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DITERPENOIDS OF THE WOOD OF *AGATHIS VITIENSIS**

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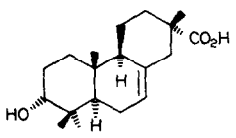
Key Word Index—*Agathis vitiensis*; Araucariaceae; Fijian kauri, diterpenoids; 3α-hydroxy-(13*S*)-16-*nor*-pimar-7-en-15-oic acid; (13*S*)-pimar-7-en-3α,15,16-triol; kaur-16-en-3α,13-diol; kauran-3α,13,16α-triol

Abstract—3α-Hydroxy-(13*S*)-16-*nor*-pimar-7-en-15-oic acid and (13*S*)-pimar-7-en-3α,15,16-triol, two new tricyclic diterpenoids, and kaur-16-en-3α,13-diol and kauran-3α,13,16α-triol, two new tetracyclic diterpenoids, have been isolated from the heartwood of the Fijian species *Agathis vitiensis*. The structures of the new compounds have been assigned from high field NMR measurements. Other constituents include agatharesinol, sitosterol, abietic acid and agathic acid.

INTRODUCTION

Agathis vitiensis Benth. & Hook f. ex Drake, the Fijian kauri, is a member of the family Araucariaceae and is a commercial native timber tree of Fiji which is now common only in the interior of the main islands. The bled resin has been examined previously and the presence of several diterpenoid acids, *viz. cis*-communic, *trans*-communic, sandaracopimaric, abietic, neoabietic, dehydroabietic, and agathic acids, has been reported [2]. Lignin chemistry of the heartwood has also been examined [3]. We describe here the isolation and structural determination of four new diterpenoids (**1**–**4**) from the heartwood. Other substances identified in the heartwood were agatharesinol [4], abietic acid, agathic acid and sitosterol.



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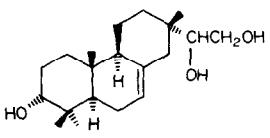

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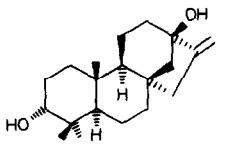

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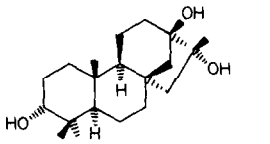

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RESULTS AND DISCUSSION

The new diterpenoids were isolated by multiple column chromatography of a methanolic extract of the heartwood. The high resolution mass spectrum of compound **1**, mp 208–210°, gave a molecular formula $C_{19}H_{30}O_3$, suggesting that it was a *nor*-diterpenoid. The IR spectrum [3420 (OH), 1695 (CO_2H), 1040 cm^{-1} (C–O)], ^1H NMR spectrum [three-proton singlets at δ 0.88, 0.95, 0.96, 1.10, and one-proton signals at 3.48 (*dd*, $J=3.0$, 3.0 Hz) and 5.44 (*dd*, $J=3.0$, 2.9 Hz)] and ^{13}C NMR spectrum (Table 1) indicated the presence of four tertiary methyl groups, a secondary hydroxyl group, a carboxyl group, and a trisubstituted double bond in the molecule. From the molecular formula compound **1** was therefore tricyclic.

The spin-correlated two-dimensional ^1H NMR spectrum (COSY) of **1** indicated the presence of the substructures **a**, **b** and **c** (Fig. 1). As the carbinyl proton (δ 3.48) in the spectrum showed weak coupling with adjacent methylene protons ($J=3.0$ Hz) and also *W*-coupling with a proton on a β-carbon atom, it was determined as equatorial, i.e. the hydroxyl group was axial. Combination of the above substructures gives a *nor*-pimarane type structure **1** in which the position of the hydroxyl group and the stereochemistry at C-13 were still unassigned. Possible positions for the hydroxyl group were C-1_{ax} or C-3_{ax}. A comparison of ^{13}C NMR chemical shifts of **1** with those of isopimaradiene (**5**) [5] (Table 1) showed that the C-18 signal of **1** exhibited a large upfield shift (δ 5.6) (Table 2) indicating that the hydroxyl group was at C-3 [6]

The stereochemistry at C-13 was assigned from the observation that the C-17 methyl protons, which occurred downfield from the other methyl protons due to their proximity to the carboxyl group, exhibited long range coupling to axial protons at δ 1.71 and 2.36 but not to the equatorial protons at δ 1.80 and 2.18. The observed

*Chemistry of Fijian Plants. Part 3. For part 2 see ref [1].

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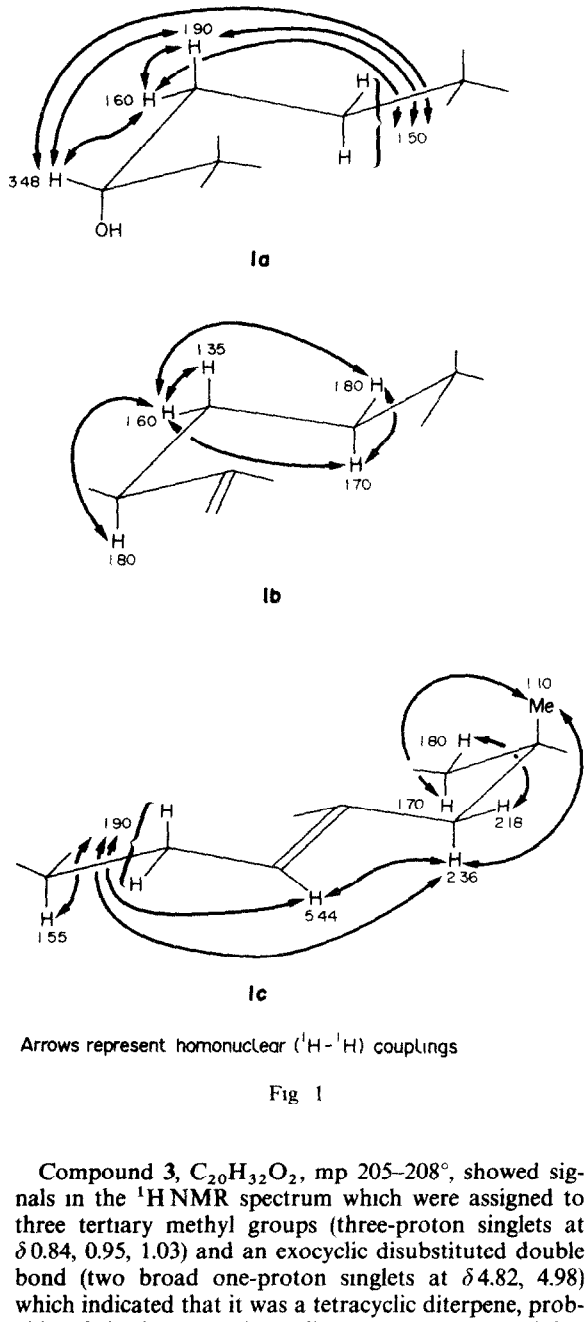
Table 1 ^{13}C NMR data of pimaranes ($CDCl_3$)

C	1	2	5	6	7
1	31 6	31 7	40 1	48 7	48 7
2	25 1	25 2	19 0	69.3	68 6
3	76.3	76 1	42.5	215 9	45.2
4	37.0	37.0*	33 1	47 4	39.1
5	43 9	44 1	50 5	52 7	46 6
6	23 1	23 1	23 5	23 8	21.8
7	123 0	122 1	121 6	120 5	35.5
8	133 8	134.9	135 2	135 9	136.5
9	51.2	51 8	52 2	51 3	50 6
10	34 9	35 0	35 6	36 1	38 9
11	19 4	19 6	20 3	20 0	18 4
12	33 1	33 1	36.4	35 5	30 2
13	42.1	37 1*	37 0	37.0	37.8
14	42 6	43 0	46 3	45.1	128.1
15	183 6	80 5	149 9	72.2	79.1
16	—	62 7	109 5	63.0	62.7
17	19 6	17 2	21.8	23 2	22.5
18	28 3	28 3	33 9	25 4	70 6
19	22 7	22 7	22.6	22 4	18 7
20	14 8	14 8	15 2	15 5	16.0

*Values may be reversed



Arrows represent homonuclear (^{1}H-^{1}H) couplings

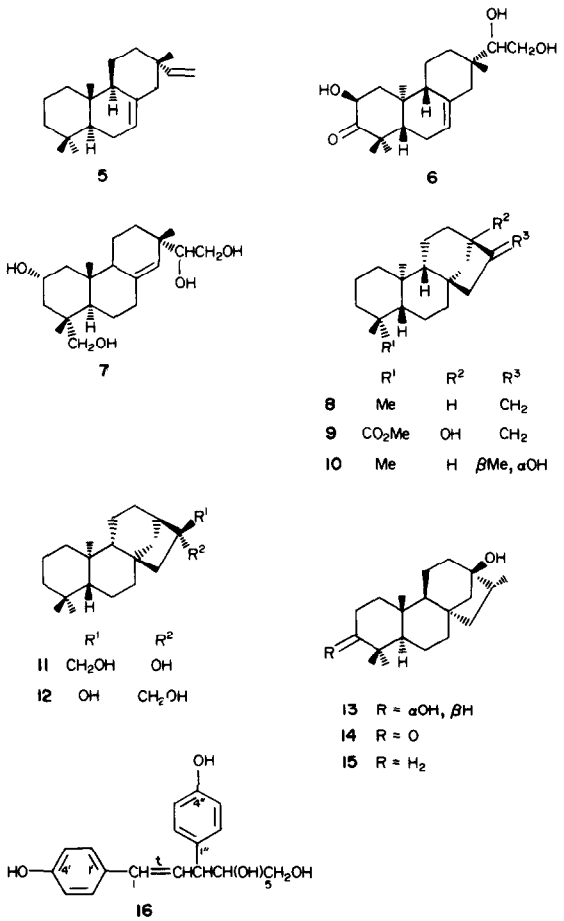
Fig 1

coupling ($^4J \approx 0.2$ Hz) is that expected [7] for a torsional angle H_AC–C–C(H_B)$_3$ of 180° and thus the C-13 methyl group is considered to be axial. Compound **1** is therefore 3α-hydroxy-(13*S*)-16-*nor*-pimar-7-en-15-oic acid.

Compound **2**, $C_{20}H_{36}O_3$, mp 170–175°, showed hydroxyl absorption (3400, 1060, 1040, 1010 cm^{-1}) in the IR spectrum but no carbonyl absorption. The ^{1}H NMR spectrum showed signals assigned to four methyl groups (three-proton singlets at δ 0.76, 0.86, 0.93, 0.95), a methine group bearing an oxygen function [a one-proton doublet of doublets at δ 3 46 (J = 3.4, 2.3 Hz)], a 1,2-dihydroxyethyl group [δ 3.34 (1H, *dd*, J = 10.8, 2.5 Hz), 3.46 (1H, *dd*, J = 10.8, 10.8 Hz), 3.75 (1H, *dd*, J = 10.8, 2.5 Hz)], and a trisubstituted double bond [δ 5.35 (1H, J = 4.1, 2.0 Hz)] The ^{1}H NMR signals were similar to those of **1** except that the signal assigned to the C-13 methyl group showed an upfield shift and new signals typical of a 1,2-dihydroxyethyl group had appeared. The ^{1}H NMR signal for the C-13 methyl group (δ 0.76) showed long range diaxial ^4J coupling to the signals at 1.89 (H-14$_{ax}$) and 1.30 (H-12$_{ax}$) and thus could be assigned an axial stereochemistry. In the ^{13}C NMR spectrum compound **2** showed similar chemical shifts to those of **1** except for the signals of C-13, C-17, and of the carbon atoms of the 1,2-dihydroxyethyl group. Consideration of the spectroscopic data leads to the structure of **2** as the 1,2-dihydroxyethyl derivative of **1**.

The stereochemistry at C-13 was confirmed as (13*S*) by comparison of the ^{13}C NMR data of **2** with that of 2β,15,16-trihydroxy-(13*S*)-*ent*-pimar-7-en-3-one (**6**) [8] which showed different chemical shifts for adjacent carbon atoms C-12 and C-14 However, chemical shifts for C-15 and C-16 were similar to those of hallol (**7**) [9] (Table 1). Data from a COSY spectrum also supported the assignment of configuration at C-13 and thus the structure of **2** was established as (13*S*)-pimar-7-ene-3α,15,16-triol

Compound **3**, $C_{20}H_{32}O_2$, mp 205–208°, showed signals in the ^{1}H NMR spectrum which were assigned to three tertiary methyl groups (three-proton singlets at δ 0.84, 0.95, 1.03) and an exocyclic disubstituted double bond (two broad one-proton singlets at δ 4.82, 4.98) which indicated that it was a tetracyclic diterpene, probably of the kaurene class. The two oxygen containing functional groups of **3** were assigned as secondary and tertiary hydroxyl groups from the IR (3400, 1100, 1060 cm^{-1}), ^{1}H NMR [one-proton triplet (J = 3 Hz) at δ 3.42], and ^{13}C NMR [δ 76.1 (*d*), 80 4 (*s*)] spectra The spin correlated two-dimensional spectrum showed the presence of the substructures **a**–**e** (Fig. 2) in which the secondary hydroxyl group in **a** was positioned at C-3 and assigned an axial configuration. The substructure **a** was only possible if the secondary hydroxyl group was at C-1 or C-3 and the latter position was favoured since this is the usually observed oxygenation site Substructure **c** was assigned to C-14 but it was not possible to assign which of the substructures **d** and **e** corresponded to C-5–C-7 or to C-9–C-12 The position of the tertiary hydroxyl group was determined by comparison of the ^{1}H and ^{13}C NMR



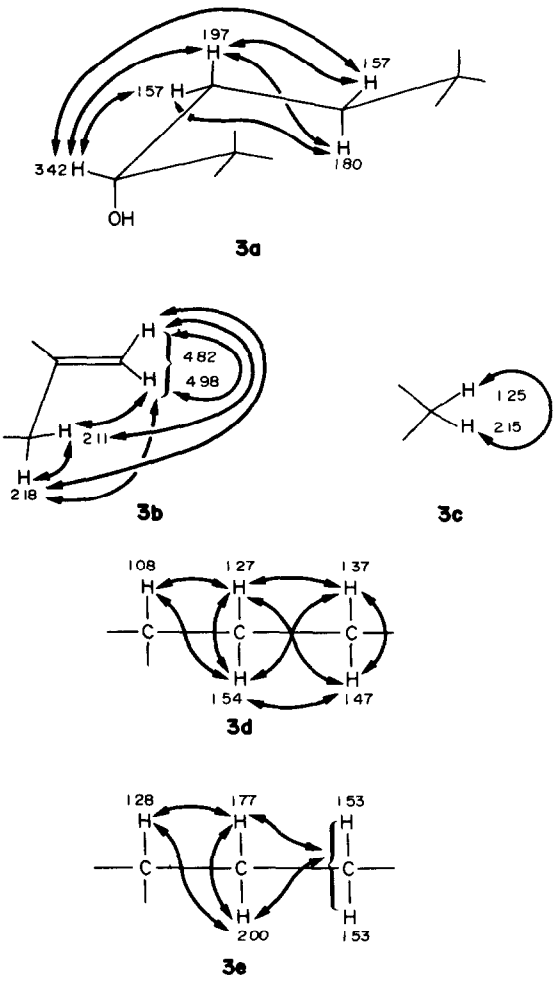


Fig. 2.

Table 2. ^{13}C NMR chemical shift differences ($CDCl_3$)

C	Δδ(1–5)	Δδ(3–8)	C	Δδ(3–8)	Δδ(4–10)
1	−8.5	−8.1	11	+1.7	+1.5
2	+6.1	+6.6	12	+7.8	+6.5
3	+33.8	+34.1	13	+36.2	+31.3
4	+3.9	+4.2	14	+7.2	+5.6
5	−6.6	−7.2	15	−1.6	−2.1
18	−5.6	−5.2	16	+0.2	+0.9

chemical shifts of **3** with those of similar compounds [10–12]. CH signals in the ^{13}C NMR spectra of such compounds are observed in the region δ 44–45 at higher field than for example C-5 or C-9 signals. In the present case the CH signals were observed at δ 48.9 and 54.3 (Table 3) showing conclusively that the C-13 position was substituted. From this data the structure **3** was determined as kaur-16-ene-3α,13-diol.

Comparison of the ^{13}C NMR data of **3** with that of *ent*-kaur-16-ene (**8**) and methyl 13-hydroxy-*ent*-kaur-16-en-18-oate (**9**) [13] (Table 3) supported the structural assignment. Differences in the chemical shifts of A- and B-rings between **3** and **8** were interpreted in terms of hydroxylation shifts caused by the presence of the 3α-hydroxyl group in **3** [6]. Chemical shifts of the C- and D-rings of **3** were similar to those of **9** which possessed the same substitution pattern in ring D.

The ^{1}H NMR spectrum of compound **4**, $C_{20}H_{34}O_3$, mp 124–126°, was similar to that of **3** except that the exocyclic double bond signals of **3** were replaced by an additional methyl singlet at δ 1.22. The chemical shift of this latter group suggested the presence of an additional tertiary hydroxyl group vicinal to a tertiary hydroxyl group at C-13. A strong peak in the mass spectrum at *m/z* 304 corresponding to the loss of water from the molecular ion was strongly indicative of a 1,2-tertiary diol. The structure of **4** was therefore assigned as kaurane-3α,13,16-triol and was confirmed from its high field NMR parameters. Chemical shifts of the A-ring carbons in the ^{13}C NMR spectrum (Table 3) were almost identical with those of **3**. Comparison of the remaining chemical shifts with those of *ent*-kauran-16α-ol (**10**) [9] also showed a close similarity (Table 3). Differences in the chemical shifts of the compounds **4** and **10** were similar to those observed between **3** and **8** (Table 2) and were due to hydroxylation at C-13. The configuration at C-16 of compound **4** is not unequivocal. However, comparison of the partial ^{13}C NMR data (Table 4) for *ent*-kauran-16α,17-diol (**11**) and *ent*-kauran-16β,17-diol (**12**) [14] suggests that the configuration of the 16-hydroxyl group of **4** is α.

Table 3 ^{13}C NMR data of kauranes ($CDCl_3$)

C	3	4	8	9	10
1	33 2	33 2	41 3	40 6	42 0
2	25 3	25 2	18.7	19.1	18 6
3	76 1	76.0	42 0	38.0	42 0
4	37.5	37 5	33 3	43.7	33 2
5	48 9	48 8	56 1	53 8	56 2
6	20.1	19 9	20 3	21.8	20.4
7	39 4	41 9	40 4	39.2	40 3
8	41.6	41 1	44 2	41.6	45 3
9	54 3	55 2	56 1	56.9	56 8
10	38 9	38 9	39 3	39 2	39 3
11	19 8	19 5	18.1	20 4	18 0
12	41.1	33 4	33.3	41 3	26.9
13	80.4	80 3	44 2	80 1	49 0
14	47 1	43.3	39 9	46 9	37 7
15	47 6	55 9	49 2	47.4	58.0
16	156.2	80.3	156 0	155 9	79.4
17	102 9	21 2	102 8	102.9	24.5
18	28 5	28 4	33.7	28 6	33.5
19	22 0	22 0	21 7	177.9	21.6
20	17 3	17 5	17 6	15 2	18.0

The absolute configuration of **3** and thus of compounds **1**, **2** and **4**, was determined by sequential hydrogenation of **3** to **13**, oxidation to **14** and Huang–Minlon reduction to afford the enantiomer **15** of (16*S*)-kauran-13-ol, of established configurations [12, 15]

EXPERIMENTAL

Mps. uncorr EIMS were obtained on an A.E.I. MS9 instrument interfaced with an A.E.I. data system DS30. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ using TMS as int standard

Leaves of the plant, collected in the Wailoku area near Suva, were matched with voucher specimens of *Agathis vitiensis* lodged in the Fiji National Herbarium, University of the South Pacific

Isolation of the diterpenoids The heartwood of *Agathis vitiensis* (950 g) was extracted (Soxhlet) with MeOH for 22 hr. The concentrated extract (7 7 g) was chromatographed on an Al_2O_3 column using *n*-hexane, Et_2O, EtOAc, and MeOH and their mixtures as eluants to yield long-chain esters (114 mg), mp 98–99°, and fractions containing **3** (85 mg), **4** (12 mg), sitosterol (25 mg), **2** (27 mg), **1** (20 mg) and agatharesinol (20 mg). Where necessary fractions containing diterpenoids were collected and rechromatographed on silica gel using C_6H_6 and $CHCl_3$ as eluants to yield pure compounds

3α-Hydroxy-(13S)-16-nor-pimar-7-en-15-oic acid (**1**) Needles (from C_6H_6), mp 208–210°, $[\alpha]_D^{18}$ −10° ($CHCl_3$. *c* 1.1), IR ν_{max}^{KBr} cm^{-1}: 3420, 2620, 1695, 1465, 1240, 1040, 880; ^{1}H NMR δ 0 88 (3H, *s*, 10-Me), 0.95 (3H, *s*, 4 ax-Me), 0 96 (3H, *s*, 4 eq-Me), 1 10 (3H, *s*, 13-Me), 1 35 (1H, *qd*, $J_{11ax,11eq}$ = 13 2 Hz, $J_{11ax,9}$ = 13 2, $J_{11ax,12ax}$ = 13 2, $J_{11ax,12eq}$ = 4.4, H-11$_{eq}$), 1 54 (1H, *m*, $J_{1eq,1ax}$ = 13 1 Hz, $J_{1eq,2eq}$ = 3.4, $J_{1eq,2ax}$ = 4 5, H-1$_{eq}$), 1 55 (1H, *d*, $J_{5,6ax}$ = 11.8 Hz, H-5$_{ax}$), 1.55 (1H, *dd*, $J_{1ax,1eq}$ = 13.1 Hz, $J_{1ax,2eq}$ = 3 4 H-1$_{ax}$), 1 60 (1H, *m*, $J_{2eq,2ax}$ = 14 2 Hz, $J_{2eq,1ax}$ = 3 4 Hz, $J_{2eq,1eq}$ = 3.4 Hz, $J_{2eq,3}$ = 2 2 Hz, H-2$_{eq}$), 1 60 (1H, *dd*, $J_{11eq,11ax}$ = 13 2 Hz, $J_{11eq,12ax}$ = 3 8, H-11$_{eq}$), 1 71 (1H, *m*, $J_{12ax,12eq}$ = 13 2 Hz, $J_{12ax,11ax}$ = 13 2 Hz, $J_{12ax,11eq}$ = 3.8, H-12$_{ax}$), 1 80 (1H, *d*, $J_{9\ 11ax}$ = 13 2 Hz, H-9), 1 80 (1H, *m*, $J_{11ax,11eq}$ = 13.2 Hz, $J_{11ax,9}$ = 13 2, $J_{11ax,12ax}$ = 13 2, $J_{11ax,12eq}$ = 4.4, H-11$_{ax}$), 1.90 (1H, *m*, $J_{2ax,2eq}$ = 14 2 Hz, $J_{2ax,1eq}$ = 4 5, $J_{2ax,3}$ = 2 2, H-2$_{ax}$), 1.90 (1H, *d*, $J_{6eq,7}$ = 2.9 Hz, H-6$_{eq}$), 1 90 (1H, *dd*, $J_{6ax,5}$ = 11 8 Hz, $J_{6ax,7}$ = 3.0, H-6$_{ax}$), 2.18 (1H, *dd*, $J_{14eq,14ax}$ = 14.0 Hz, $J_{14eq,12eq}$ = 2.5, H-14$_{eq}$), 2 36 (1H, *br d*, $J_{14ax,14eq}$ = 14 0 Hz, H-14$_{ax}$), 3 48 (1H, *dd*, $J_{3eq,2ax}$ = 3 0 Hz, $J_{3eq,2eq}$ = 3 0, H-3$_{eq}$), 5 44 (1H, *dd*, $J_{7,6ax}$ = 3 0 Hz, $J_{7,6eq}$ = 2 9, H-7), ^{13}C NMR see Table 1; MS *m/z* 306 [M]$^+$, 291 [M − Me]$^+$, 288 [M − H_2O]$^+$, 273 (Found M$^+$ 306.2198. $C_{19}H_{30}O_3$ requires M 306 2195).

(13S)-Pimar-7-ene-3α,15,16-triol (**2**) Needles (from EtOAc), mp 170–175°, $[\alpha]_D^{17}$ −22° (MeOH, *c* 1.0); IR ν_{max}^{KBr} cm^{-1} 3400, 1450, 1375, 1060, 1040, 1010, 870, ^{1}H NMR δ 0.76 (3H, *s*, 13-Me), 0 86 (3H, *s*, 10-Me), 0.95 (3H, *s*, 4$_{ax}$-Me), 0 96 (3H, *s*, 4$_{ax}$-Me), 1.30 (1H, *dd*, $J_{12ax,12eq}$ = 9.2 Hz, $J_{12ax,11ax}$ = 9 2, H-12$_{ax}$), 1 32 (1H, *m*, $J_{11ax,11eq}$ = 11.2 Hz, $J_{11ax,12ax}$ = 9 2, $J_{11ax\ 12eq}$ = 3.0, H-11$_{ax}$), 1.42 (1H, *m*, $J_{12eq,12ax}$ = 9 2 Hz, $J_{12eq,11ax}$ = 3 0, $J_{12eq,11eq}$ = 3.0, H-12$_{eq}$), 1.52 (1H, *d*, $J_{1eq,2eq}$ = 3.4 Hz, H-1$_{eq}$), 1 52 (1H, *d*, $J_{1ax,2eq}$ = 3 4 Hz, H-1$_{ax}$), 1 52 (1H, *s*, H-5$_{ax}$), 1 55 (1H, *dd*, $J_{11eq,11ax}$ = 11 2 Hz, $J_{11eq,12eq}$ = 3.0, H-11$_{eq}$), 1 59 (1H, *m*, $J_{2eq,2ax}$ = 14 4 Hz, $J_{2eq,1ax}$ = 3.4, $J_{2eq,1eq}$ = 3.4, $J_{2eq,3eq}$ = 3 4, H-2$_{eq}$), 1 72 (1H, *s*, H-9), 1 84 (1H, *d*, $J_{6eq,7}$ = 2 0 Hz, H-6$_{eq}$), 1 89 (1H, *d*, $J_{14ax,14eq}$ = 14 0, H-14$_{ax}$), 1 90 (1H, *dd*, $J_{2ax,3eq}$ = 2.3, H-2$_{ax}$), 2 06 (1H, *dd*, $J_{14eq,14ax}$ = 14 0 Hz, $J_{14eq,12eq}$ = 2 6, H-14$_{eq}$), 3 46 (1H, *dd*, $J_{3eq,2eq}$ = 3 4 Hz, $J_{3eq,2ax}$ = 2 3, H-3$_{eq}$), 3 34 (1H, *dd*, $J_{16ax,15ax}$ = 10.8 Hz, $J_{16a,16b}$ = 2 5, H-16a), 3 46 (1H, *dd*, $J_{15eq,16a}$ = 10 8 Hz, $J_{15eq,16b}$ = 10.8, H-15$_{eq}$), 3 75 (1H, *dd*, $J_{16b,15ax}$ = 10 8 Hz, $J_{16a,16b}$ = 2 5, H-16b), 5.35 (1H, *dd*, $J_{7,6ax}$ = 4.1 Hz, $J_{7,6eq}$ = 2.0, H-7); ^{13}C NMR see Table 1, MS *m/z* 322 [M]$^+$, 307 [M − Me]$^+$, 304 [M − H_2O]$^+$, 289, 261 (Found M$^+$ 322 2508. $C_{20}H_{34}O_3$ requires M 322 2508).

Kaur-16-ene-3α,13-diol (**3**). Needles (from EtOAc), mp 205–208°; $[\alpha]_D^{17}$ +28° (MeOH, *c* 1.0), IR ν_{max}^{KBr} cm^{-1} 3400, 1100, 1080, 1060, 970, 890, 880, ^{1}H NMR δ 0 84 (3H, *s*, 10-Me), 0 95 (3H, *s*, 4$_{ax}$-Me), 1 03 (3H, *s*, 4$_{eq}$-Me), 1 08 (1H, *br d*, *J* = 7 Hz, H-5 or 9), 1.25 (1H, *m*, H-14), 1 27 (1H, *m*, H-6 or 11), 1 28 (1H, *m*, H-5 or 9), 1 37 (1H, *m*, H-7 or 12), 1 47 (1H, *m*, H-7 or 12), 1 53 (2H, *m*, H_2-7 or 12), 1 54 (1H, *m*, H-6 or 11), 1 57 (1H, *m*, H-2$_{eq}$), 1.57 (1H, *m*, H-1$_{eq}$), 1 77 (1H, *m*, H-6 or 11), 1 80 (1H, *m*, H-1$_{ax}$), 1 97 (1H, *m*, H-2$_{ax}$), 2 00 (1H, *m*, H-6 or 11), 2 11 (1H, *m*, H-15), 2.15 (1H, *m*, H-14), 2 18 (1H, *m*, H-15), 3 42 (1H, *m*, H-3$_{eq}$), 4 82 (1H, *br s*, H-17), 4.98 (1H, *br s*, H-17); ^{13}C NMR see Table 2, MS *m/z* 304 [M]$^+$, 286 [M − H_2O]$^+$, 271 [M − H_2O − Me]$^+$, 268 [M − 2H_2O]$^+$, 253 [M − 2H_2O − Me]$^+$. (Found M$^+$ 304.2406 $C_{20}H_{32}O_2$ requires M 304 2403).

Kaurane-3α,13,16α-triol (**4**). Needles (from EtOAc), mp 124–126°, IR ν_{max}^{KBr} cm^{-1} 3350, 1160, 1060, 975; ^{1}H NMR δ 0 83 (3H, *s*, 4$_{eq}$-Me), 0.93 (3H, *s*, 4$_{ax}$-Me), 1.01 (1H, *s*, H-9), 1.02 (3H, *s*, 10-Me), 1 21 (3H, *s*, 16-Me), 1 23 (1H, *m*, $J_{1eq,1ax}$ = 14.2 Hz, $J_{1eq,2ax}$ = 4 0, $J_{1eq,2eq}$ = 4 0, H-1$_{eq}$), 1.24 (1H, *s*, H-11$_{ax}$), 1 25 (1H, *d*, $J_{12ax,11eq}$ = 6.7 Hz, H-12$_{ax}$), 1 27 (1H, *d*, $J_{5ax\ 6ax}$ = 12.1 Hz, H-5$_{ax}$), 1.33 (1H, *m*, $J_{6ax,6eq}$ = 12.1 Hz, $J_{6ax,7ax}$ = 12.1, $J_{6ax,5ax}$ = 12 1, $J_{6ax,7eq}$ = 3 8, H-6$_{ax}$), 1.47 (1H, *d*, $J_{6eq,6ax}$ = 12 1 Hz, H-6$_{eq}$), 1.48 (1H, *d*, $J_{7eq,6ax}$ = 3 8 Hz, H-7$_{eq}$), 1 52 (1H, *d*, $J_{15ax,15eq}$ = 14 6 Hz, H-15$_{ax}$), 1 54 (1H, *dd*, $J_{1ax,1eq}$ = 14 2 Hz, $J_{1ax,2ax}$ = 13.9, H-1$_{ax}$), 1 57 (1H, *m*, $J_{2eq,2ax}$ = 13.9 Hz, $J_{2eq,1eq}$ = 4 0,

Table 4. Partial ^{13}C NMR data for compounds **4**, **11** and **12**

C	4	11	12
13	80.3	45 5	52.6
15	55.9	53 4	56.1
16	80 3	81 6	79 7
17	21 2	66 2	69 1

$J_{2eq,3eq}$=2.7, H-2_{eq}), 1.58 (1H, *d*, $J_{7ax,6ax}$=12.1 Hz, H-7_{ax}), 1.58 (1H, *d*, $J_{11eq,12ax}$=6.7 Hz, H-11_{eq}), 1.62 (1H, *m*, $J_{12eq,12ax}$ =9.2 Hz, $J_{12eq,11ax}$=3 0, $J_{12eq,11eq}$=3.0, $J_{12eq,14eq}$=2.6, H-12_{eq}), 1.62 (1H, *d*, $J_{14ax,14eq}$=10.8 Hz, H-14_{ax}), 1.65 (1H, *d*, $J_{15eq,15ax}$=14 6 Hz, H-15_{eq}), 1.91 (1H, *d*, $J_{14eq,14ax}$=10.8 Hz, H-14_{eq}), 1.97 (1H, *m*, $J_{2ax,2eq}$=13.9 Hz, $J_{2ax,1ax}$=13.9, $J_{2ax,1eq}$ =4.0, $J_{2ax,3eq}$=2.7, H-2_{ax}), 3.35 (1H, *dd*, $J_{3eq,2ax}$=2.7 Hz, $J_{3eq,2eq}$=2.7, H-3_{eq}); ^{13}C NMR see Table 3; MS *m/z* 322 $[M]^+$, 304 $[M-H_2O]^+$, 286 $[M-2H_2O]^+$, 271 $[M-2H_2O-Me]^+$, 263 (Found: M^+ 322.2504 $C_{20}H_{34}O_3$ requires M 322.2508).

Sitosterol. Flakes (from MeOH), mp 130–134°; IR ν_{max}^{KBr} cm^{-1}: 3400, 2960, 1465, 1360, 1040, MS *m/z*: 414 $[M]^+$, 399, 396, 381. It was identical with an authentic sample by direct comparison (IR, MS, TLC, ^{1}H NMR, ^{13}C NMR). (Found: M^+ 414.3862. Calc. for $C_{29}H_{50}O$ M 414.3861).

Agatharesinol (**16**). Pale amber resin, IR ν_{max}^{film} cm^{-1} 1610, 1515, 1450, 1240, 1175, 1020, 970, 830; ^{1}H NMR: δ 3.23 (1H, *m*, $J_{5b,5a}$=5.1 Hz, $J_{5b,5\text{-}OH}$=5.5, $J_{5b,4}$=4.8, H-5b), 3.32 (1H, *m*, $J_{5a,5b}$=5.1 Hz, $J_{5a,5\text{-}OH}$=5.5, $J_{5a,4}$=5.1, H-5a), 3.38 (1H, *d*, $J_{3,4}$ =6 1 Hz, H-3), 3.74 (1H, *m*, $J_{4,3}$=6.1 Hz, $J_{4,4\text{-}OH}$=5.1, $J_{4,5a}$ =5.1, $J_{4,5b}$=4 8, H-4), 6.22 (1H, *d*, $J_{1,2}$=15.8 Hz, H-1), 6 31 (1H, *dd*, $J_{2,1}$=15.8 Hz, $J_{2,3}$=8.1, H-2), 6 66 (2H, *d*, $J_{2'',3''}$=8.5 Hz, H-3'', 5''), 6.69 (2H, *d*, $J_{2',3'}$=8.6 Hz, H-3',5'), 7.09 (2H, *d*, $J_{2'',3''}$ =8.5 Hz, H-2'',6''), 7.19 (2H, *d*, $J_{2',3'}$=8 6 Hz, H-2'6'), 9 12 (1H, *s*, OH), 9.41 (1H, *s*, OH); ^{13}C NMR: δ 51.0 (C-3), 64.0 (C-5), 74.0 (C-4), 114.6 (C-3'',5''), 115.2 (C-3',5'), 127.0 (C-2',6'), 128.3 (C-1'), 128.8 (C-2), 129.1 (C-1), 129 5 (C-2'',6''), 132.2 (C-1''), 155.3 (C-4'), 156.5 (C-4'') MS *m/z*: 225 $[M-CH(OH)CH_2OH]$.

Diterpene acids A portion of the MeOH extract was extracted with Me_2CO–*n*-hexane and filtered to remove polymeric material. Removal of solvent from the soln gave a gum which was treated with an ethereal soln of CH_2N_2 and examined by GC (OV-17, column temp 248°, injection and detector temp 275°, flow rate N_2 at 50 ml/min, H_2 at 20 ml/min; OV-101, column temp 220°, injector and detector temp 255°, flow rate N_2 40 ml/min, H_2 20 ml/min) Methyl abietate and methyl agathate were identified by comparison of R_t's with those of authentic samples

Hydrogenation of compound **3**. A soln of the diol **3** (23 mg) in EtOH (10 ml) was hydrogenated at room temp. using 20% Pd/C (70 mg) as a catalyst. The catalyst was filtrated off and the filtrate evapd to give a residue which after recrystallization from EtOAc yielded (*16R*)-*kaurane*-3α,13-*diol* (**13**) (16 mg), needles, mp 203–204°. $[\alpha]_D^{18}$ +21° (MeOH; *c* 1.0); IR ν_{max}^{KBr} cm^{-1}: 3420, 2950, 1450, 1325, 1080, 1060, 1018, 970; ^{1}H NMR. δ 0.83 (3H, *s*, 4_{eq}-Me), 0.94 (3H, *s*, 4_{ax}-Me), 0 97 (3H, *d*, *J*=5.7 Hz, 16-Me), 0.97 (1H, *dd*, $J_{9,11ax}$=14 Hz, $J_{9,11eq}$=2 2, H-9), 1.02 (3H, *s*, 10-Me), 1 28 (1H, *d*, $J_{5,6eq}$=3.0 Hz), 1.95 (1H, *m*, H-2_{ax}), 2.00 (1H, *dd*, $J_{14ax,14eq}$=10.6 Hz, $J_{14eq,12eq}$=2 1, H-14_{eq}), 3.41 (1H, *d*, *J* =2 4 Hz, H-3); MS *m/z*: 306 $[M]^+$, 288 $[M-H_2O]^+$, 273 $[M-H_2O-Me]^+$, 263. (Found: M^+ 306.2554, $C_{20}H_{34}O_2$ requires M 306.2559).

13-*Hydroxy*-(16*R*)-*kauran*-3-*one* (**14**). A soln of the diol (**13**) (12 mg) in pyridine (1 ml) was added to a soln of CrO_3 (0.10 g) in pyridine (1 ml), and the mixture was allowed to stand at room temp for 5 hr. The mixture was poured into H_2O, and the product extracted with Et_2O. The extract was washed with 5% HCl soln and H_2O, dried (Na_2SO_4) and concd to yield 13-hydroxy-(16*R*)-kauran-3-one, (10 mg) colourless oil, $[\alpha]_D^{18}$ +67° ($CHCl_3$, *c* 1.0). IR ν_{max}^{neat} cm^{-1}: 3370, 2950, 1695, 1450, 1355, 1120, 1070, 1013, 950, 750; ^{1}H NMR: δ 0.95 (1H, *m*, H-9), 0 99 (3H, *d*, *J* =6.7 Hz, 16-Me), 1.02 (3H, *s*, 10-Me), 1.06 (3H, s, 4_{ax}-Me), 1 07 (3H, *s*, 4_{eq}-Me), 1.97 (1H, *dd*, $J_{14eq,14ax}$=10.8 Hz, $J_{14eq,12eq}$=2.2, H-14_{eq}), 2.00 (1H, *m*, $J_{1eq,1ax}$=13.2 Hz, $J_{1eq,2ax}$=7.0, $J_{1eq,2eq}$ =5.3, H-1_{eq}), 2.47 (2H, *m*, H-2_{ax}, H-2_{eq}).

(*16R*)-*Kauran*-13-*ol* (**15**). A mixture of the ketone **14** (8 mg), 100% hydrazine hydrate (0.2 ml), KOH (120 mg), EtOH (2 ml) and diethylene glycol (2 ml) was heated under reflux for 1 5 hr. The EtOH, water and excess of hydrazine were removed by distillation, the temp of the soln was raised to 200°, and the refluxing was continued for 3.5 hr. The cooled soln was diluted with H_2O and extracted with Et_2O. The extract was washed with H_2O, dried (Na_2SO_4) and concd. The residue crystallized from *n*-hexane to give (16R)-*kauran*-13-*ol* (5 mg) needles, mp 136–140°, $[\alpha]_D^{19}$ +22° ($CHCl_3$, *c*=0.6) (lit. [15] for (16*S*)-enantiomer, mp 135–142°, subliming to give mp 147–148°, $[\alpha]_D^{20}$ −24.4° ± 1.4°). IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 2860, 1455, 1370, 1355, 1250, 1080, 1020; ^{1}H NMR· δ 0.79 (3H, *s*, 4_{ax}-Me), 0.84 (3H, *s*, 4_{eq}-Me), 0.97 (3H, *d*, *J* = 6.7 Hz, 16-Me), 0.99 (3H, *s*, 10-Me), 1 99 (1H, *dd*, $J_{14eq,14ax}$=10.7 Hz, $J_{14eq,12eq}$=1 7, H-14_{eq}); MS *m/z* 290 $[M]^+$, 275 $[M-Me]^+$, 257 $[M-Me-H_2O]^+$, 247 (Found: M^+ 290.2609. Calc. for $C_{20}H_{34}O$ 290.2610).

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