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NEW MONOTERPENOID GLYCOSIDES FROM *LIGUSTRUM ROBUSTUM* *

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Abstract Four new monoterpenoid glycosides, named ligurobustosides D, G, H and L, were isolated from the leaves of *Ligustrum robustum*. On the basis of spectral and chemical methods, their structures were identified as geraniol 3′-O-α-*L*-rhamnopyranosyl-4′-*cis*-p-coumaroyl-β-*D*-glucopyranoside (**1**), 6-hydroxy-3,7-dimethyl-2E, 7-octadienyl-1-ol 3′-O-α-*L*-rhamnopyranosyl-4′-trans-p-coumaroyl-β-*D*-glucopyranoside (**2**), 6-hydroxy-3, 7-dimethyl-2E, 7-octadienyl-1-ol 3′-O-α-*L*-rhamnopyranosyl-4′-*cis*-p-coumaroyl-β-*D*-glucopyranoside (**3**) and 6,7-dihydroxy-3,7-dimethyl-2E-octaenyl-1-ol 3′-O-α-*L*-rhamnopyranosyl-4′-*cis*-p-coumaroyl-β-*D*-glucopyranoside (**4**), respectively. In addition, seven known compounds, apigenin (**5**), cosmosiin(**6**), rhoifolin(**7**), D-sorbitol(**8**), arteoside(**9**), β-sitosterol(**10**) and oleanolic acid (**11**) were also obtained.

Keywords *Ligustrum robustum*; monoterpenoid glycosides; Oleaceae

粗壮女贞中的新单萜配糖体

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摘 要 从粗壮女贞(*Ligustrum robustum*)叶子中分离鉴定了4个新的单萜配糖体,命名为粗壮女贞甙D、G、H和L.通过波谱及化学方法,它们分别鉴定为香叶醇3′-O-α-*L*-吡喃鼠李糖基-4′-顺式香豆酰基-β-*D*-吡喃葡萄糖甙(**1**),6-羟基-3,7-二甲基-2E,7-葵二烯醇3′-O-α-*L*-吡喃鼠李糖基-4′-反式香豆酰基-β-*D*-吡喃葡萄糖甙(**2**),6-羟基-3,7-二甲基-2E,7-葵二烯醇3′-O-α-*L*-吡喃鼠李糖基-4′-顺式香豆酰基-β-*D*-吡喃葡萄糖甙(**3**)以及6,7-二羟基-3,7-二甲基-2E-葵烯醇3′-O-α-*L*-吡喃鼠李糖基-4′-顺式香豆酰基-β-*D*-吡喃葡萄糖甙(**4**).此外,还从该植物得到了7个已知化合物,芹菜素(**5**)、cosmosiin(**6**)、rhoifolin(**7**)、山梨糖醇(**8**)、阿克苷(**9**)、β-谷甾醇(**10**)和齐墩果酸(**11**).

关键词 粗壮女贞;单萜配糖体;木樨科
中图法分类号 Q949.776.206 ; Q946.851

Ligustrum robustum (Roxb.) Bl. mainly distributes in southwestern China and its leaves have been used as tea with antiviral and antipyretic functions[1]. Primary investigation on this plant has led to the isolation of eight new monoterpenoid glycosides, ligurobustosides A, B, C, E, F, I, J and K[2], and in a continuation of studies on its minor constituents, four new monoterpenoid glycosides, ligurobustosides D, G, H and L, were obtained. This paper deals with the isolation and idenfication of those new compounds.

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1 Materials and Methods

1.1 Instruments and materials

The ^1H and ^{13}C-NMR spectra were measured at Bruker AM-400 spectrometer using TMS as internal standard. IR spectra (KBr) were recorded on Perkin-Elmer 577 spectrometer and UV spectra (EtOH) on UV 210 spectrometer. FAB-MS data were obtained on VG Auto Spec-3000 spectrometer and optical rotations (22℃) on JASCO-20 spectrometer. Paper chromatography (PC) was carried out on Whattman paper No.1 with n-BuOH-HOAc-H_2O (4:1:5, upper phase), the spots were visualized by spraying $C_6H_5NH_2$-*o*-$C_6H_4(CO_2H)_2$-n-BuOH(2:3:200). RP-18(Lobar, 40~63 μm, length: 250 mm, Merck) and MCI GEL resin(Mitsubishi Inc.) were used.

1.2 Extraction and isolation

Ligustrum robustum (Roxb.)Bl. was collected in Guiyang, Guizhou Province and its voucher specimen is deposited in the Herbarium of Kunming Institute of Botany. Extraction procedure was described in reference[2]. Compound **1** was first obtained as a mixture with ligurobustoside C. After $AgNO_3$ silica gel column chromatography, **1** was separated with ligurobustoside C. Compounds **2** and **3** were also obtained as a mixture. After repeated column chromatography on silica gel and reversed phase materials(RP-18 silica gel and MCI Gel resin), both of the two compounds were finally purified by $AgNO_3$ silica gel column chromatography. Using the same method, compound **4** was separated from ligurobustoside K.

1.3 Acid hydrolysis

Compounds **1**, **2**, **3** and **4** were hydrolyzed with 1mol/L H_2SO_4 in φ(EtOH) = 10% water solution under reflux for 2 hours, repectively. Each reaction mixture was neutralized with a saturated solution of $NaHCO_3$ and then concentrated to dryness. The residue was used for PC analysis, in which D-glucose and L-rhamnose were detected in the four compounds by comparison with authentic samples.

1.4 Physical and chemical data

Ligurobustoside D(**1**) white amorphous powder, $C_{31}H_{44}O_{12}$, $[\alpha]_D$ = -64.7°(*c* = 0.032, MeOH). FAB-MS (positive ion) *m/z*: 631[M + Na]$^+$, 455[M-Oaglycone]$^+$, 309[M-O-aglycone-(rhamnosyl or *cis*-p-coumaroyl) + H]$^+$. UVλ_{max} (logε)/nm: 216(4.57), 280.5(4.34), 299(4.53), 314(4.32). IRν_{max}/cm^{-1}: 3400(br), 2905, 1640, 1595, 1505, 1435, 1370, 1325, 1160, 1030, 825. ^1H and ^{13}C-NMR spetra: see Tables 1 and 2.

Ligurobustoside G(**2**) white amorphous powder, $C_{31}H_{44}O_{13}$, $[\alpha]^D$ = -72.6°(*c* = 0.041, MeOH). FAB-MS (positive ion) *m/z*: 647[M + Na]$^+$, 471[M-Oaglycone]$^+$, 315[M-Oaglycone-(rhamnosyl or trans-p-coumaroyl) + H]$^+$. UVλ_{max} (logε)/nm: 204(4.67), 214.5(4.64), 332(4.51). IRν_{max}/cm^{-1}: 3450(br), 2905, 1680, 1595, 1510, 1435, 1370, 1325, 1160, 1030, 825. ^1H and ^{13}C-NMR spetra: see Tables 1 and 2.

Ligurobustoside H(**3**) white amorphous powder, $C_{31}H_{44}O_{13}$, $[\alpha]_D$ = -67.3°(*c* = 0.038, MeOH). FAB-MS (positive ion) *m/z*: 647[M + Na]$^+$, 471[M-O-aglycone]$^+$, 315[M-O-aglycone-(rhamnosyl or *cis*-p-coumaroyl) + H]$^+$. UVλ_{max} (logε)/nm: 215(4.57), 280.5(4.34), 298.5(4.55). IRν_{max}/cm^{-1}: 3400(br), 2905, 1645, 1590, 1505, 1435, 1370, 1325, 1160, 1030, 825. ^1H and ^{13}C-NMR spetra: see Tables 1 and 2.

Ligurobustoside L(**4**) white amorphous powder, $C_{31}H_{46}O_{14}$, $[\alpha]_D$ = -61.5°(*c* = 0.022, MeOH). FAB-MS (negative ion) *m/z*: 641[M-H]$^-$, 623[M-H_2O-H]$^-$, 495[M-(rhamnosyl or *cis*-p-coumaroyl)]$^-$, 325[M-(rhamnosyl or *cis*-p-coumaroyl)-O-aglycone]$^-$. UVλ_{max}(logε)/nm: 216(4.57), 280.5(4.34), 299(4.53). IRν_{max}/cm^{-1}: 3400(br), 2905, 1650, 1595, 1505, 1435, 1370, 1325, 1160, 1030, 825, 805. ^1H and ^{13}C-NMR spectra: see Tables 1 and 2.

Apigenin(**5**) yellow amorphous powder, $C_{15}H_{10}O_5$. FAB-MS (positive ion) *m/z*: 271[M + H]$^+$. UVλ_{max}/nm: 203.5, 266.5, 335. IRν_{max}/cm^{-1}: 3350, 1650, 1605, 1480, 1280, 1190, 835. ^1H-NMR (DMSO-d_6) δ: 6.72(1H, s, H-3), 6.46(1H, d, *J* = 2.2 Hz, H-6), 6.18(1H, d, *J* = 2.2 Hz, H-8), 7.89(2H, d, *J* = 8.8 Hz, H-2',6'), 6.91 (2H, d, *J* = 8.8 Hz, H-3',5'), 12.92(1H, s, 5-OH), 10.71(1H, brs, 7-OH), 10.33(1H, brs, 4'-OH). ^{13}C-NMR

(DMSO-d_6)δ: 164.1(C-2), 102.9(C-3), 181.7(C-4), 161.1(C-5), 98.8(C-6), 163.7(C-7), 93.9(C-8), 157.2 (C-9), 103.9(C-10), 121.2(C-1'), 128.4(C-2',6'), 115.9(C-3',5'), 161.4(C-4')[4].

Cosmosiin(6) yellow amorphous powder, $C_{21}H_{20}O_{10}$. FAB-MS (positive ion) m/z: 433[M + H]$^+$, 271[M-glc + H]$^+$. UVλ_{max}(logε)/nm: 204(4.11), 269(3.97), 336.5(3.95). IRν_{max}/cm^{-1}: 3400, 1650, 1600, 1585, 1490, 1340, 1290, 1180, 830. ^{1}H-NMR(DMSO-d_6)δ: 6.86(1H, s, H-3), 6.82(1H, d, J = 2.2 Hz, H-6), 6.43(1H, d, J = 2.2 Hz, H-8), 7.95(2H, d, J = 8.6 Hz, H-2',6'), 6.93(2H, d, J = 8.6 Hz, H-3',5'), 5.06(1H, d, J = 7.2 Hz, glc H-1), 12.95(1H, s, 5-OH), 10.46(1H, brs, 4'-OH). ^{13}C-NMR(DMSO-d_6)δ: 164.3(C-2), 103.1(C-3), 181.9(C-4), 161.1(C-5), 99.5(C-6), 162.9(C-7), 94.8(C-8), 156.9(C-9), 105.3(C-10), 121.0(C-1'), 128.6 (C-2',6'), 116.0(C-3',5'), 161.3(C-4'), 100.0(glc C-1), 73.1(glc C-2), 77.2(glc C-3), 69.6(glc C-4), 76.4 (glc C-5), 60.6(glc C-6)[3].

Table 1 ^{1}H-NMR spectral data of glycosides 1 ~ 4 in CD_3OD

	1		2		3		4	
H	δ	J/Hz	δ	J/Hz	δ	J/Hz	δ	J/Hz
Aglycone								
1a	4.34dd	11.9,6.0	4.26d	6.9	4.26d	6.9	4.30d	7.6
1b	4.27dd	11.9,6.0						
2	5.37t	6.0	5.40t	6.9	5.40t	6.9	5.44t	7.6
4	2.05t	6.6	2.10m		2.10m		2.31m	
							2.11m	
5		2.11t	6.5	1.67m		1 67m		1.75m
							1.39m	
6	5.10t	6.2	3.98t	6.5	3.98t	6.5		
7							4.38m	
8	1.69s		4.92d	1.6	4.92d	1.6	1.18s	
			4.82d	1.6	4.82d	1.6		
9	1.61s	1 70s		1.70s		1.14s		
10	1.69s		1.68s		1.68s		1.71s	
Glucosyl								
1'	4.36d	7.9	4.36d	8.0	4.36d	8.0	4.36d	8.0
2'	3.29t	8.2	3.54m	9.2	3.54m		3.28t	8.0
3'	3.75t	9.2	3.81t		3.75t	9.2	3.76t	9.2
4'	3.58m		4.92t	9.2	4.92t		3.58m	
5'	3.56m		3.38m		3.38m		3.55m	
6'	3.52m		3.52m		3.52m		3.52m	
Rhamnosyl								
1"	5.18d	1.5	5.18brs		5.18brs		5.18d	1.5
2"	3.91dd	3.2,1.8	3.91brs		3.91brs		3.90m	
3"	3.62m		3.59m		3.59m		3.56m	
4"	3.39t	8.8	3.40t	8.8	3.40t	8 8	3.40t	7.8
5"	3.30m		3.99t	6.4	3.99t	6 4	3.30m	
6"	1.15d	6.2	1.07d	6.0	1.15d	6.0	1.15d	6.3
Acyl moiety								
2,6	7.72d	8.7	7.46d	8.0	7.71d	8.0	7.71d	8.6
3,5	6.76d	8.7	6.80d	8.0	6.75d	8.0	6.75d	8.6
7	6.63d	12.8	7.66d	15.9	6 94d	12.8	6.94d	12.9
8	5.79d	12.8	6.34d	15.9	5.78d	12.8	5.78d	12.9

Rhoifolin(7) yellow amorphous powder, C27H30O14. FAB-MS (positive ion) m/z: 579[M + H]$^+$, 433[M-rha + H]$^+$, 271[M-rha-glc + H]$^+$. UVλ_{max}(logε)/nm: 205(4.51), 267(4.27), 335.5(4.36). IRν_{max}/cm^{-1}: 3400, 1650, 1590, 1575, 1480, 1340, 1295, 1180, 820. ^{1}H-NMR(DMSO-d_6)δ: 6.85(1H, s, H-3), 6.76(1H, d, J = 2.0 Hz, H-6), 6.44(1H, d, J = 2.0 Hz, H-8), 7.93(2H, d, J = 8.6 Hz, H-2',6'), 6.94(2H, d, J = 8.6 Hz, H-3',5'), 5.05(1H, d, J = 7.2 Hz, glc H-1), 4.54(1H, brs, rha H-1), 1.06(3H, d, J = 6.0 Hz, rha H-6), 12.95(1H, s, 5-

OH), 10.44(1H, brs, 4'-OH). ^{13}C-NMR(DMSO-d_6)δ: 164.4(C-2), 103.1(C-3), 182.0(C-4), 161.2(C-5), 99.5(C-6), 162.9(C-7), 94.8(C-8), 156.9(C-9), 105.4(C-10), 121.1(C-1'), 128.6(C-2',6'), 116.1(C-3',5'), 161.3(C-4'), 100.5(glc C-1), 73.1(glc C-2), 76.3(glc C-3), 68.3(glc C-4), 75.7(glc C-5), 66.1(glc C-6), 100.0(rha C-1), 70.4(rha C-2), 70.8(rha C-3), 70.1(rha C-4), 69.6(rha C-5), 17.8(rha C-6)[6].

D-sorbitol(**8**) colorless crystals(from MeOH), mp 161 ~ 162℃, $C_6H_{14}O_6$. FAB-MS (positive ion) m/z: 183 $[M+H]^+$, 152 $[M-CH_2OH]^+$, 121. ^{13}C-NMR(D_2O)δ: 76.1(C-3), 74.5(C-4), 72.1(C-2,5), 65.8(C-1,6)[7].

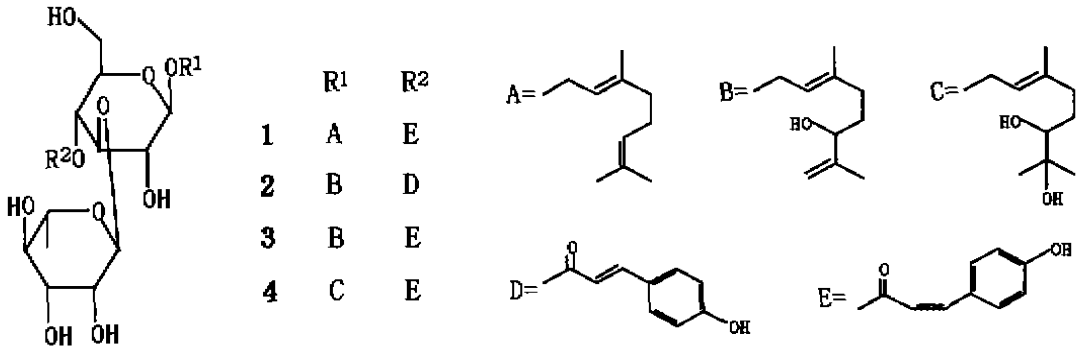
Acleoside(**9**) white amorphous powder, $C_{29}H_{36}O_{15}$. FAB-MS (positive ion) m/z: 647 $[M+Na]^+$, 625 $[M+H]^+$, 479 $[M-rha+H]^+$, 471 $[M-C_8H_9O_3]^+$. UVλ_{max}(logε)/nm: 220(4.22), 247(3.92), 292(4.00), 304(4.04), 335(4.17). IR(ν_{max}/cm^{-1}): 3400, 2920, 1690, 1600, 1515, 1480, 1280, 1160, 1040, 810. ^{1}H-NMR(CD_3OD)δ: 6.68(1H, d, J = 2.0 Hz, 2-H), 6.67(1H, d, J = 8.0 Hz, 5-H), 6.55(1H, dd, J = 8.0, 2.0 Hz, H-6), 2.78(2H, dt, J = 8.0, 2.0 Hz, H-8), 3.71(1H, dd, J = 12.0, 8.0 Hz, 7-Ha), 4.02(1H, dd, J = 8.0, 6.0 Hz, 7-Hb), 7.05(1H, d, J = 2.0 Hz, H-2'), 6.76(1H, d, J = 8.0 Hz, H-5'), 6.94(1H, dd, J = 8.0, 2.0 Hz, H-6'), 7.58(1H, d, J = 16.0 Hz, H-7'), 6.26(1H, d, J = 16.0 Hz, H-8'), 4.36(1H, d, J = 7.8 Hz, glc H-1), 5.18(1H, d, J = 1.6 Hz, rha H-1), 1.08(3H, d, J = 6.0 Hz, rha H-6). ^{13}C-NMR(CD_3OD)δ: 131.6(C-1), 116.4(C-2), 144.6(C-3), 146.1(C-4), 117.1(C-5), 121.3(C-6), 36.5(C-7), 72.2(C-8), 127.7(C-1'), 112.0(C-2'), 146.8(C-3'), 149.7(C-4'), 116.6(C-5'), 123.2(C-6'), 168.3(C-7'), 115.2(C-8'), 148.0(C-9'), 104.2(glc C-1), 76.0(glc C-2), 81.6(glc C-3), 70.7(glc C-4), 76.0(glc C-5), 62.4(glc C-6), 103.0(rha C-1), 70.1(rha C-2), 75.6(rha C-3), 71.0(rha C-4), 70.7(rha C-5), 18.5(rha C-6)[8].

Table 2 ^{13}C-NMR spectral data of glycosides 1 ~ 4 in CD_3OD

C	1	2	3	4
Aglycone				
1	66.5	66.7	66.7	66.6
2	121.4	1121 6	121 6	121.6
3	142.1	141.9	141 9	142.3
4	40.6	36.3	36.6	37 7
5	27.4	34.2	34 2	30.4
6	125.0	76.1	76.1	78.9
7	132 5	148 8	148.8	73.8
8	25.9	111.5	111.5	25.7
9	17.8	30 0	30.0	25.0
10	16.5	16.6	16.6	16.6
Glucosyl				
1'	102.9	102.9	102.9	102.8
2'	76.1	76.1	76.1	76.1
3'	81.8	81.6	81.8	81.8
4'	70.6	70.8	70.6	70.6
5	76.1	76.1	76.1	76.1
6'	62.5	62.5	62.5	62.5
Rhamnosyl				
1''	102.6	102.9	102.9	102.9
2''	72.3	72.3	782.3	72.3
3''	72.1	72.2	72 2	72.1
4''	73.8	73.9	73.9	73.8
5''	70.4	70 4	70.4	70.4
6''	18.2	18.4	17.7	18.2
Acyl moiety				
1	127.6	127.2	127.5	127.6
2,6	134.2	131.3	134.1	134.1
3,5	115.8	116.9	115.8	115.8
4	160.6	161.4	160.2	160.3
7	147.1	147.6	147.1	147.2
8	115.9	114.9	116.1	116.0
CO	167.0	168.3	166.9	166 9

β-sitosterol(**10**), colorless needles(from acetone), mp 137 ~ 138℃, $C_{29}H_{50}O$. ^{1}H-NMR ($CDCl_3$)δ: 3.50(1H, m, 3α-H), 5.33(1H, brd, J = 5.2 Hz, H-6), 2.25(2H, m, H-4), 0.98, 0.63(6H, s, 2 × CH_3), 0.90(3H, d, J = 6.6 Hz, -CH_3), 0.81(6H, d, J = 7.1 Hz, 2 × CH_3), 0.80(3H, t, J = 6.8 Hz, -CH_3). ^{13}C-NMR($CDCl_3$)δ: 140.8(C-5), 121.7(C-6), 71.8(C-3), 56.9(C-14), 56.2(C-17), 50.3(C-9), 46.0(C-4), 42.4(C-13), 39.9(C-12), 37.3(C-24), 36.6(C-1), 36.2(C-10), 34.1(C-22), 32.0(C-20), 32.0(C-8), 31.7(C-7), 29.7(C-2), 29.3(C-16), 28.3(C-11), 26.3(C-15), 24.3(C-23), 23.2(C-27), 21.1(C-28), 19.8(C-19), 19.4(C-21), 19.1(C-25), 18.8(C-29), 12.0(C-26), 11.9(C-18).

Oleanolic acid(**11**) white amorphous powder, $C_{30}H_{48}O_3$. ^{1}H-NMR(C_5D_5N)δ: 5.48 (1H, brs, H-12), 3.45(1H, dd, J = 10.2, 6.2 Hz, H-3), 1.30, 1.25, 1.04, 0.96, 0.88(21H, s, 7 × CH_3). ^{13}C-NMR(C_5D_5N)δ: 180.6(C-28), 143.6(C-13), 122.6(C-12), 79.0(C-3), 55.2(C-5), 47.6(C-9), 46.5(C-17), 45.8(C-19), 41.5(C-14), 40.9(C-18), 39.2(C-8), 38.7(C-4), 38.3(C-1), 37.0(C-10), 33.7(C-21), 33.0(C-29), 32.6(C-7), 32.4(C-22), 30.7(C-20), 28.1(C-23), 27.6(C-15), 27.1(C-2), 25.9(C-27), 23.6(C-30), 23.4(C-16), 22.8(C-11), 18.2(C-6), 17.1(C-26), 15.5(C-24), 15.3(C-25)[9].



2 Results and Discussion

Ligurobustoside D(**1**) was obtained as an amorphous powder. Its IR(1640, 1595, 1505, 1435 cm^{-1}) and UV(216, 280.5, 299, 314 nm) showed the absorptions of aromatic group and α,β-unsaturated ester. **1** was hydrolyzed with 1 mol/l H_2SO_4 in φ(EtOH) = 10% water solution and followed by paper chromatography detection showing the presence of L-rhamnose and D-glucose. The molecular formula ($C_{31}H_{44}O_{12}$) of **1** was determined by the positive ion FAB-MS spectrum, in which the molecular ion peak at m/z 631[M + Na]$^+$, and fragment ion peaks at m/z 455[M-O-aglycone]$^+$, 309[M-O-aglycone -(rhamnosyl or *cis*-p-coumaroyl) + H]$^+$ were exhibited. The ^{1}H-NMR (δ4.36, d, J = 7.9 Hz; 5.18, d, J = 1.5 Hz) and ^{13}C-NMR(δ102.9, 102.6; two anomeric sugar carbons) spectra further confirmed the existence of β-*D*-glucose and α-*L*-rhamnose. Direct comparison of its NMR data with those of ligurobustoside C suggested that **1** had the same aglycone (geraniol) and sugars (β-*D*-glucopyranose and α-*L*-rhamnopyranose), but different acyl moiety with ligurobustoside C. The ^{1}H-NMR spectrum at the aromatic region showed an A_2B_2 system belonging to a p-coumaroyl moiety [δ6.76(2H, d, J = 8.4 Hz), 7.72(2H, d, J = 8.4 Hz)]. Two olefinic proton signals which appeared as an AB system [δ5.79(1H, d, J = 12.8 Hz), 6.93(1H, d, J = 12.8 Hz)] indicated a *cis*-geometry in the p-coumaroyl moiety. Thus, the structure of **1** was established as geraniol 3′-O-α-*L*-rhamnopyranosyl-4′-*cis*-p-coumaroyl-β-*D*-glucopyran oside.

Interestingly, it was noted that **1** was unstable under light and was slowly converted to a trans isomer (ligurobustoside C). We could not get the pure compound of **1** until $AgNO_3$ silica gel column chromatography was carried out in the dark. This phenomenon had been reported[3] and we inferred that from a *cis*-p-coumaroyl moiety to a trans-p-coumaroyl one might be involved in a mechanism of free radical reaction.

Ligurobustoside G(**2**) was obtained as an amorphous powder. Its formula ($C_{31}H_{44}O_{13}$) was provided by the positive ion FAB-MS spectrum {647[M + Na]$^+$, 471[M-O-aglycone]$^+$, 315[M-O-aglycone-(rhamnosyl or trans-p-coumaroyl) + H]$^+$} and NMR spectra. After acidic hydrolysis of **2**, D-glucose and *L*-rhamnose were detected by paper chromatography. The UV (204, 214.5, 332 nm) and IR (1680, 1595, 1510, 1435, 1370, 1325, 1160, 1030 cm^{-1}) spectra of **2** suggested the presence of double bonds and conjugated aromatic ester group. Comparing the ^{1}H and ^{13}C NMR signals of **2** with those of ligurobustoside C, we could conclude that both two compounds contained identical parts: a trans-p-coumaroyl moiety and two sugar units (β-*D*-glucose and α-*L*-rhamnose), that was, rhamnose was still connected with C-3′ position of the inner glucose, while the coumaroyl moiety was also located at the C-4′ position of the inner glucose, but they had different aglycones. In the ^{1}H-NMR spectrum of the aglycone of **2**, an AB system assignable to a pair of terminal methylene olefinic protons [δ4.92(1H, d, J = 1.6 Hz), 4.82(1H, d, J = 1.6 Hz)], one olefinic methine proton [δ5.40(1H, t, J = 6.9 Hz)] and one allyl-methine proton [δ3.98(2H, t, J = 6.9 Hz)] were exhibited. Crrespondingly, in the ^{13}C NMR spectrum of the aglycone of **2**, double bond signals (δ111.5t, 148.8s) and one methine carbon signal (δ76.1d) bearing one hydroxyl group appeared, while another double bond signals (δ125.0d, 132.5s) and one methyl carbon signal (δ17.9) disappeared compared with the aglycone of ligurobustoside C. The aglycone of **2** had one more hydroxyl group than

that of ligurobustoside C, and this additional hydroxy was easily assigned at C-6 position of the aglycone, but its stereochemistry was not determined finally. Such assignments were further supported by direct comparison with the aglycone of ligurobustoside F. Thus, the structure of **2** was elucidated to be 6-hydroxy-3,7-dimethyl-2E,7-octadienyl-1-ol 3′-O-*α*-*L*-rhamnopyranosyl-4′-trans-p-coumaroyl-*β*-*D*-glucopyranoside.

Ligurobustoside H(**3**) was also obtained as an amorphous powder. Its ^1H and ^{13}C NMR spectral data were very similar to those of **2**. Both **3** and **2** were isomers due to the same molecular ion peak at *m/z* 647[M + Na]$^+$ in the positive ion FAB-MS spectra. The difference between **3** and **2** was attributed to the acyl moiety. The ^1H-NMR spectrum (an A_2B_2 system at *δ*6.75 and 7.71, 2H each, a pair of doublets, J = 8.8 Hz; an AB system at *δ*5.78 and 6.94, 1H each, a pair of doublets, J = 12.8 Hz) confirmed that the acyl moiety was a *cis*-p-coumaroyl one. The acidic hydrolysis of **3** also provided D-glucose and L-rhamnose. Thus, the structure of **3** was identified as 6-hydroxy-3,7-dimethyl-2E,7-octadienyl-1-ol 3′-O-*α*-*L*-rhamnopyranosyl-4′-*cis*-p-coumaroyl-*β*-*D*-glucopyranoside.

Ligurobustoside L(**4**), an amorphous powder, was analyzed for $C_{31}H_{46}O_{14}$ from its negative ion FAB-MS spectrum(*m/z*: 641[M-H]-, 623, 495 and 325). Its UV and IR spectra showing little difference with ligurobustosides A-K also confirmed it was a monoterpenoid glycoside of the same kind. By direct comparison of its NMR spectral data with those of ligurobustoside K, both had the same sections: two sugar units (*β*-*D*-glucose and *α*-*L*-rhamnose) detected by acidic hydrolysis and monoterpenoid aglycone(6,7-dihydroxy-3,7-dimethyl-2E-octaenyl-1-ol), and their only difference was the acyl moiety. Both **4** and ligurobustoside K were isomers for they had the same molecular formula. Based on the 1H-NMR spectrum (an A2B2 system at *δ*6.75 and 7.71, 2H each, a pair of doublets, J = 8.8 Hz; an AB system at *δ*5.78 and 6.94, 1H each, a pair of doublets, J = 12.8 Hz) and ^{13}C-NMR spectrum (*δ*134.1d, 115.8d; 147.2d, 116.0d and *α*, *β*-unsaturated carbonyl group: *δ*166.9s) of **4**, its acyl moiety was readily determined as a *cis*-p-coumaroyl group. Thus, *the structure of* **4** *was identified as* 6, 7-*dihydroxy*-3, 7-*dimethyl*-2E-*octaenyl*-1-ol 3′-O-*α*-*L*-*rhamnopyranosyl*-4′-*cis*-p-coumaroyl-*β*-*D*-glucopyranoside.

In addition, the structures of seven known compounds, apigenin(**5**), cosmosiin(**6**), rhoifolin(**7**), D-sorbitol(**8**), acteoside(**9**), *β*-sitosterol(**10**) and oleanolic acid (**11**), were confirmed by comparison with the spectral datra reported.

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