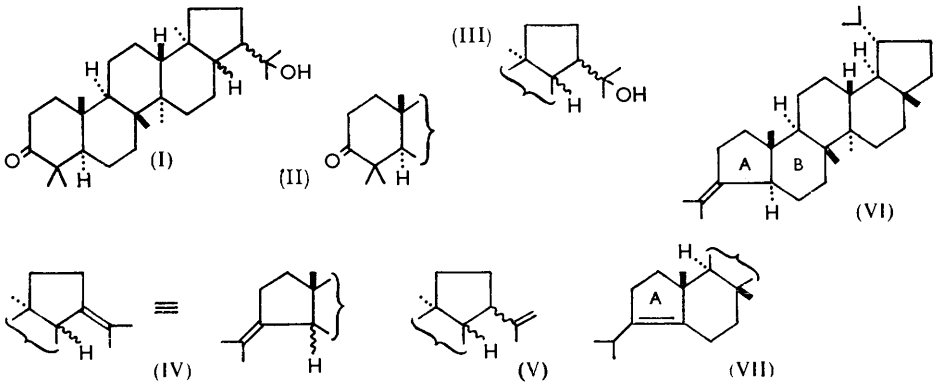
373. *The Chemistry of Triterpenes and Related Compounds. Part XXXIV.* The Structure of Hydroxyhopanone.*

By H. Fazakerley, T. G. Halsall, and E. R. H. Jones.

The structure (I) suggested [1] for hydroxyhopanone [2] has been confirmed by a study of the products of acid-catalysed isomerisation of hopenone. One of these, hopenone-I (VIII), has been prepared from γ-onocerin by Jeger and his co-workers.[3] Hydroxyhopanone is one of the few pentacyclic triterpenes biosynthesised from squalene without rearrangement of the carbon skeleton.

Structure (I) has recently been suggested [1] for hydroxyhopanone,[2] which was shown to include the structural features (II) and (III).[1] Dehydration of hydroxyhopanone with phosphoryl chloride in pyridine yielded hopenone, a mixture of the *iso*propylidene and *iso*propenyl isomers, hopenone-a (IV) and hopenone-b (V). Structure (IV) is similar to



that of γ-lupene [4] (VI) which is isomerised by acid to *iso*-γ-lupene (VII),[5,6] and in the expectation of obtaining further information about rings D and E in hydroxyhopanone acid-catalysed isomerisations were studied.

A new ketone, hopenone-I, crystallised immediately from the mixture when hopenone was treated with 8% sulphuric acid in acetic acid. A similar result was obtained with the parent hydroxyhopanone. The mother liquors from these reactions contained a lower-melting isomer, hopenone-II, which was obtained more conveniently by treating hopenone-I with 15% sulphuric acid in acetic acid. Wolff–Kishner reduction of hopenone-I gave hopene-I and from hopenone-II hopene-II was obtained with another compound (probably a hydrocarbon) which has not yet been investigated further. Hopene-II was also obtained directly by isomerisation of hopene.

The infrared spectra of hopenone-I and -II and of hopene-I and -II indicated the absence of a di- or tri-substituted double bond and it was concluded that the double bond in each compound was tetrasubstituted. The ultraviolet absorption properties are compared with those of appropriate standard substances in Table 1. The end absorption of hopenone-I and hopene-I resembles that of *iso*-γ-lupene (VII) whilst that of hopenone-II

* Part XXXIII, *J.*, 1958, 2603.

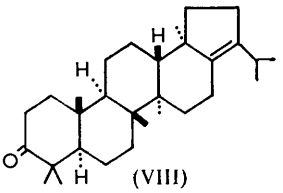
[1] Dunstan, Fazakerley, Halsall, and Jones, *Croat. Chim. Acta*, 1957, **29**, 173; cf. *Proc. Chem. Soc.*, 1957, 228.
[2] Mills and Werner, *J.*, 1955, 3132.
[3] Schaffner, Caglioti, Arigoni, and Jeger, *Helv. Chim. Acta*, 1958, **41**, 152.
[4] Heilbron, Kennedy, and Spring, *J.*, 1938, 329.
[5] Nowak, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1949, **32**, 323.
[6] Barton, de Mayo, and Orr, *J.*, 1958, 2239.

and hopene-II is similar to that of δ-amyrenone [7] which consists predominantly of olean-13(18)-en-3-one (85%), with a tetrasubstituted doubly exocyclic double bond, along with 18α-olean-12-en-3-one.[8]

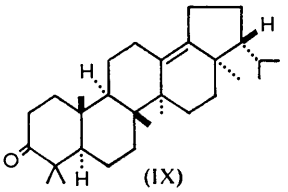
TABLE 1. *Values of* $\varepsilon_{obs.}$ *in alcohols.*

	2100 Å	2150 Å	2200 Å	$\varepsilon_{2100}/\varepsilon_{2200}$
Hopenone-I (VIII)	6250	3480	1700	3·6
Hopene-I	6950	4180	2200	3·2
iso-γ-Lupene (VII)	4950	3000	1450	3·4
Hopenone-II (IX)	9350	6050	3850	2·4
Hopene-II	8100	5700	3300	2·4
δ-Amyrenone	6220	4700	3590	1·7

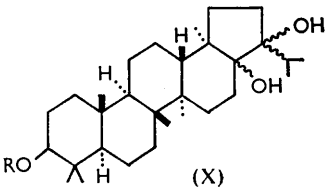
The most likely structures for hopenone-I and hopenone-II appeared to be (VIII) and (IX) although the possibility of ring E enlargement as in the sequence lupenone ⟶ lupenone-I ⟶ δ-amyrenone [7,9] could not be excluded.



(VIII)



(IX)



(X)

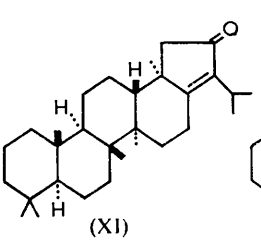
Treatment of hopenone-I with osmium tetroxide followed by reduction with lithium aluminium hydride gave as the main product a triol (X; R = H). This formed only a monoacetate, consistent with the presence of two tertiary hydroxyl groups derived from a tetrasubstituted double bond in hopenone-I. Treatment of the triol monoacetate with lead tetra-acetate gave a diketone having a strong infrared band at 1708 cm.$^{-1}$ due to two carbonyl groups and a medium band at 1403 cm.$^{-1}$ indicative of the methylene of a $-CH_2 \cdot CO-$ group. These data are consistent with structure (VIII) for hopenone-I.

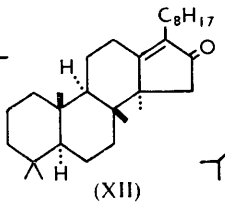
Oxidation of hopene-I with sodium dichromate in acetic acid–benzene gave as main components an αβ-unsaturated ketone (XI), $C_{30}H_{48}O$, and a saturated ketone, the structure of which is discussed later. The αβ-unsaturated ketone was shown spectroscopically to be a *cyclo*pentenone with a tetrasubstituted double bond. It had bands at 1697 (C=O), 1636 (C=C), and 1409 ($CH_2 \cdot CO$) cm.$^{-1}$ and its ultraviolet spectrum had a maximum at 2430 Å (ε = 13,200). Similar infrared bands are found with other *cyclo*pentenones, notably 16-oxo*iso*euphenyl acetate (XII) with bands at 1692 and 1637 cm.$^{-1}$.[10,11] The ultraviolet spectrum of compound (XII) ($\lambda_{max.}$ 2430 Å; ε = 12,600) is also similar, showing, as in the case of the product from hopene-I, the hypsochromic shift of *ca.* 100 Å characteristic of *cyclo*pentenones. This evidence is consistent with structure (XI) for the αβ-unsaturated ketone and provides further support for structure (VIII) for hopenone-I. Chromic acid oxidation of " anhydro-oleanolic lactone II " [12] (XIII) with a terminal ring similar to that of hopene-I also gives a product with $\lambda_{max.}$ 2400 Å. This was formulated either as the *cyclo*pentenone (XIV) or as the *iso*propylidene*cyclo*pentanone (XV); cf.[12] the latter can now be excluded.

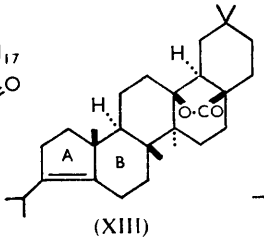
If structure (VIII) correctly represented hopenone-I then it should be possible to prepare it from γ-onocerin (XVI) [13] by conversion of the latter into the saturated diol followed by a retropinacolic dehydration at one end of the molecule and oxidation of the secondary hydroxyl group at the other. At this stage Professor O. Jeger kindly informed

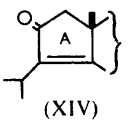
[7] Ames, Halsall, and Jones, *J.*, 1951, 450.
[8] Brownlie, Fayez, Spring, Stevenson, and Strachan, *J.*, 1956, 1377.
[9] Ames, Beton, Bowers, Halsall, and Jones, *J.*, 1954, 1905.
[10] Dawson, Halsall, and Jones, unpublished work.
[11] Arigoni, Viterbo, Dunnenberger, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1954, **37**, 2306.
[12] Ruzicka, Rudowski, Norymberski, and Jeger, *ibid.*, 1946, **29**, 210.
[13] Barton and Overton, *J.*, 1955, 2639.

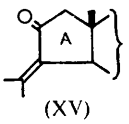
us that he was investigating the chemistry of γ-onocerin and believed that γ-onocerin could be converted into structure (VIII). He and his colleagues [3] accomplished this and the identities of the products from hydroxyhopanone and γ-onocerin were fully established by determinations of mixed melting point and comparison of infrared spectra. This


(XI)

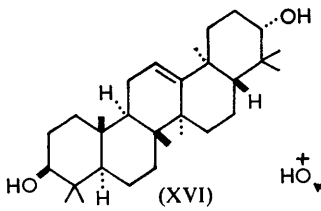

(XII)

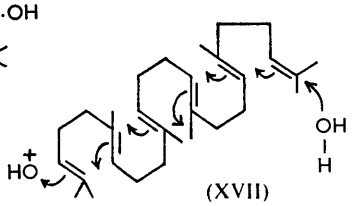

(XIII)

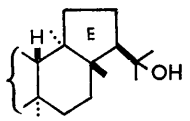

(XIV)


(XV)

relation establishes the absolute configuration of seven of the nine asymmetric centres [13,14] in hydroxyhopanone as in (I) and is consistent with its biogenesis from squalene (XVII)


(XVI)


(XVII)


(XVIII)

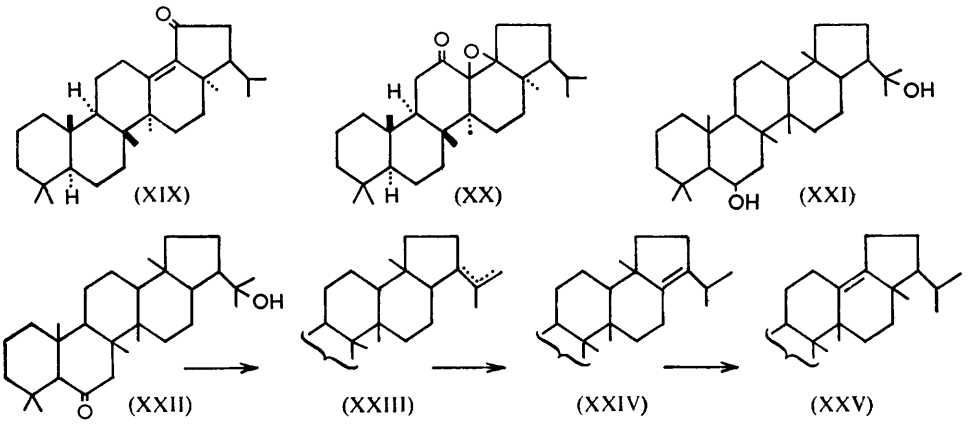
followed by subsequent oxidation of the $C_{(3)}$ hydroxyl group. A completely concerted cyclisation process [15,16] being assumed, the stereochemistry of the two remaining asymmetric centres should be as in (XVIII). [*Added, March 25th*, 1959.—Evidence has now been obtained which confirms the *trans*-fusion of rings D and E (Baddeley, Halsall, and Jones, to be published).]

The structure (IX) given to hopenone-II was based on analogies with the conversion of quinovic acid into novic acid [17] and similar rearrangements.[18,19] The nature of the two carbonyl compounds produced by oxidation of hopene-II with sodium dichromate in acetic acid provided support for this structure. The less polar, $C_{30}H_{48}O$, obtained in 40% yield, had maximal ultraviolet absorption at 2610 Å (ε, 13,900), indicative of a fully-substituted αβ-unsaturated ketone with the double bond exocyclic to two rings [cf. 4 : 4-dimethyl-15-oxocholest-8(14)-en-3β-ol: $\lambda_{max.}$ 2610 Å, ε = 14,700 [20]]. Its infrared spectrum had bands at 1697 and 1615 cm.$^{-1}$, the latter being only slightly the less intense. The band at 1697 cm.$^{-1}$ indicates a keto-group in a five-membered ring, and the high intensity of the 1615 cm.$^{-1}$ band that the αβ-unsaturated ketone is cisoid.[21,22] These data are appropriate to structure (XIX) derived from structure (IX) for hopenone-II. The more polar oxidation product (20%), $C_{30}H_{48}O_2$, gave no colour with tetranitromethane and showed no selective light absorption between 2200 Å and 2600 Å. Its infrared band at 1706 cm.$^{-1}$ was characteristic of a *cyclo*hexanone. These facts, together with the presence of weak infrared bands at 910, 890, 870, and 820 cm.$^{-1}$, probably due to an epoxide,[23]

[14] Schaffner, Viterbo, Arigoni, and Jeger, *J.*, 1956, **39**, 174.
[15] Ruzicka, "Perspectives in Organic Chemistry," Interscience, London, 1956, p. 265.
[16] Eschenmoser, Ruzicka, Jeger, and Arigoni, *ibid.*, 1955, **38**, 1890.
[17] Barton and de Mayo, *J.*, 1953, 3371.
[18] Allan, Spring, Stevenson, and Strachan, *J.*, 1955, 3371.
[19] Allan, Fayez, Spring, and Stevenson, *J.*, 1956, 457.
[20] Woodward, Patchett, Barton, Ives, and Kelly, *J. Amer. Chem. Soc.*, 1954, **76**, 2852.
[21] Cf. Eschenmoser, Schinz, Fischer, and Colonge, *Helv. Chim. Acta*, 1951, **34**, 2329.
[22] Cf. Heusser, Saucy, Anliker, and Jeger, *ibid.*, 1952, **35**, 2090.
[23] Cf. Sallmann and Tamm, *ibid.*, 1956, **39**, 1340; Bible, Placek, and Muir, *J. Org. Chem.*, 1957, **22**, 607; Meda, Camerino, Alberti, and Vercellone, *Gazzetta*, 1955, **85**, 41.

justify the formulation of this compound as the oxo-epoxide (XX), a typical product of oxidation by chromic acid.

Very recently the structure (XXI) with the same gross carbon skeleton as hydroxyhopanone has been suggested [6] for zeorin.[24] Both hydroxyhopanone (I) and zeorinone (XXII) give a similar series of products on acid isomerisation, *iso*zeorininone (XXIII) [6]



corresponding to hopenone (IV and V), zeorininone (XXIV) [6] to hopenone-I (VIII), and *neo*zeorininone (XXV) [6] to hopenone-II (IX). Oxidation of zeorininone and *neo*zeorininone gives compounds [6] analogous to those, *i.e.*, (X), (XIX), and (XX), formed from hopenone-I and hopene-II. The molecular rotation changes for the sequence zeorinone (XXII) to *neo*zeorininone (XXV) and from hydroxyhopanone to hopenone-II are given in Table 2. In Table 3 the rotations of the products of oxidation of hopene-I and hopene-II are compared with the corresponding products from zeorininone and *neo*zeorininone. Apart from the differences between zeorinone and zeorininone and between hydroxyhopane and hopenone-I, the changes are of the same sign and size, suggesting that the stereochemistry at $C_{(13)}$, $C_{(14)}$, and $C_{(18)}$ is the same in both zeorin and hydroxyhopane. The observed differences would be compatible with variations at the two centres in ring E, $C_{(17)}$ and $C_{(21)}$, and hydroxyhopanone and zeorin may differ at one or both of these centres.

TABLE 2.

	$[M]_D$	$\Delta[M]_D$		$[M]_D$	$\Delta[M]_D$
Zeorinone	+154° [a]	−23°	Hydroxyhopanone (I)	+305° [b]	−21°
*iso*Zeorininone (XXIII) ...	+131 [a]	−42	Hopenone (IV and V)	+284 [b]	+38
Zeorininone (XXIV)	+89 [a]	−97	Hopenone-I (VIII)	+322 [c]	−89
*neo*Zeorininone (XXV)	−8 [a]		Hopenone-II (IX)	+233 [d]	

[a] Ref. 24. [b] Ref. 1. [c] This is calculated from the value given for hopenone-I from γ-onocerin; cf. ref. 3. [d] This paper.

TABLE 3.

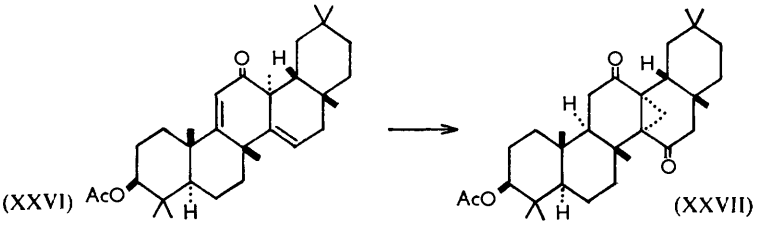
	$[M]_D$	$\Delta[M]_D$		$[M]_D$	$\Delta[M]_D$
Epoxy-ketone (XX) [a] from hopene-II	+462°	+454°	Epoxy-dione from [b] *neo*zeorinone	+413°	+421°
Hopene-II [a]	+8		*neo*Zeorininone [c]	−8	
αβ-Unsaturated ketone [a] (XIX) from hopene II	+197	+189	αβ-Unsaturated ketone [b] from *neo*zeorininone	+171	+179
Triol monoacetate [a] (X; R = Ac) from hopenone-I	+113	−145	Triol monoacetate from [b] zeorinin acetate	+266	−106
Diketone fission [a] product	−32		Diketone fission [b] product	−160	

[a] This paper. [b] Ref. 6. [c] Ref. 24.

As indicated above, one of the oxidation products from hopene-I is a saturated ketone, $C_{30}H_{48}O$, with its keto-group in a five-membered ring (indicated by a band at 1742 cm.$^{-1}$

[24] Barton and Bruun, *J.*, 1952, 1683.

of moderate intensity). It gave no colour with tetranitromethane and showed negligible absorption between 1900 and 2600 Å. This indicates the absence of a double bond and that the ketone must be hexacyclic, a new *cyclo*alkane ring having been formed during the



oxidation. It is likely that this is a *cyclo*propane ring, although no band at *ca.* 3040 cm.$^{-1}$, indicating a methylene group in such an environment,[25] was present. An example of the formation of a *cyclo*alkane ring during oxidation with chromic acid is found in the conversion of 12-oxo*iso*oleana-9(11) : 14-dien-3β-yl acetate (XXVI) by vigorous oxidation with chromic acid into a product which is probably 12 : 14-dioxo-13 : 27-*cyclo*olean-9(11)-en-3β-yl acetate (XXVII).[26,27]

Experimental

M. p.s are uncorrected. Rotations were determined for chloroform solutions at room temperature. Ultraviolet spectra were obtained on a Cary recording spectrophotometer. Measurements of end absorption were observed at maximum sensitivity in 2-mm. cells at optical densities in the range 0·3 to 0·5. Infrared spectra were determined for carbon disulphide solutions unless otherwise stated. The alumina used for chromatography was Peter Spence Grade " H " and, unless otherwise stated, was deactivated with 5% of 10% aqueous acetic acid. Light petroleum refers to the fraction with b. p. 60—80°.

Treatment of Hydroxyhopanone with 6% (*v/v*) *Sulphuric Acid in Acetic Acid.*—The ketol (1·06 g.) in acetic acid (110 c.c.) was treated, with cooling, with concentrated sulphuric acid (7·2 c.c.) in acetic acid (10 c.c.). A precipitate formed immediately. After 24 hr. at 20° this was filtered off, washed with methanol, and dried (675 mg.). Crystallisation from acetone–chloroform (3 : 1) gave hopenone-I [3-oxohop-17(21)-ene; (VIII)] as needles, m. p. 197—197·5°, $[\alpha]_D$ +93° (*c* 0·74). {Schaffner *et al.*[3] report that the rotation of this sample as determined by them is +76° (*c* 0·35). For hopenone-I from γ-onocerin they report $[\alpha]_D$ +77°} (Found: C, 84·8; H, 11·4. Calc. for $C_{30}H_{48}O$: C, 84·85; H, 11·4%). Light absorption: ε at 2100 Å = 6250; at 2150 Å = 3480; at 2200 Å = 1700; infrared bands at 1706s and 830—800w (br.) cm.$^{-1}$. Hopenone-I gave a yellow colour with tetranitromethane.

The filtrate was diluted with water. Ether extraction gave a pale yellow solid (315 mg.) chromatography and fractional crystallisation of which showed that it was a mixture of hopenone-I and lower-melting material (see hopenone-II below).

Isomerisation of Hopenone-I (VIII) *with* 15% *Sulphuric Acid in Acetic Acid.*—Hopenone-I (370 mg.) in acetic acid (65 c.c.) and benzene (25 c.c.) was treated with concentrated sulphuric acid (12·75 c.c.) in acetic acid (20 c.c.). After the mixture had been kept for 18 hr. at 20° (no precipitate) it was worked up in the usual manner to give a yellow gum (350 mg.) which was adsorbed from light petroleum (20 c.c.) on alumina (20 g.). Elution with light petroleum (20 c.c.) gave a gum (51 mg.), obtained as plates, m. p. 165—175° after softening above 140°, from methanol. Further elution with light petroleum (80 c.c.) gave a solid (222 mg.), obtained as needles (from methanol), m. p. 145—150°. Finally elution with light petroleum (100 c.c.) gave a solid (46 mg.), obtained as needles and plates (from methanol), m. p. 140—152°. Further crystallisation of the middle fraction from methanol gave *hopenone-II* (IX) as needles, m. p. 152—154°, $[\alpha]_D$ +55° (*c* 1·06) (Found: C, 84·6; H, 11·7. $C_{30}H_{48}O$ requires C, 84·85; H, 11·4%).

*Isomerisation of Hopenone.**—Hopenone (0·69 g.) was dissolved in acetic acid (55 c.c.), and

* This is the product of dehydration of hydroxyhopanone with phosphoryl chloride and is a mixture of the *iso*propylidene (hopenone-a) and *iso*propenyl (hopenone-b) isomers.

[25] Cole, *J.*, 1954, 3807.
[26] Beaton, Easton, Macarthur, Spring, and Stevenson, *J.*, 1955, 3992.
[27] Johnson and Spring, *J.*, 1954, 1556.

a mixture of acetic acid (10 c.c.) and concentrated sulphuric acid (5·5 c.c.) added. Crystals began to separate after a few minutes. After 24 hr. the solid was filtered off and crystallised from acetone–chloroform to give hopenone-I, m. p. 197—199°. Addition of water to the acidic filtrate precipitated a solid from which more hopenone-I and some hopenone-II were obtained.

Hopene-I.—Hopenone-I (223 mg.) was reduced by the Huang-Minlon procedure, diethylene glycol (60 c.c.), hydrazine hydrate (3 c.c.; 100%), and then potassium hydroxide (2·15 g.) being used. Isolation with ether afforded a solid (215 mg.) which crystallised from acetone to give *hopene-I* [hop-17(21)-ene] as needles, m. p. 178—180°, $[\alpha]_D$ +49·5° (*c* 0·98) (Found: C, 87·65; H, 12·1. $C_{30}H_{50}$ requires C, 87·75; H, 12·25%).

Hopene-II.—Hopenone-II (680 mg.) was reduced by the Huang-Minlon procedure, diethylene glycol (100 c.c.), hydrazine hydrate (4 c.c.; 100%), and then potassium hydroxide (3·3 g.) being used. Isolation in the usual manner and crystallisation of the product (620 mg.) from acetone gave *hopene-II* as plates (380 mg.), m. p. 194—196° undepressed on admixture with a sample obtained by acid isomerisation of hopene-ab (see below), $[\alpha]_D$ +2° (*c* 1·38) (Found: C, 87·5; H, 12·45. $C_{30}H_{50}$ requires C, 87·75; H, 12·25%). The mother liquor afforded plates (127 mg.), m. p. 155—157°, $[\alpha]_D$ +29·5° (*c* 0·79), the infrared spectrum of which was almost identical with that of hopene-II.

Isomerisation of Hopene with Sulphuric Acid in Acetic Acid.—Hopene (1·09 g.) was dissolved in acetic acid (220 c.c.) and benzene (70 c.c.) at 100°. Evaporation under reduced pressure removed most of the benzene. Sulphuric acid (12 c.c.) was added at 60°. After 7 hr. at 20° the precipitate (915 mg.), m. p. mainly 162—164° (solid remaining up to 174°), was isolated. Crystallisation from methanol–acetone gave two similar fractions; rotation and infrared data indicate that they are a mixture of hopene-I (*ca.* 80%) and hopene-II (*ca.* 20%).

The two fractions (667 mg.) were treated in benzene (75 c.c.) with acetic acid (255 c.c.) and concentrated sulphuric acid (45 c.c.) at 20°. After 18 hr. the precipitate was collected (437 mg.; m. p. 192—196°). The filtrate afforded a brown semi-solid (230 mg.) not yet examined. Crystallisation of the precipitate from acetone gave hopene-II as plates (395 mg.), m. p. and mixed m. p. 195—196·5°, $[\alpha]_D$ +1·5°.

γ-Lupene.—This was prepared as described by Heilbron, Kennedy, and Spring [4] but with a contact time of 9 min. γ-Lupene formed hard needles (from ethyl acetate), m. p. 193—197°, $[\alpha]_D$ −18° (*c* 1·05) (lit. value [3]: m. p. 197—199°, $[\alpha]_D$ −19·7°).

iso-*γ-Lupene.*—This was prepared by refluxing γ-lupene in acetic acid for 12 hr.[4] It formed leaflets (from acetone–methanol), m. p. 128—130°, $[\alpha]_D$ +12° (*c* 1·3) (lit. value [5]: m. p. 133—134° [evacd. capillary], $[\alpha]_D$ +14°).

δ-*Amyrenone.*—This was prepared by acid isomerisation of β-amyrenone; [7] it had m. p. 201—203°, $[\alpha]_D$ −10° (*c* 1·5) (lit. value: m. p. 200—202·5°, $[\alpha]_D$ −12°).

Hydroxylation of Hopenone-I (VIII).—Hopenone-I (940 mg.) in dioxan (10 c.c.) and pyridine (25 c.c.) was treated with osmium tetroxide (650 mg.; 1·23 mol.) at 20°; a black precipitate formed rapidly. After 67 hr. the solution was evaporated, tetrahydrofuran (20 c.c.) and lithium aluminium hydride (1 g.) were added, and the solution was refluxed for 2 hr. The product (1 g.), isolated with ether, was crystallised from acetone–methanol to give 3β : 17ξ : 21ξ-*trihydroxyhopane* (X; R = H) as laths (660 mg.), m. p. 244—246°, $[\alpha]_D$ +16·5° (*c* 1·2) (in pyridine) (Found: C, 76·4; H, 11·55. $C_{30}H_{52}O_3$,MeOH requires C, 76·55; H, 11·45%). It gave no colour with tetranitromethane. The mother liquor from the first crystallisation was evaporated, and the residue filtered in benzene–ether (1 : 1) through alumina. The product (255 mg.) formed needles (from methanol), m. p. 207—211°, $[\alpha]_D$ +22·5° (*c* 1·17) (in pyridine). The infrared spectrum was almost identical with that of the main product. The needles gave no colour with tetranitromethane. It is probably isomeric with the above triol, with the glycol grouping in the opposite and more hindered *cis* configuration.

The triol (580 mg.) in pyridine (7 c.c.) was treated with acetic anhydride (3 c.c.) for 9 hr. at 20°. Dilution with water gave a solid which was chromatographed on alumina to give *hopane*-3β : 17ξ : 21ξ-*triol* 3-*monoacetate* (X; R = Ac) (580 mg.) as needles (from acetone–methanol), m. p. 273—278° (after transition above 220°), $[\alpha]_D$ +22·5° (*c* 1·44) (Found: C, 76·25; H, 11·0. $C_{32}H_{54}O_4$ requires C, 76·45; H, 10·85).

Fission of the Triol 3-*Monoacetate* (X; R = Ac) *with Lead Tetra-acetate.*—The triol 3-monoacetate (68 mg.) in benzene (6 c.c.) and acetic acid (4 c.c.) was treated with a solution of lead tetra-acetate in acetic acid (1·48%; 5 c.c. = 1·23 mol.), and benzene (5 c.c.) was added. 1 mol.

of the oxidant was consumed in less than 20 min. at 20°. The mixture was then poured into water containing potassium iodide and sodium thiosulphate. Isolation in the usual manner afforded a 3β-*acetoxy*-17 : 21-*dioxo*-E-seco*hopane*, which crystallised from methanol as needles, m. p. 195—196°, $[\alpha]_D$ −6·5° (*c* 0·38) (Found: C, 77·15; H, 10·5. $C_{32}H_{52}O_4$ requires C, 76·75; H, 10·45%). $\nu_{max.}$ 1732s (OAc), 1708vs (br.) (2 C=O groups), 1403m (–CH_2·CO–) cm.$^{-1}$.

The diketo-acetate (47 mg.) in methanol (5 c.c.) was treated with potassium hydroxide (525 mg.) in methanol (4 c.c.) at 20° for 7 hr. and then at 90° for 2 min. Isolation in the usual manner gave the diketo-alcohol as a gum (40 mg.; insufficient for further purification); $\nu_{max.}$ 3600—3350 (br.) and 1030 (OH), 1708s (C=O), 1698ms (inflex.) (C=O) cm.$^{-1}$.

Hydroxylation of Hopene-I.—Hopene-I (145 mg.) in ether (10 c.c.) and pyridine (3 c.c.) was treated with osmium tetroxide (134 mg.) at 20° for 24 hr. The mixture was evaporated at 100°/0·2 mm. and the residual osmate heated under reflux with lithium aluminium hydride (600 mg.) in tetrahydrofuran (20 c.c.) for 1 hr. Isolation in the usual manner afforded a solid (155 mg.) which was adsorbed on alumina (9 g.) from light petroleum–benzene (7 : 3; 10 c.c.). Elution with this solvent (20 c.c.) gave a gummy solid (29 mg.). Further elution with the same solvent (60 c.c.) gave *hopane*-17ξ : 21ξ-*diol* (115 mg.) as plates (from methanol–acetone), m. p. 225—226°, $[\alpha]_D$ +12·5° (*c* 1·44) (Found: C, 80·8; H, 11·9. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%).

Oxidation of Hopene-I with Sodium Dichromate.—To hopene-I (785 mg.) in acetic acid (50 c.c.) and benzene (20 c.c.) at 50° was added sodium dichromate (2·33 g.; 12·3 mol.) in acetic acid (15 c.c.). The temperature was raised gradually during 45 min. to 83° and the solution kept at this temperature for a further 45 min. Ethanol (10 c.c.) and water were then added. Isolation with ether gave a neutral pale yellow solid (790 mg.) ($\lambda_{max.}$ 2430 Å, ε *ca.* 8000). This was adsorbed from light petroleum–benzene (9 : 1; 35 c.c.) on alumina (50 g.). This solvent (100 c.c.) eluted a solid (294 mg.) which gave a saturated *ketone* as plates (123 mg.) (from acetone–methanol), m. p. 271—273° (after change to needles above 200°), $[\alpha]_D$ +44·5° (*c* 0·92) (Found: C, 84·65; H, 11·65. $C_{30}H_{48}O$ requires C, 84·85; H, 11·35%). $\nu_{max.}$ (in Nujol): 1742ms and 1411 cm.$^{-1}$ (C=O and CH_2·CO of *cyclo*pentanone). Light absorption between 1900 and 2600 Å was negligible. It gave no colour with tetranitromethane. The mother-liquor from the first crystallisation above afforded impure αβ-unsaturated ketone (see below).

Further elution with light petroleum–benzene (9 : 1 and 8 : 2; 400 c.c.) yielded a solid (468 mg.) which gave the αβ-unsaturated ketone (XI) as needles (320 mg.) (from methanol), m. p. 172—173·5°, $[\alpha]_D$ +4° (*c* 1·0) (Found: C, 85·0; H, 11·45. $C_{30}H_{48}O$ requires C, 84·85; H, 11·4%). $\nu_{max.}$ (in Nujol): 1697vs and 1636s (C=O and C=C of *cyclo*pentenone), 1407ms (CH_2·CO) cm.$^{-1}$; $\lambda_{max.}$ 2430 Å (ε 13,200). A very pale yellow colour was given with tetranitromethane.

Oxidation of Hopene-II with Sodium Dichromate.—To hopene-II (675 mg.) in acetic acid (40 c.c.) and benzene (30 c.c.) at 50° was added sodium dichromate (2·0 g.; 12·3 mol.) in acetic acid. The method of the preceding oxidation was then employed. Isolation gave a neutral pale yellow solid (690 mg.) ($\lambda_{max.}$ 2160 Å; ε *ca.* 7300) which was adsorbed from light petroleum–benzene (10 : 1; 33 c.c.) on alumina (45 g.).

Elution with light petroleum–benzene (9 : 1; 250 c.c.) produced a solid (283 mg.) which gave the αβ-*unsaturated ketone* (XIX) as plates (from methanol), m. p. 253—254·5°, $[\alpha]_D$ +46·5° (*c* 1·0) (Found: C, 84·7; H, 11·45. $C_{30}H_{48}O$ requires C, 84·85; H, 11·4%). $\nu_{max.}$ (in Nujol): 1697s (*cyclo*pentenone), 1615s (slightly lower) (C=C), (1409) (CH_2·CO) cm.$^{-1}$. It gave a pale yellow colour with tetranitromethane.

Elution with light petroleum–benzene (1 : 1; 350 c.c.) gave several fractions (300 mg.) which on crystallisation from methanol–acetone gave the *keto-epoxide* (XX) (122 mg.) as plates, m. p. 240—243°, $[\alpha]_D$ +105° (*c* 0·97) (Found: C, 81·85; H, 10·7. $C_{30}H_{48}O_2$ requires C, 81·75; H, 11·0%). $\nu_{max.}$ (in Nujol): 1706s (six-membered ring C=O) 910, 890, 870, 820 (epoxide?) cm.$^{-1}$. There was negligible light absorption between 2000 and 2600 Å. It gave no colour with tetranitromethane.

The authors thank Mr. W. J. Dunstan for assistance in the early stages of this work. One of them (H. F.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, November 7th,* 1958].