Iridoid and Phenolic Glycosides from *Wulfenia carinthiaca*

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Two new phenylpropanoid glycosides (2′-O-acetylplantamajoside and 2′-O, 6″-O-diacetylplantamajoside), a new iridoid glycoside (10-O-(cinnamoyl)-6′-O-(desacetylalpinosidyl)-catalpol), the two known iridoid glycosides globularin and isoscrophularioside, and the known phenylpropanoid glycoside platamajoside were isolated from the methanolic extract of the underground parts of *Wulfenia carinthiaca.* Structure elucidations were based on high-resolution mass spectrometry and extensive 1-D and 2-D NMR spectroscopy.

Introduction

W. carinthiaca Jacq. (Scrophulariaceae) is a Tertiary relic, whose distribution is limited to two small areas at mount Gartnerkofel at the border of Carinthia and Friuli Venetia Giulia (Austria/Italy) and in the Prokletjia Mountains in the frontier area of Albania, Montenegro and Serbia. All in all six species of *Wulfenia* are known, all occuring in disjunct areas (Kosch, 1992). Within the Scrophulariaceae the genus *Wulfenia* is in an intermediate position between the genera *Digitalis* and *Veronica* based on morphology and anatomy (Raman, 1989) and closely related to the genera *Veronicastrum* and *Paederota* based on seed-morphology (Hong, 1984). *Wulfenia* preserves many relic characteristics as the unlimited growth of the main axis and the small variability of the leaves, the latter indicating genetic inflexibility (Lepper, 1970). The present habitats (forests and sub-alpine meadows) are located in sub-alpine altitudes ranging from 1000 to 3000 m above sea level. We report on the isolation and structure elucidation of six compounds – three iridoid glycosides and three phenylpropanoid glycosides from the underground parts of *W. carinthiaca.* The chemosystematic impact of the occurrence of these compounds is discussed briefly.

Results and Discussion

Structure elucidation

The methanolic extract (10.2 g) of underground parts of *W. carinthiaca* (74.1 g) was fractionated by silica gel column chromatography (CC) using a gradient of EtOAc, MeOH and H_2O, repeated Sephadex LH-20 CC and subsequent semi-preparative RP-18 HPLC, yielding six compounds (**1–6**, Fig. 1). Compounds **4** and **5** were identified as the known iridoids, globularin (Faure *et al.*, 1987), and isoscrophularioside, respectively (Junior, 1981) and compound **1** as the known phenylpropanoid glycoside plantamajoside (Ravn *et al.*, 1988) on the basis of NMR and MS data.

The molecular formula of compound **2** was determined as $C_{31}H_{38}O_{17}$ by HR-mass spectrometry. The ^1H and ^{13}C NMR spectral data were very similar to the data reported for **1** (Ravn *et al.*, 1988), except for additional signals assignable to an acetyl group. The HMBC spectra showed a correlation between proton H-2′ of the inner glucose moiety and the carbonyl carbon (δ_C 171.9) of the acetyl group (Table I). Conclusively, compound **2** was identified as 2′-O-acetylplantamajoside, which represents a new natural product.

Compound **3** had a molecular formula of $C_{33}H_{40}O_{18}$, as determined from HR-mass spectrometric analysis. The ^1H and ^{13}C NMR spectra were very similar to the spectra of **1** (Ravn *et al.*, 1988)

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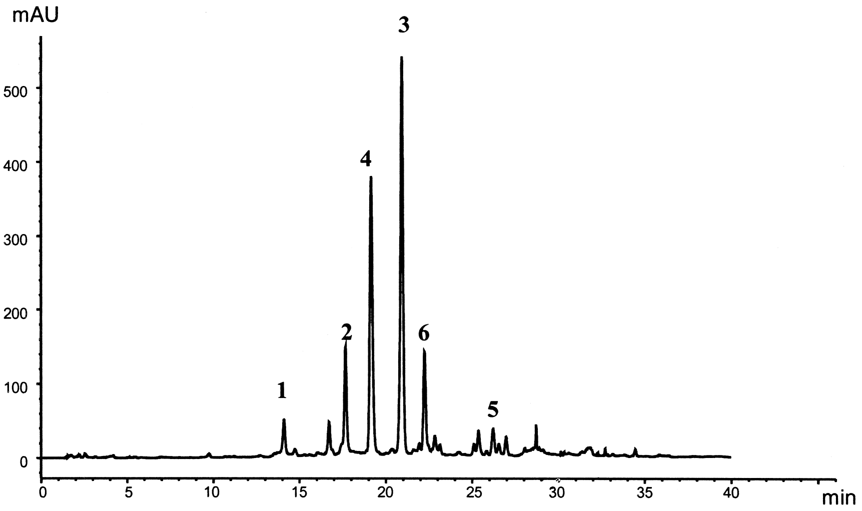

Fig. 1. HPL chromatogram from a methanolic extract of the underground parts of *Wulfenia carinthiaca*: Plantamajoside (**1**), 2′-O-acetylplantamajoside (**2**), 2′-O, 6″-O-diacetylplantamajoside (**3**), globularin (**4**), isoscrophularioside (**5**), and wulfenoside (**6**). HPLC parameters: Mobile phase A: H_2O (with 0.15% CH_3COOH), mobile phase B: MeOH; linear gradient: 0 min: 25% B, 3 min: 25% B; 25 min: 52% B; 28 min: 80% B; 30 min: 90% B; stop time: 40 min; flow-rate: 1.00 ml/min; oven temperature: 30 °C; column: Zorbax SB-C18 4.6 × 150 mm (particle size 3.5 μm); injection volume: 10 μl; detection wavelength: 205 nm.

and **2** (Table I). In addition to the signals reported for compound **1**, the signals of two acetyl groups were observed. HMBC correlations between H-2′ (δ_H 4.83) of the inner glucose moiety and a carbonyl carbon (δ_C 172.8) of one acetyl group and between the protons at C-6″ (δ_H 4.12 and 4.20) of the terminal glucose moiety and the carbonyl carbon of the second acetyl group (δ_C 172.8) (Table I) identified compound **3** as 2′-O, 6″-O-diacetylplantamajoside, another new natural product.

The molecular formula of compound **6** was determined as $C_{40}H_{48}O_{20}$ by HR mass spectrometry. ^{1}H and ^{13}C NMR spectral data (Table II) in combination with results of 2D-NMR experiments revealed the presence of two iridoid glucoside moieties and a *trans*-cinnamoyl moiety.

The presence of two β-glucose units was indicated by two anomeric proton signals at δ_H 4.76 and 4.68 (both d, J = 8.0 Hz), two pairs of signals assignable to the methylene protons at C-6 [δ_H 4.75, 4.20; δ_H 3.86, 3.65] and signals integrating for eight protons in the region between δ_H 3.2 and δ_H 3.5 (protons H-2, H-3, H-4, and H-5). Due to the downfield shifts of one pair of H-6 methylene signals it was obvious that one of the two glucose moieties was acylated in that position.

The structure of the *trans*-cinnamoyl moiety was established by ^{1}H NMR data showing two vicinal olefinic protons [δ_H 6.56 and 7.73 (J_{AX} = 16.0 Hz)] and five aromatic protons at δ_H 7.41 (3H) and δ_H 7.65 (2H).

One of the two iridoid moieties showed signals for two vicinally coupled olefinic protons at δ_H 6.37 (dd, J = 6.0 and 1.6 Hz) and δ_H 5.09 (dd, J = 5.5 and 4.8 Hz) – assignable to H-3 and H-4 – and further protons at δ_H 4.95 (d, J = 10.0 Hz, H-1), δ_H 2.29 (m, H-5), δ_H 3.91 (d, J = 8.0 Hz, H-6), δ_H 3.57 (m, H-7), δ_H 2.65 (dd, J = 9.5, 7.5 Hz, H-9) as well as δ_H 5.04 and 4.18 (both d, J = 12.5 Hz, H-10). The corresponding carbon NMR signals, included seven methines ($\delta_{C\text{-}1}$ 95.4, $\delta_{C\text{-}3}$ 141.8, $\delta_{C\text{-}4}$ 103.7, $\delta_{C\text{-}5}$ 38.6, $\delta_{C\text{-}6}$ 79.3, $\delta_{C\text{-}7}$ 62.1, $\delta_{C\text{-}9}$ 43.1), one methylene ($\delta_{C\text{-}8}$ 62.5) and one quarternary carbon ($\delta_{C\text{-}10}$ 63.1). Taking into account results from 2D NMR experiments and literature data (Morota *et al.*, 1989; Calis *et al.*, 2001) this partial structure was identified as a catalpol unit with acylations in positions C-10 of the iridoid moiety and C-6′ of the glucose moiety. The acylations in positions C-10 and C-6′ were indirectly indicated by downfield shifts for the H-10-oxymethylene protons and the H-6′-oxymethylene protons. The H-10-protons displayed shifts of δ_H 5.04 and 4.18 ppm (J_{AX} = 12.5 Hz) in comparison with the literature data for catalpol [δ_H 4.13 (J = 13.1 Hz) and 3.78 ppm (J = 13.1 Hz)] and the H-6′-oxymethylene protons, reported for catalpol showed shifts of δ_H 4.75 and 4.20 ppm in comparison with δ_H 3.90 and 3.63 ppm (Morota *et al.*, 1989).

Table I. ^{1}H and ^{13}C NMR data of compound **2** and **3**[a].

	2		**3**	
	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
3,4-Dihydroxyphenyl moiety				
α	4.08 2H, m[b]	71.9	4.08 2H, m[b]	71.8
β	2.70 2H, m[b]	36.3	2.69 2H, m[b]	36.3
1		131.8		131.8
2	6.68 1H, s	116.3	6.68 1H, s	116.3
3		144.6		144.6
4		146.0		146.1
5	6.65 1H, d (8.0)	117.2	6.66 1H, m	117.2
6	6.52 1H, d (8.0)	121.3	6.53 1H, d (8.0)	121.3
Glucose (inner)				
1′	4.49 1H, d (8.0)	102.1	4.52 1H, d (8.0)	102.0
2′	4.96 1H, m[b]	74.9	4.83 1H, m[b]	74.6
3′	4.15 1H, m	80.4	4.01 1H, m	81.1
4′	4.99 1H, m	70.5	4.96 1H, m	70.3
5′	3.64 1H, m[b]	77.8	3.64 1H, m[b]	75.2
6′	3.77 1H, dd (12.0, 2.0) 3.44 1H, dd (12.0, 5.0)	63.2	3.66 1H, dd (12.5, 2.0) 3.56 1H, dd (12.5, 5.0)	62.2
Glucose (terminal)				
1″	4.28 1H, d (8,0)	105.0	4.28 1H, d (8.0)	105.5
2″	3.01 1H, d (8.0)	74.5	3.05 1H, d (8.0)	74.5
3″	3.22 1H, m	78.0	3.25 1H, m	77.7
4″	3.06 1H, m	71.8	3.15 1H, m	71.3
5″	3.63 1H, m[b]	76.0	3.61 1H, m[b]	76.1
6″	3.65 1H, dd (12.0, 2.0) 3.60 1H, dd (12.0, 5.0)	62.2	4.20 1H, dd (12.0, 2.0) 4.12 1H, dd (12.0, 5.0)	64.7
Caffeoyl moiety				
α‴		168.4		168.4
β‴	7.57 1H, d (16.0)	147.3	7.56 1H, d (16.0)	147.2
γ‴	6.34 1H, d (16.0)	115.3	6.26 1H, d (16.0)	115.3
1‴		127.8		127.7
2‴	7.07 1H, s	116.6	7.03 1H, s	115.3
3‴		146.8		146.8
4‴		149.7		149.7
5‴	6.79 1H, d (8.0)	116.9	6.77 1H, d (7.5)	116.6
6‴	6.99 1H, d (8.0)	123.1	6.95 1H, d (7.5)	122.9
$\mathrm{CH_3\underline{C}O}$		171.9		172.7
$\mathrm{CH_3\underline{C}O}$				172.8
$\mathrm{\underline{CH_3}CO}$	1.98 3H, s	21.0	1.99 3H, s	21.2
$\mathrm{\underline{CH_3}CO}$			1.86 3H, s	20.6

[a] Measured in CD_3OD at 500 MHz and 125 MHz, respectively. Referenced to solvent signal of CD_3OD δ_C 49.00 ppm and solvent residual signals at δ_H 3.31 ppm (Gottlieb *et al.*, 1997).

[b] Signal patterns are unclear due to overlapping.

The second iridoid structure was determined as desacetylalpinoside by its NMR data (Calis *et al.*, 2001). ^{1}H NMR signals for this second iridoid moiety included an olefinic proton at δ_H 7.48 (d, J = 1.7 Hz, H-3‴) and signals at δ_H 6.35 (s, H-1‴), δ_H 3.59 (m, H-5‴), δ_H 2.57 and 1.48 (m, H-6‴), δ_H 2.47 (m, H-7‴) and δ_H 4.23 and 4.17 (m, H-10‴). The ten carbon signals for this partial structure included four methines ($\delta_{C\text{-}1'''}$ 92.0, $\delta_{C\text{-}3'''}$ 152.3, $\delta_{C\text{-}5'''}$ 38.6, and $\delta_{C\text{-}7'''}$ 34.4), two methylene ($\delta_{C\text{-}6'''}$ 31.9 and $\delta_{C\text{-}10'''}$ 58.9), three quarternary carbons ($\delta_{C\text{-}4'''}$ 114.2, $\delta_{C\text{-}8'''}$ 142.5, and $\delta_{C\text{-}9'''}$ 143.2), and one carbonyl carbon atom at δ_C 169.0.

Connectivities of the three identified partial structures (catalpol, *trans*-cinnamoyl, and desacetylalpinoside) were established by HMBC spectroscopy. Important HMBC correlations are shown in Figure 3. HMBC cross-peaks were observed from the protons in position 10 of the catalpol moiety to the carbonyl carbon signal (δ_C 168.5) of the cinnamoyl moiety and from the glucose protons in position C-6′ of the catalpol moi-

Table II. ^{1}H and ^{13}C NMR data of compound **6**^{a}.

	^{1}H NMR	^{13}C NMR		^{1}H NMR	^{13}C NMR
1	4.95 1H, d (10.0)	95.4	1‴	6.35 1H, s	92.0
3	6.37 1H, dd (6.0, 1.5)	141.8	3‴	7.48 1H, d (2.0)	152.3
4	5.09 1H, dd (6.0, 5.0)	103.7	4‴		114.2
5	2.29 1H, m	38.6	5‴	3.59 1H, m	38.6
6	3.91 1H, d (8.0)	79.3	6‴	2.57 and 1.48 2H, m	31.9
7	3.57 1H, m	62.1	7‴	2.47 2H, m	34.4
8		63.1	8‴	142.5	
9	2.65 1H, dd (9.5, 7.5)	43.1	9‴	143.2	
10	5.04 1H, d (12.5)	62.5	10‴	4.23 1H, m	58.9
	4.18 1H, d (12.5)			4.17 1H, m	
			11‴		169.0
1′	4.76 1H, d (8.0)	100.3			
2′	3.47 1H, dd (8.0, 9.5)	75.5	1⁗	4.68 1H, d (8.0)	99.9
3′	3.37 1H, m^{b}	77.8	2⁗	3.18 1H, m	74.3
4′	3.42 1H, m	70.9	3⁗	3.37 1H, m^{b}	77.8
5′	3.30 1H, m^{b}	77.9	4⁗	3.29 1H, m	71.0
6′	4.75 1H, dd (12.0, 5.0)	62.4	5⁗	3.30 1H, m^{b}	77.9
	4.20 1H, d (12.0)		6⁗	3.86 1H, dd (11.5, 2.0)	62.3
				3.65 1H, dd (11.5, 5.0)	
1″		136.1			
2″	7.65 1H,	129.1			
3″	7.41 1H, m	129.8			
4″	7.41 1H, m	131.3			
5″	7.41 1H, m	129.8			
6″	7.65 1H, m	129.1			
α	6.56 1H, d (16.0)	118.5			
β	7.73 1H, d (16.0)	146.6			
C = O		168.5			

[a] Measured in CD_3OD at 500 MHz and 125 MHz, respectively. Referenced to solvent signal of CD_3OD δ_C 49.00 ppm and solvent residual signals at δ_H 3.31 ppm (Gottlieb *et al.*, 1997).

[b] Overlapping signals.

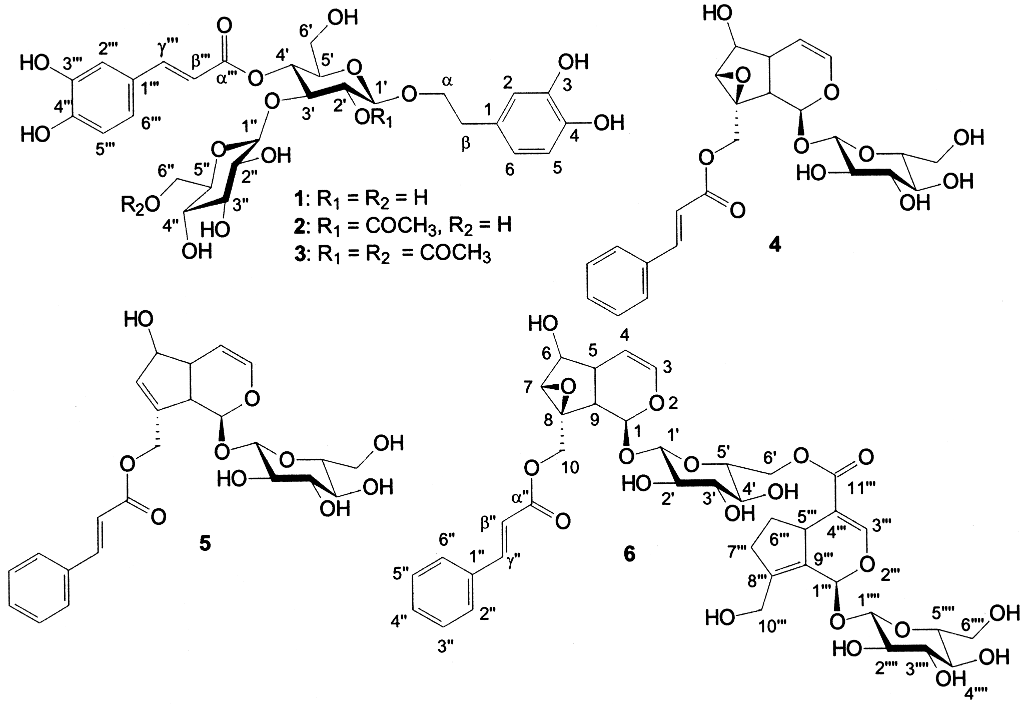

Fig. 2. Structures of phenylpropanoid glygosides (Plantamajoside (**1**), 2′-O-acetylplantamajoside (**2**), 2′-O, 6″-O-diacetylplantamajoside (**3**) and iridoid glycosides (globularin (**4**), isoscrophularioside (**5**) and wulfenoside (**6**) from *Wulfenia carinthiaca.*

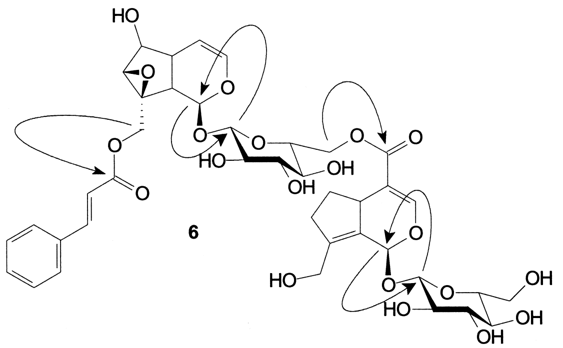

Fig. 3. Important HMBC cross-peaks observed for compound **6**.

ety to the carboyl signal of the desacetylalpinoside moiety. Thus, compound **6** was identified as 10-O-(cinnamoyl)-6′-O-(desacetylalpinosidyl)-catapol, a new natural product for which we propose the name wulfenoside.

Discussion

Iridoid glycosides and phenylpropanoid glycosides occur in many genera of the Acanthaceae, Bignoniaceae, Buddlejaceae, Globulariaceae, Lamiaceae, Lentibulariaceae, Pedaliaceae, Plantaginaceae, Scrophulariaceae and Verbenaceae (Grayer *et al.*, 1999). In Takhtajan's (1997) concept of the Scrophulariaceae *W. carinthiaca* is a member of the tribe Veroniceae. This tribe also comprises the genera *Aragoa*, *Besseya*, *Ellisiophyllum*, *Hebe*, *Lagotis*, *Picrorhiza*, *Scrofella*, *Sibthorpia*, *Synthyris*, *Veronica* and *Veronicastrum.* Recent results of DNA sequence analyses of several members of the Scrophulariaceae (Olmstead *et al.*, 2001) imply that the Scrophulariaceae *sensu* Takhtajan (1997) are not monophyletic. On this basis Olmstead *et al.* (2001) disintegrated the Scrophulariaceae in the traditional sense. Many former Scrophulariaceae genera were transferred to the new Veronicaceae family and the formerly narrowly defined Orobanchaceae now comprise many former semi-parasitic members of the Scrophulariaceae like *Bartsia*, *Melampyrum*, and *Tozzia.* In addition, some former smaller Scrophulariaceae satellite families were merged with the new narrower concept of the Scrophulariaceae (e.g. the Loganiaceae), while other small families like the Callitrichaceae, Globulariaceae, Haloragidaceae, and Plantaginaceae were merged with the former Scrophulariaceae tribes Angelonieae, Antirrhineae, Cheloneae, Digitaleae and Gratioleae to constitute the new Veronicaceae family.

The genus *Wulfenia* was not included in the study by Olmstead *et al.* (2001), but due to its close relationship with other members of the tribe Digitaleae it will also have to be included in the new Veronicaceae family. Thus, a close relationship between *Wulfenia* and the genera *Globularia* and *Plantago*, which were formerly classified in families of their own, is implied. Our phytochemical data support a close relationship of *Digitalis*, *Globularia*, *Plantago*, *Veronica*, and *Wulfenia* as plantamajoside derivatives were found in previous studies in *Digitalis purpurea* (Matsumoto *et al.*, 1987), different *Plantago* species (Ronsted *et al.*, 2000), and *Veronica fuhsii* (Ozipek *et al.*, 1999), while catalpol derivatives esterified with cinnamic acid were reported for species from the genera *Globularia* (Amer and El-Masry, 1988; Chaudhuri and Sticher, 1981; Calis *et al.*, 2002) and *Plantago* (Taskova *et al.*, 2002).

Experimental

General experimental procedures

Optical rotations were measured with a Perkin-Elmer 341 polarimeter. The IR spectra were recorded on a Bruker IFS 25 FTIR spectrometer. The samples were applied to a ZnSe disk. The spectra were recorded in a transmission mode within the range of 4000–600 cm^{-1}. The mass spectra (HR-FAB) were recorded on a Finnigan MAT 95S mass spectrometer.

^{1}H-NMR, ^{13}C-NMR (500 MHz) and 2D NMR (COSY, HMBC and HSQC) were recorded on a V-500 Varian spectrometer in CD_3OD. Column chromatography was performed using silica gel 60 (Merck, 0.040–0.063 mm, 230–400 mesh). Semi preparative reversed phase HPLC was performed on a Dionex apparatus (P 580 pump) with a LiChroCART® (250 × 10 mm) column with LiChrospher® 100 RP-18 material (particle size 10 μm). TLC was performed on silica gel 60 F_{254} Merck plates and detected with vanillin-H_2SO_4 reagent.

Plant material

W. carinthiaca was collected in September 2001 from the Botanical garden Innsbruck, Austria. Voucher specimens (MD01–2319) have been deposited in the herbarium of the Department of Pharmacognosy, Institute of Pharmacy, University of Innsbruck, Austria

Extraction and isolation

The air dried underground parts of *W. carinthiaca* (74.1 g) were crushed to coarse powder and extracted with CH_2Cl_2 and subsequently with MeOH. The MeOH extract were evaporated to dryness in vacuo. The crude extract (10.2 g) was suspended in EtOAc and fractionated by silica gel vacuum liquid chromatography employing a gradient of EtOAc, MeOH, and H_2O. Fractions containing **1–6** were subjected to Sephadex LH-20 CC. Enriched fractions of **1–6** were finally purified by semi-preparative reversed phase HPLC using a gradient of H_2O and MeOH to yield **1** (18.3 mg), **2** (15.7 mg), **3** (22.6 mg), **4** (18.2 mg), **5** (6.1 mg), and **6** (7.4 mg).

Spectroscopic data

2′-O-acetylplantamajoside (**2**): yellow amorphous powder, $[\alpha]^{20}_{D}$ – 66.7 ° (MeOH, *c* 0.02); IR (film) ν_{max} 3383 (br), 2924, 1735, 1602, 1519, 1446, 1375, 1256, 1162, 1117, 1074 856, 816 cm^{-1}; ^1H NMR and ^{13}C NMR (CD_3OD): Table 1; HR-FAB-MS *m/z* 683.21740 $[M + H]^+$ (calcd. for $C_{31}H_{39}O_{17}$, 683.21866).

2′-O, 6″-O-diacetylplantamajoside (**3**): yellow amorphous powder, $[\alpha]^{20}_{D}$ – 81,0 ° (MeOH, *c* 0.21); IR (film) ν_{max} 3395 (br), 2929, 1729, 1602, 1518, 1446, 1374, 1252, 1161, 1117, 1041, 814 cm^{-1}; ^1H NMR and ^{13}C NMR (CD_3OD): Table 1; HR-FAB-MS *m/z* 725.22912 $[M + H]^+$ (calcd. for $C_{33}H_{40}O_{18}$, 725.22921).

Wulfenoside (10-O-(cinnamoyl)-6′-(desacetylalpinosidyl)-catapol) (**6**): amorphous powder, $[\alpha]^{20}_{D}$ – 53,1 ° (MeOH, *c* 0,058); IR (film) ν_{max} 3383 (br), 2923, 1703, 1629, 1289, 1082, 879, 770, 687 cm^{-1}; ^1H NMR and ^{13}C NMR (CD_3OD): Table 2; HR-FAB-MS, *m/z* 871.265230 $[M + Na]^+$ (calcd. for $C_{40}H_{48}O_{20}Na$, 871.263664); *m/z* 849.283362 $[M + H]^+$ (calcd. for $C_{40}H_{49}O_{20}$, 849.281720)

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