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FURTHER ISOLATION OF GLYCOSIDES FROM *CYNANCHUM HANCOCKIANUM*

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ABSTRACT.—Three new glycosides, neohancosides B, C, and D, have been isolated as polyacetates **2**, **3**, and **4** from *Cynanchum hancockianum* along with neohancoside A hexaacetate [**1**]. The new compounds were established as 9-hydroxylinalool-3-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside heptaacetate [**2**], 2-hydroxyacetophenone-2-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside hexaacetate [**3**], and 6′-*O*-sinapoylsucrose octaacetate [**4**] by means of spectroscopic and chemical tools.

We previously reported eight new compounds, hancokinol, hancolupenol, hancolupenol hexacosanoate, hancolupenone, hancopregnane, hancoside, neohancoside A, and *p*-menthane-1,7,8-triol, and eleven known compounds, antofine, cynatratoside A, daucosterol, de-6-*O*-methylantofine, glaucogenins A and C, 4-hydroxy-3-methoxyacetophenone, (−)-leucanthemitol, *p*-menthane-1,8,9-triol, 1-*p*-menthene-8,9-diol, and sinapic acid, isolated from the petroleum ether-soluble (1) and -insoluble (2) and HCl-soluble portions (3) of the EtOH extract of *Cynanchum hancockianum* (Maxim.) Al. Iljinski. (Asclepiadaceae) grown in Inner Mongolia. This paper deals with the isolation and structure elucidation of compounds from the *n*-BuOH-soluble portion of the same source for the completion of this series of work.

RESULTS AND DISCUSSION

The *n*-BuOH-soluble portion afforded a mixture of inseparable compounds on repeated chromatography, showing an ir OH band and a positive Molisch coloration. However, acetylation led to the easy isolation of three new compounds, neohancosides B, C, and D, as polyacetates **2**, **3**, and **4**, together with one known compound, neohancoside A hexaacetate [**1**]. Prior to acetylation, the absence of the acetoxyl signal was unambiguously confirmed by ir and nmr (^{1}H and ^{13}C) analyses. Accordingly, **1–4** must exist in nature as the nonacetylated compounds **1a–4a**.

Neohancoside A hexaacetate [**1**], $C_{33}H_{48}O_{16}$, indicated the presence of linalool [**5**], methyl α- and β-D-glucopyranosides, and methyl α- and β-D-xylopyranosides on alkaline hydrolysis, followed by acidic methanolysis, suggesting **1** to be a linalool glycoside composed of a polyacetylglucose and a polyacetylxylose. The nmr spectra were superimposable on those of linalool-3-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside hexaacetate (2).

Neohancoside B heptaacetate [**2**], $C_{35}H_{50}O_{18}$, gave neohancoside B [**2a**], on deacetylation with MeONa/MeOH. Comparison with the nmr spectra of neohancoside A [**1a**] (2) showed that the aglycone moiety of **2a** is an analogue of **5** and the sugar moiety is composed of a β-D-glucopyranoside and a β-D-xylopyranoside arranged in the same manner as that of **1a** (Tables 1 and 2).

The aglycone moiety of **2a** displayed the presence of two tertiary methyls, four methylenes, two methines, and two quaternary carbons in DEPT experiments. On the

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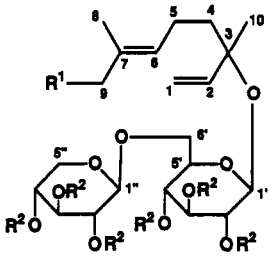
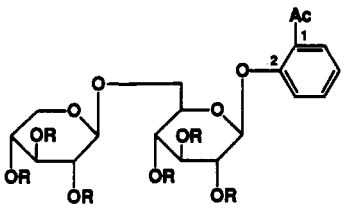
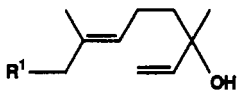


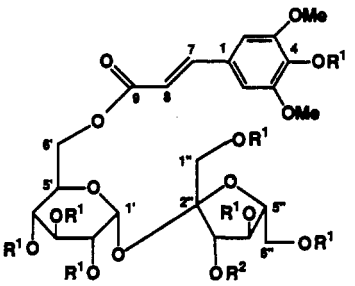
1 R^1=H, R^2=Ac
1a R^1=R^2=H
2 R^1=OAc, R^2=Ac
2a R^1=OH, R^2=H



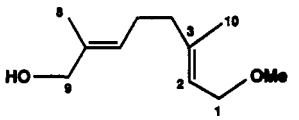
3 R=Ac
3a R=H



5 R^1=H
6 R^1=OH



4 R^1=R^2=Ac
4a R^1=R^2=H
8 R^1=H, R^2=4-*O*-methylsinapoyl



7

basis of the proton and carbon resonances, a methylene (δ_H 4.15, δ_C 68.23) contained an *O*-function, suggesting an 8- or 9-hydroxylinalool for the aglycone moiety. Determination of the 9-*O*-function was achieved by observation of an nOe between H-6 (δ_H 5.40) and H_2-9 (δ_H 4.43) in **2**.

Each proton of the sugar moieties was unambiguously assigned by HOHAHA experiments. The HMBC correlations observed between a quaternary carbon (δ_C 80.13, C-3) and an anomeric methine (δ_H 4.80, δ_C 99.54, C-1′) of a glucose and between a methylene (δ_H 4.62, 4.20, δ_C 70.03, C-6′) of a glucose and an anomeric methine (δ_H 4.88, δ_C 105.87, C-1″) of a xylose led to 9-hydroxylinalool-3-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside for **2a**.

Enzymatic hydrolysis of **2a** with a β-D-glucosidase afforded 9-hydroxylinalool [**6**] as the aglycone. The ^{1}H nmr spectrum of **6** was superimposable on that of (±)-**6** derived from (±)-**5** by SeO_2 oxidation and showed an nOe between H_2-5 (δ_H 2.08) and H_3-8 (δ_H 1.67).

Acidic methanolysis of **2a** with HCl/MeOH gave compound **7**, methyl α- and β-D-glucopyranosides, and methyl α- and β-D-xylopyranosides. Compound **7** was identical with 9-hydroxy-1-*O*-methylgeraniol (4) prepared from (±)-**6** by acidic methanolysis including dehydroxylation at C-3, rearrangement of C-1=C-2, and methoxylation at C-1. The 2*E* configuration was suggested by an nOe observed between H_2-1 (δ_H 3.90) and H_3-10 (δ_H 1.68).

Neohancoside C hexaacetate [**3**], $C_{31}H_{38}O_{17}$, afforded an aglycone, methyl α- and β-D-glucopyranosides, and methyl α- and β-D-xylopyranosides on alkaline hydrolysis,

TABLE 1. Comparison of Nmr Data for Compounds **1**, **1a**, and **2**.[a]

Position	Compound					
	1 ($CDCl_3$)		**1a** (C_5D_5N)		**2** ($CDCl_3$)	
	δ_C[b]	δ_H	δ_C[b]	δ_H[b]	δ_C	δ_H
1	115.33 t	5.22 d (11.0)	114.29 t	5.19 dd (17.5, 1.5)	115.46 t	5.21 d (11.0)
		5.18 d (18.0)		5.12 dd (10.8, 1.5)		5.17 d (19.0)
2	141.49 d	5.89 dd (18.0, 11.0)	144.52 d	6.33 dd (17.5, 10.8)	141.82 d	5.90 dd (19.0, 11.0)
3	80.83 s		80.21 s		80.56 s	
4	40.66 t	1.58 m	40.99 t	1.73 t (8.3)	40.13 t	1.60 m
5	22.32 t	2.04 m	23.22 t	2.18 m	22.02 t	2.02 m
6	123.98 d	5.21 t (7.0)	125.68 d	5.11 m	129.16 d	5.40 t (7.2)
7	131.69 s		131.14 s		130.32 s	
8	17.65 q	1.58 s	17.91 q	1.45 s	13.96 q	1.63 s
9	25.64 q	1.68 s	25.91 q	1.52 s	70.12 t	4.43 s
10	22.53 q	1.25s	24.40 q	1.41 s	22.53 q	1.24 s
1′	95.47 d	4.53 d (8.0)	99.55 d	4.80 d (7.8)	95.57 d	4.51 d (8.0)
2′	71.93 d	4.95 dd (9.2, 8.0)	75.26 d	3.83 dd (8.2, 7.8)	71.40 d	4.93 dd (9.2, 8.0)
3′	73.03 d	5.15 t (9.2)	78.86 d	4.07 t (8.2)	73.12 d	5.17 t (9.2)
4′	69.25 d	5.03 t (9.2)	71.74 d	4.06 t (8.2)	69.15 d	4.91 t (9.2)
5′	72.92 d	3.58 m	76.97 d	3.86 m	72.87 d	3.58 m
6′	68.14 t	3.77 m	70.02 t	4.61 dd (11.0, 2.0)	67.62 t	3.77 m
		3.60 m		4.21 dd (11.0, 4.5)		3.56 m
1″	100.31 d	4.57 d (7.1)	105.91 d	4.87 d (7.1)	100.15 d	4.53 d (7.1)
2″	70.13 d	4.85 dd (8.5, 7.1)	75.02 d	3.91 (8.5, 7.1)	70.47 d	4.89 dd (8.5, 7.1)
3″	71.35 d	5.14 t (8.5)	78.24 d	4.02 t (8.5)	71.22 d	5.13 t (8.5)
4″	68.26 d	4.97 dt (5.0, 8.5)	71.29 d	4.09 ddd (9.7, 8.5, 4.6)	68.71 d	4.93 dt (4.9, 8.5)
5″	61.81 t	4.12 dd (12.0, 5.0)	67.19 t	4.21 dd (11.0, 4.6)	61.85 t	4.12 dd (11.9, 4.9)
		3.38 dd (12.0, 8.5)		3.55 dd (11.0, 9.7)		3.35 dd (11.9, 8.5)
OAc	Me×6				Me×7	
	20.71–20.64 (each q)				20.99–20.63 (each q)	
	2.10–1.99 (each s)				2.06–1.98 (each s)	
	CO×6				CO×7	
	170.58–169.11 (each s)				170.95–169.08 (each s)	

[a]Chemical shift in δ (ppm); ^{13}C multiplicities from DEPT experiments; J_{HH} (Hz) in parentheses; assignments based on ^1H-^1H, ^1H-^{13}C (one-bond, long-range) COSY, HMBC and HOHAHA experiments.

[b]These data are from Y. Konda *et al.* (2).

followed by acidic methanolysis. The aglycone was proven to be 2-hydroxyacetophenone by spectroscopic (ir and ^1H nmr) analysis. Deacetylation of **3** with MeONa/MeOH was unsuccessful and afforded 2-hydroxyacetophenone and a sugar instead of neohancoside C [**3a**].

A survey of the nmr data for **3** indicated that the sugar moiety is composed of a β-D-glucopyranoside triacetate and a β-D-xylopyranoside triacetate arranged in the same manner as those of **1** and **2** (Table 3). The oxygen bridges between C-2 and C-1′ and

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

Position	^{13}C	Correlated H δ_H		C coupled with H	H coupled with H
1	114.29 t	H_A-1	5.18 d (11.0)	C-2, C-3	H-2
		H_B-1	5.11 d (17.5)	C-2, C-3	H-2
2	144.46 d	H-2	6.31 dd (17.5, 11.0)	C-3, C-4, C-10	H_2-1
3	80.12 s				
4	40.68 t	H_2-4	1.77 t (8.3)	C-2, C-3, C-5, C-6, C-10	H_2-5
5	22.78 t	H_2-5	2.30 m	C-4, C-6, C-7	H_2-4, H-6
6	125.16 d	H-6	5.62 t (7.0)		H_2-5
7	136.92 s				
8	14.12 q	H_3-8	1.66 s	C-6, C-7, C-9	
9	68.23 t	H_2-9	4.15 s	C-6, C-7	
		9-OH	6.06 s		
10	24.54 q	H_3-10	1.41 s	C-2, C-3, C-4	
1′	99.54 d	H-1′	4.80 d (8.0)	C-3, C-5′	H-2′
2′	75.26 d	H-2′	3.83 t (8.0)	C-1′, C-3′, C-4′	H-1′, H-3′
3′	78.85 d	H-3′	4.06 m	C-2′, C-4′, C-5′	H-2′
4′	71.78 d	H-4′	4.06 m	C-3′, C-6′	
5′	77.02 d	H-5′	3.87 m	C-1′, C-3′	H-4′, H_B-6′
6′	70.03 t	H_A-6′	4.62 dd (11.0, 2.0)	C-4′, C-1″	H_B-6′
		H_B-6′	4.20 dd (11.0, 4.7)	C-4′, C-1″	H-5′, H_A-6′
1″	105.87 d	H-1″	4.88 d (8.5)	C-6′, C-5″	H-2″
2″	75.00 d	H-2″	3.91 t (8.5)	C-1″	H-1″, H-3″
3″	78.20 d	H-3″	4.02 t (8.5)		H-2″, H-4″
4″	71.27 d	H-4″	4.09 ddd (10.0, 8.5, 4.0)		H-3″, H_B-5″
5″	67.16 t	H_A-5″	4.21 dd (11.0, 4.0)		H-4″, H_B-5″
		H_B-5″	3.55 dd (11.0, 10.0)		H-4′, H_A-5″

[a]In C_5D_5N; chemical shifts in δ (ppm); ^{13}C multiplicities from DEPT experiments; J_{HH} (Hz) in parentheses; assignments based on ^1H-^1H, ^1H-^{13}C (one-bond), COSY, HMBC, and HOHAHA experiments.

between C-6′ and C-1′ were verified by HMBC experiments. Thus, **3** was established as 2-hydroxyacetophenone-2-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside hexaacetate.

Neohancoside D octaacetate [**4**], $C_{39}H_{48}O_{33}$, was shown to consist of an aromatic aglycone and two polyacetylated sugars different from those of the above three compounds by nmr analysis (Table 4). The aglycone moiety was a 2-acetoxy-1,3-dimethoxybenzene (*meta*-H, δ_H 6.82, s) possessing a *trans*- olefin (δ_H 7.64, 6.46, each d, J=15.9 Hz) conjugated with a carboxyl at C-5, i.e., an acetylsinapate.

The remarkable feature of the sugar moiety was the presence of one anomeric methine (δ_H 5.69 , d, J=3.6 Hz, δ_C 90.19) and one quaternary carbon (δ_C 104.22) in addition to three methylenes, seven methines, and seven acetoxyls. The former two were correlated by ^1H-^{13}C (long-range) COSY experiments and assigned to C-1 of an α-D-glucose moiety and C-2 of a β-D-fructose moiety, respectively, in a sucrose heptaacetate by comparison with those of sucrose octaacetate (5,6).

Alkaline methanolysis of **4** gave methyl sinapate and sucrose, each of which was identical with an authentic sample.

The oxygen bridge between C-9 and C-6′ in **4** was demonstrated by ^1H-^{13}C (long-range) COSY experiments. Thus, **4** was established as 6′-*O*-sinapoylsucrose octaacetate.

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

Position	^{13}C	Correlated H δ_H		C coupled with H	H coupled with H
1	132.82 s				
2	155.21 s				
3	115.28 d	H-3	7.07 d (8.2)	C-2, C-4, C-5	H-4
4	130.23 d	H-4	7.55 ddd (8.2, 7.5, 2.0)	C-2, C-6	H-5, H-6
5	123.38 d	H-5	7.15 t (7.5)	C-2, C-3	H-6
6	129.96 d	H-6	7.64 dd (7.5, 2.0)	C-1, C-2, C-7	H-4, H-5
7	199.92 s				
8	31.60 q	H_3-8	2.55 s		
1′	98.70 d	H-1′	5.15 d (8.0)	C-2′	H-2′
2′	70.93 d	H-2′	5.30 dd (9.5, 8.0)	C-1′, C-3′, C-4′	H-1′, H-3′
3′	72.69 d	H-3′	5.28 t (9.5)	C-2	H-2′, H-4′
4′	68.52 d	H-4′	5.01 t (9.5)	C-3′	H-3′, H-5′
5′	73.92 d	H-5′	3.85 m	C-1′, C-6′	H-4′, H_B-6′
6′	67.34 t	H_A-6′	3.85 m	C-4′, C-1″	H-5′, H_B-6′
		H_B-6′	3.64 dd (11.5, 7.7)	C-1″	H-5′, H_A-6′
1″	100.48 d	H-1″	4.49 d (7.0)		H-2″
2″	70.71 d	H-2″	4.91 dd (9.0, 7.0)	C-1″, C-3″	H-1″, H-3″
3″	71.52 d	H-3″	5.12 t (9.0)	C-2″, C-4″	H-2″, H-4″
4″	68.78 d	H-4″	4.94 dt (5.3, 9.0)		H-3″, H_2-5″
5″	62.16 d	H_A-5″	4.09 dd (12.0, 5.3)	C-1″, C-3″, C-4″	H-4″, H_B-5″
		H_B-5″	3.29 dd (12.0, 9.0)	C-1″, C-4″	H-4″, H_A-5″
OAc	Me×6	20.69–20.53 (each q), 2.05–1.86 (each s)			
	CO×6	170.10–169.30 (each s)			

[a]In $CDCl_3$; chemical shifts in δ (ppm); ^{13}C multiplicities from DEPT experiments; J_{HH} (Hz) in parentheses; assignments based on ^1H-^1H COSY, HMQC, HMBC, and HOHAHA experiments.

The nonacetylated compound, neohancoside D [**4a**], was reported as an artificial product from the hydrolyzate of tenuifoliside [**8**] (7).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps (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; ^1H nmr, Varian XL-400 at 400 MHz (reference TMS); ^{13}C nmr, Varian XL-400 at 100.6 MHz (reference TMS); eims, fabms, and hrms, 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, nOe (difference), and HOHAHA experiments were performed using Varian's standard pulse sequences.

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 voucher 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). The insoluble portion was partitioned between H_2O (4 liters×4) and *n*-BuOH (4 liters×4) to yield the *n*-BuOH-soluble portion (500 g).

The *n*-BuOH-soluble portion (200 g) was chromatographed over Si gel (600 g) eluting with a mixture of $CHCl_3$ and MeOH in increasing polarity. The eluate from $CHCl_3$-MeOH (97:3→80:20) (6 liters) was discarded due to the difficult separation of the content. The eluate (40 g) from elution with $CHCl_3$-MeOH (70:30) (25 liters) was rechromatographed over Si gel (250 g) eluting with petroleum ether-Me_2CO (1:1) (26 liters). The resulting eluate was passed through an RP-8 column (40–63 μm, 20×4 cm, Merck) using MeOH-H_2O (6:4) (18 liters) as eluent to yield the crude product (35 g).

The crude product (10 g) was stirred with Ac_2O (10 g) and C_5H_5N (1 ml) at room temperature overnight. Workup of the reaction mixture gave acetylated compounds (10 g), half of which was

TABLE 4. Nmr Data for Compound **4**.[a]

Position	^{13}C	Correlated H	δ_H	H coupled with C	H coupled with H
1	132.70 s			H-8	
2	105.11 d	H-2	6.82 s	H-7	H-7, H-8
3	152.54 s			H-2, OMe	
4	130.72 s			H-2, H-6	
5	152.54 s			H-6, OMe	
6	105.11 d	H-6	6.82 s		H-7, H-8
7	145.46 d	H-7	7.64 d (15.9)	H-2, H-6	H-2, H-6, H-8
8	117.72 d	H-8	6.46 d (15.9)		H-2, H-6, H-7
9	166.41 s			H_2-6′	
3-OMe	56.35 q	Me	3.86 s		
5-OMe	56.35 q	Me	3.86 s		
1′	90.19 d	H-1′	5.69 d (3.6)	H-3′	H-2′
2′	70.41 d	H-2′	4.88 dd (9.5,3.6)	H-1′	H-1′, H-3′
3′	69.79 d	H-3′	5.46 t (9.5)	H-1′	H-2′, H-4′
4′	68.56 d	H-4′	5.12 t (9.5)		H-3′, H-5′
5′	68.70 d	H-5′	4.33 m		H-4′, H_2-6′
6′	62.05 t	H_2-6′	4.30 m		H-5′
1″	62.95 t	H_2-1″	4.19 s		
2″	104.22 s			H_2-1″	
3″	75.95 d	H-3″	5.45 d (5.7)		H-4″
4″	75.32 d	H-4″	5.35 t (5.7)		H-3″, H-5″
5″	79.37 d	H-5″	4.19 m		H-4″, H_2-6″
6″	63.83 t	H_2-6″	4.36 m		H-5″
OAc	Me×8	20.47–20.70 (each q), 2.33–1.64 (each s)			
	CO×8	170.53–168.47 (each s)			

[a]In $CDCl_3$; chemical shifts in δ (ppm); ^{13}C multiplicities from DEPT experiments; J_{HH} (Hz) in parentheses; assignments based on ^1H-^1H COSY, ^1H-^{13}C (one-bond, long-range) COSY, and HOHAHA experiments.

chromatographed over Si gel (40 g) eluting with petroleum ether-Me_2CO (85:15) (12 liters) to give **1** (14 mg), **2** (38 mg), **3** (120 mg), and **4** (250 mg).

Neobancoside A hexaacetate [**1**].—Colorless needles: mp 180–181 ($CHCl_3$) [lit. (2) mp 179.5–180.5° ($CHCl_3$)]; ir ν max (KBr) cm^{-1} 1740 (OAc); ^1H and ^{13}C nmr see Table 1. *Anal.* calcd for $C_{35}H_{48}O_{16}$, C 56.56, H 6.90; found C 56.50, H 6.95.

This compound was identified by direct comparison with an authentic sample.

Neobancoside B heptaacetate [**2**].—Colorless needles, mp 118.5–120.5° ($CHCl_3$); ir ν max (KBr) cm^{-1} 1740 (OAc); ^1H and ^{13}C nmr see Table 1; nOe H-6→H_2-9 (3.5%), H_2-9→H-6 (4.2%). *Anal.* calcd for $C_{35}H_{50}O_{18}$, C 55.41, H 6.60; found C 55.49, H 6.66.

DEACETYLATION OF **2**.—To a solution of **2** (4.0 mg) in MeOH (1 ml) was added 2.8% MeONa/MeOH (0.1 ml), and the solution was stirred at room temperature for 4h. The reaction mixture was neutralized with IR-120 (H^+) (ion exchange resin), filtered, and concentrated in vacuo. The residue was purified by preparative tlc [Si gel, $CHCl_3$-MeOH (5:1)] to yield **2a** (2.8 mg), R_f 0.13.

Neobancoside B [**2a**].—Colorless amorphous: $[\alpha]^{27}D$ −25.7° (*c*=0.28, MeOH); ir ν max (KBr) cm^{-1} 3260 (OH); ^1H and ^{13}C nmr see Table 2; fabms *m/z* $[M+Na]^+$ 487.

ENZYMATIC HYDROLYSIS OF **2a**.—A mixture of **2a** (2.8 mg) and β-glucosidase (Wako Pure Chemical Industries Ltd.) (4.0 mg) in a K_2HPO_4/citric acid buffer solution (pH=4.5, 2 ml) was stirred at 35° for 6 days. The reaction mixture was extracted with $CHCl_3$ (2 ml×4). Work up of the organic layer, followed by preparative tlc [Si gel, $CHCl_3$-MeOH (50:1)], gave **6** (1.0 mg), R_f 0.19.

9-Hydroxylinalool [**6**].—Colorless oil: ir ν max ($CHCl_3$) cm^{-1} 3600, 3500 (OH); ^1H nmr ($CDCl_3$) δ 5.90 (1H, dd, *J*=18.0, 11.0 Hz, H-2), 5.42 (1H, t, *J*=7.0 Hz, H-6), 5.23 (1H, dd, *J*=18.0, 1.3 Hz, H-1) 5.08 (1H, dd, *J*=11.0, 1.3 Hz, H-1), 4.00 (2H, s, H_2-9), 2.08 (2H, m, H_2-5), 1.67 (3H, s, H_3-8), 1.58 (2H, m,

H_2-4), 1.30 (3H, s, H_3-10); nOe H_3-8→H_2-5 (3.5%); fabms *m/z* $[M+Na]^+$ 193; hrms *m/z* $[M-H_2O]^+$ 152.1226 (152.1201 for $C_{10}H_{18}O_2-H_2O$).

PREPARATION OF (±)-**6**.—Compound (±)-**6** was prepared in 8.8% yield as a colorless oil from (±)-linalool [**5**] (Wako Pure Chemical Industries Ltd.) by the same procedure as employed for the preparation of (−)-**6** (8).

ACIDIC METHANOLYSIS OF **2a**.—A solution of **2a** (2.3 mg) in 6% HCl/MeOH (2 ml) was stirred at room temperature overnight. 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, $CHCl_3$), furnished **7** (0.6 mg), R_f 0.10, as a colorless oil, which was identified with an authentic sample (vide infra) by direct comparison. The residue from the aqueous layer was purified by preparative tlc [Si gel, $CHCl_3$-MeOH (5:1)] to give methyl α- and β-D-glucopyranosides (0.6 mg, ratio 1:1). R_f 0.17, and α- and β-D-xylopyranosides (0.6 mg, ratio 3:1), R_f 0.34, which were identified with authentic samples by nmr analysis and co-tlc.

ACIDIC METHANOLYSIS OF (±)-**6**.—A solution of (±)-**6** (3.0 mg) in 6% HCl/MeOH (2 ml) was stirred at room temperature overnight. Workup of the reaction mixture as above afforded **7** (1.5 mg), R_f 0.10 (Si gel, $CHCl_3$).

9-Hydroxy-1-O-methylgeraniol [**7**].—Colorless oil: ir ν max ($CHCl_3$) cm^{-1} 3500 (OH); ^1H nmr ($CDCl_3$) δ 5.36 (2H, m, H-2, H-6), 3.99 (2H, s, H_2-9), 3.90 (2H, d, J=7.0 Hz, H_2-1), 3.32 (3H, s, 1-OMe), 2.16–2.08 (4H, m, H_2-4, H_2-5), 1.68 (3H, s, H_3-10), 1.66 (3H, s, H_3-8); nOe H_2-1→H_3-10 (1.1%), H_2-9→H-6 (4.4%); eims *m/z* $[M]^+$ 184 (184 calcd for $C_{11}H_{20}O_2$); hrms *m/z* $[M-OH]^+$ 167.1459 (167.1436 calcd for $C_{11}H_{20}O_2$-OH).

Neohancoside C hexaacetate [**3**].—Colorless needles: mp 194–195° ($CHCl_3$); ir ν max (KBr) cm^{-1} 1740 (OAc), 1670 (Ac); ^1H and ^{13}C nmr see Table 3. *Anal.* calcd for $C_{31}H_{38}O_{17}$, C 54.55, H 5.57; found C 54.34, H 5.57.

ALKALINE HYDROLYSIS, FOLLOWED BY ACIDIC METHANOLYSIS OF **3**.—A solution of **3** (8.0 mg) in 3% KOH/MeOH (1 ml) was refluxed for 1 h, and 10% HCl (1 ml) was added. After reflux for an additional 5 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 EtOAc (5 ml×2). Workup of the organic layer, followed by preparative tlc (Si gel, $CHCl_3$), gave 2-hydroxyacetophenone (1.0 mg), R_f 0.78, as a colorless oil. The residue from the aqueous layer was dissolved in 6% HCl/MeOH (1 ml), and the whole was refluxed for 3 h. The reaction mixture was neutralized with Ag_2CO_3, filtered, and concentrated in vacuo. The residue was purified by preparative tlc [Si gel, $CHCl_3$-MeOH (5:1)] to yield methyl α- and β-D-glucopyranosides (1.4 mg, ratio 2:1), R_f 0.17, and methyl α- and β-D-xylopyranosides (1.0 mg, ratio 2. 5:1), R_f 0.34, each of which was identified with an authentic sample by nmr analysis and co-tlc.

Neohancoside D octaacetate [**4**].—Colorless needles, mp 138–140° ($CHCl_3$); ir ν max (KBr) cm^{-1} 1740 (OAc); ^1H and ^{13}C nmr see Table 4; eims *m/z* $[M+1]^+$ 885. *Anal.* calcd for $C_{39}H_{48}O_{33}$, C 52.94, H 5.43; found C 52.69, H 5.43.

ALKALINE METHANOLYSIS OF **4**.—A solution of **4** (7.7 mg) in 3% KOH/MeOH (1 ml) was stirred at room temperature for 4 h. The reaction mixture was neutralized with 1 N HCl 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 methyl sinapate (1.7 mg), R_f 0.54, as colorless needles: mp 90–92° (Et_2O); hrms *m/z* $[M]^+$ 238.0844 (238.0841 calcd for $C_{12}H_{14}O_5$). Purification of the residue from the aqueous layer by preparative tlc [Si gel, $CHCl_3$-MeOH-H_2O (14:10:1)] afforded sucrose (2.7 mg), R_f 0.20, as colorless amorphous: $[\alpha]^{21}D$ +27.5° (*c*=0.16, MeOH).

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