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DITERPENOIDS FROM LEAVES OF CRYPTOMERIA JAPONICA

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Abstract—Phytol, seven labdanes, eight abietanes, four pimaranes and three biditerpenes were isolated from the leaves of *Cryptomeria japonica*. The new compounds included 8,13-dioxo-14,15,17-trinorlabdan-19-oic acid, 12-hydroxy-11-methoxyabieta-8,11,13-trien-7-one, 6α ,11-dihydroxy-12-methoxyabieta-8,11,13-trien-7-one, 6,12-dihydroxy-11-methoxyabieta-5,8,11,13-tetraen-7-one, an acetal formed by abieta-8,11,13-triene- 6α , 7α ,11,12-tetraol and imbricataloic acid, a self-condensation product of imbricataloic acid, as well as an acetal formed by abieta-8,11,13-triene- 6α , 7β ,12-triol and 12-hydroxy-6,7-secoabieta-8,11,13-triene-6,7-dial. Their structures were determined by chemical and spectral methods.

INTRODUCTION

The Japanese cedar, Cryptomeria japonica D. Don., is a widely distributed conifer which is called 'sugi' in Japan. We recently reported on the isolation of sesquiterpernes [1], diterpenes of the abietane, kaurane and labdane type [2,3], and a triterpene chamaecydin [4] from the ethyl acetate-soluble part of the leaves of C. japonica. In a continuation of this study, we have isolated a further 24 diterpenes including seven novel compounds (6, 11, 13, 15, 21-23).

RESULTS AND DISCUSSION

The leaves of C. japonica were extracted with acetone, and the ethyl acetate-soluble portion of the extract was subjected to chromatography to give diterpenes 1-23. The known diterpenes phytol (1) [5], junicedric acid (2) [6], 13-epicupressic acid methyl ester (3) [7], copalol (4) [8], 13-oxo-14,15-dinorlabd-8(17)-en-19-oic acid methyl ester (5) [9], trans-communic acid (7) [10], cis-communic acid (8) [11], 19-acetoxyferruginol (9) [12], sugiol methyl ether (10) [13], 6 α -hydroxydemethylcryptojaponol (12) [14], 5,6-dehydrosugiol methyl ether (14) [15], cupresol (16) [16], nejukol (17) [17], isopimarinol (18) [18], isopimaric acid (19) [19, 20] and sandaracopimaric acid (20) [20, 21] were identified by comparison of their physical and spectral data (mp, [α], mass, IR, ¹H and ¹³C NMR) with the literature data.

The exact mass of the $[M]^+$ ion of 6 was found to be m/z 294.183, indicating the molecular formula $C_{17}H_{26}O_4$. The IR absorptions at 3000-2500 and

1691 cm⁻¹, indicated that **6** was a trinorditerpenoid acid containing carbonyl groups. The carbon signals at δ 182.9, 209.3 and 211.7 were attributable to a carboxyl group and two carbonyl groups. The ¹H NMR spectrum (Table 1) showed three singlets at δ 0.60, 1.28 and 2.06 attributable to two methyl groups attached to tertiary carbons and an acetyl group. The structure of **6** was assigned as 8,13-dioxo-14,15,17-trinorlabdan-19-oic acid. The carboxyl group was oriented axially at C-4 and exerted a shielding effect on Me-10, which appeared upfield at δ 0.60. Ozonolysis of a sample of isocupressic acid (previously isolated in our laboratory [3]) gave **6**, supporting further the assigned structure.

Compound 11 ($C_{21}H_{30}O_3$) contained a conjugated carbonyl group as inferred from the IR absorption at 1650 cm⁻¹, the UV absorption at 290 nm and the carbon resonance at δ 198.7. The ¹H NMR spectrum showed a methoxyl group at δ 3.76 (s) and an aromatic proton at 7.79 (s), which was obviously deshielded by an adjacent carbonyl group. The structure of 11 was determined to be 12-hydroxy-11-methoxyabieta-8,11,13-trien-7-one. The methoxyl group was assigned to the C-11 position as it showed an 8% NOE on irradiation of Me-10 at δ 1.36.

Compound 13 ($C_{21}H_{30}O_4$) was also a diterpenoid ketone, showing IR absorption at 1671 cm⁻¹ and a carbon signal at $\delta 200.6$. The ¹H NMR spectrum of 13 was similar to that of $\delta \alpha$ -hydroxydemethylcryptojaponol (12), except for an additional methoxyl resonance at $\delta 3.79$. The structure of 13 was assigned as $\delta \alpha$,11-dihydroxy-12methoxyabieta-8,11,13-trien-7-one. The C-6 hydroxyl group was intramolecularly hydrogen bonded with the carbonyl group at C-7. The H-6 coupled with H-5 ($J_{5,6} = 13.5$ Hz) and with the geminal hydroxyl proton (J = 3 Hz). The 11-hydroxyl group appeared at $\delta 6.18$ and was hydrogen bonded with the adjacent methoxyl group. Irradiation of Me-10 at $\delta 1.53$ caused a 2% NOE

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of the signal at $\delta 6.18$, supporting the assignment of the hydroxyl group at C-11.

The molecular formula $C_{21}H_{28}O_4$ of 15 was deduced by measurement of the exact mass of its $[M]^+$ ion (m/z344.198). The IR absorptions at 3383 and 1618 cm⁻¹ were attributable to the hydroxyl and conjugated carbonyl groups. By analyses of the ¹H and ¹³CNMR spectra (Tables 1 and 2), 15 was determined to be 6,12dihydroxy-11-methoxyabieta-5,8,11,13-tetraen-7-one. The carbon signals at δ 179.9, 144.5 and 143.0 were attributable to a α -hydroxyalkenone moiety. The aromatic proton at C-14 gave rise to a low field signal at δ 7.71 due to the deshielding effect of the carbonyl group at C-7. On irradiation of Me-10 at δ 1.64, a 7% NOE of the methoxyl group at δ 3.82 was observed.

Compounds 21–23 are biditerpenes and their molecular formulae were deduced to be $C_{40}H_{60}O_6$, $C_{40}H_{62}O_5$ and $C_{40}H_{56}O_5$, respectively, from the HR mass spectra. Compound 21 has an acetal moiety as it showed a proton signal at $\delta 4.99$ (t, J = 6.5 Hz) and a carbon signal at





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Table 1. ¹H NMR spectral data of diterpenoids (300 MHz, CDCl₃ solution, δ values in ppm, J values in Hz)*†

Н	11	13	15	21‡	23 §
1β	2.92 (br d, $J = 13.5$)	3.14 (m)	$3.01 \ (dd, J = 7.5, 9)$	2.86 (br $d, J = 13$)	2.35 (br $d, J = 12$)
5	1.83 (dd, J = 4.5, 13.5)	1.80 (d, J = 13.5)		1.52 (d, J = 10)	1.50 (d, J = 10)
6	2.53 (dd, J = 13.5, 18)	4.63 (dd, J = 3, 13.5)		4.55 (dd, J = 6.5, 10)	4.62 (dd, J = 8, 10)
	$2.64 \ (dd, J = 4.5, 18)$				
7				5.03 (d, J = 6.5)	5.20 (d, J = 8)
11		_	_		6.62 (s)
14	7.79 (s)	7.55 (s)	7.71 (s)	6.94 (s)	7.29 (s)
15	3.20 (sept, J = 7)	3.18 (sept, J = 7)	3.23 (sept, J = 7)	3.02 (sept, J = 7)	3.10 (sept, J = 7)
16	$1.21 \ (d, J = 7)$	1.22 (d, J = 7)	1.25 (d, J = 7)	1.21 $(d, J = 7)$	$1.11 \ (d, J = 7)$
17	1.24 (d, J = 7)	1.22 (d, J = 7)	1.27 (d, J = 7)	1.25 (d, J = 7)	1.12 (d, J = 7)
18	0.91 (s)	1.18 (s)	1.43 (s)	1.08 (s)	1.10 (s)
19	0.97 (s)	1.23 (s)	1.43 (s)	1.12 (s)	1.10 (s)
20	1.36 (s)	1.53 (s)	1.64 (s)	1.20 (s)	1.14 (s)
OH	6.06 (s)	3.81 (d, J = 3)	6.20 (s)		
		6.18 (s)	7.05 (s)		
OCH3	3.76 (s)	3.79 (s)	3.82 (s)		

*Some assignable resonances for 6 appeared at $\delta 0.60$ (s, H-20), 1.28 (s, H-18), 2.06 (s, H-16) in addition to others.

†Some assignable resonances for **22** appeared at $\delta 0.51$ (s, H-20), 1.10 (d, J = 6.5, H-16), 1.20 (s, H-18), 4.32 (br s, H-17), 4.77 (br s, H-17), 9.32 (s, H-15), 0.57 (s, H-20'), 0.91 (d, J = 6.5, H-16'), 1.21 (s, H-18'), 4.44 (br s, H-17'), 4.80 (br s, H-17'), 6.39 (t, J = 7, H-15'). †The rest of the resonances appeared at $\delta 0.57$ (s, H-20'), 0.92 (d, J = 6.5, H-16'), 1.21 (s, H-18'), 4.50 (br s, H-17'), 4.80 (br s, H-17'), 4.99 (t, J = 6.5, H-15').

§The rest of the resonances appeared at $\delta 0.70$ (s, H-18'), 1.00 (s, H-19'), 1.15 (d, J = 7, H-16'), 1.19 (d, J = 7, H-17'), 1.33 (s, H-20'), 2.99 (sept, J = 7, H-15'), 3.28 (d, J = 5, H-5'), 6.53 (s, H-7'), 6.76 (s, H-11'), 7.53 (s, H-14'), 9.91 (d, J = 5, H-6').

 δ 100.5 (d). Acid-catalysed hydrolysis of **21** (Scheme 1) gave imbricataloic acid (**24**) and $\delta\alpha$ -hydroxydemethylcryptojaponol (**12**). By analyses of the C-H COSY and HMBC spectra, **21** was determined to be an acetal formed from imbricatolic acid and abieta-8,11,13-triene- 6α ,7 α ,11,12-tetraol (25). The latter component, liberated on the acid-catalysed hydrolysis of 21, appeared to undergo autoxidation to give 12. Both H-5 and H-6 were

С	6	11	13	15	С	21	22	23
1	39.2	37.3	36.5	29.7	1, 1′	39.1, 38.8	39.2, 39.2	38.5, 37.4
2	19.6	19.1	18.9	17.6	2, 2'	19.0, 19.9	19.9, 19.9	18.8, 19.5
3	37.7	41.0	42.4	36.4	3, 3'	42.4, 38.0	38.0, 38.0	42.9, 38.5
4	44.2	33.6	34.0	36.5	4, 4′	34.2, 44.2	44.2, 44.2	33.8, 31.6
5	54.8	49.9	55.4	143.0	5, 5'	50.4, 56.4	56.4, 56.5	50.6, 63.8
6	25.4	35.6	73.3	144.5	6, 6′	75.9, 26.1	26.0, 26.0	76.6, 207.3
7	43.0	198.7	200.6	179.9	7,7′	74.4, 38.8	38.7, 38.7	74.1, 99.4
8	211.7	124.9	125.9	124.4	8, 8′	127.1, 148.1	148.2, 147.8	126.2, 126.8
9	62.1	144.0	139.7	139.9	9, 9′	132.0, 56.5	56.1, 56.4	147.5, 145.6
10	43.7	40.2	41.3	40.9	10, 10′	40.6, 40.1	40.6, 40.4	37.7, 39.4
11	16.3	152.6	146.5	148.6	11, 11′	141.1, 20.9	22.4, 21.5	109.1, 112.5
12	42.6	145.4	149.7	145.8	12, 12'	140.5, 36.6	36.0, 36.4	152.2, 153.3
13	209.3	133.9	137.7	137.6	13, 13'	132.2, 30.0	32.3, 34.1	131.4, 131.9
14		122.8	117.5	116.3	14, 14′	116.1, 40.9	147.3, 33.2	125.8, 129.0
15		27.2	26.7	26.8	15, 15'	27.4, 100.5	195.6 155.3	27.2, 26.9
16	29.9	22.1	23.4	23.5	16, 16'	22.5, 20.1	18.9, 20.1	22.4, 22.4
17		22.3	23.5	23.6	17, 17′	22.6, 106.5	106.3, 106.7	22.4, 22.4
18	29.0	33.0	35.7	27.4	18, 18'	34.7, 29.0	29.0, 29.0	35.1, 22.4
19	182.9	21.6	22.5	27.2	19, 19′	22.6, 183.2	183.8, 183.8	22.6, 22.4
20	13.2	21.2	19.0	27.9	20, 20′	21.6, 12.7	12.8, 12.8	22.3, 24.0
OCH ₃		61.4	61.9	62.0				

Table 2. ¹³C NMR spectral data for diterpenoids (75 MHz, $CDCl_3$ solution, δ values in ppm)



Scheme 1.

in axial positions as shown by the large coupling constant 10 Hz. As a 5% NOE of H-6 (at $\delta 4.55$) was observed on irradiation of H-7 (at $\delta 5.03$), these two protons must be in the *cis* relationship. Irradiation of H-15' (at $\delta 4.99$) caused a 4% NOE of H-14 (at $\delta 6.94$), but no enhancement of H-6 or H-7. Acetal 21 thus has the 15'S-configuration with H-15' and H-7 on opposite faces.

From its ¹H, ¹³C, C–H COSY and HMBC spectra, **22** was determined to be a self-condensation product of imbricataloic acid. The proton signals at $\delta 6.39$ (H-15') and 9.32 (H-15) as well as the carbon signals at $\delta 155.3$ (C-15'), 147.3 (C-14) and 195.6 (C-15) were attributed to the enal moiety. Irradiation of H-15 caused a 16% NOE of H-15', supporting the assigned *E*-configuration. The

circular dichroic spectrum of 22 showed a negative Cotton effect with $[\theta]_{min}$ at 327.5 nm, this being consistent with the 13S-configuration [3]. Ozonolysis of 22 (Scheme 2) gave 8,15-dioxo-17-norlabdan-19-oic acid (26) and 8oxo-15,17-dinorlabdane-14,19-dioic acid (28), which might be derived from an α -oxoaldehyde (27). Compound 26, having the 13S-configuration, also showed a negative Cotton effect with $[\theta]_{min}$ at 292 nm [3].

By analyses of the H–H COSY and ¹³C spectra, **23** was determined to be an acetal formed by condensation of the vicinal diol in abieta-8,11,13-triene- 6α , 7β ,12-triol with the benzaldehyde moiety in 12-hydroxy-6,7-secoabieta-8,11,13-triene-6,7-dial. The three axial protons, H-5, H-6 and H-7, displayed large coupling constants 10 Hz ($J_{5,6}$) and 8 Hz ($J_{6,7}$). Irradiation of H-7' (at δ 6.53) caused a 10% NOE of H-7 (at δ 5.20), but no enhancement of H-6. Compound **23** has the 7'S-configuration so that H-7' and H-7 are on the same face to account for the NOE study.

It is unclear whether the three biditerpenes 21-23 are natural products or artefacts.

EXPERIMENTAL

General. Analyt. TLC: Merck Silica gel 60F sheets; HPLC: Hibar Lichrosorb Si 60 (7 or 10 μ m) column (25 × 1 cm).

Plant material. The plant used in this study was introduced from Japan and was cultivated in Taipei suburb. A voucher specimen has been deposited in our laboratory. The leaves (1.4 kg) of *C. japonica* D. Don. were collected and exhaustively extracted with Me₂CO in January 1989. The Me₂CO extract was passed through a pad of charcoal, concd and re-extracted with EtOAc. The EtOAc-soluble portion (45 g) was subjected to CC on silica gel by elution with gradients of hexane and EtOAc. The appropriate frs were combined and purified by HPLC to give 17 (22 mg), 3(12 mg), 13(11 mg), 11 (3 mg), 15 (3 mg), 18 (3 mg), 1 (12 mg), 5 (14 mg), 19 (7 mg), 10 (11 mg), 20 (12 mg), 14 (4 mg), 4 (5 mg), 7 (12 mg), 8 (15 mg), 12 (14 mg), 23 (17 mg), 2 (7 mg), 9 (6 mg), 16 (7 mg), 22 (7 mg), 21 (17 mg) and 6 (17 mg), in order of increasing polarity.

Phytol (1). Oil, $[\alpha]_D^{25} + 0.16^{\circ}$ (CHCl₃; c 1.2), {lit. [5], oil, $[\alpha]_D + 0.06^{\circ}$ (neat)}.

Junicedric acid (2). Oil, $[\alpha]_{D}^{25} + 33.5^{\circ}$ (CHCl₃; c0.7), {lit. [6], gum, $[\alpha]_{D}^{25} + 30.5^{\circ}$ (EtOH; c0.59)}. ¹³C NMR (CDCl₃, 75 MHz): δ 12.9 (C-20), 19.9 (C-2), 21.1 (C-16), 21.7 (C-11), 26.0 (C-6), 28.9 (C-18), 31.1 (C-13), 36.8 (C-12), 37.9 (C-3), 38.7 (C-7), 39.1 (C-1), 40.5 (C-10), 41.6 (C-14), 44.2 (C-4), 56.3 (C-5), 56.5 (C-9), 106.6 (C-17), 147.9 (C-8), 179.8 (C-15), 184.1 (C-19).

13-Epicupressic acid methyl ester (3). Oil, $[\alpha]_D^{25} + 61.0^{\circ}$ (CHCl₃; c1.2), {lit. [7], oil, $[\alpha]_D + 64.0^{\circ}$ (EtOH)}.

Copalol (4). Oil, $[\alpha]_{D}^{25} + 31.0^{\circ}$ (CHCl₃; c 0.5), {lit. [8], oil, $[\alpha]_{D} + 30.0^{\circ}$ (CHCl₃)}.

13-Oxo-14,15-dinorlabd-8(17)-en-19-oic acid methyl ester (5). Oil, $[\alpha]_{D}^{25}$ + 37.1° (CHCl₃; c 1.4), {lit. [9], oil, $[\alpha]_{D}$ + 36.5° (CHCl₃)}. ¹³CNMR (CDCl₃, 75 MHz): δ 12.4 (C-20), 17.7 (C-11), 19.9 (C-2), 26.3 (C-6), 28.8 (C-18), 30.1 (C-16), 38.2 (C-3), 38.7 (C-7), 39.1 (C-1), 40.4 (C-10), 42.8 (C-12), 44.3 (C-4), 51.1 (OCH₃), 55.5 (C-5), 56.3 (C-9), 106.4 (C-17), 147.8 (C-8), 177.7 (C-19), 209.3 (C-13).

8,13-Dioxo-14,15,17-trinorlabdan-19-oic acid (6). Oil, $[\alpha]_{D}^{25} - 0.6^{\circ}$ (CHCl₃; c 1.7). TLC (30% EtOAc in hexane) R_f 0.27. IR ν_{max}^{neat} cm⁻¹: 3000–2500, 1691. EIMS (70 eV) m/z (rel. int.): 294 [M]⁺ (53), 279 (100), 233 (85), 215 (55), 175 (47), 139 (24), 121 (70). HRMS for C₁₇H₂₆O₄ requires 294.1832; found 294.1836.



Scheme 2.

Ozonolysis of isocupressic acid. A soln of isocupressic acid (15 mg) in CH₂Cl₂ (5 ml) was stirred at -78° and bubbled with O₃ for 5 min. Me₂S (3 ml) was then added and the mixt. stirred at 25° for 2 hr. The mixt. was concd to give 6 (13 mg).

trans-Communic acid (7). Solid, mp 130–132°; $[\alpha]_D^{25}$ + 38.0° (CHCl₃; c1.2), {lit. [10] (Me ester), mp 105–106°; $[\alpha]_D$ + 48.0° (CHCl₃)}.

cis-Communic acid (8). Gum, $[\alpha]_{\rm D}^{55} + 37.5^{\circ}$ (CHCl₃; c1.5), {lit. [11] (Me ester), mp 41-42°; $[\alpha]_{\rm D} + 45.0^{\circ}$ (CHCl₃)}.

19-Acetoxyferruginol (9). Oil, $[\alpha]_D^{25} + 52.0^{\circ}$ (CHCl₃; c0.6). ¹³C NMR (CDCl₃, 75 MHz): δ 19.0 (C-2), 19.4 (C-6), 22.5 (C-16), 22.7 (C-17), 25.6 (C-18), 26.8 (C-15), 27.3 (C-20), 30.3 (C-7), 36.0 (C-4), 37.2 (C-1), 37.4 (C-10), 38.8 (C-3), 51.3 (C-5), 67.0 (C-19), 111.1 (C-11), 126.7 (C-14), 126.8 (C-8), 131.8 (C-13), 148.0 (C-9), 150.9 (C-12), 21.0, 171.4 (OAc).

Sugiol methyl ether (10). Solid, mp $132-134^{\circ}$; $[\alpha]_{D}^{25}$ + 30.0° (CHCl₃; c1.1), {lit. [13], mp $136-137^{\circ}$; $[\alpha]_{D}$ + 32.0° (MeOH)}.

12-Hydroxy-11-methoxyabieta-8,11,13-trien-7-one (11). Solid, mp 177–178°. $[\alpha]_{D}^{30}$ + 10.0° (CHCl₃; c 0.3). TLC (50% CHCl₃ in hexane) R_f 0.37. IR ν_{max}^{KBr} cm⁻¹: 3329, 1650, 1581. UV $\lambda_{max}^{\text{MeOH}}$ nm (ε): 290 (10700), 250 (1280), 233 (12400), 225 (10600), 211 (15800). EIMS (70 eV) m/z (rel. int.): 330 [M]⁺ (100), 315 (68), 273 (25), 245 (40), 233 (33), 193 (45), 128 (10). HRMS for C₂₁H₃₀O₃ requires 330.2196; found 330.2185.

6α-Hydroxydemethylcryptojaponol (12). Solid, mp 202–203°. [α] $_{D}^{25}$ + 42.0° (CHCl₃; c 1.4), {lit. [14] (triacetate) mp 179–181°}. ¹³C NMR (CDCl₃, 75 MHz): δ18.9 (C-2), 19.9 (C-20), 22.3 (C-19), 22.4 (C-16), 22.8 (C-17), 27.3 (C-15), 34.0 (C-4), 35.4 (C-18), 37.1 (C-1), 41.0 (C-10), 41.9 (C-3), 55.0 (C-5), 73.0 (C-6), 118.1 (C-14), 122.3 (C-8), 132.2 (C-13), 138.3 (C-9), 141.1 (C-11), 146.8 (C-12), 200.1 (C-7).

6α,11-Dihydroxy-12-methoxyabieta-8,11,13-trien-7-one (13). Solid, mp 167–168°, $[\alpha]_{25}^{25}$ + 85.5° (CHCl₃; c 1.1). TLC (50% CHCl₃ in hexane) R_f 0.42. IR ν_{max}^{KRr} cm⁻¹: 3419, 1671, 1593. UV $\lambda_{max}^{\text{MeOH}}$ nm (ε): 316 (5000), 300 (4360), 274 (14 100), 247 (3830), 217 (26 400). EIMS (70 eV) m/z(rel. int.): 346 [M]⁺ (38), 331 (20), 317 (100), 299 (17), 249 (42), 203 (35), 189 (18), 128 (30). HRMS for C₂₁H₃₀O₄ requires 346.2145; found 346.2144.

5,6-Dehydrosugiol methyl ether (14). Gum, $[\alpha]_D^{25}$ + 15.0° (CHCl₃; c0.4), {lit. [15] (dehydrosugiol) mp 284-286°, $[\alpha]_D$ + 13° (EtOH)}.

6,12-Dihydroxy-11-methoxyabieta-5,8,11,13-tetraen-7one (15). Solid, mp 182–183°, $[\alpha]_D^{30} + 3.3°$ (CHCl₃; c 0.3). TLC (33% CH₂Cl₂ in hexane) R_f 0.22. IR ν_{max}^{KBr} cm⁻¹: 3383, 1618, 1585, 1554. UV $\lambda_{max}^{\text{MeOH}}$ nm (ε): 325 (2300), 298 (1800), 280 (2400), 262 (1950), 247 (3250), 235 (2700). EIMS (70 eV) m/z (rel. int.): 344 [M]⁺ (67), 329 (15), 301 (17), 275 (100), 259 (68), 256 (30), 241 (23), 231 (20). HRMS for C₂₁H₂₈O₄ requires 344.1988; found 344.1978.

Cupresol (16). Oil, $[\alpha]_D^{25} + 48.0^{\circ}$ (CHCl₃; c0.7), {lit. [16], Oil; $[\alpha]_D^{25} + 48.2^{\circ}$ (CHCl₃; c0.76)}.

Nejukol (17). Oil, $[\alpha]_D^{25} - 6.9^{\circ}$ (CHCl₃; c2.2), {lit. [17], mp 40-41°; $[\alpha]_D - 6.8^{\circ}$ (CHCl₃)}.

Isopimarinol (18). Gum, $[\alpha]_{D}^{25} - 25.2^{\circ}$ (CHCl₃; c 0.3), {lit. [18], mp 84-86°; $[\alpha]_{D} - 24.6^{\circ}$ (CHCl₃)}.

Isopimaric acid (19). Solid, mp 160–161°. $[\alpha]_D^{30} + 6.0^\circ$ (CHCl₃; *c* 0.7), {lit. [19], mp 162–164°.; $[\alpha]_D 0^\circ$ (CHCl₃)}.

Sandaracopimaric acid (20). Solid, mp 167–169°. $[\alpha]_{D}^{30} - 18.5^{\circ}$ (CHCl₃; c1.2), {lit. [21], mp 169°.; $[\alpha]_{D} - 20.0^{\circ}$ (EtOH)}.

Acetal **21** from abieta-8,11,13-triene- $6\alpha,7\alpha,11,12$ -tetraol and imbricataloic acid. Solid, mp 134–136°, $[\alpha]_D^{20} + 11°$ (CHCl₃; c 1.7), TLC (15% EtOAc in hexane) R_f 0.23. IR ν_{max}^{KBr} cm⁻¹: 3450, 3080, 3000–2500, 1687, 1610, 889, FAB-MS m/z (rel. int.): 637 [M + 1]⁺ (8), 527 (10), 442 (13), 317 (30), 299 (30), 229 (20), 154 (100), 136 (80). HRMS for C₄₀H₆₀O₆ requires 636.4392; found 636.4415.

Hydrolysis of **21**. A soln of **21** (17 mg) in CH₂Cl₂ (5 ml) was treated with 2 N HCl at 30° for 7 days. The organic phase was sepd by HPLC with elution by EtOAc-hexane (1:4) to give imbricataloic acid (4 mg) and **12** (4 mg), and unreacted **21** (10 mg). Imbricataloic acid, gum, $[\alpha]_D^{28} + 35.5^{\circ}$ (CHCl₃; c 0.4), {lit. [22] (Me ester), oil, $[\alpha]_D + 38.5^{\circ}$ (CHCl₃)}. IR ν_{max}^{act} cm⁻¹: 3079, 3000–2500, 2718, 1718, 1684, 887. ¹H NMR (CDCl₃, 300 MHz): $\delta 0.58$ (s, H-20), 0.94 (d, J = 6.5 Hz, H-16), 1.22 (s, H-18), 4.45 (br s, H-17), 4.82 (br s, H-17), 9.73 (t, J = 2.5 Hz, H-15).

Self-condensation product **22** of imbricataloic acid. Solid, mp 223-224°, $[\alpha]_D^{25} + 57^\circ$ (CHCl₃; c 0.7). TLC (30% EtOAc in hexane) R_f 0.48. IR ν_{max}^{KBr} cm⁻¹: 3080, 3000-2500, 1683, 1636, 894, 883. UV λ_{max}^{MeOH} nm (ε): 233 (11500), 214 (5500), 209 (6700). CD (MeOH): $[\theta]_{327.5} - 260$. EIMS (70 eV) m/z (rel. int.): 622 [M]⁺ (2), 604 (3), 577 (4), 558 (5), 543 (5), 327 (12), 221 (60), 175 (45), 161 (35), 121 (100). HRMS for C₄₀H₆₂O₅ requires 622.4600; found 622.4617.

Ozonolysis of 22. A soln of 22 (7 mg) in CH₂Cl₂ (5 ml) was stirred at -78° and bubbled with O₃ for 1 min. Me₂S (3 ml) was added and the mixt. stirred at 25° for 2 hr. The mixt. was sepd by HPLC with elution by EtOAc-hexane (3:7) to give 8,15-dioxo-17-norlabdan-19-oic acid (26, 4 mg) and 8-oxo-15,17-dinorlabdan-14,19-dioic acid (28, 3 mg). 26: oil, $[\alpha]_{D}^{20} - 31^{\circ}$ (CHCl₃; *c* 0.4), {lit. [3], oil; $[\alpha]_D^{20} - 31^\circ$ (CHCl₃; *c* 0.4)}. **28**: gum, $[\alpha]_D^{30} + 36.5^\circ$ (CHCl₃; c 0.3), TLC (30% EtOAc in hexane) R_f 0.29. IR v_{max}^{neat} cm⁻¹: 3000–2500, 1694. ¹HNMR (CDCl₃, 200 MHz): δ 0.55 (s, H-20), 1.12 (d, J = 7 Hz, H-16), 1.30 (s, H-18). ¹³C NMR (CDCl₃, 75 MHz): δ 13.3 (C-20), 17.2 (C-16), 19.6 (C-2), 19.9 (C-11), 25.5 (C-6), 28.7 (C-18), 33.7 (C-12), 37.6 (C-3), 39.3 (C-1), 39.8 (C-13), 43.0 (C-7), 43.8 (C-10), 44.1 (C-4), 55.0 (C-5), 62.9 (C-9), 182.4 (C-14), 183.0 (C-19), 210.8 (C-8). EIMS (70 eV) m/z (rel. int.): 224 $[M - C_4H_8CO_2]^+$ (48), 209 (100), 163 (8), 145 (5), 121 (23), 109 (12), 95 (13).

Acetal **23** from abieta-8,11,13-triene-6α,7β,12-triol and 12-hydroxy-6,7-secoabieta-8,11,13-triene-6,7-dial. Solid, mp 144–145°, $[\alpha]_{D^8}^{-8} + 31°$ (CHCl₃; c1.7), TLC (15% EtOAc in hexane) R_f 0.33. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3397, 2745, 1698, 1613, 1578, 1499. EIMS (70 eV) m/z (rel. int.): 616 [M]⁺ (8), 598 (35), 583 (13), 552 (5), 301 (27), 284 (100), 202 (80). HRMS for C₄₀H₅₆O₅ requires 616.4122; found 616.4135. Acknowledgement—We thank the National Science Council for financial support (NSC83-0208-M002-095).

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