Pergamon

0031-9422(95)00795-4

Phytochemistry, Vol. 41, No. 5, pp. 1361–1365, 1996

0031-9422/96 $15.00 + 0.00

TERPENES FROM HEARTWOOD OF *JUNIPERUS CHINENSIS*

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(*Received* 3 *August* 1995)

Key Word Index—*Juniperus chinensis*; Cupressaceae; wood; sesquiterpenes; diterpenes; norditerpene.

Abstract—A bisnorditerpene, 14 diterpenes and 12 sesquiterpenes were isolated from the heartwood of *Juniperus chinensis*. A new diterpene found (15-hydroxylabda-8(17),11*E*,13*E*-trien-19-oic acid), and three new sesquiterpenes (cedr-3-en-15-ol, junipercedrol and α-longipinen-12-ol) were found. Junipercedrol, with a new skeleton, was determined to be 2,2,6,9-tetramethyltricyclo[5.2.2.0^{3,7}]undecan-9-ol by spectral analyses and its stereochemistry was established by an X-ray analysis. This is also the first report in nature of thujopen-12-ol sesquiterpene.

INTRODUCTION

Juniperus chinensis, Cupressaceae, 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, 46 diterpenes, 12 norditerpenes, a bisnorditerpene and a secoditerpene in addition to other components from the bark and leaves [4–8]. The diterpenes include labdane-, abietane-, sempervirane-, totarane- and chinane-types. Labdane-type diterpenes are rich in the bark, whereas abietane-type diterpenes predominate in the leaves. The norditerpenes are norabietanes except for norpimarane. We report here the sesquiterpenoid and diterpenoid constituents found in the heartwood of *J. chinensis*.

RESULTS AND DISCUSSION

The acetone-soluble part of the air-dried heartwood of *J. chinensis* was concentrated and subjected to repeated column chromatography to give sesquiterpenes **1–12**, diterpenes **13–26** and a bisnorditerpene **27**. By analyses of their physical and spectroscopic properties (mp, [α], IR, mass spectrum, ^{1}H and ^{13}C NMR), the structures of known compounds were assigned: β-cuparenol (**1**) [9], α-acorenol (**2**) [10], thujopsen-12-ol (**3**) [11], isoleptographiol (**4**) [12], caryophyllene oxide (**5**) [13], 6,7-epoxycaryophyll-3(15)-en-14-ol (**6**) [14], cedrol (**8**) [15], cedran-3α-ol (**9**) [15], cedrane-3β,12-diol (**10**) [16], ferruginol (**13**) [6], hinokiol (**14**) [17], dehydroabietinol (**15**) [18], abieta-8,11,13-trien-7-one (**16**) [6], sugiol (**17**) [6], totarol (**18**) [6], sandaracopimaric acid (**19**) [6], *trans*-communic acid (**20**) [6], *cis*-communic acid (**21**) [6], agathic acid (**22**) [6], isocupressic acid (**23**) [6], acetylisocupressic acid (**24**) [19], 15-hydroxylabd-8(17)-en-19-oic acid (**26**) [20], and 15,16-bisnor-13-oxolabda-8(17), 11*E*-dien-19-oic acid (**27**) [21]. The *cis*-relationship of H-4 and the Me-1 group in **1** was confirmed by the nOe experiment, i.e. irradiation of the methyl group (at δ 1.23) caused an 11% enhancement of H-4 (at δ 4.57). This is the first report of thujopen-12-ol in nature, although it was previously prepared by oxidation of thujopsene [11]. Sandaracopimaric acid is the most abundant constituent.

Compound **7** ($C_{15}H_{24}O$) showed an IR absorption at 3331 cm^{-1} attributable to a hydroxyl group. By comparison of its ^{1}H and ^{13}C NMR spectral data with those of cedr-3-ene [15] and cedr-3-en-12-ol [15], the structure of **7** was assigned as cedr-3-en-15-ol. Compound **7** contains an allyl alcohol moiety as resonances occurred at relatively lower fields (δ 5.48, 3.99 and 3.93) than the signals of the olefinic and carbinyl protons in cedr-3-en-12-ol (at δ 5.26, 3.56 and 3.47).

The molecular formula of **11**, $C_{15}H_{26}O$, was deduced from the exact mass $[M]^+$ *m/z* 222.197. The IR absorption of a hydroxyl group appeared at 3452 cm^{-1}. The corresponding tertiary carbinyl carbon appeared at δ 76.2 (*s*) . All the carbon signals had chemical shifts smaller than 80 ppm, indicating **11** to be a tricyclic compound without double bond. Detailed analyses of the ^{1}H–^{1}H COSY and HMBC spectra led to the assignment of **11**, (junipercedrol) as 2,2,6,9-tetramethyltricyclo [5.2.2.0^{3,7}] undecan-9-ol. It is a sesquiterpene with a new skeleton. The stereochemistry of **11** was established by an X-ray analysis. By analogy to the cedrane compounds such as **8–10**, compounds **7** and **11** are considered to have, respectively, the (2*R*,6*R*,7*R*,10*R*)- and (1*R*,3*S*,6*R*,7*R*,9*R*)-configurations.

The molecular formula of **12**, $C_{15}H_{24}O$, was deduced from the exact mass $[M]^+$ *m/z* 220.182. The presence of

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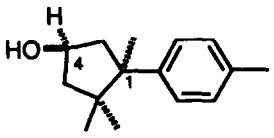

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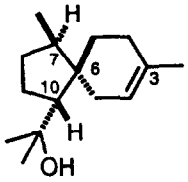

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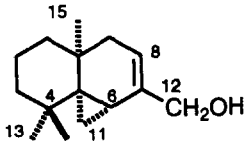

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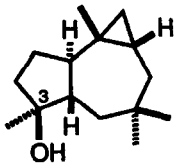

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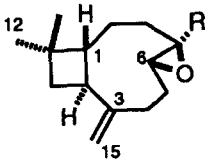
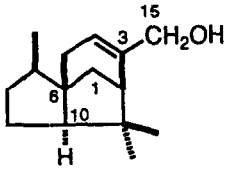


5 R = CH_3
6 R = CH_2OH



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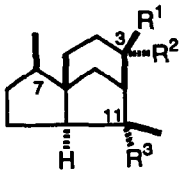
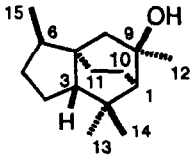
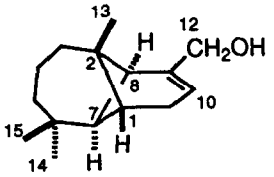


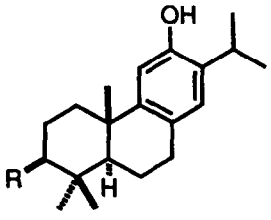


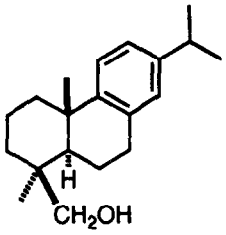


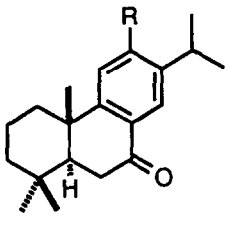
8 R^1 = OH, R^2 = R^3 = CH_3
9 R^1 = R^3 = CH_3, R^2 = OH
10 R^1 = OH, R^2 = CH_3, R^3 = CH_2OH

11

12







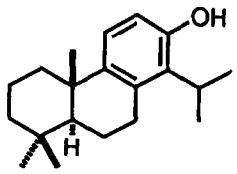
13 R = H
14 R = OH

15

16 R = H
17 R = OH

a CH_2OH group was inferred from the IR absorption at 3376 cm^{-1} and the carbinyl carbon appearing at δ 65.9 (*t*). Compound **12** contains a trisubstitiuted double bond as two olefinic carbons showed at δ 119.0 (*d*) and 151.0 (*s*). The proton resonances at δ 5.44 and 3.96 (2 H) confirmed the presence of an allylic alcohol moiety. From the ^1H–^1H COSY and HMBC spectra, compound **12**, named α-longipinen-12-ol, was assigned as 2,6,6-trimethyl-9-(hydroxymethyl)tricyclo [5.4.0.$0^{2,8}$] undec-9-ene. Except for the signals of the allylic alcohol moiety all the ^1H and ^{13}C signals of **12** were similar to those of α-longipinene [22]. By analogy to the structure of α-longipinene, compound **12** was tentatively assigned to have the (1*R*,2*S*,7*R*,8*S*)-configuration.

Compound **25** was readily assigned as 15-hydroxylabda-8(17),11*E*,13*E*-trien-19-oic acid by analyses of the IR, MS, ^1H and ^{13}C NMR spectra. The IR absorptions at 3372 and 3200–2500 cm^{-1} were attributable to the hydroxyl and carboxyl groups. The proton and carbon resonances of **25** were assigned by assistance of the ^1H–^1H and ^1H–^{13}C correlated spectra. The stereochemistry of **25** was established by NOE studies. Irradiation of methyl-10 (at δ 0.71) caused a 12% NOE of H-11 (at δ 5.70), but no enhancement of methyl-4 (at 1.24). Irradia-



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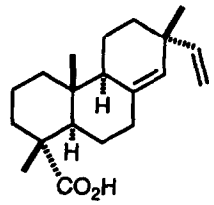

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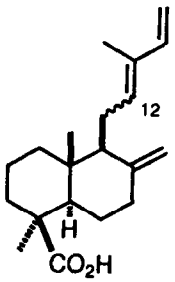
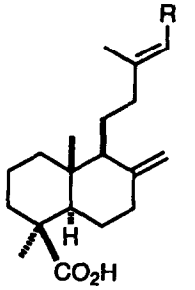
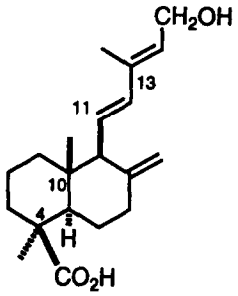


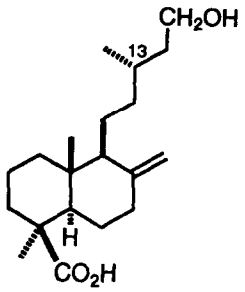
20 (12*E*)
21 (12*Z*)



22 R = CO_2H
23 R = CH_2OH
24 R = CH_2OAc



25



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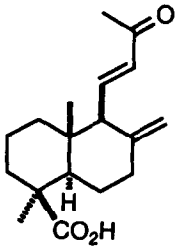


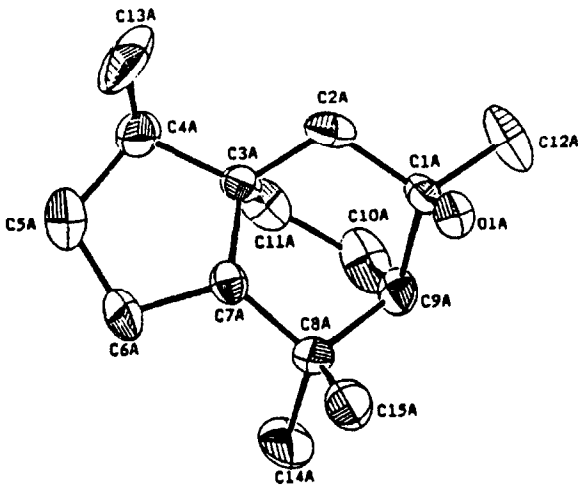
27

tion of methyl-13 (at 1.91) caused also enhancements of H-11 and H-15 (at δ 4.26), indicating the (11*E*,13*E*)-configuration. Compound **25** was assigned the (4*S*,5*R*, 9*S*,10*R*)-configuration by analogy to labdenoic acids **22–24.**

EXPERIMENTAL

Plant material. The heartwood of *Juniperus chinensis* Linn. var. *kaizuka* Hort. were collected from the plants 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 heartwood (1.1 kg) was sliced, air-dried and extracted with Me_2CO (8 l × 3). The combined extracts were treated with activated charcoal and filtered to remove coloured material. The filtrate was concd to give a residue (24 g), which was absorbed by silica gel (30 g) and then chromatographed on a column packed with 250 g of silica gel. By elution with gradients of hexane and EtOAc, compounds **5** (7 mg), **16** (12 mg), **13** (14 mg), **18** (13 mg), **2** (33 mg), **8** (20 mg), **11** (20 mg), **9** (13 mg), **6** (3 mg), **4** (7 mg), **12** (11 mg), **3** (12 mg), **7** (43 mg), **17** (8 mg), **20** (11 mg), **21** (20 mg), **1** (7 mg), **15** (4 mg), **19** (1.2 g), **27** (12 mg), **14** (8 mg), **26** (12 mg), **10** (11 mg), **24** (44 mg), **23** (15 mg), **25** (21 mg) and **22** (10 mg) were obtained in ascending order of polarity. These compounds were further purified by HPLC using a Hibar Lichrospher Si 60 (Merck, 10 μm) cloumn (25 cm × 1 cm).

β-Cuparenol (**1**). Oil, $[\alpha]_D^{30}$ + 58.3° ($CHCl_3$; *c* 0.7). ref. [9] $[\alpha]_D^{30}$ + 63.8° ($CHCl_3$). ^{13}C NMR ($CDCl_3$): δ 20.8



ORTEP drawing of **11**

Scheme 1.

(*q*), 24.5 (*q*), 25.3 (*q*), 27.0 (*q*), 43.0 (*s*), 47.3 (*t*), 50.1 (*t*), 50.7 (*s*), 70.5 (*d*), 126.7 (*d*, 2 C), 128.4 (*d*, 2 C), 135.0 (*s*), 143.5 (*s*).

α-Acorenol (**2**). Oil, R_f 0.2 (EtOAc–hexane, 1:15). $[\alpha]_D^{25}$ − 36.1° ($CHCl_3$; *c* 3.3). ref. [10] $[\alpha]_D$ − 36.1°. ^{13}C NMR ($CDCl_3$): δ 14.9 (*q*), 23.2 (*q*), 26.0 (*t*), 28.0 (*q*), 28.0 (*t*), 29.1 (*t*), 30.1 (*t*), 30.6 (*t*), 31.4 (*q*), 41.6 (*d*), 45.0 (*s*), 54.7 (*d*), 73.7 (*s*), 121.2 (*d*), 135.0 (*s*).

Thujopsen-12-ol (**3**). Oil, R_f 0.18 (EtOAc–hexane, 1:10). $[\alpha]_D^{18}$ − 82° ($CHCl_3$; *c* 1.2). ^{13}C NMR ($CDCl_3$): δ 11.4 (*t*), 18.9 (*d*), 19.4 (*t*), 26.8 (*q*), 28.5 (*q*), 29.0 (*q*), 31.7 (*s*), 33.9 (*s*), 34.6 (*s*), 36.5 (*t*), 40.2 (*t*), 40.6 (*t*), 67.1 (*t*), 116.3 (*d*), 139.4 (*s*).

Isoleptographiol (**4**). Oil, $[\alpha]_D^{28}$ + 13.2° ($CHCl_3$; *c* 0.7). ref. [12] $[\alpha]_D^{23}$ + 14.6° ($CHCl_3$; *c* 0.63).

(6*R*,7*R*)-6,7-*Epoxycaryophyll*-3(15)-*ene* (**5**). $[\alpha]_D^{25}$ −62° ($CHCl_3$; *c* 0.7). ref. [12] $[\alpha]_D^{20}$ − 79.4° ($CHCl_3$; *c* 2.32). ^{13}C NMR ($CDCl_3$): δ 17.0 (*q*), 21.6 (*q*), 27.2 (*t*), 29.8 (*t*), 29.9 (*q*), 30.2 (*t*), 34.0 (*s*), 39.1 (*t*), 40.0 (*t*), 48.7 (*d*), 51.0 (*d*), 59.0 (*s*), 63.7 (*d*), 113.0 (*t*), 152.0 (*s*).

(6*R*,7*R*)-6,7-*Epoxycaryophyll*-3(15)-*en*-14-*ol* (**6**). Oil, $[\alpha]_D^{32}$ − 38.2° ($CHCl_3$; *c* 0.3). ref. [14] $[\alpha]_D^{18}$ − 34.6° ($CHCl_3$; *c* 0.5).

Cedr-3-*en*-15-*ol* (**7**). Oil, R_f 0.17 (EtOAc–hexane, 1:10). $[\alpha]_D^{25}$ − 0.93° ($CHCl_3$; *c* 4.3). IR υ_{max}^{neat} cm^{-1}: 3331 (OH). ^1H NMR ($CDCl_3$): δ 0.82 (*d*, *J* = 7.2 Hz, Me-7), 0.93 (*s*, Me-11), 0.96 (*s*, Me-11), 1.25–1.98 (*m*, 11 H), 2.24 (*m*, 1 H), 3.93, 3.99 (2 H, AB *quartet*, *J* = 7.4 Hz, H-15), 5.48 (*m*, H-4), ^{13}C NMR ($CDCl_3$): δ 15.4 (*q*, C-14), 24.5 (*t*, C-9), 25.4 (*q*, C-13), 27.6 (*q*, C-12), 36.0 (*t*, C-8), 38.6 (*t*, C-5), 40.6 (*t*, C-1), 41.4 (*d*, C-7), 48.3 (*s*, C-11), 50.3 (*d*, C-10), 54.2 (*s*, C-6), 59.0 (*d*, C-2), 67.1 (*t*, C-15), 120.3 (*d*, C-4), 144.0 (*s*, C-3). EI-MS (70 eV) *m/z* (rel. int.): 220 $[M]^+$ (20), 202 (4), 189 (9), 177 (18), 147 (17), 135 (100). Exact mass $[M]^+$ for $C_{15}H_{24}O$ requires 220.1827. Found 220.1836.

Cedrol (**8**). Mp 80–81°, $[\alpha]_D^{25}$ + 8.5° ($CHCl_3$; *c* 2). Ref. [15] mp 86–87°, $[\alpha]_D^{28}$ + 10.5° ($CHCl_3$; *c* 5).

Cedran-3α-*ol* (**9**). Oil $[\alpha]_D^{28}$ + 10.9° ($CHCl_3$; *c* 1.3). ^{13}C NMR ($CDCl_3$); δ 15.4 (*q*), 25.4 (*t*), 28.1 (*q*), 29.0 (*q*), 30.5 (*t*), 30.6 (*q*), 34.3 (*t*), 36.9 (*t*), 39.9 (*t*), 41.8 (*s*), 41.9 (*d*), 53.4 (*s*), 56.2 (*d*), 61.5 (*d*), 73.3 (*s*).

Cedrane-3β,12-*diol* (**10**). $[\alpha]_D^{20}$ − 7° ($CHCl_3$; *c* 1.1). Ref. [15] $[\alpha]_D^{25}$ − 5° ($CHCl_3$; *c* 1.2). ^{13}C NMR ($CDCl_3$): δ 15.4 (*q*), 22.5 (*q*), 23.9 (*t*), 30.4 (*q*), 31.3 (*t*), 34.4 (*t*), 37.5 (*t*), 41.4 (*d*), 41.7 (*t*), 47.1 (*s*), 53.3 (*s*), 54.5 (*d*), 57.2 (*d*), 70.0 (*t*), 74.5 (*s*).

2,2,6,9-*Tetramethyltricyclo*[5.2.2.0^{3,7}]*undecan*-9-*ol* (**11**). White needles, mp 50–51°, $[\alpha]_D^{25}$ + 82° ($CHCl_3$; *c* 1.3). IR υ_{max}^{neat} cm^{-1}: 3452 (OH). ^1H NMR ($CDCl_3$): δ 0.78 (*d*, *J* = 7.2 Hz, Me-6), 0.88 (*m*, H-4), 0.91 (*s*, Me-2), 1.02 (*m*, H-5), 1.09 (*dd*, *J* = 2.4, 1.8 Hz, H-1), 1.25 (*s*, Me-2), 1.33 (*m*, H-11), 1.36 (*s*, Me-9), 1.36 (*m*, H-10), 1.38 (*d*, *J* = 13.2 Hz, H-8), 1.38 (*m*, H-4), 1.46 (*m*, H-6), 1.46 (*d*, *J* = 13.2 Hz, H-8), 1.54 (*m*, H-11), 1.67 (*dd*, *J* = 6.8, 1.3 Hz, H-3), 1.68 (*m*, H-10), 1.95 (*m*, H-5). ^{13}C NMR ($CDCl_3$): δ 17.8 (*q*, C-15), 21.4 (*t*, C-10), 23.6 (*t*, C-11), 27.2 (*q*, C-14), 28.5 (*t*, C-4), 32.6 (*q*, C-12), 33.7 (*q*, C-13), 34.1 (*s*, C-2), 34.6 (*t*, C-5), 39.7 (*d*, C-6), 43.4 (*s*, C-7), 47.1 (*t*, C-8), 49.1 (*d*, C-1), 50.6 (*d*, C-3), 76.2 (*s*, C-9). EI-MS (70 eV) *m/z* (rel. int.): 222 $[M]^+$ (3), 203 (13), 204 (10), 189 (10), 43 (100). Exact mass $[M]^+$ for $C_{15}H_{26}O$ requires 222.1985. Found 222.1972.

2,6,6-*Trimethyl*-9-(*hydroxymethyl*)*tricyclo*[5.4.0.0.^{2,8}]*undec*-9-*ene* (**12**). Oil, $[\alpha]_D^{25}$ + 3.0° ($CHCl_3$; *c* 1.1). IR υ_{max}^{neat} cm^{-1}: 3376 (OH), 1670, 810. ^1H NMR ($CDCl_3$): δ 0.81 (3 H, *s*, H-13), 0.81 (3 H, *s*, H-15), 0.89 (3 H, *s*, H-14), 1.31 (*m*, H-5), 1.33 (*m*, H-5), 1.45 (*br s*, H-7), 1.56 (2 H, *m*, H-4), 1.57 (*m*, H-3), 1.62 (*m*, H-3), 2.10 (*m*, H-1), 2.20 (*br s*, H-8), 2.28 (2 H, *br s*, H-11), 3.96 (2 H, *br s*, H-12), 5.44 (*br s*, H-10). ^{13}C NMR ($CDCl_3$): δ 21.7 (*t*, C-4), 23.9 (*q*, C-13), 27.8 (*q*, C-15), 28.0 (*q*, C-14), 32.8 (*s*, C-6), 34.1 (*t*, C-11), 39.0 (*t*, C-5), 39.8 (*s*, C-2), 40.1 (*d*, C-1), 40.9 (*t*, C-3), 42.6 (*d*, C-8), 59.1 (*d*, C-7), 65.9 (*t*, C-12), 119.0 (*d*, C-10), 151.0 (*s*, C-9). EI-MS (70 eV) *m/z* (rel. int.): 220 $[M]^+$ (15), 205 (5), 202 (10), 189 (23), 159 (20), 135 (100), 121 (26), 119 (48), 105 (72). Exact mass $[M]^+$ for $C_{15}H_{24}O$ requires 220.1828. Found 220.1818.

Ferruginol (**13**). $[\alpha]_D^{25}$ + 43.1°. ($CHCl_3$; *c* 1.4). Ref. [6] $[\alpha]_D$ + 40.6° (EtOH).

Hinokiol (**14**). Mp 233–235°, $[\alpha]_D^{18}$ + 77.5° ($CHCl_3$; *c* 0.8). Ref. [17] mp 234–235°, $[\alpha]_D^{18}$ + 74.4° ($CHCl_3$; *c* 1.0).

Dehydroabietinol (**15**). Oil, $[\alpha]_D^{20}$ + 44° ($CHCl_3$; *c* 0.4). Ref. [18] $[\alpha]_D^{25}$ + 43.4° ($CHCl_3$; *c* 2.0).

Abieta-8,11,13-*trien*-7-*one* (**16**). Mp 87–90°, $[\alpha]_D^{25}$ + 6° ($CHCl_3$; *c* 1.2). Ref. [6] mp 88–90°, $[\alpha]_D^{25}$ + 4° (EtOH; *c* 3.4).

Sugiol (**17**). Mp 290–293°, $[\alpha]_D^{25}$ + 24° ($CHCl_3$; *c* 0.8). Ref. [6] mp 291–293°, $[\alpha]_D^{25}$ + 25° (EtOH, *c* 8).

Totarol (**18**). Mp 131–132°, $[\alpha]_D^{20}$ + 41° ($CHCl_3$; *c* 1.3). Ref. [6] mp 131–132°, $[\alpha]_D^{20}$ + 40.2° EtOH, *c* 2.2).

Sandaracopimaric acid (**19**). Mp 173.5–175°, $[\alpha]_D^{25}$ − 3.5° ($CHCl_3$; *c* 1.2). Ref. [6] mp 174–175°, $[\alpha]_D^{25}$ − 14.4° (EtOH, *c* 1.1).

trans-*Communic acid* (**20**). Mp 130–132°, $[\alpha]_D^{30}$ + 36° ($CHCl_3$, *c* 0.9). Ref. [6] mp 130–132°, $[\alpha]_D^{25}$ + 38° (EtOH, *c* 1).

cis-*Communic acid* (**21**). ^{13}C NMR ($CDCl_3$): δ 12.8 (*q*), 19.7 (*q*), 19.9 (*t*), 22.2 (*t*), 25.8 (*t*), 29.0 (*q*), 37.8 (*t*), 38.5 (*t*), 39.2 (*t*), 40.4 (*s*), 44.2 (*s*), 56.2 (*d*), 56.6 (*d*), 107.8 (*t*), 113.2 (*t*), 131.5 (*d*), 131.6 (*s*), 133.8 (*d*), 147.9 (*s*), 184.4 (*s*).

Agathic acid (**22**). Mp 203–205°, $[\alpha]_D^{18}$ + 60° ($CHCl_3$, *c* 1.0). Ref. [6] mp 203–204°, $[\alpha]_D$ + 65° (95% EtOH).

Isocupressic acid (**23**). Oil, $[\alpha]_D^{25}$ + 41.2° ($CHCl_3$; *c* 1.5). Ref. [6] $[\alpha]_D^{25}$ + 42° ($CHCl_3$; *c* 2.5).

15-*Acetoxylabda*-8(17),13*E*-*dien*-19-*oic acid* (**24**). Mp 75–78°, $[\alpha]_D^{25}$ + 42.0° ($CHCl_3$; *c* 4.4). Ref. [19] $[\alpha]_D$ + 49° (*c* 1.1).

15-*Hydroxylabda*-8(17),11*E*,13*E*-*trien*-19-*oic acid* (**25**). Oil, $[\alpha]_D^{25}$ − 0.66° ($CHCl_3$; *c* 2.1). IR υ_{max}^{neat} cm^{-1}: 3372 (OH), 3200–2500 (acid), 1688 (C=O), 1639, 791. ^1H NMR ($CDCl_3$): δ0.71 (*s*, Me-10), 1.24 (*s*, Me-4), 1.30–2.10 (9 H, *m*), 1.91 (*s*, Me-13), 2.12–2.17 (*m*, H-7), 2.34 (*d*, *J* = 9.8 Hz, H-9), 2.41–2.46 (*m*, H-7), 4.26 (2 H, *d*, *J* = 6.9 Hz, H-15), 4.46 (*br s*, H-17), 4.73 (*br s*, H-17), 5.56 (*t*, *J* = 6.9 Hz, H-14), 5.70 (*dd*, *J* = 15.5, 9.8 Hz, H-11), 6.02 (*d*, *J* = 15.5 Hz, H-12). ^{13}C NMR ($CDCl_3$): δ 12.8 (*q*, Me-13), 13.5 (*q*, Me-10), 19.6 (*t*), 25.0 (*t*), 28.9 (*q*, Me-4), 37.2 (*t*), 38.1 (*t*), 39.8 (*s*), 40.8 (*t*), 44.1 (*s*), 55.7 (*d*, C-5), 59.3 (*t*, C-15), 60.5 (*d*, C-9), 108.0 (*t*, C-17), 127.7 (*d*, C-11), 128.4 (*d*, C-14), 136.4 (*s*, C-13), 136.7 (*d*, C-12), 149.6 (*s*, C-8), 183.0 (*s*, C-19). EI-MS (70 eV) *m/z* (rel. int.): 318 $[M]^+$ (1), 300 (62), 285 (24), 255 (10), 161 (30), 145 (46), 133 (100).

15-*Hydroxylabd*-8(17)-*en*-19-*oic acid* (**26**). Oil, $[\alpha]_D^{20}$ + 18.7° ($CHCl_3$; *c* 1.2). Ref. [20] $[\alpha]_D^{25}$ + 17.9° ($CHCl_3$). ^{13}C NMR ($CDCl_3$): δ 12.7 (*q*), 19.8 (*q*), 19.9 (*t*), 21.1 (*t*), 26.0 (*t*), 29.0 (*q*), 30.2 (*d*), 36.4 (*t*), 38.0 (*t*), 38.7 (*t*), 39.1 (*t*), 39.4 (*t*), 40.5 (*s*), 44.1 (*s*), 56.3 (*d*), 56.6 (*d*), 61.1 (*t*), 106.3 (*t*), 148.2 (*s*), 183.3 (*s*).

15,16-*Bisnor*-13-*oxolabda*-8(17),11*E*-*dien*-19-*oic acid* (**27**). Oil, $[\alpha]_D^{24}$ + 20.5° ($CHCl_3$; c 1.2). Ref. [21] $[\alpha]_D^{20}$ + 24.1° (MeOH; *c* 1.0).

Acknowledgements—We are grateful to the National Science Council of the Republic of China for financial support and to Mr Gene-Hsian Lee (Advanced Instrumentation Centre) for the X-ray diffraction of compound **11**.

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