Terpenoids. Part 7.[1] Diequatorial Opening of 2,3-Epoxides of *ent*-Kauranes and *ent*-Gibberellanes

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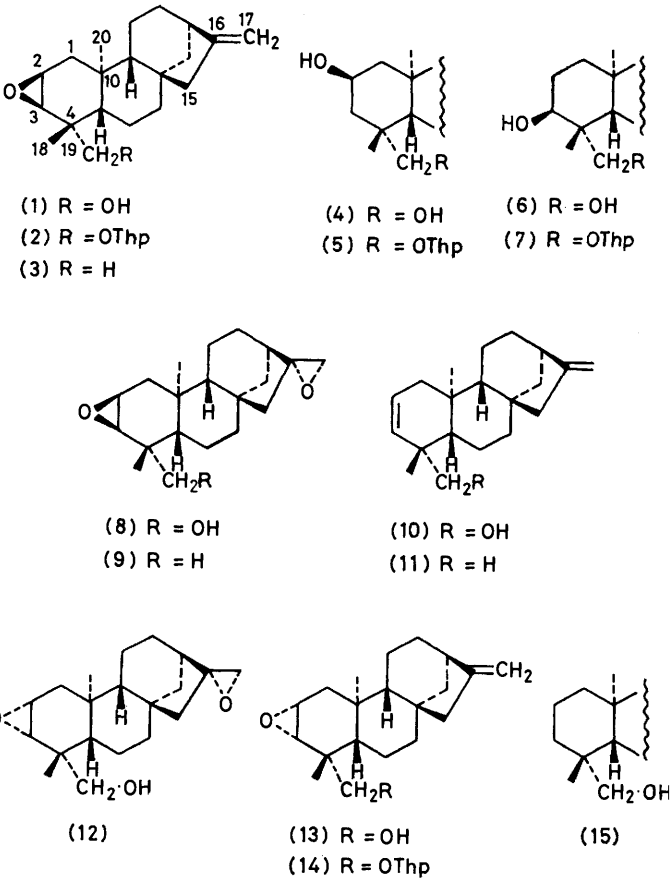
Reduction of *ent*-2α,3α-epoxykaur-16-en-19-ol (1) by hydride to the 2-equatorial alcohol (4) is attributed to participation by the 19-hydroxy-group, since the 19-tetrahydropyranyl ether (2) and the 4,4-dimethyl epoxide (24) are reduced normally to the corresponding 3-axial alcohols (7) and (26) respectively.

Reduction of *ent*-2β,3β-epoxykaur-16-en-19-ol (13) and the 19-tetrahydropyranyl ether (14) by hydride gave the 3-equatorial alcohol (19) and the 19-tetrahydropyranyl ether (23) respectively. Analogously, acidic hydrolysis of the *ent*-2β,3β-epoxides (30) and (31) in the *ent*-kaurane series, and of (40) and (41) in the *ent*-gibberellane series, afforded the diequatorial 2,3-diols. The abnormal opening of these *ent*-2β,3β-epoxides is attributed to the steric effect of the adjacent *ent*-4α-methyl group.

REQUIRING *ent*-2α-hydroxykaurenes for microbiological conversion [2] into *ent*-2α-hydroxygibberellanes,[3] we have followed up the report by Bakker *et al.*[4] that *ent*-2α,3α-epoxykaur-16-en-19-ol (1) was reduced by lithium aluminium hydride to the *ent*-2α-equatorial alcohol (4) as well as the expected *ent*-3α-axial alcohol (6). In confirming this result we have encountered other examples of the diequatorial opening of 2,3-epoxides of both *ent*-kauranes and *ent*-gibberellanes. These exceptions to the normal diaxial cleavage of epoxycyclohexanes are discussed in this paper.

Reduction by Hydride.—Bakker *et al.*[4] prepared the *ent*-2α,3α-epoxide (1) from the diepoxide (8), which they obtained as the sole product of the reaction of the dienol (10) with 3-chloroperbenzoic acid. In our hands and under similar conditions, the dienol (10) gave equal amounts of the diepoxides (8) and (12). In their n.m.r. spectra both epoxides had the same chemical shift for the 17-protons and are assumed to be *ent*-16β,17β-epoxides, formed by attack from the less hindered face.[5] The 2,3-stereochemistries of the diepoxides (8) and (12), and of the monoepoxides (1) and (13) derived from them by treatment with potassium selenocyanide,[4,6] were assigned from the chemical shifts of the 18- and 20-protons. In the less polar *ent*-2β,3β-diepoxide (12) and the corresponding monoepoxide (13), both the C-4 and C-10 methyl groups were deshielded (*ca.* 1.3 p.p.m.), as compared with those of *ent*-kaurenol (15). In the *ent*-2α,3α-epoxides (1) and (8) which corresponded to the compounds described by Bakker *et al.*[4] only the 18-protons were deshielded (*ca.* 1.3 p.p.m.). These stereochemical assignments were confirmed (see later) by the products obtained from reduction of the monoepoxides by hydride and by an alternative synthesis (see later) of the nor-ketone (30) corresponding to the *ent*-2β,3β-epoxide (13). Formation of the *ent*-2β,3β-epoxide by attack from the more hindered face of the dienol (10) is probably due to participation by the 19-hydroxy-group.[7]

With lithium aluminium hydride both the monoepoxides (1) and (13) were reduced anomalously. The *ent*-2α,3α-epoxide (1), as originally reported by Bakker *et al.*,[4] gave the *ent*-2α(*eq*)-alcohol (4) and the *ent*-3α(*ax*)-alcohol (6) in the ratio 3 : 2. However reduction of the 19-tetrahydropyranyl (Thp) ether (2) yielded only the normal *ent*-3α(*ax*)-alcohol (7). This result suggests that

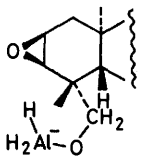


the anomalous reduction of the *ent*-2α,3α-epoxide (1) was caused by participation of the 19-hydroxy-group, directing *ent*-3β-hydride attack, perhaps through the

[1] Part 6, D. H. Bowen, C. Cloke, and J. MacMillan, *J.C.S. Perkin I*, 1975, 378.
[2] M. W. Lunnon, J. MacMillan, and B. O. Phinney, *J.C.S. Perkin I*, preceding paper.
[3] L. J. Beeley and J. MacMillan, *J.C.S. Perkin I*, 1976, 1022.
[4] H. J. Bakker, I. F. Cook, P. R. Jefferies, and J. R. Knox, *Tetrahedron*, 1974, **30**, 3631.
[5] J. R. Hanson, *J. Chem. Soc.*, 1963, 5061.
[6] C. C. J. Culvenor, *Austral. J. Chem.*, 1964, **17**, 233.
[7] H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1957, 1958.

complex (16). Ghisalberti *et al.*[8] also observed participation of the 19-hydroxy-group in the reaction of the 19-acetate of this epoxide with base, resulting in the formation of the oxetan (17). However, although reduction of the 19-Thp ether (2) gave only the 3-axial alcohol (7), the Thp group introduces a possible steric barrier to *ent*-3β-hydride attack. To interpret the abnormal reduction of (1) solely in terms of the directing effect of the 19-hydroxy-group, replacement of the hydroxy-group by hydrogen was undertaken: the 4,4-dimethyl epoxide (3) was prepared *via* the *ent*-3β-alcohol (22) and the diene (11).

Jefferies and Retallack[9] have reduced the monotosylate (20) with lithium aluminium hydride to give the *gem*-dimethyl compound (22) and the oxetan (18) in the ratio 1 : 3. In the present work the 19-*p*-bromobenzenesulphonate (21) was available from another project. Reduction of it with lithium aluminium hydride in refluxing tetrahydrofuran gave equal amounts of the required *gem*-dimethyl compound (22) and, surprisingly, *ent*-kaur-16-en-19-ol (15), but the mixture could not be separated. The latter compound was not formed at room temperature, when the main products were the



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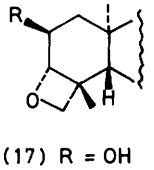
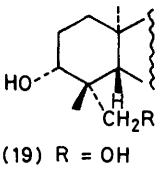
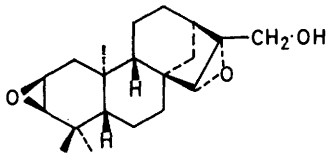


(17) R = OH
(18) R = H



(19) R = OH
(20) R = OTs
(21) R = OBs
(22) R = H
(23) R = OThp



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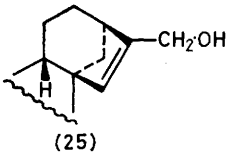

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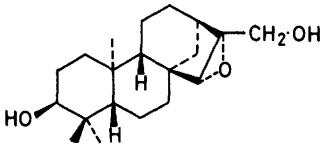

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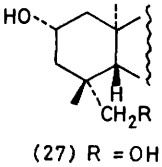


(27) R = OH
(28) R = OThp

diol (19) and the required *gem*-dimethyl compound (22); the yields were variable and small amounts of the oxetan (18) were sometimes formed but compound (22) was always the major product. The formation of *ent*-kaur-16-en-19-ol (15) at the higher temperature of reduction is probably due to reduction of the intermediate oxetan (18), since the latter, prepared by the action of base on the *p*-bromobenzenesulphonate (21), gave *ent*-kaur-16-en-19-ol (15) and the *gem*-dimethyl compound in the ratio 3 : 1 under the same conditions of reduction.

The next step, dehydration of the alcohol (22) was expected to occur smoothly with phosphoryl chloride since Ghisalberti *et al.*[8] found that the diene (11) was the sole product from this reaction. However, in our hands a mixture was obtained and shown by g.l.c.–mass spectrometry to contain one major, and four minor, isomeric products each with M^+ 270 as expected for the diene (11). Although the mixture could be resolved by analytical t.l.c. on silica gel–silver nitrate layers, preparative t.l.c. under these conditions was unsuccessful. The total product was therefore treated with 3-chloroperbenzoic acid to give one major product, which was separated from several minor products by layer chromatography and assigned the structure (24) from the following n.m.r. data. In addition to the 2- and 3-epoxide protons at δ 2.81 (d, *J* 4 Hz) and 3.22 (dd, *J* 4 and 6 Hz), respectively, the n.m.r. spectrum contained an AB system at δ 3.76 and 4.06 (*J* 13 Hz), typical of hydroxymethylene protons, and a one-proton singlet at δ 2.93 in the epoxide region. Formation of the diepoxide (24) from the diene (11) was repeatable and can be explained by rearrangement of the expected diepoxide (9) to the allylic alcohol (25) followed by further epoxidation of the 15,16-double bond. It is significant that epoxidation of the 2,3-double bond in the diene (11) gave no *ent*-2β,3β-epoxide, thereby supporting the suggestion that *ent*-2β,3β-epoxidation of the dienol (10) occurred by participation of the 19-hydroxy-group.

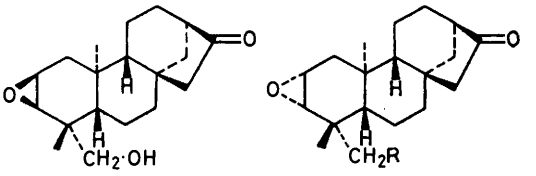
Reduction of the diepoxide (24) with lithium aluminium hydride gave only one product (g.l.c.–mass spectrometry), which formed a bistrimethylsilyl ether and was assigned the structure (26). The n.m.r. spectrum showed that the 15,16-epoxide and the 17-hydroxy-group of the parent compound were still present, and that the 2- and 3-protons of the 2,3-epoxide had been replaced by an *ent*-3β-proton with δ 3.42 and $W_{\frac{1}{2}}$ 7 Hz. Thus the *ent*-2α,3α-epoxide (24) without oxygenation at C-19 was reduced normally to the *ent*-3α(*ax*)-alcohol, supporting the view that abnormal reduction of the *ent*-2α,3α-epoxide (1) is due to participation of the 19-hydroxy-group.

In the reduction of the *ent*-2β,3β-epoxide (13) the 19-hydroxy-group was not expected to direct hydride attack, yet reduction of this epoxide with lithium aluminium hydride also gave a mixture of the *ent*-3β(*eq*)-alcohol (19) and the *ent*-2β-alcohol (27) in the ratio 3 : 2. This ratio was not substantially altered in the reduction of the 19-Thp ether (14), thereby excluding an explanation for the anomalous reduction based upon the electrophilicity of an aluminium complex with the

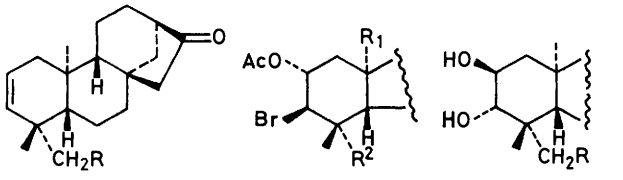
[8] E. L. Ghisalberti, P. R. Jefferies, and J. R. Knox, *Austral. J. Chem.*, 1969, **22**, 455.

[9] P. R. Jefferies and R. W. Retallack, *Austral. J. Chem.*, 1968, **21**, 1311.

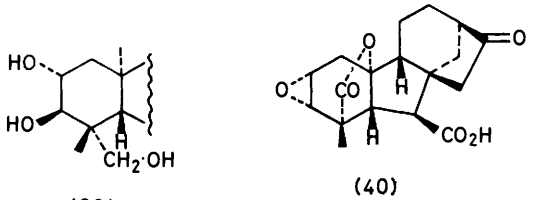
19-hydroxy-group.[10] Although it is possible that the anomalous reduction of the 19-Thp ether is due to the complexing of the Thp ether oxygen atoms and the *ent*-2β,3β-epoxide system with the aluminium, the simplest explanation of these results is that *ent*-3α-attack of



(29) (30) R = OH (31) R = H



(32) R = OH (33) R = H (34) R^1 = Me, R^2 = CH_2·OH (35) R^1 = R^2 = CO_2Me (36) R^1 = R^2 = Me (37) R = OH (38) R = H



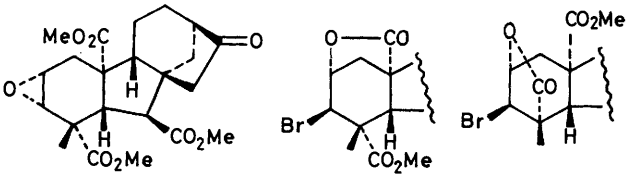
(39) (40)

hydride is sufficiently hindered by the *ent*-4α-methyl group for attack at the *ent*-2α-position to occur also. Support for this view was obtained from a study of acid-catalysed opening (see later) and from the reduction of the *ent*-2β,3β-epoxide (13) with dissolving metal where the sterically undemanding solvated electrons are known [11] to reduce sterically hindered epoxides to axial alcohols. In two experiments using lithium and hexamethylphosphoric triamide no *ent*-3β(*eq*)-alcohol (19) was detected. In one reduction, the 2-axial alcohol (27) and its endocyclic double bond isomer were the sole products; in the other the 2-axial alcohols were accompanied by some of the olefin (10), for which there is precedent.[12]

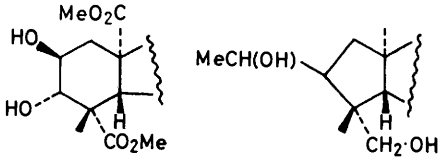
Acid-catalysed Opening.—Attention was next directed to the acid-catalysed opening of these 2,3-epoxides. To avoid the complication of acid-catalysed endomerisation of the 16-ene to the 15-ene, the nor-ketones (29) and (30) were prepared by oxidation of the corresponding *ent*-2α,3α- and 2β,3β-epoxides (1) and (13) with osmium tetraoxide–periodate. The *ent*-2β,3β-epoxy-ketone (30) was also prepared by the methods described by Beeley and MacMillan [3] from the nor-ketone (32) *via* the bromohydrin acetate (34). This preparation confirmed the *ent*-2β,3β-stereochemistry of the nor-ketone (30) and thereby the 2,3-stereochemistry of all *ent*-2,3-epoxykauranes described in this paper.

Reaction of the *ent*-2β,3β-epoxy-ketone (30) with M-sulphuric acid in tetrahydrofuran at room temperature gave one product, shown to be a triol by formation of a tristrimethylsilyl ether and recognised as the 2,3-diequatorial compound (37) from the $J_{2.3}$ value of 10 Hz and the large $W_{\frac{1}{2}}$ value of *ca.* 27 Hz for the 2-proton. Treatment of the *ent*-2α,3α-epoxy-ketone (29) under the same conditions gave a single triol, which had different mass and n.m.r. spectra from the triol (37) and is therefore formulated as the 2,3-diaxial compound (39). The signals for the equatorially related 2- and 3-protons were obscured in the n.m.r. spectrum by the 19-proton signals, and $J_{2.3}$ could not be determined.

Beeley and MacMillan [3] have noted the anomalous opening of the *ent*-2β,3β-epoxide (40) of a C_{19} gibberellin to give both 2,3-diequatorial and -diaxial diols. To provide an example of the *ent*-gibberellanes without the 19,10-lactone system, acid-catalysed opening of the *ent*-2β,3β-epoxide (41) of a C_{20} gibberellin was examined. The required epoxide (41) was prepared by treatment of the known [3] bromohydrin (35) with base. A minor product was a lactone characterised as (42) or (43) by spectroscopic data, but no attempt was made to distinguish between these alternatives. Treatment of the epoxide (41) with M-sulphuric acid gave only the diequatorial diol (44), characterised by the $J_{2.3}$ value of 10 Hz with a $W_{\frac{1}{2}}$ value for the 2-proton of *ca.* 26 Hz.



(41) (42) (43)



(44) (45)

Thus diequatorial opening of the three *ent*-2β,3β-epoxides (30), (40), and (41) was observed on treatment with M-sulphuric acid. These epoxides contain varying degrees of oxygenation at C-19, and -10 or -20 which could assist the development of a positive charge at

[10] E. Glotter, S. Greenfield, and D. Lavie, *Tetrahedron Letters*, 1967, 5261.

[11] A. S. Hallsworth and H. B. Henbest, *J. Chem. Soc.*, 1957, 4604.

[12] A. S. Hallsworth and H. B. Henbest, *J. Chem. Soc.*, 1960, 3571.

C-2 from the protonated epoxides and cause *ent*-2α-attack of water. To test this possibility the *ent*-2β,3β-epoxide (31), lacking any other oxygenation in ring A, was examined. This epoxide (31) was prepared from the alcohol (22), which was converted into the corresponding 17-nor-ketone. The latter, in contrast to its parent (22), was smoothly converted into the olefin (33) with phosphoryl chloride. Reaction of this olefin with bromine acetate gave the bromohydrin (36), which with base gave the epoxide (31). Acidic hydrolysis of this *ent*-2β,3β-epoxide (31) gave entirely the abnormal diequatorial diol (38) with $J_{2,3}$ 10 Hz and $W_{\frac{1}{2}}$ for the 2-proton 26 Hz. Thus the diequatorial opening of the *ent*-2β,3β-epoxides (30), (31), (40), and (41) is independent of oxygenation at C-10, -19, and -20.

Precedents for the anomalous opening of epoxides with acids and hydride in the absence of participating groups have been described by Barton *et al.*[13] They found that the 2β,3β-epoxides of lanostane and lanost-8-ene were reduced by lithium aluminium hydride to the equatorial 3β-alcohols and were opened by hydrobromic acid to the 2α-bromo-3β-alcohols. Barton *et al.*[12] suggested that these 2β,3β-epoxides opened diaxially in the twist-boat form. However this explanation cannot apply to the *ent*-2β,3β-epoxide (40) because of the conformational restraint imposed by the lactone bridge. Moreover *ent*-2α,3α-epoxides open normally, for example (2) or (24) as shown earlier in this paper, 2β,3β-gibberellins,[14] and 2α,3α-lanostane.[13] An alternative explanation for these facts is that, in the *ent*-2β,3β-epoxides nucleophilic attack at C-3 is hindered by the adjacent *ent*-4α-substituent. Thus nucleophilic attack occurs at C-2 to give diequatorial opening. Consistent with this suggestion is the fact that the C_{19} gibberellin epoxide (40) gave [3] a mixture of diequatorial and diaxial diols; here the lactone bridge causes the 4-methyl group to be pulled away from the line of attack at C-3.

An attempt was made to exploit the anomalous opening of *ent*-2β,3β-epoxides to prepare an *ent*-2α-methylkaur-16-ene for microbiological transformation studies. However, treatment of the epoxide (13) with methylmagnesium iodide in benzene afforded the alcohol (45), presumably by rearrangement of the epoxide followed by further reaction of the resultant aldehyde, and, as a minor product, the alcohol (19). The structure of the alcohol (45) was revealed by the n.m.r. spectrum which contained signals for the MeCH(OH) grouping at δ 1.15 and 3.67 (*J* 6 Hz). The minor product (19) may be formed either by reduction of the epoxide (13) by the Grignard reagent directly or after rearrangement to the 3-ketone followed by reduction (*cf.* ref. 15).

EXPERIMENTAL

For general experimental details see ref. 16, except for t.l.c., for which we used Merck Kieselgel HF and for i.r. spectra, which are given for solutions (*ca.* 40 mg ml^{-1}) in methylene dichloride in 0.2 mm cells. For g.l.c.–mass spectrometry of methylated (CH_2N_2) and trimethylsilylated samples see ref. 17, except for the g.l.c. columns, which are described in ref. 18.

Epoxidation of ent-*Kaura*-2,16-*dien*-19-*ol* (10).—The dienol (10) (710 mg) in chloroform (180 ml) was treated with 3-chloroperbenzoic acid (3.36 g) at 0 °C for 2 days. The mixture was washed with ice-cold aqueous 5% sodium hydroxide (2 × 100 ml), then with water. Evaporation gave a gum which was separated by multiple-elution preparative layer chromatography (p.l.c.) with acetone–n-hexane (3 : 7). Recovery from the band at lower R_F value gave *ent*-2α,3α:16β,17β-diepoxykauran-19-ol (8) (298 mg), crystallising from benzene–light petroleum as prisms, m.p. 171—175° (lit.,[4] no m.p. recorded) (Found: C, 75.3; H, 9.9. Calc. for $C_{20}H_{30}O_3$: C, 75.4; H, 9.5%); $\nu_{max.}$ 3 630, 1 026, 955, and 833 cm^{-1}; δ 1.04 (s, 20-H_3), 1.21 (s, 18-H_3), 2.20 (dd, *J* 6 and 15 Hz, 1-H), 2.80 and 2.89 (dd, *J* 5 Hz, 17-H_2), 3.24 (m, 2- and 3-H), and 3.64 and 3.90 (dd, *J* 11 Hz, 19-H_2).

Recovery from the band at higher R_F value gave ent-2β,3β:16β,17β-*diepoxykauran*-19-*ol* (12) (269 mg), crystallising from benzene as cubes, m.p. 175—182° (Found: C, 75.5; H, 9.7. $C_{20}H_{30}O_3$ requires C, 75.4; H, 9.5%); $\nu_{max.}$ 3 620, 1 030, 1 020, 954, and 847 cm^{-1}; δ 1.22 (s, 18- and 20-H_3), 2.42 (dd, *J* 15 and 2 Hz, 1-H), 2.80 and 2.89 (J_{AB} 5 Hz, 17-H_2), 3.00 (d, *J* 4 Hz, 3-H), 3.30 (m, 2-H), and 3.36 and 3.96 (J_{AB} 11 Hz, 19-H_2).

ent-2α,3α-*Epoxykaur*-16-*en*-19-*ol* (1).—The diepoxide (8) (294 mg), in methanol (30 ml) containing potassium selenocyanate (1.29 g), was refluxed for 5.5 h. The mixture was concentrated by distillation, then diluted with water and extracted with ether. The extract gave an oil (317 mg) which was purified by p.l.c. with ethyl acetate–light petroleum (3 : 2). Elution of the band at R_F 0.4 gave the *ent*-2α,3α-monoepoxide (1) (189 mg), which crystallised from benzene–light petroleum as needles, m.p. 158—160° (lit.,[4] 153—154°) (Found: C, 79.4; H, 9.9. Calc. for $C_{20}H_{30}O_2$: C, 79.4; H, 10.0%); $\nu_{max.}$ 3 640, 1 660, 880, and 830 cm^{-1}; δ 1.02 (s, 20-H_3), 1.20 (s, 18-H_3), 2.18 (dd, *J* 6 and 15 Hz, 1-H), 2.64br (s, 13-H), 3.26 (m, 2- and 3-H), 3.63 and 3.89 (J_{AB} 11 Hz, 19-H_2), and 4.74br (s) and 4.80br (s) (17-H_2).

ent-2β,3β-*Epoxykaur*-16-*en*-19-*ol* (13).—The *ent*-2β,3β-diepoxide (12) (269 mg) was treated with potassium selenocyanate (1.22 g) in methanol (30 ml) as for the *ent*-2α,3α-diepoxide (8). The oily product (270 mg) was purified by p.l.c. in ethyl acetate–light petroleum (3 : 2). Recovery from the band at R_F 0.7 gave ent-2β,3β-*epoxykaur*-16-*en*-19-*ol* (13) (149 mg), needles, m.p. 118—120° (from benzene–light petroleum) (Found: C, 79.1; H, 10.2. $C_{20}H_{30}O_2$ requires C, 79.4; H, 10.0%); $\nu_{max.}$ 3 635, 1 660, 878, and 846 cm^{-1}; δ 1.20 (s, 18- and 20-H_3), 2.40 (dd, *J* 2 and 15 Hz, 1-H), 2.66br ($W_{\frac{1}{2}}$ 10 Hz, 13-H), 2.97 (d, *J* 4 Hz, 3-H), 3.30 (m, 2-H), 3.33 and 3.95 (J_{AB} 11 Hz, 19-H_2), and 4.74 and 4.80 (17-H_2).

Reductions with Lithium Aluminium Hydride.—(a) ent-2α,3α-*Epoxykaur*-16-*en*-19-*ol* (1). The epoxide (128 mg), lithium aluminium hydride (410 mg), and tetrahydrofuran (4 ml) were heated under reflux for 6 h. To the cooled

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mixture ethyl acetate was added and the resulting suspension was poured into a solution of ammonium chloride (9 g) in water (45 ml). Extraction with ethyl acetate yielded a solid (131 mg), which was separated by p.l.c. in methanol–chloroform (1 : 19). Double development and elution of the band at R_F 0.3 gave *ent*-kaur-16-ene-2α,19-diol (4) (57 mg), crystallising from ethyl acetate as prisms, m.p. 218—219° (lit.,[4] 220—221°); $\nu_{max.}$ and δ as previously recorded; [4] *m/e* (for Me_3Si derivative) 448 (M^+, <1%), 358 (13), 268 (16), 255 (62), 143 (33), 131 (40), 129 (31), 103 (28), and 73 (100).

Elution of the band at R_F 0.4 gave *ent*-kaur-16-ene-3α,19-diol (6) (38 mg), crystallising from ethyl acetate in prisms, m.p. 204—206° (lit.,[8] 201—202°); $\nu_{max.}$ and δ as previously recorded; [8] *m/e* (for Me_3Si derivative) 448 (M^+, <1%), 358 (24), 229 (36), 189 (19), 169 (53), 147 (19), 103 (21), and 73 (100).

(b) ent-2β,3β-*Epoxykaur*-16-*en*-19-*ol* (13). The epoxide (40 mg) in tetrahydrofuran (2 ml) was reduced with lithium aluminium hydride (125 mg) as in (a). The product (46 mg) was separated by p.l.c. with ethyl acetate–light petroleum (1 : 1). Recovery from the band at R_F 0.5 gave *ent*-kaur-16-en-3β,19-diol (19) (23 mg), identical (m.p. and n.m.r. data) with authentic material.

Elution of the band at R_F 0.2 gave *ent*-kaur-16-ene-2β,19-diol (27) (14 mg), which crystallised from benzene–light petroleum as needles, m.p. 173—175° (lit.,[8] 174—175°); $\nu_{max.}$ and δ as previously recorded; [8] *m/e* (for Me_3Si derivative) 448 (M^+, <1%), 359 (9%), 268 (35), 255 (38), 247 (31), 156 (29), 121 (30), 119 (29), and 73 (100).

(c) ent-2α,3α-*Epoxy*-19-(*tetrahydropyran*-2-*yloxy*)*kaur*-16-*ene* (2). The tetrahydropyranyl ether (2) was prepared by dissolving the epoxide (1) (41 mg), dihydropyran (0.121 ml), and a crystal of toluene-*p*-sulphonic acid in methylene chloride (5 ml). The reaction was monitored by t.l.c. After 3.5 h at 20 °C the solution was washed with water, dried, and evaporated to give a gum (85 mg), which was purified by p.l.c. in ethyl acetate–light petroleum (7 : 13) to give the gummy ether (2) (43 mg); $\nu_{max.}$ 1 660, 1 138, 1 120, 1 078, 1 032, 877, and 870 cm^{-1}.

This ether (2) (34 mg) and lithium aluminium hydride (99 mg) in tetrahydrofuran (1.5 ml) were heated under reflux for 6 h. The usual work-up gave a gum (52 mg) which after p.l.c. in ethyl acetate–light petroleum (2 : 3) and elution of the band at R_F 0.7 gave *ent*-19-(tetrahydropyran-2-yloxy)kaur-16-en-3α-ol (7) (26 mg), identical (n.m.r. data and mass spectrum of Me_3Si ether) with authentic material.[2]

(d) ent-2β,3β-*Epoxy*-19-(*tetrahydropyran*-2-*yloxy*)*kaur*-16-*ene* (14). The tetrahydropyranyl ether (14) was prepared from the epoxide (13) (29 mg), dihydropyran (0.085 ml), and a crystal of toluene-*p*-sulphonic acid in methylene chloride (3.5 ml). Work-up as in (c) gave the ether (13), which after p.l.c. in ethyl acetate (3 : 7) was obtained as an oil (25 mg); $\nu_{max.}$ 1 660, 1 122, 1 120, 1 080, 1 032, 880, 870, and 850 cm^{-1}.

This epoxide (14) (25 mg) in tetrahydrofuran (1.5 ml) was heated under reflux for 6 h with lithium aluminium hydride (60 mg). Work-up as in (c) gave a gum (28 mg). Analysis of a trimethylsilylated portion by g.l.c.–mass spectrometry showed the presence of equal proportions of two isomeric tetrahydropyranyl ethers with M^+ 460 (<1%) and base peak *m/e* 85 which were identified as the Me_3Si ethers of *ent*-19-(tetrahydropyran-2-yloxy)kaur-16-en-2β- and -3β-ols, (28) and (23), as follows. Hydrolysis of the crude product with 20% acetic acid in methanol gave a mixture (1 : 1) of the diols (27) and (19), identified by g.l.c.–mass spectrometric comparison of the bistrimethylsilyl ethers with authentic samples.

Reduction of ent-2β,3β-*Epoxykaur*-16-*en*-19-*ol* (13) *with Lithium in Hexamethylphosphoric Amide*.—Lithium (100 mg) was added to hexamethylphosphoric amide (25 ml; dry and redistilled) under nitrogen and with stirring at 60 °C for 40 min. The resulting blue solution was cooled to room temperature and the epoxide (13) (42 mg) in hexamethylphosphoric amide (1.5 ml) was added. After 3 h methanol was added (discharging the orange colour), followed by water, and the pH of the solution was adjusted to 3.0 by adding 0.5M-hydrochloric acid. Extraction with ether yielded an oil (62 mg), which contained two components (t.l.c.), one with the same R_F value as the diol (27). G.l.c. showed two peaks, each of which was resolved into a doublet after trimethylsilylation. P.l.c. in ethyl acetate–light petroleum gave two bands, at R_F 0.1 and 0.75.

Elution of the band at R_F 0.1 gave a mixture (17.5 mg) of the diol (27) and its Δ^{15} isomer, δ (C_5D_5N) 1.68 (d, *J* 2 Hz, 17-H_3) and 5.14 (m, 15-H). G.l.c.–mass spectrometry of the trimethylsilylated mixture gave: (i) the Δ^{15}-isomer Me_3Si ether, shorter t_R, *m/e* 448 (M^+, 1%), 358 (7), 345 (11), 268 (11), 255 (51), 187 (20), 156 (21), 145 (25), 121 (33), 119 (65), 94 (100), and 73 (66); and (ii) the diol (27) Me_3Si ether, *m/e* 448 (M^+, <1%), 358 (18), 268 (80), 255 (73), 242 (60), 156 (56), 121 (54), 119 (58), 117 (89), 95 (70), and 73 (100).

Elution of the band at R_F 0.75 gave a mixture (18.5 mg) of the diene (10) and its Δ^{15}-isomer, δ 1.7 (d, *J* 2 Hz, 17-H_3) and 5.08 (m, 15-H). G.l.c.–mass spectrometry gave: (i) the Δ^{15}-isomer, shorter t_R, *m/e* 358 (M^+, 8%), 343 (7), 268 (6), 187 (20), 149 (22), 119 (100), 105 (46), 103 (45), and 93 (32); and (ii) the Δ^{16}-isomer longer t_R, *m/e* 358 (M^+, 7%), 343 (5), 268 (23), 255 (63), 187 (53), 175 (23), 135 (25), 119 (85), 103 (73), and 95 (100).

In a second experiment the epoxide (60 mg) in hexamethylphosphoric amide (2 ml) and lithium (200 mg) in hexamethylphosphoric amide (5 ml) gave an oil from which residual solvent was removed by column chromatography on silica gel with ethyl acetate. The resultant solid (35 mg) had the same R_F value as the diol (27), and the n.m.r. spectrum showed the presence of the diol (27) together with the isomeric 15-ene.

ent-*Kaur*-16-*en*-3β-*ol* p-*Bromobenzenesulphonate* (21).—The diol (19) (2.0 g) in pyridine (60 ml) was stirred with *p*-bromobenzenesulphonyl chloride (2.5 g) for 26 h at 20 °C. The mixture was added to water and extracted with ethyl acetate to yield a brown gum (5.0 g), which was adsorbed on silica gel and placed on a column of silica gel made up in light petroleum. Elution with 35—45% ethyl acetate in light petroleum gave the p-*bromobenzenesulphonate* (21) (2.0 g), crystallising from chloroform–light petroleum as plates, m.p. 143—145° (Found: C, 59.7; H, 7.0; Br, 14.8; S, 5.95. $C_{26}H_{35}BrO_4S$ requires C, 59.65; H, 6.7; Br, 15.3; S, 6.1%); $\nu_{max.}$ 3 620, 1 660, 1 581, 835, and 825 cm^{-1}; δ 0.92 (s, 20-H_3), 1.09 (s, 18-H_3), 2.65br (13-H), 3.28 (m, 3-H), 4.12 and 4.26 (J_{AB} 10 Hz, 19-H_2), 4.74br and 4.80br (17-H_2), and 7.74 (m, ArH_4).

Reduction by Lithium Aluminium Hydride of the p-*Bromobenzenesulphonate* (21).—(a) *At room temperature*. The *p*-bromobenzenesulphonate (800 mg) in tetrahydrofuran (35 ml) was stirred at 20 °C for 14 h with lithium aluminium hydride (900 mg). The mixture was poured into a solution

of ammonium chloride (20 g) in water (100 ml), which was then extracted with ethyl acetate to give a gum (1.4 g). P.l.c. of this gum on silica gel with ethyl acetate–light petroleum (3 : 7) and elution of the band at R_F 0.75 gave the oxetan (18) (28 mg), prisms (from ethyl acetate), m.p. 116—118° (lit.,[9] 120—121°) (Found: M^+, 286.228. Calc. for $C_{20}H_{30}O$: M, 286.230); $\nu_{max.}$ 1 658, 977, 878, and 870 cm^{-1}; δ 1.26 (s, 20-H_3), 1.32 (s, 18-H_3), 2.68br (13-H), 4.12 and 4.43 (J_{AB} 6 Hz, 19-H_2), 4.66 (m, 3-H), and 4.76 and 4.80 (17-H_2).

Extraction of the band at R_F 0.5 gave *ent*-kaur-16-en-3β-ol (22) (130 mg), which crystallised from chloroform–light petroleum as a microcrystalline powder which on heating formed needles, m.p. 168—170° (lit.,[9] 172—173°) (Found: M^+, 288.244. Calc. for $C_{20}H_{32}O$: M, 288.245); $\nu_{max.}$ 3 625, 1 657, and 877 cm^{-1}; δ 0.79 (s, 20-H_3), 1.00 (s, 19-H_2), 1.04 (s, 18-H_2), 2.66br (13-H), 3.21 (m, 3-H), and 4.75 and 4.80 (17-H_2).

Extraction of the band at R_F 0.2 gave the diol (19) (110 mg), identical (t.l.c. and n.m.r. and mass spectra) with an authentic sample.

In a repeat experiment the *p*-bromobenzenesulphonate (2.0 g), tetrahydrofuran (80 ml), and lithium aluminium hydride (2.0 g) gave the alcohol (22) (590 mg) and the diol (19) (107 mg), but none of the oxetan (18).

(b) *Under reflux.* The *p*-bromobenzenesulphonate (100 mg) in tetrahydrofuran (3 ml) was heated under reflux for 4 h with lithium aluminium hydride (100 mg). Work-up as in (a), followed by p.l.c. of the crude product on silica gel with ethyl acetate–light petroleum (1 : 4), gave from a band at R_F 0.4, a mixture (27 mg) shown by n.m.r. and g.l.c.–mass spectrometry of the Me_3Si derivatives to contain equal amounts of *ent*-kaur-16-en-19-ol (15) and *ent*-kaur-16-en-3β-ol (22). A mixture (42 mg) of the same products but in the ratio 3 : 1 was obtained by similar reduction of the oxetan (18) (46 mg) prepared from the *p*-bromobenzenesulphonate (21) essentially as described by Jefferies and Retallack.[9]

ent-2α,3α:15β,16β-*Diepoxykauran*-17-*ol* (24).—The alcohol (22) (250 mg) was treated with phosphoryl chloride (800 μl) in pyridine (12 ml) for 12 h at 20 °C and then at 100 °C for 1 h. Extraction with ethyl acetate gave an oil (315 mg), which was redissolved in ethyl acetate and passed through a column of silica gel. Concentration of the eluate gave a gum (185 mg). Analysis by g.l.c.–mass spectrometry showed one major peak with four minor components at longer retention time; all had M^+ 270. The n.m.r. spectrum showed δ 0.91, 0.96, and 1.07 (all s), 2.68br (d, $W_{\frac{1}{2}}$ 11 Hz), 4.77br and 4.81br, and 5.40 (m).

The crude product (185 mg) was treated with 3-chloroperbenzoic acid (870 mg) at 0 °C for 20 h in chloroform (30 ml). The mixture was washed with ice-cold aqueous 5% sodium hydroxide (2 × 20 ml) and then water. Evaporation under vacuum gave a residue (200 mg) which t.l.c. showed to consist of one major polar product with five minor components at higher R_F value. P.l.c. in ethyl acetate–light petroleum (3 : 7) with double development and recovery from the band at R_F 0.3 yielded ent-2α,3α:15β,16β-*diepoxykauran*-17-*ol* (24) (50 mg), which crystallised from ethyl acetate–light petroleum as needles, m.p. 182—185° (Found: C, 75.3; H, 9.5. $C_{20}H_{30}O_3$ requires C, 75.4; H, 9.5%); δ 1.02 (s, 19- and 20-H_3), 1.12 (s, 18-H_3), 2.81 (d, J 4 Hz, 3-H), 2.93 (s, 15-H), 3.22 (dd, J 4 and 5 Hz, 2-H), and 3.76 and 4.06 (J_{AB} 13 Hz, 17-H_2); $\nu_{max.}$ 3 662—3 240br, 3 610, 1 055, 925, 842, and 826 cm^{-1}.

Reduction by Lithium Aluminium Hydride of the Diepoxide (24).—The diepoxide (35 mg) in tetrahydrofuran (3 ml) was refluxed for 4 h with lithium aluminium hydride (125 mg). The usual work-up gave a solid (42 mg) which was separated by p.l.c. on silica gel with ethyl acetate–light petroleum (2 : 3). Recovery from the band at R_F 0.15 gave ent-15β,16β-*epoxykaurane*-3α,17-*diol* (26) (22 mg), which crystallised from ethyl acetate as needles, m.p. 217—223° (Found: C, 74.3; H, 10.5%; M^+, 320.236. $C_{20}H_{32}O_3$ requires C, 74.9; H, 10.1%; M, 320.235); δ 0.84 (s, 20-H_3), 0.96 (s, 19-H_3), 1.02 (s, 18-H_3), 2.94 (s, 15-H), 3.42 (m, $W_{\frac{1}{2}}$ 7 Hz, 3-H), and 3.78 and 4.06 (J_{AB} 13 Hz, 17-H_2); $\nu_{max.}$ 3 662—3 200br, 3 640, 1 062, 925, and 842 cm^{-1}.

ent-2β,3β-*Epoxy*-17-*norkauran*-16-*en*-19-*ol* (30).—(*a*) The epoxide (13) (100 mg) and osmium tetraoxide (4 crystals) in tetrahydrofuran (12.5 ml) and water (12.5 ml) were stirred at 0 °C. Sodium periodate (180 mg) was added and the mixture was allowed to warm to room temperature. After 24 h the mixture was concentrated under vacuum and an excess of water was added. Extraction with ethyl acetate and recovery gave a crude product (110 mg) which was purified by p.l.c. on silica gel doubly developed with ethyl acetate–light petroleum (3 : 2). Recovery from a band at R_F 0.4 gave the *nor-ketone* (30) (81 mg), which crystallised from benzene–light petroleum as a microcrystalline powder, m.p. 158—163° (Found: C, 75.05; H, 9.6%; M^+, 304.204. $C_{19}H_{28}O_3$ requires C, 75.0; H, 9.3%; M, 304.204); $\nu_{max.}$ 3 620, 1 740, and 843 cm^{-1}; δ 1.24 and 1.27 (both s, 18- and 19-H_3), 3.00 (d, J 4 Hz, 3-H), 3.34 (m, 2-H), and 3.38 and 3.97 (J_{AB} 11 Hz, 19-H_2).

(*b*) The olefin (32) (100 mg), lithium acetate dihydrate (540 mg), *N*-bromoacetamide (54 mg), and glacial acetic acid (6 ml) were stirred for 3 h at 20 °C. The mixture was poured into water (50 ml) and extracted with ethyl acetate to give a gum (210 mg). P.l.c. in ethyl acetate–light petroleum (2 : 3) and extraction of the band at R_F 0.2 gave ent-2β-*acetoxy*-3α-*bromo*-19-*hydroxy*-17-*norkauran*-16-*one* (34) (91 mg), which crystallised from ethyl acetate as prisms, m.p. 178—180° [Found: C, 60.9; H, 7.8%; M^+, 426.141. $C_{21}H_{31}BrO_4$ requires C, 61.3; H, 7.6%; M (for ^{79}Br), 426.140]; δ 1.21 (s, 20-H_3), 1.32 (s, 18-H_3), 2.10 (s, $MeCO_2$), 3.67 and 4.08 (J_{AB} 11 Hz, 19-H_2), 4.68 (d, J 5 Hz, 3-H), and 5.36 (q, J 5 Hz, 2-H); $\nu_{max.}$ 3 622, 1 747, 1 735, 1 230, 1 030, and 1 018 cm^{-1}; *m/e* 428 (M^+, 2.1%), 426 (M^+, 1), 367 (1), 365 (1), 337 (9), 335 (9), 287 (41), 257 (100), 189 (35), and 119 (87).

The bromoacetate (34) (87 mg) was stirred at 20 °C for 20 h with methanol (6.5 ml) and M-sodium hydroxide (0.55 ml). The solution was concentrated and diluted with water. Extraction with methylene chloride gave crystals (67 mg) which, after p.l.c. in ethyl acetate–light petroleum (1 : 1), afforded the epoxide (30) (58 mg), identical with that obtained in (a).

Acidic Hydrolysis of the ent-2β,3β-*Epoxide* (30).—The epoxide (29) (62 mg) was dissolved in tetrahydrofuran and M-sulphuric acid was added. After 17 h at room temperature, t.l.c. showed the absence of starting material, the mixture giving one spot at lower R_F value. Aqueous sodium hydrogen carbonate was added and the tetrahydrofuran was evaporated off under nitrogen. Addition of water and extraction with ethyl acetate gave the crude product (50 mg). P.l.c. in methanol–chloroform (1 : 9) and removal of the band at R_F 0.5 yielded ent-2α,3β,19-*trihydroxy*-17-*norkauran*-16-*one* (37) (37 mg), which crystallised from chloroform–light petroleum as prisms, m.p.

181—183° (Found: C, 70.9; H, 9.7. $C_{19}H_{30}O_4$ requires C, 70.8; H, 9.4%); δ ($CDCl_3$) 1.14 (s, 20-H_3), 1.26 (s, 18-H_3), 3.14 (d, *J* 10 Hz, 3-H), 3.35 and 4.10 (J_{AB} 11 Hz, 19-H_2), and 3.92 (m, $W_{\frac{1}{2}}$ 27 Hz, 2-H); δ (C_5D_5N) 1.05 (s, 20-H_3), 1.51 (s, 18-H_3), 3.51 (d, *J* 10 Hz, 3-H), 3.67 and 4.36 (J_{AB} 11 Hz, 19-H_2), and 4.27 (m, $W_{\frac{1}{2}}$ 27 Hz, 2-H); $\nu_{max.}$ 3 650—3 130br and 1 740 cm^{-1}; *m/e* (for tris-Me_3Si ether) 538 (M^+, <1%), 433 (2), 345 (100), 217 (6), 191 (28), 147 (17), 143 (13), 103 (14), and 73 (48).

ent-2α,3α-*Epoxy*-19-*hydroxy*-17-*norkauran*-16-*one* (29).—The epoxide (1) (141 mg) and five crystals of osmium tetraoxide were stirred at 0 °C in tetrahydrofuran (18 ml) and water (18 ml). Sodium periodate (254 mg) was added, and the mixture left to warm up to room temperature. After 24 h the reaction was worked up in the usual way, and the crude extract (160 mg) was purified by p.l.c. in ethyl acetate–light petroleum (1 : 1). Extraction of the band at R_F 0.2 gave the *nor-ketone* (29) (105 mg), which crystallised from ethyl acetate as prisms, m.p. 173—175° (Found: C, 74.6; H, 9.3%; M^+, 304.203. $C_{19}H_{28}O_3$ requires C, 80.0; H, 9.3%; *M*, 304.204); δ 1.12 (s, 20-H_3), 1.23 (s, 18-H_3), 3.26 (m, 2- and 3-H), and 3.63 and 3.89 (J_{AB} 11 Hz, 19-H_2); $\nu_{max.}$ 3 630, 1 738, and 828 cm^{-1}.

Acidic Hydrolysis of the ent-2α,3α-*Epoxide* (29).—The epoxide (29) (100 mg) was stirred at room temperature in tetrahydrofuran (12 ml) and M-sulphuric acid (2 ml). After 16 h the reaction was worked up as for the *ent*-2β,3β-epoxide (29) to give a crude product (70 mg). P.l.c. in methanol–chloroform (1 : 9) and elution of the band at R_F 0.4 gave ent-2β,3α,19-*trihydroxy*-17-*norkauran*-16-*one* (39) (53 mg), which crystallised from chloroform–light petroleum as microprisms, m.p. 158—160° (Found: C, 70.9; H, 9.7%; M^+, 322.214. $C_{19}H_{30}O_4$ requires C, 70.8; H, 9.4%; *M*, 322.214); δ ($CDCl_3$) 1.09 (s, 20-H_3), 1.28 (s, 18-H_3), 3.50 and 4.06 (J_{AB} 10 Hz, 19-H_2), and 3.70—4.00 (2- and 3-H); δ (C_5D_5N) 1.38 (s, 20-H_3), 1.42 (s, 18-H_3), 3.87 and 4.24 (J_{AB} 10 Hz, 19-H_2), and 4.26—4.47 (2- and 3-H); $\nu_{max.}$ 3 660—3 100br and 1 740 cm^{-1}; *m/e* (for tris-Me_3Si ether) 538 (M^+, 1%), 448 (8), 358 (36), 345 (67), 306 (24), 217 (17), 191 (38), 169 (26), 168 (30), 147 (34), 143 (58), 103 (51), and 73 (100).

Methyl ent-2β,3β-*Epoxy*-16-*oxo*-17-*norgibberellane*-7,19,20-*trioate* (41).—The bromohydrin (35) (250 mg), prepared from gibberellin A_{13} by the method of Beeley and MacMillan,[3] was dissolved in methanol (16 ml), and M-sodium hydroxide (1.4 ml) was added dropwise. The mixture was stirred for 20 h at 20 °C, then concentrated under vacuum and, after addition of water, extracted with methylene chloride to give crystals (180 mg). The crude product separated as two bands upon p.l.c. on silica gel in ethyl acetate–light petroleum (3 : 2). The band at R_F 0.4 gave the *epoxide* (41) (100 mg), which crystallised from ethyl acetate–light petroleum as needles, m.p. 188—190° (Found: C, 62.5; H, 6.3%; M^+, 420.178. $C_{22}H_{28}O_8$ requires C, 62.8; H, 6.7%; *M*, 420.177); δ 1.44 (s, 18-H_3), 1.99 (d, *J* 12 Hz, 5-H), 3.04 (d, *J* 4 Hz, 3-H), 3.06 (dd, *J* 14 and 3 Hz, 1-H), 3.28 (t, *J* 4 and 3 Hz, 2-H), 3.64 (s, CO_2Me), 3.77 (s, 2 CO_2Me), and 3.94 (d, *J* 12 Hz, 6-H); $\nu_{max.}$ 1 742, 1 728, 855, 846, and 836 cm^{-1}; *m/e* 420 (9%), 388 (76), 312 (43), 285 (51), 241 (36), 225 (100), 197 (36), and 155 (39).

Elution of the band at R_F 0.75 gave the bromolactone (42) or (43) (38 mg), which crystallised from ethyl acetate as prisms, m.p. 241—242° (Found: M^+, 468.079. Calc. for $C_{21}H_{25}{}^{79}BrO_7$: *M*, 468.079); δ 1.37 (s, 18-H_3), 2.75 (d, *J* 11 Hz, 5-H), 2.84 (d, *J* 12 Hz, 1-H), 3.72 and 3.74 (both s, 2 CO_2Me), 3.81 (d, *J* 11 Hz, 6-H), 4.78 (td, *J* 4 and 1 Hz, 2-H), and 5.18 (d, *J* 4 Hz, 3-H); $\nu_{max.}$ 1 790, 1 742, and 1 733 cm^{-1}; *m/e* 470 (M^+, 2.9%), 468 (M^+, 10), 438 (100), 436 (100), 410 (37), 408 (37), 225 (26), 197 (24), 155 (18), and 129 (16).

Acidic Hydrolysis of the Epoxide (41).—The *ent*-2β,3β-epoxide (41) (110 mg) in tetrahydrofuran (10 ml) was refluxed with M-sulphuric acid (1.5 ml) for 2 h. The mixture was neutralised with aqueous sodium hydrogen carbonate; the tetrahydrofuran was evaporated off under nitrogen and the residue was extracted with ethyl acetate to give the crude product (135 mg). P.l.c. in ethyl acetate–light petroleum (4 : 1) and elution of the band at R_F 0.15 gave *methyl* ent-2α,3β-*dihydroxy*-16-*oxo*-17-*norgibberellane*-7,19,20-*trioate* (44) (68 mg), which crystallised from ethyl acetate–light petroleum as prisms, m.p. 195—205° (Found: C, 59.9; H, 6.8. $C_{22}H_{30}O_9$ requires C, 60.3; H, 6.9%); δ 1.32 (s, 18-H_3), 2.22 (d, *J* 12 Hz, 5-H), 2.74 (dd, *J* 13 and 5 Hz, 1-H), 3.04 (d, *J* 10 Hz, 3-H), 3.64, 3.70, and 3.73 (all s, 3 CO_2Me), 3.96 (d, *J* 12 Hz, 6-H), and 4.15 (m, $W_{\frac{1}{2}}$ 26 Hz, 2-H); $\nu_{max.}$ 3 585, 3 545, 1 740, and 1 722 cm^{-1}; *m/e* (for bis-Me_3Si ether) 582 (M^+, 2%), 567 (6), 433 (100), 351 (15), 217 (18), 204 (11), 188 (19), 173 (33), and 147 (32).

Starting material (41) (37 mg) was recovered from the band at R_F 0.5.

ent-3β-*Hydroxy*-17-*norkauran*-16-*one*.—The *ent*-3β-alcohol (19) (200 mg) was dissolved in tetrahydrofuran (13 ml) and water (13 ml) at 0 °C, and a few crystals of osmium tetraoxide were added. Sodium periodate (390 mg) was then added to the mixture, which was subsequently allowed to warm to room temperature. After 12 h, work-up with ethyl acetate and subsequent p.l.c. in ethyl acetate–light petroleum (35 : 65) with removal of the band at R_F 0.3 gave the *nor-ketone* (142 mg), which crystallised from acetone–light petroleum as microprisms, m.p. 188—190° (Found: M^+, 290.226. $C_{19}H_{30}O_2$ requires *M*, 290.225); δ 0.81 (s, 20-H_3), 1.01 (s, 19-H_3), 1.10 (s, 18-H_3), and 3.23 (m, $W_{\frac{1}{2}}$ 18 Hz, 3-H); $\nu_{max.}$ 3 620 and 1 740 cm^{-1}.

ent-17-*Norkaur*-2-*en*-16-*one* (33).—*ent*-3β-Hydroxy-17-norkauran-16-one (138 mg) was dissolved in pyridine (8 ml) containing phosphoryl chloride (400 μl). The mixture was left for 12 h at 20 °C and then heated at 100 °C for 1 h. Aqueous work-up and extraction into ethyl acetate gave a pink solid (150 mg), which was redissolved in ethyl acetate and the colour removed by elution from a column of silica gel to yield the *olefin* (33) (100 mg). Recrystallisation from aqueous methanol gave needles, m.p. 108—110° (Found: M^+, 272.215. $C_{19}H_{28}O$ requires *M*, 272.214); δ 0.92 (s, 20-H_3), 0.98 (s, 19-H_3), 1.13 (s, 18-H_3), and 5.42 (m, 2- and 3-H); $\nu_{max.}$ 1 740 cm^{-1}.

ent-2β-*Acetoxy*-3α-*bromo*-17-*norkauran*-16-*one* (36).—The olefin (33) (95 mg) was dissolved in acetic acid (6 ml) and *N*-bromoacetamide (60 mg) and lithium acetate dihydrate (570 mg) were added. The mixture was stirred at room temperature for 3 h, then added to water and extracted with ethyl acetate. P.l.c. in ethyl acetate–light petroleum (3 : 7) and recovery from the band at R_F 0.5 gave the *bromo-acetate* (36) (86 mg). Recrystallisation from ethyl acetate–light petroleum afforded needles, m.p. 191—193° (Found: M^+, 410.145. $C_{21}H_{31}{}^{79}BrO_3$ requires *M*, 410.145); δ 1.14 (s, 20-H_3), 1.17 (s, 19-H_3), 1.32 (s, 18-H_3), 2.08 (s, $MeCO_2$), 4.34 (d, *J* 7 Hz, 3-H), and 5.29 (q, *J* 6 Hz, 2-H); $\nu_{max.}$ 1 740 cm^{-1}; *m/e* 412 (M^+ + 2, <1%), 410 (M^+, <1), 352 (13), 350 (12), 271 (42), 189 (13), 133 (55), and 43 (100).

ent-2β,3β-*Epoxy*-17-*norkauran*-16-*one* (31).—The bromoacetate (36) (118 mg) was stirred in methanol (9 ml) and M-sodium hydroxide (0.8 ml) at 20 °C for 5 h. The mixture was then poured into water and extracted with methylene chloride to give the *epoxide* (31) (73 mg). Recrystallisation from ethyl acetate–light petroleum gave needles, m.p. 120—124° (Found: M^+, 288.209. $C_{19}H_{28}O_2$ requires M, 288.209); δ 1.04 (s, 20-H_3), 1.11 (s, 19-H_3), 1.26 (s, 18-H_3), 2.87 (d, J 4 Hz, 3-H), and 3.28 (m, $W_{\frac{1}{2}}$ 10 Hz, 2-H); $\nu_{max.}$ 1 740, 910, 896, and 840 cm^{-1}.

Acidic Hydrolysis of the Epoxide (31).—The epoxide (30) (70 mg) in tetrahydrofuran (8 ml) was stirred with M-sulphuric acid (1.5 ml) at 20 °C for 12 h; t.l.c. then showed the absence of starting material. The solution was concentrated under vacuum, added to water, and neutralised with aqueous sodium hydrogen carbonate. Isolation with ethyl acetate followed by p.l.c. in ethyl acetate–chloroform (2 : 3) and elution of the band at R_F 0.15 gave ent-2α,3β-*dihydroxy*-17-*norkauran*-16-*one* (38) (42 mg), which crystallised from chloroform–light petroleum as needles, m.p. 175—178° (Found: M^+, 306.220. $C_{19}H_{30}O_3$ requires M, 306.219); δ (C_5D_5N) 1.07 and 1.10 (both s, 19- and 20-H_3), 1.24 (s, 18-H_3), 3.34 (d, J 10 Hz, 3-H), and 4.10 (m, $W_{\frac{1}{2}}$ 26 Hz, 2-H); $\nu_{max.}$ 3 590, 3 460, and 1 740 cm^{-1}; *m/e* (for bis-Me_3Si ether) 450 (M^+, 6%), 435 (7), 360 (5), 347 (13), 306 (43), 271 (52), 217 (37), 157 (67), 147 (73), 143 (80), 109 (62), and 73 (100).

Grignard Reaction of ent-2β,3β-*Epoxykaur*-16-*en*-19-*ol* (13).—The epoxide (13) (100 mg) was dissolved in dry benzene (20 ml) and the apparatus was flushed with nitrogen. 0.12M-Methylmagnesium iodide in ether (12 ml) was added from a syringe. The mixture was refluxed for 4 h then allowed to cool and cautiously added to ammonium chloride (2 g) in water (20 ml). The benzene was removed under vacuum and more water was added; extraction into ethyl acetate gave the crude product (244 mg). Analytical t.l.c. showed one spot corresponding in R_F value with *ent*-kaur-16-ene-3β,19-diol (19), and p.l.c. in ethyl acetate–light petroleum (1 : 1) yielded one band. Subsequent g.l.c. and n.m.r. showed this band (80 mg) to be a 3 : 1 mixture. The minor component was identified as the diol (19) by g.l.c.–mass spectrometry. Fractional crystallisation from ethyl acetate gave the major product, ent-A-*nor*-2ξ-(1-*hydroxyethyl*)*kaur*-16-*en*-19-*ol* (45) as needles, m.p. 203—205° (Found: C, 78.9; H, 11.1%; M^+, 318.254. $C_{21}H_{34}O_2$ requires C, 79.2; H, 10.8%; M, 318.256); δ 1.06 (s, 20-H_3), 1.12 (s, 19-H_3), 1.16 (d, J 6 Hz, 2′-H_3), 2.65br (13-H), 3.26 and 3.52 (J_{AB} 10 Hz, 19-H_2), 3.66 (m, J 9 and 6 Hz, 1′-H), and 4.78br (17-H_2); $\nu_{max.}$ 3 625, 3 460, 1 658, and 880 cm^{-1}.

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