973. *New Metabolites of* Gibberella fujikuroi. *Part VI.*[1] *Studies with (−)-Kaurene.*

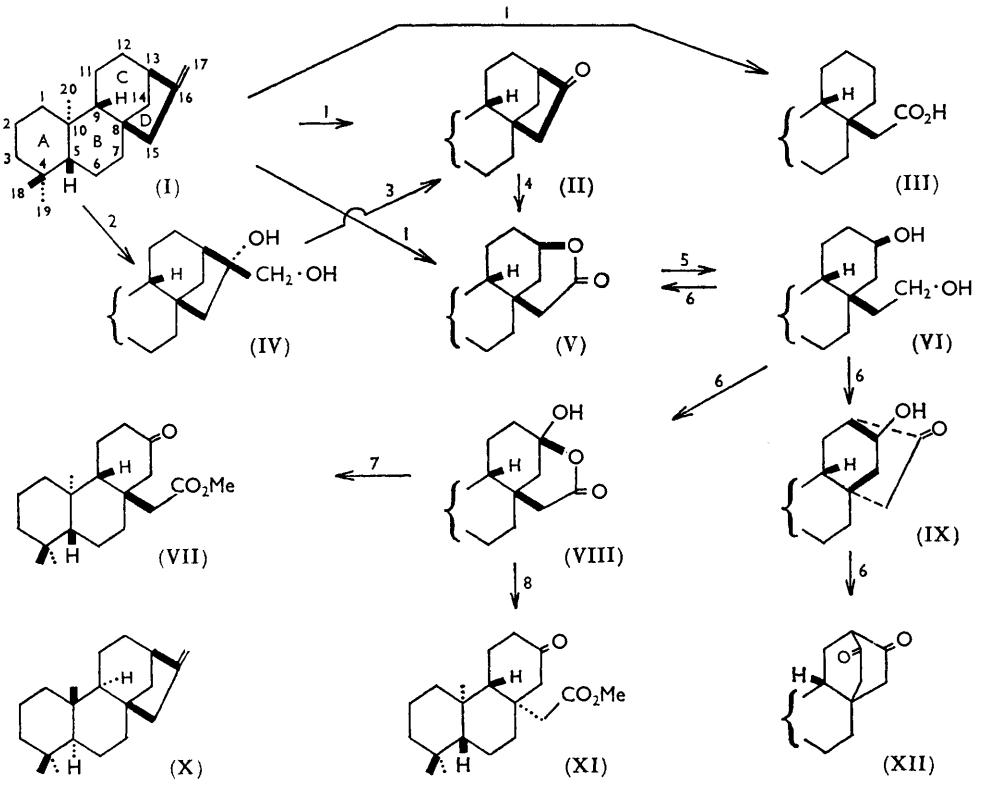
By J. R. Hanson.

(−)-Kaurene has been degraded to a keto-ester which is enantiomeric with a compound derived from (+)-phyllocladene. (−)-Kauranol is shown to have a 16α-hydroxyl group.

Both *trans-anti-cis-* and *trans-anti-trans*-skeletons exist amongst the tetracyclic diterpenes. However, the predominant stereochemistry now appears to be that of the *cis*-B/C fusion of (−)-kaurene to which the diterpene alkaloids of the atisine [2] and garryfoline [3] group, (−)-kauranol,[4,5] the kaurenolides,[5,6] and steviol [7] have been related. Cafestol,[8] the gibberellins,[9] and the grayanotoxins,[10] with an identical B/C/D ring fusion, have an obvious biogenetic relationship. As part of the problem of determining the structure and stereochemistry of the kaurenolides,[6,11] we turned our attention to the then (1960) unproved stereochemistry of (−)-kaurene. In this paper we detail our work on the hydrocarbon, some of which has been described in a preliminary communication.[12]

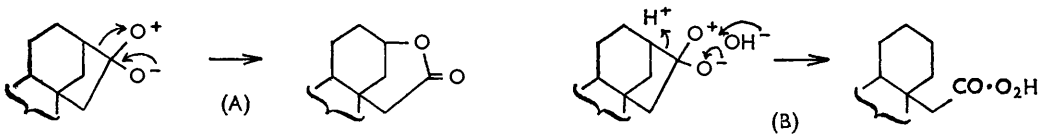
The isolation of (−)-kaurene (I) from *Gibberella fujikuroi* (Saw) Wr. ACC.917 has been described.[5] Ozonolysis of (−)-kaurene in glacial acetic acid [13] gave, as the major product, 17-nor-(−)-kauran-16-one (II) ($\nu_{max.}$ 1745 cm.$^{-1}$), which showed a positive Cotton effect in the optical rotatory dispersion curve.[6,13] Amongst the other products of ozonolysis was a δ-lactone (V) ($\nu_{max.}$ 1724, 1216 cm.$^{-1}$), identical with the product of Baeyer–Villiger oxidation of the nor-ketone. A monobasic acid, $C_{19}H_{32}O_2$ ($\nu_{max.}$ 2667, 1704 cm.$^{-1}$), which was saturated and hence tricarbocyclic, was also isolated from the ozonolysis and has been assigned structure (III). Although we could not exclude the possibility of Baeyer–Villiger oxidation during this reaction, these by-products could arise [14] from rearrangement

[1] Part V, Cross, Galt, and Hanson, 1963, 5052.
[2] Pelletier, *Tetrahedron*, 1961, **14**, 76; Dvornik and Edwards, *ibid.*, p. 54.
[3] Vorbrueggen and Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 2990.
[4] McGimpsey and Murray, *J. Appl. Chem.*, 1960, **10**, 340.
[5] Cross, Galt, Hanson, Grove, Morrison, and Curtis, *J.*, 1963, 2937.
[6] Cross, Galt, and Hanson, *J.*, 1963, 2944, 3783.
[7] Djerassi, Quitt, Mosettig, Cambie, Rutledge, and Briggs, *J. Amer. Chem. Soc.*, 1961, **83**, 3720.
[8] Scott, Sim, Ferguson, Young, and McCapra, *J. Amer. Chem. Soc.*, 1962, **84**, 3197.
[9] McCapra, Scott, Sim, and Young, *Proc. Chem. Soc.*, 1962, 185; Bourn, Grove, Mulholland, Tidd, and Klyne, *J.*, 1963, 154.
[10] Kakisawa, Yanai, Kozima, Nakanishi, and Mishima, *Tetrahedron Letters*, 1962, 115; Tallent, *J. Org. Chem.*, 1962, **27**, 2968.
[11] Cross, Galt, Hanson, and Klyne, *Tetrahedron Letters*, 1962, 145.
[12] Cross, Hanson, Briggs, Cambie, and Rutledge, *Proc. Chem. Soc.*, 1963, 17.
[13] Briggs, Cain, Davis, and Wilmhurst, *Tetrahedron Letters*, 1959, No. 8, 8 *et seq.*
[14] Cf. Bailey, *Chem. Rev.*, 1958, **58**, 925.



1, O_3; 2, OsO_4; 3, $NaIO_4$; 4, $Ph{\cdot}CO_3H$; 5, $LiAlH_4$; 6, CrO_3–H_2SO_4; 7, K_2CO_3–MeI; 8, NaOMe–MeI.

of the zwitterions (A) and (B) and, in the case of the latter, subsequent decomposition of the per-acid.



Treatment of kaurene in ether–pyridine with osmium tetroxide gave (—)-kaurane-16α,17-diol (IV) ($\nu_{max.}$ 3350 cm.$^{-1}$) in which hydroxylation was assumed to have taken place from the less hindered α-face of the molecule to form the 16α-hydroxy-derivative.[15] Cleavage of the diol with sodium periodate in aqueous methanol gave 17-nor-(—)-kauran-16-one (II).

The δ-lactone (V) was prepared in quantity by Baeyer–Villiger oxidation of the 17-nor-ketone with perbenzoic acid catalysed by toluene-*p*-sulphonic acid. Migration of the more highly substituted bond under these conditions has been observed in the oxidation of camphor [16] and in the degradation [17] of gibberellin A_7. However the free acid could not be obtained pure by alkaline hydrolysis of the lactone: refluxing with sodium hydroxide and cautious acidification at 0° followed by rapid working-up returned the starting material. Similar difficulties have recently been observed in the related degradation of veatchine.[3,18] This was avoided by reduction of the lactone with lithium aluminium hydride to the diol

[15] Cf. Briggs, Cain, Cambie, and Davis, *J.*, 1962, 1840.
[16] Cf. Sauers and Ahearn, *J. Amer. Chem. Soc.*, 1961, **83**, 2759.
[17] Cross, Galt, and Hanson, *Tetrahedron*, 1962, **18**, 451.
[18] Cf. Djerassi and Finnegan, *J. Amer. Chem. Soc.*, 1960, **82**, 4342.

(VI) ($\nu_{max.}$ 3255 cm.$^{-1}$) which on oxidation in acetone solution with 8N-chromium trioxide in sulphuric acid afforded a hydroxy-lactone (VIII) ($\nu_{max.}$ 3350, 1703 cm.$^{-1}$) as the major product. The δ-lactone (V) and a monohydroxy-ketone, $C_{19}H_{30}O_2$, were isolated as minor products of this oxidation.

The hydroxy-ketone ($\nu_{max.}$ 3450, 1710 cm.$^{-1}$) showed no significant end-absorption in the ultraviolet region, and resonances which might be ascribed to olefinic protons were absent from its nuclear magnetic resonance spectrum; hence the compound was tetracarbocyclic. Further analysis of this spectrum suggested the presence of a secondary alcohol (one-proton multiplet, τ 5·9) together with a ketone flanked by an α-methylene group (τ 7·7) and an α-methine proton (τ 7·15). On oxidation the hydroxy-ketone formed a diketone ($\nu_{max.}$ 1740, 1721 cm.$^{-1}$), the nuclear magnetic resonance spectrum of which, whilst excluding the presence of an aldehyde, showed a one-proton triplet at τ 6·8 (*J* 3 c./sec.) due to the system $-CH_2-CH(CO-)_2$. It followed that the hydroxy-ketone had the atisine skeleton (IX) arising by an internal aldol condensation of a keto-aldehyde formed during the oxidation and related to the intermediate in the inversion of the acetic acid side-chain (see below).

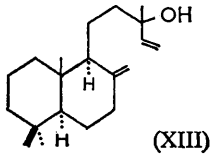
The hydroxy-lactone (VIII) could not be methylated by ethereal diazomethane. However, the methyl ester (VII) was obtained by refluxing it with methyl iodide in dry acetone in the presence of two mol. of potassium hydroxide. This keto-ester had m. p. 128—129° and infrared absorption at 1733, 1706 cm.$^{-1}$. On methylation with methyl iodide in methanol in the presence of an excess of sodium methoxide, an isomeric methyl ester (XI) was isolated (m. p. 178—179·5°; $\nu_{max.}$ 1738, 1711 cm.$^{-1}$), whose optical rotatory dispersion curve displayed a negative Cotton effect. This ester was shown to be the optical enantiomer of a degradation product of (+)-phyllocladene (X) kindly supplied by Drs. R. C. Cambie and P. S. Rutledge of the University of Auckland.[12] The infrared spectra were identical in solution and in Nujol mull, and the optical rotatory dispersion curves were mirror images. This example of the inversion of the acetic acid side-chain is analogous to the rearrangement of some degradation products of allogibberic acid in which a 1,3-diketone intermediate has been isolated.[19,20] The relation to phyllocladene proved the antipodal nature of the A/B ring fusion in (—)-kaurene and the position of the angular methyl group, and it links the (—)-kaurene group of diterpenes, not only with (+)-phyllocladene, but also with the bicyclic diterpenes of the manöol series. Edwards *et al.* have recently reported [21] a similar link between podocarpic acid and a degradation product of the alkaloid atisine.

Before the relationship with phyllocladene was complete, an attempt was made to remove the ring D (C-15 and C-16) of (—)-kaurene in the hope of achieving a similar link with a degradation product [22] or (+)-manöol (XIII). Isomerisation of kaurene with methanolic sulphuric acid gave (—)-isokaurene and the methyl ether (XIV) as a minor product. Hydroxylation of isokaurene with osmium tetroxide gave the 15,16-diol (XV) which, on oxidation with lead tetra-acetate in benzene followed by crystallisation of the gummy residue from methanol, gave a triether $C_{22}H_{38}O_3$. The structure of this ether followed from its nuclear magnetic resonance spectrum which showed resonances at τ 6·81 and 6·59 due to two methoxyl groups and a deshielded $\geq C-CH_3$ resonance at τ 8·77, in addition to the three at τ 9·16, 9·14, and 8·96 and a sharp singlet at τ 6·09 due to $\begin{matrix} O \\ C \end{matrix}\!>\!CH\cdot O$, leading to the internal ketal structure (XVII) for the ether.

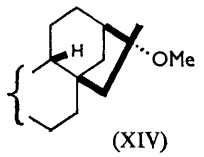
The hydrated terminal methylene group, as in phyllocladanol [23] and gibberellin A_2,[24]

[19] Grove and Mulholland, *J.*, 1960, 3007.
[20] Hanson, unpublished work.
[21] ApSimon and Edwards, *Canad. J. Chem.*, 1962, **40**, 896.
[22] Grant and Hodges, *Tetrahedron*, 1960, **8**, 261.
[23] Kondo, Immaura, and Suda, *Bull. Agric. Chem. Soc. Japan*, 1960, **24**, 65.
[24] Takahashi, Seta, Kitamura, Kawarada, and Sumiki, *Bull. Agric. Chem. Soc. Japan*, 1957, **21**, 75; Grove, *J.*, 1961, 3545.

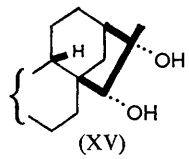
is a characteristic feature of the tetracyclic diterpenes. (—)-Kauranol,[4] which has also been isolated[5] from *Gibberella fujikuroi*, was of undefined stereochemistry at C-16.



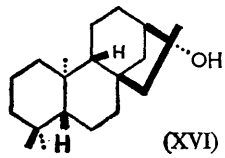
(XIII)



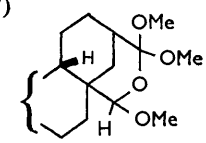
(XIV)



(XV)



(XVI)



(XVII)

Epoxidation of (—)-kaurene gave a monoepoxide which, in view of the pattern of hydrogenation, was assumed to be the 16α-epoxide, *i.e.*, attack of perbenzoic acid from the less hindered α-face. Reduction of this epoxide with lithium aluminium hydride gave (—)-kauranol which must therefore have the 16α-hydroxyl group (XVI).* Treatment with mineral acid gave the diol (IV).

Experimental

M. p.s were determined on a Kofler block and are corrected. Infrared spectra were determined for Nujol mulls on a Perkin–Elmer 221 spectrometer and nuclear magnetic resonance spectra in chloroform solution on a Varian Associates A.60 spectrometer with tetramethylsilane as an internal reference. Alumina for chromatography was acid-washed Woelm's grade II. Light petroleum refers to the fraction b. p. 60—80°. Extracts were dried over Na_2SO_4.

(—)-Kaurene, m. p. 50—50·5°, $[\alpha]_D$ −80°, $\nu_{max.}$ 3065, 1657, and 870 cm.$^{-1}$, used for this work was isolated from *Gibberella fujikuroi*.[5]

Ozonolysis of (—)-*Kaurene* (I).—Ozonised oxygen (15 mg. of O_3 per min.) was passed through (—)-kaurene (600 mg.) in acetic acid (15 ml.) for 6 min. The acetic acid was evaporated at the water-pump, and the residue was diluted with water, neutralised with sodium hydrogen carbonate, and extracted with ether. The extract was washed with water, dried, and evaporated to give a semi-crystalline residue. This was 17-nor-(—)-kauran-16-one (II) (405 mg.) which crystallised from methanol as plates, m. p. 114—116° (lit.,[13] 114—115°) (Found: C, 83·0; H, 11·0. Calc. for: $C_{19}H_{30}O$: C, 83·15; H, 11·0%), $\nu_{max.}$ 1745 cm.$^{-1}$. Chromatography on alumina and elution with 1 : 3 ethyl acetate–light petroleum gave 7β-*hydroxy*-(—)-*podocarpan*-14β-*ylacetic acid lactone* (V) (35 mg.) which crystallised from light petroleum as needles, m. p. 146—148° (Found: C, 78·2; H, 10·5. $C_{19}H_{30}O_2$ requires C, 78·6; H, 10·4%), $\nu_{max.}$ 1724, 1216 cm.$^{-1}$.

The aqueous phase was acidified with dilute hydrochloric acid, and the organic material recovered in ether and chromatographed on silica gel. Elution with 3 : 17 ethyl acetate–light petroleum gave (—)-*podocarpan*-14β-*ylacetic acid* (III) (46 mg.) which crystallised from acetone–light petroleum as needles, m. p. 144—145° (Found: C, 77·75; H, 11·0. $C_{19}H_{32}O_2$ requires C, 78·0; H, 11·0%), $\nu_{max.}$ 2667 and 1704 cm.$^{-1}$.

Baeyer–Villiger Oxidation of 17-*Nor*-(—)-*kauran*-16-*one* (II).—The nor-ketone (400 mg.) in a 0·7N-solution of perbenzoic acid in chloroform (10 ml.) containing toluene-*p*-sulphonic acid (15 mg.) was kept at 0° for 18 hr. The solution was diluted with chloroform and extracted with aqueous ferrous sulphate, dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water. Recovery gave a crystalline residue which was recrystallised from light petroleum to give the above δ-lactone (V) (350 mg.) as needles, m. p. 147—148°, identified by its infrared spectrum.

The lactone (55 mg.) in methanol (2 ml.) was heated under reflux with 0·5N-sodium hydroxide for 2 hr. The solution was diluted with a large excess of water and extracted with ether. The aqueous phase was cooled to 0°, cautiously acidified, and again extracted, this time with ethyl acetate. After drying and evaporation at 30° the gum was treated with ethereal diazomethane and chromatographed on alumina, to give the starting material (35 mg.).

* Dr. R. C. Cambie has kindly informed us that he has reached the same conclusion.

Hydroxylation of (−)-*Kaurene* (I).—Osmium tetroxide (500 mg.) was added to a solution of (−)-kaurene (350 mg.) in ether (10 ml.) and pyridine (5 ml.). The brown suspension was kept at 0° for 18 hr., diluted with ether to 100 ml., and treated with a solution of mannitol (5 g.) and potassium hydroxide (5 g.) in water (50 ml.). The mixture was refluxed for 2 hr. The organic phase was separated and the aqueous phase extracted with ether. The combined extracts were washed with dilute hydrochloric acid and water and dried. The solvent was evaporated and the residue crystallised from acetone, to give (−)-*kaurane*-16α,17-*diol* (IV) (310 mg.) as needles, m. p. 189—190° (Found: C, 75·8; H, 11·4. $C_{20}H_{34}O_2,0{\cdot}5H_2O$ requires C, 76·1; H, 11·2%), $\nu_{max.}$ 3370br cm.$^{-1}$.

Oxidation of Kaurane-16α,17-*diol with Sodium Periodate.*—The diol (250 mg.) in methanol (15 ml.) was treated with sodium periodate (500 mg.) in water (5 ml.) at room temperature for 18 hr. The solution was concentrated and then diluted with water and extracted with ether. The extract was washed with water, dried, and evaporated. The residue crystallised from methanol as plates of 17-nor-(−)-kauran-16-one (190 mg.), m. p. 115—116°, identical with the sample described above.

Reduction of the δ-*Lactone* (V).—The lactone (V) (244 mg.) in dry ether (15 ml.) was refluxed with lithium aluminium hydride (245 mg.) for 2·5 hr., then cooled and the excess of reagent was destroyed with ethyl acetate followed by water. The aqueous phase was extracted with ether and the combined ether extracts were washed with dilute hydrochloric acid and water and dried. The solvent was evaporated and the residue chromatographed on alumina. Elution with ether gave 13,16-*seco*-17-*nor*-(−)-*kaurane*-13β,16-*diol* (VI) (169 mg.) which crystallised from light petroleum as needles, m. p. 155—156° (Found: C, 77·4; H, 11·8. $C_{19}H_{34}O_2$ requires C, 77·5; H, 11·6%), $\nu_{max.}$ 3255 (OH) cm.$^{-1}$.

Oxidation of the Diol (VI).—The diol (210 mg.) in acetone (5 ml.) was treated at room temperature for 1 hr. with a solution (0·5 ml.) prepared from chromic oxide (26·67 g.) in concentrated sulphuric acid (23 ml.) and water (40 ml.) made up to 100 ml.[25] Methanol was added and the solution concentrated, diluted with water, and extracted with ethyl acetate. The extract was washed with water, dried, and evaporated, to give a semi-crystalline residue of 13-*oxo*-13,16-*seco*-17-*nor*-(−)-*kauran*-16-*oic acid* (16 ⟶ 13-*lactone form*) (VIII) (91 mg.) which crystallised from light petroleum as needles, m. p. 131—135° (Found: C, 75·1; H, 10·1. $C_{19}H_{30}O_3$ requires C, 74·5; H, 9·9%), $\nu_{max.}$ 3350 (OH of hydroxy-lactone), 1703 (C=O of lactone) cm.$^{-1}$. The product could not be methylated with ethereal diazomethane. The residue was chromatographed on silica gel. Elution with 1 : 9 ether–light petroleum gave the above δ-lactone (V) (10 mg.); further elution with 7 : 13 ethyl acetate–light petroleum gave the *hydroxy-ketone* (IX) (34 mg.) which crystallised from acetone–light petroleum as needles, m. p. 196—197° (Found: C, 78·3; H, 10·45. $C_{19}H_{30}O_2$ requires C, 78·6; H, 10·4%), $\nu_{max.}$ 3450 (OH), 1710 (cyclohexanone) cm.$^{-1}$, nuclear magnetic resonance (n.m.r.) peaks at τ 9·3, 9·2, 8·8 ($\geq C{-}CH_3$), 8·6—8·1 (ring protons), 7·7 ($CH_2{\cdot}CO$), 7·15 (multiplet) (CH·CO), 6·4 (OH), 5·9 (multiplet) ($\geq CH{\cdot}OH$).

Oxidation of the Hydroxy-ketone (IX).—The hydroxy-ketone (94 mg.) in acetone (3 ml.) was treated with the above chromic oxide reagent (0·1 ml.) at room temperature for 1 hr. The solution was concentrated, then diluted with water and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate and water and dried. The solvent was evaporated, giving a gum which crystallised from acetone as needles (58 mg.) of the *diketone* (XII), m. p. 210—211° (Found: C, 79·5; H, 9·7. $C_{19}H_{28}O_2$ requires C, 79·1; H, 9·8%), $\nu_{max.}$ 1740, 1721 cm.$^{-1}$, n.m.r. peaks at τ 9·18, 9·15, 9·12, 7·8, 6·8 (triplet, J 3 c./sec.).

Alkaline Hydrolysis of the Hydroxy-lactone (VIII).—(*a*) The compound (50 mg.) in pure acetone (5 ml.) was refluxed with methyl iodide (0·4 ml.) and potassium hydroxide (25 mg.) for 3 hr. The solution was concentrated, diluted with water, acidified with dilute hydrochloric acid, and extracted with ether. The extract was washed with sodium hydrogen carbonate solution and water and dried. The solvent was evaporated and the residue crystallised from light petroleum to give *methyl* 7-*oxo*-(−)-*podocarpan*-14β-*yl acetate* (VII) (25 mg.) as needles, m. p. 128—129° (Found: C, 74·3; H, 10·2. $C_{30}H_{32}O_3$ requires C, 74·9; H, 10·1%), $\nu_{max.}$ 1733, 1706 (ester and cyclohexanone) cm.$^{-1}$.

(*b*) The hydroxy-lactone (208 mg.) and methyl iodide (0·5 ml.) were added to a solution of sodium (53 mg.) in methanol (10 ml.) and refluxed for 4·5 hr. and the solution was then concentrated *in vacuo*. The residue was diluted with water and extracted with ether. The extract

[25] Curtis, Heilbron, Jones, and Woods, *J.*, 1953, 457.

was washed with dilute hydrochloric acid and water and dried. Evaporation of the solvent gave a residue which was chromatographed successively on silica and then alumina. Elution with 1 : 9 ethyl acetate–light petroleum gave *methyl 7-oxo-(−)-podocarpan-14α-yl acetate* (XI) (74 mg.) which crystallised from acetone as needles, m. p. 178—179·5° $[\alpha]_D^{20}$ −24° (*c* 0·2) (Found: C, 75·2; H, 10·0. $C_{20}H_{32}O_3$ requires C, 74·9; H, 10·1%), $\nu_{max.}$ 1738 and 1711 cm.$^{-1}$. The infrared spectra for a chloroform solution and a Nujol mull were identical with those of the corresponding enantiomer [12] from phyllocladene. However the mixed m. p. was depressed to 150—156°. Rotatory dispersion curve: values are for [*M*] in methanol; negative Cotton effect curve; (600 mμ) −50°; (312, trough) −3200°; (275) +3500°.

Isomerisation of (−)-Kaurene.—(−)-Kaurene (450 mg.) in methanol (25 ml.) was treated with concentrated sulphuric acid (2·5 ml.) at 0° for 18 hr. The solution was concentrated *in vacuo*, diluted with water, and extracted with ether. The extract was dried and evaporated and the residue crystallised from ethanol, to give (−)-isokaurene (210 mg.), m. p. 63°. Chromatography of the residue on alumina and elution with light petroleum gave a mixture of kaurene and isokaurene, m. p. 51—55°; further elution gave *16-methoxy-(−)-kaurene* (XIV) (39 mg.) which crystallised from acetone as needles, m. p. 97—98° (Found: C, 83·4; H, 11·9. $C_{21}H_{36}O$ requires C, 82·8; H, 11·9%).

Hydroxylation of Isokaurene.—Isokaurene (0·75 g.) in dry ether (45 ml.) containing pyridine (5 ml.) was treated with osmium tetroxide (1 g.) at 0° for 18 hr. The solution was then refluxed with mannitol (15 g.), potassium hydroxide (15 g.), ethanol (100 ml.), and water (100 ml.) for 1 hr. The organic solvents were removed *in vacuo* and the solution extracted with ether. The extract was washed with sodium hydroxide solution, dilute hydrochloric acid, and water and dried. The solvent was evaporated to give a semi-crystalline residue (0·5 g.) which was chromatographed on alumina. Elution with 3 : 17 ethyl acetate–light petroleum gave (−)-*kaurane-15α,16α-diol* (XV) (240 mg.) which crystallised from acetone–light petroleum as needles, m. p. 174—175° (Found: C, 7·80; H, 11·3. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%).

Oxidation of the Diol (XV) *by Lead Tetra-acetate.*—The diol (200 mg.) in acetic acid (10 ml.) was refluxed with lead tetra-acetate (500 mg.) for 3 hr. The solution was poured into water and extracted with ether. The extract was washed with aqueous sodium hydrogen sulphite, sodium hydrogen carbonate solution, and water, and dried. Evaporation furnished a gum which was crystallised from methanol to give the *diether* (XVII) (100 mg.) as needles, m. p. 124—125° (Found: C, 75·7; H, 10·95. $C_{22}H_{38}O_3$ requires C, 75·4; H, 10·9%), n.m.r. (40 Mc./sec. instrument) peaks at τ 9·16, 9·14, 8·96, and 8·77 ($4\gtrless C-CH_3$), 6·81 and 6·59 (MeO), and 6·09 [$CH(O)_2$].

Epoxidation of (−)-Kaurene.—(−)-Kaurene (250 mg.) was dissolved in a 0·7N-solution of perbenzoic acid in chloroform (5 ml.) and kept at 0° for 24 hr. The solution was diluted with chloroform and extracted with aqueous ferrous sulphate, water, sodium hydrogen carbonate solution, and again water, and dried. The solvent was evaporated and the residue crystallised from methanol, to give *16α,17-epoxy-(−)-kaurane* (156 mg.), as needles m. p. 113—115° (Found: C, 83·3; H, 11·2. $C_{20}H_{32}O$ requires C, 83·3; H, 11·2%).

Reduction of Kaurene Epoxide.—The epoxide (100 mg.) in dry ether (15 ml.) was heated under reflux with lithium aluminium hydride (200 mg.) for 4 hr. The excess of reagent was destroyed by ethyl acetate followed by dilute hydrochloric acid. The solution was extracted with ether, and the extract washed with water and dried. Evaporation of the solvent and crystallisation of the residue from acetone–light petroleum gave (−)-kauranol (XVI) (52 mg.) as needles, m. p. 212—214°, $[\alpha]_D^{20}$ −40° (*c* 0·3).

Treatment of (−)-Kaurene Epoxide with Mineral Acid.—The epoxide (10 mg.) in methanol (1 ml.) was refluxed with dilute hydrochloric acid (10 ml.) for 5 hr. The solution was diluted with water, and the organic material recovered with ether, to give a gum which crystallised from acetone–light petroleum as needles of (−)-kaurane-16α,17-diol (IV) (4 mg.), m. p. 189—190°, identified by the infrared spectrum.

I thank Professor W. Klyne and Miss J. Jackson for the optical rotatory dispersion measurements, Mr. B. K. Tidd for the nuclear magnetic resonance spectra, Drs. B. E. Cross and R. H. B. Galt for helpful discussion, and Mr. P. L. Hazell for technical assistance.

Imperial Chemical Industries Limited, Akers Research Laboratories,
The Frythe, Welwyn, Herts. [*Received, March 25th,* 1963.]