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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

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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 $(2-O-\beta-glucoside of cucurbitacin R)$ (8) [7] were established by ¹H and ¹³C 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 C30H50O5 by NMR and HR-FAB mass spectrometry. The IR spectrum showed absorption bands at 3400 (OH) and 1710 cm⁻¹ (CO). The ¹³C NMR spectrum of 7 revealed 30 signals (Table 1): one carbonyl (δ 217.8), eight methylene, seven methine [three of them bearing an oxygen atom (δ 70.3, 70.7 and 89.7)], six quaternary [two of them bearing an oxygen atom ($\delta 85.6$ 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): 20S, 24S-epoxy- 3β , 12 β , 23S, 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 20S,24R-epoxy-12B,25dihydroxydammaran-3-one isolated from Salvia bicolor [9]. Therefore, 7 is the 3-keto-compound of 21: 20S,24Sepoxy-12\beta,23\$,25-trihydroxydammaran-3-one.

The glycosides 10-13 were characterized as ocotillol type dammarane glycosides based on the ¹H and ¹³C 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.



Table 1. ¹³C 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	70.7ª	70.7*	70.5ª	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°	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	70.3ª	70.0ª	70.3ª	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°	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 ¹H and ¹³C 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 ¹H and ¹³C 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 ¹H-¹H COSY (assignments: see Experimental). In the phase sensitive ROESY spectrum of the acetate, cross-peaks were observed between the H-1 (δ 5.30) of rhamnosyl and the H-2 (δ 3.72) of inner glucosyl moiety, and between the H-1 (δ 4.66) of terminal glucosyl and the H-3 (δ 3.92) 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 ¹³C 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 -CH₂-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 20S,24S-epoxy-3B,12B,23S,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 (20S,24S-epoxy- $3\beta,12\beta,25$ -trihydroxydammarane) and I (24R-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-3 β ,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 12keto function [15]. From these data, 26 was assumed to be 20S,24*R*-epoxy-3 β ,25-dihydroxydammaran-12-one. The structure was further confirmed by preparation of this compound from 24 by selective oxidation of the 12hydroxyl 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 ¹H and ¹³C 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: 20S,24Repoxy- 3β , 25 ξ , 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 $\delta 3.25$ (1H, dd, J = 1.2, 10.7 Hz) was observed in the ¹H 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 μ m, Merck) were used. All solvent systems for chromatography were homogeneous. MPLC: ODS-AM 120-S50 (23 mm × 42 cm, YMC, Japan). HPLC: D-ODS-10 (YMC). Acid

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Table 2. ¹³CNMR spectral data of glycosides in pyridine- $d_5(\delta$ -value)

С	9	10	11	12	13	14	С	9	10	11	12	13	14
1	39.6	39.3	39.7	39.3	39.7	39.7	3-0-						
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	39.7ª	39.7ª	39.7ª	39.8ª	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	40.1ª	40.0ª	40.2ª	39.7	G-2-0-						
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	32.5ª	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	49.6ª	49.7°	49.8°	49.7°	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-3-0-						
16	28.6	28.6	28.6	28.5	28.6	28.6	R-1	103.6			103.0		103.7
17	49.9ª	50.0°	50.1°	50.0°	50.2 ^ь	50.0 ^ь	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°	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-3-0-						
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°	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

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1 a Die 2.10	Continuea

с	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	3-0-						
2	26.5	27.0	26.9	26.0*	27.0	26.9ª	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	39.7ª	39.7ª	39.7 ^b	39.6ª	39.7°	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	40.0ª	40.0 ^a	40.6 ^ь	40.7ª	40.6ª	G-2-0-						
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	32.5ª	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	26.0ª	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	32.6ª	32.3	32.4 ^b	31.7	32.3	31.7	G-3-0-						
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 ^ь	16.7	16.5°	16.2 ^b	16.5°	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-3-0-						
23	70.8	28.7	28.8	26.9ª	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°	26.8	27.0	21.9	G-5	76.5					
28	63.9	27.9	27.9°	27.9	27.8	27.9	G-6	62.3					
29	13.8	16.8 ^b	16.7	16.6°	16.7 ^b	16.6°							
30	18.2	18.2	18.4	16.8°	16.9 ^b	16.8°							

^{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 CHCl₃-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 CHCl₃-MeOH (15:1) and then HPLC on ODS with 60% ag. 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 CHCl₃-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 \times 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). ¹³C NMR (CDCl₃): δ (C-1-C-30) 36.0, 71.6, 213.0, 50.3, 140.5, 120.3, 23.9, 42.4, 48.4°, 33.8, 212.4, 48.7, 50.8, 48.3°, 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, $[\alpha]_D^{25} - 45.0^{\circ}$ (EtOH; *c* 0.85). ¹³C NMR (CDCl₃): 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). ¹³C NMR (CDCl₃): 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, $[\alpha]_{2}^{26}$ + 79.0° (CHCl₃; c 0.57). ¹³C NMR (CDCl₃): δ (C-1–C-30) 35.9, 71.6, 213.0, 50.2, 140.4, 120.3, 23.8, 42.3, 48.4°, 33.7, 212.3, 48.6, 50.6, 48.3°, 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 (CDCl₃): 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° (CHCl₃; c 0.67). ¹³C NMR (CDCl₃): 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. ¹H NMR (CDCl₃): δ 1.18 (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, m)dd J = 8.8, 12.9 Hz, H-15b, 4.33 (1H, m, H-16), 2.60 (1H, m, H-16)br d, J = 6.8 Hz, H-17, 0.95 (3H, s, H-18), 1.04 (3H, s, H-18)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, $[\alpha]_{b}^{5}$ + 122.3° (CHCl₃; c1.14). ¹³C NMR (CDCl₃): 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, $[\alpha]_D^{25} + 31.5^{\circ}$ (EtOH; c 1.30). ¹³C 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, $[\alpha]_D^{19} + 30.0^{\circ}$ (CHCl₃; c0.20). FAB-MS (negative) m/z: 489.3579 $[M - H]^-$ (C₃₀H₄₉O₅, requires 489.3579). IR $\nu_{max}^{CHCl_3}$ cm⁻¹: 3400 (OH), 1710 (C=O). CD (MeOH; c0.8): $[\theta]^{25} + 1903$ (291 nm): ¹H NMR (CDCl₃): δ 0.90, 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). ¹³C NMR: Table 1.

Neoalsoside A (9). Needles (Me₂CO), mp 279–280°, $[\alpha]_D^{23} - 29.8°$ (pyridine; c 1.04). Authentic sample: mp 277–279°, $[\alpha]_D^{23} - 31.5°$ (pyridine). ¹H NMR (pyridine d_5): $\delta 0.75$, 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). ¹³C NMR: Table 2. Neoalsogenin A (21). Needles (MeOH), mp 241–242°, $[\alpha]_{D^2}^{2^2}$ +17.3° (MeOH; c 0.56). ¹H NMR (CDCl₃): δ 0.78, 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). ¹³C NMR: Table 1.

Neoalsoside A2 (10). Powder, $[\alpha]_{\rm b}^{15} - 6.9^{\circ}$ (MeOH; c 1.13). FAB-MS (negative) m/z: 653.4264 $[M - H]^{-}$ (C₃₆H₆₁O₁₀, requires 653.4264). ¹H NMR (pyridine- d_5): $\delta 0.81, 0.87, 0.95, 1.00, 1.32, 1.44, 1.61$ 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). ¹³C NMR: Table 2.

Neoalsoside A3 (11). Powder, $[\alpha]_{\rm D}^{19} - 3.9^{\circ}$ (MeOH; c 1.00). FAB-MS (negative) m/z: 799.4872 $[M - H]^{-1}$ (C₄₂H₇₁O₁₄, requires 799.4843). ¹H NMR (pyridine- d_5): $\delta 0.80, 0.85, 0.94, 1.20, 1.25, 1.44, 1.61$ 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). ¹³C NMR: Table 2.

Neoalsoside A4 (12). Powder, $[\alpha]_D^{16} + 3.0^{\circ}$ (MeOH; c 0.78). FAB-MS (negative) m/z: 799.4843 $[M - H]^-$ (C₄₂H₇₁O₁₄, requires 799.4835). ¹H NMR (pyridine- d_5): $\delta 0.80, 0.88, 0.95, 0.97, 1.27, 1.44, 1.62$ 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). ¹³C NMR: Table 2.

Neoalsoside A5 (13). Powder, $[\alpha]_D^{19} + 6.8^\circ$ (MeOH; c 1.45). FAB-MS (negative) m/z: 961.5369 $[M - H]^{-1}$ $(C_{48}H_{81}O_{19}, \text{ requires 961.5371})$. ¹H NMR (pyridine- d_5): $\delta 0.81, 0.85, 0.94, 1.18, 1.25, 1.44, 1.62$ 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). ¹³CNMR: Table 2. Compound 13 was acetylated with Ac_2O and pyridine in the usual way to give an acetate. ¹H NMR (CDCl₃, 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, $[\alpha]_{\rm b}^{19} - 3.8^{\circ}$ (MeOH; c 1.14). FAB-MS (negative) m/z: 961.5341 $[M - H]^-$ (C₄₈H₈₁O₁₉, requires 961.5371). ¹H NMR (pyridine- d_5): $\delta 0.85$, 1.10, 1.42, 1.61 and 1.63 (each 3H, s, Me), 0.89 (3H $\times 2$, 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). ¹³C NMR: Table 2.

Neoalsoside C2 (15). Powder, $[\alpha]_D^{15} - 12.5^{\circ}$ (MeOH; c0.69). FAB-MS (negative) m/z: 977.5349 $[M - H]^-$ (C₄₈H₈₁O₂₀, requires 977.5321). ¹H NMR (pyridine- d_5): $\delta 0.81$, 1.09, 1.39, 1.57 and 1.60 (each 3H, s, Me), 0.85 (3H $\times 2$, 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). ¹³C NMR: Table 2.

Neoalsogenin C (22). Powder, $[\alpha]_D^{17} + 17.2^{\circ}$ (CHCl₃; c 0.99). FAB-MS (negative) m/z: 507.3683 $[M - H]^{-1}$ (C₃₀H₅₁O₆, requires 507.3685). ¹H NMR (CDCl₃): δ 0.88, 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). ¹³C NMR: Table 1.

Neoalsoside D1 (16). Powder, $[\alpha]_{D}^{16} - 18.4^{\circ}$ (MeOH; c 1.52). FAB-MS (negative) m/z: 929.5430 $[M - H]^{-}$ (C₄₈H₈₁O₁₇, requires 929.5473). ¹H NMR (pyridine-d₅): $\delta 0.83$, 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). ¹³C NMR: Table 2.

Neoalsoside E1 (17). Needles (MeOH), mp 259–261°, $[\alpha]_{16}^{16}$ + 14.1° (MeOH; c 1.14). FAB-MS (negative) m/z: 929.5488 [M-H]⁻ (C₄₈H₈₁O₁₇, requires 929.5473). ¹H NMR (pyridine-d₅): δ 0.77, 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). ¹³C 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, $[\alpha]_{\rm D}^{1.7} + 10.0^{\circ}$ (CHCl₃: c 0.70). ¹H NMR (CDCl₃): $\delta 0.77$, 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). ¹³C NMR: Table 1. Compound, **24**: Powder, $[\alpha]_{15}^{15}$ + 19.7° (CHCl₃; c 1.07). ¹H NMR (CDCl₃): δ 0.77, 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). ¹³C 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, $[\alpha]_D^{27} - 15.6^{\circ}$ (MeOH; c 0.64). FAB-MS (negative) m/z: 913.5530 [M - H]⁻ (C₄₈H₈₁O₁₆, requires 913.5523). ¹H NMR (pyridine- d_5): $\delta 0.80, 0.90, 0.95, 1.17, 1.21, 1.23, 1.42$ 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). ¹³C NMR: Table 2.

Neoalsoside G1 (19). Powder, $[\alpha]_{1}^{19} - 3.9^{\circ}$ (MeOH; c 1.72), FAB-MS (negative) m/z: 927.5257 $[M - H]^{-1}$ (C₄₈H₇₉O₁₇, requires 927.5316). ¹H NMR (pyridine- d_5): $\delta 0.79$, 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). ¹³C NMR: Table 2.

Neoalsogenin G (26). Needles (Me₂CO), mp 209–211°, $[\alpha]_D^{24} + 47.6°$ (CHCl₃; 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]⁻ (C₃₀H₄₉O₄, requires 473.3631). ¹H NMR (CDCl₃): δ 0.76, 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). ¹³C NMR: Table 1.

Preparation of **26** [15]. A soln of **24** (34 mg) in Ac₂O (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 H₂O, and then extracted with Et₂O. The Et₂O layer was evapd and the residue was chromatographed on silica gel with CHCl₃-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, $[\alpha]_D^{20} - 10.4^{\circ}$ (MeOH; c 0.48). FAB-MS (negative) m/z: 929.5476 $[M - H]^-$ (C₄₈H₈₁O₁₇, requires 929.5473). ¹H NMR (pyridine- d_5): $\delta 0.75$, 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). ¹³C NMR: Table 2.

Neoalsogenin H (27). Powder, FAB-MS (negative) m/z: 475.3824 $[M-H]^-$ (C₃₀H₅₁O₄, requires 475.3787). ¹H NMR (CDCl₃): δ 0.77, 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). ¹³C NMR: Table 1.

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