Pergamon

Phytochemistry, Vol. 35, No. 5, pp. 1279–1284, 1994
Elsevier Science Ltd
Printed in Great Britain.
0031-9422/94 \$6.00+0.00

ABIETANES AND KAURANES FROM LEAVES OF *CRYPTOMERIA JAPONICA*

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(*Received* 10 *August* 1993)

Key Word Index—*Cryptomeria japonica*; Taxodiaceae; leaves; diterpenes; abietane-type; kaurane-type.

Abstract—Totarol, 14 abietanes, two secoabietanes and four *ent*-kaurane derivatives were isolated from the leaves of *Cryptomeria japonica*. The new compounds included 6,12-dihydroxyabieta-5,8,11,13-tetraen-7-one, 6β-hydroxyferruginol, 7α,8α-epoxy-6α-hydroxyabieta-9(11),13-dien-12-one, (5*R*,10*S*)-12-methoxyabieta-6,8,11,13-tetraene, *ent*-kaur-15-en-17-al and (+)-16-acetylkaurane-16,17-diol. 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 [1]. Its constituents have been extensively studied [2–12]. The leaves are reported to contain diterpenes ferruginol (**1**), sugiol (**5**), xanthoperol, kaurane, kaurene and phyllocladene. We report herein novel diterpenes of abietane- and kaurene-types (**11–14**, **20** and **21**) isolated from the ethyl acetate-soluble part of the leaves of *C. japonica*.

RESULTS AND DISCUSSION

Ten known abietane-type diterpenes, ferruginol (**1**) [13, 14], 6,7-dehydroferruginol (**2**) [13], 6,7-dehydroferruginol methyl ether (**3**) [13], 7-dehydroabietanone (**4**) [15], sugiol (**5**) [14, 16], 6α-hydroxysugiol (**6**) [14], hinokiol (**7**) [17], 11-hydroxysugiol (**8**) [18], cryptojaponol (**9**) [19] and 5-epixanthoperol (**10**) [20], a secoabietane dialdehyde (**15**), 12-hydroxy-6,7-secoabieta-8,11,13-triene-6,7-dial [21] and its methyl ether (**16**) [21], as well as totarol (**17**) [22], were identified by comparison of their physical and spectral data (mp, [α], mass, IR, ^{1}H and ^{13}C NMR) with the literature. The methyl ethers **3** and **16** are reported for the first time from a natural source, although they have been prepared by methylation of **2** and **15**, respectively [21]. The C-5 chirality of **16** was confirmed by NOE of the aldehyde signal at δ9.86 upon irradiation of Me-10 at δ1.49.

The molecular formula $C_{20}H_{26}O_3$ of **11** was deduced from its exact mass $[M]^+$ at *m/z* 314.188. The IR absorption at 1675 cm^{-1} was attributable to a conjugated carbonyl group. The ^{1}H NMR spectrum (Table 1) showed no olefinic proton, whereas the ^{13}C NMR spectrum (Table 2) exhibited two olefinic carbons at δ141.1 and 143.7. An α-hydroxy-α,β-unsaturated ketone was inferred from these spectral data. An aromatic proton H-14 occurring at a low field δ7.99 (*s*) indicated **11** is an abietane-type diterpene having the carbonyl group at C-7. The positions of C-5 at δ141.1 and C-7 at δ179.7 were deduced from a HMBC spectrum by correlation with C-18 and C-14, respectively. Compound **11** was assigned as 6,12-dihydroxyabieta-5,8,11,13-tetraen-7-one, an enol tautomer of 5-epixanthoperol (**10**). It was found that **10** yielded *ca* 50% of **11** on standing in $CDCl_3$ for two months.

Compound **12** ($C_{20}H_{30}O_2$) showed the exact mass at *m/z* 302.224. The structure was determined to be 6β-hydroxyferruginol by analysis of its NMR spectra (Tables 1 and 2). The compound has an equatorial H-6α, which exhibited small coupling constants with C-5 and C-7 protons ($J_{5,6} = 2$ Hz, $J_{6,7\beta} = 6$ Hz and $J_{6,7\alpha} = 3$ Hz).

Compound **13** ($C_{20}H_{28}O_3$) showed the exact mass $[M]^+$ at *m/z* 316.203. The ^{13}C NMR spectrum (Table 2) showed a signal at δ187.1 attributable to a carbonyl group and resonances at δ126.2, 138.6, 149.5 and 162.5 attributable to two C=C double bonds. Taking these data and two alkenyl proton resonances at δ6.03 (*s*) and 6.30 (*s*), we considered **13** contained a cyclohexa-2,5-dienone moiety. Further evidence from the ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY, HMBC and NOE experiments support the structural assignment of **13** as 7α,8α-epoxy-6α-hydroxyabieta-9(11),13-dien-12-one. The axial H-6β (at δ4.40) appeared to couple with the axial H-5α ($J = 9$ Hz), but not with the equatorial H-7β (at δ3.72). Irradiation of H-7β or Me-10 caused 7.9 or 5.6% NOE of H-6β, respectively, supporting the assigned stereochemistry. The HMBC spectrum revealed that H-11 at δ6.30 was correlated with C-8, C-10 and C-13, whereas H-14 at δ6.03 was correlated with C-9 and C-12. Compound **13**

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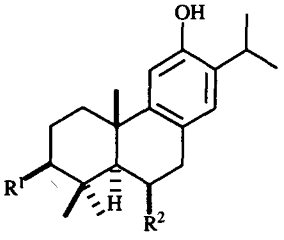
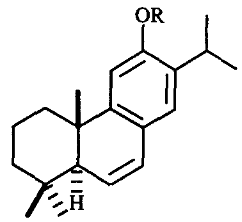
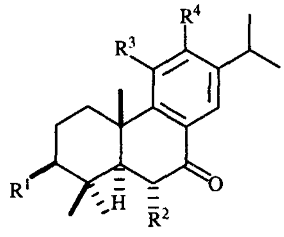


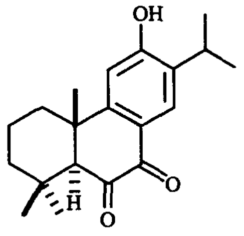
	R1	R2
1	H	H
7	OH	H
12	H	OH



	R
2	H
3	Me



	R1	R2	R3	R4
4	H	H	H	H
5	H	H	H	OH
6	H	OH	H	OH
8	H	H	OH	OH
9	H	H	OH	OMe



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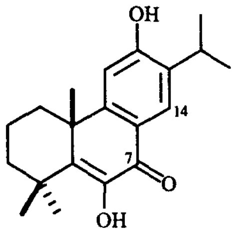

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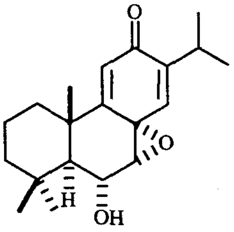

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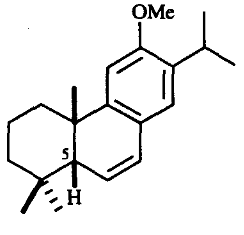

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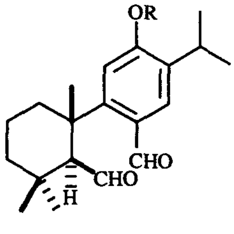
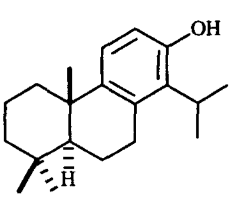


	R
15	H
16	Me



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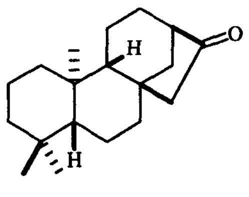

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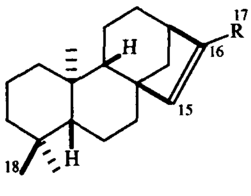
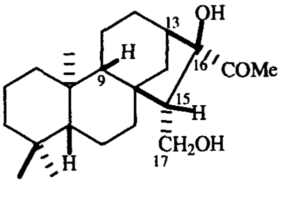


	R
19	CH_2OH
20	CHO



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was subjected to acid-catalysed isomerization (0.1 M HCl, MeOH, CH_2Cl_2, 25°C, 16 hr) to give a main product **6**, presumably via opening of the epoxy ring to form an enol intermediate as shown in Scheme 1.

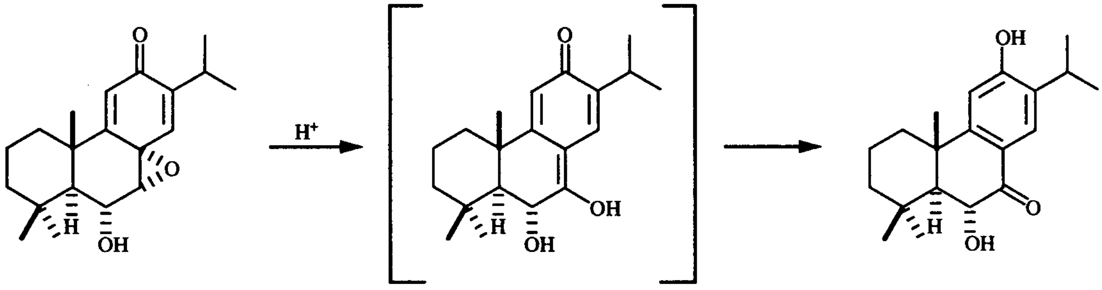
By analysis of the ^{1}H NMR spectrum, **14** ($C_{21}H_{30}O$) was assigned as (5*R*,10*S*)-12-methoxyabieta-6,8,11,13-tetraene, the C-5 epimer of **3**. The coupling constant of 6 Hz between the equatorial H-5β and the vinyl H-6 in **14** is larger than the value of 2.5 Hz between the axial H-5α and H-6 in **3**. On the other hand, **3** showed a W-shape coupling between H-5α and H-7 ($J = 3$ Hz), whereas **14** lacked this phenomenon. The 5,10-*cis* configuration was concluded by observing a 13.5% NOE of H-5 upon irradiation of the Me-10 group at δ1.07. The H-18

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

H	**11**	**12**	**13**	**14***	**20**	**21†**
5		1.65 (*d*, $J=2$)	1.21 (*d*, $J=9$)	1.77 (*d*, $J=6$)	0.80 (*dd*, $J=12$, 2)	0.73 (*dd*, $J=12$, 2)
6		4.29 (*ddd*, $J=2$, 3, 6)	4.40 (*d*, $J=9$)	5.82 (*dd*, $J=10$, 6)		
7		2.68 (*dd*, $J=16$, 3), 3.26 (*dd*, $J=16$, 6)	3.72 (*s*)	6.44 (*d*, $J=10$)		
9					1.06 (*bd*, $J=12$)	1.08 (*bd*, $J=12$)
11	6.82 (*s*)	6.59 (*s*)	6.30 (*s*)	6.73 (*s*)		
13					3.01 (*bd*, $J=5$)	3.15 (*bs*)
14	7.99 (*s*)	6.89 (*s*)	6.03 (*s*)	6.81 (*s*)	1.36 (*dd*, $J=10.5$, 5), 2.17 (*dd*, $J=10.5$, 1)	0.43 (*dd*, $J=12$, 5), 1.80 (*dd*, $J=12$, 2)
15	3.16 (*sept*, $J=7$)	3.11 (*sept*, $J=7$)	2.96 (*sept*, $J=7$)	3.22 (*sept*, $J=7$)	6.55 (*s*)	2.46 (*dd*, $J=9$, 2)
16	1.25 (*d*, $J=7$)	1.21 (*d*, $J=7$)	1.06 (*d*, $J=7$)	1.17 (*d*, $J=7$)		
17	1.28 (*d*, $J=7$)	1.23 (*d*, $J=7$)	1.08 (*d*, $J=7$)	1.17 (*d*, $J=7$)	9.70 (*s*)	4.14 (*dd*, $J=19$, 9), 4.92 (*dd*, $J=19$, 2)
18	1.41 (*s*)	1.07 (*s*)	1.07 (*s*)	0.34 (*s*)	0.85 (*s*)	0.82 (*s*)
19	1.41 (*s*)	1.08 (*s*)	1.07 (*s*)	0.87 (*s*)	0.79 (*s*)	0.75 (*s*)
20	1.46 (*s*)	1.14 (*s*)	1.19 (*s*)	1.07 (*s*)	1.04 (*s*)	0.94 (*s*)

*The methoxy group in **14** appeared at δ3.82 (*s*).

†The acetyl group in **21** appeared at δ2.52 (*s*).



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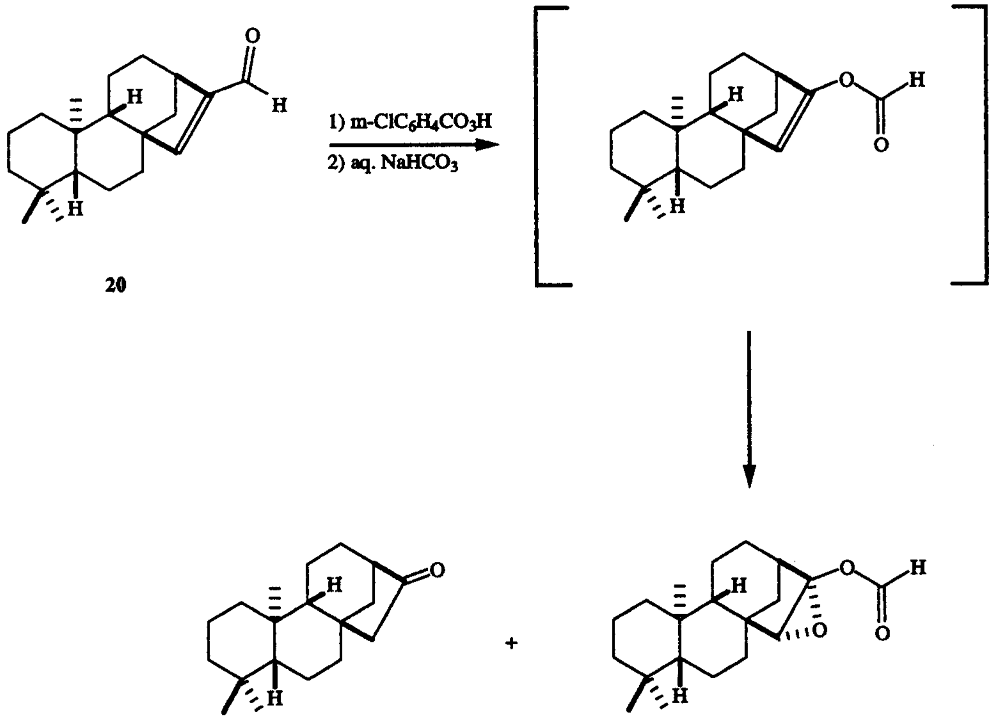
Scheme 1.



20 18 A

Scheme 2.

resonance occurred at a remarkably high field, δ0.34, due to the shielding effect of the B-ring.

The known compounds *ent*-17-norkauran-16-one (**18**) [23] and *ent*-kaur-15-en-17-ol (**19**) [24] are laevorotatory. Compound **18** showed a carbon resonance at δ222.8 (C-16) attributable to a strained ketone. The new diterpene aldehyde **20** ($C_{20}H_{30}O$), *ent*-kaur-15-en-17-al, was correlated by oxidation of the alcohol **19** with manganese dioxide (CH_2Cl_2, 20°, 16 hr). When **20** was subjected to oxidation with *meta*-chloroperbenzoic acid (CH_2Cl_2, 0°, 1 hr) followed by treatment with aqueous sodium bicarbonate, the ketone **18** and an epoxyformate A were obtained (Scheme 2). The uncommon structure of **21** ($C_{22}H_{36}O_3$), $[\alpha]_D^{25}+62.5°$, was assigned as (+)-16-acetylkaurane-16,17-diol. The acetyl group showed an IR absorption at 1700 cm^{-1} and a singlet at δ2.52 (*s*) in the ^1H NMR spectrum. Assignments of proton and carbon resonances in **21** were assisted by ^{13}C–^1H COSY and HMBC spectra. The H-15 and two geminal protons at C-17 appeared as an ABX pattern, at δ2.46 (*dd*, $J=9$, 2 Hz), 4.14 (*dd*, $J=19$, 9 Hz) and 4.92 (*dd*, $J=19$, 2 Hz). The stereochemistry was determined by NOE experiments, i.e. irradiation of the acetyl group at δ2.52 caused a 7.2% enhancement of H-13 resonance at δ3.15 and irradiation of H-9 at δ1.08 caused a 23.8% enhancement of H-15 resonance. Since **18**–**21** were found in the same plant, the

Table 2. ^{13}C NMR spectral data of new compounds (CDCl$_3$ solution, δ values in ppm)*

C	**11**	**12**	**13**	**14***	**20**	**21†**
1	33.6	39.0	38.1	35.5	40.4	40.4
2	17.6	19.0	18.1	19.3	18.5	18.5
3	37.9	42.7	43.2	42.1	42.0	41.8
4	35.9	34.1	34.7	35.1	33.3	33.1
5	141.1	58.9	58.2	52.5	55.9	55.6
6	143.7	68.6	66.4	125.9	18.7	19.8
7	179.7	38.9	70.9	128.1	38.2	37.9
8	120.9	123.5	56.2	127.4	51.0	46.0
9	154.9	148.4	162.5	141.6	46.8	56.7
10	40.3	38.1	38.0	37.0	39.8	39.5
11	111.4	109.8	126.2	105.7	18.4	17.1
12	157.7	151.3	187.1	156.4	25.3	26.4
13	133.8	131.3	149.5	133.6	38.0	42.1
14	125.6	126.6	138.6	124.7	43.0	36.1
15	26.9	26.8	26.3	26.5	162.3	45.0
16	22.3	22.2	21.3	22.7	148.5	117.7
17	22.5	22.4	21.3	22.8	189.5	79.7
18	28.2	34.6	35.3	20.6	33.5	33.5
19	27.5	22.7	22.4	31.3	21.5	21.5
20	35.1	22.7	21.6	33.4	17.7	17.4

*The methoxy group in **14** appeared at δ55.7.

†The acetyl group in **21** appeared at δ28.3 and 201.8

dextrorotatory compound **21** was still considered an *ent*-kaurane derivative. However, it is unclear whether **21** is a natural product or an artefact.

In summary, we isolated totarol, 14 abietanes, two secoabietanes and four *ent*-kaurane derivatives from the leaves of *C. japonica*. Among the new compounds, the enol **11**, epoxydienone **13**, 5,10-*cis* abietane **14** and kauranediol had an additional acetyl group at C-16 worth special note.

EXPERIMENTAL

General. Merck silica gel 60F sheets were used for analytical TLC. HPLC was carried out on a Hibar Lichrosorb Si 60 (7 or 10 μm) column (25 × 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$_2$CO. The Me$_2$CO 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 gradients of hexane and EtOAc. The appropriate frs were combined and purified by HPLC to give **14** (10 mg), **3** (10 mg), **4** (5 mg), **17** (7 mg), **1** (35 mg), **20** (16 mg), **2** (5 mg), **16** (16 mg), **21** (11 mg), **12** (5 mg), **15** (18 mg), **13** (20 mg), **10** (5 mg), **11** (15 mg), **6** (12 mg), **9** (16 mg), **18** (6 mg), **19** (27 mg), **5** (27 mg), **8** (10 mg) and **7** (22 mg) in the order of increasing polarity.

Compounds **1–10**, **15–19**. Ferruginol (**1**): oily solid. $[\alpha]_D^{20}+39.5^\circ$ (CHCl$_3$; *c* 1.3). 6,7-Dehydroferruginol (**2**): oil. $[\alpha]_D^{25}-62^\circ$ (CHCl$_3$; *c* 0.5). 6,7-Dehydroferruginol methyl ether (**3**): oil. $[\alpha]_D^{25}-87^\circ$ (CHCl$_3$; *c* 1). ^{13}C NMR (CDCl$_3$): δ19.1 (C-2), 20.1 (C-18), 22.5 (C-16, 17), 22.9 (C-19), 26.4 (C-15), 32.6 (C-20), 32.9 (C-4), 36.1 (C-1), 38.0 (C-10), 41.1 (C-3), 51.1 (C-5), 55.6 (MeO), 104.8 (C-11), 124.4 (C-14), 125.8 (C-8), 127.3 (C-6), 127.4 (C-7), 133.8 (C-13), 147.0 (C-9), 156.4 (C-12), 7-Dehydroabietanone (**4**): solid. Mp 85–87°. $[\alpha]_D^{30}+13.5^\circ$ (CHCl$_3$; *c* 0.5). ^{13}C NMR (CDCl$_3$): δ18.8 (C-2), 21.2 (C-19), 23.3 (C-16), 23.7 (C-17), 23.8 (C-20), 32.5 (C-18), 33.2 (C-4), 33.5 (C-15), 36.2 (C-6), 37.8 (C-10), 37.9 (C-1), 41.3 (C-3), 49.3 (C-5), 123.6 (C-12), 124.8 (C-11), 130.7 (C-8), 132.4 (C-14), 146.5 (C-13), 153.8 (C-9), 199.9 (C-7). Sugiol (**5**): solid. Mp 292–293°. $[\alpha]_D^{30}+26.0^\circ$ (EtOH; *c* 1.5). 6α-Hydroxysugiol (**6**): solid. Mp 207–208°. $[\alpha]_D^{25}+35.3^\circ$ (CHCl$_3$; *c* 0.5). ^{13}C NMR (CDCl$_3$): δ18.8 (C-2), 21.8 (C-19), 22.2 (C-16), 22.4 (C-17), 24.7 (C-20), 26.8 (C-15), 34.1 (C-4), 35.8 (C-18), 38.8 (C-1), 39.2 (C-10), 42.9 (C-3), 55.9 (C-5), 73.9 (C-6), 110.2 (C-11), 121.8 (C-8), 127.2 (C-14), 133.4 (C-13), 156.5 (C-9), 158.9 (C-12), 199.7 (C-7). Hinokiol (**7**): solid. Mp 233–235°. $[\alpha]_D^{30}+74^\circ$ (EtOH; *c* 1.1). ^{13}C NMR (acetone-d_6): δ15.9 (C-19), 19.7 (C-6), 22.7 (C-16), 22.9 (C-17), 25.1 (C-20), 27.2 (C-15), 28.5 (C-18), 28.8 (C-2), 30.7 (C-7), 37.8 (C-1), 37.9 (C-10), 39.5 (C-4), 50.8 (C-5), 78.3 (C-3), 111.3 (C-11), 126.1 (C-8), 126.9 (C-14), 132.6 (C-13), 148.3 (C-9), 153.0 (C-12), 11-Hydroxysugiol (**8**): solid. Mp 192–193°. $[\alpha]_D^{26}+21^\circ$ (CHCl$_3$; *c* 1). ^{13}C NMR (CDCl$_3$): δ18.6 (C-20), 19.0 (C-2), 21.5 (C-19), 22.3 (C-16), 22.5 (C-17), 27.2 (C-15), 33.1 (C-18), 33.4 (C-4), 35.5 (C-1), 36.7 (C-6), 40.1 (C-10), 41.0 (C-3), 50.2 (C-5), 118.0 (C-14), 125.2 (C-8), 131.9 (C-13), 138.7 (C-9), 141.2 (C-11), 146.5 (C-12), 199.5 (C-7). Cryptojaponol (**9**): solid. Mp 203–204°. $[\alpha]_D^{25}+25^\circ$ (CHCl$_3$; *c* 1.6). ^{13}C NMR (CDCl$_3$): δ18.0 (C-2), 18.9 (C-20), 21.5 (C-19), 23.4 (C-16), 23.5 (C-17), 26.7 (C-15), 33.1 (C-18), 33.5 (C-4), 35.6 (C-6), 36.3 (C-1), 40.2 (C-10), 41.3 (C-3), 50.3 (C-5), 61.8 (MeO), 117.3 (C-14), 128.8 (C-8), 138.1 (C-11), 139.1 (C-13), 146.5 (C-9), 149.1 (C-12), 199.1 (C-7). 5-Epixanthoperol (**10**): solid. Mp 205–207°. $[\alpha]_D^{25}+25^\circ$ (CHCl$_3$; *c* 0.5). 12-Hydroxy-6,7-secoabieta-8,11,13-triene-6,7-dial (**15**): solid. Mp 191–192°. $[\alpha]_D^{30}+20^\circ$ (MeOH$_3$; *c* 1.2). 12-Methoxy-6,7-secoabieta-8,11,13-triene-6,7-dial (**16**): oil. $[\alpha]_D^{25}+51^\circ$ (CHCl$_3$; *c* 1). ^{13}C NMR (CDCl$_3$): δ19.5 (C-2), 22.3 (C-16, 17, 19), 23.4 (C-20), 26.5 (C-15), 30.6 (C-18), 32.2 (C-1), 33.6 (C-4), 37.6 (C-3), 40.9 (C-10), 55.4 (MeO), 64.9 (C-5), 109.2 (C-11), 127.6 (C-8), 133.2 (C-14), 135.0 (C-13), 151.0 (C-9), 160.7 (C-12), 191.4 (C-7), 205.6 (C-6). Torarol (**17**): solid. Mp 125–126°. $[\alpha]_D^{30}+40.2^\circ$ (EtOH$_3$; *c* 0.5). *ent*-17-Norkauran-16-one (**18**): solid. Mp 109–110°. $[\alpha]_D^{20}-20^\circ$ (CHCl$_3$; *c* 0.5). ^{13}C NMR (CDCl$_3$): δ18.0 (C-20), 18.5 (C-11), 18.6 (C-2), 19.3 (C-6), 21.6 (C-19), 29.7 (C-12), 33.3 (C-4), 33.6 (C-18), 37.5 (C-7), 39.5 (C-10), 40.4 (C-1), 41.0 (C-14), 41.9 (C-3), 42.5 (C-8), 48.0 (C-9), 55.0 (C-13), 55.2 (C-15), 56.1 (C-5), 222.8 (C-16). *ent*-Kaur-15-en-17-ol (**19**): solid. Mp 85–86°. $[\alpha]_D^{25}-33^\circ$ (CHCl$_3$; *c* 1). ^{13}C NMR (CDCl$_3$): δ17.6 (C-20), 18.6 (C-2, 11), 19.2 (C-6), 21.6 (C-19), 25.7 (C-12), 33.3 (C-4), 33.5 (C-18), 39.3 (C-7), 39.5 (C-10), 40.5 (C-1), 41.2 (C-13), 42.1 (C-3), 43.9 (C-14), 48.4 (C-9), 49.0 (C-8), 56.0 (C-5), 61.3 (C-17), 136.1 (C-15), 146.0 (C-16).

6,12-*Dihydroxyabieta*-5,8,11,13-*tetraen*-7-*one* (**11**). Needles from CHCl$_3$. Mp 189–190°. $[\alpha]_D^{26}-8.5^\circ$ (CHCl$_3$;

c 0.9). TLC (20% EtOAc in hexane) R_f 0.55. IR ν_{max}^{KBr} cm^{-1}: 3326, 1675, 1601, 1502, 1380. UV λ_{max}^{MeOH} nm (ε): 335 (7900), 309 (6140), 281 (7480), 261 (3510), 250 (6270), 236 (4540). EIMS (70 eV) m/z rel. int.: 314 $[M]^+$ (100), 299 (16), 271 (42), 245 (75), 229 (30), 215 (26), 203 (20). HRMS for $C_{20}H_{26}O_3$ requires: 314.1883. Found: 314.1881.

6β-Hydroxyferruginol (**12**). Oily solid. $[\alpha]_D^{20}+9.4°$ ($CHCl_3$; c 0.5). TLC ($CHCl_3$–hexane–EtOAc, 10:9:1) R_f 0.33. IR ν_{max}^{Neat} cm^{-1}: 3378, 1613, 1499, 1373. EIMS (70 eV) m/z rel. int.: 302 $[M]^+$ (100), 287 (24), 269 (81), 227 (53), 199 (31), 157 (27), 149 (19). HRMS for $C_{20}H_{30}O_2$ requires: 302.2247. Found: 302.2242.

*7α,8α-Epoxy-6α-hydroxyabieta-*9(11),13-*dien-*12-*one* (**13**). Oil. $[\alpha]_D^{25}-42.5°$ ($CHCl_3$; c 2). TLC (13% EtOAc in hexane) R_f 0.32. IR ν_{max}^{Neat} cm^{-1}: 3411, 1649, 1614, 1379, 1232, 921. UV $\lambda_{max}^{CHCl_3}$ nm (ε): 261 (9300), 250 (7900). EIMS (70 eV) m/z rel. int.: 316 $[M]^+$ (63), 301 (40), 287 (80), 273 (20), 231 (55), 203 (100), 163 (52). HRMS for $C_{20}H_{28}O_3$ requires: 316.2039. Found: 316.2031.

(5R,10S)-12-*Methoxyabieta-*6,8,11,13-*tetraene* (**14**). Oil. $[\alpha]_D^{28}-266°$ ($CHCl_3$; c 1). TLC (hexane) R_f 0.56. IR ν_{max}^{Neat} cm^{-1}: 3022, 1601, 1493, 1380, 1362, 1246. UV λ_{max}^{MeOH} nm (ε): 281 (8900), 245 (1900), 222 (25 600). EIMS (70 eV) m/z rel. int.: 298 $[M]^+$ (49), 283 (15), 241 (9), 227 (22), 216 (100), 199 (35), 173 (38). HRMS for $C_{21}H_{30}O$ requires: 298.2298. Found: 298.2296.

ent-*Kaur-*15-*en-*17-*al* (**20**). Crystals from EtOAc–hexane (6:94). Mp 115–116°. $[\alpha]_D^{25}-99°$ ($CHCl_3$; c 1). TLC (6% EtOAc in hexane) R_f 0.45. IR ν_{max}^{KBr} cm^{-1}: 2795, 1660, 1596. UV λ_{max}^{MeOH} nm (ε): 248 (7700), 217 (940). EIMS (70 eV) m/z rel. int.: 286 $[M]^+$ (80), 271 (65), 253 (22), 175 (37), 123 (71), 109 (45), 91 (100). HRMS for $C_{20}H_{30}O$ requires: 286.2298. Found: 286.2304. A soln of **20** (25 mg, obtained from oxidation of **19** with MnO_2) in CH_2Cl_2 (5 cm^3) was stirred with m-CPBA (1.2 equiv) at 0° for 1 hr and treated subsequently with 0.5 M aq. $NaHCO_3$ (3 ml) for 1 hr. The organic phase was concd and sepd by HPLC with elution of EtOAc–hexane (4.5:95.5) to give the ketone **18** (2.5 mg) and the epoxyformate A (5 mg) accompanied by recovery of **20** (15 mg). A: solid. Mp 78–79°. $[\alpha]_D^{25}-5°$ ($CHCl_3$; c 0.5). TLC (4.5% EtOAc in hexane) R_f 0.42. IR ν_{max}^{KBr} cm^{-1}: 1745, 1182, 971. EIMS (70 eV) m/z rel. int.: 318 $[M]^+$ (5), 303 (9), 290 (70), 275 (40), 257 (25), 247 (30), 229 (25), 123 (100). ^{1}H NMR ($CDCl_3$): δ0.76 (dd, $J=12$, 2 Hz, H-5), 0.78 (s, H-19), 0.85 (s, H-18), 0.99 (s, H-20), 1.08 (bd, $J=12$ Hz, H-9), 2.75 (bd, $J=5$ Hz, H-13), 3.20 (s, H-15), 8.10 (s, HCO_2). ^{13}C NMR ($CDCl_3$): δ17.5 (C-20), 18.1 (C-11), 18.4 (C-2, 6), 21.5 (C-19), 25.6 (C-12), 32.8 (C-7), 33.3 (C-4), 33.5 (C-18), 34.9 (C-14), 37.1 (C-13), 39.1 (C-10), 40.4 (C-1), 41.9 (C-3), 42.5 (C-8), 50.4 (C-9), 55.9 (C-5), 65.3 (C-15), 86.6 (C-16), 159.5 (HCO_2). HRMS for $C_{20}H_{30}O_3$ requires: 318.2196. Found: 318.2190.

(+)-16-*Acetylkaurane-*16,17-*diol* (**21**). Crystals from hexane. Mp 170–171°. $[\alpha]_D^{25}+62.5°$ ($CHCl_3$; c 0.9). TLC (10% EtOAc in hexane) R_f 0.40. IR ν_{max}^{KBr} cm^{-1}: 3450, 3380, 1700. EIMS (70 eV) m/z rel. int.: 348 $[M]^+$ (2), 330 (8), 314 (30), 299 (40), 271 (28), 217 (25), 177 (57), 163 (100). HRMS for $C_{22}H_{36}O_3$ requires: 348.2666. Found: 348.2658.

Acknowledgement—We are grateful to the National Science Council for financial support.

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