35. New Triterpene Saponins from *Herniaria glabra*

by **Michaela Freiler, Gottfried Reznicek, Johann Jurenitsch***, and **Wolfgang Kubelka**

Institute of Pharmacognosy, University of Vienna, A–1090 Vienna

and **Wolfram Schmidt** and **Manfred Schubert-Zsilavecz***

Department of Organic Chemistry I, University of Ulm, D–89081 Ulm

and **Ernst Haslinger***

Institute of Pharmaceutical Chemistry, University of Graz, A–8010 Graz

and **Josef Reiner**

Department of Organic Chemistry I, University of Bayreuth, D–95447 Bayreuth

Dedicated to Prof. *K. Hiller* on the occasion of his 65th birthday

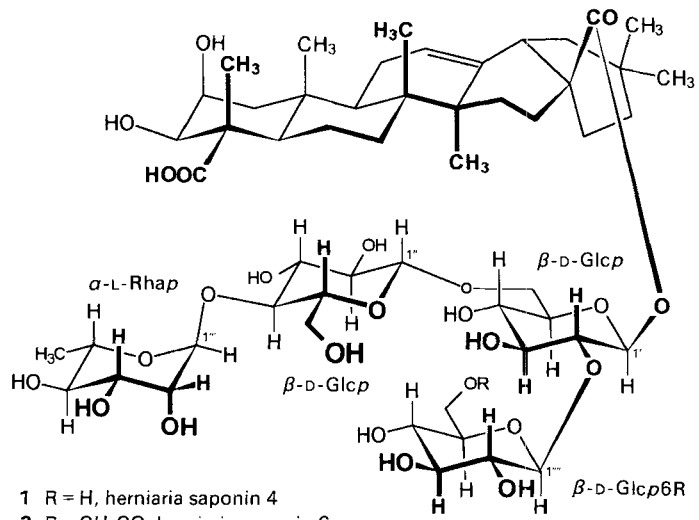
(8.XII.95)

Three new saponins **1–3** were isolated from *Herniaria glabra* by means of prep. HPLC and TLC. The structures were established mainly by a combination of 2D-NMR techniques (COSY, TOCSY, ROESY, HMQC, and HMBC) as *O*-α-L-rhamnopyranosyl-(1 → 4)-*O*-β-D-glucopyranosyl-(1 → 6)-*O*-[β-D-glucopyranosyl-(1 → 2)]-β-D-glucopyranosyl medicagen-28-ate (herniaria saponin 4; **1**), *O*-β-D-glucopyranosyl-(1 → 3)-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-[β-(3*R*)-D-apiofuranosyl-(1 → 3)]-β-D-4-*O*-acetylfucopyranosyl 3-*O*-(β-D-glucuronopyranosyl)-16α-hydroxymedicagen-28-ate (herniaria saponin 5; **2**), and *O*-α-L-rhamnopyranosyl-(1 → 4)-*O*-β-D-glucopyranosyl-(1 → 6)-*O*-[β-D-6-*O*-acetylglucopyranosyl-(1 → 2)]-β-D-glucopyranosyl medicagen-28-ate (herniaria saponin 6; **3**).

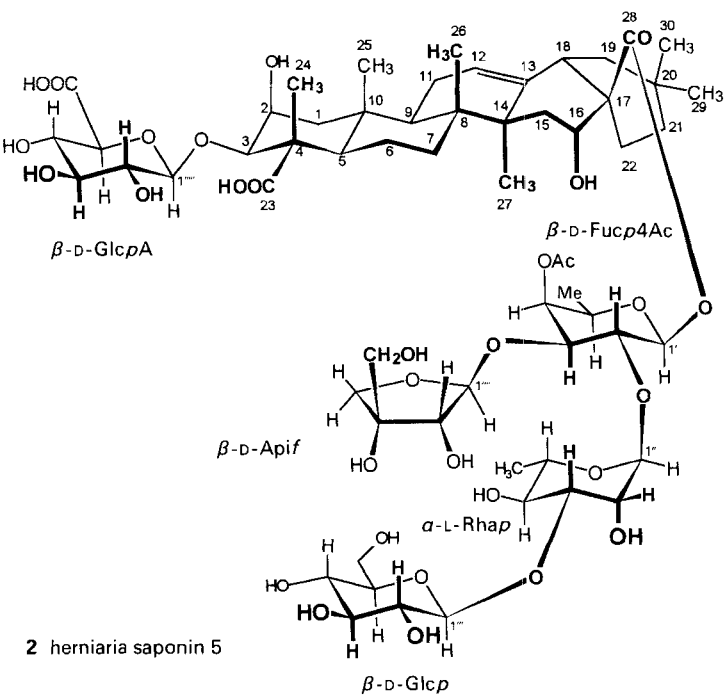
1. Introduction. – The saponins from *Herniaria glabra* L. are claimed to be responsible for the diuretic activity of the aerial parts of this plant. In previous publications [1] [2], we reported the isolation of herniaria saponins 1–3 representing glycosides of medicagenic acid (2β,3β-dihydroxyolean-12-ene-23,28-dioic acid).

This paper deals with the isolation and structure elucidation of three further main saponins, herniaria saponin 4 (**1**) and 6 (**3**), glycosides of medicagenic acid, and herniaria saponin 5 (**2**), a derivative from 16α-hydroxymedicagenic acid [3], synonym of zanhic acid [4].

2. Results and Discussion. – *Isolation.* A crude plant extract was prepared from dried aerial parts with 80% MeOH/H_2O and further extracted with H_2O-saturated BuOH. This extract was defatted by CH_2Cl_2 extraction and prefractionated by column chromatography over silica gel using different mobile phases. Herniaria saponins 4 (**1**) and 5 (**2**) were obtained by prep. HPLC (reversed-phase silica gel), by prep. TLC (silica gel), and by final purification using prep. HPLC again. Herniaria saponin 6 (**3**) was directly isolated from a crude MeOH extract by solid-phase extraction using *C-18* cartridges and final purification by prep. HPLC.



1 R = H, herniaria saponin 4
3 R = CH_3CO, herniaria saponin 6



2 herniaria saponin 5

Structure of **1**–**3**. The LSI-MS (Liquid Secondary-Ion Mass Spectrometry) provided information about the molecular weights of the saponins **1**–**3** and of the aglycones, as well as about the sequence of the sugar moieties. The absolute configuration for each of the sugar moieties was determined by GC/MS after hydrolysis and reaction with (−)-(*R*)-butan-2-ol according to *Reznicek et al.* [5].

NMR measurements and LSI-MS showed that **1** (herniaria saponin 4) was the 2-deacetyl derivative of the previously described herniaria saponin 2 [1]. All δ(H) and δ(C) are identical to those published for herniaria saponin 2, except those which are directly influenced by the structural change in position 2.

Herniaria saponin 6 (**3**) was investigated by COSY-45, TOCSY [6], ROESY [7], HMQC [8], and HMBC [9] experiments, and full assignment of all ^{1}H- and ^{13}C-resonances was obtained. The aglycone and the oligosaccharide part are similar with those of **1**, except that C(6) of the terminal glucopyranosyl residue is acetylated, which was confirmed by the well documented acetylation shift of the protons at C(6'''') as well as by the correlation cross-peaks from these protons to the acetyl carbonyl resonance in the HMBC spectrum.

The aglycone of **2** is 16α-hydroxymedicagenic acid. This was established by COSY, ROESY, and H,C-shift correlation spectra, which also gave the full assignment of the ^{1}H- and ^{13}C-resonances (see *Table 1*). On the basis of these measurements, it was possible to indicate that **2** is a bisdesmosidic saponin, which contains a glucuronic-acid residue attached to C(3) and a branched oligosaccharide chain connected to the carboxy function in position 17. This was verified by a H,C-correlation signal between H–C(1') and the resonance of the carboxy C-atom. Additional H,H- and H,C-COSY experiments led to the unambiguous assignment of all ^{1}H- and ^{13}C-resonances (see *Table 2*). The nature of the sugar residues was deduced from the values of the vicinal coupling constants in a monosaccharide unit and confirmed later by hydrolysis and GC/MS analysis as mentioned above.

The desired sequence information was obtained by ROESY and HMBC experiments, showing that the 4-*O*-acetylfucopyranosyl residue was a branching point, bearing an apiofuranosyl residue at C(3) and a Glc*p*-(1 → 3)-Rha*p* disaccharide moiety at C(2). By comparison of the δ(C) of the apiofuranosyl residue with published values [10–12], we concluded the configuration of this monosaccharide to be β-D. The saponin contains, therefore, a β-(3*R*)-D-apiofuranosyl residue, and the structure of herniaria saponin 5 (**2**)

Table 1. *^{1}H- and ^{13}C-NMR Data* ((D$_4$)methanol) *of the Aglycone of* **2**, *the Zanhic-Acid Moiety*

	δ(^{13}C) [ppm]	δ(^{1}H) [ppm][a])		δ(^{13}C) [ppm]	δ (^{1}H) [ppm][a])
CH_2(1)	44.9	1.28, 2.12	H–C(16)	74.8	4.42
H–C(2)	71.1	4.29	C(17)	47.8	
H–C(3)	86.6	4.08	H–C(18)	42.5	2.95
C(4)	53.4		CH_2(19)	48.1	2.26, 1.05
H–C(5)	53.2	1.60	C(20)	31.5	
CH_2(6)	21.8	1.58, 1.18	CH_2(21)	36.5	1.89, 1.18
CH_2(7)	33.9	1.56, 1.40	CH_2(22)	31.3	1.88, 1.88
C(8)	41.4		C(23)	183.1	
H–C(9)	48.8	1.63	Me(24)	13.6	1.40
C(10)	37.4		Me(25)	17.4	1.28
CH_2(11)	24.7	1.98, 1.93	Me(26)	18.1	0.83
H–C(12)	123.4	5.35	Me(27)	25.2	0.97
C(13)	143.8		C(28)	179.1	
C(14)	43.0		Me(29)	33.3	0.84
CH_2(15)	36.4	1.76, 1.39	Me(30)	25.2	0.96

[a]) The first mentioned δ refers to the axial, the second to the equatorial H-atom.

Table 2. *^{1}H- and ^{13}C-NMR Data* ((D$_4$)methanol) *of the Monosaccharides of* **2**

	δ(^{13}C) [ppm]	δ(^{1}H) [ppm]	J(H,H)[a] [Hz]		δ(^{13}C) [ppm]	δ(^{1}H) [ppm]	J(H,H)[a] [Hz]
4-*O*-Acetyl-β-D-fucopyranose				α-L-Rhamnopyranose			
H–C(1′)	95.1	5.45	^3J(1′,2′) = 7.9	H–C(1″)	102.1	5.15	^3J(1″,2″) = 1.6
H–C(2′)	75.9	3.82	^3J(2′,3′) = 9.6	H–C(2″)	71.3	4.15	^3J(2″,3″) = 3.2
H–C(3′)	81.0	3.89	^3J(3′,4′) = 3.4	H–C(3″)	83.0	3.69	^3J(3″,4″) = 9.4
H–C(4′)	74.7	5.24	^3J(4′,5′) = 0.3	H–C(4″)	72.6	3.54	^3J(4″,5″) = 9.4
H–C(5′)	71.1	3.84	^3J(5′,6′) = 6.8	H–C(5″)	70.3	3.77	^3J(5″,6″) = 6.1
CH$_3$(6′)	16.6	1.05		CH$_3$(6″)	18.5	1.27	
*C*H$_3$COO	20.8	2.14					
CH$_3$*C*OO	172.5			β-D-Apiofuranose			
				H–C(1‴)	112.7	5.13	^3J(1‴,2‴) = 2.1
β-D-Glycopyranose				H–C(2‴)	78.6	3.92	
H–C(1‴)	105.5	4.45	^3J(1‴,2‴) = 7.4	C(3‴)	80.6		
H–C(2‴)	75.4	3.28	^3J(2‴,3‴) = 9.0	CH$_2$(4‴)	75.5	3.74, 3.96	^2J(4‴a,4‴b) = 9.7
H–C(3‴)	77.7	3.38	^3J(3‴,4‴) = 9.5	CH$_2$(5‴)	65.4	3.54, 3.54	^2J(5‴a,5‴b) = 11.6
H–C(4‴)	71.3	3.33	^3J(4‴,5‴) = 9.2				
H–C(5‴)	77.8	3.35	^3J(5‴,6‴a) = 5.3	β-D-Glucuronic acid			
			^3J(5‴,6‴b) = 2.6	H–C(1⁗)	105.2	4.42	^3J(1⁗,2⁗) = 7.8
CH$_2$(6‴)	62.5	3.88	^2J(6‴a,6‴b) = 11.4	H–C(2⁗)	74.8	3.26	^3J(2⁗,3⁗) = 8.6
		3.70		H–C(3⁗)	77.5	3.38	^3J(3⁗,4⁗) = 8.5
				H–C(4⁗)	73.4	3.47	^3J(4⁗,5⁗) = 8.6
				H–C(5⁗)	75.7	3.88	
				C(6⁗)	178.1		

[a]) ΔJ(H,H) = 0.1 Hz.

is established as *O*-β-D-glucopyranosyl-(1 → 3)-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-[β-(3*R*)-D-apiofuranosyl-(1 → 3)]-β-D-4-*O*-acetylfucopyranosyl 3-*O*-(β-D-glucuronopyranosyl)-16α-hydroxymedicagen-28-ate.

Experimental Part

General. NMR Spectra: *Bruker-AMX-500* spectrometer (500.13 (^{1}H) and 125.76 MHz (^{13}C)); data processing with *Aspect-X32* computer using UXNMR software; 5-mm reverse probe head; [D$_4$]methanol solns. at 303 K; MeOH as internal standard (δ(^{1}H) 3.3, and δ(^{13}C) 49.0); typical parameters: 90°-pulses, ^{1}H 9.6–10 ms, ^{13}C 10.3 ms; WALTZ ^{1}H-decoupling pulse 112 ms; GARP ^{13}C-decoupling pulse 60 ms; MLEV-17 pulse 20.5 ms. COSY: 45° mixing pulse. TOCSY: phase-sensitive using TPPI, mixing time 100 ms (100 MLEV-17 cycles plus two trim pulses of 2.5 ms each). ROESY: phase-sensitive using TPPI, spinlock cw pulse (250 ms). HMQC: phase-sensitive using TPPI, BIRD sequence, GARP-decoupled. HMBC: phase-sensitive using TPPI, delay to achieve long-range couplings: 71 ms (J(C,H) = 7 Hz). LSI-MS: *MAT 8500* (*Finnigan*), matrix glycerol, 4.5 kV Cs beam, negative-ion mode.

Plant Material. Herniaria glabra L. was cultivated in the garden of the Institute of Pharmacognosy, University of Vienna; a voucher specimen is deposited in the herbarium of the Institute of Pharmacognosy, University of Vienna, Austria.

Isolation of Herniaria Saponin 4 (**1**) *and 5* (**2**). Air-dried above-ground parts (1 kg) from *H. glabra* were extracted exhaustively with 80% MeOH/H$_2$O. The org. solvent was removed and the aq. soln. extracted with H$_2$O-saturated BuOH (3 ×). After evaporation, the residue was defatted by CH$_2$Cl$_2$. A first fractionation of the crude BuOH extract (60 g) was carried out by repeated CC (silica gel *60 Merck* (0.063–0.200 mm), CHCl$_3$/MeOH/H$_2$O 6:4:1 and H$_2$O-sat. BuOH). Further purification of the saponin mixture was performed by prep. HPLC

(*Lichrospher RP-8*, 7 μm (16 × 250 mm), MeOH/H_2O (54% MeOH for **1** and 58% MeOH for **2**) adjusted to pH 3 with CF_3COOH, flow 11 ml/min, UV detection (206 nm)) and prep. TLC (silica gel *60 Merck* (0.25 mm), $CHCl_3$/MeOH/H_2O 6:4:1 adjusted to pH 3 with CF_3COOH). To avoid hydrolysis of the glycosides, BuOH was added in excess when evaporating the solvent under reduced pressure. Herniaria saponins 4 (**1**) and 5 (**2**) were obtained after final prep. HPLC under the same conditions as above.

Isolation of Herniaria Saponin 6 (**3**). The MeOH extract (3.2 g) was dissolved in 300 ml of dest. H_2O and applied to *C-18* cartridges in portions of 20 ml each (*InChrom, Clean-up C-18*, 5000 mg; preconditioned with MeOH). Each cartridge was rinsed with 100 ml of H_2O, 35% MeOH/H_2O, and 40 ml of $CHCl_3$ to remove polar and nonpolar impurities. Finally, the saponin complex was eluted from the cartridges with 60% MeOH/H_2O. After removing the org. solvent, herniaria saponin 6 (**3**) was isolated from the residue (400 mg) by repeated prep. HPLC (conditions as for **1** see above).

Herniaria Saponin 4 (= O-α-L-*Rhamnopyranosyl-(1 → 4)*-O-β-D-*glucopyranosyl-(1 → 6)*-O-*[β*-D-*glucopyranosyl-(1 → 2)]*-β-D-*glucopyranosyl Medicagen-28-ate*; **1**). White powder. M.p. 231–233° (uncorr.). $[\alpha]_{20}^{D} = +3.7$ ($c = 0.135$, MeOH). ^{1}H-NMR (500 MHz, CD_3OD): 1.22 (H_{ax}–C(1)); 2.06 (H_{eq}–C(1)); 4.05 (H–C(2)); 3.83 (H–C(3)); 1.57 (H–C(5)); 1.69 (H_{ax}–C(6)); 1.32 (H_{eq}–C(6)); 1.54 (H_{ax}–C(7)); 1.31 (H_{eq}–C(7)); 1.61 (H–C(9)); 2.04 (H_{ax}–C(11)); 1.92 (H_{eq}–C(11)); 5.26 (H–C(12)); 1.76 (H_{ax}–C(15)); 1.16 (H_{eq}–C(15)); 2.07 (H_{ax}–C(16)); 1.73 (H_{eq}–C(16)); 2.86 (H–C(18)); 1.67 (H_{ax}–C(19)); 1.14 (H_{eq}–C(19)); 1.23 (H_{ax}–C(21)); 1.11 (H_{eq}–C(21)); 1.81 (H_{ax}–C(22)); 1.48 (H_{eq}–C(22)); 1.30 (Me(24)); 1.26 (Me(25)); 0.95 (Me(26)); 1.15 (Me(27)); 0.79 (Me(29)); 0.90 (Me(30)); 5.40 (*d*, $J(1',2') = 7.9$, H–C(1')); 3.82 (*t*, $J(2',3') = 9.2$, H–C(2')); 3.65 (*t*, $J(3',4') = 8.5$, H–C(3')); 3.45 (*t*, $J(4',5') = 9.8$, H–C(4')); 3.53 (*m*, $J(5',6'a) = 5.5$, $J(5',6'b) = 2.4$, H–C(5')); 3.80 (*dd*, $J = 11.5$, H_a–C(6')); 4.05 (*dd*, $J = 11.5$, H_b–C(6')); 4.38 (*d*, $J(1'',2'') = 7.8$, H–C(1'')); 3.22 (*t*, $J(2'',3'') = 9.2$, H–C(2'')); 3.46 (*t*, $J(3'',4'') = 8.8$, H–C(3'')); 3.52 (*t*, $J(4'',5'') = 10.3$, H–C(4'')); 3.29 (*m*, $J(5'',6''a) = 4.4$, $J(5'',6''b) = 2.3$, H–C(5'')); 3.81 (*dd*, $^2J = 11.3$, H_b–C(6'')); 3.65 (*dd*, $^2J = 11.3$, H_a–C(6'')); 4.84 (*d*, $J(1''',2''') = 1.8$, H–C(1''')); 3.83 (*dd*, $J(2''',3''') = 3.9$, H–C(2''')); 3.64 (*dd*, $J(3''',4''') = 9.2$, H–C(3''')); 3.39 (*t*, $J(4''',5''') = 9.8$, H–C(4''')); 3.95 (*m*, $J(5''',6''') = 6.3$, H–C(5''')); 1.25 (*d*, Me(6''')); 4.79 (*d*, $J(1'''',2'''') = 7.8$, H–C(1'''')); 3.19 (*t*, $J(2'''',3'''') = 9.8$, H–C(2'''')); 3.33 (*t*, $J(3'''',4'''') = 8.8$, H–C(3'''')); 3.14 (*t*, $J(4'''',5'''') = 10.5$, H–C(4'''')); 3.28 (*m*, $J(5'''',6''''a) = 7.2$, $J(5'''',6''''b) = 2.8$, H–C(5'''')); 3.89 (*dd*, $^2J = 11.4$, H_b–C(6'''')); 3.64 (*dd*, $^2J = 11.4$, H_a–C(6'''')). ^{13}C-NMR (125 MHz, CD_3OD): 45.4 (C(1)); 72.3 (C(2)); 76.8 (C(3)); 52.6 (C(4)); 52.6 (C(5)); 22.0 (C(6)); 33.7 (C(7)); 41.2 (C(8)); 48.2 (C(9)); 37.1 (C(10)); 23.7 (C(11)); 123.7 (C(12)); 145.1 (C(13)); 43.1 (C(14)); 29.6 (C(15)); 24.7 (C(16)); 48.2 (C(17)); 42.5 (C(18)); 47.2 (C(19)); 31.6 (C(20)); 34.9 (C(21)); 33.3 (C(22)); 13.8 (C(24)); 17.4 (C(25)); 18.0 (C(26)); 26.5 (C(27)); 178.4 (C(28)); 33.5 (C(29)); 24.4 (C(30)); 94.2 (C(1')); 78.1 (C(2')); 78.7 (C(3')); 70.9 (C(4')); 79.8 (C(5')); 69.7 (C(6')); 104.5 (C(1'')); 75.4 (C(2'')); 76.9 (C(3'')); 78.1 (C(4'')); 76.9 (C(5'')); 62.0 (C(6'')); 103.0 (C(1''')); 72.5 (C(2''')); 72.3 (C(3''')); 73.8 (C(4''')); 70.7 (C(5''')); 17.8 (C(6''')); 103.7 (C(1'''')); 75.9 (C(2'''')); 78.1 (C(3'''')); 72.6 (C(4'''')); 78.2 (C(5'''')); 63.8 (C(6'''')). LSI-MS: 1133 ($[M - H]^-$), 987 ($[M - H -$ deoxyhexose$]^-$), 971 ($[M - H -$ hexose$]^-$), 825 ($[M - H -$ deoxyhexose $-$ hexose$]^-$), 633 ($[M - H -$ deoxyhexose $-$ hexose $-$ hexose$]^-$), 501 ([aglycone $- H]^-$).

Herniaria Saponin 5 (= O-β-D-*Glucopyranosyl-(1 → 3)*-O-α-L-*rhamnopyranosyl-(1 → 2)*-O-*[β-(3*R*)*-D-*apiofuranosyl-(1 → 3)]*-β-D-*4*-O-*acetylfucopyranosyl 3*-O-*(β*-D-*Glucuronopyranosyl)-16α-hydroxymedicagen-28-ate*; **2**). White powder. M.p. 266–268° (uncorr.). $[\alpha]_{20}^{D} = -23.2$ ($c = 0.125$, MeOH). LSI-MS: 1321 ($[M - H]^-$), 1145 ($[M - H -$ glucuronic acid$]^-$), 1189 ($[M - H -$ pentose$]^-$), 1159 ($[M - H -$ hexose$]^-$), 1013 ($[M - H -$ glucuronic acid $-$ pentose$]^-$), 517 ([aglycone $- H]^-$).

Herniaria Saponin 6 (= O-α-L-*Rhamnopyranosyl-(1 → 4)*-O-β-D-*glucopyranosyl-(1 → 6)*-O-*[β*-D-*6*-O-*acetylglucopyranosyl-(1 → 2)]*-β-D-*glucopyranosyl Medicagen-28-ate*; **3**). White powder. M.p. 217–219° (uncorr.). $[\alpha]_{20}^{D} = +7.2$ ($c = 0.177$, MeOH). ^{1}H-NMR (500 MHz, CD_3OD): 1.20 (H_{ax}–C(1)); 2.08 (H_{eq}–C(1)); 4.08 (H–C(2)); 3.97 (H–C(3)); 1.59 (H–C(5)); 1.68 (H_{ax}–C(6)); 1.33 (H_{eq}–C(6)); 1.52 (H_{ax}–C(7)); 1.32 (H_{eq}–C(7)); 1.59 (H–C(9)); 2.02 (H_{ax}–C(11)); 1.92 (H_{eq}–C(11)); 5.28 (H–C(12)); 1.72 (H_{ax}–C(15)); 1.18 (H_{eq}–C(15)); 2.00 (H_{ax}–C(16)); 1.70 (H_{eq}–C(16)); 2.82 (H–C(18)); 1.68 (H_{ax}–C(19)); 1.13 (H_{eq}–C(19)); 1.21 (H_{ax}–C(21)); 1.12 (H_{eq}–C(21)); 1.80 (H_{ax}–C(22)); 1.48 (H_{eq}–C(22)); 1.32 (Me(24)); 1.27 (Me(25)); 0.93 (Me(26)); 1.13 (Me(27)); 0.79 (Me(29)); 0.90 (Me(30)); 5.38 (*d*, $J(1',2') = 7.8$, H–C(1')); 3.67 (*t*, $J(2',3') = 9.3$, H–C(2')); 3.46 (*t*, $J(3',4') = 8.7$, H–C(3')); 3.42 (*t*, $J(4',5') = 9.9$, H–C(4')); 3.52 (*m*, $J(5',6'a) = 5.7$, $J(5',6'b) = 2.5$, H–C(5')); 3.81 (*dd*, $J = 11.6$, H_a–C(6')); 4.19 (*dd*, $J = 11.6$, H_b–C(6')); 4.42 (*d*, $J(1'',2'') = 7.9$, H–C(1'')); 3.21 (*t*, $J(2'',3'') = 9.3$, H–C(2'')); 3.45 (*t*, $J(3'',4'') = 8.8$, H–C(3'')); 3.52 (*t*, $J(4'',5'') = 10.4$, H–C(4'')); 3.27 (*m*, $J(5'',6''a) = 4.3$, $J(5'',6''b) = 2.3$, H–C(5'')); 3.81 (*dd*, $^2J = 11.2$, H_b–C(6'')); 3.69 (*dd*, $^2J = 11.2$, H_a–C(6'')); 4.82 (*d*, $J(1''',2''') = 1.9$, H–C(1''')); 3.82 (*dd*, $J(2''',3''') = 3.8$, H–C(2''')); 3.62 (*dd*, $J(3''',4''') = 9.2$, H–C(3''')); 3.40 (*t*, $J(4''',5''') = 9.7$,

H–C(4‴)); 3.96 (*m*, $J(5‴,6‴) = 6.2$, H–C(5‴)); 1.28 (*d*, Me(6‴)); 4.77 (*d*, $J(1⁗,2‴) = 7.8$, H–C(1⁗)); 3.19 (*t*, $J(2⁗,3‴) = 9.8$, H–C(2⁗)); 3.36 (*t*, $J(3⁗,4⁗) = 8.8$, H–C(3⁗)); 3.20 (*t*, $J(4⁗,5⁗) = 10.4$, H–C(4⁗)); 3.46 (*m*, $J(5⁗,6⁗a) = 7.1$, $J(5⁗,6⁗b) = 2.9$, H–C(5⁗)); 4.18 (*dd*, $^2J = 11.4$, H_a–C(6⁗)); 4.32 (*dd*, $^2J = 11.4$, H_b–C(6⁗)); 2.07 (*s*, MeCOO). ^{13}C-NMR (125 MHz, CD_3OD): 45.6 (C(1)); 71.9 (C(2)); 76.4 (C(3)); 52.8 (C(4)); 52.8 (C(5)); 22.0 (C(6)); 33.8 (C(7)); 41.2 (C(8)); 49.7 (C(9)); 37.4 (C(10)); 23.6 (C(11)); 123.6 (C(12)); 145.0 (C(13)); 43.0 (C(14)); 29.7 (C(15)); 24.7 (C(16)); 47.92 (C(17)); 42.5 (C(18)); 47.1 (C(19)); 31.6 (C(20)); 34.9 (C(21)); 33.2 (C(22)); 182.0 (C(23)); 13.3 (C(24)); 17.3 (C(25)); 17.8 (C(26)); 26.5 (C(27)); 178.0 (C(28)); 33.5 (C(29)); 23.6 (C(30)); 93.8 (C(1′)); 78.8 (C(2′)); 75.2 (C(3′)); 70.8 (C(4′)); 78.1 (C(5′)); 69.2 (C(6′)); 104.2 (C(1″)); 75.3 (C(2″)); 76.7 (C(3″)); 79.6 (C(4″)); 76.8 (C(5″)); 61.9 (C(6″)); 103.0 (C(1‴)); 72.4 (C(2‴)); 72.2 (C(3‴)); 73.8 (C(4‴)); 70.7 (C(5‴)); 17.8 (C(6‴)); 104.2 (C(1⁗)); 75.6 (C(2⁗)); 78.0 (C(3⁗)); 72.1 (C(4⁗)); 79.1 (C(5⁗)); 65.6 (C(6⁗)); 21.0 (*Me*COO); 172.7 (Me*C*OO). LSI-MS: 1175 ($[M - H]^-$), 1029 ([M – H – deoxyhexose]$^-$), 971 ([M – H – acetylhexose]$^-$), 867 ([M – H – deoxyhexose – hexose]$^-$), 663 ([M – H – deoxyhexose – acetylhexose – hexose]$^-$), 501 ([aglycone – H]$^-$).

HPLC and GC/MS instruments were financed by the support of the Austrian *Bundesministerium für Wissenschaft und Forschung*.

REFERENCES

[1] G. Reznicek, J. Cart, S. Korhammer, W. Kubelka, J. Jurenitsch, E. Haslinger, *Pharmazie* **1993,** *48,* 450.
[2] H. Schröder, M. Schubert-Zsilavecz, G. Reznicek, J. Cart, J. Jurenitsch, E. Haslinger, *Phytochemistry* **1993,** *34,* 1609.
[3] G. Klein, J. Jurenitsch, W. Kubelka, *Sci. Pharm.* **1982,** *50,* 216.
[4] M. Z. Dimbi, R. Warin, C. Delaude, R. Huls, *Bull. Soc. Chim. Belg.* **1984,** *93,* 323.
[5] G. Reznicek, O. Susman, K. Böhm, *Sci. Pharm.* **1993,** *61,* 35.
[6] D. Bax, D. G. Davis, *J. Magn. Reson.* **1985,** *65,* 355.
[7] A. A. Bothner-By, R. L. Stephens, J. Lee, C. D. Warren, W. Jeanloz, *J. Am. Chem. Soc.* **1984,** *106,* 811.
[8] A. Bax, S. Subramanian, *J. Magn. Reson.* **1986,** *67,* 565.
[9] A. Bax, M. F. Summers, *J. Am. Chem. Soc.* **1986,** *108,* 2093.
[10] J. R. Snyder, A. S. Serriani, *Carbohydrate Res.* **1987,** *166,* 85.
[11] G. A. Gross, O. Sticher, C. Anklin, *Helv. Chim. Acta* **1987,** *70,* 91.
[12] H. Ishii, K. Tori, T. Tozyo, Y. Yoshimura, *J. Chem. Soc., Perkin Trans. 1* **1984,** 661.