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TWO NEW GLYCOSIDES, HANCOSIDE AND NEOHANCOSIDE A, FROM *CYNANCHUM HANCOCKIANUM*

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ABSTRACT.—Two new glycosides, hancoside [**1**] and neohancoside A [**2**] have been isolated from *Cynanchum hancockianum* along with five known compounds, antofine, cynatratoside A, daucosterol, (−)-leucanthemitol, and sinapic acid. Compounds **1** and **2** are established as 3β,14β,15β-trihydroxypregn-5-en-20-one 3β-*O*-β-D-(6-*O*-sinapoyl)-glucopyranosyl-(1→2)-β-D-glucopyranoside [**1**] and linalool 3-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside [**2**] by spectroscopic analysis.

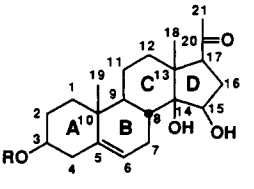
In the course of the studies on *Cynanchum hancockianum* (Maxim.) Al. Iljinski. (Asclepiadaceae) grown in Inner Mongolia, we reported four new pentacyclic triterpenes, hancokinol, hancolupenone, hancolupenol, and hancolupenol hexacosanoate, from the petroleum ether-soluble portion of the EtOH extract of *C. hancockianum* (1). Our further investigations have led to the isolation of a new steroid glycoside **1** and a new monoterpene glycoside **2**. This paper deals with the isolation and structure elucidation of these compounds by spectroscopic analysis.

RESULTS AND DISCUSSION

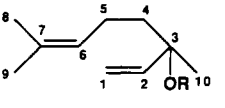
Compounds **1** and **2** were obtained along with five known compounds, antofine, cynatratoside A, daucosterol, (−)-leucanthemitol, and sinapic acid, on chromatography (Si gel) of the petroleum ether-insoluble portion of the EtOH extract of the same plant source eluting with a mixture of $CHCl_3$ and MeOH.

Compound **1**, hancoside, $C_{44}H_{62}O_8$, showed positive Liebermann-Burchard and Molisch color reactions regarded as indicative of a steroid glycoside. The ir spectrum provided hydroxyl (3400 cm^{-1}) and carbonyl bands (1736, 1724 cm^{-1}). Examination of the nmr data obtained indicated the presence of three structure units, A, B, and C.

Unit A (aglycone moiety) was composed of three methyls, seven methylenes, six methines, and five quaternary carbons detected by DEPT experiments. 2D nmr analysis revealed the presence of three independent proton-spin systems, C-1–C-4 (four-carbon chain), C-6–C-12 except C-10 (six-carbon chain), and C-15–C-17 (three-carbon



1 R=β-D-(6-*O*-sinapoyl)glucopyranosyl-(1→2)-β-D-glucopyranosyl



2 R=β-D-xylopyranosyl-(1→6)-β-D-glucopyranosyl

3 R=H, 17α-Ac

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chain), and two propyl fragments, C-19–C-10–C-5 and C-18–C-13–C-14, comprised of one methyl and two quaternary carbons, respectively, suggesting a steroid framework built up by a combination among them. Two angular methyls (δ_H 0.99, δ_C 16.74, C-18; δ_H 0.88, δ_C 19.96, C-19) were unambiguously assigned by the 2D correlations to the surrounding protonated and quaternary carbons. The presence of an acetyl comprised of a methyl (δ_H 2.07, δ_C 31.38, C-21) and a quaternary carbon (δ_C 214.66, C-20) was confirmed by ^{1}H-^{13}C (long-range) COSY experiments. The HMBC correlation of a methine (δ_H 2.50, δ_C 60.62, C-17) to H_3-21 led to 17-Ac. A one-proton signal at δ_H 5.39 (δ_C 123.08, C-6) was attributed to a trisubstituted olefinic proton (H-6) possessing two neighboring methylenes (δ_H 2.72, 2.58, δ_C 39.29, C-4; δ_H 2.64, 2.29, δ_C 26.28, C-7) and a quaternary carbon (δ_c 37.73, C-10) (HMBC). A quaternary carbon (δ_C 82.07, C-14) was correlated to H-17 and H_3-18 (HMBC). A methine (δ_H

TABLE 1. Nmr Data for the Steroid Moiety of **1**.[a]

Carbon	δ_C	Correlated H[b] δ_H	C coupled with H[c]	H coupled with H[d]
C-1	37.63 t	H-1α 0.91 dt(3.5, 13.5)	C-5, C-9, C-10 (H_3-19)	H-1β, H_2-2
		H-1β 1.58 dt(13.5, 3.5)		H-1α, H_2-2
C-2	30.35 t	H-2α 2.07 m		H_2-1, H-2β H-3
		H-2β 1.77 dq(3.5, 13.5)		H_2-1, H-2α, H-3
C-3	79.04 d	H-3 3.80 m (W_H = 28.0)		H_2-2, H_2-4
C-4	39.29 t	H-4α 2.72 dd(14.0, 4.0)	C-2, C-3, C-5, C-6, C-10	H-3, H-4β
		H-4β 2.58 brt(14.0)		H-3, H-4α
C-5	140.81 s			
C-6	123.08 d	H-6 5.39 m	C-4, C-7, C-10	H_2-7
C-7	26.28 t	H_A-7 2.64 brd(16.0)		H-6, H_B-7, H-8
		H_B-7 2.29 m	C-14	H-6, H_A-7, H-8
C-8	37.48 d	H-8 1.81 dt(4.5, 11.0)	C-9, C-14	H_2-7, H-9
C-9	45.99 d	H-9 ca. 1.14	C-10, C-11	H-8
C-10	37.73 s			
C-11	20.81 t	H_2-11 ca. 1.18	C-9	
C-12	38.16 t	H_2-12 ca. 1.18	C-9, C-14 (H_3-18)	
C-13	48.69 s		(H_3-18)	
C-14	82.07 s		(H_3-18)	
C-15	74.05 d	H-15 4.42 m		H_2-16
C-16	35.73 t	H_A-16 2.34 m	C-14, C-17	H-15, H_B-16, H-17
		H_B-16 2.03 m	C-15, C-17	H-15, H_A-16, H-17
C-17	60.62 d	H-17 2.50 dd(10.0, 4.5)	C-12, C-13, C-14, C-15, C-16 (H_3-18)	H_2-16
C-18	16.74 q	H_3-18 0.99 s	C-12, C-13, C-14, C-17	
C-19	19.96 q	H_3-19 0.88 s	C-1, C-5, C-9, C-10	
C-20	214.66 s		(H_3-21)	
C-21	31.38 q	H_3-21 2.07 s	C-17	

[a]Spectra were taken in C_5D_5N.
[b]^{1}H-^{13}C (one-bond) COSY. Figures in parentheses are coupling constants (Hz).
[c]HMBC. Letters in parentheses refer to ^{1}H-^{13}C (long-range) COSY.
[d]^{1}H-^{1}H COSY.

4.42, δ_C 74.05, C-15) was linked to a methylene (δ_H 2.34, 2.03, δ_C 35.73, C-16) and H-17 (HMBC). The carbon or proton resonances suggested the 14 and 15 positions carry oxygen functions. A methine (δ_H 3.80, δ_C 79.04, C-3) with an oxygen function was placed between two methylenes (δ_H 2.07, 1.77, δ_C 30.35, C-2; δ_H 2.72, 2.58, δ_C 39.29, C-4) by ^{1}H-^{1}H COSY experiments. The oxygen function was assigned to be equatorial on the basis of coupling (W_H = 28 Hz) observed for H-3.

Assuming a chair form for ring A and ring C and a half-chair form for ring B, the stereochemistry was examined on the basis of NOESY experiments (Figure 1). The enhancements linking H-8 to H_3-18 (13-Me) and H_3-19 (10-Me) indicated these groups to be axial (β) with respect to related rings. The orientations (α and β) refer to 10β-Me. An nOe observed between H-9 and H-15 show H-9 and C-14–C-15 to be axial (α) with respect to ring C, resulting in the B/C/D trans-cisoid-cis, H-9/10-Me trans configuration with 14β,15β-di-*O*-functions. 17β-Ac was determined on the basis of nOe's observed between H_2-12 and H-17 and between H_3-18 and H_3-21. Thus, these findings led to a pregn-5-en-20-one with 3β,14β,15β-tri-*O*-functions for unit A.

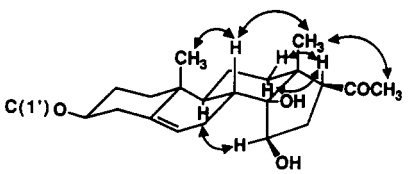

FIGURE 1. The nOe of **1**.

Unit B (sugar moiety) indicated the presence of carbons and their corresponding protons arising from two β-D-glucopyranoses in the nmr spectra (Table 2). The position and splitting multiplicity of each proton were unambiguously clarified by HOHAHA experiments. The mutual HMBC correlations (Figure 2) between a methine (δ_H 3.98, δ_C 85.69, C-2′) of glucose I and an anomeric methine (δ_H 5.18, δ_C 106.93, C-1″) of glucose II demonstrated two glucoses to combine with each other at the 2′ and 1″ positions. Thus, unit B was established as a β-sophoroside (2).

Unit C (sinapic acid moiety) showed the presence of carbons and their corresponding protons arising from a sinapic acid in the nmr spectra by comparison with those of an authentic sinapic acid (Table 2).

It was clarified that unit A and unit B are combined with each other at the 3 and 1′ positions by the HMBC correlation between H-3 and an anomeric methine (δ_H 4.97, δ_C 100.70, C-1′) of glucose I. HMBC experiments also showed the correlation between a methylene (δ_H 5.06, 4.92, δ_C 64.98, C-6″) of glucose II and a carboxyl carbon (δ_C 167.85, C-9‴) of a sinapic acid, determining unit B to join with unit C at 6″-OH as a sinapate. These findings indicated 3β,14β,15β-trihydroxypregn-5-en-20-one 3β-*O*-β-D-(6-*O*-sinapoyl)glucopyranosyl-(1→2)-β-D-glucopyranoside for **1**.

Acidic methanolysis of **1** afforded compound **3**, methyl α- and β-D-glucopyranosides, and methyl sinapate. A glance at the changes observed in the ^{1}H and ^{13}C resonances of ring A suggested **3** to be the aglycone of **1**. However, discrepancies in the carbon resonances were found at other positions remote from ring A. It has been reported that the C-12 and C-20 signals in C/D *cis*-17β-pregnanes appear at a lower field than those in 17α isomers, and the C-18 resonances are shifted upfield (3). The epimerization shifts, $\Delta\delta$ (C-12) = +7.88, $\Delta\delta$ (C-18) = −3.22 and $\Delta\delta$ (C-20) = +5.06 ppm, observed between **1** and **3** pointed out **3** to be the 17α-isomer of aglycone, i.e., 17-*epi*-

TABLE 2. Nmr Data for Sugar and Sinapic Acid Moieties of **1**.[a]

Carbon	δ_C	Correlated H[b] δ_H	C coupled with H[c]
C-1′	100.70 d	H-1′ 4.97 d(9.0)	C-3, C-5′
C-2′	85.69 d	H-2′ 3.98 t(9.0)	C-1′, C-3′, C-1″
C-3′	78.31 d	H-3′ 4.24 t(9.0)	
C-4′	71.35 d	H-4′ 4.11 t(9.0)	C-5′
C-5′	78.42 d	H-5′ 3.79 m	
C-6′	62.75 t	H_A-6′ 4.40 dd(12.0, 2.5)	C-4′
		H_B-6′ 4.24 dd(12.0, 4.5)	
C-1″	106.93 d	H-1″ 5.18 d(8.0)	C-2′
C-2″	76.69 d	H-2″ 4.06 dd(9.0, 8.0)	C-1″, C-3″
C-3″	78.24 d	H-3″ 4.15 t(9.0)	C-4″
C-4″	71.35 d	H-4″ 4.13 t(9.0)	
C-5″	75.99 d	H-5″ 4.07 m	C-1″
C-6″	64.98 t	H_A-6″ 5.06 brd(11.0)	C-4″, C-9‴
		H_B-6″ 4.92 dd(11.0, 4.8)	
C-1‴	125.30 s		(H-8‴)
C-2‴	106.90 d	H-2‴ 6.87 s	C-3‴, C-4‴, C-7‴
C-3‴	139.20 s		
C-4‴	149.40 s		(H-2‴, H-6‴)
C-5‴	139.20 s		
C-6‴	106.90 d	H-6‴ 6.87 s	C-4‴, C-5‴, C-7‴
C-7‴	146.20 d	H-7‴[d] 7.85 d(16.0)	C-9‴ (H-2‴, H-6‴)
C-8‴	115.57 d	H-8‴[d] 6.56 d(16.0)	C-1‴
C-9‴	167.85 s		(H-7‴)
3‴-OMe	56.55 q	Me 3.72 s	
5‴-OMe	56.55 q	Me 3.72 s	
4‴-OH		11.53 s	

[a]Spectra were taken in C_5D_5N.
[b]^{1}H-^{13}C (one-bond) COSY. Assignments were confirmed by HOHAHA experiments. Figures in parentheses are coupling constants (Hz).
[c]HMBC. Letters in parentheses refer to ^{1}H-^{13}C (long-range) COSY.
[d]These protons were coupled with each other (^{1}H-^{1}H COSY).

hancogenine, on the basis of the above-mentioned findings. Compound **3** must be formed via an acid-mediated enolization during the rection.

It is known that C/D *cis*-17β(17*S*)- and 17α(17*R*)-pregnanes show a positive and a negative Cotton effect (carbonyl n→π*), respectively, on the ORD spectra (4,5). A positive cd Cotton effect at 290.5 nm observed for **1** corresponded to 17β-Ac (17*S*). A negative one observed at 292 nm indicated 17α-Ac(17*R*) for **3**. In addition, the glycosidation shifts of β,β′-carbons, $\Delta\delta_{1-3}$ (C-2) = −2.46 and $\Delta\delta_{1-3}$ (C-4) = −4.19 ppm, led to 3β(eq)-OH(3*S*) (2). These observations were in accord with the stereochemistry of **1** deduced above.

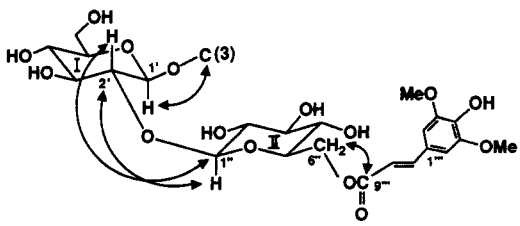

FIGURE 2. HMBC of **1**.

Compound **2**, neohancoside A, $C_{21}H_{36}O_{10}$, showed a positive Molisch color reaction. The ir spectrum indicated a hydroxyl band (3350 cm^{-1}). Acidic methanolysis revealed the presence of linalool and methyl α- and β-D-xylopyranosides. 2D nmr analysis also showed **2** to consist of linalool, a glucose, and a xylose (Table 3).

TABLE 3. Nmr Data for **2**.[a]

Carbon	δ_C	Correlated H[b] δ_H	C coupled with H[c]	H coupled with H[d]
C-1	114.29 t	H_A-1 5.19 dd(17.5, 1.5)	C-3	H_B-1, H-2
		H_B-1 5.12 dd(10.8, 1.5)	C-3	H_A-1, H-2
C-2	144.52 d	H-2 6.32 dd(17.5, 10.8)	C-3, C-10	H_2-1
C-3	80.21 s			
C-4	40.99 t	N_2-4 1.73 t(8.3)	C-3, C-6, C-10	H_2-5
C-5	23.22 t	H_2-5 2.18 m	C-4	H_2-4, H-6
C-6	125.68 d	H-6 5.11 m		H_2-5, H_3-8, H_3-9
C-7	131.14 s			
C-8	17.91 q	H_3-8 1.45 s	C-5, C-6, C-7	H-6
C-9	25.91 q	H_3-9 1.52 s	C-5, C-6, C-7, C-8	H-6
C-10	24.40 q	H_3-10 1.41 s	C-2, C-3, C-4	
C-1′	99.55 d	H-1′ 4.80 d(7.8)	C-3	H-2′
C-2′	75.26 d	H-2′ 3.83 dd(8.2, 7.8)	C-3′	H-1′
C-3′	78.86 d	H-3′ 4.07 t(8.2)		
C-4′	71.74 d	H-4′ 4.06 t(8.2)	C-3′	
C-5′	76.97 d	H-5′ 3.86 m	C-3′	
C-6′	70.02 t	H_A-6′ 4.61 dd(11.0, 2.0)		H_B-6′
		H_B-6′ 4.21 dd(11.0, 4.5)	C-1″	H_A-6′
C-1″	105.91 d	H-1″ 4.87 d(7.1)	C-6′	
C-2″	75.02 d	H-2″ 3.91 dd(8.5, 7.1)	C-1″, C-3″	
C-3″	78.24 d	H-3″ 4.02 t(8.5)	C-2″, C-4″	
C-4″	71.29 d	H-4″ 4.09 ddd(9.7, 8.5, 4.6)		H_2-5″
C-5″	67.19 d	H_A-5″ 4.21 dd(11.0, 4.6)	C-1″, C-3″, C-4″	H-4″
		H_B-5″ 3.55 dd(11.0, 9.7)	C-1″, C-3″, C-4″	H-4″

[a]Spectra were taken in $CDCl_3$.

[b]^1H-^{13}C (one-bond) COSY. Assignments of protons of sugar moiety were confirmed by HOHAHA experiments. Figures in parentheses are coupling constants (Hz).

[c]HMBC.

[d]^1H-^1H COSY.

Three tertiary methyls (δ_H 1.45, δ_C 17.91, C-8; δ_H 1.52, δ_C 25.91, C-9; δ_H 1.41, δ_C 24.40, C-10), three methylenes (δ_H 5.19, 5.12, δ_C 114.29, C-1; δ_H 1.73, δ_C 40.99, C-4; δ_H 2.18, δ_C 23.22, C-5), two methines (δ_H 6.32, δ_C 144.52, C-2; δ_H 5.11, δ_C 125.68, C-6) and two quaternary carbons (δ_C 80.21, C-3; δ_C 131.14, C-7) were attributable to a linalool by comparison with those of linalool. The remaining protons and carbons were assigned to those of a glucose and a xylose by 2D nmr spectroscopy and comparison with those of sugars. The position and splitting multiplicity of each proton were unambiguously determined by HOHAHA experiments.

The HMBC correlations (Figure 3) between C-3 and an anomeric methine (δ_H

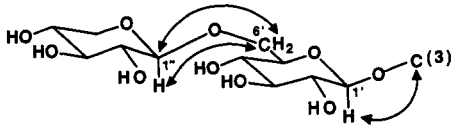

FIGURE 3. HMBC of **2**.

4.80, δ_C 99.55, C-1′) of a glucose and between a methylene (δ_H 4.21, δ_C 70.02, C-6′) of a glucose and an anomeric methine (δ_H 4.87, δ_C 105.91, C-1″) of a xylose led to linalool 3-*O*-β-D-xylopyranosyl-(1↦6)-β-D-glucopyranoside as the structure for **2**.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points (uncorrected) were determined on a micro hot-stage apparatus. Specific rotations were taken on a JASCO DPI-181 polarimeter. Spectra were recorded on the following spectrometers: ir, Hitachi 260-30; uv, Hitachi EPS-2U; cd, JASCO J-20; ^{1}H nmr, Varian XL-400 at 400 MHz (reference TMS); ^{13}C nmr, Varian XL-400 at 100.6 MHz (reference TMS); eims, fabms, and fdms, JEOL JMS DX-300; elemental analysis, Perkin-Elmer 240B.

All nmr spectra were taken at a probe temperature of 20° using a 5-mm tube. 2D nmr, DEPT, and NOESY experiments were performed using Varian's standard pulse sequences (6).

EXTRACTION AND ISOLATION.—The roots of *C. hancockianum* were collected in Inner Mongolia. Plant material was identified by Prof. Y. Guo, Shenyang College of Pharmacy, and a specimen is deposited in the Herbarium of Shenyang College of Pharmacy.

The air-dried, powdered plant material (15 kg) was extracted with boiling EtOH (30 liters × 4) for 5 h. The EtOH extract (2.4 kg) obtained was extracted with $CHCl_3$-MeOH (9:1) (5 liters). MeOH-H_2O (6:4) (2.5 liters) was added to a syrup obtained from the soluble portion, and the whole was extracted with petroleum ether (1.4 liters × 5) (1).

The insoluble portion was concentrated in vacuo to a syrup and taken up in $CHCl_3$ (2 liters). The $CHCl_3$ solution was poured into petroleum ether (6 liters) with stirring to yield a precipitate (200 g). The precipitate (130 g) was chromatographed over Si gel (460 g) eluting with a mixture of $CHCl_3$ and MeOH in increasing polarity. First elution with $CHCl_3$-MeOH (97:3↦95:5) (30 liters) gave antofine (7,8) (1.3 g), cynatratoside A (9) (140 mg), daucosterol (2.6 g), and sinapic acid (92 mg). Elution with $CHCl_3$-MeOH (90:10) (7.5 liters) afforded the eluate (4.3 g) which was rechromatographed over Si gel (45 g) eluting with $CHCl_3$-MeOH (93:7) (12 liters) to yield **1** (60 mg) along with two unidentified compounds (12, 8 mg) showing positive Liebermann-Burchard and Molisch color reactions. The eluate (4.8 g) from subsequent elution with $CHCl_3$-MeOH (93:7) (6 liters) was rechromatographed over Si gel (40 g) eluting with petroleum ether-Me_2CO (1:1) (8.5 liters) to yield **2** (60 mg) together with (−)-leucanthemitol (10) (80 mg).

The known compounds were identified by spectroscopic analysis and direct comparisons with authentic samples.

Hancoside [**1**].—Colorless granules: mp 185–187° (MeOH); $[\alpha]^{27}_D$ −12.31° (c = 0.13, dioxane); ir ν max (KBr) cm^{-1} 3400, 1736, 1724, 1630; uv λ max (MeOH) ε (nm) 4120 (223), 4700 (238), 5500 (324); cd ($c = 1.23 \times 10^{-3}$, dioxane) $[\theta]^{24}$ (nm) 0 (329.5), +2700 (290.5) (positive maximum), +600 (254.2) (negative maximum), +15400 (209) (positive maximum); fabms *m/z* $[M + 1]^+$ 879; ^{1}H nmr and ^{13}C nmr, see Tables 1 and 2. *Anal.* calcd for $C_{44}H_{62}O_{18}$, C 60.12, H 7.11; found C 59.86, H 6.90.

ACIDIC METHANOLYSIS OF **1**.—A solution of **1** (5.0 mg) in 2 N HCl (0.5 ml) and MeOH (1 ml) was refluxed for 8 h. The reaction mixture was neutralized with Ag_2CO_3, filtered and concentrated in vacuo. The residue was partitioned between H_2O (2 ml) and $CHCl_3$ (5 ml × 2). Workup of the organic layer, followed by preparative tlc [Si gel, $CHCl_3$-MeOH (100:1)], gave **3** (1.3 mg), R_f 0.08, and **5** (1.0 mg), R_f 0.54. Concentration of the aqueous layer in vacuo yielded **4** (2.4 mg) (ratio 2:1), R_f 0.17 [Si gel, $CHCl_3$-MeOH (5:1)].

17-epi-*Hancogenine* [**3**].—Colorless needles: mp 218–220° (C_6H_6/hexane); $[\alpha]^{22}_D$ −44.2° (c = 0.09, dioxane); ir ν max ($CHCl_3$) cm^{-1} 3340, 1730, 1702; uv λ max (MeOH) ε (nm) 6000 (284); cd ($c = 8.6 \times 10^{-4}$, dioxane); $[\theta]^{22}$ (nm) 0 (330), −3170 (292) (negative maximum), 0 (234); ^{1}H nmr ($CDCl_3$) δ 5.38 (1H, d, J = 5.0 Hz, H-6), 4.53 (1H, ddd, J = 9.5, 5.0, 3.5 Hz, H-15), 3.72 (1H, m, W_H = 26.0 Hz, H-3), 3.50 (1H, t, J = 9.5 Hz, H-17), 2.90 (1H, dt, J = 14.0, 9.5 Hz, H_A-16), 2.55 (1H, dd, J = 18.0, 10.5 Hz, H-7α), 2.48 (2H, m, H_2-4), 2.36 (1H, dt, J = 18.0, 5.0 Hz, H-7β), 2.02 (3H, s, H_3-21), 2.01 (1H, m, H-8), 1.96 (1H, m, H-2α), 1.77 (1H, ddd, J = 14.0, 9.5, 3.5 Hz, H_B-16), 1.71 (1H, dt, J = 14.0, 4.0 Hz, H-1β), 1.65 (1H, dt, J = 4.0, 11.0 Hz, H-2β), 1.35 (3H, s, H_3-18), 1.33 (2H, m, H_2-11), 1.24 (1H, m, H-9), 1.14 (2H, m, H_2-12), 1.04 (1H, ddd, J = 14.0, 11.0, 4.0 Hz, H-1α), 0.92 (3H, s, H_3-19), 6.42 (1H, d, J = 5.0 Hz, 15-OH, coupled with H-15), 6.04 (1H, br s, 3-OH), 5.07 (1H, s, 14-OH); ^{13}C nmr ($CDCl_3$) δ 209.60 (s, C-20), 140.50 (s, C-5), 122.05 (d, C-6), 83.81 (s, C-14), 71.33 (d, C-3), 71.16 (d, C-15), 59.90 (d, C-17), 48.71 (s, C-13), 46.56 (d, C-9), 43.48 (t, C-4), 37.87 (t, C-1), 37.87 (d, C-8), 37.54 (s, C-10), 34.52 (t, C-16), 32.71 (t, C-2), 31.93 (q, C-21), 30.28 (t, C-12), 26.70 (t, C-7), 20.73 (t, C-11), 19.96 (q, C-18, C-19); fabms *m/z* $[M + Na]^+$ 371 (348 for $C_{21}H_{32}O_4$); hrms *m/z* $[M - H_2O]^+$ 330.2197 (330.2194 for $C_{21}H_{30}O_3$).

Methyl α- and β-D-glucopyranosides.—These compounds were identified with authentic samples by nmr analysis and co-tlc.

Methyl sinapate.—Colorless needles: mp 90–92° (Et_2O); hrms *m/z* $[M]^+$ 238.0860 (238.0841 for $C_{12}H_{14}O_5$). This compound was identical with an authentic sample by mixed melting point, ir and nmr spectra.

Neohancoside A [**2**].—Colorless granules: mp 84–86° (MeOH); $[\alpha]^{23}D$ −27.7° (*c* = 0.62, MeOH); ir ν max (KBr) cm^{-1} 3350, 1620; fdms *m/z* $[M+Na]^+$ 471; ^1H and ^{13}C nmr see Table 3. *Anal.* calcd for $C_{21}H_{36}O_{10}$, C 56.23, H 8.09; found C 56.05, H 8.02.

Neohancoside A hexaacetate.—This compound was prepared in the usual manner using Ac_2O and C_5H_5N. Colorless needles: mp 179.5–180.5° ($CHCl_3$); ir ν max (KBr) cm^{-1} 1740; ^{13}C nmr ($CDCl_3$) δ (aglycone moiety) 141.49 (d, C-2), 131.69 (s, C-7), 123.98 (d, C-6), 115.33 (t, C-1), 80.83 (s, C-3), 40.66 (t, C-4), 25.64 (q, C-9), 22.53 (q, C-10), 22.32 (t, C-5), 17.65 (q, C-8); (sugar moiety) 100.31 (d, C-1″), 95.47 (d, C-1′), 73.03 (d), 72.93 (d), 71.92 (d), 71.35 (d), 70.13 (d), 69.25 (d), 68.26 (d), 68.14 (t), 61.81 (t), 20.71–20.64 (each q, Me × 6), 170.58–169.11 (each s, CO × 6). *Anal.* calcd for $C_{33}H_{48}O_{16}$, C 56.56, H 6.90; found C 56.40; H 6.85.

ACIDIC METHANOLYSIS OF **2**.—A solution of **2** (5.0 mg) in 6.5% HCl/MeOH (2 ml) was refluxed for 8 h. The reaction mixture was neutralized with Ag_2CO_3, filtered and concentrated in vacuo. The residue was partitioned between H_2O (2 ml) and $CHCl_3$ (5 ml × 2). Workup of the organic layer afforded unidentified materials (1.7 mg) instead of linalool, the occurrence of which was clearly recognized at the initial stage by co-tlc (Si gel, $CHCl_3$) with an authentic sample (R_f 0.68). Concentration of the aqueous layer in vacuo gave a mixture (2.4 mg) of methyl α- and β-D-glucopyranosides R_f 0.17, and methyl α- and β-D-xylopyranosides R_f 0.34, which were identical with authentic samples by co-tlc [Si gel, $CHCl_3$-MeOH (5:1)].

Cynatratoside A.—Colorless needles: mp 207–208.5° (Me_2CO) [lit. (9) mp 209–210°]. The ir and nmr (^1H, ^{13}C) data were in accord with those described by Zhang *et al.* (9). Eims *m/z* $[M]^+$ 504. *Anal.* calcd for $C_{28}H_{40}O_8 \cdot \frac{1}{2}H_2O$, C 65.47, H 8.04; found C 65.62, H 8.02.

(−)-Leucanthemitol.—Colorless prisms, mp 129–130° (MeOH) [lit. (10) mp 113.5°]; $[\alpha]^{17}D$ −96.37° (*c* = 0.38, MeOH) [lit. (10) $[\alpha]D$ −101.5° (*c* = 1.5, H_2O)]. The ir and nmr (^1H, ^{13}C) data were in accord with those described by Plouvier (10). Eims *m/z* $[M-18]^+$ 128. *Anal.* calcd for $C_6H_{10}O_4$, C 49.30, H 6.90; found C 49.49, H 7.05.

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