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SESQUITERPENES FROM LEAVES OF *CRYPTOMERIA JAPONICA*

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Key Word Index—*Cryptomeria japonica*; Taxodiaceae; leaves; sesquiterpenes.

Abstract—Twenty-seven sesquiterpenes were isolated from leaves of *Cryptomeria japonica*. The new compounds included elem-1-en-4,11-diol, 11-acetoxyeudesman-4α-ol, eudesmane-5α,11-diol, 3-eudesmene-1β,11-diol, 1β-acetoxy-3-eudesmen-11-ol, 4-eudesmene-1β,11-diol, 1β-acetoxy-4-eudesmen-11-ol, 7-epi-γ-eudesmol, 7-epi-4-eudesmene-1β,11-diol, 1β-acetoxy-4(15)-eudesmen-11-ol. Their structures were determined by chemical and spectral methods.

INTRODUCTION

The Japanese cedar, *Cryptomeria japonica* D. Don., is a widely distributed conifer called 'sugi' in Japanese. We recently reported the isolation and structural determination of chamaecydin triterpene [1], abietane, kaurane and labdane diterpenes [2, 3] from the ethyl acetate-soluble part of the leaves of *C. japonica*. As a continuation of this study, we describe herein, 27 constituents of sesquiterpenes including 10 novel compounds **5**, **8**, **9**, **11**, **12**, **14–17**, and **23**.

RESULTS AND DISCUSSION

The leaves of *C. japonica* were extracted with acetone. The ethyl acetate-soluble portion of the extract was subjected to chromatography to give sesquiterpenes **1–27**. The known compounds epitodomatuic acid (**1**) [4], epijuvabione (**2**) [4], 11-hydroxy-4,5-secoeudesmane-4,5-dione (**3**) [5], elemol (**4**) [6], cryptomeridiol (**6**) [7], 4-epicryptomeridiol (**7**) [8], α-eudesmol (**10**) [9, 10], γ-eudesmol (**13**) [9], 6-eudesmene-1β,4β-diol (**18**) [11], oplodiol (**19**) [10, 12], β-eudesmol (**20**) [13], 4(15)-eudesmene-1β,11-diol (**21**) [14], 4(15)-eudesmene-1β,6α-diol (**22**) [15, 16], α-cadinol (**24**) [17], T-cadinol (**25**) [18], oplopanone (**26**) [19] and cedrol (**27**) [20] were identified by comparison of their physical and spectral data (mp, [α], mass, IR, ^{1}H and ^{13}C NMR) with literature.

The molecular formula, $C_{15}H_{28}O_2$, of **5** was inferred from its exact mass 240.209. The ^{13}C NMR spectrum showed signals for a terminal double bond at δ153.3 (*d*) and 109.5 (*t*). The signals for two isopropanol moieties appeared at δ1.17 (Me), 1.18 (3 Me), 72.7 (*s*) and 75.4 (*s*). The proton resonance at δ1.57 was assigned to H-5 by means of C–H COSY and HMBC. As H-5 appeared as a double of doublet (J = 12, 3 Hz), it was in the axial orientation. Compound **5** had chemical shifts for C-7 and C-10 at δ49.5 (*d*) and 40.3 (*s*), close to the values for those signals in elemol. The structure of **5** was determined to be elem-1-en-4,11-diol and its (5*R*,7*R*,10*S*)-configuration was tentatively assigned by analogy to that of elemol. Compound **5** was unstable in $CDCl_3$ solution. A product **5a**, (1*S*)-elemane-1,4,11-triol, was obtained presumably by the acid-catalysed hydration of **5**. The *S*-configuration was determined by Horeau's method [21]. Compound **5** can be also regarded as a hydration derivative of elemol (**4**).

From spectral analyses, **8** ($C_{17}H_{30}O_3$) was readily determined to be 11-acetoxyeudesman-4α-ol. It showed the IR absorption at 1723 cm^{-1} and carbon resonances at δ22.4 and 170.5 for the acetoxy group. The structure of **8** was confirmed as it was saponified to yield cryptomeridiol (**6**). Two C-11 methyl groups in **6** appearing at δ1.16 were deshielded to δ1.40 and 1.43 in **8** as the C-11 hydroxyl group was converted to the acetoxy group.

An eudesmanediol (**9**) ($C_{15}H_{28}O_2$) exhibited the parent peak in the mass spectrum at m/z 240.209. The C–H COSY and HMBC experiments led to the assignment of **9** as eudesmane-5α,11-diol. Irradiation of Me-10 (at δ0.93) caused 7% NOE of Me-4 (at δ0.81) and 10% NOE of H-6β (at δ1.28). The signal of H-6α appeared at a relatively low field δ1.72 presumably due to the deshielding effect of the 5α-hydroxyl group. The large coupling constant 12.5 Hz between H-6β and H-7 was in agreement with their axial positions.

Based on the spectral analyses, two isomers ($C_{15}H_{26}O_2$) **11** and **14**, were assigned as 3-eudesmene-1β,11-diol and 4-eudesmene-1β,11-diol, respectively. Two olefinic carbons in **11** occurred at δ119.5 (*d*) and 135.4 (*s*), whereas those in **14** appeared at δ123.8 (*s*) and 133.6 (*s*). The H-1 in **11** was axially oriented to exhibit its resonance as a double of doublet (at δ3.50) with 10 and 6.5 Hz coupling constants. The resonance of H-1 in **14** also showed a similar pattern (*dd*, J = 9, 7 Hz). An allylic

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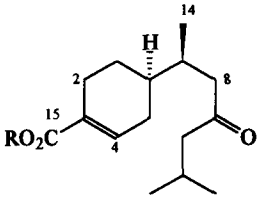

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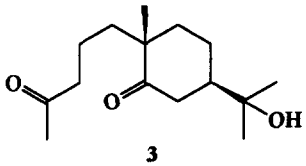

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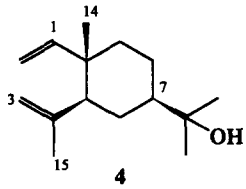

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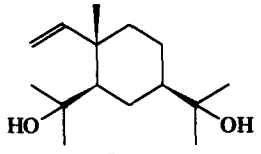

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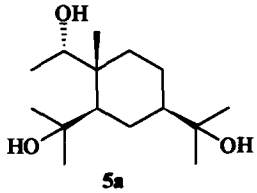

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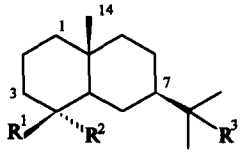
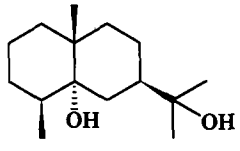


	R^1	R^2	R^3
6	CH_3	OH	OH
7	OH	CH_3	OH
8	CH_3	OH	OAc



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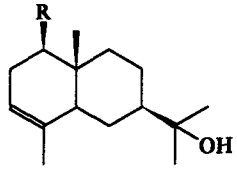
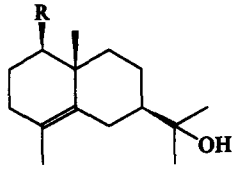
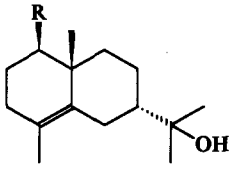


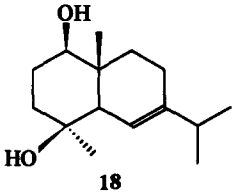
10 R = H
11 R = OH
12 R = OAc



13 R = H
14 R = OH
15 R = OAc



16 R = H
17 R = OH



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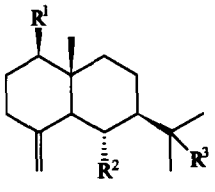
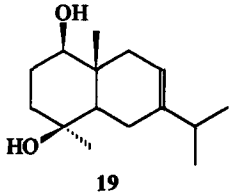


	R^1	R^2	R^3
20	H	H	OH
21	OH	H	OH
22	OH	OH	H
23	OAc	H	OH



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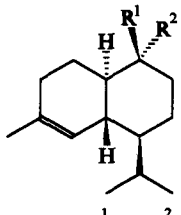
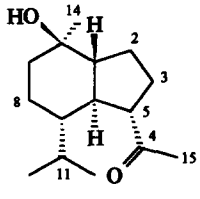


	R^1	R^2
24	CH_3	OH
25	OH	CH_3



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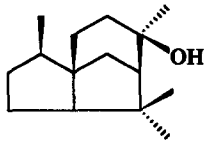

27

proton H-5 appearing at δ1.66 (*dd*, J = 9, 3 Hz) also conformed to the *trans*-fused configuration of **11**. The C-7 resonances of **11** and **14** occurred at δ49.2 and 49.7 close to the value of C-7 (δ50.0) in α-eudesmol (**10**).

Compounds **12** and **15** are 1β-acetoxy-3-eudesmen-11-ol and 1β-acetoxy-4-eudesmen-11-ol, the acetates of **11** and **14**, respectively. Due to the inductive effect of acetoxy groups, the H-1 resonances in **12** and **15** occurred at low fields δ4.74 (*dd*, J = 9.5, 6.5 Hz) and 4.67 (*dd*, J = 8, 8 Hz). Saponification of **12** and **15** gave, respectively, the corresponding diol **11** and **14**.

Compounds **16** ($C_{15}H_{26}O$) and **17** ($C_{15}H_{26}O_2$) were determined to be 7-epi-γ-eudesmol and 7-epi-4-eudesmene-1β,11-diol, respectively. The coupling constants between the C-7 and C-6 protons were small (2–3.5 Hz) as the C-7 protons were on equatorial positions. The C-7 signals in **16** and **17** appeared at δ44.1, whereas those signals in their 7-epimers **13** and **14**

Table 1. ^{1}H NMR spectral data of new compounds ($CDCl_3$ solution, δ values in ppm, J values in Hz)*†

H	5	9	11	12	14	15	16	17	23
1	6.04 (*dd*, *J* = 10.5,17.5)	1.12 (*m*)	3.50 (*dd*, *J* = 6.5,10)	4.74 (*dd*, *J* = 6.5,9.5)	3.41 (*dd*, *J* = 7.9)	4.67 (*dd*, *J* = 8.8)		3.50 (*dd*, *J* = 8.8)	4.64 (*dd*, *J* = 4.5, 11.5)
		1.95 (*m*)							
2	4.92 (*dd*, *J* = 1,10.5)	1.35 (*m*)	1.86 (*dd*, *J* = 10,13.5)	2.00 (*dd*, *J* = 9.5,13.5)	1.65 (*m*)				
	5.00 (*dd*, *J* = 1,17.5)	1.60 (*m*)	2.27 (*dd*, *J* = 6.5,13.5)	2.34 (*dd*, *J* = 6.5,13.5)	1.20 (*m*)				
3	1.17 (s)	1.35 (*m*)	5.25 (*br s*)	5.24 (*br s*)	1.95 (*ddd*, *J* = 3,3,12.5)	1.96 (*ddd*, *J* = 2,3,12)			2.13 (*ddd*, *J* = 5,12,13.5)
		1.40 (*m*)			2.15 (*ddd*, *J* = 2,9.5,12.5)	2.20 (*ddd*, *J* = 2,9,12)			2.29 (*ddd*, *J* = 2,5,13.5)
5	1.57 (*dd*, *J* = 3,12)		1.66 (*dd*, *J* = 3,9)	1.85 (*brd*, *J* = 12)					1.78 (*dd*, *J* = 2,12)
6		1.28 (*dd*, *J* = 12.5,12.5)			1.64 (*ddd*, *J* = 1.5,9,13.5)	1.70 (*dd*, *J* = 9,13.5)	2.10 (*dd*, *J* = 2,15)	2.01 (*dd*, *J* = 3.5,15)	
		1.72 (*dd*, *J* = 2.5,12.5)			2.58 (*ddd*, *J* = 2.5,3,13.5)	2.60 (*ddd*, *J* = 2,3,13.5)	2.69 (*dd*, *J* = 2,15)	2.59 (*dd*, *J* = 3,15)	
12	1.18 (s)	1.15 (s)	1.18 (s)	1.18 (s)	1.17 (s)	1.18 (s)	1.17 (s)	1.15 (s)	1.17 (s)
13	1.18 (s)	1.15 (s)	1.19 (s)	1.19 (s)	1.17 (s)	1.18 (s)	1.23 (s)	1.21 (s)	1.17 (s)
14	1.15 (s)	0.93 (s)	0.72 (s)	0.81 (s)	0.97 (s)	1.05 (s)	1.06 (s)	1.02 (s)	0.72 (s)
15	1.18 (s)	0.81 (*d*, *J* = 7)	1.59 (s)	1.59 (s)	1.55 (s)	1.57 (s)	1.66 (s)	1.63 (s)	4.51 (*d*, *J* = 1)
									4.75 (*d*, *J* = 1)
OAc				2.02 (s)		2.03 (s)			2.01 (s)

*Some assignable resonances for **8** appeared at δ0.84 (s, H-14), 1.08 (s, H-15), 1.40 (s, H-12), 1.43 (s, H-13), 1.94 (s, OAc) in addition to others.
†The rest appeared at δ1.0–2.0 overlapping with other signals.

appeared at lower fields ($\Delta\delta$ = 5 ppm) [22]. In contrast, the C-11 signals of the isopropanol moieties in **16** and **17** occurred at lower fields than those in **13** and **14**.

Compound **23** showed IR absorption at 3453 (broad) and 1711 cm^{-1} attributable to hydroxyl and acetyl groups. The exact mass at *m/z* 280.202 indicated the molecular formula $C_{17}H_{28}O_3$ and an intense signal at *m/z* 202 was attributable to the fragment derived by elimination of water and acetic acid $[M - H_2O - HOAc]^+$. By analysis of the ^{1}H and ^{13}C NMR spectra, the structure of **23** was determined to be 1β-acetoxy-4-(15)-eudesmen-11-ol. To confirm this structural assignment, **23** was saponified to give the eudesmenediol **21**.

In summary, a series of known and new sesquiterpenes were isolated from the leaves of *C. japonica*. The structures of new sesquiterpenes were determined by analyses of their spectra. The acetates **8**, **12**, **15** and **23** were correlated with their corresponding alcohols by saponification.

EXPERIMENTAL

General. Merck silica gel 60F sheets were used for analyt. TLC. HPLC was carried out on a Hibar Lichrosorb Si 60 (7 μm or 10 μm) column (25 cm × 1 cm).

Plant material. The plant used in this study is introduced from Japan and cultivated in suburban Taipei. A voucher specimen has been deposited in our laboratory. The leaves (1.4 kg) of *C. japonica* D. Don. were exhaustively extracted with Me_2CO. The Me_2CO extract was passed through a pad of charcoal, concd and re-extracted with EtOAc. The EtOAc-soluble portion (45 g) was chromatographed on a silica gel column by elution with gradient of hexane and EtOAc. The appropriate frs were combined and purified by HPLC to give **16** (20 mg), **2** (16 mg), **24** (12 mg), **25** (8 mg), **27** (22 mg), **23** (27 mg), **4** (12 mg), **10** (8 mg), **20** (13 mg), **8** (27 mg), **15** (10 mg), **12** (11 mg), **13** (15 mg), **26** (20 mg), **9** (21 mg), **1** (15 mg), **19** (8 mg), **17** (3 mg), **22** (12 mg), **11** (14 mg), **14** (50 mg), **3** (3 mg), **21** (15 mg), **18** (5 mg), **7** (35 mg), **5** (5 mg) and **6** (25 mg), in order of increasing polarity.

Epitodomatuic acid (**1**). Oil, $[\alpha]_D^{20}$ + 71° ($CHCl_3$; *c* 1.5), lit. [4], Oil, $[\alpha]_D^{25}$ + 71.2° ($CHCl_3$; *c* 1.07).

Epijuvabione (**2**). Oil, $[\alpha]_D^{25}$ + 60° ($CHCl_3$; *c* 1.6), lit. [4], Oil, $[\alpha]_D^{25}$ + 60° ($CHCl_3$; *c* 1.18).

11-*Hydroxy*-4,5-*secoeudesmane*-4,5-*dione* (**3**). Oil, $[\alpha]_D^{15}$ + 50° ($CHCl_3$; *c* 0.3), lit. [5], Oil, $[\alpha]_D^{24}$ + 46° ($CHCl_3$; *c* 0.39). ^{13}C NMR ($CDCl_3$, 75 MHz): δ18.3 (C-2), 21.9 (C-8), 23.1 (C-14), 27.2 (C-12), 27.4 (C-13), 29.9 (C-15), 36.3 (C-9), 37.3 (C-1), 39.8 (C-6), 44.3 (C-3), 47.1 (C-10), 49.6 (C-7), 72.0 (C-11), 209.1 (C-4), 215.8 (C-5).

Elemol (**4**). Oil, $[\alpha]_D^{25}$ − 6° ($CHCl_3$; *c* 1.8), lit. [6], mp 52–53°; $[\alpha]_D$ − 5.82° ($CHCl_3$; *c* 3.4). ^{13}C NMR ($CDCl_3$, 75 MHz): δ16.6 (C-14), 22.5 (C-8), 24.7 (C-15), 27.1 (C-12, 13), 28.5 (C-6), 39.7 (C-10), 39.9 (C-9), 49.3 (C-7), 52.7 (C-5), 72.7 (C-11), 109.9 (C-2), 112.0 (C-3), 147.9 (C-4), 150.2 (C-1).

Elem-1-*en*-4,11-*diol* (**5**). Oil, $[\alpha]_D^{15}$ − 14° ($CHCl_3$; *c* 0.5). TLC (50% EtOAc in hexane) R_f 0.44. IR ν_{max}^{neat} cm^{-1}: 3388, 3081, 1625, 914. EIMS (70 eV) *m/z* (rel. int.): 240 $[M]^+$

Table 2. ^{13}C NMR spectral data of new compounds (75 MHz, $CDCl_3$ solution, δ values in ppm)

C	5	8	9	11	12	14	15	16	17	23
1	153.3	41.0	33.0	76.3	78.2	78.3	80.3	39.4	75.4	80.7
2	109.5	20.2	22.2	32.3	29.1	27.1	23.9	18.9	26.9	28.0
3	31.5	43.6	30.5	119.5	119.0	31.9	31.5	32.7	31.3	33.8
4	75.4	72.2	32.4	135.4	135.3	123.8	124.0	126.0	125.1	148.2
5	55.7	54.8	75.2	46.5	46.4	133.6	133.4	135.0	133.6	48.7
6	23.0	21.2	32.1	23.9	23.7	26.5	26.3	25.4	25.2	24.2
7	49.5	47.2	45.2	49.2	49.1	49.7	49.7	44.1	44.1	47.6
8	25.5	22.1	21.3	21.9	21.8	22.8	22.7	22.6	21.8	21.9
9	43.8	44.4	36.3	35.0	34.9	38.8	38.6	38.1	33.5	36.6
10	40.3	34.6	37.6	37.4	36.3	39.4	38.4	34.4	39.5	39.1
11	72.7	85.1	72.5	72.9	72.8	72.7	72.6	74.6	74.1	72.7
12	27.5	23.5	26.9	26.7	26.7	26.7	26.7	27.8	27.4	27.0
13	28.2	23.7	27.0	27.6	27.6	27.1	27.2	29.8	29.4	27.2
14	17.1	18.6	22.7	9.5	10.6	17.3	18.4	25.9	19.2	11.2
15	26.6	22.5	14.9	20.9	21.2	18.9	18.9	19.6	19.3	107.2
OAc		170.5			171.0		171.0			170.9
		22.4			20.7		21.3			21.2

(10), 239 (95), 221 (7), 154 (20), 134 (55), 98 (65), 43 (100). HRMS for $C_{15}H_{28}O_2$ requires 240.2091; found 240.2085.

(1S)-*Elemane*-1,4,11-*triol* (**5a**). This was obtained when **5** stood in $CDCl_3$ soln for 2 weeks. White crystals from $CHCl_3$–hexane (1:1), mp 93–94°, $[\alpha]_D^{30}$ − 3.3° ($CHCl_3$; *c* 0.3). TLC (30% EtOAc in hexane) R_f 0.47. IR ν_{max}^{KBr} cm^{-1}: 3435. ^1H NMR ($CDCl_3$, 300 MHz): δ0.82 (*s*, H-14), 1.05 (*s*, H-15), 1.07 (*d*, *J* = 6.5 Hz, H-2), 1.18 (*s*, H-3), 1.20 (*s*, H-12), 1.21 (*s*, H-13), 1.50 (*dd*, *J* = 3, 12 Hz, H-5), 3.45 (*q*, *J* = 6.5 Hz, H-1). ^{13}C NMR ($CDCl_3$, 75 MHz): δ13.5 (C-2), 14.0 (C-14), 21.8 (C-6), 21.9 (C-8), 24.0 (C-15), 27.1 (C-12), 27.8 (C-13), 30.4 (C-3), 36.0 (C-9), 43.5 (C-10), 49.5 (C-7), 58.1 (C-5), 72.9 (C-11), 78.8 (C-4), 81.6 (C-1). EIMS (70 eV) *m/z* (rel. int.): 225 $[M - H_2O - Me]^+$ (42), 207 (3), 178 (70), 163 (50), 135 (100), 121 (18), 95 (15). HRMS for $[C_{15}H_{30}O_3 - H_2O - Me]$ requires 225.1856; found 225.1855. A sample of **5a** was treated with (±)-2-phenylbutanoic anhydride in pyridine at 25° for 1 hr. The recovered 2-phenylbutanoic acid after work up showed levorotation, **5a** was thus assigned to have (1*S*)-configuration [21].

Cryptomeridiol (**6**). Mp 136–137°. $[\alpha]_D^{25}$ − 33° ($CHCl_3$; *c* 1.5), lit. [7], *mp* 137.5°; $[\alpha]_D^{20}$ − 21.7° ($CHCl_3$; *c* 2.5).

4-*Epicryptomeridiol* (**7**). Mp 81–82°. $[\alpha]_D^{25}$ + 4° ($CHCl_3$; *c* 2.5), lit. [8], mp 81–82°; $[\alpha]_D$ + 3.8° ($CHCl_3$; *c* 0.22).

11-*Acetoxyeudesman*-4α-ol (**8**). Oil, $[\alpha]_D^{25}$ −13° ($CHCl_3$; *c* 2.7). TLC (9% EtOAc in CH_2Cl_2) R_f 0.33. IR ν_{max}^{neat} cm^{-1}: 3423, 1723. EIMS (70 eV) *m/z* (rel. int.): 282 $[M]^+$ (2), 281 $(M - H)^+$ (7), 222 $[M - MeCOOH]^+$ (35), 204 (52), 189 (21), 161 (20), 149 (35), 109 (25), 81 (30), 43 (100). HRMS for $C_{17}H_{30}O_3$ requires 282.2196; found 282.2175.

Saponification of **8**. A soln of **8** (20 mg) in EtOH (5 ml) was treated with 10% KOH in EtOH (2 ml) at 25° for 16 hr. The mixt. was extracted with Et_2O and sepd by HPLC (30% EtOAc in hexane) to give **8** (10 mg) and **6** (8 mg).

Eudesmane-5α-11-*diol* (**9**). Solid, mp 66–67°. $[\alpha]_D^{25}$ + 38° ($CHCl_3$; *c* 2.1). TLC (15% EtOAc in $CHCl_3$) R_f 0.32. IR ν_{max}^{KBr} cm^{-1}: 3465. EIMS (70 eV) *m/z* (rel. int.): 240 $[M]^+$ (13), 222 (12), 207 (22), 181 (20), 164 (18), 149 (42), 126 (100), 112 (82). HRMS for $C_{15}H_{28}O_2$ requires 240.2090; found 240.2092.

α-*Eudesmol* (**10**). Oil, $[\alpha]_D^{25}$ + 28° ($CHCl_3$; *c* 0.8), lit. [9], mp 75°; $[\alpha]_D$ + 28.6° ($CHCl_3$; *c* 1.86).

3-*Eudesmene*-1β-11-*diol* (**11**). Needles from $CHCl_3$–hexane (7:3), mp 144–145°. $[\alpha]_D^{25}$ − 4° ($CHCl_3$; *c* 1.4), TLC (33% EtOAc in CH_2Cl_2) R_f 0.52. IR ν_{max}^{KBr} cm^{-1}: 3333. EIMS (70 eV) *m/z* (rel. int.): 238 $[M]^+$ (7), 220 (15), 202 (5), 177 (15), 121 (25), 93 (38), 59 (100). HRMS for $C_{15}H_{26}O_2$ requires 238.1934; found 238.1939.

1β-*Acetoxy*-3-*eudesmen*-11-*ol* (**12**). Oil, $[\alpha]_D^{28}$ + 15.5° ($CHCl_3$; *c* 1.1). TLC (20% EtOAc in hexane) R_f 0.4. IR ν_{max}^{neat} cm^{-1}: 3443, 1730. EIMS (70 eV) *m/z* (rel. int.): 280 $[M]^+$ (1), 262 (3), 235 (13), 220 (20), 203 (85), 187 (30), 159 (35), 145 (50), 43 (100). HRMS for $C_{17}H_{28}O_3$ requires 280.2039; found 280.2058. Saponification of **12** (10 mg) by a procedure similar to that for **8** gave **11** (8 mg).

γ-*Eudesmol* (**13**). Mp 72–73°. $[\alpha]_D^{25}$ + 21° ($CHCl_3$; *c* 1.5), lit. [9], mp 73–74°; $[\alpha]_D$ + 18.7° ($CHCl_3$; *c* 0.7).

4-*Eudesmene*-1β,11-*diol* (**14**). Crystals from CH_2Cl_2–hexane (6:4), mp 137–138°. $[\alpha]_D^{15}$ + 61° ($CHCl_3$; *c* 5.0). TLC (33% EtOAc in CH_2Cl_2) R_f 0.38. IR ν_{max}^{KBr} cm^{-1}: 3436. EIMS (70 eV) *m/z* (rel. int.): 238 $[M]^+$ (15), 220 (100), 203 (40), 187 (35), 159 (48), 133 (35), 119 (25). HRMS for $C_{15}H_{26}O_2$ requires 238.1934; found 238.1932.

1β-*Acetoxy*-4-*eudesmen*-11-*ol* (**15**). Oil, $[\alpha]_D^{28}$ + 60° ($CHCl_3$; *c* 1.0). TLC (20% EtOAc in hexane) R_f 0.44. IR ν_{max}^{neat} cm^{-1}: 3451, 1731. EIMS (70 eV) *m/z* (rel. int.): 280 $[M]^+$ (8), 262 (30), 220 (12), 202 (75), 187 (70), 159 (100),

145 (40), 131 (70). HRMS for $C_{17}H_{28}O_3$ requires 280.2039; found 280.2065. Saponification of **15** (10 mg) by a procedure similar to that for **8** gave **14** (8 mg).

7-Epi-γ-eudesmol (**16**). Oil, $[\alpha]_D^{25}$ − 45° ($CHCl_3$; *c* 2.0). TLC (50% $CHCl_3$ in hexane) R_f 0.3. IR ν_{max}^{neat} cm^{-1}: 3419. EIMS (70 eV) *m/z* (rel. int.): 222 $[M]^+$ (22), 204 (95), 189 (80), 161 (100), 149 (25), 133 (35), 119 (18). HRMS for $C_{15}H_{26}O$ requires 222.1985; found 222.1988.

7-Epi-4-eudesmene-1β,11-diol (**17**). Oil, $[\alpha]_D^{25}$ − 15° ($CHCl_3$; *c* 0.2). TLC (30% EtOAc in hexane) R_f 0.25. IR ν_{max}^{neat} cm^{-1}: 3395, 1647. EIMS (70 eV) *m/z* (rel. int.): 238 $[M]^+$ (4), 220 (15), 202 (10), 187 (11), 159 (17), 105 (20), 59 (60), 43 (100). HRMS for $C_{15}H_{26}O_2$ requires 238.1934; found 238.1938.

6-Eudesmene-1β,4β-diol (**18**). Mp 137–139°. $[\alpha]_D^{25}$ − 25° ($CHCl_3$; *c* 0.5), lit. [11], oil; $[\alpha]_{436nm}^{24}$ − 35.4° ($CHCl_3$; *c* 1.0). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.6 (C-14), 21.4 (C-12), 21.7 (C-13), 22.7 (C-8), 27.0 (C-2), 29.4 (C-15), 35.1 (C-9), 35.3 (C-11), 38.1 (C-10), 38.7 (C-3), 49.8 (C-5), 71.1 (C-4), 78.4 (C-1), 115.4 (C-6), 136.0 (C-7).

Oplodiol (**19**). Mp 106–107°, $[\alpha]_D^{25}$ − 52° ($CHCl_3$; *c* 0.8), lit. [10], mp 107–108°; $[\alpha]_D^{27}$ − 58.0° ($CHCl_3$; *c* 1.0).

β-Eudesmol (**20**). Mp 79–80°, $[\alpha]_D^{25}$ + 56° ($CHCl_3$; *c* 1.3), lit. [13], mp 79–80°; $[\alpha]_D$ + 56.6° ($CHCl_3$; *c* 2.0).

4(15)-Eudesmene-1β,11-diol (**21**). Mp 156–157°, $[\alpha]_D^{30}$ + 56° ($CHCl_3$; *c* 1.5), lit. [14], mp 156–157°; $[\alpha]_D^{31}$ + 56.4° ($CHCl_3$; *c* 1.5).

4(15)-Eudesmene-1β,6α-diol (**22**). Oil, $[\alpha]_D^{25}$ + 7.5° ($CHCl_3$; *c* 1.2), lit. [15], gum; $[\alpha]_{436nm}^{24}$ + 16° ($CHCl_3$; *c* 0.1). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.6 (C-14), 18.2 (C-8), 16.2 (C-12), 21.1 (C-13), 26.0 (C-11), 31.9 (C-2), 35.1 (C-3), 36.3 (C-9), 41.7 (C-10), 49.3 (C-7), 55.9 (C-5), 67.0 (C-6), 79.0 (C-1), 107.8 (C-15), 146.2 (C-4).

1β-Acetoxy-4(15)-eudesmen-11-ol (**23**). Oil, $[\alpha]_D^{30}$ + 29° ($CHCl_3$; *c* 2.2). TLC (EtOAc–$CHCl_3$–hexane, 5:50:45) R_f 0.27. IR ν_{max}^{neat} cm^{-1}: 3453, 3079, 1711, 888. EIMS (70 eV) *m/z* (rel. int.): 202 $[M - H_2O - HOAc]^+$ (15), 162 (100), 147 (65), 133 (20), 119 (18), 106 (16), 59 (18). HRMS for $C_{17}H_{28}O_3$ requires 280.2039; found 280.2021. Saponification of **23** (20 mg) by a procedure similar to that for **8** gave **21** (16 mg).

α-Cadinol (**24**). Mp 70–71°, $[\alpha]_D^{25}$ − 45° ($CHCl_3$; *c* 0.8), lit. [17], mp 72.5°; $[\alpha]_D$ − 39.4° ($CHCl_3$; *c* 1.32).

T-Cadinol (**25**). Oil, $[\alpha]_D^{25}$ − 5° ($CHCl_3$; *c* 1.2), lit. [18], oil; $[\alpha]_D^{30}$ − 4.7° ($CHCl_3$; *c* 4.4).

Oplopanone (**26**). Mp 96–97°, $[\alpha]_D^{32}$ − 16° ($CHCl_3$; *c* 2.0), lit. [19], mp 96–97°; $[\alpha]_D^{25.5}$ − 20.0° (dioxane; *c* 0.571). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.6 (C-12), 20.2 (C-14), 21.9 (C-13), 23.0 (C-8), 25.3 (C-2), 28.6 (C-3), 29.4 (C-15), 29.5 (C-11), 42.0 (C-9), 46.7 (C-7), 49.4 (C-1), 55.7 (C-6), 57.0 (C-5), 73.0 (C-10), 211.4 (C-4).

Cedrol (**27**). Mp 80–81°, $[\alpha]_D^{25}$ + 3° ($CHCl_3$; *c* 2.2), lit. [20], mp 86–87°; $[\alpha]_D^{28}$ + 9.9° ($CHCl_3$; *c* 5).

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