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TRITERPENE GLYCOSIDES FROM *Cussonia paniculata*. II. ACETYLATED GLYCOSIDES FROM LEAVES

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*Structures of 13 new acetylated triterpene glycosides from leaves of Cussonia paniculata (Araliaceae) were established as 28-O-(2-O-acetyl- and 3-O-acetyl-α-L-rhamnopyranosyl)-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosides of 23-hydroxybetulinic acid (**1a** and **1b**) and hederagenin (**2a** and **2b**), 3-O-α-L-arabinopyranosyl-28-O-(2-O-acetyl- and 3-O-acetyl-α-L-rhamnopyranosyl)-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glycopyranosides of oleanic (**3a** and **3b**) and ursolic (**3c** and **3d**) acids, 3-O-α-L-arabinopyranosyl-28-O-(4-O-acetyl-, 2-O-acetyl-, and 3-O-acetyl-α-L-rhamnopyranosyl)-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosides of hederagenin (**4**, **5a** and **5b**), and 3-O-β-D-glucopyranosyl-(1→2)-O-α-L-arabinopyranosyl-28-O-(2-O-acetyl- and 3-O-acetyl-α-L-rhamnopyranosyl)-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosides of oleanic acid (**6a** and **6b**). The structures of the compounds were established using chemical methods and NMR spectroscopy.*

Key words: acetylated triterpene glycosides; glycosides of oleanic, ursolic, and 23-hydroxybetulinic acids and hederagenin; *Cussonia paniculata*; Araliaceae.

We previously reported [1] the isolation and structure of eight unacetylated glycosides from leaves of *Cussonia paniculate* Eckl. et Zeih. In the present article, the glycoside composition of the leaves of this plant is studied. It was noted previously [1] that the leaves contain a large quantity of acylated glycosides according to two-dimensional (2D) TLC [2]. The proof of structure of these is given herein.

Glycoside F (**3**) was obtained during separation of the purified total triterpene glycosides [1] as a pure compound by TLC in various solvent systems whereas fractions E, G, and I formed a group of glycosides with similar chromatographic mobilities. Rechromatography of fraction E produced glycosides E_1 (**1**) and E_2 (**2**); fraction G, G_1 (**4**), G_2, and G_3 (**5**) [1]; fraction I, I_1, I_2, and I_3 (**6**).

Total acid hydrolysis of **1** produced rhamnose and glucose in addition to the aglycon, which had the same chromatographic mobility as hederagenin. However, the color the chromatographic band differed from it upon development by phosphotungstic acid. The progenin obtained by alkaline hydrolysis was identical to the aglycon. This indicated that the aglycon had no carbohydrate chain on C-3. We assumed that the aglycon, like hederagenin, contained one additional hydroxyl in addition to the usual hydroxyl on C-3 and carboxyl on C-28. Then, we used NMR spectroscopy to establish the structures of the aglycon and the carbohydrate chain and to determine the type of acyl group and its location.

Six signals were found in the ^{13}C NMR spectrum of **1** in the range of anomeric C atoms (95-108 ppm). However, the chromatographic mobility of the glycoside showed that it should contain three carbohydrate residues. Obviously, **1** contained two isomeric glycosides with different acetylated carbohydrate fragments because signals for two O-acetyls (methyl and carbonyl C atoms) were observed in the spectrum at 21.0, 21.2, 171.1, and 171.2 ppm. Signals of the corresponding anomeric protons were found from the signals of the anomeric C atoms in the 2D HSQC spectrum.

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We concluded from the results of total acid hydrolysis and the magnitudes of the SSCC of the anomeric protons (four signals with $J_{1,2}$ = 8 Hz and two with $J_{1,2}$ = 1.5 Hz) that each of the isomeric trisaccharide chains contained two glucose units and one rhamnose. Furthermore, the isomers apparently differed only in the position of the acetyl.

Based on the 2D TOCSY spectrum, signals of the remaining skeletal protons for each of the glucopyranose units were found from the signals of the anomeric protons. Signals of the rhamnopyranose units were found primarily from the two proximal doublets for H-6 protons in the high-field region of the spectrum.

Signals for each proton in each of the six monosaccharide units could be assigned unambiguously using the COSY spectrum. After signals for all H atoms were assigned based on the HSQC spectrum, signals for the C atoms were completely assigned. The magnitudes of the chemical shifts for the C and H atoms in the glucose units showed that they were similar to those of glucopyranose units in the trisaccharide fragment Rha$^1\rightarrow^4$Glc$^1\rightarrow^6$Glc$\rightarrow$, which is typical of Araliaceae glycosides [1, 3]. However, the chemical shifts of the rhamnopyranose units were substantially different. Obviously the acetyl was located on the rhamnopyranose units. The magnitudes of the chemical shifts for the H atoms of the rhamnopyranose units showed that the signal for H-2 for one of them was located at an unusually low field ($\Delta\delta$ > 1 ppm) compared with the unacetylated trisaccharide; for the other isomeric unit, that for H-3.

The magnitudes of the chemical shifts for the C atoms showed that C-2 of one of the rhamnose units experienced a positive α-effect (1.7 ppm) whereas the neighboring C atoms showed negative β-effects (3.9 ppm for C-1 and 2.4 ppm for C-3). In the other rhamnose unit, C-3 experienced a positive α-effect (2.4 ppm); C-3 (2.5 ppm) and C-4 (2.2 ppm), negative β-effects.

The location of the acetyl was also confirmed using the HMBC spectrum, in which a cross-peak was observed between rhamnose H-2 and the carbonyl C of one of the acetyls in one glycoside and between rhamose H-3 and the carbonyl C of the other acetyl in the isomeric glycoside.

Furthermore, the types of bonds between glycosides of the monosaccharide units and of the carbohydrate fragment to the aglycon were determined using the HMBC spectrum and the observed correlations of the anomeric protons. Based on these results, the carbohydrate fragments on aglycon C-28 are 2-O-acetyl- and 3-O-acetyl-α-L-rhamnopranosyl-(1$\rightarrow$4)-O-β-D-glucopyranosyl-(1$\rightarrow$6)-O-β-D-glucopyranosyls, which were described previously only once in glycosides of *Astrantia major* (Umbelliferae) [4]. They are observed for the first time in glycosides of plants from the family Araliaceae.

Preliminary analysis of the ^{13}C NMR spectrum of **1** with ATP-editing showed that a very low-field signal appeared at 175.1 ppm. This was assigned unambiguously to the carboxyl C because of the chemical shift. Two signals at 150.9 and 110.0 ppm were observed for olefinic C atoms. Furthermore, 25 signals for aglycon C atoms were observed at high field.

These results led to the preliminary conclusion that the aglycon had a carboxyl, one double bond, a usual unglycosylated hydroxyl on C-3 (δ_C 73.4 ppm), and another primary hydroxyl (δ_C 67.7 ppm) presumed to be on C-23. The signals for the C atoms of the double bond, namely a quaternary one (according to ATP-editing) at 150.9 ppm and a secondary one (in a =CH_2 group) at 110.0 ppm, had chemical shifts that corresponded completely to C atoms of the double bond in an isopropenyl sidechain of lupane-type triterpenoids [5]. This led to the assumption that the aglycon was of this type.

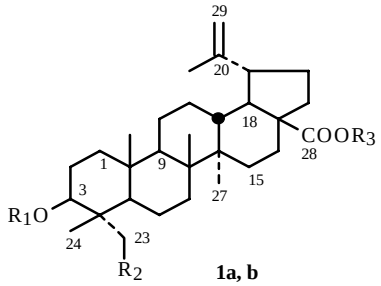
A comparison of the chemical shifts for the aglycon C atoms and those in the literature for 28-O-glycosides of betulinic and 3-epibetulinic acids [6] enabled most of the signals for C atoms in rings C, D, and E and the isopropenyl sidechain to be assigned. The remaining signals for C atoms in rings A and B were assigned by comparing chemical shifts for signals of C atoms in analogous rings of 28-O-glycosides of 23,27-dihydroxybetulinic acid [5] and hederagenin [7]. This led to the conclusion that the additional hydroxyl was located on C-23 and the aglycon was 3β,23-dihydroxylup-20(29)-en-28-oic acid or 23-hydroxybetulinic acid.

Rather recently a glycoside of this aglycon was isolated from *Oplopanax elatus* (Araliaceae) [8]. Signals for H atoms of the aglycon of **1** were completely assigned using the 2D HSQC spectrum. The 2D COSY and TOCSY spectra confirmed that the signals of the H atoms were correctly assigned (by analyzing cross-peaks of vicinal protons and those forming isolated spin systems). Furthermore, examinations of the HMBC spectrum for cross-peaks between signals for C and H atoms separated by several (three) bonds and the ROESY spectrum for spatially proximal H atoms also confirmed that the assignments were correct.

Thus, **1** is a mixture of two isomeric and chromatographically inseparable glycosides designated E_{1a} (**1a**) and E_{1b} (**1b**) with the structures 28-O-(2-O-acetyl- and 3-O-acetyl-α-L-rhamnopyranosyl)-(1$\rightarrow$4)-O-β-D-glucopyranosyl-(1$\rightarrow$6)-O-β-D-glucopyranosides of 23-hydroxybetulinic acid, respectively. The glycosides occur in the fraction in a 1:1 ratio according to the ratio of the integrated intensities of the signals for identical C atoms in the isomeric carbohydrate fragments. Glycosides **1a** and **1b** are the new triterpene glycosides. Tables 1 and 2 list the ^{13}C and ^{1}H NMR spectral data for **1a** and **1b**.

TABLE 1. ^{13}C Chemical Shifts of Aglycons in **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **3c**, **3d**, **4**, **5a**, **5b**, **6a**, and **6b** and ^{1}H in **1a** and **1b** (δ, ppm, 0 = TMS, C_5D_5N)

C atom	Compound					
	2a, **2b**	**3a**, **3b**, **6a**, **6b**	**4**, **5a**, **5b**	**3c**, **3d**	**1a**, **1b**	**1a**, **1b**
1	38.8	38.8	38.8	39.0	39.1	1.64; 1.00
2	27.6	26.5	26.1	26.5	27.4	1.93; 1.89
3	73.6	88.8	82.1	88.8	73.4	4.14
4	42.8	39.5	43.5	39.5	42.9	-
5	48.6	55.9	47.7	55.9	48.7	1.40
6	18.6	18.5	18.3	18.5	18.5	1.72; 1.45
7	32.8	33.1	32.9	33.5	34.3	1.50; 1.30
8	39.9	39.9	40.0	40.1	41.2	-
9	48.1	48.0	48.3	48.0	51.0	1.40
10	37.3	37.0	37.0	37.0	37.2	-
11	23.8	23.7	23.9	23.7	21.1	1.35; 1.16
12	122.9	122.8	122.9	126.0	26.1	1.84; 1.24
13	144.2	144.1	144.2	138.4	38.4	2.62
14	42.2	42.1	42.2	42.5	42.2	-
15	28.3	28.2	28.3	28.7	30.1	1.99; 1.18
16	23.4	23.3	23.4	24.6	32.3	2.60; 1.46
17	47.0	47.0	47.1	48.4	57.0	-
18	41.7	41.7	41.7	53.2	49.8	1.70
19	46.3	46.3	46.3	39.1	47.4	3.34
20	30.8	30.7	30.8	39.3	150.9	-
21	34.0	34.0	34.1	30.7	30.8	2.13; 1.40
22	32.5	32.4	32.6	36.7	36.8	2.19; 1.47
23	67.9	28.2	64.6	28.2	67.7	4.11; 3.67
24	13.0	16.9	13.6	16.9	12.8	1.00
25	16.0	15.6	16.3	15.7	16.4	1.13
26	17.6	17.5	17.6	17.6	16.8	0.87
27	26.0	26.0	26.1	23.7	26.1	0.96
28	176.2	176.7	176.7	176.2	175.1	-
29	33.1	33.1	33.1	17.3	110.0	4.86; 4.73
30	23.7	23.7	23.8	21.2	19.5	1.72



1a, b

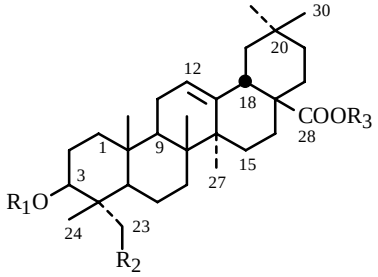
	R_1	R_2	R_3
1a:	H	OH	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*α*-L-Rha*p*^{2}← OAc
1b:	H	OH	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*α*-L-Rha*p*^{3}← OAc

Total acid hydrolysis of **2** produced rhamnose and glucose in addition to hederagenin. The progenin produced by alkaline hydrolysis of **2** was identical to the aglycon, which indicated that aglycon C-3 did not contain a carbohydrate. Signals in the ^{13}C NMR spectrum for a 28-O-glycosylated hederagenin were assigned based on literature data [7]. The remaining signals for the carbohydrate fragments were completely identical to those of the carbohydrates in **1a** and **1b**. Thus, **2** was a mixture (1:1) of two isomeric and chromatographically inseparable glycosides E_{2a} (**2a**) and E_{2b} (**2b**) with the structures 28-O-(2-O-acetyl- and 3-O-acetyl-*α*-L-rhamnopyranosyl)-(1→4)-O-*β*-D-glucopyranosyl-(1→6)-O-*β*-D-glucopyranosides of hederagenin, respectively. Glycosides **2a** and **2b** are the new compounds. Tables 1 and 2 list the ^{13}C and ^{1}H NMR spectral data for **2a** and **2b**.

TABLE 2. ^{13}C and ^{1}H Chemical Shifts of Carbohydrates in **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **3c**, **3d**, **4**, **5a**, **5b**, **6a**, and **6b** (δ, ppm, 0 = TMS, C_5D_5N)

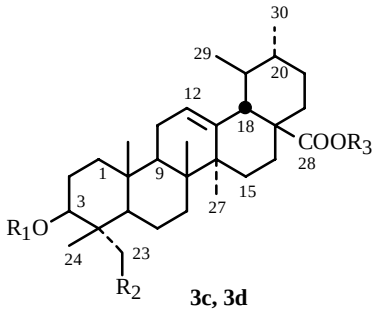
C atom	Compound			C atom	Compound			H atom	Compound		
	3a, **3b**, **3c**, **3d**	**4**, **5a**, **5b**	**6a**, **6b**		**1a**, **2a**, **3a**, **3c**, **5a**, **6a**	**1b**, **2b**, **3b**, **3d**, **5b**, **6b**	**4**		**1a**, **2a**, **3a**, **3c**, **5a**, **6a**	**1b**, **2b**, **3b**, **3d**, **5b**, **6b**	**4**
1	107.1	106.7	104.7	1	95.5	95.4	95.6	1	6.12	6.12	6.19
2	72.7	73.1	80.3	2	73.7	73.7	73.9	2	4.08	4.08	4.11
3	74.4	74.7	73.3	3	78.4	78.4	78.7	3	4.20	4.20	4.20
4	69.3	69.7	68.2	4	70.6	70.7	70.9	4	4.26	4.26	4.26
5	66.4	66.9	64.8	5	77.9	77.8	78.1	5	4.04	4.04	4.08
						69.1	69.2	6A	4.59	4.59	4.64
								6B	4.28	4.28	4.31
Glc-1			105.5	Clc-1	104.5	104.7	104.8	Glc-1	4.94	4.88	4.99
2			76.1	2	75.3	75.2	75.5	2	3.88	3.86	3.91
3			78.0	3	76.2	76.2	76.5	3	4.07	4.02	4.13
4			71.5	4	77.1	78.0	77.6	4	4.36	4.28	4.40
5			78.1	5	77.0	76.8	77.3	5	3.59	3.49	3.63
6			62.5	6	61.0	61.2	61.3	6A	4.23	4.14	4.18
								6B	4.05	4.05	4.05
				Rha-1	98.9	102.4	102.2	Rha-1	5.64	5.71	5.84
				2	74.2	70.0	72.5	2	5.75	4.76	4.63
				3	70.3	76.1	70.4	3	4.63	5.77	4.54
				4	74.0	70.7	76.0	4	4.17	4.46	5.78
				5	70.0*	70.4*	67.5	5	4.95	4.95	4.97
				6	18.3	18.4	18.0	6	1.66	1.64	1.43
				OAc	21.0**	21.2**	21.2	OAc	2.00	2.03	2.03
					171.2	171.1	170.9				

Average chemical shifts are given in Tables 1 and 2 in columns with several compounds. Deviations from the average are less than ±0.1 ppm for individual compounds. Signals between atoms marked * and ** were arbitrarily assigned.



2a, b; 3a, b; 4; 5a, b; 6a, b

	R_1	R_2	R_3
2a:	H	OH	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*α*-L-Rha*p*^{2}←OAc
2b:	H	OH	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*α*-L-Rha*p*^{3}←OAc
3a:	*α*-L-Ara*p*→	H	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*α*-L-Rha*p*^{2}←OAc
3b:	*α*-L-Ara*p*→	H	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*a*-L-Rha*p*^{3}←OAc
4:	*α*-L-Ara*p*→	OH	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-α-L-Rha*p*^{4}←OAc
5a:	*α*-L-Ara*p*→	OH	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*α*-L-Rha*p*^{2}←OAc
5b:	*α*-L-Ara*p*→	OH	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*α*-L-Rha*p*^{3}←OAc
6a:	*β*-D-Glc*p*-(1→2)-*α*-L-Ara*p*	H	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*α*-L-Rha*p*^{2}←OAc
6b:	*β*-D-Glc*p*-(1→2)-*α*-L-Ara*p*	H	←*β*-D-Glc*p*-(6←1)-*β*-D-Glc*p*-(4←1)-*α*-L-Rha*p*^{3}←OAc



3c, 3d

	R_1	R_2	R_3
3c:	α-L-Ara*p*	H	$\leftarrow\beta$-D-Glc*p*-(6$\leftarrow$1)-β-D-Glc*p*-(4$\leftarrow$1)-*a*-L-Rha*p*$^2\leftarrow$OAc
3d:	α-L-Ara*p*	H	$\leftarrow\beta$-D-Glc*p*-(6$\leftarrow$1)-β-D-Glc*p*-(4$\leftarrow$1)-α-L-Rha*p*$^3\leftarrow$OAc

The acid hydrolysate of **3** contained arabinose, glucose, rhamnose, and the aglycon, which was oleanolic acid according to TLC. The progenin of this glycoside was obtained by alkaline hydrolysis and was identical by TLC to the 3-O-α-L-arabinopyranoside of oleanolic acid [1]. Signals in the ^{13}C NMR spectrum for C atoms of the α-L-arabinopyranosyl fragment and the 2-O-acetyl- and 3-O-acetyl-α-L-rhamnopyranosyl-(1$\rightarrow$4)-O-β-D-glucopyranosyl-(1$\rightarrow$6)-O-β-D-glucopyranosyl fragments described above for **1** and **2** were assigned using literature data [3]. However, like for previously described glycosides of fractions B and H [1], the signals of the aglycon part of the ^{13}C NMR spectrum were consistent with the presence of two aglycons, oleanolic and ursolic acids, in a 4:1 mole ratio. The HMBC spectrum of **3** showed cross-peaks from H-1 of one of the glucose units to carboxyl C-28 of both oleanolic and ursolic acids. Thus, **3** was a mixture of four isomeric chromatographically inseparable glycosides F_{1a} (**3a**), F_{1b} (**3b**), F_{2a} (**3c**), and F_{2b} (**3d**) with the structures 3-O-α-L-arabinopyranosyl-28-O-(2-O-acetyl- and 3-O-acetyl-α-L-rhamnopyranosyl)-(1$\rightarrow$4)-O-β-D-glucopyranosyl-(1$\rightarrow$6)-O-β-D-glucopyranosides of oleanolic and ursolic acids, respectively.

The presence of four isomeric glycosides was also proved as follows. Although the intensities of the signals for aglycon C atoms differed significantly (4:1), those for identical atoms in the 2-O- and 3-O-acetylated trisaccharide fragments were practically identical (1:1). This indicates unambiguously that isomeric glycosides of the aglycon with 2-O- and 3-O-acetylated trisaccharide fragments of both oleanolic and ursolic acids were present. Glycosides **3a**-**3d** are new. Tables 1 and 2 list the ^{13}C and ^{1}H NMR spectral data for **3a**-**3d**.

Total acid hydrolysis of **4** and **5** showed glucose, arabinose, rhamnose, and hederagenin according to TLC. The progenins that were formed by alkaline hydrolysis of **4** and **5** were identical to hederagenin 3-O-α-L-arabinopyranoside according to TLC [1]. It was assumed based on these data that **4** and **5** were isomers at the acyl group. Signals for α-L-arabinopyranose and disubstituted hederagenin were assigned in the ^{13}C NMR spectra of **4** and **5** using literature data [3]. The remaining signals for the carbohydrate on aglycon C-28 were assigned as described above for **1**. Another three signals were observed in the ^{13}C NMR spectrum of **4** in the region of anomeric C atoms. These were used to find doublets for the anomeric protons in the HSQC spectrum. Doublets at 4.99 and 6.19 ppm with SSCC 8 Hz belong to glucopyranoses; the doublet at 5.84 with SSCC about 1.5 Hz, to rhamnopyranose. Signals for H atoms of the aglycon C-28 carbohydrate were completely assigned using 2D COSY and TOCSY spectra.

Signals in the ^{13}C NMR spectrum were assigned using the proton spectrum and the HSQC spectrum. Signals for C atoms at 21.2 and 170.9 ppm were assigned to an acetyl ester. The α- and β-effects on the H and C atoms of the carbohydrate of **4** compared with the unsubstituted trisaccharide [3] showed that rhamnose C-4 had an O-acetyl. The location of the acetate was also confirmed using the HMBC spectrum, in which a cross-peak was observed between rhamnose H-4 and an acetate carbonyl C atom.

The types of bonds between the carbohydrate units were determined using the HMBC spectrum. Thus, **4** is hederagenin 3-O-α-L-arabinopyranosyl-28-O-(4-O-acetyl-α-L-rhamnopyranosyl)-(1$\rightarrow$4)-O-β-D-glucopyranosyl-(1$\rightarrow$6)-O-β-D-glucopyranoside. This glycoside is new. Furthermore, the 4-O-acetyl-α-L-rhamnopryanosyl-(1$\rightarrow$4)-O-β-D-glucopyranosyl-(1$\rightarrow$6)-O-β-D-glucopyranosyl fragment has not been found previously in triterpene glycosides. Tables 1 and 2 list the ^{13}C and ^{1}H NMR spectral data for **4**.

The chemical shifts for ^{1}H and ^{13}C atoms in the aglycon C-28 carbohydrate of **5** that remained after signals of the 3-O-α-L-arabinopyranosyl fragment were assigned agreed completely with those of the carbohydrate in **1**. Thus, **5** is not a pure compound but consists of two isomeric acetylated glycosides **5a** and **5b** with the structures hederagenin 3-O-α-L-arabinopyranosyl-28-O-(2-O-acetyl- and 3-O-acetyl-α-L-rhamnopyranosyl)-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosides in a 1:1 mole ratio. Glycosides **5a** and **5b** are the new compounds. Tables 1 and 2 list the ^{13}C and ^{1}H NMR spectral data for **5a** and **5b**.

The acid hydrolysate of **6** contained arabinose, glucose, rhamnose, and oleanolic acid according to TLC. The progenin obtained by alkaline hydrolysis of **6** was oleanolic acid 3-O-β-D-glucopyranosyl-(1→2)-O-α-L-arabinopyranoside according to TLC [1]. Signals in the ^{13}C and ^{1}H NMR spectra of **6** were assigned by analogy with oleanolic acid 3-O-β-D-glucopyranosyl-(1→2)-O-α-L-arabinopyranoside [1] and the carbohydrates in **1a** and **1b**. It was demonstrated that **6** is a mixture of oleanolic acid 3-O-β-D-glucopyranosyl-(1→2)-O-α-L-arabinopyranosyl-28-O-(2-O-acetyl- and 3-O-acetyl-α-L-rhamnopyranosyl)-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucpyranosides (**6a** and **6b**) in a 1:1 mole ratio. However, isomeric glycosides of ursolic acid were not found in **6**. Glycosides **6a** and **6b** are new. Tables 1 and 2 list the ^{13}C and ^{1}H NMR spectral data for **6a** and **6b**.

EXPERIMENTAL

General comments have been published [1].

Separation of Glycosides. The separation of glycoside fractions E, F, G_1, and G_3 has been reported [1]. Glycosides E_1 (**1**, 40 mg) and E_2 (**2**, 43 mg) were prepared by separating fraction E (90 mg) using preparative chromatography on Silpearl microsphere silica gel with elution by water-saturated $CHCl_3$:*i*-C_3H_7OH (2:1). Glycoside I_3 was isolated by separating fraction I (181 mg) over Silpearl silica gel with elution by water-saturated $CHCl_3$:*i*-C_3H_7OH (4:1) to afford I_1 (57 mg), I_2 (67 mg), and I_3 (**6**, 50 mg).

Glycosides 1a and 1b. Acid hydrolysis produced glucose, rhamnose, and the aglycon that had the same chromatographic mobility as hederagenin but gave a chromatographic band of a different color on development by phosphotungstic acid. The progenin formed by alkaline hydrolysis had the same chromatographic mobility as the aglycon.

Glycosides 2a and 2b. Acid hydrolysis produced glucose, rhamnose, and hederagenin. The progenin formed by alkaline hydrolysis had the same chromatographic mobility as the aglycon.

Glycosides 3a, 3b, 3c, and 3d. Acid hydrolysis produced arabinose, glucose, rhamnose, and oleanolic acid. The progenin formed by alkaline hydrolysis was identified by TLC as oleanolic acid 3-O-α-L-arabinopyranoside [1].

Glycoside 4. Acid hydrolysis produced arabinose, glucose, rhamnose, and hederagenin. The progenin formed by alkaline hydrolysis was ideentified by TLC as hederagenin 3-O-α-L-arabinopyranoside [1].

Glycosides 5a and 5b. Acid hydrolysis, like for **4**, produced arabinose, glucose, rhamnose, and hederagenin. The progenin formed by alkaline hydrolysis was identified by TLC as hederagenin 3-O-α-L-arabinopyranoside [1].

Glycosides 6a and 6b. Acid hydrolysis produced arabinose, glucose, rhamnose, and oleanolic acid. The progenin formed by alkaline hydrolysis was identified by TLC as oleanolic acid 3-O-β-D-glucopyranosyl-(1→2)-O-α-L-arabinopyranoside [1].

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