Pergamon 0031-9422(95)00417-3 Phytochemistry, Vol. 41, No. 1, pp. 255–261, 1996

0031-9422/96 $15.00 + 0.00

DITERPENOIDS FROM LEAVES OF *CRYPTOMERIA JAPONICA*

WEN-CHIUNG SU, JIM-MIN FANG and YU-SHIA CHENG*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

(*Received in revised form* 5 *May* 1995)

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

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

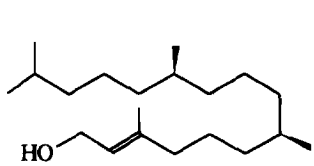
The leaves of *C. japonica* were extracted with acetone, and the ethyl acetate-soluble portion of the extract was subjected to chromatography to give diterpenes **1**–**23**. The known diterpenes phytol (**1**) [5], junicedric acid (**2**) [6], 13-epicupressic acid methyl ester (**3**) [7], copalol (**4**) [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], 6α-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, ^{1}H and ^{13}C 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 δ182.9, 209.3 and 211.7 were attributable to a carboxyl group and two carbonyl groups. The ^{1}H NMR spectrum (Table 1) showed three singlets at δ0.60, 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 δ0.60. Ozonolysis of a sample of isocupressic acid (previously isolated in our laboratory [3]) gave **6**, supporting further the assigned structure.

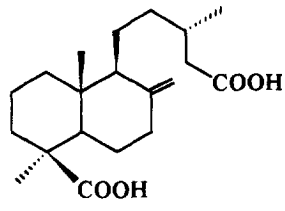
Compound **11** ($C_{21}H_{30}O_3$) contained a conjugated carbonyl group as inferred from the IR absorption at 1650 cm^{-1}, the UV absorption at 290 nm and the carbon resonance at δ198.7. The ^{1}H NMR spectrum showed a methoxyl group at δ3.76 (*s*) and an aromatic proton at 7.79 (*s*), which was obviously 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 δ1.36.

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 δ200.6. The ^{1}H NMR spectrum of **13** was similar to that of 6α-hydroxydemethylcryptojaponol (**12**), except for an additional methoxyl resonance at δ3.79. The structure of **13** was assigned as 6α,11-dihydroxy-12-methoxyabieta-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 δ6.18 and was hydrogen bonded with the adjacent methoxyl group. Irradiation of Me-10 at δ1.53 caused a 2% NOE

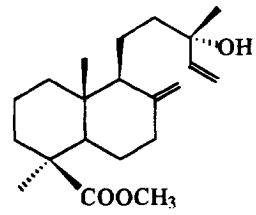
*Author to whom correspondence should be addressed.



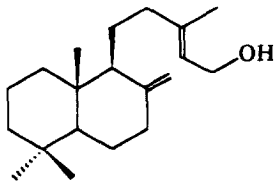
1



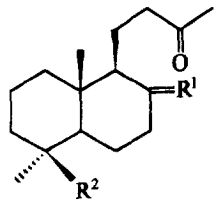
2



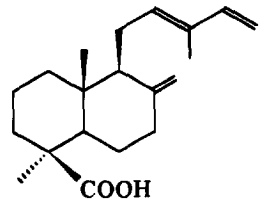
3



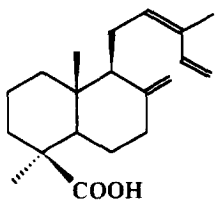
4



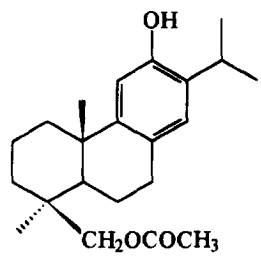
	R¹	R²
5	CH_2	$COOCH_3$
6	O	COOH



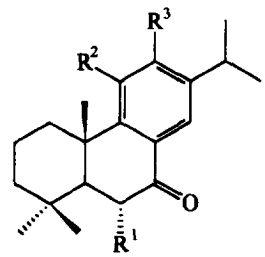
7



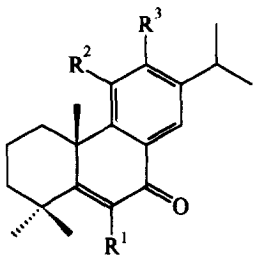
8



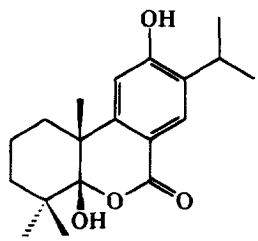
9



	R¹	R²	R³
10	H	H	OCH_3
11	H	OCH_3	OH
12	OH	OH	OH
13	OH	OH	OCH_3



	R¹	R²	R³
14	H	H	OCH_3
15	OH	OCH_3	OH

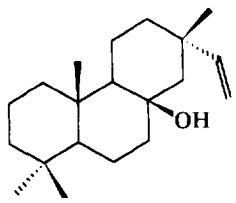


16

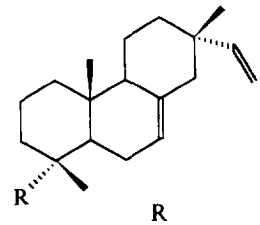
of the signal at δ6.18, supporting the assignment of the hydroxyl group at C-11.

The molecular formula $C_{21}H_{28}O_4$ of **15** was deduced by measurement of the exact mass of its $[M]^+$ ion (*m/z* 344.198). The IR absorptions at 3383 and 1618 cm^{-1} were attributable to the hydroxyl and conjugated carbonyl groups. By analyses of the ^1H and ^{13}C NMR spectra (Tables 1 and 2), **15** was determined to be 6,12-dihydroxy-11-methoxyabieta-5,8,11,13-tetraen-7-one. The carbon signals at δ179.9, 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 δ7.71 due to the deshielding effect of the carbonyl group at C-7. On irradiation of Me-10 at δ1.64, a 7% NOE of the methoxyl group at δ3.82 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 δ4.99 (t, J = 6.5 Hz) and a carbon signal at



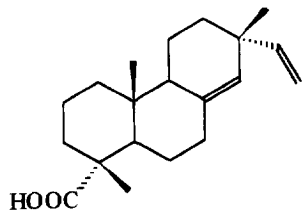
17



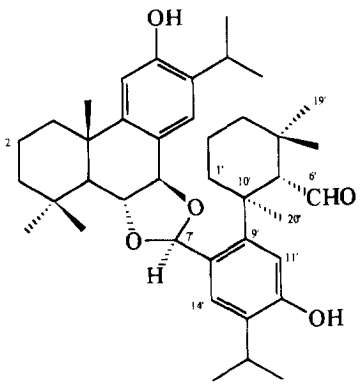
R

18 CH_2OH

19 COOH



20



23

Table 1. ^{1}H NMR spectral data of diterpenoids (300 MHz, $CDCl_3$ solution, δ values in ppm, J values in Hz)*†

H	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*)		
OCH_3	3.76 (*s*)	3.79 (*s*)	3.82 (*s*)		

*Some assignable resonances for **6** appeared at δ0.60 (*s*, H-20), 1.28 (*s*, H-18), 2.06 (*s*, H-16) in addition to others.

†Some assignable resonances for **22** appeared at δ0.51 (*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′).

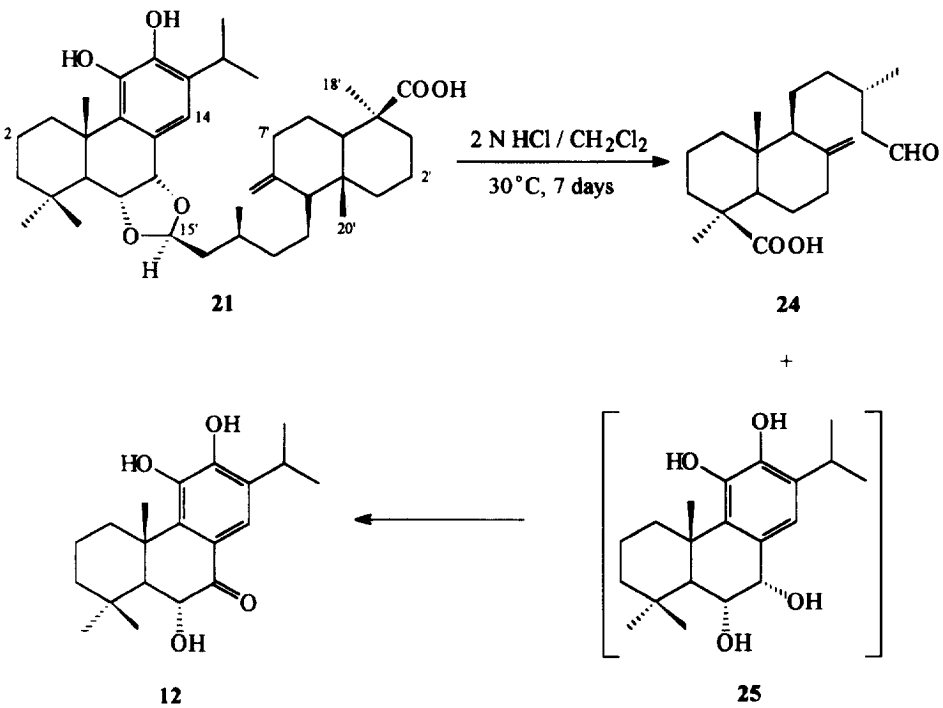
‡The rest of the resonances appeared at δ0.57 (*s*, H-20′), 0.92 (*d*, J = 6.5, H-16′), 1.21 (*s*, H-18′), 4.50 (*br s*, H-17′), 4.80 (*br s*, H-17′), 4.99 (*t*, J = 6.5, H-15′).

§The rest of the resonances appeared at δ0.70 (*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′).

δ100.5 (*d*). Acid-catalysed hydrolysis of **21** (Scheme 1) gave imbricataloic acid (**24**) and 6α-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,7α,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

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

C	6	11	13	15	C	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				



Scheme 1.

in axial positions as shown by the large coupling constant 10 Hz. As a 5% NOE of H-6 (at δ4.55) was observed on irradiation of H-7 (at δ5.03), these two protons must be in the *cis* relationship. Irradiation of H-15′ (at δ4.99) caused a 4% NOE of H-14 (at δ6.94), 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, ^{13}C, C–H COSY and HMBC spectra, **22** was determined to be a self-condensation product of imbricataloic acid. The proton signals at δ6.39 (H-15′) and 9.32 (H-15) as well as the carbon signals at δ155.3 (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 13*S*-configuration [3]. Ozonolysis of **22** (Scheme 2) gave 8,15-dioxo-17-norlabdan-19-oic acid (**26**) and 8-oxo-15,17-dinorlabdane-14,19-dioic acid (**28**), which might be derived from an α-oxoaldehyde (**27**). Compound **26**, having the 13*S*-configuration, also showed a negative Cotton effect with $[\theta]_{min}$ at 292 nm [3].

By analyses of the H–H COSY and ^{13}C 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 δ6.53) caused a 10% NOE of H-7 (at δ5.20), 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 μm) 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 Me_2CO in January 1989. The Me_2CO 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° ($CHCl_3$; *c* 1.2), {lit. [5], oil, $[\alpha]_D$ + 0.06° (neat)}.

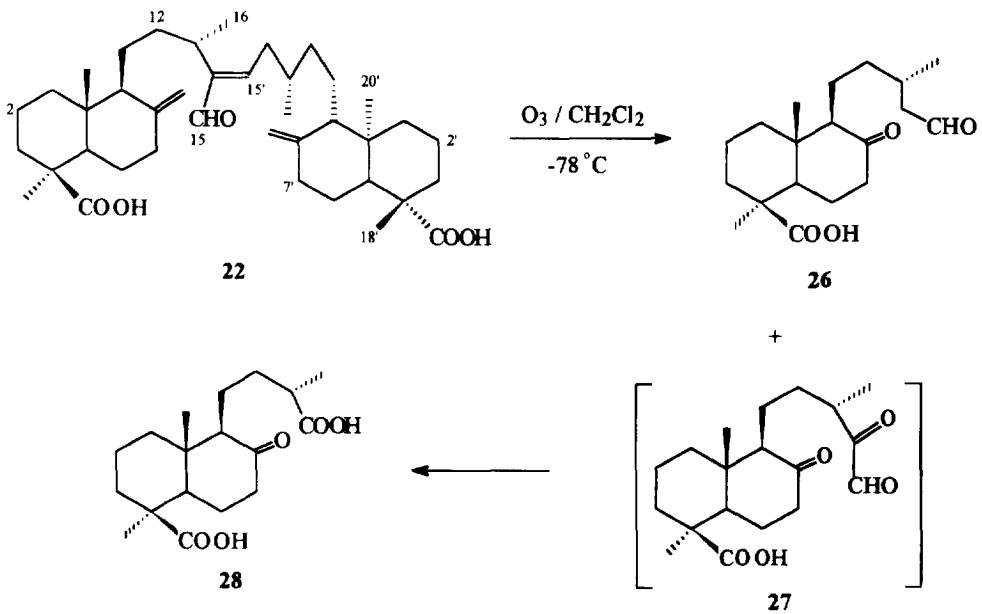
Junicedric acid (**2**). Oil, $[\alpha]_D^{25}$ + 33.5° ($CHCl_3$; *c* 0.7), {lit. [6], gum, $[\alpha]_D^{25}$ + 30.5° (EtOH; *c* 0.59)}. ^{13}C NMR ($CDCl_3$, 75 MHz): δ12.9 (C-20), 19.9 (C-2), 21.1 (C-16), 21.7 (C-11), 26.0 (C-6), 28.9 (C-18), 31.1 (C-13), 36.8 (C-12), 37.9 (C-3), 38.7 (C-7), 39.1 (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° ($CHCl_3$; *c* 1.2), {lit. [7], oil, $[\alpha]_D$ + 64.0° (EtOH)}.

Copalol (**4**). Oil, $[\alpha]_D^{25}$ + 31.0° ($CHCl_3$; *c* 0.5), {lit. [8], oil, $[\alpha]_D$ + 30.0° ($CHCl_3$)}.

13-*Oxo*-14,15-*dinorlabd*-8(17)-en-19-*oic acid methyl ester* (**5**). Oil, $[\alpha]_D^{25}$ + 37.1° ($CHCl_3$; *c* 1.4), {lit. [9], oil, $[\alpha]_D$ + 36.5° ($CHCl_3$)}. ^{13}C NMR ($CDCl_3$, 75 MHz): δ12.4 (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 (OCH_3), 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° ($CHCl_3$; *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 $C_{17}H_{26}O_4$ requires 294.1832; found 294.1836.



Scheme 2.

Ozonolysis of isocupressic acid. A soln of isocupressic acid (15 mg) in CH_2Cl_2 (5 ml) was stirred at $-78°$ and bubbled with O_3 for 5 min. Me_2S (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° ($CHCl_3$; *c* 1.2), {lit. [10] (Me ester), mp 105–106°; $[\alpha]_D$ + 48.0° ($CHCl_3$)}.

cis-*Communic acid* (**8**). Gum, $[\alpha]_D^{25}$ + 37.5° ($CHCl_3$; *c* 1.5), {lit. [11] (Me ester), mp 41–42°; $[\alpha]_D$ + 45.0° ($CHCl_3$)}.

19-*Acetoxyferruginol* (**9**). Oil, $[\alpha]_D^{25}$ + 52.0° ($CHCl_3$; *c* 0.6). ^{13}C NMR ($CDCl_3$, 75 MHz): δ19.0 (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°; $[\alpha]_D^{25}$ + 30.0° ($CHCl_3$; *c* 1.1), {lit. [13], mp 136–137°; $[\alpha]_D$ + 32.0° (MeOH)}.

12-*Hydroxy*-11-*methoxyabieta*-8,11,13-*trien*-7-*one* (**11**). Solid, mp 177–178°. $[\alpha]_D^{30}$ + 10.0° ($CHCl_3$; *c* 0.3). TLC (50% $CHCl_3$ in hexane) R_f 0.37. IR ν_{max}^{KBr} cm^{-1}: 3329, 1650, 1581. UV λ_{max}^{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 $C_{21}H_{30}O_3$ requires 330.2196; found 330.2185.

6α-*Hydroxydemethylcryptojaponol* (**12**). Solid, mp 202–203°. $[\alpha]_D^{25}$ + 42.0° ($CHCl_3$; *c* 1.4), {lit. [14] (triacetate) mp 179–181°}. ^{13}C NMR ($CDCl_3$, 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°, $[\alpha]_D^{25}$ + 85.5° ($CHCl_3$; *c* 1.1). TLC (50% $CHCl_3$ in hexane) R_f 0.42. IR ν_{max}^{KBr} cm^{-1}: 3419, 1671, 1593. UV λ_{max}^{MeOH} nm (ε): 316 (5000), 300 (4360), 274 (14100), 247 (3830), 217 (26400). 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 $C_{21}H_{30}O_4$ requires 346.2145; found 346.2144.

5,6-*Dehydrosugiol methyl ether* (**14**). Gum, $[\alpha]_D^{25}$ + 15.0° ($CHCl_3$; *c* 0.4), {lit. [15] (dehydrosugiol) mp 284–286°, $[\alpha]_D$ + 13° (EtOH)}.

6,12-*Dihydroxy*-11-*methoxyabieta*-5,8,11,13-*tetraen*-7-*one* (**15**). Solid, mp 182–183°, $[\alpha]_D^{30}$ + 3.3° ($CHCl_3$; *c* 0.3). TLC (33% CH_2Cl_2 in hexane) R_f 0.22. IR ν_{max}^{KBr} cm^{-1}: 3383, 1618, 1585, 1554. UV λ_{max}^{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 $C_{21}H_{28}O_4$ requires 344.1988; found 344.1978.

Cupresol (**16**). Oil, $[\alpha]_D^{25}$ + 48.0° ($CHCl_3$; *c* 0.7), {lit. [16], Oil; $[\alpha]_D^{25}$ + 48.2° ($CHCl_3$; *c* 0.76)}.

Nejukol (**17**). Oil, $[\alpha]_D^{25}$ − 6.9° ($CHCl_3$; *c* 2.2), {lit. [17], mp 40–41°.; $[\alpha]_D$ − 6.8° ($CHCl_3$)}.

Isopimarinol (**18**). Gum, $[\alpha]_D^{25}$ − 25.2° ($CHCl_3$; *c* 0.3), {lit. [18], mp 84–86°; $[\alpha]_D$ − 24.6° ($CHCl_3$)}.

Isopimaric acid (**19**). Solid, mp 160–161°. $[\alpha]_D^{30}$ + 6.0° ($CHCl_3$; *c* 0.7), {lit. [19], mp 162–164°.; $[\alpha]_D$ 0° ($CHCl_3$)}.

Sandaracopimaric acid (**20**). Solid, mp 167–169°. $[\alpha]_D^{30}$ − 18.5° ($CHCl_3$; *c* 1.2), {lit. [21], mp 169°.; $[\alpha]_D$ − 20.0° (EtOH)}.

Acetal **21** *from abieta*-8,11,13-*triene*-6α,7α,11,12-*tetraol and imbricataloic acid.* Solid, mp 134–136°, $[\alpha]_D^{20}$ + 11° ($CHCl_3$; *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 $C_{40}H_{60}O_6$ requires 636.4392; found 636.4415.

Hydrolysis of **21**. A soln of **21** (17 mg) in CH_2Cl_2 (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° ($CHCl_3$; *c* 0.4), {lit. [22] (Me ester), oil, $[\alpha]_D$ + 38.5° ($CHCl_3$)}. IR ν_{max}^{neat} cm^{-1}: 3079, 3000–2500, 2718, 1718, 1684, 887. ^1H NMR ($CDCl_3$, 300 MHz): δ0.58 (*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° ($CHCl_3$; *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 $C_{40}H_{62}O_5$ requires 622.4600; found 622.4617.

Ozonolysis of **22**. A soln of **22** (7 mg) in CH_2Cl_2 (5 ml) was stirred at $-78°$ and bubbled with O_3 for 1 min. Me_2S (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° ($CHCl_3$; *c* 0.4), {lit. [3], oil; $[\alpha]_D^{20}$ − 31° ($CHCl_3$; *c* 0.4)}. **28**: gum, $[\alpha]_D^{30}$ + 36.5° ($CHCl_3$; *c* 0.3), TLC (30% EtOAc in hexane) R_f 0.29. IR ν_{max}^{neat} cm^{-1}: 3000–2500, 1694. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.55 (*s*, H-20), 1.12 (*d*, *J* = 7 Hz, H-16), 1.30 (*s*, H-18). ^{13}C NMR ($CDCl_3$, 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°, $[\alpha]_D^{28}$ + 31° ($CHCl_3$; *c* 1.7), TLC (15% EtOAc in hexane) R_f 0.33. IR ν_{max}^{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 $C_{40}H_{56}O_5$ requires 616.4122; found 616.4135.

Acknowledgement—We thank the National Science Council for finanical support (NSC83-0208-M002-095).

REFERENCES

1. Su, W.-C., Fang, J.-M. and Cheng, Y.-S. (1995) *Phytochemistry* **39**, 603.
2. Su, W.-C., Fang, J.-M. and Cheng, Y.-S. (1994) *Phytochemistry* **35**, 1279.
3. Su, W.-C., Fang, J.-M. and Cheng, Y.-S. (1994) *Phytochemistry* **37**, 1109.
4. Su, W.-C., Fang, J.-M. and Cheng, Y.-S. (1993) *Phytochemistry* **34**, 779.
5. Demole, E. and Lederer, E. (1958) *Bull. Soc. Chim. Fr.* 1128.
6. Calderon, J. S., Quijano, L., Gomez-Garibay, F., Moran, M. and Rios, T. (1987) *Phytochemistry* **26**, 2639.
7. Carman, R. M., Craig, W. G. and Shaw, I. M. (1973) *Aust. J. Chem.* **26**, 209.
8. Cambie, R. C., Grant, P. K., Huntrakul, C. and Weston, R. J. (1969) *Aust. J. Chem.* **22**, 1691.
9. De Pascual Teresa, J., San Feliciano, A. and Egido, T. (1976) *An. Quim.* **72**, 865.
10. Arya, V. P., Erdtman, H. and Kubota, T. (1961) *Tetrahedron* **16**, 255.
11. Thomas, B. R. (1966) *Acta Chem. Scand.* **20**, 1074.
12. Cambie, R. C., Cox, R. E. and Sidwell, D. (1984) *Phytochemistry* **23**, 333.
13. Wenkert, E., Campello, J. P., McChesney, J. D. and Watts, D. J. (1974) *Phytochemistry* **13**, 2545.
14. Fraga, B. M., Gonzalez, A. G., Herrera, J. R., Luis, J. G. and Ravelo, A. G. (1986) *Phytochemistry* **25**, 269.
15. Kupchan, S. M., Karim, A. and Marcks, C. (1969) *J. Org. Chem.* **34**, 3912.
16. Jolad, S. D., Hoffmann, J. J., Schram, K. H., Cole, J. R., Bates, R. B. and Tempesta, M. S. (1984) *J. Nat. Prod.* **47**, 983.
17. Corbett, R. E. and Smith, R. A. J. (1967) *J. Chem. Soc. (C)* 300.
18. Baldwin, D. E., Loeblich, V. M. and Lawrence, R. V. (1958) *J. Org. Chem.* **23**, 25.
19. Harris, G. C. and Sanderson, T. F. (1948) *J. Am. Chem. Soc.* **70**, 2079.
20. Wenkert, E. and Buckwalter, B. L. (1972) *J. Am. Chem. Soc.* **94**, 4367.
21. Edwards, O. E., Nicolson, A. and Rodger, M. N. (1960) *Can. J. Chem.* **38**, 663.
22. Spalding, B. P., Zinkel, D. F. and Roberts, D. R. (1971) *Phytochemistry* **10**, 3289.