Terpenoids. Part II.[1] Some Ring D Derivatives of 13β-Kaurane

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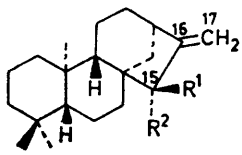
Metal hydride reduction of 13β-kaur-16-en-15-one afforded the 1,4-reduction product, (16*R*)-13β-kauran-15β-ol but none of the expected 1,2-reduction product, 13β-kaur-16-en-15β-ol; in concentrated solution, a dimer (19) was a minor product. Treatment of 13β-kaur-16-en-15α-ol with aqueous acid in methanol yielded a dimeric ether (20) in addition to 17-hydroxy- and 17-methoxy-13β-kaur-15-ene. The four isomers of 13β-kauran-15-ol were prepared; their m.p.s and optical rotations differed from those reported previously.

A previously noted division of *Cryptomeria japonica* into producers of *ent*-kaurene or 13β-kaurene has been confirmed for fifteen additional varieties.

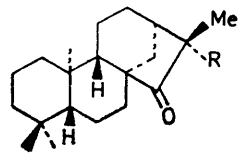
In Part I [1] a twist envelope conformation for ring D in the *ent*-kaur-16-en-15-ols (1) and (2) was suggested on the basis of the J values for the allylic coupling between the 15- and 17-protons. A similar conformation in the 16-carbonium ion, obtained by protonation of these alcohols, was also proposed [1] to explain the difference in the rate of 15,16-hydride shift in the acid-catalysed rearrangement of the two alcohols. The isomer (1) and

[1] Part I, M. F. Barnes and J. MacMillan, *J. Chem. Soc.* (*C*), 1967, 361.

its 16-deuterio-analogue (3) readily yielded the (16*R*)-ketones (4) and (5), respectively; under the same conditions, the isomer (2) was stable. The present work sought to extend this study to the 13β-kaurane (phyllocladane) series.



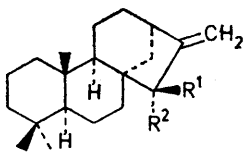
(1) R^1 = OH, R^2 = H
(2) R^1 = H, R^2 = OH
(3) R^1 = OH, R^2 = ^{2}H



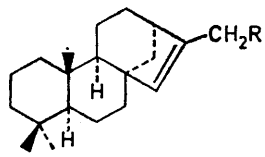
(4) R = H
(5) R = ^{2}H

A source of 13β-kaurene (6) was required. Appleton *et al.*[2] have examined ten varieties of *Cryptomeria japonica* and found that two contained 13β-kaurene. The other eight varieties contained *ent*-kaurene but none contained both diterpene hydrocarbons. In an independent study we examined the leaves of fifteen varieties of *C. japonica* and obtained similar results. G.l.c. analyses of light petroleum extracts showed that three varieties contained 13β-kaurene but no *ent*-kaurene. The remaining twelve varieties contained *ent*-kaurene but no 13β-kaurene. The identity of the diterpene hydrocarbons was confirmed by isolation. *C. japonica* clearly exists in two distinct chemotaxonomic groups which must contain independent cyclase systems for geranylgeranyl pyrophosphate. Since *ent*-kaurene is an established biosynthetic intermediate for the gibberellin group of plant hormones, the acids from the *ent*-kaurene and 13β-kaurene varieties of *C. japonica* were examined for gibberellin-like biological activity. Both showed weak but equal activity in the lettuce hypocotyl bio-assay. However in an extensive g.l.c.–mass spectral examination of derivatives of the acids, no gibberellins could be identified.[3] Nor could the growth habit of the fifteen varieties of *C. japonica* be correlated with the presence or absence of *ent*-kaurene.

Soxhlet extraction of *C. japonica* var. *pendula* on a large scale gave a mixture of 13β-kaur-16-ene (6) and



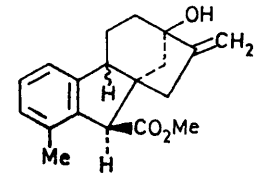
(6) R^1 = R^2 = H
(7) R^1 = H, R^2 = OH
(8) R^1R^2 = O
(9) R^1 = OH, R^2 = H



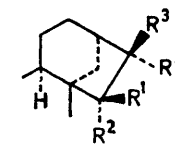
(10) R = H
(11) R = OH
(12) R = OMe

13β-kaur-15-ene (10) in yields of 0·5 and 0·2%, respectively. The isomer (10) was absent in light petroleum extracts made at room temperature. Isomerisation of the 16-ene (6) to the 15-ene (10) by heating the crude cold extract of *C. japonica* has been previously noted[4] and may be caused by the presence of abietic acid, which is known[5] to induce the analogous isomerisation of *ent*-kaur-16-ene to *ent*-kaur-15-ene.

13β-Kaur-16-ene (6) was isomerised by iodine in boiling benzene to an equilibrium mixture containing 98% of 13β-kaur-15-ene (10). Similar equilibration[1] of 2nd kaur-15-ene and -16-ene yielded a mixture containing 75% of the endocyclic double bond isomer. The higher proportion of the 15-ene in the 13β-kaurenes shows the greater preference for sp^2-hybridisation at C-15 due to the relief of steric compression with the 10-methyl group. Sensitised photo-oxygenation of 13β-kaur-16-ene (6) gave the known[6] 15-en-17-ol (11) in 40% yield. Similarly 13β-kaur-15-ene (10) was converted in over 85% yield into the known[6,7] 16-en-15α-ol (7). The stereochemistry of the 15α-ol (7) was deduced from the reasonable preference for reaction on the less hindered α-face and was confirmed by n.m.r. studies (to be described in a later paper). Barnes *et al.*[8] have suggested that the



(13) 9β*H*
(14) 9α*H*



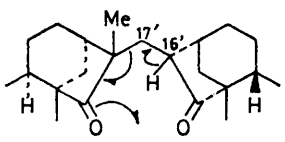
	R^1	R^2	R^3	R^4
(15)	OH	H	Me	H
(16)	H	OH	Me	H
(17)	OH	H	H	Me
(18)	H	OH	H	Me

failure to photo-oxygenate methyl epiallogibberate (13), in contrast to the 9α*H*-epimer (14), might indicate different conformations of ring D in the two epimers as a result of the differing C-9 stereochemistries. However the yield (40%) of 13β-kaur-15-en-17-ol (11) from the photo-oxygenation of 13β-kaur-16-ene (6) is only slightly lower than that (55%)[1] of *ent*-kaur-15-en-17-ol from *ent*-kaur-16-ene and indicates little if any effect of the stereochemistry at C-9 on the ease of photo-oxygenation of these diterpenes.

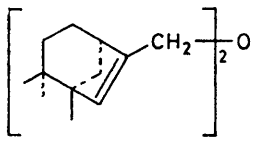
Reduction of 13β-kaur-16-en-15-one (8), obtained by oxidation of the 16-en-15α-ol (7), with sodium borohydride or lithium aluminium hydride failed to yield 13β-kaur-16-en-15β-ol (9). The fully saturated alcohol, the (16*R*)-15β-ol (15), was obtained even under very mild conditions. This result contrasts with the smooth reduction of *ent*-kaur-16-en-15-one to the corresponding 16-en-15β-ol.[1] This difference between the two series is probably due to the steric compression in the transition state for 1,2-hydride addition between the developing 15β-hydroxy-group and the 10β-methyl function,

[2] R. A. Appleton, R. McCrindle, and K. H. Overton, *Phytochemistry*, 1968, **7**, 135.
[3] P. N. Strong, B.Sc. Thesis, University of Bristol, 1969.
[4] R. McCrindle, personal communication.
[5] S. Nagahama, *Bull. Chem. Soc. Japan*, 1963, **36**, 753.
[6] L. H. Briggs, B. F. Cain, R. C. Cambie, and B. R. Davis, *J. Chem. Soc.*, 1962, 1840.
[7] L. H. Briggs, R. C. Cambie, and P. S. Rutledge, *J. Chem. Soc.*, 1963, 5374.
[8] M. F. Barnes, R. C. Durley, and J. MacMillan, *J. Chem. Soc.* (*C*), 1970, 1341.

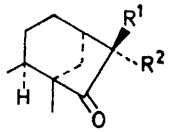
allowing 1,4-addition to predominate. 1,4-Reduction of enones with sodium borohydride is rare.[9] Reduction of the enone (8) with lithium aluminium hydride in concentrated solution gave small amounts of the dimer (19), whose structure was deduced from the mass (M^+ 574), i.r. ($\nu_{C=O}$ 1730 cm^{-1}, five-membered ring ketone), and n.m.r. spectra. The last showed five methyl singlets and a one-proton multiplet (τ 6·45) which was assigned to the 16′-proton since the signal collapsed on irradiation at τ 8·43, the expected chemical shift for the 17′-protons. This low chemical shift for the 16′-proton may be caused by deshielding from both carbonyl groups. Fragmentation in the mass spectrum is also in accord with structure (19). McLafferty rearrangement of the parent ion [see arrows in (19)] gives the base peak at *m/e* 288. The formation of the dimer (19) can be rationalised in terms of hydride attack at C-17, followed by a Michael-type addition of the resulting anion to the enone (8).



(19)



(20)



(21) R^1 = Me, R^2 = H
(22) R^1 = H, R^2 = Me

The failure to prepare 13β-kaur-16-en-15β-ol (9) precluded a comparison of the rates of acid-catalysed 15,16-hydride shift in the two 15-epimeric allylic alcohols. The available 15α-ol (7) was much less stable to acid than its counterpart in the *ent*-kaurane series.[1] However there was no evidence for 15,16-hydride shift since neither (16*R*)- nor (16*S*)-13β-kauran-15-one [(21) and (22)] was detected. The products depended upon the reaction conditions. At 0° in methanol containing concentrated hydrochloric acid, the major product was a non-polar dimer which was decomposed by chromatography or molecular distillation to a mixture of starting material (7) and 13β-kaur-15-en-17-ol (11). From this evidence and the spectroscopic properties of a sample containing 20% of the alcohols (7) and (11) as the only impurities, the structure (20) was assigned to the dimer. The n.m.r. spectrum contained a vinylic proton signal at τ 4·31, showing allylic coupling to methyleneoxy-protons at τ 5·94 and the presence of a 15,16-double bond was indicated by the shielded 10-methyl singlet at τ 9·29.[10] At 60°, the major product of the reaction of the 15α-ol (7) and methanolic hydrochloric acid was 17-methoxy-13β-kaur-15-ene (12) whose structure was assigned on the basis of spectroscopic data, listed in the Experimental section. All three products (11), (12), and (20) are clearly derived by reactions of the intermediate allylic cation, with water, methanol, and the 16-en-15α-ol (7), respectively.

The four isomers of 13β-kauran-15-ol were prepared in the following way for n.m.r. studies (to be reported in a subsequent paper). The (16*R*)- and (16*S*)-kauran-15α-ols [(16) and (18), respectively] were obtained as a separable mixture by hydrogenation of the 16-en-15α-ol (7), the 16*R*-isomer predominating as expected for preferential α-hydrogenation. The isomers were characterised by their separate oxidation to the known [7,11,12] (16*R*)- and (16*S*)-13β-kauran-15-ones [(21) and (22), respectively]. Thus prepared, these ketones were shown to contain less than 1% of each other by g.l.c. The (16*R*)- and (16*S*)-13β-kauran-15β-ols [(15) and (17), respectively] were prepared from 13β-kaur-16-en-15α-ol (7) by the following route. Oxidation gave the 16-en-15-one (8), which underwent hydrogenation from the α-face exclusively to provide the (16*R*)-15-one (21). Epimerisation of the (16*R*)-ketone (21) with aqueous alkali gave an equilibrium mixture of the (16*R*)- and (16*S*)-ketones [(21) and (22), respectively] containing 60% of the 16*S*-epimer (22). This xture could not be separated by crystallisation or adsorption chromatography and was directly reduced with lithium aluminium hydride to a mixture of (16*R*)- and (16*S*)-13β-kauran-15β-ols [(15) and (17), respectively], which were readily separated by preparative t.l.c. and characterised by their separate oxidation to the (16*R*)- and (16*S*)-ketones (21) and (22).

The four epimeric alcohols (15)—(18) have been described by Turner *et al.*[12] and three of them (16)—(18) by Briggs *et al.*[7] The m.p. and optical rotation values obtained in the present work differ from those quoted by the previous workers (see Table). Our alcohols were shown to be greater than 99% pure by g.l.c. and the assigned stereochemistries were confirmed by n.m.r. studies (to be reported).

Reported m.p.s and optical rotations (chloroform solutions) for the isomers of 13β-kauran-15-ols

Isomer		Present work	Turner *et al.*[12]	Briggs *et al.*[7]
(15)	M.p. (°C)	104—105	104—105	
	$[\alpha]_D$ (°)	−9	+13	
(16)	M.p.	105—109	114·5—115·3	Oil
	$[\alpha]_D$	+11	−6·6	
(17)	M.p.	103—104	94—95	157·5—158
	$[\alpha]_D$	+21		−3
(18)	M.p.	Oil	81—82	111—115·5
	$[\alpha]_D$		−35	−12

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Silica gel M.F.C. (Hopkin and Williams)

[9] H. O. House, ' Modern Synthetic Methods,' Benjamin, New York, 1965, p. 40.
[10] Y. Kitahara and A. Yoshikoshi, *Bull. Chem. Soc. Japan*, 1964, **37**, 890.
[11] R. Henderson and R. Hodges, *Tetrahedron*, 1960, **11**, 226.
[12] R. B. Turner, K. H. Ganshirt, P. E. Shaw, and J. D. Tauber, *J. Amer. Chem. Soc.*, 1966, **88**, 1776.

and Mallinkrodt SilicAR T.L.C.-7G were used for column and thin-layer chromatography respectively. I.r. spectra were obtained on a Perkin-Elmer 257 spectrophotometer for Nujol mulls except where stated otherwise. Optical rotations were recorded on a Perkin-Elmer 141 polarimeter for methanolic solutions unless otherwise stated. N.m.r. spectra were obtained with a Varian HA100 spectrometer for deuteriochloroform solutions with tetramethylsilane as internal standard. Mass spectrometry was carried out with an A.E.I. MS9 spectrometer and the data were processed by an on-line Linc 8 computer.[13] G.l.c. was carried out on a Pye 104 dual column gas chromatograph fitted with flame ionisation detectors. Silanised glass columns (5 ft × $\frac{5}{32}$ in int. diam.) were packed with 2% QF-1 or 2% SE-33 on demineralised and silanised Gaschrom A. Retention indices were determined by use of n-alkane standards. Light petroleum boiled at 60—80°.

Extraction and Identification of Diterpene Hydrocarbons.—The foliage, together with light terminal shoots of varieties of *Cryptomeria japonica*, was dried at 25° for 3 weeks and extracted with refluxing light petroleum. After evaporation *in vacuo*, the residue was taken up in light petroleum and subjected to column chromatography over grade 1 neutral alumina. The diterpene hydrocarbons were identified by comparison with authentic samples of *ent*-kaurene and 13β-kaurene, by g.l.c., m.p., and optical rotation. The following varieties gave *ent*-kaurene: Elegans; Compacta; Viminalis; Hong Kong No. 31 (101–88); Jirdai–Sugi; Hong Kong No. 23 (101–88); Selaginiodes 365–04 Rovelli; Yenko–Sugi 252–08; Kusari Sugi 252–08 Yokohama No. 15; No. 29 25–93 Japan China; Vitellina 566–04 Rovelli No. 12; and 101–88 Hong Kong No. 27. The following varieties gave 13β-kaurene: Hong Kong No. 13 (101–88); Pendula 528–13 Veitch 4007 No. 16; and Lobbii No. 11.

Isolation of 13β-*Kaurene.*—*C. japonica* pendula cuttings (2·35 kg) were dried for 3 weeks at 25° in air. The leaves (1·04 kg) were then removed, and Soxhlet-extracted with light petroleum (15 l) for 7 days. Evaporation gave a dark green oil, which was dried (P_2O_5) to constant weight (76·1 g) and chromatographed on grade 1 neutral alumina (700 g). Elution with light petroleum gave a mixture (7·3 g) of 13β-kaur-16-ene (6) and 13β-kaur-15-ene (10), which was separated by preparative t.l.c. on silica gel impregnated with silver nitrate (10%) to give 13β-kaur-16-ene (6) (5·1 g) as plates, m.p. 97—98° (from methanol); $[\alpha]_D^{22}$ +15·6°; $\nu_{max.}$ 3070, 1658, and 873 cm^{-1}; τ 9·21, 9·17, and 9·10 (each 3H, s) and 5·03br (2H, s); and 13β-kaur-15-ene (10) (2·1 g) as needles, m.p. 113—113·5° (from ethanol–light petroleum); $[\alpha]_D^{22}$ +24° (*c* 0·2); $\nu_{max.}$ 3055, 1638, and 828 cm^{-1}; τ 9·29, 9·22, and 9·18 (each 3H, s), 8·37 (3H, d, $J_{15,17}$ 2 Hz), and 4·75br (1H, s).

13β-*Kaur*-15-*ene* (10).—13β-Kaur-16-ene (6) (15 mg) and iodine (20 mg) in benzene (15 ml) were heated under reflux for 9 h. The cooled mixture was washed with sodium thiosulphate solution (2 × 10 ml) and water (2 × 10 ml), dried, and evaporated to give 13β-kaur-15-ene (10) (15 mg), containing only 2% 13β-kaur-16-ene (6) (by g.l.c.), which crystallised from ethanol–light petroleum as needles, m.p. 113—113·5°, physical data identical with those of the product (10) already described.

13β-*Kaur*-15-*en*-17-*ol* (11).—13β-Kaur-16-ene (6) (20 mg) and haematoporphorin (5 mg) were dissolved in pyridine (5 ml) in a vertical glass tube (int. diam. 2·0 cm). The solution was irradiated for 96 h in a stream of dry oxygen by four fluorescent tubes (Phillips TL4W/33) mounted 2—3 cm away. The solution was evaporated below 40° and the resultant crude hydroperoxide was reduced overnight in ethanol (10 ml) containing acetic acid (2 drops) and sodium iodide (500 mg). The dark residue obtained by evaporation was recovered in ether and washed with sodium thiosulphate. Preparative t.l.c. on silica gel gave 13β-kaur-15-en-17-ol (11) (8 mg) as needles, m.p. 115—119° (from light petroleum); $[\alpha]_D^{22}$ +7° (*c* 0·46); $\nu_{max.}$ 3590, 3300, and 839 cm^{-1}; τ 9·28, 9·21, and 9·18 (each 3H, s), 5·90br (2H, s), and 4·45br (1H, s).

13β-*Kaur*-16-*en*-15α-*ol* (7).—13β-Kaur-15-ene (10) (250 mg) and haematoporphyrin (20 mg) in pyridine (20 ml) were oxygenated and irradiated as just described for 72 h. Work-up in the usual way gave an oil (290 mg), which was chromatographed on silica gel (30 g). Elution with light petroleum gave a mixture of 13β-kaur-16-ene and 13β-kaur-15-ene (80 mg); elution with 10% acetone–benzene gave 13β-kaur-16-en-15α-ol (7) (150 mg) as needles, m.p. 112—113° (from methanol); $[\alpha]_D^{22}$ +40° (*c* 0·24); $\nu_{max.}$ 3600, 3470, 3080, 1660, 900, and 839 cm^{-1}; τ 9·21, 9·16, and 9·09 (each 3H, s), 5·65br (1H, s), 5·06 (1H, s), and 4·90 (1H, s).

13β-*Kaur*-16-*en*-15-*one* (8).—13β-Kaur-16-en-15α-ol (7) (125 mg) in pyridine (5 ml) was added to a stirred suspension of chromium trioxide (200 mg) in pyridine (5 ml) at 0°. After 3·5 h at room temperature, the mixture was poured into ether (20 ml), washed with brine and water, dried, and evaporated to give 13β-kaur-16-en-15-one (121 mg), which crystallised from acetone as needles, m.p. 112—114°; $[\alpha]_D^{22}$ +71·3°; o.r.d. $[\phi]_{250}$ 0, $[\phi]_{234}$ +4450, $[\phi]_{207}$ −6260; c.d. $\Delta\varepsilon_{410}$ 0, $\Delta\varepsilon_{370}$ −0·95, $\Delta\varepsilon_{354}$ −1·09, $\Delta\varepsilon_{300}$ 0, $\Delta\varepsilon_{270}$ 0, $\Delta\varepsilon_{245}$ −1·97, $\Delta\varepsilon_{218}$ +3·62, $\Delta\varepsilon_{195}$ +3·16; $\lambda_{max.}$ 235 nm (ε 6740); $\nu_{max.}$ 1725, 1645, and 928 cm^{-1}; τ 9·25, 9·19, and 9·17 (each 3H, s), and 4·98 and 4·20 (each 1H, s).

Reduction of 13β-*Kaur*-16-*en*-15-*one* (8).—(a) *Lithium aluminium hydride.* 13β-Kaur-16-en-15-one (8) (25 mg) was added to a suspension of lithium aluminium hydride in sodium-dried ether (25 ml). The mixture was boiled for 9 h. Water (10 ml) was added and the solution stirred for a further 5 min. The solution was extracted with brine and water, dried, and evaporated to give an oil (24·2 mg). Preparative t.l.c. on three silica plates (0·3 mm × 20 × 20 cm) [benzene–petroleum (3 : 2) as eluant] gave (16*R*)-13β-kauran-15β-ol (15) (18 mg) as needles, m.p. 104—105° (from light petroleum), identical with the product formed by lithium aluminium hydride reduction of (16*R*)-kauran-15-one; and the dimer (19) (5 mg), m.p. 286—288°; $\nu_{max.}$ 1730, 1100, and 950 cm^{-1}; τ 9·22 and 9·18 (each 6H, s), 9·08 and 9·05 (each 3H, s), and 6·45 (1H, m). Lithium aluminium hydride reduction of 13β-kaur-16-en-15-one (8) in dilute ethereal solution (0·1 mg per ml) produced (16*R*)-13β-kauran-15β-ol (15) in quantitative yield.

(b) *Sodium borohydride.* Sodium borohydride reduction of 13β-kaur-16-en-15-one gave (16*R*)-13β-kauran-15β-ol as the only isolable product.

Acid Treatment of 13β-*Kaur*-16-*en*-15α-*ol* (7).—(a) *At* 0°. 13β-Kaur-16-en-15α-ol (7) (25 mg) was dissolved in methanol (5 ml) and ether (2·5 ml) at 0°, and hydrochloric acid (1 ml) was added. The solution was stirred for 4·5 h at 0°. The organic solvents were removed at room temperature and the residue extracted with ether (3 × 2 ml); the extract was washed, dried, and evaporated to give an oil (25 mg), shown by t.l.c. to be a *ca.* 1 : 1 mixture of starting material and a compound of high R_F value. Preparative t.l.c. was carried

[13] R. Binks, R. L. Cleaver, J. S. Littler, and J. MacMillan, *Chem. in Brit.*, 1971, **7**, 8.

out on two silica gel plates (0·3 mm × 20 × 20 cm), with benzene–light petroleum (3 : 2). Elution of the band of high R_F value with benzene gave a mixture of three compounds, the original compound of high R_F value and two polar materials identified as 13β-kaur-16-en-15α-ol (7) and 13β-kaur-15-en-17-ol (11) by comparison with authentic samples. The following spectroscopic data were obtained for an 80% pure sample of the compound of high R_F value which was assigned structure (20) [the 20% impurity was a mixture of the alcohols (7) and (11)]: $\nu_{max.}$ 3590, 3350, 1035, 900, and 840 cm^{-1}; τ 9·29, 9·22, and 9·18 (each 6H, s), 5·94br (4H, s), and 4·31br (2H, s).

(b) *At* 60°. When the foregoing reaction was carried out at 60°, although dimer (20) was formed, the major product, partially purified by t.l.c. on silica gel plates, was identified as 17-methoxy-13β-kaur-15-ene (12), $\nu_{max.}$ 1100 and 840 cm^{-1}; τ 9·28, 9·22, 9·18, and 6·74br (each 3H, s), and 4·44br (1H, s).

Hydrogenation of 13β-*Kaur*-16-*en*-15α-*ol* (7).—13β-Kaur-16-en-15α-ol (20 mg) in ethanol (10 ml) was hydrogenated over 2% palladium–barium carbonate (20 mg) at room temperature and pressure for 3 h. After removal of the catalyst by filtration through sodium sulphate, evaporation gave a white crystalline solid (20 mg). Preparative t.l.c. on three silica plates (0·4 mm × 20 × 20 cm) with 5% acetone–light petroleum yielded (16*R*)-13β-kauran-15α-ol (16) (16·5 mg), R_F 0·4, m.p. 105—109° (from light petroleum) (Found: M^+, 290·260. Calc. for $C_{20}H_{34}O$: *M*, 290·261); $[\alpha]_D^{22}$ +11°; $\nu_{max.}$ 3580 and 3480 cm^{-1}; τ 9·22, 9·18, and 9·10 (each 3H, s), 8·96 (3H, d, $J_{16,17}$ 6·5 Hz), 6·27 (1H, d, $J_{15.16}$ 4 Hz); and (16*S*)-13β-kauran-15α-ol (18) (3 mg), R_F 0·5, a clear oil (Found: M^+, 290·260. Calc. for $C_{20}H_{34}O$: *M*, 290·261); $\nu_{max.}$ (film) 3600 and 3450 cm^{-1}, τ 9·22, 9·18, and 9·10 (each 3H, s), 9·10 (3H, d, $J_{16.17}$ 7·5 Hz), and 5·84 (1H, d, $J_{15.16}$ 8 Hz).

(16*R*)-13β-*Kauran*-15-*one* (21).—13β-Kaur-16-en-15-one (8) (27 mg) in ethanol (10 ml) was hydrogenated over 5% palladium–charcoal (30 mg) for 5·5 h. After removal of the catalyst by filtration, evaporation yielded (16*R*)-13β-kauran-15-one (21) (25 mg) as plates, m.p. 103—104° (from methanol); $[\alpha]_D^{22}$ −64°; o.r.d. $[\phi]_{400}$ −730, $[\phi]_{327}$ −7110, $[\phi]_{289}$ +6390, $[\phi]_{218}$ +2210, $[\phi]_{206}$ +4180; c.d. $\Delta\varepsilon_{350}$ 0, $\Delta\varepsilon_{311}$ −2·82, $\Delta\varepsilon_{250}$ 0, $\Delta\varepsilon_{230}$ 0, $\Delta\varepsilon_{208}$ −0·67; $\lambda_{max.}$ 300 nm (ε 81); $\nu_{max.}$ 1730 cm^{-1}; τ 9·21 (3H, s), 9·18 (6H, s), and 8·97 (3H, d, $J_{16.17}$ 7·0 Hz).

(16*R*)-13β-*Kauran*-15β-*ol* (15).—(16*R*)-13β-Kauran-15-one (10 mg), in sodium-dried ether (2 ml), was added to a stirred suspension of lithium aluminium hydride (10 mg) in sodium-dried ether (2 ml). After 3 h at room temperature, work-up in the usual way gave (16*R*)-13β-kauran-15β-ol (9 mg) as needles, m.p. 104—105° (from light petroleum) (Found: M^+, 290·260. Calc. for $C_{20}H_{34}O$: *M*, 290·261); $[\alpha]_D^{22}$ −9°; $\nu_{max.}$ 3610 and 3480 cm^{-1}; τ 9·21 and 9·18 (each 3H, s), 9·06 (3H, d, $J_{20,?} < 1$ Hz), 9·12 (3H, d, $J_{16.17}$ 7·2 Hz), and 6·14 (1H, dd, $J_{15.16}$ 11, $J_{15.OH}$ 6 Hz).

Epimerisation of (16R)-13β-*Kauran*-15-*one* (21).—(16*R*)-13β-Kauran-15-one (21) (50 mg) was refluxed in 1% sodium hydroxide in methanol (10 ml). The reaction was monitored by g.l.c. After 3 h under reflux the mixture was cooled and evaporated and the residue was partitioned between water and ether. Work-up in the usual way yielded a mixture (4 : 6) of epimeric (16*R*)- and (16*S*)-13β-kauran-15-ones (20 mg).

Further treatment with base did not alter the ratio of 16*R*- to 16*S*-epimers.

(16S)-13β-*Kauran*-15β-*ol* (17).—A mixture of (16*S*)-13β-kauran-15-one (22) (62%) and (16*R*)-13β-kauran-15-one (21) (38%) (50 mg) in sodium-dried ether (10 ml) was added to a stirred suspension of lithium aluminium hydride (50 mg) in sodium-dried ether (30 ml) at room temperature. After 3 h, water was added and the mixture was stirred for a further 5 min. Work-up in the usual way gave an oil (51 mg). Preparative t.l.c. on three silica plates (0·4 mm × 20 × 20 cm) developed with benzene–light petroleum (3 : 2) yielded (16*R*)-13β-kauran-15β-ol (15) (19 mg), needles, m.p. 104—105° (from methanol), and the (16*S*)-13β-ol (17) (28 mg), needles, m.p. 103—104° (from methanol) (Found: M^+, 290·258. Calc. for $C_{20}H_{34}O$: *M*, 290·261); $[\alpha]_D^{22}$ +21°; $\nu_{max.}$ 3580 and 3440 cm^{-1}; τ 9·23, 9·19, and 9·03 (each 3H, s), 8·98 (3H, d, $J_{16.17}$ 7·0 Hz), and 6·76 (1H, d, $J_{15.16}$ 5·5 Hz).

Oxidation of (16R)-13β-*Kauran*-15β-*ol* (15).—(16*R*)-13β-Kauran-15β-ol (15) (15 mg) in dry pyridine (5 ml) was added to a stirred suspension of chromium trioxide (20 mg) in dry pyridine (5 ml) at 0°. The mixture was allowed to warm to room temperature and stirred for 3 h. Recovery of the product in ether in the usual way gave (16*R*)-13β-kauran-15-one (21) (14 mg), crystallised from acetone as plates, m.p. 103—104°. G.l.c. showed the complete absence of (16*S*)-13β-kauran-15-one (22).

(16*S*)-13β-*Kauran*-15-*one* (22).—(16*S*)-13β-Kauran-15β-ol (17) (25 mg) in dry pyridine (5 ml) was oxidised with chromium trioxide (35 mg) in dry pyridine (5 ml) at 0° as in the previous experiment. Recovery of the product in ether gave (16*S*)-13β-kauran-15-one (22) (25 mg) as plates, m.p. 128·5—129·5° (from acetone); $[\alpha]_D^{22}$ −64° (*c* 0·42); o.r.d. $[\phi]_{400}$ −1990, $[\phi]_{330}$ −6850, $[\phi]_{289}$ +2860, $[\phi]_{223}$, −4850, $[\phi]_{203}$ 0; c.d. $\Delta\varepsilon_{340}$ 0, $\Delta\varepsilon_{311}$ −2·05, $\Delta\varepsilon_{250}$ 0, $\Delta\varepsilon_{20}$, −2·43; $\lambda_{max.}$ 303 nm (ε 66); $\nu_{max.}$ 1725 cm^{-1}; τ 9·22, 9·17, and 9·15 (each 3H, s), and 8·94 (3H, d, $J_{16.17}$ 7·5 Hz).

Oxidation of (16R)-13β-*Kauran*-15α-*ol* (16).—(16*R*)-13β-Kauran-15α-ol (16) (15 mg) in dry pyridine (5 ml) was oxidised by chromium trioxide (20 mg) in dry pyridine (5 ml) at 0° as before. The usual work-up gave (16*R*)-13β-kauran-15-one (21) (14 mg), m.p. 103—104°, identical with that formed by hydrogenation of 13β-kaur-16-en-15-one (8).

Oxidation of (16S)-13β-*Kauran*-15α-*ol* (18).—(16*S*)-13β-Kauran-15α-ol (18) (7 mg) was similarly oxidised to give (16*S*)-13β-kauran-15-one (22) (5·5 mg), identical with that obtained by oxidation of (16*S*)-13β-kauran-15β-ol (17).

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