Structures of Four New Triterpenes from the Rhizomes of *Polypodium juglandifolium*

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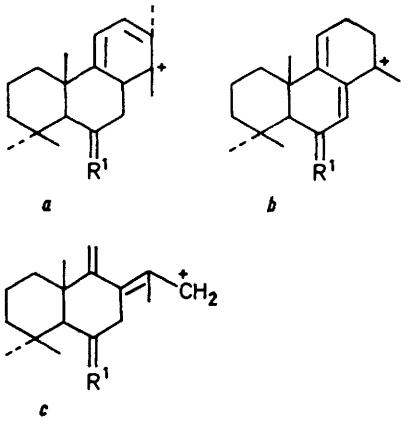
Four new triterpenes isolated from the rhizomes of *Polypodium juglandifolium* have been identified on the basis of chemical and spectral evidence as fern-9(11)-en-6α-ol (I), fern-9(11)-en-20β-ol (III), 24,24-dimethyl-9,19-cyclolanost-25-en-3β-ol (V), and hopan-29-ol (VII). The acetates of the last two compounds occur in the same plant material.

No report of chemical work on the fern *Polypodium juglandifolium* H. B. Willd. has appeared so far. From the petroleum extract of the rhizomes of this plant, by an elaborate process of chromatography, we have isolated six crystalline compounds (A—F in order of separation). Subsequently B and C turned out to be the acetates of E and F, respectively. Compounds A, D, E, and F were identified as triterpenes from their colour reactions and spectral properties. The tetranitromethane colour reaction showed that all except F (and its acetate C) were unsaturated.

Compound A, $C_{30}H_{50}O$, an alcohol, resisted acetylation with acetic anhydride–pyridine at room temperature but gave an acetate on heating with this reagent. It was not oxidised by chromic oxide–pyridine but was by chromic oxide–sulphuric acid. The mass spectral fragmentation of the resulting ketone showed that it could be a fernene or arborene derivative with an 8,9- or 9,11-double bond.[1] The ketone gave under Huang-Minlon conditions a hydrocarbon identified as fern-9(11)-ene. The i.r. spectrum of the ketone showed that the carbonyl group was present in a six-membered ring. The fragments *a*—*c* in the mass spectrum restricted the choice to rings A and B. The resistance offered by compound A to acetylation and oxidation showed that the hydroxy-group was at position 6 or 7. On treatment with phosphoryl chloride–pyridine at low temperature compound A lost a molecule of water. The product (anhydro-A) did not show u.v. absorption characteristic of a conjugated diene but when treated with warm 1% sulphuric acid in acetic acid for a short time it was changed into an isomer having u.v. absorption typical of a 6,8-diene. These observations ruled out position 7 and indicated position 6 as the location of the hydroxy-group. In the n.m.r. spectrum of compound A the $W_{\frac{1}{2}}$ value of the C*H*·OH signal showed that this proton is axial (β), so that compound A may be identified as fern-9(11)-en-6α-ol (I). The easy dehydration referred to earlier may be attributed to the molecular strain resulting from the

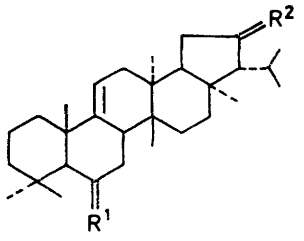


interaction between the 6α-OH and the 4α-Me group, which is relieved on dehydration. For the conjugated diene other likely structures [$\Delta^{5,7}$ and $\Delta^{7,9(11)}$] were ruled out on the basis of the observed $\lambda_{max.}$ value. The original anhydro-A may have the $\Delta^{6,9(11)}$-structure.

Compound D, $C_{30}H_{50}O$, could be easily acetylated with acetic anhydride–pyridine, and oxidised with chromic oxide in either pyridine or sulphuric acid at low temperature, resulting in the same ketone. The mass spectral fragmentations of the alcohol and ketone showed that they were fernene or arborene derivatives with an 8,9- or 9,11-double bond.[1] Huang-Minlon reduction of the ketone yielded a hydrocarbon identified as fern-9(11)-ene. The fragments *a*—*c* in the mass spectrum showed that the carbonyl group was in rings D or E. Since i.r. data showed the carbonyl group to be in a five-membered ring, positions 19 or 20 were possible; thus compound D would have to be a 19- or 20-alcohol. A choice was possible from a consideration of the stability of the DE

[1] K. Nishimoto, M. Ito, S. Natori, and T. Ohmoto, *Tetrahedron*, 1968, 735.

ring junction in the oxo-derivative. Fern-9(11)-ene has a *trans* DE ring fusion and the ketone from which it was

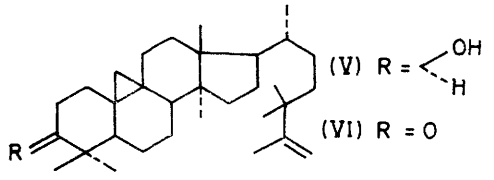


(I) R^1 =  , R^2=H_2

(II) R^1 = O, R^2 = H_2

(III) R^1 = H_2, R^2 = 

(IV) R^1 = H_2, R^2 = O



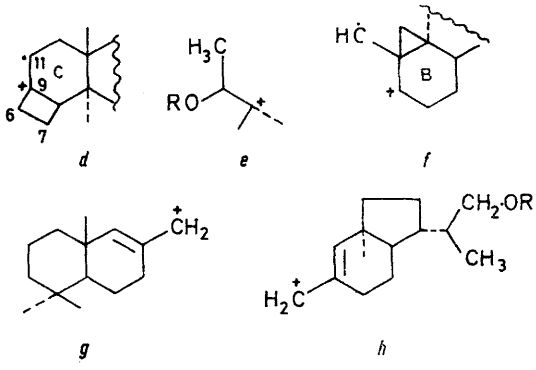
(V) R =

(VI) R = O

formed could be expected to have the same stereochemistry. A *trans* ring junction with an oxo-group adjoining it is known to be less stable than the *cis* equivalent, and would be expected to undergo isomerisation, particularly in the presence of acids.[2] The ketone was stable to both hot mineral acid and alkali. This ruled out position 19 for the oxo-group. When the ketone was reduced with sodium borohydride, two epimeric alcohols were formed. A Dreiding model showed that a 20β- (equatorial) alcohol is almost unhindered but not a 20α-alcohol. Evidently the major reduction product is the 20β-alcohol. Since the natural alcohol is identical with the major reduction product it is identified as fern-9(11)-en-20β-ol (III). This is supported by its ease of acetylation and oxidation.

Compound E, $C_{32}H_{54}O$, was an alcohol which was easily acylated. I.r. and n.m.r. spectra showed that it had a terminal methylene group which could be easily hydrogenated under catalytic conditions. N.m.r. signals at δ 0.31 and 0.54 showed that the compound has a cyclopropane ring (possibly 9,19- as in cycloartanol). The mass spectrum showed that it was a C_{32} tetracyclic triterpene with a cyclopropane ring (9,19) (see fragments *d* and *f*) and a C_{10} side chain, possibly the usual steroidal side chain with an ethyl or *gem*-dimethyl system on C-24. Since the grouping CH_3–C=CH_2 present in the parent had disappeared in the dihydro derivative (n.m.r. and i.r. evidence), the double bond was located at position 25. The alcohol was easily oxidised to the corresponding ketone. In its properties the alcohol showed general similarities to cycloneolitsol and the ketone to cyclobalanone (see Experimental section). Cycloneolitsol was synthesised by Labriola and Ourisson [3] in the course of work designed to prove the structure of cycloneolitsin,[4] which is its methyl ether and occurs in a higher plant [*Neolitsea dealbata* (Lauraceae)]. Cyclobalanone was isolated by Tachi *et al.*[5] also from a higher plant [*Quercus glauca* (syn. *Cyclobalanopsis gluaca*) (Fagaceae)]; the alcohol was also prepared by these authors by reduction of the ketone. A direct comparison of our ketone with cyclobalanone supplied by Professor Y. Tachi showed that they were identical. Our alcohol (E) showed a $W_{1/2}$ value for the C*H*OH n.m.r. signal of 13 Hz (*ax*,*ax*-coupling), which showed that the OH is equatorial. Hence this compound is 24,24-dimethyl-9,19-cyclolanost-25-en-3β-ol (V).

As will be seen from the data given in the Experimental section, the alcohol and the acetate obtained by us have m.p.s. considerably lower than those reported, though the optical rotations show general agreement. To eliminate the possibility of our alcohol being the 3α-epimer of the form (3β) reported by earlier workers, our ketone was reduced with sodium borohydride. This gave only one product, expected to have the hydroxy-group in the equatorial (3β) configuration. The m.p. of this product was close to that given by earlier workers (see Experimental section), so that it could be taken to be the 3β-compound. It had an i.r. spectrum identical with that of the lower-melting alcohol isolated as such from the plant or by saponification of the naturally occurring acetate. This observation was surprising but



d *e* *f* *g* *h*

it helped to show that our natural alcohol is also a 3β-compound, supporting the conclusion from the n.m.r. spectrum mentioned earlier. In an attempt to clinch the issue the natural (lower melting) alcohol was permethylated by Hakomori's method (NaH–Me_2SO–MeI); the methyl ether (3-*O*-methyl compound) had m.p. and optical rotation agreeing with those reported [3] (see Experimental section) for cycloneolitsin (3β-methoxy-compound). Thus there seems little doubt that the natural alcohol obtained by us is the 3β-isomer in spite

[2] G. Ourisson, P. Crabbe, and O. R. Rodig, 'Tetracyclic Triterpenes,' Hermann, London, 1964, p. 79.

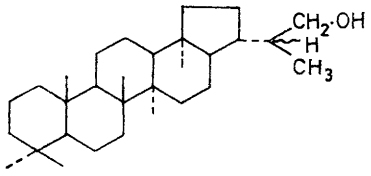
[3] R. Labriola and G. Ourisson, *Tetrahedron*, 1971, 1901.

[4] E. Ritchie, R. G. Senior, and W. C. Taylor, *Austral. J. Chem.*, 1969, **22**, 2371.

[5] Y. Tachi, S. Taga, Y. Kamano, and M. Komatsu, *Chem. and Pharm. Bull. (Japan)*, 1971, **19**, 2193.

of its lower m.p. A solution of the natural (low m.p.) alcohol in chloroform–methanol was seeded with the higher melting alcohol to see if the whole of it would now crystallise in the higher melting form. However this did not happen; instead the crystals obtained melted at 151—152°. Evidently the substance is capable of existing in more than one form. Even for the acetate, widely differing m.p.s have been reported by earlier workers. It may well be that there is an impurity not eliminated by crystallisation and not detected by t.l.c. The complete identity of the i.r. spectra of the lower and higher melting forms of the alcohol may be fortuitous.

Compound F, $C_{30}H_{52}O$, an alcohol, easily formed an acetate, but strangely showed some resistance to oxidation. The i.r. spectrum of the oxidised product (CrO_3–C_5H_5N) showed that it was an aldehyde. Owing to its sparing solubility its n.m.r. spectrum could not be taken. Further oxidation to the carboxylic acid proved difficult (CrO_3–H_2SO_4 on the alcohol or aldehyde). Reduction of the aldehyde with borohydride gave back the parent alcohol. Hence the parent alcohol appears to be primary. The CH_2OAc n.m.r. signal of the acetate confirmed this. The mass spectrum of the compound confirmed the molecular weight and the fragments *g* and *h* and the fragment *m/e* 369 [$M - CH_3CHCH_2OH$(or Ac)] provided evidence for the presence of a hopane, isohopane, or neohopane skeleton with a hydroxy-group at C-29 or 30. At this stage a synthetic approach appeared feasible, and hopan-29-ol was synthesised by hydroboration of diploptene. The resulting primary alcohol was identical with the natural alcohol. Hence compound F was hopan-29-ol (VII). Ensminger *et al.*



(VII)

prepared hopan-29-ol as an intermediate in their synthesis of homohopane.[6] However to our knowledge details of the experiments or the properties of the alcohol have not been published so far.

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage apparatus. Rotations were taken for solutions in chloroform. I.r. spectra were recorded with a Perkin-Elmer Infracord 137 instrument for KBr discs. N.m.r. spectra were taken for solutions in [^{2}H]chloroform with tetramethylsilane as internal standard and a Varian A-60 instrument.

Isolation.—The petroleum extract (4 g) of the powdered rhizomes (2 kg) was chromatographed over silica gel. Petroleum–benzene (1 : 1) eluted a mixture of three compounds, separated by re-chromatography followed by preparative t.l.c. on silica gel into A (70 mg), B (50 mg), and C (40 mg). Benzene eluted first compound D (75 mg) and later a mixture of two compounds separated by preparative t.l.c. on silica gel into E (50 mg) and F (40 mg). In a subsequent extraction from plant material collected a year later (3 kg of powder), compound A was absent and the yields of the other compounds showed considerable variation.

Compound A: Fern-9(11)-en-6α-ol (I)—This formed *needles* (from n-hexane), m.p. 241°, $[\alpha]_D$ −74.8° (*c* 0.86) (Found: C, 84.6; H, 12.0. $C_{30}H_{50}O$ requires C, 84.5; H, 11.7%), $\nu_{max.}$ 3 700, 845, and 815 cm^{-1}; δ 0.68—1.2 (8 × Me), 2.03br (OH), 4.28 (1 H, *m*, $W_{\frac{1}{2}}$ 17 Hz, C*H*·OH), and 5.36 (1 H, *m*, C=CH). The *acetate* (Ac_2O–C_5H_5N; 140 °C; 2 h) formed cubic crystals (from chloroform–methanol), m.p. 200°, $[\alpha]_D$ −84.6° (*c* 0.78) (Found: C, 81.9; H, 11.4. $C_{32}H_{52}O_2$ requires C, 82.0; H, 11.1%); $\nu_{max.}$ 1 725, 1 240, 845, and 810 cm^{-1}; δ 0.7—1.1 (8 × Me), 1.96 (Ac), 5.13 (1 H, m, C*H*·OAc), and 5.28 (1 H, m, C=CH).

The 6-Ketone (II).—An ice-cold solution of compound (I) (10 mg) in dry acetone (8 ml) was treated with Jones reagent (containing 10 mg of CrO_3) and left in the ice-bath for ½ h and then at room temperature for 3 h. The product (8 mg) crystallised from chloroform–methanol as plates, m.p. 222—223°, $[\alpha]_D$ +16.7° (*c* 0.60), $\nu_{max.}$ 1 730, 840, and 815 cm^{-1}; *m/e* 424 (M^+, 32%), 409 (M—Me, 100), 271 [(*a*; R^1 = O), 16], 257 [(*b*; R^1 = O), 10], and 245 [(*c*; R^1 = O), 10].

Deoxy-A [*Fern-9(11)-ene*].—To a solution of the ketone (II) (10 mg) in diethylene glycol (2 ml), 80% hydrazine hydrate (0.2 ml) was added, and the mixture was refluxed at 210 °C for 4 h. Potassium hydroxide (25 mg) was added and after removal of water and excess of hydrazine by distillation the mixture was refluxed for 8 h. The product was cooled and diluted with water, and the solid was filtered off, washed, dried, and crystallised as plates (from methanol), m.p. 169° (8 mg), identical with authentic fern-9(11)-ene (mixed m.p., t.l.c., and i.r. spectrum).

Anhydro-A. An ice-cold solution of the alcohol (I) (10 mg) in dry pyridine (1 ml) was treated with freshly distilled phosphoryl chloride (0.2 ml), and left in the ice-bath for ½ h and at room temperature for 2 h. The product (8 mg) crystallised from chloroform–methanol as plates, m.p. 152° (Found: C, 88.5; H, 12.0. Calc. for $C_{30}H_{48}$: C, 88.2; H, 11.8%).

Isomerisation of anhydro-A. The substance (8 mg) was warmed on a water-bath with glacial acetic acid containing 1% sulphuric acid (2 ml) till it had dissolved completely and then left at room temperature for ½ h. The product (6 mg), isolated by diluting with water and filtering, crystallized from methanol as plates, m.p. 127—129° (Found: C, 87.9; H, 12.1. Calc. for $C_{30}H_{48}$: C, 88.2; H, 11.8%); $\lambda_{max.}$ (MeOH) 269 nm (log ε 4.060) (Calc.: 273 nm).

Compound D: Fern-9(11)-en-20β-ol (III).—This formed *needles* (from chloroform–methanol), m.p. 186°, $[\alpha]_D$ −30.2° (*c* 1.29) (Found: C, 84.4; H, 11.4. $C_{30}H_{50}O$ requires C, 84.5; H, 11.7%), $\nu_{max.}$ 3 500, 835, and 810 cm^{-1}; δ 0.75—1.07 (8 × Me), 2.05br (OH), 4.33 (1 H, m, C*H*·OH), and 5.33 (1 H, m, C=CH); *m/e* 426 (M^+, 20%), 411 (M − Me, 87), 393 (411 − H_2O, 32), 257 [(*a*; R^1 = H_2), 22], 243 [(*b*; R^1 = H_2), 100], and 231 [(*c*; R^1 = H_2), 28]. The *acetate* (Ac_2O–C_5H_5N; room temp.; 16 h) formed plates (from chloroform–methanol), m.p. 201°, $[\alpha]_D$ +17.8° (*c* 0.56) (Found: C, 82.1; H, 11.4. $C_{32}H_{52}O_2$ requires C, 82.0; H, 11.1%), $\nu_{max.}$ 1 725, 1 240, 845, and 810 cm^{-1}; δ 0.7—1.07 (8 × Me), 2.01 (Ac), 5.05 (1 H, m, C*H*·OAc), and 5.25 (1 H, m, C=CH).

[6] A. Ensminger, P. Albrecht, G. Ourisson, B. J. Kimble, J. R. Maxwell, and G. Eglinton, *Tetrahedron Letters*, 1972, 3861.

The 20-*ketone* (IV). (Jones reagent, 0 °C for 1/2 h, then room temp., for 2 h; or CrO_3–C_5H_5N, room temp., 16 h) formed needles (from chloroform–methanol), m.p. 181°, $[\alpha]_D$ −100.0° (*c* 0.56) (Found: C, 85.1; H, 11.6. $C_{30}H_{48}O$ requires C, 84.9; H, 11.4%), $\nu_{max.}$ 1 745, 845, and 815 cm^{-1}; *m/e* 424 (M^+, 21%), 409 (M − Me, 100), 257 [(*a*; $R^1 = H_2$), 6], 243 [(*b*; $R^1 = H_2$), 42], and 231 [(*c*; $R^1 = H_2$), 10].

Reduction of the ketone (IV). A solution of the ketone (IV) (10 mg) in methanol–dioxan (1 : 1; 3 ml) was treated with sodium borohydride (10 mg) and set aside at room temperature for 2 h. The product (8 mg) crystallised from chloroform–methanol as needles, m.p. 185—186°, identical with compound D (III) (mixed m.p., t.l.c., and i.r. spectrum).

Deoxy-D [*fern*-9(11)-*ene*]. This was prepared from the ketone (IV) in the same manner as deoxy-A from the ketone (II). The product crystallised from methanol as plates, m.p. 166—168°, identical with authentic fern-9(11)-ene (mixed m.p., t.l.c., and i.r. spectrum).

Compound E: 24,24-*Dimethyl*-9,19-*cyclolanost*-25-*en*-3β-*ol* (V).—This formed needles (from chloroform–methanol), m.p. 120—122° (could not be improved further), $[\alpha]_D$ +42.0° (*c* 0.62) (lit.,[3] m.p. 183—185°, $[\alpha]_D$ +48°; lit.,[5] m.p. 172—173°, $[\alpha]_D$ +22°) (Found: C, 84.2; H, 12.2. Calc. for $C_{32}H_{54}O$: C, 84.5; H, 11.8%); $\nu_{max.}$ 3 450 and 885 cm^{-1}; δ 0.31 (1 H) and 0.54 (1 H) (two d, *J* 5 Hz, 19-H_2), 0.78—1.06 (7 × Me), 1.65 (*s*, CH_3–C=C), 3.20 (1 H, m, $W_{\frac{1}{2}}$ 13 Hz, C*H*·OH), and 4.70 (2 H, s, C=CH_2); *m/e* 454 (M^+, 8%), 439 (M — Me, 11), 436 ($M - H_2O$, 11), 421 (M — Me — H_2O, 19), 393 ($M - C_3H_7 - H_2O$, 11), 367 (*f*, 8), 315 (M — side chain, 24), 314 (*d*, 15), 87 [(*e*; R = H), 21], and 83 (100). The *acetate* (Ac_2O–C_5H_5N; room temp.; 16 h) formed needles (from chloroform–methanol), m.p. 111—112° (could not be improved further), identical (mixed m.p., t.l.c. and i.r. spectrum) with compound B (see later).

The 3-*ketone* (VI). An ice-cold solution of compound E (15 mg) in dry acetone (5 ml) was treated with Jones reagent (containing 15 mg of CrO_3). The product (10 mg) crystallised from methanol as plates, m.p. 186–187°, $[\alpha]_D$ + 14.0° (*c* 0.56) (lit.,[5] m.p. 187—190°; $[\alpha]_D$ + 20°) (Found: C, 84.6; H, 12.0. Calc. for $C_{32}H_{52}O$: C, 84.9; H, 11.7%); $\nu_{max.}$ 1 710 and 885 cm^{-1}, identical with authentic cyclobalanone (mixed m.p., t.l.c., and i.r. spectrum).

Reduction of the ketone (VI). A solution of the ketone (VI) (10 mg) in methanol–dioxan (1 : 1; 3 ml) was treated with sodium borohydride (10 mg) and set aside at room temperature for 4 h. The product (8 mg) crystallised from chloroform–methanol as plates, m.p. 182—184°, having the same R_F value in t.l.c. and same i.r. spectrum as the natural alcohol (of m.p. 120—122°).

Methyl ether of compound E. A mixture of sodium hydride (50% dispersion in oil; 20 mg) and dimethyl sulphoxide (4 ml) was kept at 70 °C for 1 h in an oil-bath. A solution of natural compound E (20 mg) in dimethyl sulphoxide (4 ml) was added slowly and the mixture was maintained at the same temperature for another 2 h. After cooling in ice the mixture was treated with methyl iodide (2 ml) and left overnight. The product was purified by preparative t.l.c. and crystallised from chloroform–methanol as plates, m.p. 179—182°, $[\alpha]_D$ + 72.0° (*c* 0.50) (lit.,[3] m.p. 172—174°, $[\alpha]_D$ + 63.0°); *m/e* 468 (M^+, 4%), 453 (M — Me, 8), 436 (M — MeOH, 29), 421 (M — Me — MeOH, 71), 393 (M — MeOH — C_3H_7, 19), 367 (*f*, 16), 329 (M — side chain, 6), 314 (*d*, 10), 135 (100), and 69 [(*e*; R = Me) — MeOH, 4].

Compound B (O-*Acetyl-E*).—This formed needles (from chloroform–methanol), m.p. 112—113° (could not be improved further), $[\alpha]_D$ + 48.0° (*c* 0.83) (lit.,[3] m.p. 177—181°, $[\alpha]_D$ + 58°; lit.,[5] m.p. 149—152°) (Found: C, 81.9; H, 11.6. Calc. for $C_{34}H_{56}O_2$: C, 82.2; H, 11.3%); $\nu_{max.}$ 1 725, 1 250, and 885 cm^{-1}; δ 0.30 (1 H) and 0.48 (1 H) (two d, *J* 5 Hz, 19-H_2), 0.82—1.01 (7 × Me), 1.65 (s, MeC=C), 1.95 (Ac), 4.43br (1 H, C*H*·OAc), and 4.60 (2 H, s, C=CH_2); *m/e* 496 (M^+, 5%), 481 (M — Me, 8), 436 (M — AcOH, 27), 421 (M — Me — AcOH, 27), 393 ($M - C_3H_7$ — AcOH, 16), 367 (*f*, 12) 357 (M — side chain, 7), 314 (*d*, 15), 69 [(*e*; R = Ac) — AcOH, 17] and 43 (Ac^+, 100).

Deacetylation of compound B. A solution of B (10 mg) in benzene (5 ml) was refluxed for 3 h with alcoholic 20% potassium hydroxide (5 ml). The product (8 mg), needles (from chloroform–methanol), m.p. 120—121° (could not be improved further), was identical with compound E(mixed m.p., t.l.c., and i.r. spectrum).

Dihydro-B. A solution of B (30 mg) in ethyl acetate (25 ml) was hydrogenated [10% Pd–C (15 mg)] at atmospheric pressure for 5 h. Filtration, evaporation, and crystallisation from chloroform–methanol gave plates, m.p. 122—123°, $[\alpha]_D$ + 40.0° (*c* 0.80) (Found: C, 81.6; H, 11.8. Calc. for $C_{34}H_{58}O_2$: C, 81.9; H, 11.6%), $\nu_{max.}$ 1 725 and 1 248 cm^{-1}; δ 0.33 (1 H) and 0.58 (1H) (two d, *J*5 Hz, 19–H_2), 0.73—0.97 (9 × Me), 2.0 (Ac) and 4.58 (1 H, m, C*H*·OAc).

Compound F: Hopan-29-*ol* (VII).—This formed *needles* (from chloroform–methanol), m.p. 241—242° (Found: C, 83.8; H, 11.8. $C_{30}H_{52}O$ requires C, 84.1; H, 12.1%), $\nu_{max.}$ 3 400 cm^{-1}; *m/e* 428 (M^+, 14%), 413 (M — Me, 6), 369 (M — $MeCHCH_2OH$, 10), 207 [(*h*; R = H), 4], 191 (*g*, 4), and 176 (191 — Me, 100). The *acetate* (Ac_2O–C_5H_5N; room temp.; 16 h) formed needles (from n-hexane), m.p. 200°, identical (mixed m.p., t.l.c., and i.r. spectrum), with compound C (see later).

Aldehyde from compound F. This was prepared by oxidation (CrO_3–C_5H_5N) for 1/2 h at 0 °C followed by 24 h at room temp. The *product* was purified by passing through a small column of silica gel and crystallised from chloroform; m.p. 297—300° (Found: C, 84.3; H, 11.4. $C_{30}H_{50}O$ requires C, 84.5; H, 11.7%); $\nu_{max.}$ 1 710 cm^{-1}. The aldehyde was reduced with sodium borohydride in the same manner as the ketone from compound D. The product, m.p. 240—241°, was identical with compound F (mixed m.p., t.l.c., and i.r. spectrum).

Compound C (*O-Acetyl-F*).—This formed *needles* (from n-hexane), m.p. 199—200°, $[\alpha]_D$ + 34.0° (*c* 0.83) (Found: C, 82.0; H, 11.8. $C_{32}H_{54}O_2$ requires C, 81.7; H, 11.5%); $\nu_{max.}$ 1 725 and 1 225 cm^{-1}; δ 0.77—1.01 (7 × Me), 2.08 (Ac), and 4.0 (2 H, m, CH_2·OAc); *m/e* 470 (M^+, 1%), 410 (M — AcOH, 2), 395 (410 — Me, 4), 369 (M — $MeCHCH_2$-OAc, 11), 249 [(*h*; R = Ac), 30], 191 (*g*, 20), and 189 (249 — AcOH, 100).

Deacetylation of compound C. This was performed as described for B. The product crystallised from chloroform–methanol as needles, m.p. 240—241°, identical with compound F (mixed m.p., t.l.c., and i.r. spectrum).

Synthesis of Hopan-29-*ol* (VII).—To a solution of diploptene (20 mg) in dry tetrahydrofuran (2 ml), powdered sodium borohydride (30 mg) was added, followed by freshly distilled boron trifluoride–ether complex (0.4 ml) in dry tetrahydrofuran (2 ml). The mixture was shaken, left at room temperature for 1 h, treated with aqueous 3N-sodium hydroxide (1 ml) and 30% hydrogen peroxide (1 ml), and

left at room temperature for 1 h. Water was added, the mixture was extracted with ether, and the ethereal solution was washed, dried, and evaporated. The product (18 mg) was purified by preparative t.l.c. and crystallised as needles from chloroform–methanol; m.p. 238—240°, identical with natural compound F (mixed m.p., t.l.c., and i.r. spectrum).

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