				
5	CH	42.4	3.03 t	6.5	3.02 t	6.5
6	CH	75.4	4.80 m		4.80 m	
7	CH	131.8	6.0 d	2.0	6.01 d	1.0
8	C	146				
9	CH	46.2	2.63 t	8.5	2.62 t	8.0
10	CH ₂	63.8	4.80 m 4.94 d	15.0	4.20 d 4.45 d	15.0 15.0
11	C	169.3				
12	CH ₃	52.8	3.74 s		3.74 s	
<u>CO</u> CH ₃	C	172.5				
CO <u>CH</u> ₃	<u>CH</u> ₃	20.8	2.08 s			
Glucose						
1'	CH	100.6	4.71 d	8.0	4.72 d	8.0
2'	CH	74.9	3.23 dd	8.5/8.0	3.23 dd	8.5/8.0
3'	CH	78.6	3.37 t	8.5	3.37 t	8.5
4'	CH	71.6	3.26 m		3.26 m	
5'	CH	77.9	3.26 m		3.26 m	
6a'	CH ₂	63.0	3.61 dd	12.0/6.0	3.61 dd	12.0/6.0
6b'			3.85 dd	12.0/2.0	3.85 dd	12.0/2.0

Deacetyl-daphylloside (7): UV (MeOH) λ_{max} 231.1 nm, IR (KBr) ν_{max} 3424 (OH), 1721.2 (C=O), 1635.1 (C=C), 1702 (C=O) cm^{-1} , ESI-MS m/z 404 $[\text{M}]^+$, 427 $[\text{M}+\text{Na}]^+$ (calc. for $\text{C}_{17}\text{H}_{24}\text{O}_{11}$), ^1H NMR (300 MHz, CD_3OD) (Table 3).

Astragalin [= kaempferol 3-O- β -glucopyranoside] (8): UV (MeOH) λ_{max} 350.5, 267.43 nm, IR (KBr) ν_{max} 3673 (OH), 1607 (C=C), 1732.8 (C=O) cm^{-1} , ESI-MS m/z 448 $[\text{M}]^+$, 447 $[\text{M}-\text{H}]^-$ (calc. for $\text{C}_{21}\text{H}_{20}\text{O}_{11}$), ^1H NMR (300 MHz, CD_3OD) and ^{13}C NMR (75.4 MHz, CD_3OD) data (Table 4).

Rutin [= quercetin 3-O- rutinoside] (9): UV (MeOH) λ_{max} 365, 255 nm, IR (KBr) ν_{max} 3421.3 (OH), 1603.7 (C=C), 1654.6 (C=O), 808.3 (C-O-C) cm^{-1} , ESI-MS m/z 610 $[\text{M}]^+$, 609 $[\text{M}-\text{H}]^-$ (calc. for $\text{C}_{27}\text{H}_{30}\text{O}_{16}$), ^1H NMR (300 MHz, CD_3OD) and ^{13}C NMR (75.4 MHz, CD_3OD) data (Table 4).

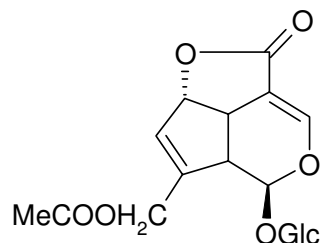
Table 4. ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data of compounds **8-9**.

Position	DEPT	8			9		
		δ_C (ppm)	δ_H (ppm)	J (Hz)	δ_C (ppm)	δ_H (ppm)	J (Hz)
Aglycone							
2	C	158.6			158.5		
3	C	135.4			135.6		
4	C	179.4			179.2		
5	C	163.0			162.8		
6	CH	100.3	6.18 d	1.0	100.4	6.16 d	2.0
7	C	167.3			167.4		
8	CH	95.1	6.37 brs		95.2	6.34 d	1.5
9	C	158.9			159.1		
10	C	105.4			105.2		
1'	C	122.8			123.0		
2'	CH	132.3	8.04 d	9.0	117.6	7.68 d	1.5
3'	C	116.1	6.87 d	9.0	145.8		
4'	C	161.6			149.9		
5'	CH	116.1	6.87 d	9.0	116.0	6.86 d	8.5
6'	CH	132.3	8.04 d	9.0	123.6	7.62 dd	8.5/2.0
Glucose							
1''	CH	104.2	5.22 d	7.5	104.9	5.07 d	8.5
2''	CH	75.7	3.19 m		75.7	3.47 m	
3''	CH	78.1	3.42 m		77.2	3.32 m	
4''	CH	71.3	3.42 m		71.3	3.27 m	
5''	CH	78.4	3.42 m		78.2	3.42 m	
6''	CH ₂	62.6	3.52 dd	12.0/4.5	68.6	3.38 m	10.5
			3.68 dd	12.0/2.0		3.80 d	
Ramnoz							
1'''					102.4	4.51 d	1.0
2'''					72.1	3.63 dd	3.5/1.5
3'''					72.2	3.53 dd	9.5/3.5
4'''					73.9	3.28 m	
5'''					69.7	3.44 m	
6'''					17.9	1.12 d	6.5

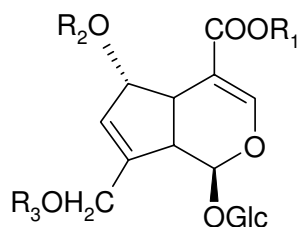
Betulalbuside A (10): UV (MeOH) λ_{max} 232.5 nm, IR (KBr) ν_{max} 3452.3 (OH), 2361.4 (C-H), 1637.3 (C=C), 1122.0 (-C-O-) cm⁻¹, ESI-MS m/z 332 [M]⁺, 355 [M+Na]⁺, 687 [2M+Na]⁺ (calc. for C₁₆H₂₈O₇), ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data (Table 5).

(2E)-2,6-dimethyl-2,7-octadien-1,6-diol-6-O-β-glucopyranoside (11): UV (MeOH) λ_{max} 232.5 nm, IR (KBr) ν_{max} 3452.3 (OH), 2361.4 (C-H), 1637.3 (C=C), 1122.0 (-C-O-) cm⁻¹, ESI-MS m/z 332 [M]⁺,

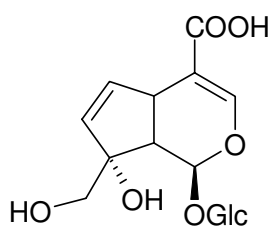
355 [M+Na]⁺, 687 [2M+Na]⁺(calc. for C₁₆H₂₈O₇), ¹H NMR (300 MHz, CD₃OD) and ¹³C NMR (75.4 MHz, CD₃OD) data (Table 5).



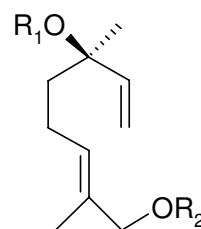
Asperuloside (1)



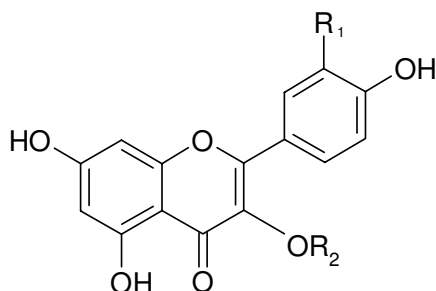
R ₁	R ₂	R ₃	Compound
H	H	COMe	Asperulosidic acid (2)
H	H	H	Deacetyl-asperulosidic acid (3)
H	COMe	H	6- <i>O</i> - <i>epi</i> -acetylscandoside (5)
Me	H	COMe	Daphylloside (6)
Me	H	H	Deacetyl-daphylloside (7)



Monotropein (4)



R ₁	R ₂	Compound
H	Glc	Betulalbuside A (10)
Glc	H	(2E)-2,6-dimethyl-2,7-octadien-1,6-diol-6- <i>O</i> -β-glucopyranoside (11)



R ₁	R ₂	Compound
H	Glc	Astragalín (8)
OH	Glc and rha	Rutin (9)

Figure. Chemical structures of the isolated compounds.

Table 5. ^1H NMR (300 MHz, CD_3OD) and ^{13}C NMR (75.4 MHz, CD_3OD) data of compounds **10-11**.

Position	DEPT	10			11		
		δ_C (ppm)	δ_H (ppm)	J	δ_C (ppm)	δ_H (ppm)	J (Hz)
Aglycone							
1	CH_2	70.1	3.03		66.4	3.74	
2	C	131.2			135.1		
3	CH	127.8	5.39 brt	7.0	123.7	5.28 t	7.0
4	CH_2	21.9			21.5	1.97 m	
5	CH_2	41.8	1.41 m	6.5	40.9	1.47 m	
r 6	C	73.5			78.9		
7	CH	146.0	5.90 t	10.5	143.5	5.84 t	10.5
8	CH_2	110.9	4.94 d 5.12 m	10.5/2.0	114.4	5.22 d 5.12 m	1.5
9	CH_3	13.6	1.57 s		13.4	1.52 s	
10	CH_3	27.5	1.14 s		22.9	1.27 s	
Glucose							
1'	CH	101.5	4.08	7.8	98	4.15 d	7.5
2'	CH	73.4	2.95 m		73.4	2.95 m	
3'	CH	76.5	3.11 m		76.7	3.03 m	
4'	CH	70.2			70.2		
5'	CH	76.8	2.97 m		77.0		
6'	CH_2	61.1	3.69 t	11.5	61.2	3.42 m	

Discussion

The n-butanol extract obtained from the methanolic extract of the aerial parts of *Galium verum* subsp. *verum* L. was fractionated by silica gel column chromatography, followed by open CC on silica gel, Sephadex LH 20 and C_{18} medium pressure liquid chromatography (MPLC) to yield compounds 1-11. Their structures were identified as asperuloside (**1**)³¹, asperulosidic acid (**2**)^{31,32}, deacetyl-asperulosidic acid (**3**)^{32,33}, monotropein (**4**)^{32,33}, 6-*O*-*epi*-acetylscandoside (**5**)³⁴, daphylloside (**6**)^{31,32}, deacetyl-daphylloside (**7**)³³, astragalinalin (**8**)³⁵, rutin (**9**)³⁵, betulalbuside A (**10**)³⁶ and (2E)-2,6-dimethyl-2,7-octadien-1,6-diol-6-*O*- β -glucopyranoside (**11**)³⁶ by comparison of their spectroscopic (NMR and MS) data with those published in the literature. To our knowledge, asperuloside, asperulosidic acid, deacetyl-asperulosidic acid, monotropein, daphylloside, deacetyl-daphylloside, astragalinalin and rutin have been reported from different *Galium* species. This study is the first report of the isolation and structure elucidation of 6-*O*-*epi*-acetylscandoside and acyclic monoterpene glycosides from *Galium* species. As is known, *Galium* species are rich in iridoids. These compounds are of assistance from a chemotaxonomy point of view in the order *Tubiflorae*. Acyclic monoterpene glycosides were isolated from *Galium* species for the first time. This is a special feature of *Galium*.

Conclusion

In this study, 7 iridoid glycosides, asperuloside, asperulosidic acid, deacetyl-asperulosidic acid, monotropein, 6-*O*-*epi*-acetylscandoside, daphylloside and deacetyl-daphylloside; 2 flavonol glycosides, astragalín and rutin; and 2 monoterpene glycosides, betulalbuside A and (2E)-2,6-dimethyl-2,7-octadien-1,6-diol-6-*O*- β -glucopyranoside, were isolated and identified from the aerial parts of *Galium verum* subsp. *verum* L.

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