

中国科学院昆明植物研究所
植物化学开放研究实验室

论文汇编

(1998年)

COLLECTED RESEARCH PAPERS

LABORATORY OF PHYTOCHEMISTRY,
KUNMING INSTITUTE OF BOTANY,
ACADEMIA SINICA



云南科技出版社

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中国科学院昆明植物研究所
植物化学开放研究实验室
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绪 言

本汇编收集了 1998 年植物化学开放研究实验室在国内外各类刊物中发表的 50 余篇论文。本汇编收集的论文是全室研究技术人员和客座研究人员、访问学者、合作研究的国内外专家以及全体研究生们通力合作、团结进取、钻研拼搏的成果。在编辑过程中，得到了作者及相关人员的大力支持和帮助，在此编者谨向所有支持和关心这本《中国科学院昆明植物研究所植物化学开放实验室论文汇编(1998)》印刷出版的同志，表示衷心感谢！

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1999 年 6 月

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MONOTERPENOID GLYCOSIDES FROM *LIGUSTRUM ROBUSTUM*

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Key Word Index—*Ligustrum robustum*; Oleaceae; monoterpene glycosides; ligustrobustosides A, B, C, E, F, I, J and K.

Abstract—Eight new monoterpene glycosides named ligustrobustosides A, B, C, E, F, I, J and K were isolated from the leaves of *Ligustrum robustum*. Their structures were established as geraniol (3'-O- α -L-rhamnopyranosyl- β -D-glucopyranoside), geraniol (3'-O- α -L-rhamnopyranosyl-4'-caffeoyle- β -D-glucopyranoside), geraniol (3'-O- α -L-rhamnopyranosyl-4'-p-coumaroyl- β -D-glucopyranoside), geraniol (3'-O- α -L-rhamnopyranosyl-6'-O-p-coumaroyl- β -D-glucopyranoside), 6-hydroxy-3,7-dimethyl-2E,7-octadienyl-(3'-O- α -L-rhamnopyranosyl-6'-O-p-coumaroyl- β -D-glucopyranoside), 7-hydroxy-3,7-dimethyl-2E,5E-octadienyl-(3'-O- α -L-rhamnopyranosyl-4'-O-p-coumaroyl- β -D-glucopyranoside), geraniol-[(3''-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl)-(4'-O-p-coumaroyl- β -D-glucopyranoside)], 6,7-dihydroxy-3,7-dimethyl-2E-octadienyl-(3'-O- α -L-rhamnopyranosyl-4'-O-p-coumaroyl- β -D-glucopyranoside) respectively, by spectroscopic and chemical methods. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Ligustrum robustum has long been used as the replacement of tea and it possesses activity against inflammation and influenza [1]. Some monoterpene glycosides have been isolated from the genus *Ligustrum* [2], but there is no report concerning the chemical study on this plant up to now. From the glycosidic extract of the leaves of *L. robustum*, we have isolated eight new monoterpene glycosides. Interestingly, all their aglycones were elucidated to be geraniol or its derivatives rather than phenylethanoids, but p-coumaroyl (or caffeoyle) group was still acting as their aromatic ester moieties, except in the case of ligustrobustoside A. This paper describes the isolation and identification of all these new compounds, ligustrobustosides A (1), B (2), C (3), E (4), F (5), I (6), J (7) and K (8).

RESULTS AND DISCUSSION

A combination of silica gel column chromatography and reversed-phase silica gel column chromatography led to the isolation of compound 1–8. Ligustrobustoside A (1), was obtained as an amorphous powder. Its IR spectrum (3400, 1595, 1440 and

1030 cm^{-1}) only indicated the presence of double bonds and hydroxyls. The molecular formula ($\text{C}_{22}\text{H}_{38}\text{O}_{10}$) of 1 was determined by the positive ion FAB-mass spectrum, in which the molecular ion peak at m/z 485 $[\text{M} + \text{Na}]^+$ and fragment ion peak at m/z 309 $[\text{M} - \text{C}_{10}\text{H}_{17}\text{O}]^+$ were exhibited. The ^1H NMR (δ 4.28, d , $J = 7.9$ Hz; 5.14, d , $J = 1.5$ Hz) and ^{13}C NMR (δ 102.7, 102.8: two anomeric sugar carbons) spectra showed the existence of two sugar units. Direct comparison of its NMR data with those of cistanoside [3] and paper chromatography detection suggested that 1 had the following structure: aglycone-Glc-Rha. The difference between 1 and cistanoside was only the aglycone. From the remaining sets of 10 carbon signals assignable to the aglycone of 1, the monoterpene was easily proved to be geraniol. ^1H - ^1H COSY spectrum indicated two discrete spin systems characteristics of geraniol. Both systems each contained an olefinic proton, the one (δ_{H} 5.36) coupled with the non-equivalent geminal protons of an oxygen-bearing methylene group, and the other (δ_{H} 5.10) to a methylene group which in turn coupled with another vinylic methylene group (Table 1). The ^{13}C NMR chemical shifts are in good agreement with those reported for geraniol glycoside [4] and geraniol [5], the latter, with the expected differences at C-1, C-2 and C-3. The possibility of the aglycone being nerol is excluded by the chemical shifts of C-4 and C-9 [6]. GC-mass spectral analysis unambiguously identified the aglycone as

* Author to whom correspondence should be addressed.

Table 1. ¹H NMR spectral data of glycosides 1–8 in CD₃OD

H	1	2	3	4	5	6	7	8
Aglycone								
1	4.33 <i>dd</i> (11.9, 6.3) 4.25 <i>dd</i> (11.9, 7.7)	4.33 <i>dd</i> (11.8, 6.2) 4.26 <i>dd</i> (11.8, 7.6)	4.34 <i>dd</i> (11.9, 6.1) 4.27 <i>dd</i> (11.9, 7.5)	4.25 <i>d</i> (7.0)	4.26 <i>d</i> (6.8)	4.28 <i>d</i> (7.2)	4.28 <i>d</i> (7.4)	4.30 <i>d</i> (7.6)
2	5.36 <i>t</i> (6.8)	5.37 <i>t</i> (6.5)	5.37 <i>t</i> (6.0)	5.34 <i>t</i> (7.0)	5.36 <i>t</i> (6.8)	5.21 <i>t</i> (7.2)	5.37 <i>t</i> (7.4)	5.44 <i>t</i> (7.6)
4	2.04 <i>t</i> (7.0)	2.04 <i>t</i> (6.8)	2.05 <i>t</i> (6.6)	2.02 <i>t</i> (6.4)	2.08 <i>m</i>	2.76 <i>br d</i> (4.8)	2.06 <i>t</i> (6.4)	2.31 <i>m</i> 2.11 <i>m</i>
5	2.12 <i>t</i> (7.0)	2.11 <i>t</i> (6.3)	2.11 <i>t</i> (6.5)	2.07 <i>t</i> (6.4)	1.65 <i>m</i>	5.62 <i>dt</i> (9.8, 4.8)	2.12 <i>t</i> (6.4)	1.75 <i>m</i> 1.39 <i>m</i>
6	5.10 <i>t</i> (6.4)	5.09 <i>t</i> (6.9)	5.10 <i>t</i> (6.2)	5.07 <i>t</i> (6.4)	4.00 <i>dd</i> (9.6, 6.4)	4.86 <i>d</i> (9.8)	5.12 <i>t</i> (6.2)	
7								4.38 <i>m</i>
8	1.67 <i>s</i>	1.68 <i>s</i>	1.69 <i>s</i>	1.64 <i>s</i>	4.90 <i>d</i> (1.6) 4.79 <i>d</i> (1.6)	1.29 <i>s</i>	1.68 <i>s</i>	1.18 <i>s</i>
9	1.60 <i>s</i>	1.60 <i>s</i>	1.61 <i>s</i>	1.57 <i>s</i>	1.68 <i>s</i>	1.29 <i>s</i>	1.61 <i>s</i>	1.14 <i>s</i>
10	1.68 <i>s</i>	1.68 <i>s</i>	1.69 <i>s</i>	1.64 <i>s</i>	1.65 <i>s</i>	1.68 <i>s</i>	1.68 <i>s</i>	1.71 <i>s</i>
Glucosyl								
1'	4.28 <i>d</i> (7.9)	4.33 <i>d</i> (7.6)	4.36 <i>d</i> (7.9)	4.31 <i>d</i> (8.1)	4.31 <i>d</i> (8.1)	4.39 <i>d</i> (7.6)	4.36 <i>d</i> (7.8)	4.36 <i>d</i> (8.0)
2'	3.30 <i>t</i> (8.2)	3.30 <i>m</i>	3.29 <i>t</i> (8.2)	3.32 <i>t</i> (8.4)	3.31 <i>d</i> (8.4)	3.30 <i>t</i> (9.2)	3.30 <i>t</i> (8.0)	3.28 <i>t</i> (8.2)
3'	3.48 <i>t</i> (8.8)	3.81 <i>t</i> (9.2)	3.80 <i>t</i> (9.2)	3.52 <i>t</i> (9.0)	3.52 <i>d</i> (8.8)	3.81 <i>t</i> (9.2)	3.80 <i>t</i> (9.0)	3.82 <i>t</i> (9.2)
4'	3.34 <i>t</i> (8.4)	3.58 <i>m</i>	3.58 <i>m</i>	3.39 <i>t</i> (9.2)	3.39 <i>t</i> (9.3)	3.58 <i>m</i>	3.58 <i>m</i>	3.58 <i>m</i>
5'	3.25 <i>m</i>	3.55 <i>m</i>	3.56 <i>m</i>	3.52 <i>t</i> (8.8)	3.52 <i>t</i> (8.8)	3.55 <i>m</i>	3.56 <i>m</i>	3.55 <i>m</i>
6'	3.87 <i>dd</i> (12.0, 2.1) 3.69 <i>dd</i> (12.0, 2.1)	*	*	4.36 <i>dd</i> (10.8, 6.4) 4.50 <i>d</i> (10.8)	4.36 <i>dd</i> (10.4, 6.2) 4.50 <i>d</i> (10.4)	3.60 <i>m</i>	3.62 <i>m</i>	3.60 <i>m</i>
Rham- nosyl								
1''	5.14 <i>d</i> (1.5)	5.18 <i>d</i> (1.7)	5.18 <i>d</i> (1.5)	5.17 <i>d</i> (1.6)	5.17 <i>d</i> (1.4)	5.18 <i>br s</i>	5.03 <i>br s</i>	5.18 <i>d</i> (1.5)
2''	3.93 <i>dd</i> (3.2, 1.8)	3.92 <i>dd</i> (3.2, 1.8)	3.91 <i>dd</i> (3.2, 1.8)	3.94 <i>t</i> (3.3)	3.94 <i>t</i> (3.3)	3.91 <i>m</i>	3.90 <i>m</i>	3.90 <i>m</i>
3''	3.67 <i>m</i>	3.60 <i>m</i>	3.62 <i>m</i>	3.70 <i>dd</i> (9.4, 3.3)	3.70 <i>dd</i> (9.6, 3.3)	3.57 <i>m</i>	3.55 <i>m</i>	3.56 <i>m</i>
4''	3.39 <i>t</i> (9.2)	3.40 <i>t</i> (8.8)	3.39 <i>t</i> (8.8)	3.39 <i>t</i> (9.4)	3.39 <i>t</i> (9.6)	3.40 <i>t</i> (8.8)	3.86 <i>m</i>	3.40 <i>t</i> (7.8)
5''	3.23 <i>m</i>	3.29 <i>m</i>	3.30 <i>m</i>	4.00 <i>m</i>	4.01 <i>m</i>	3.35 <i>m</i>	3.32 <i>m</i>	3.30 <i>m</i>
6''	1.23 <i>d</i> (6.2)	1.09 <i>d</i> (6.2)	1.08 <i>d</i> (6.2)	1.24 <i>d</i> (6.1)	1.23 <i>d</i> (6.1)	1.07 <i>d</i> (6.1)	1.02 <i>d</i> (6.2)	1.07 <i>d</i> (6.3)
Rham- nosyl								
1*							5.18 <i>br s</i>	
2*							3.88 <i>m</i>	
3*							3.54 <i>m</i>	
4*							3.65 <i>m</i>	
5*							3.41 <i>m</i>	
6*							1.08 <i>d</i> (6.2)	
Ester								
2'''		7.06 <i>d</i> (1.8)	7.46 <i>d</i> (8.8)	7.45 <i>d</i> (8.4)	7.45 <i>d</i> (8.6)	7.47 <i>d</i> (8.4)	7.48 <i>d</i> (8.2)	7.47 <i>d</i> (8.6)
3'''			6.81 <i>d</i> (8.8)	6.80 <i>d</i> (8.4)	6.80 <i>d</i> (8.6)	6.80 <i>d</i> (8.4)	6.82 <i>d</i> (8.2)	6.80 <i>d</i> (8.6)
5'''		6.94 <i>dd</i> (8.2, 1.8)	6.81 <i>d</i> (8.8)	6.80 <i>d</i> (8.4)	6.80 <i>d</i> (8.6)	6.80 <i>d</i> (8.4)	6.82 <i>d</i> (8.2)	6.80 <i>d</i> (8.5)
6'''		6.78 <i>d</i> (8.2)	7.46 <i>d</i> (8.8)	7.45 <i>d</i> (8.4)	7.45 <i>d</i> (8.6)	7.47 <i>d</i> (8.4)	7.46 <i>d</i> (8.2)	7.47 <i>d</i> (8.6)
7'''		7.59 <i>d</i> (15.8)	7.66 <i>d</i> (16.0)	7.63 <i>d</i> (15.9)	7.63 <i>d</i> (15.8)	7.66 <i>d</i> (15.9)	7.66 <i>d</i> (15.8)	6.66 <i>d</i> (15.9)
8'''		6.27 <i>d</i> (15.8)	6.34 <i>d</i> (16.0)	6.34 <i>d</i> (15.9)	6.34 <i>d</i> (15.8)	6.34 <i>d</i> (15.9)	6.33 <i>d</i> (15.8)	6.34 <i>d</i> (15.9)

* Showed spectral data overlapped by H₂O peak; coupling constants (*J* values in Hz) are shown in parentheses.

geraniol, not nerol. Accordingly, **1** is geraniol (3'-*O*- α -L-rhamnopyranosyl- β -D-glucopyranoside).

Ligobustoside **B** (**2**), was obtained as an amorphous powder. Its IR (3450, 1685, 1620, 1590, 1505 and 1435 cm^{-1}) and UV (214.5, 244.5, 299 and 331.5 nm) all showed the absorptions of aromatic group and α,β -unsaturated ester. The molecular formula ($\text{C}_{31}\text{H}_{44}\text{O}_{13}$) of **2** was confirmed by the molecular ion peak at m/z 647 $[\text{M} + \text{Na}]^+$. Its ^{13}C NMR spectra exhibited signals for 31 carbons. Comparison of these resonances with those of **1** revealed that **2** was very similar to **1** except for additional 9 carbon signals. The remaining part was readily assigned as caffeoyl moiety, while further compared with acteoside [7]. Furthermore, significant shift differences of +0.4, -3.1 and -1.8 ppm observed for C-4', C-3' and C-5' of the inner glucose indicated that acylation of caffeic acid occurred at C-4' position of the glucose. Thus, **2** is geraniol (3'-*O*- α -L-rhamnopyranosyl-4'-caffeoyl- β -D-glucopyranoside).

Ligobustoside **C** (**3**), was also obtained as an amorphous powder. Its ^1H and ^{13}C NMR spectral data very similar to those of **2**. From the positive ion FAB-mass spectrum (molecular ion peak at m/z 631 $[\text{M} + \text{Na}]^+$), the molecular formula of **3** ($\text{C}_{31}\text{H}_{44}\text{O}_{12}$) was concluded only differing from **2** by the decrease of one hydroxyl group. The ^1H NMR spectrum (an AB system at δ 7.46 and 6.81, 2H each, a pair of doublets, $J_{\text{AB}} = 8.8$ Hz) of **3** confirmed that the acyl moiety was a *trans*-*p*-coumaric acid which was also connected with C-4' position of the inner glucose, since in the ^{13}C NMR spectrum of **3**, such glucosyl C-4' shifted downfield from δ 70.3 to 70.8, while its C-3' and C-5' shifted upfield to δ 81.6 (-3.2 ppm) and δ 76.1 (-1.8 ppm), respectively (Table 2), based on direct ^{13}C NMR spectral comparison between **3** and **1**. Therefore, **3** is geraniol (3'-*O*- α -L-rhamnopyranosyl-4'-*p*-coumaroyl- β -D-glucopyranoside). Ligobustoside **C** (**3**) was detected to have anticholinergic (*in vitro*, 100 $\mu\text{g ml}^{-1}$) effects.

Ligobustoside **E** (**4**) was obtained as an amorphous powder. Its IR (3400, 1680, 1620, 1595, 1505 and 1435 cm^{-1}) and UV (205.5, 229, 315 nm) spectra exhibited the characteristic FAB-mass spectrum (631 $[\text{M} + \text{Na}]^+$, 455 $[\text{M} - \text{O aglycone}]^+$ and 309 $[\text{455-rhamnopyranosyl (or } p\text{-coumaroyl)} + \text{H}]^+$). The ^1H NMR spectrum at the aromatic region showed an A_2B_2 system belonging to a *p*-coumaroyl moiety [δ 6.80 (2H, d , $J = 8.4$ Hz), δ 7.45 (2H, d , $J = 8.4$ Hz)]. Two olefinic proton signals which appeared as an AB system [δ 6.34 (1H, d , $J = 15.9$ Hz), 7.63 (1H, d , $J = 15.9$ Hz)] indicated a *trans*-geometry in their moiety. ^1H NMR signals of two anomeric carbon protons at δ 5.17 (1H, d , $J = 1.6$ Hz) and 4.31 (1H, d , $J = 8.1$ Hz), as well as one secondary group of rhamnose at δ 1.24 (3H, d , $J = 6.1$ Hz) are consistent with the configurations for α -L-rhamnose and β -D-glucose. Two olefinic protons assignable to the aglycone moiety appearing at δ_{H} 5.07 (1H, t , $J = 6.0$ Hz) and δ_{H} 5.34 (1H, t , $J = 7.0$ Hz) confirmed that the aglycone was geraniol (Table 1).

The difference between **4** and ligobustoside **C** (**3**) was the position of *p*-coumaroyl moiety at the inner glucose. In compound **4** the *p*-coumaroyl moiety was assigned at C-6' of the inner glucose based on the following facts. Comparing the ^{13}C NMR signals of **4** with those ligobustoside **A** (**1**), the chemical shifts corresponding to C-6' of the glucose in **4** shifted downfield to δ 64.7 (+1.9 ppm), while chemical shift of C-5' and C-3' shifted upfield to δ 75.5 (-2.4 ppm) and δ 84.3 (-0.5 ppm), respectively (Table 2). Moreover, C-3' of the inner glucose shifted downfield from 81.6 to 84.3 (+2.7 ppm) due to the disappearance of esterification β effect, when comparing with ligobustoside **C** (**3**). On the other hand, the COLOC spectrum showed an important correlation spot between methylene protons of the glucosyl C-6' and carbonyl carbon of *p*-coumaroyl moiety. ^1H - ^1H and ^1H - ^{13}C COSY experiments also supported the above-mentioned results. Thus, **4** is geraniol (3'-*O*- α -L-rhamnopyranosyl-6'-*O*-*p*-coumaroyl- β -D-glucopyranoside). Ligobustoside **E** (**4**) was shown to possess the function of Ca^{2+} -antagonism (*in vitro*, 100 $\mu\text{g ml}^{-1}$).

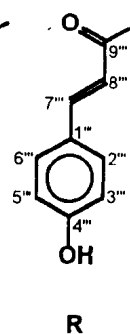
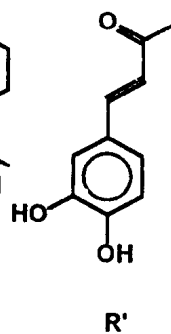
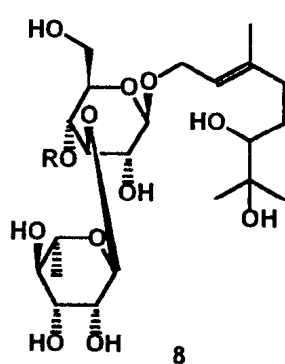
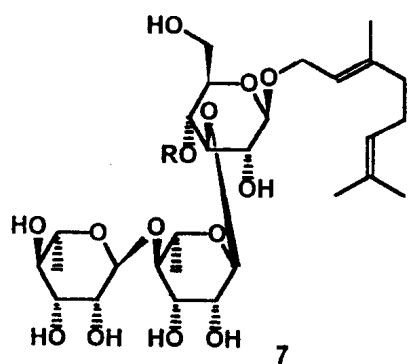
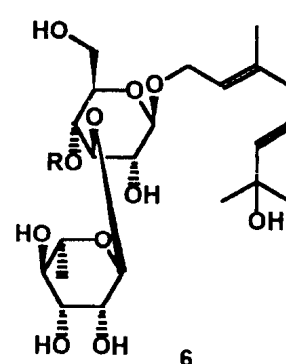
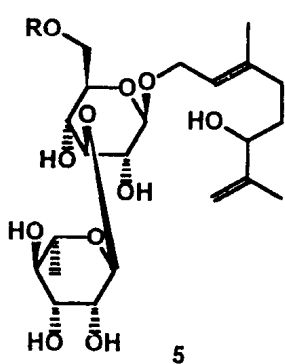
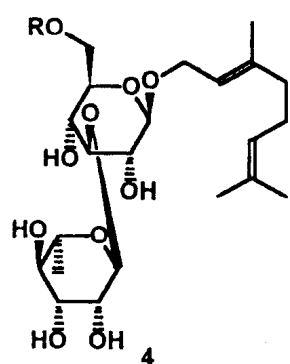
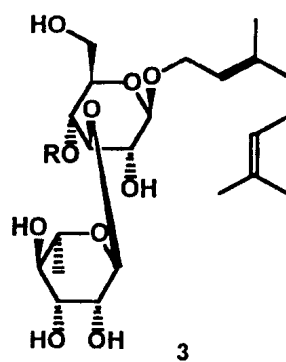
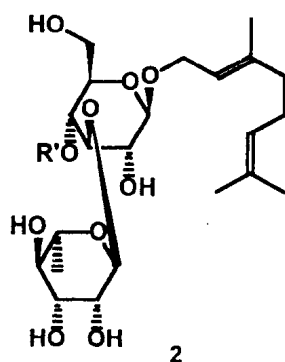
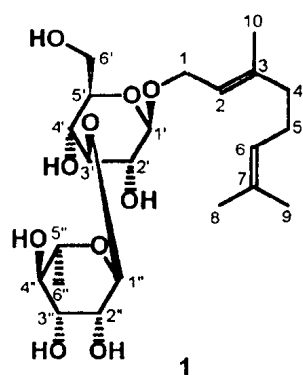
Ligobustoside **F** (**5**), an amorphous powder, analysed for $\text{C}_{31}\text{H}_{44}\text{O}_{13}$ from its positive ion FAB-mass spectrum (647 $[\text{M} + \text{Na}]^+$, 471 and 325) and NMR spectra. Its UV and IR spectra suggested the presence of double bonds and conjugated aromatic ester group same as ligobustoside **E** (**4**). Comparing the ^1H and ^{13}C NMR signals of **5** with those of **4**, we could come to the conclusion that both **5** and **4** contained identical parts: coumaroyl moiety and sugar units (β -D-glucose and α -L-rhamnose), that was, rhamnose was still connected with C-3' position of the glucose, while the coumaroyl moiety was also located at the C-6' position of the inner glucose, but they had different aglycones. From the ^1H NMR spectrum corresponding to the aglycone of **5** an AB system assignable to a pair of terminal methylene olefinic protons [δ 4.90 (1H, d , $J_{\text{AB}} = 1.6$ Hz), 4.79 (1H, d , $J_{\text{AB}} = 1.6$ Hz)], one olefinic methine proton [δ 5.36 (1H, t , $J = 6.8$ Hz)] one allyl-alcoholic methine [δ 4.00 (1H, dd , $J = 9.6, 6.4$ Hz)] were exhibited. Correspondingly, in the ^{13}C NMR spectrum of the aglycone of **5**, double bonds signals (δ 148.7 s , δ 111.5 t) and one methine carbon signal (δ 76.1 d) bearing one hydroxyl group appeared, while another double bond signals (δ 125.0 d , 132.5 s) and one methyl carbon signal (δ 17.9) disappeared, by comparing with compound **4**. Compound **5** had one more hydroxyl group than **4** (Table 2), and this additional hydroxy was assigned at C-6 of the aglycone according to biosynthesis, which is proved by comparison of NMR spectral data of the aglycone of **5** with those of 7-(6*R*-hydroxyl-3,7-dimethyl-2*E*,7-octadienyloxy) coumarin [8] 3,7-dimethyl-2*E*,7-octadiene-1,6-diol [9] also supported the result mentioned above. However, the stereochemistry of such hydroxyl group at C-6 was not determined finally. Thus, **5** is 6-hydroxy-3,7-dimethyl-2*E*,7-octadienyl-(3'-*O*- α -L-rhamnopyranosyl-6'-*O*-*p*-coumaroyl- β -D-glucopyranoside).

Table 2. ^{13}C NMR spectral data of glycosides 1–8 in CD_3OD

H	1	2	3	4	5	6	7	8
Aglycone								
1	66.4	66.5	66.5	66.3	66.3	66.6	66.5	66.6
2	121.5	121.4	121.4	121.3	121.4	122.2	121.4	121.6
3	141.9	142.0	142.1	142.2	142.1	140.8	142.1	142.3
4	40.6	40.6	40.6	40.6	36.6	43.4	40.6	37.7
5	27.4	27.4	27.4	27.4	34.2	137.6	27.4	30.4
6	125.0	125.0	125.0	125.0	76.1	128.7	125.1	78.9
7	132.5	132.5	132.5	132.5	148.7	82.4	132.5	73.8
8	25.9	25.9	25.9	25.9	111.5	24.9	25.9	25.7
9	17.7	17.8	17.8	17.9	29.9	24.9	17.7	25.0
10	16.5	16.5	16.5	16.5	16.6	16.6	16.5	16.6
Glucosyl								
1'	102.7	103.0	102.9	102.4	102.5	102.7	102.6	102.8
2'	75.5	76.1	76.1	75.5	75.5	76.1	76.1	76.1
3'	84.8	81.7	81.6	84.3	84.3	84.3	81.6	81.6
4'	70.3	70.7	70.8	70.6	70.6	70.7	70.7	70.8
5'	77.9	76.1	76.1	75.5	75.5	76.1	76.1	76.1
6'	62.8	62.4	62.5	64.7	64.7	62.4	62.4	62.5
Rhamnosyl								
1''	102.8	102.6	102.6	102.7	102.7	103.0	102.6	102.9
2''	72.3	72.3	72.3	72.3	72.3	72.3	72.7	72.3
3''	72.3	72.1	72.1	72.3	72.3	72.1	70.3	72.1
4''	74.0	73.8	73.8	70.0	70.4	73.8	81.6	73.8
5''	70.1	70.4	70.4	70.1	70.1	70.4	68.8	70.4
6''	17.9	18.5	18.4	17.9	17.9	18.4	19.1	18.4
Rhamnosyl								
1*							103.4	
2*							72.8	
3*							72.3	
4*							73.8	
5*							70.3	
6*							17.7	
Ester								
1'''		127.7	127.1	127.2	127.2	127.1	127.0	127.2
2'''		115.3	131.3	131.1	131.2	131.3	131.4	131.3
3'''		146.8	116.9	116.9	116.9	116.9	117.1	116.9
4'''		149.9	161.4	161.2	161.2	161.4	161.4	161.4
5'''		116.5	116.9	116.9	116.9	116.9	117.1	116.9
6'''		123.2	131.3	131.1	131.2	131.3	131.4	131.3
7'''		114.7	147.6	146.8	146.8	147.6	147.6	147.6
8'''		148.0	114.8	115.0	115.0	114.8	114.8	114.9
CO		168.3	168.3	169.0	169.0	168.3	168.1	168.3

Ligurobustoside I (6), was obtained as an amorphous powder. Its molecular formula ($\text{C}_{31}\text{H}_{44}\text{O}_{13}$) was provided by the negative ion FAB-mass spectrum, in which the molecular ion peak at m/z 623 $[\text{M}-\text{H}]^-$ and the fragment ion peaks at m/z 477 $[\text{M}-\text{Rha}]^-$ and 325 $[\text{M}-\text{Rha}-\text{O aglycone}]^-$ were exhibited. The ^1H and ^{13}C NMR spectra of 6 showed it possessed a *trans-p*-coumaroyl moiety [δ_{H} 7.47 (2H, *d*, $J = 8.4$ Hz, H-2''',6'''), 6.80 (2H, *d*, $J = 8.4$ Hz, H-3''',5''') and 7.66 (1H, *d*, $J = 15.9$ Hz, H-7'''), 6.34 (1H, *d*, $J = 15.9$ Hz,

H-8'''); δ_{C} 131.3 (*d*, C-2''',6'''), 116.9 (*d*, C-3''',5''') and 147.6 (*d*, C-7'''), 114.8 (*d*, C-8''') and two sugar units: β -D-glucose [δ_{H} 4.39 (1H, *d*, $J = 7.6$ Hz) and δ_{C} 102.7 *d*] and -L-rhamnose [δ_{H} 5.18 (1H, *br s*) and δ_{C} 103.0 *d*]. Furthermore 6, the connection positions of *p*-coumaroyl moiety, glucose and rhamnose one another were identical with those of ligurobustoside C (3). However, 6 had a different aglycone from 3. The aglycone of 6 was deduced as follows. From its ^{13}C NMR spectrum, the aglycone was shown to possess three



methyl groups (two of them were identical), three olefinic methines, one olefinic quarternary carbon, one quarternary carbon bearing one hydroxy and two methylene groups. The ^1H NMR spectrum of **6** revealed the presence of a pair of *E*-double bond signals [δ_{H} 5.62 (1H, *dt*, $J = 9.8, 4.8$ Hz, 5-H), 4.86 (1H, *d*, $J = 4.8$ Hz, 6-H)] belonging to the aglycone. The chemical shifts of H-8 and H-9 required an oxygen function at C-7 and the broadened doublet at 2.76 (2H, $J = 4.8$ Hz) indicated that a methylene group should be placed between two double bonds (Table 1). The aglycone of **6** was thus identified as a geraniol derivative where by allylic rearrangement a 7-hydroxyl group was introduced. Such assignment was further confirmed by comparing with 1-acetoxy-7-hydroxy-3,7-dimethylocta-2*E*,5*E*-diene isolated from *Jasonia montana* [10]. Therefore, **6** is 7-hydroxy-3,7-dimethyl-2*E*,5*E*-octadienyl-(3'-*O*- α -L-rhamnopyranosyl-4'-*O*-*p*-coumaroyl- β -D-glucopyranoside).

Ligubustoside **7** (**7**), an amorphous powder, showed characteristic absorptions of a *trans*-*p*-coumaroyl moiety in the IR and UV spectra. From the NMR spectral data, **7** was readily considered as a monoterpenoid glycoside similar to those identified previously. Further examination of ^1H NMR spectrum of **7** showed its aglycone was also geraniol same as those of ligubustosides A–C. However, **7** had one additional rhamnosyl moiety, when comparing with ligubustoside C (**3**), and this was confirmed by the appearance of the additional ^1H NMR signal [δ_{H} 5.18 (1H, *br s*, Rha, H-1)] and ^{13}C NMR signal [δ_{C} 103.4 *d* (Rha, C-1)]. Based on the negative ion FAB-mass spectrum of **7**, its molecular formula ($\text{C}_{37}\text{H}_{54}\text{O}_{16}$) was determined by the molecular ion peak at m/z 753 [$\text{M}-\text{H}$] $^-$, while the fragment ion peaks at m/z 607 [$\text{M}-\text{Rha}$] $^-$, 461 [$\text{M}-2\text{Rha}$] $^-$ and 325 [$\text{M}-2\text{Rha}-\text{O aglycone}$] $^-$ indicated that such additional rhamnose was linked to terminal rhamnose corresponding to ligubustoside C (**3**). Moreover, the *p*-coumaroyl moiety was confirmed to be located at the C-4' position of the inner glucose due to the typical ^{13}C NMR signals [δ_{C} 81.6 *d* (Glc, C-3') and 70.7 *d* (Glc, C-4')]. The remaining problem was the connection position of the additional rhamnose, and this was solved by consideration of ^{13}C NMR signals (60–85 ppm) belonging to sugar moiety. The additional rhamnose was easily proved to be attached to the C-4'' position of terminal rhamnose corresponding to ligubustoside C (**3**), since the C-4'' signal of such terminal rhamnose shifted downfield from δ 73.8 to 81.6 (+7.8 ppm), while the signals of C-3'' and C-5'' shifted upfield from δ 72.1 to 70.3 (–1.8 ppm) and from δ 70.4 to 68.8 (–1.6 ppm), respectively (Table 2). The similar situation occurring in *Ligustrum purpurascens* [11] also supported this assignment. Consequently, ligubustoside **7** (**7**) is geraniol-[3'-*O*- α -L-rhamnopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl-4'-*O*-*p*-coumaroyl- β -D-glucopyranoside].

Ligubustoside **K** (**8**), an amorphous powder, showed its molecular formula ($\text{C}_{31}\text{H}_{48}\text{O}_{14}$) from the result of the negative ion FAB-mass spectrum [m/z

641 [$\text{M}-\text{H}$] $^-$, 623 [$\text{M}-\text{H}_2\text{O}-\text{H}$] $^-$, 495 [$\text{M}-\text{rhamnosyl}$ (or *p*-coumaroyl)] $^-$ and 325 [$\text{M}-\text{rhamnosyl}$ (or *p*-coumaroyl)-O aglycone] $^-$ (base peak)]. Its IR and UV spectra had little difference with ligubustosides B–J also confirmed it was a monoterpenoid glycoside of same kind. By direct comparison of its NMR spectral data with those of ligubustosides C (**3**), both had the same sections: two sugar units (β -D-glucose and α -L-rhamnose) and *p*-coumaroyl moiety (a characteristics A_2B_2 system and an *E*-double bond AB system), and their only difference was attributed to aglycone. The aglycone of **8** was identified as follows. Its ^{13}C NMR spectrum showed it was a derivative of geraniol with the reduction of C_6-C_7 double bond, owing to the disappearance of δ_{C} 125.0 *d* and 132.5 *s* and the appearance of δ_{C} 78.9 *d* (C-6) and 73.8 *s* (C-7), when comparing with the aglycone of compound **3**. Two methyl signals belonging to H-8 and H-9 obviously shifted from δ_{H} 1.69 *s* and 1.61 *s* (in the aglycone of **3**) to 1.18 *s* and 1.14 *s*, respectively. Furthermore, remarkable variation occurred in C_4-H_2 splitting into two groups (δ_{H} 2.31 *m* and 2.11 *m*) and C_5-H_2 splitting into two groups (δ_{H} 1.75 *m* and 1.39 *m*), since the chiral C-6 appeared. In contrast, no complicated splitting situations in 4- CH_2 (δ_{H} 2.05 *t*) and 5- CH_2 (δ_{H} 2.11 *t*) in the aglycone of **3** were observed. Based on all these facts, ligubustoside **K** (**8**) is 6,7-dihydroxy-3,7-dimethyl-2*E*-octaenyl-(3'-*O*- α -L-rhamnopyranosyl-4'-*O*-*p*-coumaroyl- β -D-glucopyranoside).

EXPERIMENTAL

General. NMR spectra were recorded in CD_3OD . GC analysis was finished in GC-9A instrument (column: SE-54 type; temp.: 230°). CC and TLC: silica gel, Si 60 (Lobar, 40–63 μm , length: 250 mm, diameter: 250 mm, Merck), RP-18 (Lobar, 40–63 μm , length: 250 mm, Merck) and Diaion HP-20 (Mitsubishi Kasei).

Plant material. The leaves of *Ligustrum robustum* (Roxb.) Bl. was collected in Guiyang, Guizhou Province. A voucher specimen has been deposited in the Herbarium of Kunming Institute of Botany.

Isolation of glycosides. Dried and powdered leaves (2.5 kg) of *Ligustrum robustum* were extracted with 95% EtOH (4 \times 10 l) at room temp. After the removal of solvent, the EtOH extract (350 g) was defatted with petrol (60–90°) and then partitioned with CHCl_3 and H_2O \times 3. The H_2O layer was applied to D 101 resin column eluting with H_2O until sugars and proteins etc. were removed, and then exchanged eluent for 95% EtOH. The residue (160 g) was chromatographed on silica gel developing with $\text{CHCl}_3-\text{MeOH}-\text{H}_2\text{O}$ (from 50:10:1 to 10:10:1) to separate into six frs (I–VI).

Fr. I was repeatedly chromatographed on silica gel H until the colourful substances were removed, and then subjected to reversed-phase silica gel (RP-8) eluting with $\text{MeOH}-\text{H}_2\text{O}$ (7:3) to yield compounds **1** (130 mg) and **2** (240 mg). From fr. II we obtained a mixt. (3.5 g) after repeated CC eluting with $\text{EtOAc}-i\text{-PrOH}$

(30:1). A part (800 mg) of this mixt. was further subjected to medium pressure reversed-phase chromatography (RP-18) eluting with MeOH-H₂O (6:4) to afford **3** (140 mg). After repeated silica gel and reversed-phase silica gel CC (RP-18) eluting with MeOH-H₂O (3:2), other compounds [**4** (78 mg), **5** (65 mg), **6** (120 mg), **7** (85 mg) and **8** (140 mg)] were obtained from frs III-IV.

Ligurobustoside A (1). C₃₂H₃₈O₁₀. $[\alpha]_D^{22} = -48.3^\circ$ ($c = 0.032$, MeOH). FAB-MS (positive ion) m/z : 485 [M+Na]⁺, 309 [M-C₁₀H₁₇O₂]⁺. ¹H and ¹³C NMR spectra: see Tables 1 and 2.

Acid hydrolysis of 1. Compound **1** (10 mg) was hydrolysed with 1M H₂SO₄ in 10% EtOH under reflux for 2 hr. The reaction mixt. was neutralized with a satd soln of NaHCO₃ and concd to dryness. The residue was used for PC analysis. D-glucose and L-rhamnose were detected by comparison with authentic samples.

Enzymatic hydrolysis of 1. Compound **1** (10 mg) and β-D-glucosidase (10 mg) were dissolved in acetate buffer (5 ml, PH5) at 37° for 24 hr. The reaction residue was extracted with ether. The ether extract was then applied to GC analysis. The R_f of the aglycone of **1** was consistent with that of geraniol.

Ligurobustoside B (2). C₃₁H₄₄O₁₃. $[\alpha]_D^{22} = -72.2^\circ$ ($c = 0.021$, MeOH). FAB-MS (positive ion) m/z : 647 [M+Na]⁺, 471 [M-O aglycone]⁺, 325 [M-O aglycone-(rhamnosyl or *p*-coumaroyl)+H]⁺. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 203 (4.78), 214.5 (4.62), 244.5 (4.27), 299 (4.38), 331.5 (4.50). ¹H and ¹³C NMR spectra: see Tables 1 and 2.

Ligurobustoside C (3). C₃₁H₄₄O₁₂. $[\alpha]_D^{22} = -75.4^\circ$ ($c = 0.040$, MeOH). FAB-MS (positive ion) m/z : 631 [M+Na]⁺, 455 [M-O aglycone]⁺, 309 [M-O aglycone-(rhamnosyl or *p*-coumaroyl)+H]⁺. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 203.5 (4.66), 216 (4.57), 280.5 (4.34), 299 (4.53), 315.5 (4.62). ¹H and ¹³C NMR spectra: see Tables 1 and 2.

Alkaline hydrolyses of compounds 2 and 3. Compounds **2** and **3** (2 mg each) were hydrolysed with 2M KOH (50% EtOH) for one day. From the two reaction systems, compound **1** was detected by LC (RP-18 plate, MeOH-H₂O, 7:3).

Ligurobustoside E (4). C₃₁H₄₄O₁₂. $[\alpha]_D^{22} = -67.2^\circ$ ($c = 0.030$, MeOH). FAB-MS (positive ion) m/z : 631 [M+Na]⁺, 455 [M-O aglycone]⁺, 309 [M-O aglycone-(rhamnosyl or *p*-coumaroyl)+H]⁺. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 205.5 (4.71), 229 (4.08), 315 (4.35). ¹H and ¹³C NMR spectra: see Tables 1 and 2.

Ligurobustoside F (5). C₃₁H₄₄O₁₃. $[\alpha]_D^{22} = -70.5^\circ$ ($c = 0.028$ MeOH). FAB-MS (positive ion) m/z : 647 [M+Na]⁺, 471 [M-O aglycone]⁺, 325 [M-O aglycone-(rhamnosyl or *p*-coumaroyl)+H]⁺. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 205.5 (4.70), 226 (4.25), 312.5 (4.56). ¹H and ¹³C NMR spectra: see Tables 1 and 2.

Ligurobustoside I (6). C₃₁H₄₄O₁₃. $[\alpha]_D^{22} = -57.8^\circ$ ($c = 0.058$, MeOH). FAB-MS (negative ion) m/z : 623 [M-H]⁻, 477 [M-Rha]⁻, 325 [M-O aglycone-rhamnosyl (or *p*-coumaroyl)]⁻. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 205.5 (4.68), 228 (4.32), 313 (4.58). ¹H and ¹³C NMR spectra: see Tables 1 and 2.

Ligurobustoside J (7). C₃₇H₅₄O₁₆. $[\alpha]_D^{22} = -87.6^\circ$ ($c = -0.068$, MeOH). FAB-MS (negative ion) m/z : 753 [M-H]⁻, 607 [M-Rha]⁻, 461 [M-2Rha]⁻ and 325 [M-2Rha-O aglycone]⁻. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 205 (4.94), 229 (4.20), 316 (4.45). ¹H and ¹³C NMR spectra: see Tables 1 and 2.

Ligurobustoside K (8). C₃₁H₄₆O₁₄. $[\alpha]_D^{22} = -65.2^\circ$ ($c = 0.028$, MeOH). FAB-MS (negative ion) m/z : 641 [M-H]⁻, 623 [M-H₂O-H]⁻, 495 [M-rhamnosyl (or *p*-coumaroyl)]⁻ and 325 [M-rhamnosyl (or *p*-coumaroyl)-O aglycone]⁻. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 205 (4.71), 226 (4.26), 315 (4.57). ¹H and ¹³C NMR spectra: see Tables 1 and 2.

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