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The Chemistry of the Triterpenes and Related Compounds. Part XXXII.* The Chemistry of Hydroxyhopanone

W. J. Dunstan, H. Fazakerley, T. G. Halsall, and E. R. H. Jones

Dyson Perrins Laboratory, Oxford University

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The functional groups of hydroxyhopanone, a saturated $C_{30}H_{50}O_2$ pentacyclic triterpene keto-alcohol have been characterised and a tentative structure for hydroxyhopanone is proposed.

In a detailed investigation of the constituents of dammar resin, Mills and Werner¹ described the isolation of a number of neutral and acidic substances. Hydroxyhopanone was separated from the other neutral components by extensive chromatography and crystallisation and was characterised as a saturated $C_{30}H_{50}O_2$ keto-alcohol, containing a tertiary or hindered secondary hydroxyl group. Unlike most of the other triterpene-like constituents of the resin it is saturated to tetranitromethane and is therefore probably pentacyclic.

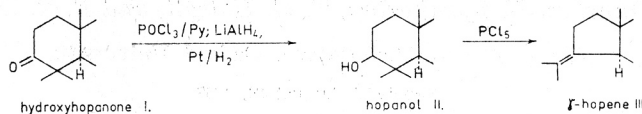
We have now devised a simpler procedure for isolating this substance by taking advantage of its sparing solubility in ether and approximately 3 g. of hydroxyhopanone can be obtained from each kilogramme of the resin. Its greater availability has made possible some advances in our understanding of its chemistry.

Largely as a result of the pioneering and stimulating work of Ruzicka, Jeger, and their colleagues at Zurich, the detailed structures of the major groups of triterpenes have now been almost completely clarified. Today, in examining any new triterpenoid substance, once the nature of the functional groups has been ascertained it is then often only necessary to carry out appropriate modifications of those functional groups in order to obtain a derivative of one of the many triterpenes of known structure. This has been our immediate aim in the present investigation although we realised right at the outset that, containing no ethylenic linkage, hydroxyhopanone could hardly belong to the α - or β -amyrin groups.

Mills and Werner¹ had shown that hydroxyhopanone gave a positive Zimmermann reaction, that the carbonyl group was reactive towards ketonic reagents and that in carbon bisulphide it showed an infrared band at 1706 cm^{-1} corresponding to a carbonyl group in a 6-membered ring. It seemed probable that this oxygen function was in the 3-position, where oxygen is found in almost all tetra- and penta-cyclic triterpenes, and this was proved in the now classical way developed by the Ruzicka school.² Elimination of the hydroxyl function from hydroxyhopanone (I) was achieved by dehydration with phosphoryl chloride in pyridine; the mixture of unsaturated ketones (hope-

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nes) so obtained was reduced first with lithium aluminium hydride (hope-nols) and then catalytically to produce hopanol (II), the alcohol group of which is derived from the original ketonic group of hydroxyhopanone. Dehydration with phosphorus pentachloride was accompanied by retropinacolinic rearrangement and the product, γ -hopene (III), gave acetone in 40% yield on ozonolysis. It can therefore be concluded that the carbonyl group is at the 3-position in a »normal« triterpenoid ring A. Reduction of (I) with lithium aluminium

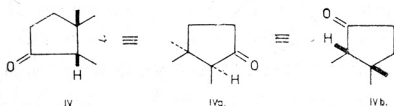


hydride or sodium borohydride gave a diol, hopanediol, which with acetic anhydride in pyridine gave only a monoacetate. The molecular rotation differences ($\Delta_1 M_D = 10$ and $\Delta_3 M_D = 117$)³ for these changes in the 3-functional groups are inconclusive, being in between the characteristic values for the amyryn and lupeol groups.

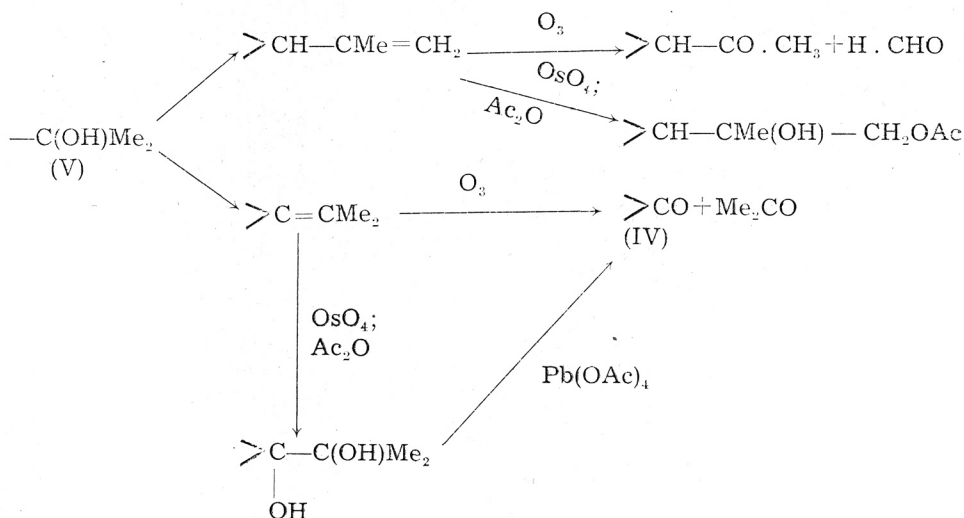
Wolff-Kishner reduction of hydroxyhopanone yielded hydroxyhopane, vigorous oxidation of which with chromic acid gave, in 10% yield, oxotrisnorhopane, $C_{27}H_{44}O$. Since the infrared spectrum of the latter includes a strong band at 1738 cm^{-1} it must contain a carbonyl group on a 5-membered ring which, in the parent ketol, carried a 3-carbon side-chain. The infrared spectrum of the ketone also includes a band at 1411 cm^{-1} attributed to the bending vibrations of the CH_2 group or groups flanking the carbonyl group.^{4, 5} The intensity of this band, which should be proportional to the number of adjacent CH_2 groups (cf. 6, 7, 8), was comparable to that in the spectrum of 15-oxoergost-22-en-3 β -ol⁹, cf. 10 indicating only one methylene group next to the carbonyl group. More precise evidence was provided by quantitative bromination studies (done in comparison with 3 β -acetoxyandrostan-17-one) and deuterium exchange experiments (for which we are indebted to Professor E. J. Corey and Dr. D. N. Jones of the University of Illinois), both of which indicated that three hydrogen atoms could be replaced by enolisation of the ketone.

If the reasonable assumption is made that the carbonyl group is adjacent to a ring junction as in (IV), and not next to a carbon atom carrying an alkyl group, then some conclusions can be drawn regarding the stereochemistry of the attachment of the 5-membered ring. Oxotrisnorhopane has a high positive rotation ($+139^\circ$), comparable with that of 3-keto-A-norcholanic acid ($+133^\circ$)¹¹ and the ΔCO value of $+405^\circ$ (the saturated hydrocarbon, trisnorhopane, was obtained by Wolff-Kishner reduction) agrees very closely with those of ring A norketones in the triterpene series^{2, 12, 13} (e. g. $+395^\circ$ for the ketone obtained by oxidation of the retropinacolinic dehydration product of lupeol). Professor Carl Djerassi^{cf. 11} has kindly determined for us the optical rotatory dispersion characteristics of oxotrisnorketohopane in the range $7000\text{--}3000\text{ \AA}$ which he finds to correspond very precisely to those of 3-keto-A-norcholanic acid and to be significantly different from those of related 5-membered ring ketones which he has examined. It can reasonably be concluded that the trisnorketone

is to be represented by (IV) (equivalent to IVa and IVb) but since this represents the more stable form of attachment of a five- to a six-membered ring it cannot be assumed that this *cis*-junction is present in hydroxyhopanone itself.



When preparing a dinitrophenylhydrazone from hydroxyhopanone Mills and Werner¹ observed that the formation of the derivative was accompanied by dehydration under the acidic conditions employed. This suggested that further evidence regarding the location of the hydroxyl group could be obtained by dehydration experiments, but clearly care would have to be exercised in drawing conclusions from experiments done under acidic conditions. As already mentioned treatment of hydroxyhopanone with phosphoryl chloride-pyridine gave a mixture of unsaturated ketones, an *isopropenyl* isomer being present, according to infrared analysis, to the extent of ca. 20%. Ozonolysis of the mixture gave both acetone and formaldehyde. Dehydration of hydroxyhopanone with phosphoryl chloride in pyridine gave a mixture of hydrocarbons, an *isopropenyl* isomer being present, according to infrared analysis, to the extent of ca. 20%. Ozonolysis gave oxotrisnorhopane (IV) and another substance, as yet impure but probably a C₂₉-ketone (with infrared band at 1715 cm⁻¹), which was also isolated from the non-volatile neutral fraction. Confirmatory evidence was obtained by osmic acid oxidation of the hydrocarbon mixture from which, after acetylation, a diol and a diol-monoacetate were obtained. The former, on lead tetracetate oxidation, gave trisnorketohopane in 85% yield. These results can best be understood if hydroxyhopanone contains the 3-carbon grouping (V).

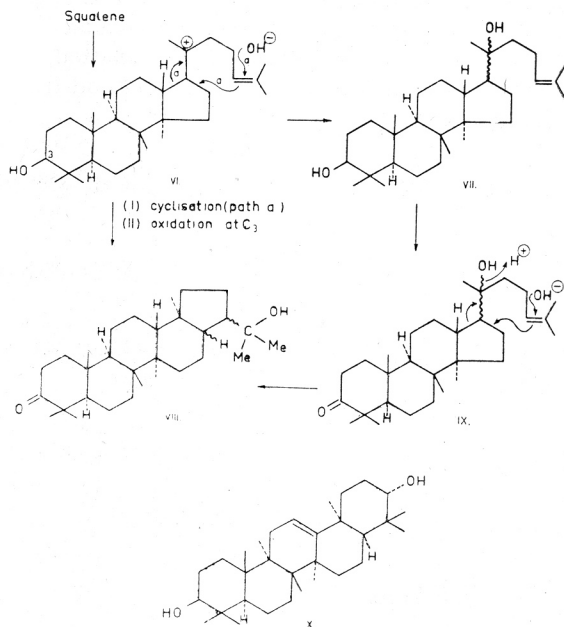


A saturated hydrocarbon provisionally designated hopane (although it may have the isopropyl side chain in the opposite configuration to that in hydroxyhopanone) was then obtained by catalytic reduction of the mixture of hydrocarbons referred to above and appropriate comparisons were made. The obvious candidate was lupane, although the non-existence of a lupene isomer containing an isopropylidene group attached to ring E made the possibility of identity unlikely and this proved to be the case. Hopane cannot be a stereoisomer of lupane with the isopropyl group in the β -configuration since oxotrisnorhopane is not identical with the $C_{(27)}$ -ketone from lupeol.¹⁴ Professor D. H. R. Barton informed us privately some time ago that zeorin¹⁵ contained a five-membered ring (a similar conclusion has now been reached by Ryabinin and Matyukhin¹⁶) but hopane was quite different from zeorinane.

TABLE I

	M. P.	$[\alpha]_D$
Hopane	197—198 ⁰	+ 43 ⁰
Lupane	184	— 1 ⁰
Zeorinane	186—187	+ 12 ⁰

A tentative structure for hydroxyhopanone is VIII. This has structural analogies with dammarenediol I and II (VII; isomeric at $C_{(20)}$)¹⁷ and even more with hydroxydammarenone I and II (diptercarpol)^{18, 19, 20} (IX; isomeric at $C_{(20)}$)¹⁷ all of which are found alongside hydroxyhopanone in dammar resin.¹ In addition VIII is fairly closely related to γ -onocerin (X).²² If structure VIII



is correct its biogenesis could occur from squalene either *via* a completely concerted process involving the ion VI postulated by Ruzicka and his colleagues^{22, 23, 24} as a key intermediate in the biogenesis of triterpenes, followed by oxidation of the C₍₃₎ hydroxyl group or, indirectly, *via* dammarenediol and hydroxydammarenone as indicated. Comparisons with appropriate zeirin and γ -onocerin derivatives are at present being made.

EXPERIMENTAL

Melting points were determined on a Kofler block and are corrected. Rotations were determined in chloroform at room temperature. The alumina used for chromatography was Peter Spence Grade »H«. Light petroleum refers to the fraction with b.p. 60–80°. The resin used was obtained from Messrs. M. Hamburger and Sons Ltd., London and is described as »Pale Bold Indonesia Dammar«.

Isolation of Hydroxyhopanone

Finely ground resin (1 kg.) was extracted with methanol (4 l.) by simmering for 1 hr. After the mixture had stood overnight, the undissolved material (ca. 350 g.) was filtered off and the extract evaporated under reduced pressure. The residue, in 100 g. batches, was dissolved in ether (450 ml.) and the dammar acids removed by shaking with potassium hydroxide solution (5%; 250 ml.) and then with water. The ethereal solution was dried with magnesium sulphate and its volume adjusted to 4.5 ml. per 1 g. of extract used. Attempts to carry out these steps on a larger scale resulted in much poorer yields. The solution was kept at 0° for several days and was then decanted from the solid which separated and which generally firmly adhered to the sides of the flask. The solid was washed with ether and crystallised from acetone or isopropyl alcohol to give hydroxyhopanone as needles (0.34 g. per 100 g. of resin), m.p. 255° [α]_D + 69° (c. 0.78) (Found: C, 81.35; H, 11.55. Calc. for C₃₀H₅₀O₂: C, 81.4; H, 11.4%). Mills and Werner¹ give m.p. 252–256° [α]_D + 64° (c. 1.68).

Dehydration of Hydroxyhopanone with Phosphoryl Chloride

Hydroxyhopanone (0.6 g) in pyridine (55 ml.) was treated with phosphoryl chloride (6 ml.) and kept overnight. After dilution with water ethereal extraction afforded an isomeric mixture (hopenone) of hopenone-a and hopenone-b which crystallised from acetone-methanol (3:1) as needles, m.p. 192–195°, [α]_D + 67° (c, 0.96) (Found: C, 84.55; H, 11.35. C₃₀H₄₈O requires C, 84.85; H, 11.4%). Infrared absorption in CS₂: bands at 885 and 1705 cm⁻¹.

The hopenone (0.5 g.) in light petroleum (80 ml.) was adsorbed on alumina (200 g.) which had been deactivated with 5% of 5% acetic acid. The column was eluted with light petroleum. Six fractions of 200 ml. each, followed by nine of 100 ml. each and a further four of 200 ml. each were collected. Fractions 6 and 7 contained 0.27 g. of solid; fractions 8 and 9 no solid; and fractions 10 and 11 contained 0.14 g. Crystallisation of fractions 6 and 7 from acetone gave hopenone-a (*iso*-propylidene isomer) as needles, m.p. 189–193°, [α]_D + 67° (c, 0.96). Infrared absorption in CS₂: no band at 885 cm⁻¹. Fractions 10 and 11 were crystallised from acetone to give hopenone-b as needles, m.p. 194°. Infrared absorption in CS₂: band at 885 cm⁻¹.

Ozonolysis of Hopenone

Hopenone (0.31 g.) in acetic acid was treated with ozonised oxygen for 55 min. at 20°. The mixture was then steam-distilled into a solution of dimedone (300 mg.) in methanol (15 ml.). 100 ml. of steam distillate was collected and after it had been partially neutralised with potassium hydroxide solution there separated a thick precipitate of formaldimedone (94 mg.; 44% yield), m.p. and mixed m.p. 191°. The filtrate obtained on filtering the precipitate was steam-distilled into a methanolic solution of 2:4-dinitrophenylhydrazine containing a few drops of concentrated hydrochloric acid. The precipitate which formed was chromatographed in benzene on alumina. Elution with benzene afforded acetone 2:4-dinitrophenylhydrazone

(75 mg.; 44% yield), m. p. and mixed m. p. 126°. The infrared spectrum (CS₂ solution) of the residue from the steam-distillation had a band at 1738 cm⁻¹.

Ozonolysis of Hopenone-a

Hopenone-a (45 mg.) in acetic acid (10 ml.) was treated with ozonised oxygen for 25 minutes at 20°. On working up the reaction mixture as above no formaldehyde resulted. Acetone 2:4-dinitrophenylhydrazone (15 mg.; 60% yield), m. p. and mixed m. p. 125–126°, was obtained.

Lithium Aluminium Hydride Reduction of Hopenone

Hopenone (110 mg.) in tetrahydrofuran (10 ml.) and lithium aluminium hydride (100 mg.) were heated under reflux for 30 min. After careful addition of water and acidification, ethereal extraction afforded *hopenol* which crystallised from methanol-acetone as plates, m. p. 195° (Found: C, 84.2; H, 11.7; C₃₀H₅₀O requires C, 84.45; H, 11.8%). Reduction of hopenone with sodium borohydride gave the same product.

Catalytic Hydrogenation of Hopanol

Hopenol (270 mg.) in acetic acid (20 ml.) was hydrogenated over Adams's catalyst (50 mg.) for 10 hr. when one mole of hydrogen was taken up. After removal of the catalyst by filtration, dilution with water gave a precipitate which was crystallised from methanol-acetone to give *hopanol* as needles, m. p. 214°, depressed on admixture with lupanol, $[\alpha]_D + 32^{\circ}$ (c, 1.89) (Found: C, 83.75; H, 12.2; C₃₀H₅₂O requires C, 84.05; H, 12.25%). The hopanol gave no colour with tetranitromethane in chloroform.

Dehydration of Hopanol with Phosphorus Pentachloride

Hopanol (40 mg.) in light petroleum was treated with phosphorus pentachloride (30 mg.). After evolution of hydrogen chloride had ceased water was added and the light petroleum layer separated, dried and poured on to a column of alumina (3.5 g.) deactivated with 5% of 5% acetic acid. Elution of the column with light petroleum gave only one fraction which was crystallised from acetone-methanol (1:3) to give γ -*hopene* as feathery needles, m. p. 151°. Its infrared spectrum showed no bands due to hydroxyl groups.

The γ -*hopene* (34 mg.) in acetic acid (7 ml.) was treated with ozonised oxygen for 20 min. at 18°. After it had been diluted with water and ferrous sulphate (ca. 1.5 g.) had been added, the reaction mixture was steam-distilled into a methanolic solution of 2:4-dinitrophenylhydrazine (200 mg. in 10 ml.) containing conc. sulphuric acid (1 ml.). Water was added to the distillate and the resulting precipitate was dissolved in benzene and adsorbed on alumina (70 g.). Elution with benzene gave acetone 2:4-dinitrophenylhydrazone (8.1 mg.; 41% yield), m. p. and mixed m. p. 126°.

Lithium Aluminium Hydride Reduction of Hydroxyhopanone

Hydroxyhopanone (0.14 g.) in tetrahydrofuran (15 ml.) was heated under reflux for 30 min. with lithium aluminium hydride. Careful addition of water and acidification gave a precipitate which was crystallised from acetone to give *hopanediol* as lustrous needles, m. p. 282–284° $[\alpha]_D + 40^{\circ}$ (c, 0.76) (Found: C, 80.9; H, 12.0. C₃₀H₅₂O₂ requires C, 81.0; H, 11.8%). The same compound was also obtained by reduction with sodium borohydride. Acetylation of hydroxyhopanol with acetic anhydride-pyridine at 100° for 5 hr. gave the *monoacetate* which crystallised from methanol-acetone as needles, m. p. 231–232°, $[\alpha]_D + 40^{\circ}$ (c, 0.86) (Found: C, 78.55; H, 11.2. C₃₂H₅₄O₃ requires C, 78.95; H, 11.2%).

Wolff-Kishner Reduction of Hydroxyhopanone

Hydroxyhopanone (345 mg.) was heated with diethylene glycol (40 ml.) and hydrazine hydrate (2.5 ml.; 100%) under reflux for 1 hr. The excess of hydrazine and water was removed by distillation, potassium hydroxide (600 mg.) was added, and the solution was heated at 200–210° for 4½ hr. After dilution with water ethereal extraction afforded a solid which was crystallised from acetone-methanol to give *hydroxyhopane* as needles (295 mg.), m. p. 245–246°, $[\alpha]_D + 45^{\circ}$ (Found: C, 84.05;

H, 12.0. $C_{30}H_{50}O$ requires C, 84.0; H, 12.25%). The infrared spectrum of hydroxyhopane showed no carbonyl band.

Dehydration of Hydroxyhopane

The alcohol (500 mg.) in pyridine (20 ml.) was treated with phosphoryl chloride (3 ml.) at 20° for 16 hr. Working up in the usual manner gave a solid (480 mg.), m. p. 175—176.5°, ϵ at $885\text{ cm}^{-1} = 45$, which was crystallised from methanol to give hopene as needles, m. p. 176.5—178°, $[\alpha]_D + 38^\circ$ (Found: C, 87.5; H, 12.45. $C_{30}H_{50}$ requires C, 87.75; H, 12.25%). Light absorption: ϵ 1980 Å = 9600; ϵ 2100 Å = 5750; ϵ 2200 Å = 2625. Infrared absorption in CS_2 : band at 885 cm^{-1} , $\epsilon = 34$. This intensity indicates that hopene contains about 20% of the isopropenyl isomer, based on the intensity ($\epsilon = 159$) of the band at 885 cm^{-1} of α -lupene, and 80% of the isopropylidene isomer.

Hydroxylation of Hopene

Hopene (1.49 g.) (ratio of hopene-a to hopene-b = 7:3) in ether (50 ml.) and pyridine (15 ml.) was treated with osmium tetroxide (1.29 g.; 1.4 mole) for 17 hr. at 20°, and then heated under reflux for 30 min. The solution was evaporated under reduced pressure and the residue in ether (70 ml.) and tetrahydrofuran (40 ml.) was heated under reflux with lithium aluminium hydride²⁵ (1.5 g.) for 1 hr. Isolation with ether afforded an almost colourless solid (1.2 g.) which was acetylated in pyridine (25 ml.) and acetic anhydride (5 ml.) for 15 hr. at 20°. Dilution with water followed by ether extraction gave a solid (1.25 g.).

The solid was adsorbed from light petroleum-benzene (3:2; 90 ml.) on alumina (deactivated with 5% of 5% acetic acid). After elution with the same solvent (400 ml.) of a small unsaturated fraction (60 mg.) elution with light petroleum-benzene (2:3; 800 ml.) gave a fraction (340 mg.) which crystallised from acetone-methanol to give hopene-b glycol monoacetate as plates, m. p. 213—215°, $[\alpha]_D + 39^\circ$ (c, 1.16) (Found: C, 78.75; H, 11.4. $C_{32}H_{54}O_3$ requires C, 78.95; H, 11.2%). Elution with benzene (1:1) gave a fraction (680 mg.) which gave hopene-a glycol as elongated plates (from acetone-methanol), m. p. 260—265°, $[\alpha]_D + 31^\circ$ (c, 0.98) (Found: C, 80.9; H, 11.8. $C_{30}H_{52}O_2$ requires C, 81.0; H, 11.8%). No colour with tetranitromethane.

Oxotrisnorhopane

a) Hydroxyhopane (440 mg.) in acetic acid (40 ml.) was treated dropwise with a solution of chromic acid (550 mg., 5 mole) in aqueous acetic acid (70%; 10 ml.) at 75—80° during 2 hr. Methanol (5 ml.) was then added and the solution diluted with water. Isolation in the usual way gave a yellow neutral fraction (315 mg.) and an acidic fraction (50 mg.). The neutral fraction was adsorbed from light petroleum (20 ml.) on alumina (20 g.) (deactivated with 5% of 5% acetic acid). Elution with light petroleum (50 ml.) gave a solid (35 mg.), m. p. 130°. Infrared absorption in »Nujol«, bands at 1740 (s) (five membered ring C=O) and 1712 (ms) cm^{-1} (methyl ketone). Further elution with light petroleum (80 ml.) gave a fraction (78 mg.) which was crystallised from acetone to give oxotrisnorhopane as feathery needles, m. p. 222—224.5° (which changed on standing for 2 months to 240—241° without change of crystalline form), $[\alpha]_D + 139^\circ$ (c, 1.12) (Found: C, 84.25; H, 11.25. $C_{27}H_{44}O$ requires C, 84.3; H, 11.5%). No colour with tetranitromethane. Zimmermann reaction: pink (20°); violet (90°). Light absorption in EtOH— $CHCl_3$ (4:1): broad max. at 2880—2950 Å; $\epsilon = 29.5$. Infrared absorption in CCl_4 solution: bands at 1738 cm^{-1} and 1413 cm^{-1} ($\epsilon = 42$) (cf. 15-oxoergost-22-en-3 β -ol⁹ which has a band at 1412 cm^{-1} in CCl_4 , $\epsilon = 39.5$ and methyl 16-oxoeburico-7:9(11)-dien-21-oate²⁶ which has a band at 1412 cm^{-1} , $\epsilon = 42$). Both these compounds have one $-CH_2-$ group α to the C=O).

b) Hopene (890 mg.) in chloroform (100 ml.) was treated with ozonised oxygen for 2 hr. at 0° until a test portion gave no colour with tetranitromethane. Zinc dust (2 g.) and acetic acid (10 ml.) were added and the mixture kept at 0° for 30 min. Isolation with ether gave a pale yellow fraction (810 mg.) which was adsorbed from light petroleum on alumina (40 g.). Elution with light petroleum gave starting material (10 mg.). Elution with light petroleum-benzene (8:2; 200 ml.) gave a solid (355 mg.) which crystallised from acetone as needles (220 mg.), m. p. 200—210°.

the infrared spectrum of which indicated that it was a mixture of oxotrisnorhopane and the C₍₂₉₎ methyl ketone. Further elution with light petroleum-benzene (7:3; 300 ml.) gave a solid (147 mg.) which crystallised from acetone-methanol to give oxotrisnorhopane as needles, m. p. and mixed m. p. 220—224°, $[\alpha]_D + 139^\circ$ (c, 0.71).

c) Hopene-a glycol (495 mg.) in benzene (50 ml.) was treated with a solution of lead tetraacetate in acetic acid (42 ml.; 1.47% \equiv 1.2 mole) at 30° for 6½ hr. and then at 20° for 16 hr. The solution was poured into potassium iodide solution containing sodium thiosulphate. Isolation with ether gave a solid (450 mg.) which was adsorbed from light petroleum (25 ml.) on alumina (30 g.) (deactivated with 5% of 5% acetic acid). Elution with light petroleum gave oxotrisnorhopane (375 mg.; 85%) as needles (from acetone-methanol), m. p. and mixed m. p. 240—241.5°, $[\alpha]_D + 142^\circ$ (c, 0.68). Elution with benzene (200 ml.) gave starting material (65 mg.).

The trisnor-ketone was heated in pyridine (10 ml.) with hydroxylamine hydrochloride (560 mg.) for 1½ hr. Isolation in the usual way gave *oxotrisnorhopane oxime* as hard plates (from acetone-methanol), m. p. 246—248°, $[\alpha]_D + 95.5^\circ$ (c, 1.08) (Found: N, 3.55. C₂₇H₄₅ON requires N, 3.5%).

Optical Rotatory Dispersion of Oxotrisnorhopane

$[\alpha]_{7000 \text{ \AA}} + 60^\circ$, $[\alpha]_{5890} + 125^\circ$, max. at 3200 Å, $[\alpha]_{\text{max}} + 1970^\circ$.

Bromination Experiments

Oxotrisnorhopane was brominated as follows using androstan-17-on-3β-yl acetate as control. A known amount of ketone (ca. 35 mg.) in chloroform (1 ml.) was treated with a solution of bromine in acetic acid (1.9%; 7 ml.) and the mixture made up to 10 ml. The solutions were kept at 40° ($\pm 1^\circ$). At intervals 1 ml portions were withdrawn and the bromine estimated by titration against 0.005 N sodium thiosulphate solution in the usual way.

TABLE II

Ketone	Moles bromine consumed after days				
	1	2	3	4	5
Oxotrisnorhopane (i)	3.1	3.25	3.33	3.35	—
(ii)	3.15	3.25	3.3	—	3.4
Androstan-17-on-3β-yl acetate (i)	1.95	2.2	2.2	2.2	—

(i) in the dark; (ii) in daylight.

Deuteration experiment

Oxotrisnorhopane, m. p. 221—224.5° (30 mg.) in 0.11 N solution of deuterium bromide (prepared using 99.99% pure deuterium oxide) in methylene chloride (150 ml.) was allowed to stand at room temperature (26—33°) in a tightly stoppered flask for 6 days in total darkness. The solution was evaporated under reduced pressure at 30° to furnish a yellow-white solid. Traces of deuterium bromide were removed by adding two 30 ml. portions of dry methylene chloride to the residue and evaporating under reduced pressure. The residue was crystallized from methylene chloride-acetone at 30° (by evaporation of the methylene chloride) to furnish fine needles, m. p. 226.5—228° (25 mg.). Deuterium analysis (carried out by Mr. J. Nemeth using the falling drop method) showed 7.05 absolute atomic per cent of deuterium (\equiv 3.1 D atoms taken up).

Trisnorhopane

Oxotrisnorhopane (89 mg.) in diethylene glycol (30 ml.) and hydrazine hydrate (3 ml.; 100%) were heated under reflux for 1 hr. The excess of hydrazine hydrate and water was removed by distillation and potassium hydroxide (0.5 g.) added. The

reaction mixture was heated under reflux at 200—210° for 4½ hr. After dilution with water isolation in the usual way gave a solid (85 mg.) which was filtered through alumina (5 g.) in light petroleum. Crystallisation from acetone gave *trisorhopane* as plates, m. p. 218.5—220.5° (change of crystal shape at 160°), $[\alpha]_D + 34.5^\circ$ (c 1.11) (Found: C, 87.6; H, 12.3. C₂₇H₄₆ requires C, 87.5; H, 12.5%).

Hydrogenation of Hopene

Hopene (406 mg.) in ethanol (200 ml.) was hydrogenated over Adams's catalyst (140 mg.) for 10 hr. Hydrogen equivalent to one double bond was absorbed. Removal of the catalyst and evaporation gave a solid which still contained a small amount of unsaturated material as indicated by a faint yellow colour with tetranitromethane in chloroform. The unsaturated material was removed by the procedure of Anderson and Nabenhauer.²⁷ The resulting product had m. p. 182°. It was dissolved in light petroleum (40 ml.) and adsorbed on alumina. Elution with light petroleum gave only one fraction which was crystallised from isopropyl alcohol-acetone to give *hopane* as needles, m. p. 189°, raised by repeated crystallisation to 198° $[\alpha]_D + 43^\circ$ (c, 1.69) (Found: C, 87.7; H, 12.2. C₃₀H₅₂ requires C, 87.3; H, 12.7%). Hopane gave no colour with tetranitromethane in chloroform.

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Kemija triterpena i njima sličnih spojeva. XXXII. Kemija hidroksihopanona.

W. J. Dunstan, H. Fazakerley, T. G. Halsall i E. R. H. Jones

Određene su funkcionalne grupe hidroksihopanona zasićenog pentacikličkog triterpenskog ketoalkohola, $C_{30}H_{50}O_2$. Predložena je za sada najvjerojatnija struktura hidroksihopanona.

DYSON PERRINS LABORATORY
UNIVERSITY OXFORD

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