Pergamon

0031-9422(94)00608-3

Phytochemistry, Vol. 38, No. 2, pp. 465–472, 1995

0031-9422/95 $9.50 + 0.00

DAMMARANE GLYCOSIDES FROM AERIAL PARTS OF *NEOALSOMITRA INTEGRIFOLIOLA**

SEIJI FUJITA, RYOJI KASAI,† KAZUHIRO OHTANI, KAZUO YAMASAKI, MING-HUA CHIU,‡ RUI-LIN NIE‡ and OSAMU TANAKA§

Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine, Kasumi, Minami-Ku, Hiroshima 734, Japan; ‡Kunming Institute of Botany, Chinese Academy of Science, Kunming, Yunnan, China; §Suzugamine Women's College, Inokuchi, Nishi-ku, Hiroshima 733, Japan

(*Received* 15 *June* 1994)

Key Word Index—*Neoalsomitra integrifoliola*; Cucurbitaceae; aerial parts; dammarane glycosides; neoalsosides A2, A3, A4, A5, C1, C2, D1, E1, F1, G1 and H1; neoalsogenins B, C, G and H; 20,24-epoxydammarane triterpenes.

Abstract—From the aerial parts of *Neoalsomitra integrifoliola*, a new 20,24-epoxydammarane triterpene and 11 new glycosides were isolated along with a known cucurbitacin glycoside, seven known cucurbitacins and neoalsoside A. The latter compound has previously been isolated from the rhizomes of this plant. The structures of the new compounds have been established by spectroscopic and chemical means.

INTRODUCTION

Neoalsomitra integrifoliola (Cogn.) Hutch. is a vine growing in the southern region of China and the Malay Peninsula. Two authors of this paper and their coworkers have already reported the isolation and structural elucidation of a dammarane glycoside named neoalsoside A from the rhizomes of this plant [1]. As part of our ongoing study on the glycosides of Chinese cucurbitaceous plants, we investigated the constituents of the aerial parts of this plant collected in Xishuangbanna, South-Yunnan, China and isolated a new dammarane triterpene and 11 new dammarane glycosides together with neoalsoside A, seven known cucurbitacins and a known cucurbitacin glycoside. The present paper deals with the isolation, identification and structural determination of these compounds.

The methanolic extract of the aerial parts of *N. integrifoliola* was chromatographically separated on a silica gel column into five main fractions. These fractions, upon repeated silica gel or reversed phase silica gel chromatography, followed by HPLC (ODS), afforded seven triterpenes (**1**–**7**) and 13 glycosides (**8**–**20**). Of these, **7** and **10**–**20** are new compounds, and were named neoalsogenin B, neoalsosides A2, A3, A4, A5, C1, C2, D1, E1, F1, G1 and H1, respectively.

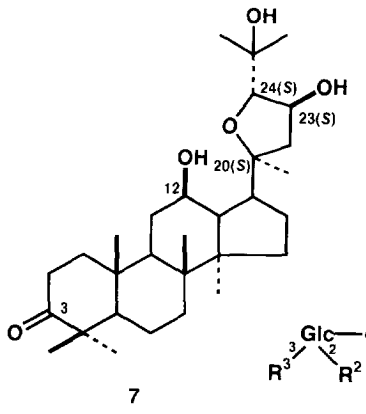
The characterization of known cucurbitacins D (**1**) [2], L (**2**) [3], R (**3**) [3], G (**4**) [4] and H (**5**) [5], hexanor cucurbitacin D (**6**) [6] and arvenin IV (2-*O*-β-glucoside of cucurbitacin R) (**8**) [7] were established by ^{1}H and ^{13}C NMR studies [8]. Glycoside **9** was identified as neoalsoside A by comparison of spectral and physical data with those of an authentic sample [1].

The molecular formula of new triterpene **7** was determined as $C_{30}H_{50}O_5$ by NMR and HR-FAB mass spectrometry. The IR spectrum showed absorption bands at 3400 (OH) and 1710 cm^{-1} (CO). The ^{13}C NMR spectrum of **7** revealed 30 signals (Table 1): one carbonyl (δ217.8), eight methylene, seven methine [three of them bearing an oxygen atom (δ70.3, 70.7 and 89.7)], six quaternary [two of them bearing an oxygen atom (δ85.6 and 70.8)] and eight methyl carbons. These data can be accommodated on the ocotillol type dammarane triterpene having two secondary hydroxyl, one tertiary hydroxyl and one ketone functions. The carbon signals of **7** appeared at almost the same positions as those of neoalsogenin A (**21**): 20*S*, 24*S*-epoxy-3β,12β,23*S*,25-tetrahydroxydammarane, the aglycone of **9**, except for some signals which closely matched those assigned to the A-ring and two methyl carbons on the C-4 of 20*S*,24*R*-epoxy-12β,25-dihydroxydammaran-3-one isolated from *Salvia bicolor* [9]. Therefore, **7** is the 3-keto-compound of **21**: 20*S*,24*S*-epoxy-12β,23*S*,25-trihydroxydammaran-3-one.

The glycosides **10**–**13** were characterized as ocotillol type dammarane glycosides based on the ^{1}H and ^{13}C NMR spectral data. Acid hydrolysis of **10**–**13** afforded neoalsogenin A (**21**) as a common aglycone, and only D-glucose was detected in the hydrolysate of **10**, and D-glucose and L-rhamnose were observed in those of **11**–**13**, as the sugar component. Clearly these glycosides

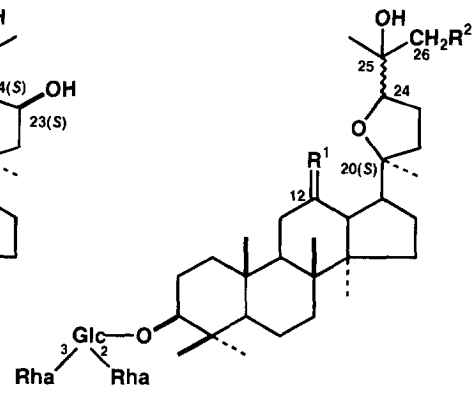
*Part 1 in the series 'Studies on the constituents of aerial parts of *Neoalsomitra integrifoliola*'.

†Author to whom correspondence should be addressed.



7

	R^1	R^2	R^3
9	H	Rha	Rha
10	H	H	H
11	H	Rha	H
12	H	H	Rha
13	H	Rha	Glc
14	OH	Rha	Rha
15	OH	Rha	Glc
21	aglycone of **9-13**		
22	aglycone of **14-15**		



	R^1	R^2	C-24	C-25
16	β-OH, H	H	*S*	
17	β-OH, H	H	*R*	
18	H_2	H	*R*	
19	O	H	*R*	
20	H_2	OH	*R*	*R*
23	aglycone of **16**			
24	aglycone of **17**			
25	aglycone of **18**			
26	aglycone of **19**			
27	aglycone of **20**			

Table 1. ^{13}C NMR spectral data of aglycones in $CDCl_3$ (δ-value)

C	7	21	22	23	24	25*	26	27
1	39.7	39.0	38.6	39.0	39.0	39.1	38.6	39.1
2	34.4	27.1	27.1	27.5	27.5	27.4	27.2	27.4
3	217.8	78.8	76.3	78.9	78.9	79.0	78.6	79.0
4	47.4	38.9	42.0	39.0	39.0	39.0	38.9	39.0
5	55.4	56.0	50.4	56.1	56.0	55.9	55.8	55.9
6	19.7	18.3	18.4	18.4	18.3	18.3	18.4	18.3
7	34.1	34.8	34.5	34.9	34.9	35.3	35.1	35.3
8	39.8	39.7	39.8	39.8	39.8	40.4	40.4	40.3
9	49.6	50.3	50.3	50.3	50.6	50.8	54.3	50.7
10	36.9	37.1	37.1	37.3	37.2	37.2	37.7	37.2
11	32.0	31.6	31.6	31.7	31.4	21.6	39.8	21.5
12	70.7[a]	70.7[a]	70.5[a]	70.6	71.0	25.7	211.5	25.4
13	49.2[b]	48.9[b]	49.0[b]	48.9	49.4	43.0	57.1	43.2
14	52.2	52.2	52.2	52.2	52.1	50.1	55.8	50.1
15	32.2	32.2	32.2	32.3	32.6	31.5	32.0	31.3
16	28.5	28.5	28.5	28.6	28.6	27.4	25.0	27.0
17	49.3[b]	49.3[b]	49.3[b]	49.0	48.0	49.5	42.6	49.9
18	15.2	15.6	15.5	15.5	15.4	15.5	15.6	15.4
19	16.1	16.3	16.6	16.3	16.3	16.3	16.1	16.2
20	85.6	85.4	85.6	87.2	86.5	86.4	85.2	87.4
21	26.5	26.4[c]	26.5	28.9	27.6	23.6	25.6	22.9
22	40.4	40.5	40.4	31.7	31.2	35.7	34.3	35.9
23	70.3[a]	70.0[a]	70.3[a]	25.1	25.0	26.1	26.5	26.3
24	89.7	89.6	89.7	87.5	85.5	83.3	83.6	83.7
25	70.8	70.8	70.8	70.1	70.1	71.4	71.1	71.4
26	25.6	25.8	25.7	24.3	26.2	24.3	24.4	71.2
27	29.8	29.7	29.7	28.0	27.9	27.4	27.7	20.5
28	26.7	28.0[c]	71.5	28.0	28.0	28.0	28.0	28.0
29	20.9	15.4	11.2	15.3	15.3	15.3	15.3	15.4
30	17.8	17.9	17.9	17.8	18.2	16.5	16.7	16.4

*Data taken from ref. [14].

[a–c]Interchangeable assignments.

are all 3-*O*-glycosides of **21** based on the observation of glycosylation shifts for carbon signals due to the C-2, C-3 and C-29 (Tables 1 and 2). The ^{1}H and ^{13}C NMR spectra of **10** revealed the presence of one unit of β-glucopyranose. Accordingly, the structure of glycoside **10** is formulated as shown. Compounds **11**–**13** showed signals attributable to one unit each of β-glucopyranose and α-rhamnopyranose for **11** and **12**, and two units of β-glucopyranose and one unit of α-rhamnopyranose for **13** in their ^{1}H and ^{13}C NMR spectra. By comparing the sugar carbon signals of each glycoside with their common aglycone (**21**), the glycosylation shift was observed for the signals due to the C-2 of the glucosyl moiety of **11**, the C-3 of the glucosyl of **12**, and both C-2 and C-3 of the inner glucosyl of **13**.

Consequently, the structures of **11** and **12** were characterized as shown. The disposition of the terminal glucosyl and rhamnosyl linkages on the inner glucose moiety of **13** was determined by ROE experiment. The assignments of the proton signals due to the sugar moieties of the acetylated compound of **13** were performed by ^{1}H–^{1}H COSY (assignments: see Experimental). In the phase sensitive ROESY spectrum of the acetate, cross-peaks were observed between the H-1 (δ5.30) of rhamnosyl and the H-2 (δ3.72) of inner glucosyl moiety, and between the H-1 (δ4.66) of terminal glucosyl and the H-3 (δ3.92) of inner glucosyl moiety. These results led to the formulation of **13** as shown.

Acid hydrolysis of glycosides **14** and **15** yielded a new common aglycone named neoalsogenin C (**22**). A comparison of the ^{13}C NMR spectrum of **22** with that of **21** showed that one of the methyl signals attributable to C-28 and C-29 of **21** was replaced by a signal associated with $-CH_2-O-$, and the signals due to C-3, C-5 and C-28–Me or C-29–Me were displaced upfield, and the signal due to C-4 was displaced downfield on going from **21** to **22**; while other resonances of **22** corresponded closely to those of **21**. These observations indicate that **22** is the C-28 or C-29 hydroxylated compound of **21**. These carbon shift differences are almost identical with those found when going from oleanolic acid, having two geminal methyl groups on the C-4, to hederagenin where the equatorial methyl group (C-23) at C-4 is hydroxylated [10]. The data demonstrate the presence of a hydroxyl group on the C-28 of **22**. The structure of **22** is thus determined as 20*S*,24*S*-epoxy-3β,12β,23*S*,25,28-pentahydroxydammarane. D-Glucose and L-rhamnose were identified in the hydrolysates of **14** and **15**. The carbon signals of the sugar moieties of **14** and **15** were essentially superimposable on those of **9** and **13**, respectively, and the glycosylation shifts were observed for the signals due to carbons around C-3 of both compounds. Accordingly, the structures of glycosides **14** and **15** are formulated as shown.

All of the following compounds are the 3-*O*-glycosides of a 23,24-epoxy-dammarane type triterpene; furthermore, they have the same sugar chain as that of **9** (and **14**). These results were also obtained by similar means to those described above.

Glycosides **16** and **17** have the same molecular formula ($C_{48}H_{82}O_{17}$), and acid hydrolysis of these glycosides provided aglycones **23** from **16** and **24** from **17**. The detailed analyses of the spectral data suggested that the structures of **23** and **24** can be formulated as two known compounds: 20 (*S*)-protopanaxadiol oxides II (20*S*,24*S*-epoxy-3β,12β,25-trihydroxydammarane) and I (24*R*-epimer of the oxide II), respectively [11]. The identification of **23** and **24** was performed by comparison of the physical and spectral data with those of authentic samples [11]. Hence, the structures of **16** and **17** are formulated as shown.

Glycoside **18** was analysed for the molecular formula $C_{48}H_{82}O_{16}$. Acid hydrolysis of **18** yielded an aglycone (**25**) which was identified as ocotillol II (20*S*,24*R*-epoxy-3β,25-dihydroxydammarane) by comparison of the physical and spectral data with those of an authentic sample [11–14]. Thus, glycoside **18** is formulated as shown.

A new aglycone (**26**, $C_{30}H_{50}O_4$) named neoalsogenin G was obtained on acid hydrolysis of glycoside **19**. The IR spectrum showed a carbonyl band at 1703 cm^{-1}. The NMR data demonstrated that **26** is also an ocotillol type dammarane triterpene. Its CD spectrum exhibited a characteristic curve, 285 nm ([θ] $-$3098), due to the 12-keto function [15]. From these data, **26** was assumed to be 20*S*,24*R*-epoxy-3β,25-dihydroxydammaran-12-one. The structure was further confirmed by preparation of this compound from **24** by selective oxidation of the 12-hydroxyl group [15]. Based on these results, the structure of **19** is formulated as shown.

Hydrolysis of glycoside **20** afforded a new aglycone (**27**) named neoalsogenin H ($C_{30}H_{52}O_4$). The ^{1}H and ^{13}C NMR spectra revealed the presence of seven methyl groups and one hydroxyl methylene group. On going from **25** to **27**, one of the two carbon signals due to C-26 and 27 was shifted upfield ($-$6.9 ppm) and another was shifted downfield (+ 46.9 ppm), while other signals remained almost unshifted (Table 1), indicating the structure of **27** as the 26-hydroxyl compound of **25**: 20*S*,24*R*-epoxy-3β,25ξ,26-trihydroxydammarane. The configuration of C-25 was determined by NOE experiment. The important and diagnostic NOEs observed in the NOE differential spectrum of **27** are illustrated in Fig. 1. A concentration, temperature and solvent-independent OH proton signal at δ3.25 (1H, *dd*, J=1.2, 10.7 Hz) was observed in the ^{1}H NMR of **27** being attributable to the intramolecular hydrogen bonding between 26-hydroxyl group and the oxygen of the tetrahydrofuran-ring (Fig. 1). The NOE data permit the assignment of the *R*-configuration at the C-25 of **27**, while it would be impossible to take any conformation that will give rise to all these NOEs at the same time in the case of the *S*-epimer, based on careful examination of the Dreiding model (Fig. 1). Therefore, the structure of **20** can be formulated as shown.

EXPERIMENTAL

General. Mps: uncorr.; NMR: TMS as int. standard; CC: silica gel (Kieselgel 60, 70–230 mesh, Merck) and silanized silica gel (LiChroprep RP-18, 40–63 μm, Merck) were used. All solvent systems for chromatography were homogeneous. MPLC: ODS-AM 120-S50 (23 mm $\times$ 42 cm, YMC, Japan). HPLC: D-ODS-10 (YMC). Acid

Table 2. ^{13}C NMR spectral data of glycosides in pyridine-d_5(δ-value)

C	9	10	11	12	13	14	C	9	10	11	12	13	14
1	39.6	39.3	39.7	39.3	39.7	39.7	3-*O*-						
2	26.8	26.8	27.0	26.7	26.9	26.5	G-1	105.0	107.0	105.4	106.7	104.9	104.3
3	88.6	88.8	88.8	89.0	88.7	81.4	G-2	78.0	75.8	79.8	76.0	78.6	78.0
4	39.9	39.7[a]	39.7[a]	39.7[a]	39.8[a]	43.7	G-3	87.3	78.8	78.0	83.8	89.4	87.0
5	56.6	56.5	56.8	56.4	56.9	48.5	G-4	70.5	71.9	72.3	69.9	70.1	70.6
6	18.5	18.5	18.6	18.5	18.6	18.2	G-5	77.9	78.4	78.0	78.3	78.4	77.8
7	35.1	35.2	35.3	35.2	35.3	34.9	G-6	62.5	63.1	63.0	62.8	62.9	62.4
8	39.9	40.0[a]	40.1[a]	40.0[a]	40.2[a]	39.7	G-2-*O*-						
9	50.5	50.6	50.7	50.6	50.7	50.7	R-1	102.1		101.7		101.6	102.2
10	37.0	37.0	37.1	37.0	37.2	36.9	R-2	71.9		72.4		72.5	71.9
11	32.5	32.6[b]	32.6[b]	32.6[b]	32.6	32.5[a]	R-3	72.4		72.6		72.3	72.5
12	70.7	70.6	70.7	70.5	70.7	70.7	R-4	73.5		74.2		74.0	73.6
13	49.6[a]	49.7[c]	49.8[c]	49.7[c]	49.8[b]	49.7[b]	R-5	70.2		69.5		69.7	70.2
14	52.3	52.3	52.4	52.3	52.4	52.4	R-6	18.4		18.6		18.5	18.4
15	32.5	32.5[b]	32.5[b]	32.5[b]	32.6	32.6[b]	G-3-*O*-						
16	28.6	28.6	28.6	28.5	28.6	28.6	R-1	103.6			103.0		103.7
17	49.9[a]	50.0[c]	50.1[c]	50.0[c]	50.2[b]	50.0[b]	R-2	72.6			72.8		72.6
18	15.5	15.6	15.7	15.6	15.7	15.6	R-3	72.4			72.6		72.5
19	16.7	16.6[d]	16.7[d]	16.6[d]	16.7[c]	17.2	R-4	73.7			74.2		73.7
20	85.2	85.2	85.3	85.2	85.3	85.2	R-5	70.3			69.9		70.2
21	27.6	27.7	27.5	27.7	27.4	27.7	R-6	18.5			18.7		18.5
22	42.1	42.2	42.3	42.2	42.4	42.1	G-3-*O*-						
23	70.8	70.8	70.9	70.8	70.9	70.9	G-1					104.0	
24	91.5	91.6	91.5	91.6	91.5	91.5	G-2					75.2	
25	70.2	70.2	70.3	70.2	70.4	70.2	G-3					77.8	
26	26.6	26.6	26.6	26.6	26.6	26.6	G-4					71.6	
27	29.7	29.8	29.7	29.8	29.7	29.8	G-5					77.2	
28	27.9	28.1	28.1	28.0	28.1	63.8	G-6					62.5	
29	16.7	16.8[d]	16.9[d]	16.7[d]	16.8[c]	13.8							
30	18.2	18.1	18.2	18.1	18.2	18.2							

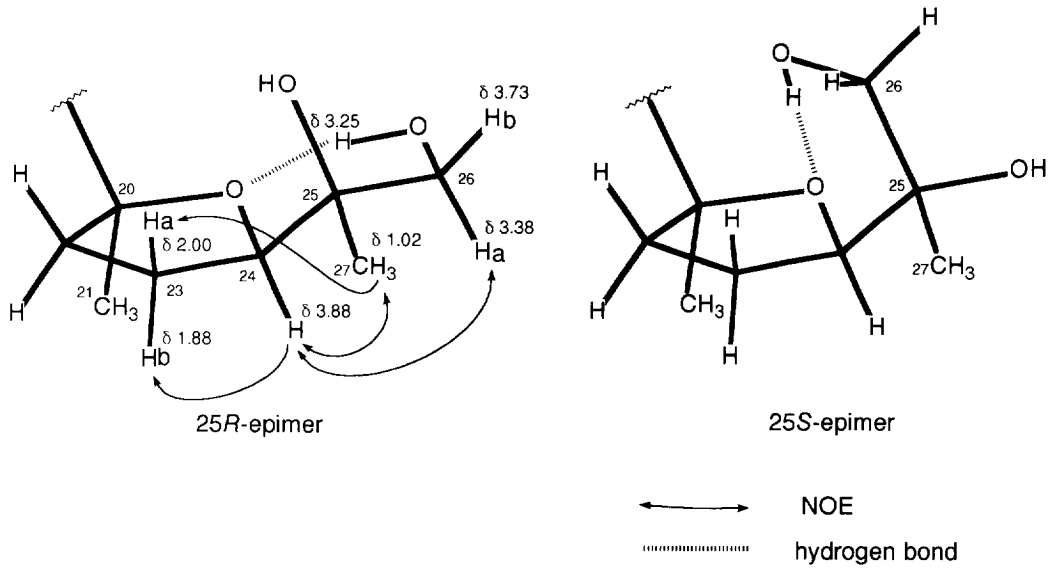


Fig. 1. NOEs detected for **27**.

hydrolysis of glycosides and identification of resulting monosaccharides: see ref. [16].

Plant material. Aerial parts of *N. integrifoliola* (Cogn.) Hutch were collected in Xishuangbanna, South-Yunnan, China, and identified by Prof. Guoda Tao. A voucher specimen is deposited in the Herbarium of the Kunming Institute of Botany.

Extraction and separation. Dried and powdered aerial

Table 2. (*Continued*)

C	15	16	17	18	19	20	C	15	16	17	18	19	20
1	39.7	39.7	39.6	39.6	39.9	39.6	3-*O*-						
2	26.5	27.0	26.9	26.0[a]	27.0	26.9[a]	G-1	104.2	105.1	105.0	105.0	105.0	105.0
3	81.3	88.7	88.5	88.7	88.3	88.8	G-2	78.7	78.1	78.0	78.0	78.1	78.0
4	43.7	39.7[a]	39.7[a]	39.7[b]	39.6[a]	39.7[a]	G-3	89.6	87.4	87.4	87.4	87.4	87.5
5	48.7	56.7	56.7	56.5	56.3	56.6	G-4	69.7	70.8	70.8	70.7	70.8	70.4
6	18.2	18.5	18.4	18.4	18.5	18.4	G-5	78.4	78.0	78.0	77.8	78.0	78.0
7	34.9	35.2	35.1	35.6	34.6	35.6	G-6	62.6	62.6	62.6	62.5	62.6	62.6
8	40.0	40.0[a]	40.0[a]	40.6[b]	40.7[a]	40.6[a]	G-2-*O*-						
9	50.7	50.6	50.8	51.0	54.6	51.0	R-1	101.6	102.2	102.2	102.1	102.2	102.2
10	36.9	37.1	37.0	37.0	37.4	37.0	R-2	72.5	72.0	72.0	72.0	72.1	72.1
11	32.5[a]	32.7	31.7	21.7	39.1	21.8	R-3	72.4	72.5	72.5	72.4	72.5	72.6
12	70.5	70.4	71.2	26.0[a]	210.5	26.5[b]	R-4	74.0	73.6	73.6	73.5	73.6	73.7
13	49.5[b]	49.5	48.4	43.1	57.3	43.3	R-5	69.7	70.0	70.2	70.1	70.2	70.2
14	52.4	52.3	52.2	50.2	55.9	50.2	R-6	18.6	18.4	18.4	18.4	18.4	18.4
15	32.6[a]	32.3	32.4[b]	31.7	32.3	31.7	G-3-*O*-						
16	28.6	25.8	25.5	27.5	25.1	27.4[b]	R-1		103.7	103.7	103.7	103.7	103.7
17	50.0[b]	49.5	49.8	50.2	43.2	50.2	R-2		72.5	72.6	72.4	72.6	72.5
18	15.6	15.7	15.5	15.5	15.6	15.6	R-3		72.6	72.5	72.6	72.5	72.4
19	17.2	16.7[b]	16.7	16.5[c]	16.2[b]	16.5[c]	R-4		73.8	73.8	73.7	73.7	73.6
20	85.2	87.1	86.8	86.2	85.4	86.4	R-5		70.2	70.4	70.3	70.4	70.8
21	27.7	26.9	26.9	23.1	25.2	23.1	R-6		18.6	18.6	18.5	18.6	18.6
22	42.1	32.7	32.9[b]	36.2	35.8	36.5	G-3-*O*-						
23	70.8	28.7	28.8	26.9[a]	26.7	27.3	G-1	104.0					
24	91.5	88.5	85.6	84.2	84.7	81.6	G-2	75.1					
25	70.2	70.0	70.4	71.1	71.2	73.5	G-3	77.9					
26	26.6	26.6	27.2	26.1	26.5	68.9	G-4	71.4					
27	29.7	29.1	27.6[c]	26.8	27.0	21.9	G-5	76.5					
28	63.9	27.9	27.9[c]	27.9	27.8	27.9	G-6	62.3					
29	13.8	16.8[b]	16.7	16.6[c]	16.7[b]	16.6[c]							
30	18.2	18.2	18.4	16.8[c]	16.9[b]	16.8[c]							

[a–d]Interchangeable assignments.

parts of *N. integrifoliola* (1.5 kg) were extracted with hot MeOH. After removal of the solvent by evapn, the MeOH extract (81 g) was chromatographed on a column of silica gel with $CHCl_3$–MeOH (4:1–1:1) to give 5 frs. Fr. 1 was suspended in H_2O, and then extracted with *n*-hexane and EtOAc, successively. The EtOAc extract afforded **1** (0.0046%), **2** (0.0027%), **3** (0.0032%), **6** (0.0011%) and **7** (0.0003%) by CC on silica gel with $CHCl_3$–MeOH (15:1) and then HPLC on ODS with 60% aq. MeOH and finally HPLC on D-PBMN-5 S-5 120A Polyamine II (YMC) with 99% aq. MeCN. Fr. 2 was sepd into 5 frs by CC on silica gel with $CHCl_3$–MeOH (7:1). These frs were purified by HPLC on ODS to give **5** (0.007%) from fr.2-1, **4** (0.004%) from fr.2-2 with 60% MeOH and **8** (0.002%) as well as **10** (0.002%) from fr. 2-3 with 72% MeOH. Fr. 2-4 gave **12** (0.002%) by HPLC on ODS with 71% MeOH. Fr. 3 was sepd into 4 frs by MPLC with 65–100% MeOH. These frs were subjected to HPLC on ODS to afford **11** (0.019%) from fr.3-1 with 73% MeOH, **16** (0.011%) and **19** (0.019%) from fr.3-2 with 78% MeOH, **20** (0.0005%) from fr.3-3 with 85% MeOH, and **17** (0.006%) as well as **18** (0.002%) from fr.3-4 with 85% MeOH. Fr. 4 was sepd into 6 frs by MPLC with 65% MeOH. Fr.4-2 was purified by HPLC on ODS with 65% MeOH to give **14** (0.043%). Fr.4-3 yielded **9** (1.24%) by HPLC on TSK-gel Amide-80 (21.5 mm × 30 cm, Tosoh) with 82% MeCN. Fr.5 was sepd into 8 frs by CC on silica gel with EtOAc–EtOH–H_2O (30:5:2–6:2:1). Glycoside **13** (0.011%) from fr.5-6 and **15** (0.001%) from fr.5-7 were obtained by HPLC on ODS with 70% MeOH and 58% MeOH, respectively.

Cucurbitacin D (**1**). Powder, $[\alpha]_D^{25}$ +48.5° (EtOH; *c* 0.89). ^{13}C NMR ($CDCl_3$): δ(C-1–C-30) 36.0, 71.6, 213.0, 50.3, 140.5, 120.3, 23.9, 42.4, 48.4[a], 33.8, 212.4, 48.7, 50.8, 48.3[a], 45.5, 71.4, 57.3, 20.0, 20.1, 78.2, 24.0, 202.6, 119.0, 155.9, 71.1, 28.8, 29.5, 21.3, 29.3, 19.3 (see ref. [2]).

Cucurbitacin L (**2**). Powder, $[\alpha]_D^{25}$ −45.0° (EtOH; *c* 0.85). ^{13}C NMR ($CDCl_3$): δ(C-1–C-30) 114.9, 144.6, 198.7, 47.5, 136.8, 120.7, 23.6, 41.6, 48.8[a], 34.7, 212.9, 48.9, 50.7, 48.3[a], 45.6, 71.0, 57.7, 19.8, 20.2, 79.2, 24.5, 215.5, 30.9, 36.9, 70.3, 28.7, 29.8, 20.0, 27.9, 18.3.

Cucurbitacin R (**3**). Powder, $[\alpha]_D^{25}$ +56.1° (EtOH; *c* 1.14). ^{13}C NMR ($CDCl_3$): δ(C-1–C-30) 36.0, 71.7, 212.8, 49.2, 140.5, 120.4, 23.9, 42.4, 48.4[a], 33.8, 212.2, 48.7, 50.8, 48.3[a], 45.4, 71.1, 57.8, 19.8, 20.0, 79.2, 24.5, 215.4, 30.9, 36.9, 70.3, 28.8, 29.9, 21.3, 29.4, 18.9,

Cucurbitacin G (**4**). Powder, $[\alpha]_D^{26}$ +79.0° ($CHCl_3$; *c* 0.57). ^{13}C NMR ($CDCl_3$): δ(C-1–C-30) 35.9, 71.6, 213.0, 50.2, 140.4, 120.3, 23.8, 42.3, 48.4[a], 33.7, 212.3, 48.6, 50.6, 48.3[a], 45.4, 70.9, 57.4, 19.8, 20.0, 79.4, 24.2, 215.4, 38.3, 74.2, 72.2, 24.6, 25.7, 21.2, 29.1, 18.9. ^1H NMR ($CDCl_3$): δ 1.15 (1H, *m*, H-1a), 2.23 (1H, *ddd*, *J* = 3.4, 6.1, 12.6 Hz, H-1b), 4.36 (1H, *ddd*, *J* = 3.9, 6.1, 12.8 Hz, H-2),

3.61 (1H, *d*, J=3.9 Hz, H-2-OH), 5.72 (1H, *br d*, J =5.8 Hz, H-6), 1.90 (1H, *m*, H-7a), 2.34 (1H, *m*, H-7b), 1.90 (1H, *m*, H-8), 2.67 (1H, *br d*, J=13.2 Hz, H-10), 2.60 (1H, *d*, J=14.9 Hz, H-12a), 3.18 (1H, *d*, J=14.9 Hz, H-12b), 1.34 (1H, *br d*, J=13.6 Hz, H-15a), 1.79 (1H, *dd*, J=9.0, 13.6 Hz, H-15b), 4.29 (1H, *br dd*, J=7.1, 9.0 Hz, H-16), 2.49 (1H, *br d*, J = 7.1 Hz, H-17), 0.90 (3H, *s*, H-18), 1.00 (3H, *s*, H-19), 1.35 (3H, *s*, H-21), 2.62 (1H, *dd*, J=1.7, 17.1 Hz, H-23a), 2.91 (1H, *dd*, J=10.0, 17.1 Hz, H-23b), 3.85 (1H, *br d*, J=10.0 Hz, H-24), 1.12 (3H, *s*, H-26), 1.15 (3H, *s*, H-27), 1.27 (3H, *s*, H-28), 1.21 (3H, *s*, H-29), 1.29 (3H, *s*, H-30).

Cucurbitacin H (**5**). Powder, $[\alpha]_D^{26}$ +58.2° ($CHCl_3$; *c* 0.67). ^{13}C NMR ($CDCl_3$): δ(C-1–C-30) 35.6, 71.5, 212.9, 50.2, 140.3, 120.2, 23.8, 42.3, 48.3, 33.6, 212.2, 48.5, 50.7, 48.3, 45.2, 71.3, 55.8, 19.8, 20.0, 79.3, 23.4[a], 213.9, 39.3, 74.3, 72.1, 24.5[a], 25.6[a], 21.2, 29.3, 18.9. ^{1}H NMR ($CDCl_3$): δ1.18 (1H, *m*, H-1a), 2.25 (1H, *m*, H-1b), 4.40 (1H, *dd*, J =5.9, 11.3 Hz, H-2), 5.76 (1H, *br s*, H-6), 1.93 (1H, *m*, H-7a), 2.38 (1H, *m*, H-7b), 1.93 (1H, *m*, H-8), 2.72 (1H, *br d*, J =12.9 Hz, H-10), 2.65 (1H, *d*, J=14.4 Hz, H-12a), 3.24 (1H, *d*, J=14.4 Hz, H-12b), 1.37 (1H, *m*, H-15a), 1.83 (1H, *dd* J=8.8, 12.9 Hz, H-15b), 4.33 (1H, *m*, H-16), 2.60 (1H, *br d*, J=6.8 Hz, H-17), 0.95 (3H, *s*, H-18), 1.04 (3H, *s*, H-19), 1.41[a] (3H, *s*, H-21), 2.54 (1H, *br d*, J=16.6 Hz, H-23a), 2.97 (1H, *dd*, J=9.0, 16.6 Hz, H-23b), 3.94 (1H, *br d*, J = 9.0 Hz, H-24), 1.32[a] (3H, *s*, H-26), 1.16[a] (3H, *s*, H-27), 1.25 (3H, *s*, H-28), 1.20 (3H, *s*, H-29), 1.30 (3H, *s*, H-30).

Hexanorcucurbitacin D (**6**). Powder, $[\alpha]_D^{15}$ +122.3° ($CHCl_3$; *c* 1.14). ^{13}C NMR ($CDCl_3$): δ(C-1–C-21) 35.9, 71.6, 211.9, 50.3[a], 140.4, 120.2, 23.9, 42.8, 48.7[b], 33.7, 210.9, 47.0, 49.9[a], 48.9[b], 44.9, 71.5, 67.6, 19.7, 20.0, 208.0, 31.4, (C-28–C-30) 21.2, 29.3, 19.0.

Arvenin (**8**). Powder, $[\alpha]_D^{25}$ +31.5° (EtOH; *c* 1.30). ^{13}C NMR (pyridine-d_5): δ(C-1–C-30) 38.5, 77.9, 212.8, 49.2[a], 140.8, 120.4, 24.1, 42.7, 48.8[a], 34.3, 211.5, 48.7, 51.0, 48.7[a], 46.3, 70.3, 58.7, 19.8, 20.3, 80.1, 25.4, 216.0, 32.7, 35.1, 69.1, 28.8, 29.8, 21.7, 30.1, 18.8; (G-1–G-6) 104.2, 75.9, 78.7, 71.3, 78.4, 62.6.

Neoalsogenin B (**7**). Powder, $[\alpha]_D^{19}$ +30.0° ($CHCl_3$; *c* 0.20). FAB-MS (negative) *m/z*: 489.3579 $[M-H]^-$ ($C_{30}H_{49}O_5$, requires 489.3579). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1710 (C=O). CD (MeOH; *c* 0.8): $[\theta]^{25}$ +1903 (291 nm): ^{1}H NMR ($CDCl_3$): δ0.90, 0.97, 1.03, 1.05, 1.06, 1.23, 1.25 and 1.28 (each 3H, *s*, Me), 3.53 (1H, *ddd*, J =4.6, 10.5, 10.7 Hz, H-12a), 1.79 (1H, *dd*, J=9.8, 10.5 Hz, H-13), 2.17 (1H, *m*, H-17), 4.55 (1H, *ddd*, J=8.0, 8.3, 8.3 Hz, H-23), 3.59 (1H, *d*, J=8.3 Hz, H-24). ^{13}C NMR: Table 1.

Neoalsoside A (**9**). Needles (Me_2CO), mp 279–280°, $[\alpha]_D^{23}$ −29.8° (pyridine; *c* 1.04). Authentic sample: mp 277–279°, $[\alpha]_D^{23}$ −31.5° (pyridine). ^{1}H NMR (pyridine-d_5): δ0.75, 0.82, 0.90, 1.11, 1.17, 1.40, 1.58 and 1.60 (each 3H, *s*, Me), 3.30 (1H, *dd*, J=4.0, 11.7 Hz, H-3), 3.75 (1H, *ddd*, J=4.8, 9.9, 10.0 Hz, H-12a), 1.96 (1H, *dd*, J=9.5, 9.9 Hz, H-13), 2.27 (1H, *ddd*, J=4.0, 9.5, 10.3 Hz, H-17), 5.06 (1H, *m*, H-23), 4.21 (1H, *d*, J=8.1 Hz, H-24), 4.83 (1H, *d*, J=7.5 Hz, H-1 of Glc), 5.95 (1H, *br s*, H-1 of Rha), 5.72 (1H, *br s*, H-1 of Rha), 1.65 (3H, *d*, J=6.1 Hz, H-6 of Rha), 1.61 (3H, *d*, J = 6.8 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

Neoalsogenin A (**21**). Needles (MeOH), mp 241–242°, $[\alpha]_D^{22}$ +17.3° (MeOH; *c* 0.56). ^{1}H NMR ($CDCl_3$): δ0.78, 0.98, 1.04, 1.23, 1.27 and 1.29 (each 3H, *s*, Me), 0.90 (3H ×2, *s*, Me), 3.20 (1H, *dd*, J=5.0, 11.4 Hz, H-3), 3.53 (1H, *ddd*, J=4.8, 10.4, 10.4 Hz, H-12a), 1.79 (1H, *dd*, J=9.9, 10.4 Hz, H-13), 2.18 (1H, *ddd*, J=4.4, 9.9, 11.0 Hz, H-17), 4.56 (1H, *ddd*, J=7.7, 8.2, 9.2 Hz, H-23), 3.61 (1H, *d*, J = 8.2 Hz, H-24). ^{13}C NMR: Table 1.

Neoalsoside A2 (**10**). Powder, $[\alpha]_D^{15}$ −6.9° (MeOH; *c* 1.13). FAB-MS (negative) *m/z*: 653.4264 $[M-H]^-$ ($C_{36}H_{61}O_{10}$, requires 653.4264). ^{1}H NMR (pyridine-d_5): δ0.81, 0.87, 0.95, 1.00, 1.32, 1.44, 1.61 and 1.63 (each 3H, *s*, Me), 3.38 (1H, *dd*, J=4.4, 11.7 Hz, H-3), 3.81 (1H, *m*, H-12a), 2.01 (1H, *dd*, J=9.9, 9.9 Hz, H-13), 2.34 (1H, *m*, H-17), 5.06 (1H, *ddd*, J=8.0, 8.1, 8.1 Hz, H-23), 4.24 (1H, *d*, J =8.1 Hz, H-24), 4.95 (1H, *d*, J=7.7 Hz, H-1 of Glc). ^{13}C NMR: Table 2.

Neoalsoside A3 (**11**). Powder, $[\alpha]_D^{19}$ −3.9° (MeOH; *c* 1.00). FAB-MS (negative) *m/z*: 799.4872 $[M-H]^-$ ($C_{42}H_{71}O_{14}$, requires 799.4843). ^{1}H NMR (pyridine-d_5): δ0.80, 0.85, 0.94, 1.20, 1.25, 1.44, 1.61 and 1.64 (each 3H, *s*, Me), 3.35 (1H, *dd*, J=4.4, 11.7 Hz, H-3), 3.79 (1H, *m*, H-12a), 2.00 (1H, *dd*, J=9.7, 9.9 Hz, H-13), 2.28 (1H, *m*, H-17), 5.07 (1H, *m*, H-23), 4.25 (1H, *d*, J=8.1 Hz, H-24), 4.96 (1H, *d*, J=7.3 Hz, H-1 of Glc), 6.58 (1H, *br s*, H-1 of Rha), 1.73 (3H, *d*, J = 6.2 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

Neoalsoside A4 (**12**). Powder, $[\alpha]_D^{16}$ +3.0° (MeOH; *c* 0.78). FAB-MS (negative) *m/z*: 799.4843 $[M-H]^-$ ($C_{42}H_{71}O_{14}$, requires 799.4835). ^{1}H NMR (pyridine-d_5): δ0.80, 0.88, 0.95, 0.97, 1.27, 1.44, 1.62 and 1.64 (each 3H, *s*, Me), 3.32 (1H, *dd*, J=4.4, 11.8 Hz, H-3), 3.81 (1H, *m*, H-12a), 2.01 (1H, *dd*, J=9.9, 10.3 Hz, H-13), 2.31 (1H, *m*, H-17), 5.06 (1H, *m*, H-23), 4.25 (1H, *d*, J=7.9 Hz, H-24), 4.84 (1H, *d*, J=7.9 Hz, H-1 of Glc), 6.12 (1H, *br s*, H-1 of Rha), 1.72 (3H, *d*, J=6.0 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

Neoalsoside A5 (**13**). Powder, $[\alpha]_D^{19}$ +6.8° (MeOH; *c* 1.45). FAB-MS (negative) *m/z*: 961.5369 $[M-H]^-$ ($C_{48}H_{81}O_{19}$, requires 961.5371). ^{1}H NMR (pyridine-d_5): δ0.81, 0.85, 0.94, 1.18, 1.25, 1.44, 1.62 and 1.64 (each 3H, *s*, Me), 3.38 (1H, *dd*, J=4.0, 11.5 Hz, H-3), 3.80 (1H, *m*, H-12a), 2.00 (1H, *dd*, J=9.9, 9.9 Hz, H-13), 2.31 (1H, *m*, H-17), 5.07 (1H, *m*, H-23), 4.24 (1H, *d*, J=8.1 Hz, H-24), 4.88 (1H, *d*, J=7.3 Hz, H-1 of Glc), 6.10 (1H, *br s*, H-1 of Rha), 5.15 (1H, *d*, J=7.7 Hz, H-1 of Glc), 1.72 (3H, *d*, J=6.1 Hz, H-6 of Rha). ^{13}C NMR: Table 2. Compound **13** was acetylated with Ac_2O and pyridine in the usual way to give an acetate. ^{1}H NMR ($CDCl_3$, sugar moiety): δ(H-1–6 of Glc), 4.34 (1H, *dd*, J=7.9 Hz), 3.72 (1H, *dd*, J=7.9, 9.0 Hz), 3.92 (1H, *d*, J=9.0, 9.3 Hz), 4.76 (1H, *dd*, J=9.3, 10.1 Hz), 3.53 (1H, *ddd*, J=2.6, 5.3, 10.1 Hz), 4.02 (1H, *dd*, J=2.6, 12.3 Hz), 4.11 (1H, *dd*, J=5.3, 12.3 Hz); (H-1–6 of Glc′) 4.66 (1H, *d*, J=7.9 Hz), 4.76 (1H, *dd*, J=7.9, 9.4 Hz), 5.22 (1H, *dd*, J=9.2, 9.4 Hz), 5.00 (1H, *dd*, J=9.2, 10.2 Hz), 3.67 (1H, *ddd*, J=2.2, 4.2, 10.2 Hz), 3.96 (1H, *dd*, J=2.2, 12.6 Hz), 4.39 (1H, *dd*, J=4.2, 12.6 Hz); (H-1–6 of Rha) 5.30 (1H, *br d*, J=1.3 Hz), 5.24 (1H, *br dd*, J=1.3, 3.8 Hz), 5.27 (1H, *br dd*, J=3.8, 10.3 Hz), 5.00 (1H, *dd*, J =10.3, 10.3 Hz), 4.28 (1H, *dq*, J=10.3, 6.2 Hz), 1.08 (3H, *d*, J=6.2 Hz).

Neoalsoside C1 (**14**). Powder, $[\alpha]_D^{19}$ − 3.8° (MeOH; *c* 1.14). FAB-MS (negative) *m/z*: 961.5341 $[M-H]^-$ ($C_{48}H_{81}O_{19}$, requires 961.5371). ^{1}H NMR (pyridine-d_5): δ0.85, 1.10, 1.42, 1.61 and 1.63 (each 3H, *s*, Me), 0.89 (3H × 2, *s*, Me), 4.18 (1H, *m*, H-3), 3.75 (1H, *m*, H-12a), 1.99 (1H, *dd*, *J* = 9.9, 10.3 Hz, H-13), 2.27 (1H, *ddd*, *J* = 4.0, 9.5, 9.9 Hz, H-17), 5.09 (1H, *m*, H-23), 4.24 (3H, *m*, H-28 and H-24), 5.05 (1H, *d*, *J* = 7.7 Hz, H-1 of Glc), 6.03 (1H, *br s*, H-1 of Rha), 5.65 (1H, *br s*, H-1 of Rha), 1.69 (3H, *d*, *J* = 6.2 Hz, H-6 of Rha), 1.63 (3H, *d*, *J* = 6.2 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

Neoalsoside C2 (**15**). Powder, $[\alpha]_D^{15}$ − 12.5° (MeOH; *c* 0.69). FAB-MS (negative) *m/z*: 977.5349 $[M-H]^-$ ($C_{48}H_{81}O_{20}$, requires 977.5321). ^{1}H NMR (pyridine-d_5): δ0.81, 1.09, 1.39, 1.57 and 1.60 (each 3H, *s*, Me), 0.85 (3H × 2, *s*, Me), 4.14 (1H, *m*, H-3), 3.73 (1H, *m*, H-12a), 1.95 (1H, *dd*, *J* = 9.9, 9.9 Hz, H-13), 2.26 (1H, *m*, H-17), 5.05 (1H, *m*, H-23), 4.24 (3H, *m*, H-28 and H-24), 5.00 (1H, *d*, *J* = 7.9 Hz, H-1 of Glc), 6.03 (1H, *br s*, H-1 of Rha), 5.05 (1H, *d*, *J* = 7.7 Hz, H-1 of Glc), 1.69 (3H, *d*, *J* = 6.0 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

Neoalsogenin C (**22**). Powder, $[\alpha]_D^{17}$ + 17.2° ($CHCl_3$; *c* 0.99). FAB-MS (negative) *m/z*: 507.3683 $[M-H]^-$ ($C_{30}H_{51}O_6$, requires 507.3685). ^{1}H NMR ($CDCl_3$): δ0.88, 0.91, 0.94, 1.04, 1.24, 1.27 and 1.29 (each 3H, *s*, Me), 3.63 (1H, *dd*, virtual coupling, H-3), 3.53 (1H, *ddd*, *J* = 4.8, 10.4, 10.4 Hz, H-12a), 1.78 (1H, *dd*, *J* = 9.7, 10.4 Hz, H-13), 2.16 (1H, *m*, H-17), 4.56 (1H, *ddd*, *J* = 7.9, 7.9, 8.1 Hz, H-23), 3.61 (1H, *d*, *J* = 8.1 Hz, H-24), 3.41 (1H, *d*, *J* = 10.3 Hz, H-28a), 3.71 (1H, *d*, *J* = 10.3 Hz, H-28b). ^{13}C NMR: Table 1.

Neoalsoside D1 (**16**). Powder, $[\alpha]_D^{16}$ − 18.4° (MeOH; *c* 1.52). FAB-MS (negative) *m/z*: 929.5430 $[M-H]^-$ ($C_{48}H_{81}O_{17}$, requires 929.5473). ^{1}H NMR (pyridine-d_5): δ0.83, 0.94, 1.02, 1.13, 1.20 and 1.46 (each 3H, *s*, Me), 1.33 (3H × 2, *s*, Me), 3.32 (1H, *dd*, *J* = 4.0, 11.7 Hz, H-3), 3.75 (1H, *m*, H-12a), 2.01 (1H, *m*, H-13), 2.30 (1H, *m*, H-17), 4.17 (1H, *m*, H-24), 4.87 (1H, *d*, *J* = 7.5 Hz, H-1 of Glc), 5.99 (1H, *br s*, H-1 of Rha), 5.76 (1H, *br s*, H-1 of Rha), 1.64 (3H, *d*, *J* = 6.2 Hz, H-6 of Rha), 1.61 (3H, *d*, *J* = 6.8 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

Neoalsoside E1 (**17**). Needles (MeOH), mp 259–261°, $[\alpha]_D^{16}$ + 14.1° (MeOH; *c* 1.14). FAB-MS (negative) *m/z*: 929.5488 $[M-H]^-$ ($C_{48}H_{81}O_{17}$, requires 929.5473). ^{1}H NMR (pyridine-d_5): δ0.77, 0.92, 0.97, 1.13, 1.19, 1.26, 1.29 and 1.47 (each 3H, *s*, Me), 3.34 (1H, *dd*, *J* = 4.0, 11.7 Hz, H-3), 3.71 (1H, *ddd*, *J* = 5.0, 10.1, 11.0 Hz, H-12a), 1.81 (1H, *dd*, *J* = 9.9, 10.1 Hz, H-13), 2.25 (1H, *ddd*, *J* = 4.0, 9.9, 10.0 Hz, H-17), 3.96 (1H, *dd*, *J* = 6.8, 8.4 Hz, H-24), 4.84 (1H, *d*, *J* = 7.5 Hz, H-1 of Glc), 5.99 (1H, *br s*, H-1 of Rha), 5.76 (1H, *br s*, H-1 of Rha), 1.68 (3H, *d*, *J* = 6.2 Hz, H-6 of Rha), 1.65 (3H, *d*, *J* = 6.0 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

20(S)-*Protopanaxadiol oxide II* (*aglycone of* **16**) (**23**) and 20(S)-*protopanaxadiol oxide I* (*aglycone of* **17**, *pyxinol*) (**24**). Compound **23**: powder, $[\alpha]_D^{17}$ + 10.0° ($CHCl_3$: *c* 0.70). ^{1}H NMR ($CDCl_3$): δ0.77, 0.88, 0.90, 0.97, 1.00, 1.09, 1.22 and 1.26 (each 3H, *s*, H-29, 19, 30, 28, 18, 26, 27 and 21, respectively), 3.18 (1H, *dd*, *J* = 5.0, 11.4 Hz, H-3), 3.51 (1H, *ddd*, *J* = 4.7, 10.4, 10.4 Hz, H-12a), 1.68 (1H, *dd*, *J* = 10.0, 10.4 Hz, H-13), 2.24 (1H, *ddd*, *J* = 4.7, 10.0, 10.8 Hz, H-17), 3.87 (1H, *dd*, *J* = 5.4, 10.8 Hz, H-24). ^{13}C NMR: Table 1. Compound, **24**: Powder, $[\alpha]_D^{15}$ + 19.7° ($CHCl_3$; *c* 1.07). ^{1}H NMR ($CDCl_3$): δ0.77, 0.85, 0.90, 0.97, 0.98, 1.10, 1.24 and 1.27 (each 3H, *s*, H-29, 19, 30, 28, 18, 26, 27 and 21, respectively), 3.18 (1H, *dd*, *J* = 5.0, 11.3 Hz, H-3), 3.51 (1H, *ddd*, *J* = 4.6, 10.6, 10.6 Hz, H-12a), 1.67 (1H, *dd*, *J* = 10.0, 10.6 Hz, H-13), 2.19 (1H, *ddd*, *J* = 3.7, 10.0, 10.8 Hz, H-17), 3.58 (1H, *dd*, *J* = 6.8, 8.8 Hz, H-24). ^{13}C NMR: Table 1. The authentic samples of **23** and **24** were synthesized from 20 (*S*)-protopanaxadiol according to the method of ref. [11].

Neoalsoside F1 (**18**). Powder, $[\alpha]_D^{27}$ −15.6° (MeOH; *c* 0.64). FAB-MS (negative) *m/z*: 913.5530 $[M-H]^-$ ($C_{48}H_{81}O_{16}$, requires 913.5523). ^{1}H NMR (pyridine-d_5): δ0.80, 0.90, 0.95, 1.17, 1.21, 1.23, 1.42 and 1.44 (each 3H, *s*, Me), 3.35 (1H, *dd*, *J* = 4.0, 11.7 Hz, H-3), 4.14 (1H, *m*, H-24), 4.88 (1H, *d*, *J* = 7.5 Hz, H-1 of Glc), 6.01 (1H, *br s*, H-1 of Rha), 5.77 (1H, *br s*, H-1 of Rha), 1.69 (3H, *d*, *J* = 6.2 Hz, H-6 of Rha), 1.65 (3H, *d*, *J* = 6.2 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

Neoalsoside G1 (**19**). Powder, $[\alpha]_D^{19}$ − 3.9° (MeOH; *c* 1.72), FAB-MS (negative) *m/z*: 927.5257 $[M-H]^-$ ($C_{48}H_{79}O_{17}$, requires 927.5316). ^{1}H NMR (pyridine-d_5): δ0.79, 0.84, 1.12, 1.13, 1.19, 1.23, 1.39 and 1.44 (each 3H, *s*, Me), 3.28 (1H, *dd*, *J* = 4.0, 11.7 Hz, H-3), 3.13 (1H, *d*, *J* = 9.5 Hz, H-13), 2.76 (1H, *ddd*, *J* = 4.0, 10.0, 10.0 Hz, H-17), 4.06 (1H, *m*, H-24), 4.83 (1H, *d*, *J* = 7.3 Hz, H-1 of Glc), 5.98 (1H, *br s*, H-1 of Rha), 5.75 (1H, *br s*, H-1 of Rha), 1.68 (3H, *d*, *J* = 6.1 Hz, H-6 of Rha), 1.64 (3H, *d*, *J* = 6.8 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

Neoalsogenin G (**26**). Needles (Me_2CO), mp 209–211°, $[\alpha]_D^{24}$ + 47.6° ($CHCl_3$; *c* 0.36). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1703 (C=O). CD (MeOH; *c* 1.0): $[\theta]^{25}$ − 3098 (285 nm). FAB-MS (negative) *m/z*: 473.3621 $[M-H]^-$ ($C_{30}H_{49}O_4$, requires 473.3631). ^{1}H NMR ($CDCl_3$): δ0.76, 0.79, 0.92, 0.98, 0.98, 1.19 and 1.20 (each 3H, *s*, Me), 1.09 (3H × 2, *s*, Me), 3.18 (1H, *dd*, *J* = 4.9, 11.3 Hz, H-3), 2.19 (2H, *m*, H-11), 2.88 (1H, *d*, *J* = 9.5 Hz, H-13), 2.56 (1H, *ddd*, *J* = 4.7, 9.5, 10.8 Hz, H-17), 3.68 (1H, *dd*, *J* = 6.0, 8.9 Hz, H-24). ^{13}C NMR: Table 1.

Preparation of **26** [15]. A soln of **24** (34 mg) in Ac_2O (1.0 ml) and pyridine (1.0 ml) was allowed to stand overnight at 5°. After working-up in the usual way, the resulting acetate (39 mg) was oxidized with CrO_3 (100 mg) and pyridine (3 ml) on standing at room temp. for 50 hr. After work-up, the resulting keto-acetate (22 mg) was saponified with 10% NaOH in MeOH (3 ml) on standing at room temp. overnight. The reaction mixt. was diluted with H_2O, and then extracted with Et_2O. The Et_2O layer was evapd and the residue was chromatographed on silica gel with $CHCl_3$–MeOH (20:1) to give a keto-compound (15 mg). This was identical with **26** by comparison of the spectral data and physical constants.

Neoalsoside H1 (**20**). Powder, $[\alpha]_D^{20}$ − 10.4° (MeOH; *c* 0.48). FAB-MS (negative) *m/z*: 929.5476 $[M-H]^-$ ($C_{48}H_{81}O_{17}$, requires 929.5473). ^{1}H NMR (pyridine-d_5): δ0.75, 0.83, 0.89, 1.13, 1.15, 1.19 and 1.42 (each 3H, *s*, Me), 3.34 (1H, *dd*, *J* = 4.0, 11.5 Hz, H-3), 4.06 (1H, *m*, H-24), 3.99 (2H, *s*, H-26), 4.85 (1H, *d*, *J* = 7.3 Hz, H-1 of Glc), 5.98 (1H, *br s*, H-1 of Rha), 5.74 (1H, *br s*, H-1 of Rha), 1.66

(3H, *d*, J = 6.1 Hz, H-6 of Rha), 1.62 (3H, *d*, J = 6.0 Hz, H-6 of Rha). ^{13}C NMR: Table 2.

Neoalsogenin H (**27**). Powder, FAB-MS (negative) *m/z*: 475.3824 $[M-H]^-$ ($C_{30}H_{51}O_4$, requires 475.3787). ^{1}H NMR ($CDCl_3$): δ0.77, 0.84, 0.87, 0.95, 0.97, 1.02 and 1.12 (each 3H, *s*, H-29, 19, 30, 18, 28, 27 and 21, respectively), 3.20 (1H, *dd*, J=4.9, 10.7 Hz, H-3), 1.53 (2H, *m*, H-12), 1.54 (1H, *m*, H-13), 1.77 (1H, *m*, H-17), 2.00 (1H, *m*, Ha-23), 1.88 (1H, *m*, Hb-23), 3.88 (1H, *dd*, J=7.3, 7.5 Hz, H-24), 3.38 (1H, *dd*, J=1.2, 11.2 Hz, Ha-26), 3.73 (1H, *dd*, J=10.7, 11.2 Hz, Hb-26), 3.25 (1H, *dd*, J=1.2, 10.7 Hz, OH-26). ^{13}C NMR: Table 1.

Acknowledgements—We wish to thank the Research Center for Molecular Medicine, Hiroshima University School of Medicine, for the use of NMR. This study was financially supported by Grant-in-Aid for the Mombusho International Scientific Research Program (No. 03044103, 1991–1993) from the Ministry of Education, Science and Culture.

REFERENCES

1. Chiu, M.-H., Nie, R.-L., Nagasawa, H., Isogai, A., Zhou, J. and Suzuki A. (1992) *Phytochemistry* **31**, 2451.
2. Kupchan, S. M., Sigel, C. W., Guttman, L. J., Restivo, R. J. and Bryan, R. F. (1972) *J. Am. Chem. Soc.* **94**, 1353.
3. Rao, M. M., Meshulam, H. and Lavie, D. (1974) *J. Chem. Soc. Perkin Trans. I* 2252.
4. Rehm, S., Enslin, P. R., Meeuse, A. D. J. and Wessels, J. H. (1957) *J. Sci. Food Agric* **8**, 679.
5. Enslin, P. R., Rehm, S. and Rivett, D. E. A. (1957) *J. Sci. Food Agric.* **8**, 673.
6. Rao, M. M., Meshulam, H. and Lavie, D. (1972) *J. Chem. Soc. Perkin Trans. I* 2552.
7. Yamada, Y., Hagiwara, K., Iguchi, K., Suzuki, S. and Hsu, H.-Y. (1978) *Chem. Pharm. Bull.* **26**, 3107.
8. Vande Velde, V. and Lavie, D. (1983) *Tetrahedron* **39**, 317.
9. Valverde, S., Escudero, J., Lopez, J. C. and Rabanal, R. M. (1985) *Phytochemistry* **24**, 111.
10. Kizu, H. and Tomimori, T. (1982) *Chem. Pharm. Bull.* **30**, 3340.
11. Nagai, M., Tanaka, N., Tanaka, O and Ichikawa, S. (1973) *Chem. Pharm. Bull.* **21**, 2061.
12. Warnhoff, E. W. and Halls, C. M. M. (1965) *Can. J. Chem.* **43**, 3311.
13. Ohmoto, T., Nikaido, T. amd Ikuse, M. (1978) *Chem. Pharm. Bull.* **26**, 1437.
14. Tanaka, R., Masuda, K. and Matsunaga, S. (1993) *Phytochemistry* **32**, 472.
15. Kasai, R., Shinzo, K. and Tanaka, O. (1976) *Chem. Pharm. Bull.* **24**, 400.
16. Hara, S., Okabe, H. and Mihashi, K. (1987) *Chem. Pharm. Bull.* **35**, 501.