Pergamon

0031-9422(95)00020-8

Phytochemistry, Vol. 39, No. 3, pp. 591–602, 1995

0031-9422/95 $9.50 + 0.00

DAMMARANE GLYCOSIDES FROM AERIAL PART OF *NEOALSOMITRA INTEGRIFOLIOLA**

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(*Received* 27 *September* 1994)

Key Word Index—*Neoalsomitra integrifoliola*; aerial part; Cucurbitaceae; neoalsosides I1, I2, J1, K1, L1, M1, M2, M3, N1, O1 and O2; neoalsogenin M; dammarane glycosides.

Abstract—From the aerial part of *Neoalsomitra integrifoliola*, eleven new dammarane glycosides were isolated. The structures were elucidated by chemical and spectral means.

INTRODUCTION

Neoalsomitra integrifoliola (COGN.) HUTCH. is a Cucurbitaceous vine distributed from the southern area of China to the Malay Peninsula. From the rhizomes of this plant, 20,24-epoxydammarane glycoside named neoalsoside A (**1**) has been isolated [2]. In a previous paper [1], we reported the isolation and structural elucidation of 20, 24-epoxydammarane triterpene and glycosides: 3-oxo-neoalsogenin A (**2**), neoalsosides A2 (**3**), A3, (**4**), A4 (**5**), A5 (**6**), C1 (**7**), C2 (**8**), D1 (**9**), E1 (**10**), F1 (**11**), G1 (**12**) and H1 (**13**) from the aerial part of this plant.

Further investigation of the aerial part of the same plant afforded 11 new dammarane glycosides named neoalsosides I1 (**14**), I2 (**15**), J1 (**16**), K1 (**17**), L1 (**18**), M1 (**19**), M2 (**20**), M3 (**21**), N1 (**22**), O1 (**23**) and O2 (**24**). The present paper deals with the structural determination of these new glycosides.

RESULTS AND DISCUSSION

The methanolic extract of the aerial part of *N. integrifoliola* on repeated column chromatography gave 11 new glycosides (**14**–**24**), together with **1**–**13** and eight cucurbitane compounds reported in our previous paper [1].

Glycoside **14** had the molecular formula $C_{48}H_{84}O_{18}$ by the FABMS and ^{13}C NMR spectrometry. Hydrolysed products could not be obtained after enzymatic hydrolysis of **14** with various enzymes (crude hesperidinase, crude naringinase, crude pectinase, etc). On the other hand, acid hydrolysis of **14** afforded two analogous compounds (**25** and **26**) as the aglycone (Scheme 1). These were identified as 20*S*,24*S*-epoxy-dammarane-3β-12β, 25-triol (aglycone of **9**) and its 20*R*-epimer, respectively. The authentic sample of **26** was obtained from 20 (*R*)-protopanaxadiol (**27**) by oxidation of the double bond with *m*-chloroperbenzoic acid [3, 4], together with **28** (Scheme 2). The carbon signals attributable to the cyclized side chain of **25** or **26** could not be observed in the ^{13}C NMR spectrum of **14**, showing that neither **25** or **26** was the genuine aglycone of **14**.

It is known that 12β,20-dihydroxydammarane type triterpenes easily effected acid-catalysed epimerization to yield a mixture of their 20*S*- and 20*R*-epimers [5]. Furthermore, it has been reported that acid treatment of a cycloartane compound having a 20,24,25-trihydroxylated side chain yielded its 20,24-epoxy-compound [6]. From these reports, and the result of acid hydrolysis of **14**, it was assumed that the genuine aglycone of **14** would be 3β,12β,20ξ,24ξ,25-pentahydroxydammarane while **25** and **26** were artifacts formed from the genuine aglycone during the course of acid hydrolysis of **14** by epimerization and cyclization of the side chain.

The estimated structure of the genuine aglycone of **14** was confirmed, and configuration of C-24 was simultaneously determined as follows. The side chain double bond of 20(*S*)-betulafolienetriol (**29**) [7] was oxidized with osmium tetraoxide to yield two 24, 25-glycols (**30** and **31**, Scheme 2). These two isomers did not show significant differences of the chemical shifts in the ^1H and ^{13}C NMR spectra. The configurations of C-24 of **30** and **31** were confirmed as *R* and *S*, respectively, by the CD measurement in the presence of Eu(fod)$_3$, which was the diol complexation method for the determination of absolute configuration of vicinal glycols [8]. Acid treatment of **30**

*Part 2 in the series 'Studies on the Constituents of Aerial Part of *Neoalsomitra integrifoliola*'. For Part 1 see ref. [1].

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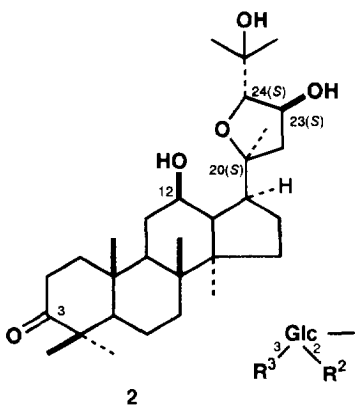
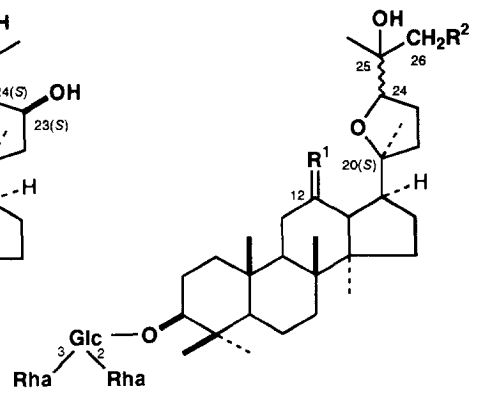
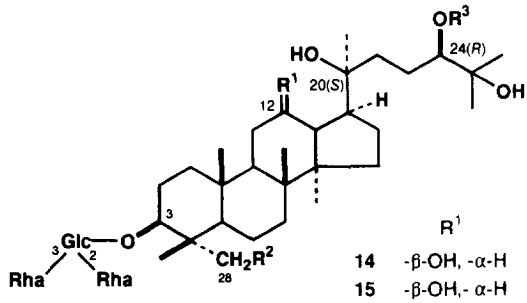


2

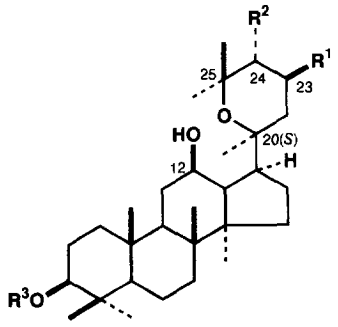
	R^1	R^2	R^3
1	-H	-Rha	-Rha
3	-H	-H	-H
4	-H	-Rha	-H
5	-H	-H	-Rha
6	-H	-Rha	-Glc
7	-OH	-Rha	-Rha
8	-OH	-Rha	-Glc



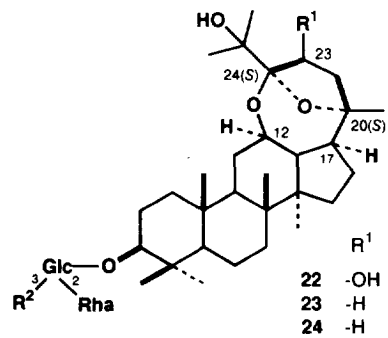
	R^1	R^2	C-24	C-25
9	-β-OH, -α-H	-H	(*S*)	
10	-β-OH, -α-H	-H	(*R*)	
11	$=H_2$	-H	(*R*)	
12	=O	-H	(*R*)	
13	$=H_2$	-OH	(*R*)	(*R*)



	R^1	R^2	R^3
14	-β-OH, -α-H	-H	-H
15	-β-OH,- α-H	-H	-Glc
16	-β-OH, -α-H	-OH	-H
17	$=H_2$	-H	-H
18	=O	-H	-H

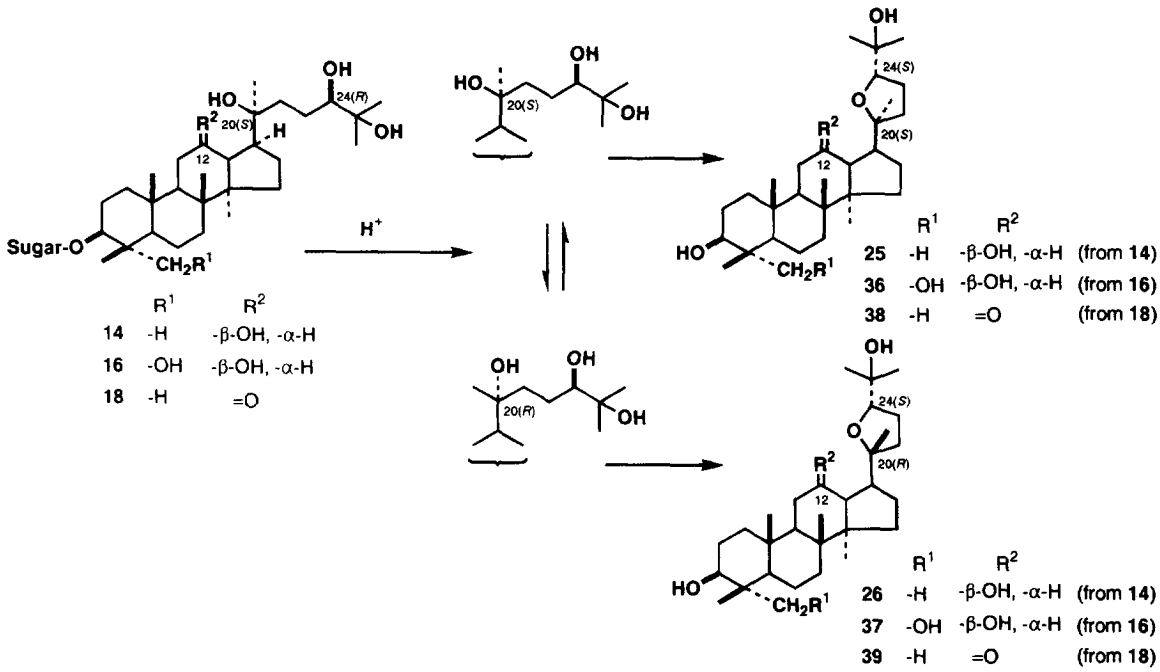


	R^1	R^2	R^3	C-23	C-24
19	-OH	-OH	-O-Glc^2-Rha	(*S*)	(*R*)
20	-OH	-OH	-O-Glc^2-Rha $^{1\,3}$ Rha	(*S*)	(*R*)
21	-O-Glc	-OH	-O-Glc^2-Rha $^{1\,3}$ Rha	(*S*)	(*R*)
40	-OH	-OH	-H	(*S*)	(*R*)
41	-H	-H	-H		

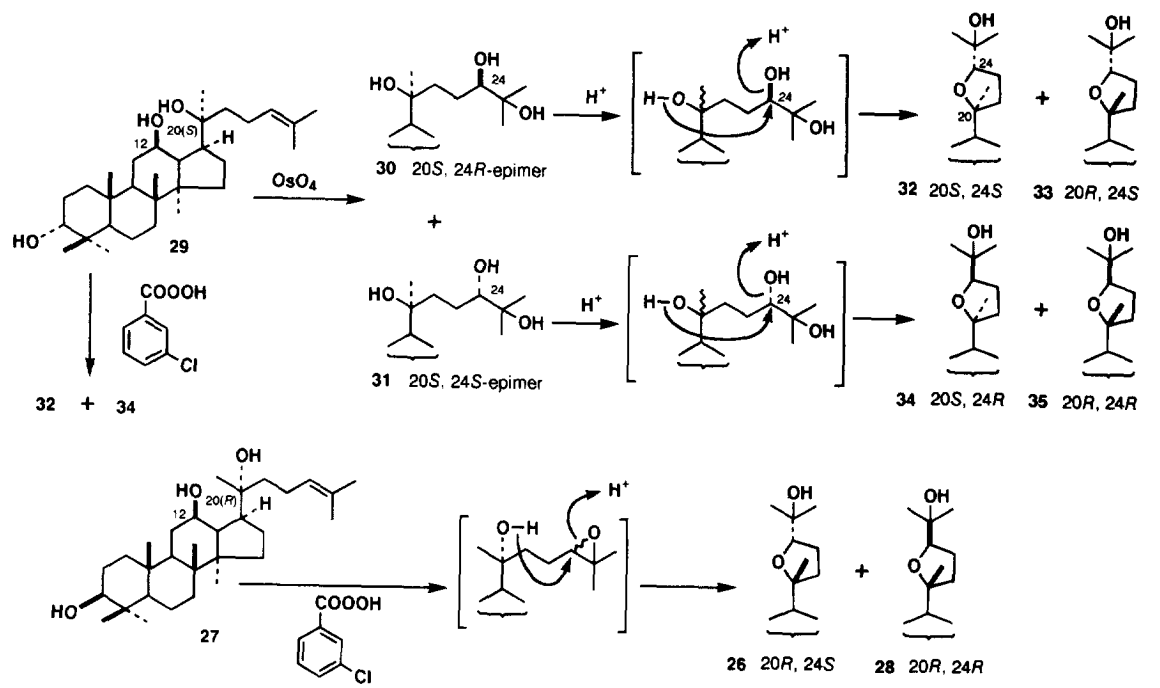


	R^1	R^2	C-23
22	-OH	-Rha	(*S*)
23	-H	-H	
24	-H	-Rha	

and **31** afforded a mixture of two 20,24-epoxy-compounds: **32** and **33** from **30** and **34** and **35** from **31**. Compounds **32** and **34** were identified as betulafolienetriol oxide II (20*S*,24*S*-epoxy) and I (20*S*,24*R*-epoxy), respectively, authentic samples of which were synthesized in an independent procedure from **29** by oxidation with *m*-chloroperbenzoic acid described above in the case of **27** [3, 4]. On the other hand, compounds **33** and **35** were characterized as 20*R*-epimers of **32** and **34**, respectively, by comparison of the carbon resonances due to the cyclized side chain of **26** (20*R*,24*S*-epoxy-epimer) and **28** (20*R*,24*R*-epoxy-epimer). This, it was confirmed that on



Scheme 1. Acid-catalysed epimerization and cyclization of the side chain of **14**, **16** and **18**.



Scheme 2. Synthetic routes to **26**, **28** and **30**–**35**.

acid treatment, 12β,20ξ,24ξ,25-tetrahydroxydammaranes were converted to two diastereomers of the corresponding 20,24-epoxy-compound through a mixture of 20*S*- and 20*R*-compounds as the intermediates, and subsequent ring formation of the side chain with inversion of the configuration on C-24 illustrated in Scheme 2.

The carbons of the cyclized side chain of **25** and **26** were superimposed by those in the ^{13}C NMR spectra of **32** and **33**, respectively. Therefore, the genuine aglycone of **14** was characterized as 12β, 20ξ, 24*R*, 25-tetrahydroxydammarane. It has been reported that in the ^{13}CNMR spectra of dammarane triterpenes having 12β,20ξ-

Table 1. ^{13}C chemical shifts of aglycones and dammarane triterpenes

C	25*	26*	28*	32*	33*	24*	35†	30†	31†	36*	38*	40†	41†
1	39.0	39.0	38.9	33.5	33.6	33.5	33.5	34.2	34.1	38.6	38.6	39.5	39.5
2	27.5	27.5	27.5	25.4	25.5	25.3	25.4	26.5[a]	26.5[a]	27.1	27.2	28.3	28.3
3	78.9	78.9	78.8	76.0	76.2	76.4	76.2	75.2	75.2	76.4	78.6	78.1	78.0
4	39.0	39.0	38.9	37.5	37.6	37.5	37.5	38.1	38.1	42.0	38.9	39.6	39.6
5	56.1	55.9	55.9	49.5	49.6	49.6	49.5	49.8	49.8	50.4	55.8	56.4	56.5
6	18.4	18.3	18.3	18.2	18.3	18.2	18.2	18.6	18.6	18.4	18.4	18.8	18.8
7	34.9	34.9	34.9	34.6	34.9	34.7	34.8	35.2	35.2	34.6	34.3	35.1	35.2
8	39.8	39.8	39.8	39.9	40.1	40.0	40.0	40.2	40.2	39.7	40.4	40.1	40.1
9	50.3	50.0	50.1	50.0	49.9	50.3	49.8	50.3	50.3	50.3	54.4	50.5	50.5
10	37.3	37.2	37.2	37.2	37.4	37.3	37.3	37.6	37.6	37.1	37.7	37.4	37.4
11	31.7	30.7	30.6	31.6	30.6	31.2	30.4	31.9[b]	32.0[b]	31.7	39.7	32.2	32.3
12	70.6	70.5	70.5	70.5	70.5	71.1	70.6	71.0	71.0	70.5	211.2	70.6	70.5
13	48.9	49.1	49.0	48.7	49.1	49.2	48.9	48.4	48.5	48.8	57.3	49.5	49.3
14	52.2	51.6	51.9	52.2	51.8	52.2	51.7	51.8	51.8	52.2	56.0	52.3	52.2
15	32.3	31.3	31.3	32.1	31.3	32.6	31.3	31.9[b]	31.3[b]	32.2	32.0	31.9	32.0
16	28.6	26.9	26.8	28.5	27.0	28.6	26.8	26.9	26.8	28.5	24.8	27.8	27.3
17	49.0	50.5	50.7	48.8	50.5	47.9	50.6	54.5	54.8	48.9	43.0	52.5	52.5
18	15.5	15.6	15.5	15.4	15.7	15.4	15.5	15.8	15.9	15.5	15.6	15.7	15.8
19	16.3	16.2	16.2	16.1	16.0	16.1	16.0	16.4	16.4	16.6	16.1	16.6	16.0
20	87.2	86.3	86.4	87.3	86.3	86.6	86.4	73.2	73.4	87.2	85.3	79.4	78.1
21	28.9	19.3	21.3	28.8	19.3	27.5	21.3	27.4	27.3	28.9	26.6	27.4	26.7
22	31.7	38.1	39.1	31.5	38.2	31.1	39.1	33.8	33.5	31.6	36.5	37.4	27.3
23	25.1	25.5	25.9	25.0	25.5	25.0	25.9	26.7[a]	26.5[a]	25.1	26.2	67.2	16.6
24	87.5	85.4	86.5	87.1	85.4	85.3	86.4	80.0	79.9	87.4	87.6	80.9	36.7
25	70.1	71.0	70.2	70.1	71.0	70.5	70.2	72.7	72.8	70.1	70.3	79.2	73.9
26	24.3[a]	25.3[a]	24.7[a]	24.1[a]	25.3[a]	26.0[a]	24.6[a]	25.9[c]	25.9[c]	24.2[a]	23.9[a]	30.4	32.8
27	28.0[a]	27.3[a]	27.9[a]	27.8[a]	27.3[a]	27.8[a]	28.0[a]	26.1[c]	26.1[c]	28.0[a]	27.7[a]	24.6	28.2
28	28.0	28.0	28.0	28.3	28.3	28.3	28.3	29.3	29.3	71.6	28.0	28.7	28.7
29	15.3	15.4	15.3	22.0	22.1	22.0	22.1	22.5	22.5	11.2	15.3	16.3	16.3
30	17.8	17.0	16.9	17.2	17.1	18.2	17.0	16.9	16.9	17.8	16.6	18.0	18.0

[a]–[c]Interchangeable assignments.
*Measured in $CDCl_3$.
†Measured in pyridine-d_5.

dihydroxy groups, the major difference between the 20*S*- and 20*R*-epimers was observed in the chemical shifts of C-13, C-16, C-17, C-20 and C-21 [9]. The remaining stereochemistry with respect to C-20 of **14** was deduced to be identical to that of **29** from the agreement of the chemical shifts of these carbons in both compounds. Consequently, the structure of **14** was characterized as 3*β*,12*β*,20*S*,24*R*,25-pentahydroxydammarane.

Acid hydrolysis of **14** yielded D-glucose and L-rhamnose. The ^1H and ^{13}C NMR spectra demonstrated that **14** had one *β*-D-glucopyranosyl and two *α*-L-rhamnopyranosyl moieties. The carbon signals assignable to the sugar moiety and the carbons around C-3 of **14** closely corresponded to those of **1** (Table 2). Thus, the structure of **14** was established as shown.

The molecular formula of glycoside **15** was determined as $C_{54}H_{94}O_{23}$. Acid hydrolysis of **15** also gave **25** and **26**, and D-glucose and L-rhamnose were identified in the hydrolysate. Comparison of the ^{13}C NMR spectra of **14** and **15** indicated that **15** had the same trisaccharide unit as that of **14** and an additional *β*-D-glucopyranosyl unit (Table 2). Furthermore, the glycosylation shifts [10] were observed for the signals due to the carbons around C-24, suggesting that **15** was a bisglycoside of a common aglycone to that of **14**. On enzymatic hydrolysis with crude hesperidinase, glycoside **15** liberated **14** as a partially hydrolysed product. Based on these results, the structure of glycoside **15** can be formulated as shown.

The ^{13}C NMR spectrum showed that glycoside **16**, $C_{48}H_{84}O_{19}$, had the same sugar chain as that of **14** (Table 2). Two compounds **36** and **37** were obtained as the acid hydrolysis products of **16**, assuming that the genuine aglycone of **16** was also a congener of **14** for the same reason described above in the case of **14** and **15**. Compound **36** (and **37**) was identified as the 28-hydroxylated compound of **25** (and **26**) by comparison of the ^{13}C NMR spectra of **36** and **25** (**37** and **26**); a typical hydroxylation shift was observed for the carbon signals of C-3–C-5, C-28 and C-29 by the 28-hydroxylation of this type of triterpene [11] (Table 2). By comparison of the ^{13}C NMR spectra of **16** and **36**, the glycosylation shifts were observed for the signals due to the carbons around C-3. Thus, the structure of glycoside **16** was established as shown.

The IR spectrum of glycoside **18**, $C_{48}H_{82}O_{18}$, showed an absorption band due to the carbonyl group at

Table 2. ^{13}C chemical shifts of glycosides in pyridine-d_5

C	1	4	14	29*	15	16	13	17	18	19	20	21	22	23	24
1	39.6	39.7	39.5	34.1	39.4	39.6	39.6	39.6	39.9	39.4	39.6	39.5	39.6	39.5	39.6
2	26.8	27.0	27.0[a]	26.3	26.9[a]	26.4[a]	26.5[a]	26.9[a]	27.0[a]	26.8	26.8	26.8	26.9	27.0	26.9
3	88.6	88.8	88.7	75.2	88.7	81.4	88.8	88.8	88.3	88.6	88.6	88.6	88.7	88.7	88.6
4	39.9	39.7[a]	39.6[b]	38.0	39.7[b]	43.6	39.7	39.7[b]	39.6[b]	39.5	39.6	39.6	39.7	39.7	39.7
5	56.6	56.8	56.6	49.6	56.6	48.5	56.6	56.5	56.3	56.5	56.6	56.5	56.6	56.5	56.4
6	18.5	18.6	18.5	18.6	18.5	18.1	18.4	18.4	18.5	18.4	18.5	18.4	18.4	18.4	18.4
7	35.1	35.3	35.2	35.1	35.2	34.9	35.6	35.6	34.5	34.9	35.1	35.0	35.0	35.0	35.0
8	39.9	40.1[a]	40.0[b]	40.1	40.1[b]	40.0	40.6	40.6[b]	40.7[b]	39.9	40.0	40.0	40.1	40.0	39.9
9	50.5	50.7	50.4	50.2	50.3	50.6	51.0	50.8	54.4	50.2	50.3	50.3	50.0	50.0	50.0
10	37.0	37.1	37.0	37.5	37.0	36.8	37.0	37.0	37.4	36.8	36.9	36.9	37.2	37.0	37.1
11	32.5	32.6[b]	32.0[c]	31.8	32.5[c]	32.1[b]	21.8	21.8	39.0	32.0	32.1	31.7	28.9	29.6	29.6
12	70.7	70.7	71.0	70.9	71.2	71.1	26.5[a]	25.5	211.9	70.4	70.7	70.5	74.0	73.7	73.7
13	49.6[a]	49.8[c]	48.5	48.3	48.8	48.4	43.3	42.(	56.6	49.3	49.5	49.5	49.5	48.9	49.0
14	52.3	52.4	51.8	51.6	51.7	51.8	50.2	50.6	55.9	52.2	52.3	52.2	48.8	49.3	49.3
15	32.5	32.5[b]	31.5[c]	31.2	31.2[c]	31.5[b]	31.7	31.6	32.0	31.7	31.8	32.1	32.0	32.0	32.0
16	28.6	28.6	26.8[a]	26.9	26.8[a]	27.0[a]	27.4[a]	28.0	24.6	27.6	27.8	27.8	23.2	23.5	23.5
17	49.9[a]	50.1[c]	54.5	54.5	55.1	54.5	50.2	51.0	44.5	52.3	52.5	52.3	52.8	53.1	53.1
18	15.5	15.7	15.8	15.8[a]	16.1	15.8	15.6	15.6	15.8	15.5	15.6	15.7	16.0	16.1	16.1
19	16.7	16.7[d]	16.5[d]	16.3[a]	16.4[d]	17.0[c]	16.5[b]	16.5[c]	16.2[c]	16.4[a]	16.6[a]	16.6[a]	16.2	16.1	16.1
20	85.2	85.3	73.3	72.9	73.6	73.3	86.4	74.3	73.5	79.3	79.2	78.6	86.0	88.1	88.1
21	27.6	27.5	27.5[e]	26.9	27.7[e]	27.4	23.1	26.3[d]	26.8	27.4	27.6	27.3	28.2	27.6	27.6
22	42.1	42.3	33.8	35.7	31.0	33.8	36.5	39.3	39.5	37.2	37.3	36.0	39.6	30.0	30.0
23	70.8	70.9	26.7[a]	22.8	26.8[a]	26.8[a]	27.3	26.6[a]	26.7[a]	67.0	67.1	78.6	72.9	36.1	36.1
24	91.5	91.5	80.1	126.2	90.9	80.1	81.6	80.0	79.8	80.7	80.9	80.3	109.3	113.0	113.0
25	70.2	70.3	72.8	130.5	73.7	72.8	73.5	72.7	72.8	79.1	79.4	79.5	73.7	73.9	74.0
26	26.5[b]	26.6[e]	25.9[f]	25.8	24.4[f]	25.9[d]	68.9	25.9[d]	25.9[d]	30.3	30.4	30.2	25.3[a]	25.7[a]	25.6[a]
27	29.7[b]	29.7[e]	26.1[f]	17.6	26.6[f]	26.1[d]	21.9	26.1[d]	26.1[d]	24.5	24.6	24.3	25.2[a]	25.1[a]	25.1[a]
28	27.9	28.1	27.9[e]	29.3	28.0[e]	63.7	27.9	27.8	27.8	27.8	27.9	27.8	28.0	28.0	28.0
29	16.7	16.9[d]	16.8[d]	22.4	16.8[d]	13.8	16.6[b]	16.7[c]	16.6[c]	16.8[a]	16.7[a]	16.7[a]	17.0	17.0	16.8
30	18.2	18.2	17.1[d]	16.9	17.0[d]	17.1[c]	16.8[b]	16.8[c]	17.2	17.8	18.0	17.9	18.2	17.6	17.7

Table 2. *continued*

C	1	4	14	29*	15	16	13	17	18	19	20	21	22	23	24
3*O*-sugar															
Glc-1	105.0	105.4	105.0		105.0	104.3	105.0	105.0	105.0	105.3	105.0	104.9	105.0	105.0	104.9
2	78.0[c]	79.8	78.0[g]		78.0[g]	77.9[e]	78.0	77.9[e]	78.0	79.7	78.0	78.6[b]	78.0	78.0[b]	77.9[b]
3	87.3	78.0	87.3		87.3	87.0	87.5	87.4	87.2	78.1[b]	87.4	87.3	87.7	78.3[b]	87.5
4	70.5[d]	72.3[f]	70.7[h]		70.8[h]	70.6[f]	70.4[c]	70.7[f]	70.2[e]	72.0[c]	70.6[b]	70.7[c]	70.5[b]	72.3[c]	70.5[c]
5	77.9[c]	78.0	77.9[g]		77.9[g]	77.8[e]	78.0	78.0[e]	78.0	77.7[b]	78.0	77.9[d]	78.0	77.7[b]	78.0[b]
6	62.5	63.0	62.6		62.6	62.4	62.6	62.6	62.5	62.7	62.6	62.5[c]	62.7	63.0	62.7
Rha-1	102.1	101.7	102.1		102.2	102.2	102.2	102.1	102.2	101.6	103.7	102.1	102.1	101.7	102.1
2	71.9	72.4[f]	72.0[i]		72.0[i]	71.9[g]	72.1[d]	72.0[g]	71.9[f]	72.3[c]	72.6[c]	72.0[f]	72.1[c]	72.5[c]	72.0[d]
3	72.4[c]	72.6[f]	72.4[i]		72.4[i]	72.4[g]	72.6[d]	72.4[g]	72.4[f]	72.4[c]	72.4[c]	72.4[f]	72.6[c]	72.6[c]	72.6[d]
4	73.5[f]	74.2	73.5[j]		73.5[j]	73.5[h]	73.7[c]	73.5[h]	73.5[g]	74.0	73.5	73.5	73.8[d]	74.2	73.5[e]
5	70.2[d]	69.5	70.2[h]		70.2[h]	70.2[f]	70.2[c]	70.1[f]	70.2[e]	69.5	70.4[b]	70.1[c]	70.2[b]	69.6	70.1[c]
6	18.4[g]	18.6	18.4[k]		18.4[k]	18.4[i]	18.4[f]	18.4	18.4[h]	18.5	18.5[d]	18.4[g]	18.4[e]	18.7	18.4[f]
Rha-1	103.6		103.7		103.7	103.6	103.7	103.7	103.7		102.1	103.7	103.7		103.7
2	72.6[c]		72.6[i]		72.6[i]	72.6[g]	72.5[d]	72.5[g]	72.5[f]		72.0[e]	72.6[f]	72.5[c]		72.4[d]
3	72.4[e]		72.4[i]		72.4[i]	72.4[g]	72.4[d]	72.4[g]	73.4[f]		72.4[c]	72.4[f]	72.5[c]		72.4[d]
4	73.7[f]		73.7[j]		73.7[j]	73.6[h]	73.6[e]	73.7[h]	73.7[g]		73.5	73.7	73.6[d]		73.7[e]
5	70.3[d]		70.4[h]		70.4[h]	70.2[f]	70.8[c]	70.4[f]	70.3[e]		70.2[b]	70.3[c]	70.8[b]		70.8[c]
6	18.5[g]		18.6[k]		18.6[k]	18.5[i]	18.6[f]	18.4	18.6[h]		18.4[d]	18.5[g]	18.6[e]		18.5[f]
23- or 24-*O*-sugar															
Glc-1					106.1							106.2			
2					76.0							76.1			
3					78.7							78.7[b]			
4					71.3							71.5			
5					78.0[g]							78.0[d]			
6					62.6							62.6[e]			

*Data taken from ref. [9].

[a–k]Interchangeable assignments.

1705 cm^{-1}. The carbon resonances of the aglycone and sugar moieties could be identified by comparison of the ^{13}C NMR spectra of **18** and **14**, except for the signals due to the carbons around C-12 (Table 2). The carbon signal (δ71.0) corresponding to the C-12 of **14** was lacking in the spectrum of **18** and was replaced by a ketone signal (δ211.9), indicating that **18** was the 12-keto-compound of **14**. The acid hydrolysis of **18** afforded **38** and **39**, the former of which was identified as 20*S*,24*S*-epoxy-3β,25-dihydroxydammaran-12-one converted from **25** by oxidation of the 12-hydroxyl group according to the reported procedure [12]. Thus, the structure of **18** was represented as shown.

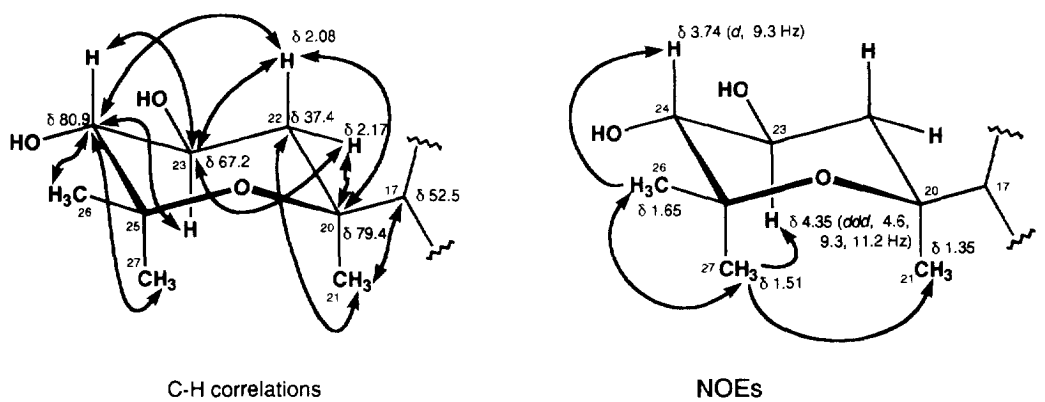
The molecular formula, $C_{48}H_{84}O_{17}$, of glycoside **17** corresponded to the monodeoxy-compound of **14**. Moreover, inspection of the ^{13}C NMR spectrum suggested that **17** was the 12-deoxy-compound of **14**, and resonances of the carbons assigned to the sugar and aglycone moieties appeared at almost the same positions as those of **13** except for the signals due to the side chain. Consequently, the structure of glycoside **17** was determined as shown.

The acid hydrolysis of glycosides **19**, **20** and **21** afforded a new common aglycone named neoalsogenin M (**40**), $C_{30}H_{52}O_5$. The ^{13}C NMR of **40** showed 30 signals (Table 1): eight methylene, eight methine [four of them bearing an oxygen atom (δ67.2, 70.6, 78.1 and 80.9)], six quaternary [two of them bearing an oxygen atom (δ79.2 and 79.4)] and eight methyl carbons. In the HMBC spectrum of **40**, C–H long-range correlations were observed as shown in Scheme 3. Beside, the carbon signals of **40** were observed essentially at the same positions as those of 20 (*S*)-panaxadiol (**41**) [13], exclusive of the signals attributable to the cyclized side chain. From these results, it was assumed that the structure of **40** could be represented as a 20*S*,25-epoxy-3β,12β,23ξ,24ξ-tetrahydroxydammarane. The result of the NOE experiments (Scheme 3) and the coupling patterns of the two carbinyl protons: H-23 (δ4.35, *ddd*, J = 4.6, 9.3, 11.2 Hz) and H-24 (δ3.74, *d*, J = 9.3 Hz), displayed that the chiral centres of C-23 and C-24 had *S*- and *R*-configurations, respectively, and that its cyclized side chain had a chair conformation. These observations led to the formulation of aglycone (**40**) as shown.

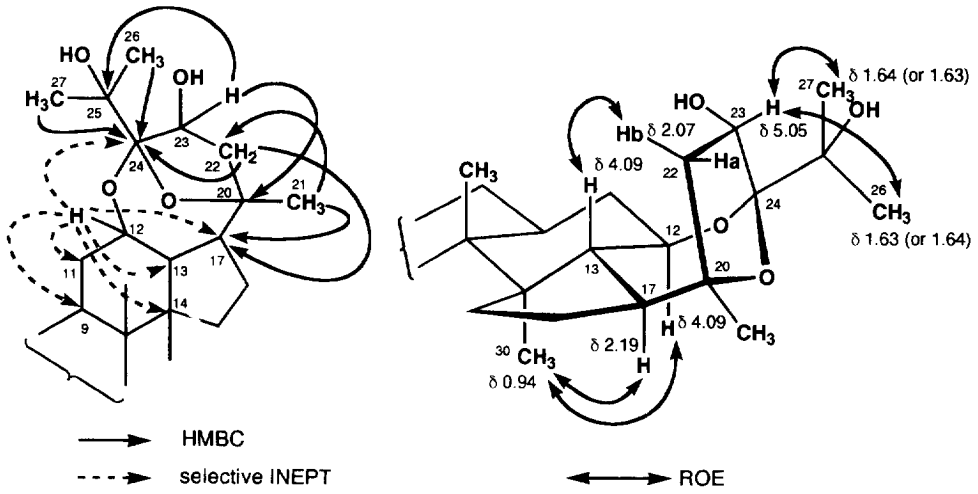
Glycosides **19**, **20** and **21** had the molecular formulae $C_{42}H_{72}O_{14}$, $C_{48}H_{82}O_8$ and $C_{54}H_{91}O_{23}$, respectively. These glycosides liberated D-glucose and L-rhamnose on acid hydrolysis. Comparison of the ^{13}C NMR spectra and their common aglycone (**40**) revealed that glycosides **19** and **20** were both the 3-*O*-glycosides of **40**. The ^{13}C NMR spectra showed that the sugar moieties of glycosides **19** and **20** were identical with those of glycosides **4** and **1**, respectively (Table 2). Accordingly, the structures of **19** and **20** were represented as shown.

The observation of the glycosylation shifts around C-3 and C-23 in the ^{13}C NMR spectrum of **21** disclosed that **21** was a 3- and 23-*O*-bisglycoside of **40**. On enzymatic hydrolysis with crude hesperidinase, glycoside **21** afforded **20** as a partially hydrolysed product. Consequently, the structure of **21** was established as shown.

Glycoside **22** was an unstable compound under acidic or alkaline conditions. The molecular formula, $C_{48}H_{80}O_{18}$, of **22** was less two hydrogens than that of **1**. Acid hydrolysis of **22** yielded D-glucose and L-rhamnose. By comparison of the ^{13}C NMR spectra of **22** and **1**, the carbon resonances of **1** attributable to the A and B-rings, and four methyl groups on these rings as well as the sugar moiety (Table 2) were essentially the same as those of **22**. In addition, the signal at δ91.5 corresponding to C-24 of **1** was lacking in the spectrum of **22** and was replaced by the signal at δ109.3. In the HMBC spectrum of **22**, the C–H long range correlations of the side chain moiety were observed as illustrated in Scheme 4, exhibiting that **22** had an analogous cyclized side chain to that of **1**, except for the presence of the C-24 ketal carbon. The information with respect to the remaining one of two ketal-bonds of C-24 could not be obtained from the above HMBC experiment of **22**. In order to resolve this problem, a selective INEPT experiment, which is a more high-sensitive method, was performed. The irradiation of the carbinyl proton of **22** at δ4.09 (H-12) disclosed the obvious C–H long range correlation between the C-24 and H-12 (Scheme 4). Thus, the ketal structure of **22** was



Scheme 3. HMBC and NOE correlations of cyclized side chain of **40**.



Scheme 4. HMBC, selective INEPT and ROE correlations of **22**.

proposed as shown. The detailed analyses of the H–H COSY and HETCOR spectra of **22** further supported this structure.

The absolute configurations of the C-12, C-17, C-20, C-23 and C-24 of **22** were deduced from the ROE experiment (Scheme 4) and examination of the Dreiding model. The ROEs were observed between (i) H-30 and H-12, (ii) H-30 and H-17, and (iii) H-13 and H-22b to establish the *R*-configuration of C-12 and the *S*-configurations of C-17, C-20 and C-24. Furthermore, the *S*-configuration of C-23 was confirmed by observation of the ROE between H-23 and both H-26 and H-27 of **22** (Scheme 4). On the basis of the evidence, the structure of **22** was characterized as shown.

Glycosides **23**, $C_{42}H_{70}O_{13}$, and **24**, $C_{48}H_{80}O_{17}$, were also unstable compounds under acidic or alkaline conditions. The ^{13}C NMR spectra of **23** and **24** suggested that both compounds had a common aglycone. Comparison of the ^{13}C NMR spectra of **22** and **23** (or **24**) exhibited that the carbinyl carbon signal (δ72.9) due to C-23 of **22** was replaced by the methylene carbon signal (δ36.1) in the spectrum of **23** (or **24**) (Table 2), showing that the aglycone of **23** and **24** was a 23-deoxy-compound of **22**. D-Glucose and L-rhamnose were identified in the acid hydrolysates of both compounds. The signals assigned to the carbons of the sugar moieties and around C-3 of the aglycone of **23** and **24** were in good agreement with those of **4** and **22**, respectively. Based on the results, the structures of **23** and **24** were determined 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 × 42 cm, YMC, Japan). HPLC: D-ODS-10 (YMC).

Acid hydrolysis of glycosides. Each glycoside dissolved in 8% HCl–dioxane was heated at 85° for 1 hr. After dilution with H_2O, the reaction mixt. was extracted with $CHCl_3$. The organic layer was concd, and the residue was purified by HPLC using aq. MeOH to afford corresponding aglycones. Detection and identification of the resulting monosaccharides from the H_2O layer were performed by the reported method [14].

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 sepn. Dried and powdered aerial 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. 3 was purified by CC on silica gel with EtOAc–EtOH–H_2O (30:5:2), and then MPLC on ODS with 65–100% MeOH to give 4 frs. These frs were subjected to HPLC on ODS to afford **9** (yield from dried plants, 0.011%), **12** (0.005%) and **22** (0.007%) from fr. 3–2 with 78% MeOH, and **10** (0.006%), **11** (0.002%), **23** (0.003%) and **24** (0.001%) 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 **7** (0.02%) and **18** (0.003%). Fr. 4–3 yielded **1** (1.24%) and **19** (0.004%) by HPLC on TSK-gel Amide-80 with 82% MeCN. Fr. 4–4 afforded **14** (0.043%) and **20** (0.043%) by HPLC on ODS with 37% 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 **17** (0.001%) from fr. 5–4, **6** (0.011%) and **16** (0.004%) from fr. 5–6 were obtained by HPLC on ODS with 74% and 70% MeOH, respectively. Fr. 5–7 was further sepd into 3 frs by MPLC on ODS using 60% MeOH. These frs were purified by HPLC on ODS to give **21** (0.001%) from fr. 5–7–2 with 69% MeOH and **15** (0.004%) from fr. 5–7–3 with 70% MeOH. The isolation of **2**–**5**, **8**, **13** and cucurbitane compounds was described in our preceding paper [1].

Neoalsoside II (**14**). Powder, $[\alpha]_D^{19}$ − 19.3° (MeOH; *c* 1.26). FABMS (negative) *m/z*: 947.5577 $[M-H]^-$ ($C_{48}H_{83}O_{18}$ requires: *m/z* 947.5578). ^{1}H NMR (pyridine-d_5): δ0.80, 0.95, 0.96, 1.15, 1.22, 1.47, 1.51 and 1.54 (each 3H, *s*, Me), 3.34 (1H, *dd*, *J* = 4.0, 11.7 Hz, H-3), 3.88 (1H, *m*, H-12), 2.08 (1H, *dd*, *J* = 10.4, 10.6 Hz, H-13), 2.40 (1H, *m*, H-17), 3.81 (1H, *d*, *J* = 9.9 Hz, H-24), 4.85 (1H, *d*, *J* = 7.5 Hz, H-1 of Glc), 5.97 (1H, *br s*, H-1 of Rha), 5.74 (1H, *br s*, H-1 of Rha'), 1.68 (3H, *d*, *J* = 6.1 Hz, H-6 of Rha), 1.63 (3H, *d*, *J* = 6.2 Hz, H-6 of Rha'). ^{13}C NMR: see Table 2.

Compound **25**. Powder, $[\alpha]_D^{17}$ + 10.0° ($CHCl_3$; *c* 0.70). FABMS (negative) *m/z*: 475.3792 $[M-H]^-$ ($C_{30}H_{51}O_4$ requires: *m/z* 475.3788). ^{1}H NMR ($CDCl_3$): δ1.00 (1H, *ddd*, *J* = 4.6, 13.2, 13.2 Hz, H-1a), 1.73 (1H, *m*, H-1b), 1.62 (2H, *m*, H-2), 3.18 (1H, *dd*, *J* = 5.0, 11.4 Hz, H-3), 0.73 (1H, *dd*, *J* = 2.5, 11.1 Hz, H-5), 1.46 (1H, *m*, H-6a), 1.55 (1H, *m*, H-6b), 1.29 (1H, *m*, H-7a), 1.43 (1H, *m*, H-7b), 1.46 (1H, *dd*, *J* = 2.7, 10.3 Hz, H-9), 1.15 (1H, *ddd*, *J* = 2.7, 10.3, 10.4 Hz, H-11a), 1.92 (1H, *m*, H-11b), 3.51 (1H, *ddd*, *J* = 4.7, 10.4, 10.4 Hz, H-12), 1.68 (1H, *dd*, *J* = 10.0, 10.4 Hz, H-13), 1.08 (1H, *m*, H-15a), 1.51 (1H, *m*, H-15a), 1.28 (1H, *m*, H-16a), 1.95 (1H, *m*, H-16b), 2.24 (1H, *ddd*, *J* = 4.7, 10.0, 10.8 Hz, H-17), 1.00 (3H, *s*, H-18), 0.88 (3H, *s*, H-19), 1.26 (3H, *s*, H-21), 1.73 (1H, *ddd*, *J* = 7.1, 11.2, 11.2 Hz, H-22a), 1.93 (1H, *m*, H-22b), 1.84 (1H, *ddd*, *J* = 5.4, 11.2, 11.2 Hz, H-23a), 2.05 (1H, *m*, H-23b), 3.87 (1H, *dd*, *J* = 5.4, 10.8 Hz, H-24), 1.09 (3H, *s*, H-26), 1.22 (3H, *s*, H-27), 0.97 (3H, *s*, H-28), 0.77 (3H, *s*, H-29), 0.90 (3H, *s*, H-30). ^{13}C NMR: see Table 1.

Compound **26**. Powder, $[\alpha]_D^{22}$ + 13.3° ($CHCl_3$; *c* 0.45). FABMS (negative) *m/z* 475.3772 $[M-H]^-$ ($C_{30}H_{51}O_4$ requires: *m/z* 475.3788). ^{1}H NMR ($CDCl_3$): δ0.99 (1H, *m*, H-1a), 1.76 (1H, *m*, H-1b), 1.63 (2H, *m*, H-2), 3.20 (1H, *dd*, *J* = 5.2, 11.3 Hz, H-3), 0.74 (1H, *br d*, *J* = 11.0 Hz, H-5), 1.52 (1H, *m*, H-6a), 1.60 (1H, *m*, H-6b), 1.28 (1H, *m*, H-7a), 1.54 (1H, *m*, H-7b), 1.42 (1H, *dd*, *J* = 3.0, 13.8 Hz, H-9), 1.22 (1H, *m*, H-11a), 1.88 (1H, *m*, H-11b), 3.57 (1H, *ddd*, *J* = 5.2, 10.4, 10.5 Hz, H-12), 1.72 (1H, *dd*, *J* = 10.5, 10.5 Hz, H-13), 1.06 (1H. *ddd*, *J* = 1.7, 8.8, 12.0 Hz, H-15a), 1.58 (1H, *m*, H-15b), 1.26 (1H, *m*, H-16a), 1.91 (1H, *m*, H-16b), 2.03 (1H, *ddd*, *J* = 6.3, 10.5, 10.7 Hz, H-17), 100 (3H, *s*, H-18), 0.89 (3H, *s*, H-19), 1.20 (3H, *s*, H-21), 1.75 (2H, *m*, H-22), 1.94 (2H, *m*, H-23), 3.89 (1H, *dd*, *J* = 7.3, 7.3 Hz, H-24), 1.14 (3H, *s*, H-26), 1.24 (3H, *s*, H-27), 0.98 (3H, *s*, H-28), 0.78 (3H, *s*, H-29), 0.90 (3H, *s*, H-30). ^{13}C NMR: see Table 1.

Oxidation of **27** *with* m-*chloroperbenzoic acid* [3, 4]. A soln of **27** (60 mg) and *m*-chloroperbenzoic acid (60 mg) in $CHCl_3$ was allowed to stand for 3 hr at 0°. After work-up as usual, the crude product was purified by CC on silica gel with $CHCl_3$–Me_2CO (3:1) to give **26** and **28** (25 mg and 18 mg).

Compound **28**. Powder, $[\alpha]_D^{22}$ + 19.4° ($CHCl_3$; *c* 1.24). FABMS (negative) *m/z*: 475.3787 $[M-H]^-$ ($C_{30}H_{53}O_5$ requires: *m/z* 475.3788). ^{1}H NMR (pyridine-d_5): δ0.77, 0.87, 0.88. 0.96, 0.99, 1.10, 1.18, 1.22 (each 3H, *s*, Me), 3.18 (1H, *br d*, *J* = 9.3 Hz, H-3), 3.54 (1H, *ddd*, *J* = 5.1, 10.4, 10.4 Hz, H-12), 1.70 (1H, *dd*, *J* = 10.4, 10.4 Hz, H-13), 2.04 (1H, *ddd*, *J* = 6.0, 10.4, 10.8 Hz, H-17), 3.85 (1H, *dd*, *J* = 5.3, 9.9 Hz, H-24). ^{13}C NMR: see Table 1.

Oxidation of **29** *with* OsO_4. A soln of **29** (315 mg) and OsO_4 (200 mg) in dry pyridine (3 ml) was left at room temp. for 2 days. The reaction mixt. was diluted with MeOH, and then was allowed to stand for 1 hr under a stream of H_2S. The resulting ppt was filtered off, and the filtrate was concd. The residue was purified by CC on silica gel with $CHCl_3$–MeOH (17:1) followed by HPLC on ODS with 77% MeOH to give **30** (89 mg) and **31** (79 mg).

Compound **30**. Powder $[\alpha]_D^{25}$ + 1.0° (MeOH; *c* 1.03). FABMS (negative) *m/z*: 475.3963 $[M-H]^-$ ($C_{30}H_{53}O_5$ requires: *m/z* 477.3944). ^{1}H NMR (pyridine-d_5): δ0.77, 0.88, 0.88, 0.98, 1.18, 1.42, 1.48, 1.51 (each 3H, *s*, Me), 3.57 (1H, *br s*, H-3), 3.81 (1H, *m*, H-12), 2.06 (1H, *dd*, *J* = 10.4, 10.5 Hz, H-13), 2.29 (1H, *ddd*, *J* = 7.1, 10.3, 10.5 Hz, H-17), 3.83 (1H, *br d*, *J* = 7.2 Hz, H-24). ^{13}C NMR: see Table 1.

Compound **31**. Powder, $[\alpha]_D^{25}$ + 28.2° (MeOH; *c* 1.56). FABMS (negative) *m/z*: 477.3950 $[M-H]^-$ ($C_{30}H_{53}O_5$ requires: *m/z* 477.3944). ^{1}H NMR (pyridine-d_5): δ0.76, 0.88, 0.89, 0.98, 1.18, 1.42, 1.45, 1.49 (each 3H, *s*, Me), 3.57 (1H, *br s*, H-3), 3.81 (1H, *m*, H-12), 2.10 (1H, *dd*, *J* = 10.3, 10.6 Hz, H-13), 2.30 (1H, *m*, H-17), 3.85 (1H, *br d*, *J* = 7.0 Hz, H-24). ^{13}C NMR: see Table 1.

Selective acetylation of **30** *and* **31**. Compounds **30** and **31** were converted to their 3,12-diacetyl derivatives, because both were insoluble in CCl_4 for measurement of the CD spectra. To a soln of **30** (38 mg) in dry Me_2CO was added anhydrous $CuSO_4$ (100 mg), and the mixt. was refluxed for 4 hr. After cooling the reaction mixt. was filtered, and the filtrate was evapd to dryness. The residue (40 mg) was acetylated with Ac_2O and pyridine followed by the usual work-up to give 3,12-diacetyl-24,25-isopropylidene derivative of **30** (40 mg). A soln of this compound in 2N HCl (1 ml) and MeOH (10 ml) was refluxed for 6 hr. After cooling, the reaction mixt. was neutralized with Ag_2CO_3, and the solids were filtered off. The filtrate was concd, and the residue was purified by CC on silica gel with $CHCl_3$–Me_2CO (3:1) to give the 3,12-diacetyl compound of **30** (8 mg) (**30**-Ac).

Compound **30**-*Ac*. Powder, $[\alpha]_D^{26}$ − 18.4° ($CHCl_3$; *c* 0.76). CD: $\Delta\varepsilon_{312}$ − 2.1 [CCl_4; 1.0×10^{-4} M of Eu (fod)$_3$, 1.4×10^{-3} M of sample]. ^{1}H NMR ($CDCl_3$): δ0.84, 0.89, 0.89, 1.00, 1.03, 1.17, 1.19, 1.23 (each 3H, *s*, Me), 4.63 (1H, *dd*, *J* = 2.8, 2.8 Hz, H-3), 4.74 (1H, *ddd*, *J* = 4.9, 10.4, 10.7 Hz, H-12), 3.35 (1H, *dd*, *J* = 1.7, 9.6 Hz, H-24), 2.07 (3H, *s*, OAc), 2.10 (3H, *s*, OAc). Compound **31** (40 mg) was also converted to its 3,12-diacetyl derivative (**31**-Ac, 7 mg) by the same procedure.

Compound **31**-*Ac*. Powder, $[\alpha]_D^{22}$ − 5.4° ($CHCl_3$; *c* 0.56). CD: $\Delta\varepsilon_{318}$ + 0.8 [CCl_4, 1.0×10^{-4} M of Eu (fod)$_3$, 1.4×10^{-3}M of sample]. ^{1}H NMR ($CDCl_3$): δ0.84, 0.88, 0.88, 1.00, 1.02, 1.14, 1.19, 1.25 (each 3H, *s*, Me), 4.62 (1H, *dd*, *J* = 2.8, 2.9 Hz, H-3), 4.75 (1H, *ddd*, *J* = 5.0, 10.4, 10.8 Hz, H-12), 3.44 (1H, *dd*, *J* = 2.0, 10.4 Hz, H-24), 2.05 (3H, *s*, OAc), 2.09 (3H, *s*, OAc).

Acid treatment of **30** *and* **31**. Compounds **30** and **31** were treated with acid under the same conditions as the acid hydrolysis of glycosides (see General procedure), and the crude products were purified by HPLC on ODS with aq. MeOH to give **32** and **33** from **30**, and **33** and **34** from **31**.

Compound **32**, powder, $[\alpha]_D^{20}$ − 11.2° ($CHCl_3$; *c* 1.16). FABMS (negative) *m/z*: 475.3790 $[M-H]^-$ ($C_{30}H_{51}O_4$ requires: *m/z* 475.3788). ^1H NMR ($CDCl_3$): δ0.85, 0.90, 0.94, 1.02, 1.10, 1.24, 1.26, 1.27 (each 3H, *s*, Me), 3.39 (1H, *br s*, H-3), 3.54 (1H, *ddd*, *J* = 4.6, 10.3, 10.3 Hz, H-12), 1.68 (1H, *dd*, *J* = 10.1, 10.3 Hz, H-13), 2.25 (1H, *ddd*, *J* = 4.6, 10.1, 10.6 Hz. H-17), 3.88 (1H, *dd*, *J* = 5.3, 10.6 Hz, H-24). ^{13}C NMR: see Table 1.

Compound **33** (12 mg), powder, $[\alpha]_D^{20}$ − 15.0° ($CHCl_3$; *c* 0.40). FABMS (negative) *m/z*: 475.3775 $[M-H]^-$ ($C_{30}H_{51}O_4$ requires: *m/z* 475.3788). ^1H NMR ($CDCl_3$): δ1.30 (1H, *ddd*, *J* = 3.4, 13.5, 13.5 Hz, H-1a), 1.49 (1H, *m*, H-1b), 1.56 (1H, *m*, H-2a), 1.95 (1H, *m*, H-2b), 3.39 (1H, *dd*, *J* = 2.9, 2.9 Hz, H-3), 1.26 (1H, *m*, H-5), 1.43 (2H, *m*, H-6), 1.25 (1H, *m*, H-7a), 1.58 (1H, *m*, H-7b), 1.53 (1H, *m*, H-9), 1.20 (1H, *m*, H-11a), 1.92 (1H, *m*, H-11b), 3.56 (1H, *ddd*, *J* = 5.1, 10.4, 10.4 Hz, H-12), 1.71 (1H, *dd*, *J* = 10.4, 10.5 Hz, H-13), 1.04 (1H, *ddd*, *J* = 1.7, 8.6, 12.1 Hz, H-15a), 1.52 (1H, *m*, H-15b), 1.22 (1H, *m*, H-16a), 1.86 (1H, *m*, H-16b), 2.02 (1H, *ddd*, *J* = 6.3, 10.5, 10.6 Hz, H-17), 0.99 (3H, *s*, H-18), 0.89 (3H, *s*, H-19), 1.19 (3H, *s*, H-21), 1.71 (2H, *m*, H-22), 1.89 (2H, *m*, H-23), 3.87 (1H, *dd*, *J* = 7.3, 7.3 Hz, H-24), 1.26 (3H, *s*, H-26), 1.23 (3H, *s*, H-27), 0.94 (3H, *s*, H-28), 0.84 (3H, *s*, H-29), 0.90 (3H, *s*, H-30). ^{13}C NMR: see Table 1.

Compound **34**. Powder, $[\alpha]_D^{20}$ + 2.0° ($CHCl_3$, *c* 0.49). FABMS (negative) *m/z*: 475.3785 $[M-H]^-$ ($C_{30}H_{51}O_4$, requires 475.3788). ^1H NMR ($CDCl_3$): δ1.30 (1H. *m*, H-1a), 1.44 (1H, *m*, H-1b), 1.56 (1H, *m*, H-2a), 1.92 (1H, *m*, H-2b), 3.40 (1H, *dd*, *J* = 2.7, 2.7 Hz, H-3), 1.23 (1H, *m*, H-5), 1.26 (1H, *m*, H-6a), 1.42 (1H, *m*, H-6b), 1.27 (1H, *m*, H-7a), 1.49 (1H, *m*, H-7b), 1.57 (1H, *m*, H-9), 1.08 (1H, *m*, H-11a), 1.95 (1H, *m*, H-11b), 3.52 (1H, *ddd*, *J* = 4.6, 10.5, 10.5 Hz, H-12), 1.67 (1H, *dd*, *J* = 9.8, 10.2 Hz, H-13), 1.13 (1H, *m*, H-15a), 1.54 (1H, *m*, H-15b), 1.29 (1H, *m*, H-16a), 1.98 (1H, *m*, H-16b), 2.19 (1H, *ddd*, *J* = 3.9, 9.0, 11.0 Hz, H-17), 0.98 (3H, *s*, H-18), 0.87 (3H, *s*, H-19), 1.26 (3H, *s*, H-21), 1.66 (1H, *m*, H-22a), 1.86 (1H, *m*, H-22b), 1.87 (1H, *m*, H-23a), 2.04 (1H, *m*, H-23b), 3.84 (1H, *dd*, *J* = 6.6, 8.8 Hz, H-24), 1.10 (3H, *s*, H-26), 1.28 (3H, *s*, H-27), 0.94 (3H, *s*, H-28), 0.84 (3H, *s*, H-29), 0.92 (3H, *s*, H-30). ^{13}C NMR: see Table 1.

Compound **35**. Powder $[\alpha]_D^{20}$ + 7.0° ($CHCl_3$; *c* 0.43). FABMS (negative) *m/z*: 475.3783 $[M-H]^-$ ($C_{30}H_{51}O_4$ requires: *m/z* 475.3788). ^1H NMR ($CDCl_3$): δ1.29 (1H, *m*, H-1a), 1.45 (1H, *m*, H-1b), 1.55 (1H, *m*, H-2a), 1.96 (1H, *m*, H-2b), 3.40 (1H, *dd*, *J* = 2.7, 2.7 Hz, H-3), 1.25 (1H, *m*, H-5), 1.44 (2H, *m*, H-6), 1.27 (1H, *m*, H-7a), 1.54 (1H, *m*, H-7b), 1.58 (1H, *m*, H-9), 1.21 (1H, *m*, H-11a), 1.92 (1H, *m*, H-11b), 3.56 (1H, *ddd*, *J* = 5.1, 10.5, 10.5 Hz, H-12), 1.71 (1H, *dd*, *J* = 10.5, 10.5 Hz, H-13), 1.06 (1H, *ddd*, *J* = 1.5, 8.5, 12.0 Hz, H-15a), 1.50 (1H, *m*, H-15b), 1.21 (1H, *m*, H-16a), 1.92 (1H, *m*, H-16b), 2.06 (1H, *ddd*, *J* = 5.9, 10.5, 10.7 Hz, H-17), 1.00 (3H, *s*, H-18), 0.90 (3H, *s*, H-19), 1.20 (3H, *s*, H-21), 1.80 (1H, *m*, H-22a), 1.82 (1H, *m*, H-22b), 1.86 (1H, *m*, H-23a), 1.98 (1H, *m*, H-23b), 3.86 (1H, *dd*, *J* = 5.4, 10.0 Hz, H-24), 1.16 (3H, *s*, H-26), 1.23 (3H, *s*, H-27), 0.94 (3H, *s*, H-28), 0.84 (3H, *s*, H-29), 0.91 (3H, *s*, H-30). ^{13}C NMR: see Table 1.

Neoalsoside I2 (**15**). Powder, $[\alpha]_D^{16}$ − 17.7° (MeOH; *c* 0.57). FABMS (negative) *m/z*: 1109.6120 $[M-H]^-$ ($C_{54}H_{93}O_{23}$ requires: *m/z* 1109.6106). ^1H NMR (pyridine-d_5): δ0.84, 0.97, 1.12, 1.15, 1.23, 1.45, 1.48 and 1.50 (each 3H, *s*, Me), 3.34 (1H, *dd*, *J* = 4.4, 11.5 Hz, H-3), 3.89 (1H, *ddd*, *J* = 5.3, 10.0, 10.5, H-12), 2.11 (1H, *dd*, *J* = 10.5, 10.5 Hz, H-13), 2.37 (1H, *ddd*, *J* = 7.9, 10.5, 10.5 Hz, H-17). 3.90 (1H, *d*, *J* = 10.0 Hz, H-24), 4.85 (1H, *d*, *J* = 7.5 Hz, H-1 of Glc), 5.98 (1H, *br s*, H-1 of Rha), 5.75 (1H, *br s*, H-1 of Rha'), 5.22 (1H, *d*, *J* = 7.9 Hz, H-1 of Glc'), 1.67 (3H, *d*, *J* = 6.0 Hz, H-6 of Rha), 1.64 (3H, *d*, *J* = 6.1 Hz, H-6 of Rha'). ^{13}C NMR: see Table 2.

Enzymatic hydrolysis of **15**. A soln of **15** (50 mg) and crude hesperidinase (5 mg) in H_2O was incubated for 24 hr at 37°. The reaction mixt. was extracted with *n*-BuOH, and the BuOH layer was evapd to dryness. The residue was purified by HPLC on ODS with 73% MeOH to give an amorphous powder (25 mg) which was identified as **14**.

Neoalsoside J1 (**16**). Powder, $[\alpha]_D^{16}$ − 13.0° (MeOH; *c* 1.08). FABMS (negative) *m/z*: 963.5522 $[M-H]^-$ ($C_{48}H_{83}O_{19}$ requires: *m/z* 963.5527). ^1H NMR (pyridine-d_5): δ0.89, 0.98, 1.11, 1.46, 1.52, 1.52 and 1.55 (each 3H, *s*, Me), 4.07 (1H, *m*, H-3), 3.88 (1H, *m*, H-12), 2.09 (1H, *dd*, *J* = 10.3, 10.4 Hz, H-13), 2.35 (1H, *m*, H-17), 3.82 (1H, *d*, *J* = 10.1 Hz, H-24), 4.32 (2H, *m*, H-28), 5.10 (1H, *d*, *J* = 7.5 Hz, H-1 of Glc), 6.07 (1H, *br s*, H-1 of Rha), 5.76 (1H, *br s*, H-1 of Rha'), 1.69 (3H, *d*, *J* = 6.1 Hz, H-6 of Rha), 1.64 (3H, *d*, *J* = 6.2 Hz, H-6 of Rha'). ^{13}C NMR: see Table 2.

Compound **36**. Powder, FABMS (negative) *m/z*: 491.3736 $[M-H]^-$ ($C_{30}H_{51}O_5$ requires: *m/z* 491.3737). ^1H NMR ($CDCl_3$): δ0.88, 0.89, 0.93, 1.00, 1.13, 1.19 and 1.24 (each 3H, *s*, Me), 3.63 (1H, *dd*, virtual coupling, H-3), 3.56 (1H, *ddd*, *J* = 5.3, 10.7, 10.7 Hz, H-12), 1.69 (1H, *dd*, *J* = 10.3, 10.7 Hz, H-13), 2.02 (1H, *m*, H-17), 3.89 (1H, *dd*, *J* = 7.3, 7.3 Hz, H-24), 3.42 (1H, *d*, *J* = 9.9 Hz, H-28a), 3.72 (1H, *d*, *J* = 9.9 Hz, H-28b). ^{13}C NMR: see Table 1.

Compound **37**. Powder, FABMS (negative) *m/z*: 491.3715 $[M-H]^-$ ($C_{30}H_{51}O_5$ requires: *m/z* 491.3737). ^1H NMR ($CDCl_3$) δ0.88, 0.91, 0.93, 1.01, 1.10, 1.23 and 1.27 (each 3H, *s*, Me), 3.64 (1H, *dd*, virtual coupling, H-3), 3.52 (1H, *ddd*, *J* = 4.8, 10.1, 10.3 Hz, H-12), 1.68 (1H, *dd*, *J* = 9.9, 10.1 Hz, H-13), 2.25 (1H, *ddd*, *J* = 4.8, 9.9, 10.8 Hz, H-17), 3.88 (1H, *dd*, *J* = 5.5, 11.0 Hz, H-24), 3.42 (1H, *d*, *J* = 10.3 Hz, H-28a), 3.72 (1H, *d*, *J* = 10.3 Hz, H-28b).

Neoalsoside K1 (**17**). Powder, $[\alpha]_D^{27}$ − 18.7° (MeOH; *c* 0.75). FABMS (negative) *m/z*: 931.5667 $[M-H]^-$ ($C_{48}H_{83}O_{17}$ requires: *m/z* 931.5629). ^1H NMR (pyridine-d_5): δ0.77, 0.94, 0.96, 1.16, 1.22, 1.47, 1.53 and 1.56 (each 3H, *s*, Me), 3.35 (1H, *dd*, *J* = 4.0, 11.7 Hz, H-3), 3.82 (1H, *d*, *J* = 9.2 Hz, 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'), 1.69 (3H, *d*, *J* = 6.0 Hz, H-6 of Rha), 1.65 (3H, *d*, *J* = 6.0 Hz, H-6 of Rha'). ^{13}C NMR: see Table 2.

Neoalsoside L1 (**18**). Powder, $[\alpha]_D^{16}$ − 11.4° (MeOH; *c* 1.13). IR (nujor) cm^{-1}: 1705 (CO). FABMS (negative) *m/z*: 945.5471 $[M-H]^-$ ($C_{48}H_{81}O_{18}$ requires: *m/z* 945.5422). ^1H NMR (pyridine-d_5): δ0.77, 0.86, 1.12, 1.13, 1.20, 1.46, 1.50 and 1.53 (each 3H, *s*, Me), 3.29 (1H, *dd*, *J* = 4.0, 11.5 Hz, H-3), 3.36 (1H, *d*, *J* = 9.7 Hz, H-13), 2.77 (1H, *m*, H-17), 3.78 (1H, *d*, *J* = 10.3 Hz. H-24), 4.83 (1H, *d*, *J* = 7.5 Hz, H-1 of Glc), 5.95 (1H, *br s*, H-1 of

Rha), 5.73 (1H, *br s*, H-1 of Rha'), 1.67 (3H, *d*, $J = 6.1$ Hz, H-6 of Rha), 1.64 (3H, *d*, $J = 6.2$ Hz, H-6 of Rha'). ^{13}C NMR: see Table 2.

Compound **38**. Powder, $[\delta]_D^{19}$ + 36.2° ($CHCl_3$; *c* 0.94). FABMS (negative) *m/z*: 473.3646 $[M - H]^-$ ($C_{30}H_{49}O_4$ requires: *m/z* 473.3631). ^{1}H NMR ($CDCl_3$): δ0.98 (1H, *m*, H-1a), 1.57 (1H, *m*, H-1b), 1.61 (2H, *m*, H-2), 3.17 (1H, *dd*, $J = 4.6, 11.2$ Hz, H-3), 0.76 (1H, *m*, H-5), 1.41 (1H, *m*, H-6a), 1.64 (1H, *m*, H-6b), 1.26 (1H, *m*, H-7a), 1.41 (1H, *m*, H-7b), 1.68 (1H, *m*, H-9), 2.19 (2H, *m*, H-11), 2.94 (1H, *d*, $J = 9.5$ Hz, H-13), 1.16 (1H, *m*, H-15a), 1.73 (1H, *m*, H-15b), 1.63 (1H, *m*, H-16a), 1.80 (1H, *m*, H-16b), 2.51 (1H, *ddd*, $J = 4.4, 9.5, 9.8$ Hz, H-17), 1.18 (3H, *s*, H-18), 0.91 (3H, *s*, H-19), 1.01 (3H, *s*, H-21), 1.65 (1H, *m*, H-22a), 1.91 (1H, *ddd*, $J = 7.6, 10.7, 11.0$ Hz, H-22b), 1.85 (1H, *m*, H-23a), 1.70 (1H, *m*, H-23b), 3.68 (1H, *dd*, $J = 5.6, 10.0$ Hz, H-24), 1.09 (3H, *s*, H-26), 1.16 (3H, *s*, H-27), 0.96 (3H, *s*, H-28), 0.78 (3H, *s*, H-29), 0.73 (3H, *s*, H-30), ^{13}C NMR: see Table 1. Compound **38** was prepd from **25** by the reported procedure [12] as follows. Compound **25** (33 mg) was acetylated with Ac_2O and pyridine at 5° overnight to give 3-*O*-monoacetate (31 mg). A soln of the acetate in pyridine and CrO_3 (100 mg) was left for 50 hr at room temp. After work-up as usual to yield 12-keto compound (22 mg) followed by deacetylation with 5% methanolic NaOH to give **38** (15 mg).

Compound **39**. Powder, FABMS (negative) *m/z*: 473.3630 $[M - H]^-$ ($C_{30}H_{49}O_4$ requires: *m/z* 473.3631). ^{1}H NMR ($CDCl_3$): δ0.76 (3H, *s*, H-30), 0.80 (3H, *s*, H-29), 0.93 (3H, *s*, H-19), 0.98 (3H, *s*, H-28), 1.07 (3H *s*, H-21), 1.14 (3H, *s*, H-26), 1.17 (3H, *s*, H-27), 1.21 (3H, *s*, H-18), 3.19 (1H, *dd*, $J = 4.9, 11.1$ Hz, H-3), 2.23 (2H, *br d*, $J = 8.6$ Hz, H-11). 2.97 (1H, *d*, $J = 9.7$ Hz, H-13), 2.53 (1H, *ddd*, $J = 4.8, 9.7, 10.9$ Hz, H-17), 3.71 (1H, *dd*, $J = 5.5, 9.5$ Hz, H-24).

Neoalsoside M1 (**19**). Powder, $[\alpha]_D^{15}$ 0° (MeOH; *c* 1.13). FABMS (negative) *m/z*: 799.4828 $[M - H]^-$ ($C_{42}H_{71}O_{14}$ requires: *m/z* 799.4842). ^{1}H NMR (pyridine-d_5): δ0.76, 0.82, 0.91, 1.14, 1.21, 1.41, 1.57 and 1.71 (each 3H, *s*, Me), 3.31 (1H, *dd*, $J = 4.0, 11.5$ Hz, H-3), 3.73 (1H, *m*, H-12), 1.92 (1H, *dd*, $J = 9.9, 10.1$ Hz, H-13), 2.16 (1H, *m*, H-17), 4.42 (1H, *m*, H-23), 3.80 (1H, *d*, $J = 9.4$ Hz, H-24), 4.92 (1H, *d*, $J = 7.0$ Hz, H-1 of Glc), 6.52 (1H, *br s*, H-1 of Rha), 1.68 (3H, *d*, $J = 6.0$ Hz, H-6 of Rha). ^{13}C NMR: see Table 2.

Neoalsoside M2 (**20**). Powder, $[\alpha]_D^{19}$ − 6.7° (MeOH; *c* 1.39). FABMS (negative) *m/z*: 945.5424 $[M - H]^-$ ($C_{48}H_{81}O_{18}$ requires: *m/z* 945.5423). ^{1}H NMR (pyridine-d_5): δ0.76, 0.82, 0.91, 1.10, 1.17, 1.42, 1.57 and 1.71 (each 3H, *s*, Me), 3.29 (1H, *dd*, $J = 4.0, 11.5$ Hz, H-3), 3.73 (1H, *ddd*, $J = 4.8, 10.1, 10.8$ Hz, H-12), 1.92 (1H, *dd*, $J = 10.1, 10.1$ Hz, H-13), 2.16 (1H, *m*, H-17), 4.42 (1H, *m*, H-23), 3.80 (1H, *d*, $J = 9.5$ Hz, H-24), 4.81 (1H, *d*, $J = 7.5$ Hz, H-1 of Glc), 5.93 (1H, *br s*, H-1 of Rha), 5.71 (1H, *br s*, H-1 of Rha'), 1.64 (3H, *d*, $J = 6.2$ Hz, H-6 of Rha), 1.61 (1H, *d*, $J = 6.1$ Hz, H-6 of Rha'). ^{13}C NMR: see Table 2.

Neoalsoside M3 (**21**). Powder, $[\alpha]_D^{27}$ − 4.1° (MeOH; *c* 0.69). FABMS (negative) *m/z*: 1107.5900 $[M - H]^-$ ($C_{54}H_{91}O_{23}$ requires: *m/z* 1107.5949). ^{1}H NMR (pyridine-d_5): δ0.85, 0.91, 1.16, 1.22, 1.36 1.58 and 1.69 (each 3H, *s*, Me), 3.35 (1H, *dd*, $J = 4.0, 11.5$ Hz, H-3), 3.74 (1H, *m*, H-12), 1.88 (1H, *dd*, $J = 10.8, 10.8$ Hz, H-13), 2.17 (1H, *m*, H-17), 4.54 (1H, *m*, H-23), 3.93 (1H, *d*, $J = 9.3$ Hz, H-24), 4.86 (1H, *d*, $J = 7.7$ Hz, H-1 of Glc), 5.51 (1H, *d*, $J = 7.9$ Hz, H-1 of Glc), 6.00 (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*, $J = 6.1$ Hz, H-6 of Rha'). ^{13}C NMR: see Table 2.

Aglycone (**40**) *of* **19**–**21**. Needles (from MeOH), mp 278–281° (decomp.), $[\alpha]_D^{22}$ + 45.0° (pyridine; *c* 1.29). FABMS (negative) *m/z*: 491.3712 $[M - H]^-$ ($C_{30}H_{51}O_5$ requires: *m/z* 491.3730). ^{1}H NMR (pyridine-d_5): δ0.87 (1H, *m*, H-1a), 1.59 (1H, *ddd*, $J = 3.4, 3.6, 9.5$ Hz, H-1b), 1.73 (1H, *m*, H-2a), 1.77 (1H, *m*, H-2b), 3.34 (1H, *dd*, $J = 5.7, 10.6$ Hz, H-3), 0.73 (1H, *dd*, $J = 2.5, 9.4$ Hz, H-5), 1.30 (1H, *m*, H-6a), 1.47 (1H, *m*, H-6b), 1.13 (1H, *ddd*, $J = 2.2, 2.2, 9.8$ Hz, H-7a), 1.35 (1H, *m*, H-7b), 1.41 (1H, *dd*, $J = 2.9, 13.4$ Hz, H-9), 1.30 (1H, *ddd*, $J = 10.1, 12.4, 13.4$ Hz, H-11a), 2.00 (1H, *ddd*, $J = 2.9, 4.9, 12.4$ Hz, H-11b), 3.68 (1H, *ddd*, $J = 4.9, 10.1, 10.1$ Hz, H-12), 1.88 (1H, *dd*, $J = 10.1, 10.3$ Hz, H-13), 0.87 (1H, *m*, H-15a), 1.35 (1H, *m*, H-15b), 1.33 (1H, *m*, H-16a), 1.77 (1H, *m*, H-16b), 2.15 (1H, *ddd*, $J = 5.6, 10.3, 10.4$ Hz, H-17), 0.80 (3H, *s*, H-18), 0.78 (3H, *s*, H-19), 1.35 (3H, *s*, H-21), 2.08 (1H, *dd*, $J = 11.2, 12.6$ Hz, H-22a), 2.17 (1H, *dd*, $J = 4.6, 12.6$ Hz, H-22b), 4.35 (1H, *ddd*, $J = 4.6, 9.3, 11.2$ Hz, H-23), 3.74 (1H, *d*, $J = 9.3$ Hz, H-24), 1.65 (3H, *s*, H-26), 1.51 (3H, *s*, H-27), 1.13 (3H, *s*, H-28), 0.93 (3H, *s*, H-29), 0.83 (3H, *s*, H-30). ^{13}C NMR: see Table 1.

Neoalsoside N1 (**22**). Powder, $[\alpha]_D^{22}$ − 24.2° (pyridine; *c* 1.53). FABMS (negative) *m/z*: 943.5271 $[M - H]^-$ ($C_{48}H_{79}O_{18}$ requires: *m/z* 943.5265). ^{1}H NMR (pyridine-d_5): δ0.79 (1H, *ddd*, $J = 3.4, 12.4, 13.5$ Hz, H-1a), 1.39 (1H, *m*, H-1b), 1.77 (1H, *m*, H-2a), 2.18 (1H, *m*, H-2b), 3.32 (1H, *dd*, $J = 4.1, 11.7$ Hz, H-3), 0.70 (1H, *br d*, $J = 11.7$ Hz, H-5), 1.38 (1H, *m*, H-6a), 1.49 (1H, *m*, H-6b), 1.17 (1H, *m*, H-7a), 1.54 (1H, *m*, H-7b), 1.34 (1H, *m*, H-9), 1.54 (1H, *m*, H-11a), 1.87 (1H, *m*, H-11b), 4.09 (1H, *m*, H-12), 1.88 (1H, *dd*, $J = 10.3, 12.1$ Hz, H-13), 1.08 (1H, *m*, H-15a), 1.68 (1H, *m*, H-15b), 1.00 (1H, *m*, H-16a), 1.58 (1H, *m*, H-16b), 2.19 (1H, *m*, H-17), 0.94 (3H, *s*, H-18), 0.73 (3H, *s*, H-19), 1.29 (3H, *s*, H-21), 2.03 (1H, *dd*, $J = 6.6, 13.5$ Hz, H-22a), 2.07 (1H, *dd*, $J = 9.3, 13.5$ Hz, H-22b), 5.05 (1H, *dd*, $J = 6.6, 9.3$ Hz, H-23), 1.63 and 1.64 (each 3H, *s*, H-26 or H-27), 1.20 (3H, *s*, H-28), 1.12 (3H, *s*, H-29), 0.94 (3H, *s*, H-30), 4.83 (1H, *d*, $J = 7.3$ Hz, H-1 of Glc), 5.94 (1H, *d*, $J = 0.9$ Hz, H-1 of Rha), 5.69 (1H, *d*, $J = 1.3$ Hz, H-1 of Rha'), 1.65 (3H, *d*, $J = 6.1$ Hz, H-6 of Rha), 1.60 (3H, *d*, $J = 6.1$ Hz, H-6 of Rha'). ^{13}C NMR: see Table 2.

Neoalsoside O1 (**23**). Powder, $[\alpha]_D^{22}$ − 22.4° (pyridine; *c* 0.85). FABMS (negative) *m/z*: 781.4772 $[M - H]^-$ ($C_{42}H_{69}O_{13}$ requires: *m/z* 781.4737). ^{1}H NMR (pyridine-d_5): δ0.80, 0.93, 0.97, 1.20, 1.25, 1.32, 1.57 and 1.62 (each 3H, *s*, Me), 3.34 (1H, *dd*, $J = 4.2, 11.5$ Hz, H-3), 3.97 (1H, *m*, H-12), 1.75 (1H, *m*, H-13), 2.25 (1H, *m*, H-17), 4.96 (1H, *d*, $J = 7.5$ Hz, H-1 of Glc), 6.60 (1H, *br s*, H-1 of Rha), 1.73 (3H, *d*, $J = 6.2$ Hz, H-6 of Rha). ^{13}C NMR: see Table 2.

Neoalsoside O2 (**24**). Powder, $[\alpha]_D^{22}$ − 25.6° (pyridine; *c* 1.56). FABMS (negative) *m/z*: 927.5303 $[M - H]^-$ ($C_{48}H_{79}O_{17}$ requires: *m/z* 927.5316). ^{1}H NMR (pyridine-d_5): δ0.78 (1H, *m*, H-1a), 1.44 (1H, *m*, H-1b), 1.78 (1H, *m*, H-2a), 2.22 (1H, *m*, H-2b), 3.33 (1H, *dd*, $J = 3.9, 11.9$ Hz,

H-3), 0.71 (1H, *br d*, J = 7.5 Hz, H-5), 1.42 (1H, *m*, H-6a), 1.47 (1H, *m*, H-6b), 1.22 (1H, *m*, H-7a), 1.51 (1H, *m*, H-7b), 1.32 (1H, *m*, H-9), 1.39 (1H, *m*, H-11a), 1.81 (1H, *m*, H-11b), 3.95 (1H, *ddd*, J = 5.9, 10.1, 10.1 Hz, H-12), 1.75 (1H, *m*, H-13), 1.10 (1H, *m*, H-15a), 1.69 (1H, *m*, H-15b), 1.11 (1H, *m*, H-16a), 1.64 (1H, *m*, H-16b), 2.25 (1H, *m*, H-17), 0.98 (3H, *s*, H-18), 0.81 (3H, *s*, H-19), 1.32 (3H, *s*, H-21), 1.46 (1H, *m*, H-22a), 2.02 (1H, *m*, H-22b), 2.00 (1H, *m*, H-23a) 2.83 (1H, *m*, H-23b), 1.55 and 1.60 (each 3H, *s*, H-26 or H-27), 1.22 (3H, *s*, H-28), 1.14 (3H, *s*, H-29), 0.94 (3H, *s*, H-30), 4.84 (1H, *d*, J = 7.5 Hz, H-1 of Glc), 5.94 (1H, *br s*, H-1 of Rha), 5.70 (1H, *br s*, H-1 of Rha'), 1.66 (3H, *d*, J = 6.1 Hz, H-6 of Rha), 1.61 (3H, *d*, J = 6.4 Hz, H-6 of Rha'). ^{13}C NMR: see Table 2.

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 Mombusho International Scientific Research Program (No. 03044103, 1991–1993) from the Ministry of Education, Science and Culture.

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