DITERPENES FROM THE BARK OF *JUNIPERUS CHINENSIS*

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Key Word Index—*Juniperus chinensis*; Cupressaceae; bark; diterpenes; labdane-type; abietane-type; totarane-type; secoabietane; sandaracopimaric acid.

Abstract—Eighteen diterpenes were isolated from the bark of *Juniperus chinensis*. The new compounds include the *E*- and *Z*-isomers of 12,15-dihydroxylabda-8(17),13-dien-19-oic acid, the *E*- and *Z*-isomers of 2 α -hydroxycommunic acid as well as 15,16-bisnor-8,17-epoxy-13-oxolabd-11*E*-en-19-oic acid, whose structures were determined by spectral methods. An epoxy communic acid, 12,13-epoxylabda-8(17),14-dien-19-oic acid and the isomer of dihydroxy communic acid, 12,13-dihydroxylabda-8(17),14-dien-19-oic acid, were isolated for the first time from a natural source.

INTRODUCTION

Juniperus chinensis is a common ornamental tree [1]. The compounds hinokiflavone and kayaflavone have been previously reported in this plant [2, 3]. We recently isolated 13 lignans and 16 diterpenes in addition to other components from the leaves [4, 5]. The diterpenes include semperviranes, abietanes, totaranes and a new chinane-type having isopropyl groups at the C-12, C-13, C-14 and C-11 positions, respectively [5]. We report here 18 diterpenes, including labdanes, abietanes and totaranes, found in the bark of *J. chinensis*.

RESULTS AND DISCUSSION

The acetone soluble part of the bark of *J. chinensis* *kaizuka* was extracted with ethyl acetate and the extract subjected to chromatography to give the diterpene components. The known compounds were readily identified as sandaracopimaric acid (**1**) [6, 7], ferruginol (**2**) [8], 7-dehydroabietanone (**3**) [9], sugiol (**4**) [7], 6 α -hydroxy-7-oxoferruginol (**5**) [10], 6,7-secoferruginol-6,7-dial (**6**) [7, 11], totarol (**7**) [5, 12], totarolone (**8**) [13], communic acid (**9**, *cis/trans* = 1:3) [14, 15], isocupressic acid (**10**) [15, 16] and agathic acid (**11**) [17, 18] by analyses of their physical and spectral properties (mp, $[\alpha]$, IR, mass, ^1H and ^{13}C NMR spectra). Sandaracopimaric acid was the predominant component.

The IR spectrum of **12a** showed the presence of carboxylic acid. The ^1H NMR spectrum (Table 1) revealed some structural characteristics such as a moiety of allylic alcohol $\text{R}_2\text{C}=\text{CHCH}_2\text{OH}$ appearing at δ 4.09 (*d*) and 5.33 (*t*), a secondary alcohol appearing at δ 4.05 (*dd*), an exocyclic double bond appearing at δ 4.68 (*s*) and 4.85 (*s*),

as well as three methyl groups appearing at δ 1.59 (*s*), 1.17 (*s*) and 0.63 (*s*). By analysis of the ^{13}C NMR spectrum of **12a** and comparison with the literature [19], **12a** is assigned as 12,15-dihydroxylabda-8(17),13*E*-dien-19-oic acid. Compound **12a** was dextrorotatory, $[\alpha]_{\text{D}} + 33^\circ$, whereas the reported compound isolated from *Guizotia scabra* (Heliantheae) [19] is laevorotatory, $[\alpha]_{\text{D}} - 29^\circ$. By analogy to the structures of other chemical constituents such as **10** and **11**, compound **12a** is probably a labdane diterpene having the (4*S*,9*S*,10*R*,12*S*)-configuration, whereas the previously reported compound (absolute configuration unknown) is the enantiomer of **12a**. The ^{13}C NMR resonances of **12b** were very close to the values of the corresponding signals of **12a** (Table 2), except for a methyl resonance (C-16) of **12b** appearing at lower field (δ 17.0). A NOE experiment by irradiating the corresponding methyl group at C-13 (δ 1.67) caused 19% enhancement of H-14 (δ 5.41). Thus **12b** is assigned as 12,15-dihydroxylabda-8(17), 13*Z*-dien-19-oic acid, a 13*Z*-isomer of **12a**.

Compound **13a** had an exact mass at m/z 318.218 attributable to a molecular formula $\text{C}_{20}\text{H}_{30}\text{O}_3$. The IR spectrum showed characteristic absorptions of carboxylic acid. The UV absorption at 227 nm indicated the presence of a conjugated diene. The resonances of the corresponding olefinic protons appeared at δ 5.37 (*t*), 6.30 (*dd*, $J = 17, 11$ Hz), 4.87 (*d*, $J = 11$ Hz) and 5.03 (*d*, $J = 17$ Hz) in addition to a proton (H-2) geminal to a hydroxyl group occurring at δ 4.13 (*dddd*, $J = 12, 12, 4, 4$ Hz). Irradiation of the signal of the Me-10 group caused an NOE effect on H-2, supporting the axial orientation of H-2. The ^1H and ^{13}C NMR spectra of **13a** and **b** were similar except for the signals of C-14 and C-16. By comparison with the spectra of *trans*- and *cis*-communic acids [14, 20], **13a** and **b** are assigned as 2 α -hydroxy-*trans*-communic acid and 2 α -hydroxy-*cis*-communic acid, respectively. Compound **13b** having the 12*E*-configuration showed H-12 at higher field

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(δ 5.26) and H-14 at lower field (δ 6.75) compared to the corresponding resonances of **13a**.

An epoxy communic acid, 12,13-epoxylabda-8(17),14-dien-19-oic acid (**14**) was isolated. The methyl ester of **14** has been previously synthesized by epoxidation of the methyl ester of *trans*-communic acid [21, 22]. The constituents of the bark of *J. chinensis* also include diastereomers of dihydroxy communic acid, 12,13-dihydroxylabda-8(17),14-dien-19-oic acid (**15**). The (12*R*,13*S*)-isomer **15a** was purified, whereas the (12*R*,13*R*)-isomer **15b** was contaminated with (12*S*,13*R*)-isomers. The stereochemistry was determined by detailed analysis of their 1H NMR spectra. The two C-17 protons in the (12*R*)-isomer **15a** showed at δ 4.42 and 4.82 ($\Delta\delta = 0.4$ ppm), the corresponding protons in **15b** appeared at δ 4.43 and 4.84 ($\Delta\delta = 0.4$ ppm). According to the literature [22, 23], the two C-17 protons in the (12*S*)-isomer showed a smaller difference in chemical shifts (4.89–4.75 = 0.14 ppm). The dihydroxylabdanoic acids **12a**, **b** having

the (12*S*)-configuration also exhibited small chemical shift differences between the two C-17 protons ($\Delta\delta < 0.2$ ppm, see Table 1). The methyl esters of **15a**, **b** have been previously prepared by hydrolysis of the methyl ester of the epoxy communic acid [21, 22]. The H-16 in **15a** appeared at higher field (δ 1.25) than that of **15b** (δ 1.30) [22].

The ^{13}C NMR spectrum of **16** showed 18 carbon signals, and the exact mass at m/z 306.182 led to a molecular formula $C_{18}H_{26}O_4$. The resonance at δ 180 (*s*) was attributable to the carbon of a carboxylic acid, the resonances at δ 140 (*d*), 136 (*d*) and 197 (*s*) were ascribed to $CH=CH-C=O$ of a conjugated ketone. The 1H NMR spectrum showed a resonance at δ 2.19 (*s*, 3 H) attributable to a methyl ketone. Compound **16** is assigned as 15,16-bisnor-8,17-epoxy-13-oxolabd-11*E*-en-19-oic acid. Two oxirane protons appeared at δ 2.56 and 2.74, which showed no NOE by irradiation of the Me-10 signal at δ 0.89. Thus, the C-8/O bond is considered to have the

Table 1. ^1H NMR spectral data of compounds **12a**, **b**, **13a**, **b** and **16** (CDCl_3 solution, δ values in ppm, J values in Hz)

H	12a	12b	13a	13b	16
1	1.03 <i>ddd</i> (13, 13, 4), 1.8 <i>m</i>	1.04 <i>m</i> , 1.81 <i>m</i>	1.05 <i>dd</i> (12, 12), 2.39 <i>d</i> (12)	1.05 <i>ddd</i> (12, 12, 3), 2.39 <i>dd</i> (12, 4)	1.05 <i>m</i> , 1.48 <i>m</i>
2	1.43 <i>m</i> , 1.90 <i>ddd</i> (10, 4, 1)	1.48 <i>m</i> , 1.90 <i>m</i>	4.15 <i>dddd</i> (12, 12, 4, 4)	4.13 <i>dddd</i> (12, 12, 4, 4)	1.47 <i>m</i> , 1.89 <i>m</i>
3	1.03 <i>ddd</i> (13, 13, 4), 2.09 <i>m</i>	1.04 <i>m</i> , 2.12 <i>m</i>	1.05 <i>dd</i> (12, 12), 2.15 <i>dd</i> (12, 4)	1.05 <i>dd</i> (12, 12), 2.15 <i>dd</i> (J 12, 4)	1.06 <i>m</i> , 2.1 <i>m</i>
5	1.32 <i>dd</i> (11, 4)	1.33 <i>m</i>	1.31 <i>m</i>	1.28 <i>m</i>	1.25 <i>m</i>
6	1.82 <i>m</i> , 1.95 <i>m</i>	1.86 <i>m</i> , 1.97 <i>m</i>	1.93 <i>m</i>	1.92 <i>m</i>	2.04 <i>m</i> , 2.09 <i>m</i>
7	1.85 <i>m</i> , 2.34 <i>m</i>	1.83 <i>m</i> , 2.37 <i>m</i>	1.94 <i>m</i> , 2.35 <i>m</i>	1.92 <i>m</i> , 2.35 <i>m</i>	1.42 <i>m</i> , 1.48 <i>m</i>
9	1.48 <i>m</i>	1.42 <i>m</i>	1.80 <i>m</i>	1.80 <i>m</i>	2.30 <i>d</i> (10)
11	1.57 <i>m</i> , 1.68 <i>m</i>	1.70 <i>m</i> , 1.62 <i>m</i>	2.18 <i>m</i> , 2.42 <i>m</i>	2.19 <i>m</i> , 2.41 <i>m</i>	6.36 <i>dd</i> (16, 10)
12	4.05 <i>dd</i> (10, 4)	4.57 <i>dd</i> (13, 6)	5.37 <i>t</i> (7)	5.26 <i>t</i> (6)	6.07 <i>d</i> (16)
14	5.33 <i>t</i> (6)	5.41 <i>t</i> (7)	6.30 <i>dd</i> (17, 11)	6.75 <i>dd</i> (17, 11)	2.19 <i>s</i>
15	4.09 (2H) <i>d</i> (6)	3.80 <i>dd</i> (13, 7), 4.05 <i>dd</i> (13, 7)	4.87 <i>d</i> (11), 5.03 <i>d</i> (17)	5.07 <i>d</i> (11), 5.16 <i>d</i> (17)	
16	1.59 <i>s</i>		1.73 <i>s</i>	1.75 <i>s</i>	
17	4.68 <i>s</i> , 4.85 <i>s</i>	4.71 <i>s</i> , 4.87 <i>s</i>	4.48 <i>s</i> , 4.86 <i>s</i>	4.49 <i>s</i> , 4.86 <i>s</i>	2.56 <i>d</i> (4), 2.74 <i>d</i> (4)
18	1.17 <i>s</i>	1.18 <i>s</i>	1.29 <i>s</i>	1.28 <i>s</i>	1.26 <i>s</i>
20	0.63 <i>s</i>	0.63 <i>s</i>	0.64 <i>s</i>	0.62 <i>s</i>	0.89 <i>s</i>

Coupling constants (J in Hz) in parentheses.Table 2. ^{13}C NMR spectral data of compounds **12a**, **b**, **13a**, **b** and **16** (CDCl_3 solution, δ values in ppm)

C	12a	12b	13a	13b	16
1	39.7 <i>t</i>	40.7 <i>t</i>	46.5 <i>t</i>	46.4 <i>t</i>	40.6 <i>t</i>
2	20.6 <i>t</i>	21.6 <i>t</i>	64.9 <i>d</i>	64.8 <i>d</i>	19.8 <i>t</i>
3	38.7 <i>t</i>	39.7 <i>t</i>	47.8 <i>t</i>	47.7 <i>t</i>	37.7 <i>t</i>
4	44.4 <i>s</i>	45.5 <i>s</i>	45.1 <i>s</i>	45.1 <i>s</i>	43.9 <i>s</i>
5	56.5 <i>d</i>	57.5 <i>d</i>	55.5 <i>d</i>	55.4 <i>d</i>	54.8 <i>d</i>
6	26.8 <i>t</i>	27.8 <i>t</i>	25.3 <i>t</i>	25.3 <i>t</i>	22.9 <i>t</i>
7	39.2 <i>t</i>	40.0 <i>t</i>	38.2 <i>t</i>	38.2 <i>t</i>	36.0 <i>t</i>
8	149.0 <i>s</i>	150.8 <i>s</i>	147.0 <i>s</i>	146.9 <i>s</i>	58.1 <i>s</i>
9	52.6 <i>d</i>	53.3 <i>d</i>	56.5 <i>d</i>	56.4 <i>d</i>	57.4 <i>d</i>
10	40.5 <i>s</i>	41.5 <i>s</i>	41.3 <i>s</i>	41.3 <i>s</i>	40.8 <i>s</i>
11	29.8 <i>t</i>	30.4 <i>t</i>	23.4 <i>t</i>	22.3 <i>t</i>	140.3 <i>d</i>
12	76.7 <i>d</i>	68.2 <i>d</i>	133.2 <i>d</i>	130.9 <i>d</i>	135.8 <i>d</i>
13	139.0 <i>s</i>	139.9 <i>s</i>	133.7 <i>s</i>	131.9 <i>s</i>	197.0 <i>s</i>
14	128.0 <i>d</i>	129.0 <i>d</i>	141.5 <i>d</i>	133.7 <i>d</i>	27.9 <i>q</i>
15	58.7 <i>t</i>	59.0 <i>t</i>	110.1 <i>t</i>	113.5 <i>t</i>	
16	10.3 <i>q</i>	17.0 <i>q</i>	11.9 <i>q</i>	19.7 <i>q</i>	
17	106.0 <i>t</i>	106.6 <i>t</i>	108.5 <i>t</i>	108.7 <i>t</i>	50.5 <i>t</i>
18	29.5 <i>q</i>	28.4 <i>q</i>	28.9 <i>q</i>	28.8 <i>q</i>	28.8 <i>q</i>
19	179.0 <i>s</i>	179.0 <i>s</i>	182.4 <i>s</i>	182.5 <i>s</i>	180.0 <i>s</i>
20	13.5 <i>q</i>	14.4 <i>q</i>	13.7 <i>q</i>	13.7 <i>q</i>	13.9 <i>q</i>

axial orientation indicating *S*-chirality at C-8. Related bisnorlabdanes have been found in the constituents of *Juniperus thurifera* [23] and *Platycladus orientalis* [22].

EXPERIMENTAL

Plant material. The bark of *Juniperus chinensis* Linn. var. *kaizuka* Hort. was collected from the plant grown in the surroundings of the Department of Chemistry of the

National Taiwan University. A voucher specimen is deposited in the Herbarium of our University. The air-dried bark (0.23 kg) was soaked in Me_2CO (5 l) for 1 week. The Me_2CO extract was concd, diluted with H_2O and extracted $\times 4$ with EtOAc (1 l each). The combined EtOAc extracts were concd to give an oil (20 g), which was absorbed by 25 g of silica gel and then chromatographed on a column packed with 250 g of silica gel. Compounds **3** (69 mg), **7** (11 mg), **2** (73 mg), **6** (6 mg), **14** (4 mg), **1** (3.2 g), **4** (80 mg), **10** (2 mg), **9** (1 g), **8** (96 mg), **5** (7 mg), **15** (6 mg), **16** (21 mg), **13b** (3.5 mg), **13a** (10 mg) and **11** (8 mg) were obtained by elution with gradients of EtOAc in hexane in ascending order of polarity (2.5–50%), whereas **12a** (7 mg) and **b** (3 mg) were obtained by elution with EtOAc– CHCl_3 (1:1).

Sandaracopimaric acid (1). Mp 174–175°. $[\alpha]_{\text{D}}^{25}$ –14.4° (EtOH; c 1.1).

Ferruginol (2). Mp 56–57°. $[\alpha]_{\text{D}}^{25}$ +40.6° (CHCl_3 ; c 3.6).

7-Dehydroabietanone (3). Mp 87–90°. $[\alpha]_{\text{D}}^{25}$ +4° (EtOH; c 3.4).

Sugiol (4). Mp 291–293°. $[\alpha]_{\text{D}}^{25}$ +25° (EtOH; c 8).

6 α -Hydroxy-7-oxoferruginol (5). Mp 207–208°. $[\alpha]_{\text{D}}^{25}$ +35.3° (MeOH; c 0.33).

6,7-Secoferruginol-6,7-dial (6). Mp 191–192°. $[\alpha]_{\text{D}}^{25}$ +20° (MeOH; c 0.2).

Totarol (7). Mp 131–132°. $[\alpha]_{\text{D}}^{25}$ +40.2° (EtOH; c 2.2).

Totarolone (8). Mp 188–189°. $[\alpha]_{\text{D}}^{25}$ +101.5° (MeOH; c 3.2).

Communic acid (9, a mixture of 12*E*- and 12*Z*-isomers, 3:1). Mp 130–132°. $[\alpha]_{\text{D}}^{25}$ +38° (EtOH; c 1.0).

Isocupressic acid (10). Mp 117–120°. $[\alpha]_{\text{D}}^{25}$ +14° (EtOH; c 1.5).

Agathic acid (11). Mp 203–204°. $[\alpha]_{\text{D}}^{25}$ +58° (CHCl_3 ; c 0.8).

12,15-Dihydroxyabda-8(17),13E-dien-19-oic acid (**12a**). Solid, mp 178–180°. $[\alpha]_D^{25} + 33.3^\circ$ (EtOH; *c* 0.4). IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 3500–2500, 1690 (CO₂H). EIMS (70 eV) *m/z* (rel. int.) 318 [M–H₂O]⁺ (4), 300 (18), 285 (21), 235 (17), 221 (19), 207 (11), 189 (50), 121 (80), 81 (80), 55 (100). Exact mass for C₂₀H₃₀O₃, [M–H₂O]⁺, requires 318.2196. Found 318.2206.

12,15-Dihydroxyabda-8(17),13Z-dien-19-oic acid (**12b**). Solid, mp 186–188°. $[\alpha]_D^{25} + 9^\circ$ (MeOH; *c* 0.45). IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 3500–2500, 1690 (CO₂H), 1630, 1600, 882. EIMS (70 eV) *m/z* (rel. int.) 336 [M]⁺ (2), 318 [M–H₂O]⁺ (16), 300 (28), 285 (33), 235 (38), 189 (90), 121 (87), 83 (100).

2 α -Hydroxy-trans-communic acid (**13a**). Solid, mp 121–122°. $[\alpha]_D^{25} + 16.6^\circ$ (MeOH; *c* 0.2). IR $\nu_{\max}^{\text{neat}} \text{ cm}^{-1}$: 3600–3200, 1688 (CO₂H), 1640, 1026, 910. UV $\lambda_{\max}^{\text{MeOH}} \text{ nm}$ (ϵ): 227 (3600). EIMS (70 eV) *m/z* (rel. int.) 318 [M]⁺ (18), 300 [M–H₂O]⁺ (20), 285 (12), 255 (19), 199 (20), 187 (26), 173 (67), 79 (100), 55 (64). Exact mass for C₂₀H₃₀O₃, [M–H₂O]⁺, requires 318.2196. Found 318.2184.

2 α -Hydroxy-cis-communic acid (**13b**). Solid, mp 132–133°. $[\alpha]_D^{25} + 18.7^\circ$ (CHCl₃; *c* 0.35). IR $\nu_{\max}^{\text{neat}} \text{ cm}^{-1}$: 3600–3200, 1682 (CO₂H), 1640, 988, 890. UV $\lambda_{\max}^{\text{CHCl}_3} \text{ nm}$ (ϵ): 245 (1600). EIMS (70 eV) *m/z* (rel. int.) 318 [M]⁺ (29), 300 (33), 285 (24), 255 (37), 199 (26), 187 (28), 173 (80), 79 (100), 55 (62). Exact mass [M]⁺ for C₂₀H₃₀O₃ requires 318.2196. Found 318.2184.

12,13-Epoxyabda-8(17),14-dien-19-oic acid (**14**). Oil. $[\alpha]_D^{25} + 24^\circ$ (CHCl₃; *c* 0.2). ¹H NMR (CDCl₃): δ 0.56 (3H, s, H-20), 1.22 (3H, s, H-18), 1.36 (3H, s, H-16), 2.87 (*dd*, *J* = 6, 4 Hz, H-12), 4.45 (s, H-17), 4.84 (s, H-17), 5.27 (*dd*, *J* = 10, 1.4 Hz, H-15), 5.29 (*dd*, *J* = 17, 1.4 Hz, H-15), 5.78 (*dd*, *J* = 17, 10 Hz, H-14). Exact mass [M]⁺ for C₂₀H₃₀O₃ requires 318.2196. Found 318.2182.

12,13-Dihydroxyabda-8(17),14-dien-19-oic acid. (12*R*, 13*S*)-Isomer **15a**, oil, $[\alpha]_D^{25} + 18^\circ$ (CHCl₃; *c* 0.7). ¹H NMR (CDCl₃): δ 0.58 (3H, s), 1.22 (3H, s, H-18), 1.25 (3H, s, H-16), 3.48 (1H, *d*, *J* = 10 Hz, H-12), 4.42 (1H, s, H-17), 4.82 (1H, s, H-17), 5.19 (1H, *dd* *J* = 10, 1 Hz, H-15), 5.33 (1H, *dd*, *J* = 17, 1 Hz, H-15), 5.91 (1H, *dd*, *J* = 17, 10 Hz, H-14). ¹³C NMR (CDCl₃): δ 12.5 (C-20), 19.8 (C-2), 23.1 (C-11), 25.0 (C-18), 26.1 (C-6), 28.7 (C-16), 38.3 (C-3), 38.5 (C-7), 39.3 (C-1), 39.9 (C-10), 44.3 (C-4), 51.9 (C-9), 56.3 (C-5), 75.3 (C-13), 77.5 (C-12), 106.8 (C-17), 114.2 (C-15), 141.1 (C-14), 147.8 (C-8), 177.6 (C-19). Exact mass for C₂₀H₃₀O₃ [M–H₂O]⁺ requires 318.2196. Found 318.2202. (12*R*,13*R*)-Isomer **15b**, ¹H NMR (CDCl₃ *inter alia*): δ 1.30 (3H, s, H-16), 3.45 (1H, *d*, *J* = 10 Hz, H-12), 4.43 (1H, s, H-17), 4.84 (1H, s, H-17), 5.20 (1H, *d*, *J* = 10 Hz, H-15), 5.33 (1H, *d*, *J* = 17 Hz, H-15), 5.91 (1H, *dd*, *J* = 17, 10 Hz, H-14). (12*S*,13*R*)-Isomers, ¹H NMR (CDCl₃, *inter alia*): δ 3.38/3.39 (*d*, *J* = 10 Hz, H-12), 4.75 (s, H-17), 4.89 (s, H-17), 5.17 (*d*, *J* = 10 Hz, H-15), 5.33 (*d*, *J* = 17 Hz, H-15), 5.90 (*dd*, *J* = 17, 10 Hz, H-14).

15,16-Bisnor-8,17-epoxy-13-oxolabd-11E-en-19-oic acid (**16**). Oil, $[\alpha]_D^{25} + 7^\circ$ (CHCl₃; *c* 1.0). IR $\nu_{\max}^{\text{neat}} \text{ cm}^{-1}$: 3600–3200, 1700 (C=O), 1688, 1640, 1252, 1000, 890. UV $\lambda_{\max}^{\text{MeOH}} \text{ nm}$ (ϵ): 227 (1833). EIMS (70 eV) *m/z* (rel. int.): 306

[M]⁺ (3), 275 (50), 263 (10), 167 (9), 121 (41), 55 (36), 43 (100). Exact mass [M]⁺ for C₁₈H₂₆O₄ requires 306.1831. Found 306.1823.

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