Pergamon 0031-9422(93)E0190-P

Phytochemistry, Vol. 36, No. 3, pp. 709-716, 1994

0031-9422/94 $7.00+0.00

MONOTERPENOID AND PHENYLETHANOID GLYCOSIDES FROM *LIGUSTRUM PEDUNCULARE*

ZHENG-DAN HE, SHINICHI UEDA, MASAKO AKAJI, TETSURO FUJITA, KENICHIRO INOUE* and CHONG-REN YANG†

Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan; *Gifu Pharmaceutical University, 5-6-1 Mitahora-higashi, Gifu 502, Japan; †Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences, 650204, Kunming, Yunnan, China

(*Received* 25 *October* 1993)

Key Word Index—*Ligustrum pedunculare*; Oleaceae; leaves; phenylethanoid glycosides; lipedosides A-I, A-II; monoterpene glycosides; lipedosides B-I–B-VI.

Abstract—Two new phenylethanoid glycosides, lipedosides A-I and A-II as well as six new monoterpene glycosides, lipedosides B-I–B-VI were isolated together with three known constituents, osmanthuside B, anatolioside and linalool from *Ligustrum pedunculare*. Their structures have been elucidated by chemical and spectroscopic methods.

INTRODUCTION

Ku-Ding-Cha, a well known traditional drinking tea, has been used in south China for a long time. Many species belonging to different families and genera are used as its original materials (Table 1) [1]. *Ligustrum pedunculare* has long been used as a variety of Ku-Ding-Cha. In continuation of our investigations on the constituents of oleaceous plants and Ku-Ding-Cha [1–3], we have isolated linalool (**12**), three phenylethanoid glycosides and seven monoterpene glycosides from *L. pedunculare*. This paper describes the isolation and structural elucidation of two new phenylethanoid glycosides, lipedosides A-I (**1**) and A-II (**2**), as well as six new monoterpene glycosides, lipedosides B-I (**6**), B-II (**7**), B-III (**8**), B-IV (**9**), B-V (**10**) and B-VI (**11**).

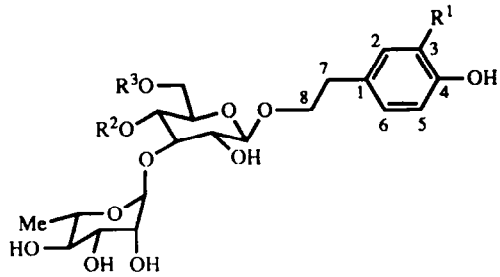
RESULTS AND DISCUSSION

A methanolic extract of the dry leaves of *L. pedunculare* was fractionated as described in the Experimental section to give two new phenylethanoid glycosides, lipedosides A-I (**1**) and A-II (**2**), as well as six new monoterpene glycosides, lipedosides B-I (**6**), B-II (**7**), B-III (**8**), B-IV (**9**), B-V (**10**) and B-VI (**11**) together with three known compounds, linalool (**12**), osmanthuside B (**3**) [4] and anatolioside (**5**) [7].

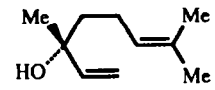
Table 1. Original species of Ku-Ding-Cha in different areas of China

Species	Family	Place
Ligustrum pedunculare Rehd.	Oleaceae	Sichuan
L. purpurascens Y.C. Yang	Oleaceae	Yunnan
L. japonicum var. *pubescens* Koidz.	Oleaceae	Guizhou
L. robustrum (Roxb.) Bl.	Oleaceae	Guizhou
Ilex cornuta Lindl. ex Paxt.	Aquifoliaceae	Zhejiang
I. kudincha C. J. Tseng	Aquifoliaceae	Guangxi
I. latifolia Thunb.	Aquifoliaceae	Zhejiang Hunan
Cratoxylum prunifolium (Kurz) Dyer	Guttiferae	Guangxi
Ehretia thyrsiflora (S. et Z.) Nakai	Ehretiaceae	Guangxi
Photinia serruiata Lindl.	Rosaceae	Zhejiang

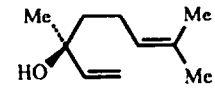
Lipedoside A-I (**1**), a powder, analysed for $C_{29}H_{36}O_{14}$ from its HR-FAB mass spectrum (*m/z* 609.2214 [M + H]$^+$). The UV (λ_{max}^{EtOH} nm: 200, 213, 225, 317) and IR (ν_{max}^{KBr} cm^{-1}: 3400, 1700, 1630, 1610, 1515) suggested the presence of hydroxyl, ester and conjugated aromatic groups. The ^{1}H NMR spectrum at the aromatic region exhibited an A_2B_2 system belonging to a *p*-coumaroyl moiety [δ6.79 (2H, *d*, J = 8.6 Hz), δ7.45 (2H, *d*, J = 8.6 Hz)]. The two olefinic proton signals which appeared as an AB-system (J = 15.9 Hz) indicated a *trans*-geometry in the moiety. ^{1}H NMR signals of two anomeric protons at δ5.20 (1H, *d*, J = 1.6 Hz) and δ4.32 (1H, *d*, J = 8.0 Hz), as well as one secondary methyl group of rhamnose at δ1.08 (3H, *d*, J = 6.3 Hz) are consistent with the configurations for α-L-rhamnose and β-D-glucose. Comparing the ^{13}C NMR signals of **1** with those of **3** [4], the chemical shifts assignable to C-3 of the aglycone moiety in **1** shifted downfield to δ144.6, while chemical shifts of C-2, C-4 and C-6 shifted upfield to δ116.3, δ146.1 and δ121.3, respectively (Table 2). An ABX-system assignable to the aglycone moiety appeared at δ6.48 (1H, *dd*, J = 8.2, 1.8 Hz), δ6.56 (1H, *d*, J = 1.8 Hz) and δ6.67 (1H, *d*, J = 8.2 Hz) (Table 3) [5]. These results indicate that two hydroxyl groups are located at C-3 and C-4 of the aglycone of **1**. Alkali hydrolysis of **1** gave a compound, whose spectral and physical data were in good accordance with those of [2-(3,4-dihydroxyphenyl)-ethyl]-(3-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside (**4**) (Tables 2 and 3). Thus, lipedoside A-I (**1**) was identified as [2-(3,4-dihydroxyphenyl)-ethyl]-(3-*O*-α-L-rhamnopyranosyl)-(4-*O*-*p*-coumaroyl)-β-D-glucopyranoside.



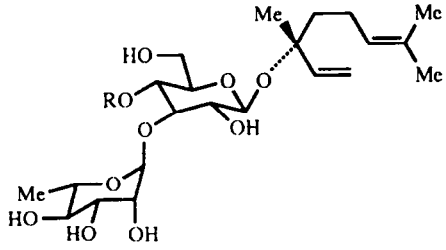
1 R^1=OH, R^2=*p*-coumaroyl, R^3=H
2 R^1=OH, R^2=H, R^3=*p*-coumaroyl
3 R^1=R^3=H, R^2=*p*-coumaroyl
4 R^1=OH, R^2= R^3=H



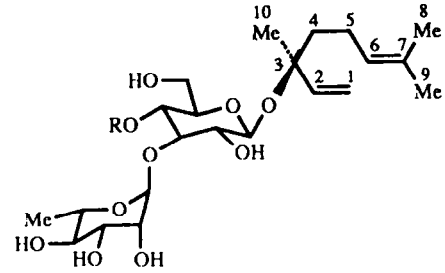
12a



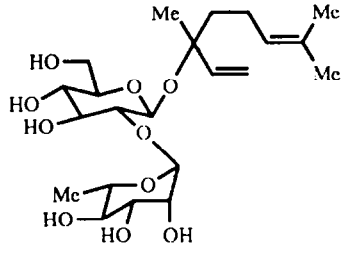
12b



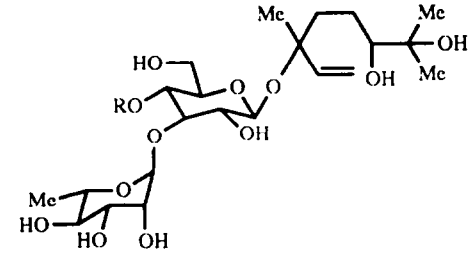
6a R=H
7a R=*cis*-*p*-coumaroyl
8a R=*trans*-*p*-coumaroyl



6b R=H
7b R=*cis*-*p*-coumaroyl
8b R=*trans*-*p*-coumaroyl



5



9 R=H
10 R=*cis*-*p*-coumaroyl
11 R=*trans*-*p*-coumaroyl

Compound **1** formerly obtained from *L. purpurascens* was a mixture of *Z* and *E* isomers [1]. Thus, optically active lipedoside A-I (**1**) is a new phenylethanoid glycoside.

Lipedoside A-II (**2**), a powder, analysed for $C_{29}H_{36}O_{14}$ from its HR-FAB mass spectrum (*m/z* 609.2191 [M + H]$^+$). The UV and IR spectra were similar to those of **1**. The ^{1}H NMR spectrum of **2** was also very similar to that of **1**, indicating an A_2B_2- and an ABX-system which belong to the *trans*-*p*-coumaroyl and the same aglycone moiety, respectively (Table 3). When comparing the ^{1}H NMR signals of **2** with those of **1**, the chemical shift assignable to H-4 of **2** in the glucosyl moiety shifted upfield from δ4.90 (1H, *t*, *J* = 8 Hz) to δ3.47 (1H, *t*, *J* = 8 Hz), but the chemical shift of H_2-6 shifted downfield from δ3.67 (1H, *dd*, *J* = 12, 5.5 Hz) and δ3.90 (1H, *dd*, *J* = 12, 2 Hz) to δ4.34 (1H, *dd*, *J* = 12, 6 Hz) and δ4.52 (1H, *dd*, *J* = 12, 2 Hz), respectively (Table 3). The signal of C-6 of **2** compared with that of **1** shifted downfield from δ62.4 to δ64.7 (Table 2). Thus, the *p*-coumaroyl moiety should be located at the C-6 of the glucosyl moiety in **2** [6]. Furthermore, alkali hydrolysis of **2** gave a known compound **4**. The structure of lipedoside A-II (**2**) has thus been elucidated as [2-(3,4-dihydroxyphenyl)-ethyl]-(3-*O*-α-L-rhamnopyranosyl)-(6-*O*-*p*-coumaroyl)-β-D-glucopyranoside.

Lipedoside B-I (**6**), a powder, analysed for $C_{22}H_{38}O_{10}$ from its HR-FAB mass spectrum (*m/z* 485.2352 [M + Na]$^+$). The IR spectrum showed characteristic absorptions at 3400 (OH groups) and 1640 (C=C) cm^{-1}. The ^{1}H NMR spectrum showed the following signals belonging to a monoterpene moiety: (i) an ABX system of three olefinic protons on a monosubstituted double bond at δ5.18 (1H, *dd*, *J* = 10.8, 1.3 Hz, H-1a), δ5.22 (1H, *dd*, *J*

Table 2. ^{13}C NMR spectral data of glycosides **1**–**4** (in CD_3OD)

C	1	2	3	4
Aglycone				
1	131.3	131.4	130.6	131.5
2	116.3	116.4	130.9	116.3
3	144.6	144.6	116.1	144.6
4	146.1	146.1	156.6	146.0
5	117.1	117.1	116.1	117.1
6	121.3	121.3	130.9	121.3
7	36.6	36.7	36.3	36.4
8	72.3	72.3	72.2	72.0
Glucosyl				
1	104.2	104.4	104.1	104.1
2	76.0	75.7	75.9	75.5
3	81.6	84.0	81.6	84.7
4	70.4	70.4	70.6	70.8
5	76.2	75.4	76.1	77.8
6	62.4	64.7	62.3	62.2
Rhamnosyl				
1	103.0	102.7	102.9	102.6
2	72.1	72.3	72.0	72.2
3	72.3	72.5	72.2	72.5
4	73.9	74.0	73.8	73.7
5	70.3	70.0	70.3	70.0
6	18.4	17.9	18.4	17.9
p-Coumaroyl				
1	126.1	127.1	127.0	—
2	131.2	131.2	131.3	—
3	116.9	116.9	116.8	—
4	161.4	161.2	161.3	—
5	116.9	116.9	116.8	—
6	131.2	131.2	131.3	—
7	147.6	146.9	147.6	—
8	114.8	114.9	114.7	—
CO	168.3	169.1	168.2	—

= 17.6, 1.3 Hz, H-1b) and δ5.92 (1H, *dd*, *J* = 17.6, 10.8 Hz, H-2); (ii) an olefinic proton at δ5.09 (1H, *m*, H-6); (iii) two set signals of CH_2 at δ1.60 (2H, *dd*, *J* = 10.5, 5.1 Hz, H-4), δ2.04 (2H, *m*, H-5); (iv) three methyl signals at δ1.37 (3H, *s*, H-10) as well as δ1.65 and δ1.58 (each 3H, *s*, H-8, 9). These ^1H NMR signals together with the ^{13}C NMR data (Tables 4 and 5) assigned to the monoterpene moiety were in accordance with those reported for the linaloyl moiety in monoterpene glycosides [7, 8]. The remaining signals in the ^1H and ^{13}C NMR spectra were consistent with the presence of one molecule of glucose and rhamnose as the sugar moieties. The anomeric protons of β-D-glucose and α-L-rhamnose were observed at δ4.35 (1H, *d*, *J* = 7.8 Hz) and δ5.14 (1H, *d*, *J* = 1.7 Hz), respectively. When comparing the ^{13}C NMR signals of **6** with those of anatolioside (**5**), the chemical shift assignable to C-2 of the glucosyl moiety in **6** shifted upfield from δ79.8 to δ75.5, while the C-3 signal shifted downfield from δ78.2 to δ84.8. These signals were assigned by ^1H–^1H COSY and ^1H–^{13}C COSY experiments. The (^1H–^{13}C) long range COSY experiment of **6** showed the ^3J interaction between the anomeric proton of rhamnose and the C-3 of glucose. The rhamnosyl group should, thus, be conjugated at C-3 of the glucosyl moiety. Enzymatic hydrolysis of compound **6** gave (*R*)-linalool (**12a**) and (*S*)-linalool (**12b**) as a mixture (**12a**:**12b** = 13:87), L-rhamnose and D-glucose [9]. Accordingly, lipedoside B-I was characterized as a mixture (*R*:S = 13:87) of 3 (*R*)- and 3 (*S*)-linaloyl-(3-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside (**6a** and **b**).

Lipedoside B-II (**7**), a powder, analysed for $C_{31}H_{44}O_{12}$ from its HR-FAB mass spectrum indicating an ion peak at *m/z* 631.2758 $[M+Na]^+$. It showed UV maxima at 201, 225 and 317 nm. IR bands appeared at 3400, 2900, 1710, 1600 and 1515 cm^{-1}. Its ^1H and ^{13}C NMR data were assignable by ^1H–^1H COSY and ^1H–^{13}C COSY experiments. The ^1H and ^{13}C NMR spectra of **7** were similar to those of **6** except for the appearance of one more set of signals for a *p*-coumaroyl group (Tables 4 and 5). The ^1H NMR spectrum exhibited an A_2B_2-system of the phenyl moiety [δ6.76 (2H, *d*, *J* = 8.7 Hz), 7.71 (2H, *d*, *J* = 8.7 Hz)] and an AB-system of *cis*-olefinic protons [δ5.78 (1H, *d*, *J* = 12.9 Hz) and δ6.93 (1H, *d*, *J* = 12.9 Hz)], which belongs to the *cis*-*p*-coumaroyl moiety. When comparing the ^1H and ^{13}C NMR signals of **7** with those of **6**, the chemical shift assignable to the glucosyl H-4 of **7** shifted downfield from δ3.32 to δ4.85, while the signals of C-3 and 5 of **7** shifted upfield by 2.68 and 1.29 ppm, respectively. The (^1H–^{13}C) long range COSY experiment of **7** showed the ^3J interaction between the carbonyl carbon of the *p*-coumaroyl group and the H-4 of glucose. Alkaline hydrolysis of **7** gave **6** which was identified with an authentic specimen, by IR, ^1H and ^{13}C NMR spectra. These results indicate that the *cis*-*p*-coumaroyl group is conjugated to the glucosyl moiety at C-4. The hydrolysate **6** was further hydrolysed with enzyme to give (*R*)-linalool (**12a**) and (*S*)-linalool (**12b**) as a mixture (**12a**:**12b** = 13:87), in addition to L-rhamnose and D-glucose. The structure of lipedoside B-II was thus concluded to be a mixture (*R*:*S* = 13:87) of 3 (*R*)- and 3 (*S*)-linaloyl-(3-*O*-α-L-rhamnopyranosyl)-(4-*O*-*cis*-*p*-coumaroyl)-β-D-glucopyranoside (**7a** and **b**).

Lipedoside B-III (**8**) was obtained as a powder. It analysed for $C_{31}H_{44}O_{12}$ from its HR-FAB mass spectrum (*m/z* 631.2730 $[M+Na]^+$). The UV spectrum showed absorption maxima at 201, 225 and 317 nm. IR bands appeared at 3400, 2920, 1710, 1600 and 1515 cm^{-1}. Its ^1H and ^{13}C NMR spectra showed that **8** was closely related to **7**, except for the *trans*-form of the *p*-coumaroyl moiety (Tables 4 and 5). Furthermore, the structure of **8** was examined by the ^1H–^1H, ^1H–^{13}C COSY and ^1H–^{13}C long range COSY NMR spectra as well as by alkaline and enzymatic hydrolysis. From the evidence described above, glycosides **7a** and **8a** as well as **7b** and **8b** are a pair of *Z*/*E* epimers, respectively. The structure of lipedoside B-III was concluded to be a mixture (*R*:*S* = 13:87) of 3 (*R*)- and 3 (*S*)-linaloyl-(3-*O*-α-L-rhamnosyl)-(4-*O*-trans-*p*-coumaroyl)-β-D-glucopyranoside (**8a** and **b**).

Lipedoside B-IV (**9**), a powder, analysed for $C_{22}H_{40}O_{12}$ from its HR-FAB mass spectrum (*m/z* 497.2534 $[M+H]^+$). The IR spectra of **9** showed similar absorption bands to those of **6** (3400, 2920, 1640 and 1080 cm^{-1}). The main difference between the ^1H NMR data of **9** and **6** was the upfield shift of the aglycone H-6

Table 3. ^{1}H NMR spectral data of glycosides **1**–**4** (in CD_3OD)

H	1	2	3	4
Aglycone				
2	6.56 (1H, *d*, 1.8)	6.65 (1H, *d*, 2.1)	7.07 (1H, *d*, 8.6)	6.71 (1H, *d*, 2.0)
3			6.72 (1H, *d*, 8.6)	–
5	6.67 (1H, *d*, 8.2)	6.69 (1H, *dd*, 8.0)	6.72 (1H, *d*, 8.6)	6.73 (1H, *d*, 8.1)
6	6.48 (1H, *dd*, 8.2, 1.8)	6.55 (1H, *dd*, 8.0, 2.1)	7.07 (1H, *d*, 8.6)	6.52 (1H, *dd*, 8.1, 2.0)
7	2.80 (2H, *t*, 6.7)	2.79 (2H, *t*, 7.0)	2.84 (2H, *t*, 6.8)	2.78 (2H, *t*, 7.2)
8	3.73 (*m*)	3.72 (*m*)	3.74 (*m*)	3.66 (*m*)
	4.02 (*m*)	4.05 (*m*)	4.11 (*m*)	3.91 (*m*)
Glucosyl				
1	4.32 (1H, *d*, 8.0)	4.34 (1H, *d*, 7.9)	4.38 (1H, *d*, 8.1)	4.30 (1H, *d*, 8.3)
2	3.49 (1H, *t*, 8.0)	3.43 (1H, *t*, 7.9)	3.47 (1H, *t*, 8.1)	3.45 (1H, *d*, 8.3)
3	3.61 (1H, *t*, 8.0)	3.58 (1H, *t*, 8.0)	3.62 (1H, *t*, 8.1)	3.60 (1H, *d*, 8.3)
4	4.90 (1H, *t*, 8.0)	3.47 (1H, *t*, 8.0)	4.91 (1H, *t*, 8.1)	3.45 (1H, *d*, 8.3)
5	3.59 (1H, *m*)	3.60 (1H, *m*)	3.57 (1H, *m*)	3.58 (1H, *m*)
6	3.67 (1H, *dd*, 12, 5.5)	4.34 (1H, *dd*, 12, 6)	3.65 (1H, *dd*, 12, 6)	3.62 (1H, *dd*, 12.1, 6)
	3.90 (1H, *dd*, 12, 2)	4.52 (1H, *dd*, 12, 2)	3.85 (1H, *dd*, 12, 2)	3.85 (1H, *dd*, 12.1, 2)
Rhamnosyl				
1	5.20 (1H, *d*, 1.6)	5.20 (1H, *d*, 1.6)	5.22 (1H, *d*, 1.6)	5.18 (1H, *d*, 1.5)
2,3	3.72 (2H, *m*)	3.70 (2H, *m*)	3.73 (2H, *m*)	3.69 (2H, *m*)
4	3.40 (1H, *t*, 9.5)	3.43 (1H, *t*, 9.1)	3.41 (1H, *t*, 9.2)	3.42 (1H, *t*, 9.2)
5	4.00 (1H, *m*)	3.91 (1H, *m*)	3.90 (1H, *m*)	3.95 (1H, *m*)
6	1.08 (3H, *d*, 6.3)	1.06 (3H, *d*, 6.2)	1.10 (3H, *d*, 6.1)	1.10 (1H, *d*, 6.3)
p-Coumaroyl				
2,6	7.45 (2H, *d*, 8.6)	7.46 (2H, *d*, 8.7)	7.46 (2H, *d*, 8.6)	–
3,5	6.79 (2H, *d*, 8.6)	6.80 (2H, *d*, 8.7)	6.81 (2H, *d*, 8.6)	–
7	7.65 (1H, *d*, 15.9)	7.62 (1H, *d*, 16.0)	7.67 (1H, *d*, 16.1)	·
8	6.33 (1H, *d*, 15.9)	6.34 (1H, *d*, 16.0)	6.34 (1H, *d*, 16.1)	·

Coupling constants (*J* values in Hz) are shown in parentheses.

signal of **6** from δ5.09 to 3.37 in **9** (Table 4). The ^{13}C NMR signal of the aglycone C-6 and C-7 of **9** also shifted upfield from δ125.6 and 132.1 in **6** to δ 80.1 and δ74.1, respectively (Table 5). These results indicate that the aglycone of **9** was 3,7-dimethyloct-1-ene-3,6,7-triol [10]. In addition, the ^{1}H NMR spectrum of **9** displayed two anomeric protons at δ4.45 (J = 7.8 Hz) and δ5.15 (J = 1.6 Hz) which were consistent with the configurations for β-D-glucose and α-L-rhamnose. One methyl group of rhamnose was observed at δ1.24 (J = 6.3 Hz). The ^{13}C NMR spectrum of **9** also showed signals for glucosyl and rhamnosyl groups. The chemical shifts of the sugar moieties of **9** were similar to those of **6**. From a ^{1}H–^{13}C long range COSY experiment on **9**, two anomeric carbons of the glucosyl and rhamnosyl groups were shown to be joined to C-1 of the aglycone and C-3 of the glucosyl moiety, respectively. Thus, the structure of lipedoside B-IV was concluded to be 3-(6,7-dihydroxy-3,7-dimethyloct-1-enyl)-3-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside (**9**).

Lipedoside B-V (**10**), a powder analysed for $C_{31}H_{46}O_{14}$ by its HR-FAB mass spectrum (*m/z* 643.2932 $[M+H]^+$). Its UV and IR spectra showed similar absorption bands to those of **7**. Comparison of the ^{1}H and ^{13}C NMR data of **10** and **9** suggested that their aglycone moieties were identical (Tables 4 and 5). In addition to the glucosyl and rhamnosyl moieties, a set of *cis*-*p*-coumaroyl signals was observed in **10**. Alkaline hydrolysis of **10** gave **9**. A ^{1}H–^{13}C long range COSY experiment on **10**, in a similar way to that described for **7**, led to the structure of lipedoside B-V being deduced as 3-(6,7-dihydroxy-3,7-dimethyloct-1-enyl)-(3-α-L-rhamnopyranosyl)-(4-*O*-*cis*-*p*-coumaroyl)-β-D-glycopyranoside (**10**).

Lipedoside B-VI (**11**), a powder, analysed for $C_{31}H_{46}O_{14}$ by its HR-FAB mass spectrum (*m/z* 643.2942 $[M+H]^+$). The ^{1}H and ^{13}C NMR spectra of **11** were similar to those of **10**, except for the appearance of a *trans*-*p*-coumaroyl unit in **11** instead of the *cis*-*p*-coumaroyl unit in **10** (Tables 4 and 5). The ^{1}H–^{1}H, ^{1}H–^{13}C COSY and ^{1}H–^{13}C long range COSY experiments on **11** were also carried out to reveal the ^3J interaction between the anomeric proton of the rhamnosyl and the C-3 of glucosyl moieties. Alkaline hydrolysis of **11** gave **9**. Thus, the structure of lipedoside B-VI was established to be 3-(6,7-dihydroxy-3,7-dimethyloct-1-enyl)-(3-α-L-rhamnopyranosyl)-(4-*O*-*trans*-*p*-coumaroyl)-β-D-glucopyranoside (**11**).

EXPERIMENTAL

^{1}H (200 and 300 MHz) and ^{13}C (50 and 75 MHz) NMR: TMS as int. standard. HR-FAB-MS, FAB-MS: glycerol as matrix. CC and TLC: silica gel, Si 60 (Lobar, 40–63 μm, length: 250 mm, diameter: 25 mm, Merck), Rp-18 (Lobar, 40–63 μm, length: 250 mm, diameter: 25 mm, Merck) and Diaion HP-20 (Mitsubishi Kasei).

Table 4. ^{1}H NMR spectral data of glycosides **5–11** in (CD_3OD)

H	5	6	7	8	9	10	11
Aglycone							
1a	5.18 (1H, *dd*, 10.8, 1.3)	5.18 (1H, *dd*, 10.8, 1.3)	5.21 (1H, *dd*, 10.9, 1.3)	5.22 (1H, *dd*, 10.9, 1.2)	5.17 (1H, *dd*, 10.9, 1.3)	5.20 (1H, *dd*, 11.0, 1.6)	5.94 (1H, *dd*, 17.8, 11.0)
1b	5.24 (1H, *dd*, 18.0, 1.3)	5.22 (1H, *dd*, 17.6, 1.3)	5.24 (1H, *dd*, 17.8, 1.3)	5.25 (1H, *dd*, 17.8, 1.2)	5.24 (1H, *dd*, 17.8, 1.3)	5.27 (1H, *dd*, 17.5, 1.6)	5.21 (1H, *dd*, 11.0, 1.6)
2	5.94 (1H, *dd*, 18.0, 10.8)	5.92 (1H, *dd*, 17.6, 10.8)	5.92 (1H, *dd*, 17.8, 10.9)	5.93 (1H, *dd*, 17.8, 10.9)	5.92 (1H, *dd*, 17.8, 10.9)	5.93 (1H, *dd*, 17.5, 11.0)	5.26 (1H, *dd*, 17.8, 1.6)
4	1.60 (2H, *dd*, 10.5, 5.1)	1.60 (2H, *dd*, 10.5, 5.1)	1.60 (2H, *dd*, 10.5, 5.1 Hz)	1.60 (2H, *dd*, 10.5, 5.0)	1.71 (2H, *br t*, 12.5)	1.77 (2H, *br t*, 12.9)	1.77 (2H, *br t*, 12.9)
5	2.01 (2H, *m*)	2.04 (2H, *m*)	2.04 (2H, *m*)	2.04 (2H, *m*)	1.54 (1H, *br dt*, 12.5, 4.3)	1.68 (1H, *br dt*, 13.0, 4.1)	1.67 (1H, *br dt*, 12.9, 4.2)
					1.88 (1H, *br dt*, 12.5, 4.3)	1.95 (1H, *br dt*, 13.0, 4.1)	1.93 (1H, *br dt*, 12.9, 4.2)
6	5.00 (1H, *m*)	5.09 (1H, *m*)	5.10 (1H, *m*)	5.10 (1H, *m*)	3.37 (*m*)	3.45 (*m*)	3.47 (*m*)
8	1.66 (3H, *s*)	1.65 (3H, *s*)	1.66 (3H, *d*, 0.7)	1.66 (3H, *d*, 0.6)	1.16 (3H, *s*)	1.18 (3H, *s*)	1.17 (3H, *s*)
9	1.59 (3H, *s*)	1.58 (3H, *s*)	1.59 (3H, *d*, 0.7)	1.59 (3H, *d*, 0.6)	1.12 (3H, *s*)	1.12 (3H, *s*)	1.12 (3H, *s*)
10	1.38 (3H, *s*)	1.37 (3H, *s*)	1.38 (3H, *s*)	1.39 (3H, *s*)	1.37 (3H, *s*)	1.39 (3H, *s*)	1.40 (3H, *s*)
Glucosyl							
1	4.42 (1H, *d*, 7.4)	4.35 (1H, *d*, 7.8)	4.40 (1H, *d*, 7.9)	4.43 (1H, *d*, 7.9)	4.45 (1H, *d*, 7.8)	4.48 (1H, *d*, 7.9)	4.56 (1H, *d*, 7.9)
2	3.41 (1H, *dd*, 7.4, 9.5)	3.28 (1H, *t*, 7.8)	3.40–3.35 (*m*)	3.52 (1H, *dd*, 7.9, 9.2)	3.42 (1H, *dd*, 7.8, 9.2)	3.43–3.37 (*m*)	3.51 (1H, *dd*, 7.9, 9.0)
3	3.45 (1H, *t*, 9.5)	3.48 (1H, *t*, 7.8)	3.72 (1H, *t*, 9.2)	3.78 (1H, *dd*, 7.9, 9.2)	3.44 (1H, *t*, 9.2)	3.74 (1H, *t*, 9.3)	3.51 (1H, *dd*, 7.9, 9.0)
4	3.30 (1H, *t*, 9.5)	3.32 (1H, *t*, 7.8)	4.85 (1H, *t*, 9.2)	4.90 (1H, *t*, 9.2)	3.33 (1H, *t*, 9.2)	4.86 (1H, *t*, 9.3)	4.92 (1H, *t*, 9.0)
5	3.19 (1H, *m*)	3.18 (1H, *m*)	3.40–3.35 (*m*)	3.36 (1H, *m*)	3.20 (1H, *m*)	3.43-3.37 (*m*)	3.38 (1H, *m*)
6	3.68 (1H, *dd*, 12, 6)	3.68 (1H, *dd*, 12, 6.2)	3.48 (1H, *dd*, 12, 5.7)	3.52 (*m*)	3.66 (1H, *dd*, 12, 6)	3.48 (1H, *dd*, 12.1, 5.6)	3.54 (*m*)
	3.85 (1H, *dd*, 12, 2)	3.82 (1H, *dd*, 12, 2)	3.58 (1H, *dd*, 12, 2)		3.87 (1H, *dd*, 12, 2)	3.58 (1H, *dd*, 12.1, 2.1)	
Rhamnosyl							
1	5.30 (1H, *d*, 1.7)	5.14 (1H, *d*, 1.7)	5.17 (1H, *d*, 1.7)	5.19 (1H, *d*, 1.7)	5.15 (1H, *d*, 1.6)	5.21 (1H, *d*, 1.6)	5.20 (1H, *d*, 1.6)
2	3.95 (1H, *dd*, 1.7, 3.4)	3.92 (1H, *dd*, 1.7, 3.5)	3.93 (1H, *dd*, 1.7, 3.4)	3.92 (1H, *dd*, 1.7, 3.5)	3.95 (1H, *dd*, 1.6, 3.5)	3.93 (1H, *dd*, 1.6, 3.5)	3.91 (1H, *dd*, 1.6, 3.5)
3	3.71 (1H, *dd*, 3.4, 9.5)	3.70 (1H, *dd*, 3.5, 9.5)	3.60 (1H, *dd*, 3.4, 9.6)	3.59 (1H, *dd*, 3.5, 9.6)	3.72 (1H, *dd*, 3.5, 9.6)	3.61 (1H, *dd*, 3.5, 9.7)	3.60 (1H, *dd*, 3.4, 9.5)
4	3.46 (1H, *t*, 9.5)	3.43 (1H, *t*, 9.5)	3.39 (1H, *t*, 9.6)	3.29 (1H, *t*, 9.6)	3.48 (1H, *t*, 9.6)	3.40 (1H, *dd*, 9.7)	3.29 (1H, *t*, 9.5)
5	4.11 (1H, *m*)	4.06 (1H, *m*)	3.64 (1H, *m*)	3.56 (1H, *m*)	4.1 (1H, *m*)	3.66 (1H, *m*)	3.55 (1H, *m*)
6	1.22 (3H, *d*, 6.2)	1.25 (3H, *d*, 6.1)	1.16 (3H, *d*, 6.2)	1.08 (3H, *d*, 6.2)	1.24 (3H, *d*, 6.3)	1.15 (3H, *d*, 6.2)	1.09 (3H, *d*, 6.2)
p-Coumaroyl							
2,6	—	—	7.71 (2H, *d*, 8.7)	7.46 (2H, *d*, 8.7)	—	7.72 (2H, *d*, 8.6)	7.45 (2H, *d*, 8.6)
3,5		—	6.76 (2H, *d*, 8.7)	6.81 (2H, *d*, 8.7)	—	6.79 (2H, *d*, 8.6)	6.83 (2H, *d*, 8.6)
7	—	—	6.93 (1H, *d*, 12.9)	7.66 (1H, *d*, 16.0)		6.94 (1H, *d*, 12.8)	7.67 (1H, *d*, 15.9)
8	—	—	5.78 (1H, *d*, 12.9)	6.33 (1H, *d*, 16.0)	—	5.80 (1H, *d*, 12.8)	6.31 (1H, *d*, 15.9)

Coupling constants (*J* values in Hz) are shown in parentheses.

Table 5. ^{13}C NMR spectral data of glycosides **5**–**11** (in CD_3OD)

C	5	6	7	8	9	10	11
Aglycone							
1	116.0	115.8	115.9	116.0	115.5	115.6	115.4
2	144.6	144.3	144.2	144.3	144.6	144.6	144.5
3	81.8	81.4	81.5	81.6	81.4	81.5	81.5
4	42.8	42.6	42.6	42.6	39.9	39.9	39.7
5	23.8	23.6	23.6	23.7	26.5	26.4	26.4
6	125.6	125.6	125.6	125.7	80.1	80.1	80.0
7	132.2	132.1	132.1	132.2	74.1	73.8	73.8
8	25.9	25.9	25.9	25.9	26.1	26.1	25.9
9	17.8	17.7	17.8	17.8	24.7	24.6	24.7
10	22.6	23.2	23.2	23.2	24.0	24.0	23.9
Glucosyl							
1	98.3	99.3	99.3	99.4	99.3	99.3	99.2
2	79.8	75.5	75.7	75.7	75.8	75.9	75.7
3	78.2	84.8	82.1	81.9	84.7	81.8	81.8
4	72.0	70.3	70.6	70.8	70.1	70.8	70.7
5	77.6	77.4	76.1	76.3	77.6	76.4	76.2
6	62.8	62.7	62.5	62.5	63.0	62.5	62.4
Rhamnosyl							
1	101.9	102.7	103.0	103.0	102.5	103.1	103.0
2	72.3	72.3	72.3	72.4	72.4	72.4	72.3
3	72.1	72.2	72.1	72.1	72.3	72.1	72.0
4	74.0	73.9	73.8	73.8	74.0	74.0	73.9
5	69.9	70.0	70.3	70.4	70.1	70.4	70.3
6	18.1	17.9	18.2	18.4	17.9	18.2	18.4
p-Coumaroyl							
1		—	127.4	127.1		127.5	127.0
2,6		—	134.2	131.3		134.3	131.3
3,5			115.8	116.9		115.6	116.8
4	—	—	160.3	161.4		160.3	161.3
7		—	147.2	147.6	—	147.2	147.5
8		—	115.9	114.8	—	115.9	114.8
CO	—		166.9	168.3		166.9	168.3

Plant material. Dried leaves of *L. pedunculare* Rehd. grown in the Chendu city, Sichuan Province, China, were purchased in 1989.

Isolation of glycosides. Dried leaves (2.15 kg) were extracted with hot MeOH (20 l × 4) under reflux. The extract was concd *in vacuo* to give a residue (675 g), which was dissolved in H_2O (1 l). The aq. suspension was extracted with hexane and EtOAc, successively. The hexane, EtOAc and H_2O layers were concd *in vacuo* to give residues of 18.9, 184.3 and 174.8 g, respectively. The H_2O extract (174.8 g) was fractionated by CC on Diaion HP-20, eluted with H_2O–MeOH with increasing MeOH content to afford frs A–F. Frs D and E were subjected to silica gel CC with $CHCl_3$–MeOH (8:1) as eluent and purified by LC on Si 60 (Lobar, 40–63 μm, Merck), respectively. Fr. D yielded glycosides **1** (101.5 mg) and **3** (305.1 mg), whereas Fr. E gave glycoside **2** (151.3 mg). Frs B, C and F were subjected to silica gel CC with $CHCl_3$–MeOH (8:1) as eluent and purified by LC on Si 60 and Rp-18 to yield seven monoterpene glycosides: **5** (25.1 mg), **6** (201.2 mg), **7** (110.3 mg), **8** (95.4 mg), **9** (30.1 mg), **10** (180.1 mg) and **11** (103.6 mg). The hexane extract (18.9 g) was fractionated by CC on silica gel and Sephadex LH-20, eluting with hexane–$CHCl_3$ with increasing $CHCl_3$ content and MeOH to afford Fr.G. Compound **12** (10.1 mg) was obtained by purification of Fr. G on Si 60 CC with hexane–$CHCl_3$ (1:1) as eluent.

Lipedoside A-I (**1**). Powder. $[\alpha]_D^{32}$ −118.0° (MeOH; *c* 0.06). UV λ_{max}^{EtOH} nm (log ε): 200 (4.28), 213 (4.00), 225 (4.10), 317 (4.28). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1700, 1630, 1610, 1515, 1450, 1170, 830. ^{13}C and ^1H NMR: see Tables 2 and 3. HR-FAB-MS *m/z*: found 609.2214 $[M+H]^+$ ($C_{29}H_{37}O_{14}$ requires 609.2183), 631 $[M+Na]^+$, 455 [M − *O*-aglycone]$^+$, 309 [M − *O*-aglycone − (rhamnosyl or coumaroyl) + H]$^+$, 147 [rhamnosyl or coumaroyl]$^+$, 137 [aglycone]$^+$. Positive ion FAB-MS, *m/z*: 631 $[M+Na]^+$, 609 $[M+H]^+$, 461 [M − (rhamnosyl or *p*-coumaroyl)]$^+$. (Found: C, 57.1; H, 6.0 $C_{29}H_{36}O_{14}$ requires: C, 57.2; H, 6.0%).

Lipedoside A-II (**2**). Powder. $[\alpha]_D^{32}$ −112.0° (MeOH; *c* 0.13) UV λ_{max}^{EtOH} nm (log ε): 200 (4.40), 213 (4.10), 225 (4.18), 318 (4.20). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1700, 1630, 1610, 1515, 1450, 1170, 830. ^1H and ^{13}C NMR: see Tables 2 and 3. HR-FAB-MS *m/z*: found 609.2191 $[M+H]^+$($C_{29}H_{37}O_{14}$ requires 609.2183), 631 $[M+Na]^+$, 455 [M − *O*-aglycone]$^+$, 309 [M − *O*-aglycone − (rhamnosyl or coumaroyl) + H]$^+$, 147 [rhamnosyl or coum-

aroyl]$^+$, 137 [aglycone]$^+$. Positive ion FAB-MS, *m/z*: 631 [M+Na]$^+$, 315 [M−rhamnosyl−*p*-coumaroyl+H]$^+$. (Found: C, 57.5; H, 5.8. $C_{29}H_{36}O_{14}$ requires: C, 57.2; H, 6.0%).

Osmanthuside B (**3**). Powder. $[\alpha]_D^{32}$ −102.4° (MeOH; *c* 0.14). UV λ_{max}^{EtOH} nm (log ε): 200 (4.38), 213 (4.12), 225 (4.20), 316.5 (4.30). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1700, 1630, 1610, 1515, 1450, 1170, 830. ^{1}H and ^{13}C NMR: see Tables 2 and 3. Positive ion FAB-MS, *m/z*: 615 [M+Na]$^+$, 593 [M+H]$^+$, 447 [M−(rhamnosyl or *p*-coumaroyl)+2H]$^+$. (Found: C, 58.6; H, 6.1. Calcd for $C_{29}H_{36}O_{13}$ C, 58.8; H, 6.1%).

Alkaline hydrolysis of compound **1**. A soln of **1** (50.2 mg) in MeOH (3 ml) and 1 M NaOH (3 ml) was stirred for 3 hr at room temp. The reaction mixt. was neutralized with 5% HCl, then extracted with Et_2O and *n*-BuOH. The *n*-BuOH extract was chromatographed on a silica gel column eluting with $CHCl_3$–MeOH–H_2O (50:10:1) to afford **4** (20.2 mg).

Alkaline hydrolysis of compound **2**. A soln of **2** (47.8 mg) in MeOH (3 ml) and 1 M NaOH (3 ml) was stirred for 3 hr at room temp. The reaction mixt. was neutralized with 5% HCl, then extracted with Et_2O and *n*-BuOH. The *n*-BuOH extract was chromatographed on a silica gel column eluting with $CHCl_3$–MeOH–H_2O (50:10:1) to afford **4** (12.1 mg).

[2-(3,4-*dihydroxyphenyl*)-*ethyl*]-(3-O-α-L-*rhamnopyranosyl*)-β-D-*Glucopyranoside* (**4**). Powder, $[\alpha]_D^{32}$ −76.3° (MeOH; *c* 0.09). UV λ_{max}^{EtOH} nm (log ε): 201 (4.12), 221 (4.00), 283 (3.50), 315 (3.30). ^{13}C and ^{1}H NMR: see Tables 2 and 3. Positive ion FAB-MS, *m/z*: 485 [M+Na]$^+$, 315 [M−rhamnosyl]$^+$. (Found: C, 52.1; H, 6.6. Calcd for $C_{20}H_{30}O_{12}$: C, 51.9; H, 6.5%).

Anatolioside (**5**). Powder, $[\alpha]_D^{32}$ −68.6° (MeOH; *c* 0.12). UV λ_{max}^{EtOH} nm (log ε): 203 (4.10). IR ν_{max}^{KBr} cm^{-1}: 3400, 2980, 2920, 1640, 1080, 1040. ^{1}H and ^{13}C NMR: see Tables 4 and 5. Positive ion FAB-MS, *m/z*: 485 [M+Na]$^+$, 463 [M+H]$^+$. (Found: C, 57.3; H, 8.2. Calcd for $C_{22}H_{38}O_{10}$: C, 57.1; H, 8.3%).

Lipedoside B-I (**6**). Powder. $[\alpha]_D^{32}$ − 48.3° (MeOH; *c* 0.15). UV λ_{max}^{EtOH} nm (log ε): 203 (4.20). IR ν_{max}^{KBr} cm^{-1}: 3400, 2980, 2920, 1640, 1080, 1040. ^{1}H and ^{13}C NMR: see Tables 4 and 5. HR-FAB-MS *m/z*: found 485.2352 [M+Na]$^+$ ($C_{22}H_{38}O_{10}Na$ requires 485.2363), 309 [M−*O*-aglycone]$^+$, 147 [M−*O*-aglycone−*O*-rhamnosyl+H]$^+$, 147 [rhamnosyl]$^+$, 137 [aglycone]$^+$. Positive ion FAB-MS, *m/z*: 485 [M+Na]$^+$, 463 [M+H]$^+$. (Found: C, 57.2; H, 8.2. $C_{22}H_{38}O_{10}$ requires: C, 57.1; H, 8.3%).

Lipedoside B-II (**7**). Powder. $[\alpha]_D^{32}$ −67.0° (MeOH; *c* 0.12). UV λ_{max}^{EtOH} nm (log ε): 201 (4.40), 225 (4.19), 317 (4.10). IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 2900, 1710, 1600, 1515, 1450, 1415, 1400, 1150, 1030, 840, 820. ^{1}H and ^{13}C NMR: see Tables 4 and 5. HR-FAB-MS *m/z*: found 631.2758 [M+Na]$^+$ ($C_{31}H_{44}O_{12}Na$ requires 631.2730), 455 [M−*O*-aglycone]$^+$, 445 [M−(*O*-rhamnosyl or *O*-coumaroyl)]$^+$, 309 [M−*O*-aglycone−(rhamnosyl or coumaroyl)+H]$^+$, 147 [rhamnosyl or coumaroyl]$^+$, 137 [aglycone]$^+$. Positive ion FAB-MS, *m/z*: 631 [M+Na]$^+$. (Found: C, 61.4; H, 7.2. $C_{31}H_{44}O_{12}$ requires: C, 61.2; H, 7.2%).

Lipedoside B-III (**8**). Powder. $[\alpha]_D^{32}$ −91.7° (MeOH; *c* 0.13). UV λ_{max}^{EtOH} nm (log ε): 201 (4.40), 225 (4.18), 317 (3.38). IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 2900, 1710, 1600, 1515, 1450, 1415, 1380, 1160, 1030, 840, 820. ^{1}H and ^{13}C NMR: see Tables 4 and 5. HR-FAB-MS *m/z*: found 631.2758 [M+Na]$^+$ ($C_{31}H_{44}O_{12}Na$ requires 631.2730), 455 [M−*O*-aglycone]$^+$, 445 [M−(*O*-rhamnosyl or *O*-coumaroyl)]$^+$, 309 [M−*O*-aglycone−(rhamnosyl or coumaroyl)+H]$^+$, 147 [rhamnosyl or coumaroyl]$^+$, 137 [aglycone]$^+$. Positive ion FAB-MS, *m/z*: 631 [M+Na]$^+$. (Found: C, 61.3; H, 7.1. $C_{31}H_{44}O_{12}$ requires: C, 61.2; H, 7.3%).

Lipedoside B-IV (**9**). Powder. $[\alpha]_D^{32}$ −78.1° (MeOH; *c* 0.09). UV λ_{max}^{EtOH} nm (log ε): 204 (4.10). IR ν_{max}^{KBr} cm^{-1}: 3400, 2980, 2920, 1640, 1080, 1040, ^{1}H and ^{13}C NMR: see Tables 4 and 5. HR-FAB-MS *m/z*: found 497.2534 [M+H]$^+$ ($C_{22}H_{41}O_{12}$ requires 497.2598), 309 [M−*O*-aglycone]$^+$, 187 [*O*-aglycone]$^+$, 147 [rhamnosyl]$^+$. Positive ion FAB-MS, *m/z*: 497 [M+H]$^+$. (Found: C, 53.3; H, 7.9. $C_{22}H_{40}O_{12}$ requires: C, 53.2; H, 8.1%).

Lipedoside B-V (**10**). Powder. [α] −85.1° (MeOH; *c* 0.29). UV λ_{max}^{EtOH} nm (log ε): 200 (4.42), 225 (4.20), 308 (4.01). IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 2900, 1710, 1600, 1515, 1450, 1415, 1400, 1150, 1030, 840, 820. ^{1}H and ^{13}C NMR: see Tables 4 and 5. HR-FAB-MS *m/z*: found 643.2932 [M+H]$^+$($C_{31}H_{47}O_{14}$ requires 643.2966), 665 [M+Na]$^+$, 479 [M−(*O*-rhamnosyl or *O*-coumaroyl)]$^+$, 455 [M−*O*-aglycone]$^+$, 309 [M−*O*-aglycone−(rhamnosyl or coumaroyl)+H]$^+$, 185 [aglycone−2H]$^+$, 147 [rhamnosyl or coumaroyl]$^+$. Positive ion FAB-MS, *m/z*: 643 [M+H]$^+$. (Found: C, 58.1; H, 7.2. $C_{31}H_{46}O_{14}$ requires: C, 57.9; H, 7.2%).

Lipedoside B-VI (**11**). Powder. $[\alpha]_D^{32}$ −102.3° (MeOH; *c* 0.10). UV λ_{max}^{EtOH} nm (log ε): 200 (4.18), 225 (4.30) and 309 (4.18). IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 2900, 1710, 1600, 1515, 1450, 1415, 1400, 1150, 1030, 840, 820. ^{1}H and ^{13}C NMR: see Tables 4 and 5. HR-FAB-MS *m/z*: found 643.2942 [M+H]$^+$ ($C_{31}H_{47}O_{14}$ requires 643.2966), 665 [M+Na]$^+$, 479 [M−(*O*-rhamnosyl or *O*-coumaroyl)]$^+$, 455 [M−*O*-aglycone]$^+$, 309 [M−*O*-aglycone−(rhamnosyl or coumaroyl)+H]$^+$, 185 [aglycone−2H]$^+$, 147 [rhamnosyl or coumaroyl]$^+$. Positive ion FAB-MS, *m/z*: 681 [M+Na]$^+$. (Found: C, 56.4; H, 7.1. $C_{31}H_{46}O_{14}$ requires: C, 57.9; H, 7.2%).

Linalool (**12a, b**). Oil. $[\alpha]_D^{30}$ +16.8° (MeOH; *c* 0.14). ^{1}H NMR (CD_3OD, 200 MHz): δ 5.83 (1H, *dd*, *J* = 17.5, 10.4 Hz, H-6), 5.09 (1H, *dd*, *J* = 17.5, 1.5 Hz, H-7b), 5.03 (1H, *dd*, *J* = 10.4, 1.5 Hz, H-7a), 4.77 (1H, *m*, H-4), 1.91 (2H, *m*, H_2-3), 1.50 (3H, *s*, H_3-8), 1.41 (3H, *s*, H_3-9), 1.27 (3H, *s*, H_3-10). ^{13}C NMR (CD_3OD, 75 MHz): δ 146.2 (C-6), 131.9 (C-5), 125.6 (C-4), 112.0 (C-7), 73.7 (C-1), 43.4 (C-2), 27.6 (C-9), 25.9 (C-8), 23.7 (C-3), 20.1 (C-10). FAB-MS, *m/z* ($C_{10}H_{18}O$): 153, 135, 93, 79. GC-MS: β-DEX 120 fused-silica capillary column, 30 m × 0.25 mm i.d. col. temp.: 220°, col. pres.: 125 kpa (He, 30 ml sec^{-1}), sample: 1 μl (split 80:1), R_t: 25.41 min. The linalool is a mixt. of **12a** and **b** (*R*:*S* = 13:87)[9].

Enzymatic hydrolysis of compound **6**. A mixt. of **6** (50 mg) and naringinase (120 mg) in citrate buffer (40 ml, pH 4) was stirred for 2 hr at 40°. The reaction mixt. was

extracted with Et_2O. The solvent was distilled off to give (*S*)-linalool (**12b**) containing 13% of (*R*)-linalool (**12a**), which was confirmed by $[\alpha]_D$, GC-MS [9]. The H_2O phase was neutralized with 0.1 M NaOH, then concd to give a residue, which was fractionated by silica gel CC with $CHCl_3$–MeOH–H_2O (14:6:1) to yield L-rhamnose (6.1 mg) and D-glucose (5.7 mg). L-Rhamnose: TLC, R_f 0.46 ($CHCl_3$–MeOH–H_2O, 14:6:1, 2 developments); $[\alpha]_D^{30}$ +7.8° (H_2O; *c* 0.16). D-Glucose: TLC, R_f 0.12 ($CHCl_3$–MeOH–H_2O, 14:6:1, 2 developments); $[\alpha]_D^{30}$ +41.3° (H_2O; *c* 0.08).

Alkaline hydrolysis of compound **7**. A soln of the glycoside (30.1 mg) in MeOH (3 ml) and 1 M NaOH (3 ml) was stirred for 3 hr at room temp. and neutralized with 5% HCl, then extracted with Et_2O and EtOAc. The Et_2O extract gave a *cis–trans* mixt. (molar ratio 1:2.5) of Me *p*-coumarate. The EtOAc extract was chromatographed on a silica gel column eluting with $CHCl_3$–MeOH (9:1) to afford **6** (14.2 mg).

Alkaline hydrolysis of compound **8**. A soln of the glycoside (30.5 mg) in MeOH (3 ml) and 1 M NaOH (3 ml) was stirred for 3 hr at room temp. and neutralized with 5% HCl, then extracted with Et_2O and EtOAc. The Et_2O extract gave a *cis–trans* mixt. (molar ratio 1:2.5) of Me *p*-coumarate. The EtOAc extract was chromatographed on a silica gel column eluting with $CHCl_3$–MeOH (9:1) to afford **6** (12.3 mg).

Alkaline hydrolysis of compound **10**. A soln of the glycoside (45.2 mg) in MeOH (3 ml) and 1 M NaOH (3 ml) was stirred for 3 hr at room temp. and neutralized with 5% HCl, then extracted with Et_2O and EtOAc. The Et_2O extract gave a *cis–trans* mixture of Me *p*-coumarate. The EtOAc extract was chromatographed on a silica gel column eluting with $CHCl_3$–MeOH (9:2) to afford **9** (18.3 mg).

Alkaline hydrolysis of compound **11**. A soln of the glycoside (43.9 mg) in MeOH (3 ml) and 1 M NaOH (3 ml) was stirred for 3 hr at room temp. and neutralized with 5% HCl, then extracted with Et_2O and EtOAc. The Et_2O extract gave a *cis–trans* mixt. of Me *p*-coumarate. The EtOAc extract was chromatographed on a silica gel column eluting with $CHCl_3$–MeOH (9:2) to afford **9** (16.3 mg)

Acknowledgements—We are grateful to Dr N. Akimoto, Faculty of Pharmaceutical Sciences, Kyoto University, for the determination of HR-FAB mass spectra, the members of the Microanalytical Center, Kyoto University for elemental analyses, Ms T. Terada, Institute for Chemical Research, Kyoto University, for determination of FAB mass spectra, Profs M. Shimada and T. Umezawa, Wood Research Institute, Kyoto University for providing the opportunity to use a β-DEX 120 fused-silica capillary column and Dr M. Yoshikura and Mr K. Ohsaki, San-Ei Gen F. F. I., Inc. for standard samples of (*R*) and (*S*)-linalool and for capillary column GC and GC-MS respectively.

REFERENCES

1. He, Z. D., Liu, Y. Q. and Yang, C. R. (1992) *Acta Bot. Yunnan* **14**, 328.
2. He, Z. D., Shi, Z. M. and Yang, C. R. (1990) *Acta Bot. Sinica* **32**, 544.
3. Kuwajima, H., Morita, M., Takaishi, K., Inoue, K., Fujita, T., He, Z. D. and Yang, C. R. (1992) *Phytochemistry* **31**, 1277.
4. Kobayashi, H., Karasawa, H., Miyase, T. and Fukushima, S. (1984) *Chem. Pharm. Bull.* **32**, 3880.
5. He, Z. D. and Yang, C. R. (1991) *Phytochemistry* **30**, 701.
6. Miyase, T., Ishino, M., Akahori, C., Ueno, A., Ohkawa, Y. and Tanizawa, H. (1991) *Phytochemistry* **36**, 2015.
7. Calis, I., Yuruker, A., Wright, A. D. and Sticher, O. (1991) *Planta Med.* **57**, Suppl. **2**, A80.
8. Calis, I., Yuruker, A., Ruegger, H., Wright, A. D. and Sticher, O. (1993) *Helv. Chim. Acta* **76**, 416.
9. Tanaka N., Sakai, H., Murakami, T., Saiki, Y., Chen, C. M. and Iitaka, Y. (1986) *Chem. Pharm. Bull.* **34**, 1015.
10. Williams, P. J., Strauss, C. R. and Wilson, B. (1980) *Phytochemistry* **19**, 1137.