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The Constitution and Stereochemistry of Rimuene[1]

By J. D. Connolly, R. McCrindle, R. D. H. Murray, and K. H. Overton

The published chemical and spectroscopic properties of rimuene suggest (V) or (VI) as probable structures for this hydrocarbon. The constitution and stereochemistry represented by (V) has been established by conversion of rimuene and the diene (VIII) from erythroxydiol-Y, respectively, into the C_{19} hydrocarbon (XII) and its antipode and has been confirmed by a total synthesis.[2]

The conversion of rimuene into isophyllocladene with boiling formic acid which has been used as key evidence for the structure and stereochemistry of rimuene, could not be substantiated with pure rimuene.

The problem posed by the constitution and stereochemistry of rimuene has attracted a degree of interest which is certainly disproportionate to its complexity and, as it turns out, also to the importance of rimuene in terpene chemistry. As Ireland has commented [2] in introducing his total synthesis of rimuene, this interest undoubtedly arose initially from Wenkert's proposal [3] that rimuene might occupy a central intermediate position in the biosynthesis of certain tetracyclic diterpenoids, and was sustained by the subsequent failure of successive proposed structures capable of performing this role, to survive closer scrutiny.[4] Undoubtedly the

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[1] Preliminary communication, J. D. Connolly, R. McCrindle, R. D. H. Murray, and K. H. Overton, *Tetrahedron Letters*, 1964, 1983.

[2] R. E. Ireland and L. N. Mander, *Tetrahedron Letters*, 1964, 3453.

[3] E. Wenkert, *Chem. and Ind.*, 1955, 282.

[4] (*a*) R. E. Ireland and P. W. Schiess, *J. Org. Chem.*, 1963, **28**, 6; (*b*) R. F. Church and R. E. Ireland, *ibid.*, p. 17.

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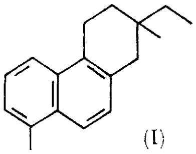
scarcity of natural rimuene, the supply of which is virtually confined to the New Zealand " rimu " tree, has had its share in substantially delaying the final solution of the problem.

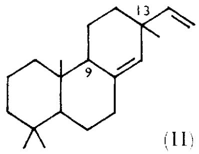
Our interest in the constituents of *Erythroxylon monogynum* caused us to study the problem of rimuene, of which the significant recorded facts are as follows:

While drastic dehydrogenation of rimuene yields pimanthrene, partial dehydrogenation of dihydrorimuene yields [5] a hydrocarbon whose physical constants were identical with those recorded for the hydrocarbon (I) obtainable from both 13-epimeric pimaric acids. Moreover, the infrared and n.m.r. properties of rimuene and dihydrorimuene are consonant with the presence of a vinylidene group and one trisubstituted ethylenic linkage, having one adjacent methylene group as in (II).[5] The position of the nuclear double bond appeared to be defined by the formation [5] of 1,2,8-trimethylphenanthrene on successive epoxidation, Grignard reaction, and dehydrogenation of dihydrorimuene. It had furthermore been reported [6] that hot formic acid converted rimuene into isophyllocladene and a mixture of abieta-8(14),12- and -7,13-dienes. The synthesis [4] of the four pimaradienes (II) epimeric at C-9 and C-13, none of which corresponded to rimuene, made untenable proposals based on this gross structure. The subsequent elucidation [4b,7] of the constitution of isopimaric acid and hence of isopimaradiene (III) and its non-identity with rimuene, left three C-9 and/or C-13 epimers of that structure for consideration. However, for a variety of reasons which have been discussed elsewhere,[8] these also seemed unlikely candidates.

While other pimaradienes, such as the $\Delta^{9(11),15}$-isomer, could not be decisively rejected on the available evidence, our work on the tricyclic erythroxydiols [9] irresistibly attracted us to a rosane structure (IV) for rimuene and at the same time provided us with the means of putting our supposition to the test. On this basis rimuene could most plausibly be formulated as (V) or (VI) (or their antipodes), with either configuration at C-13. In this connection two facts appeared to us to favour (V). (1) The signal in the n.m.r. spectrum of one quaternary methyl group in rimuene and dihydrorimuene but not in tetrahydrorimuene is notably high at τ 9·38 when compared with the published values [8] for the pimaradienes and would be accommodated by (V), where the C-9 methyl group lies above the olefinic double bond and hence in a shielding zone.[10] (2) On the basis of dehydrogenation experiments, Carman [11] had considered as probable the location of the nuclear double bond in ring B of rimuene.

We were at the outset concerned to confirm the reported conversion [6] of rimuene into isophyllocladene, since this would not only lend support to our proposed structure (V) but additionally define the C-13 configuration in rimuene and thereby indicate whether direct correlation with the erythroxydiols and rosenonolactone was possible. However, when g.l.c.-pure rimuene, m. p. 55—55·5°; $[\alpha]_D$ +56° was refluxed with 90% formic acid for 48 hours,[6] g.l.c. showed the complete absence of isophyllocladene in the product. Treated under the same conditions, isophyllocladene survived to the extent of about 35—40%; three other major products were detected, which did not correspond in retention time to those formed from rimuene. We did not feel at liberty, therefore, to avail ourselves in our structural arguments of the supposed relationship between rimuene and isophyllocladene.


(I)



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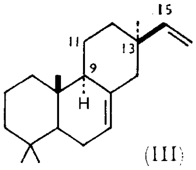

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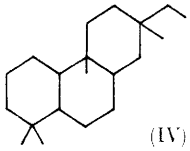
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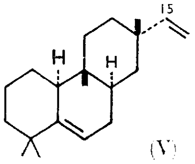
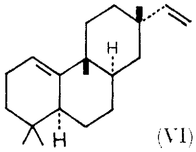
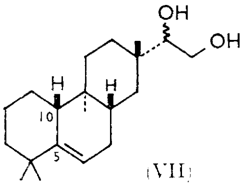


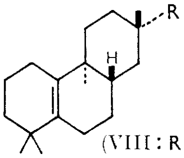
(V)



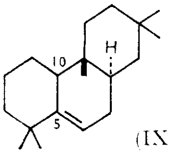
(VI)



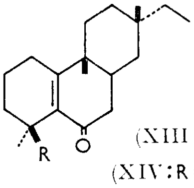
(VII)
(X : $\Delta^{5(10)}$-Isomer)



(VIII : R = $CH{:}CH_2$)
(XI : R = Me)



(IX)
(XII : $\Delta^{5(10)}$-Isomer)



(XIII : R = Me)
(XIV : R = CO_2Me)

The problem of inter-relating rimuene with the erythroxydiols was a relatively simple one. When we embarked on this project, the dehydration product

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[5] L. H. Briggs, B. F. Cain, and J. K. Wilmshurst, *Chem. and Ind.*, 1958, 599.

[6] L. H. Briggs, B. F. Cain, and R. C. Cambie, *Tetrahedron Letters*, 1959, 17.

[7] W. Antkowiak, O. E. Edwards, R. Howe, and J. W. ApSimon, *Canad. J. Chem.*, 1965, **43**, 1257.

[8] E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. McChesney, *J. Org. Chem.*, 1965, **30**, 713. We are grateful to Professor Wenkert for the Manuscript of this Paper before publication.

[9] J. D. Connolly, R. McCrindle, R. D. H. Murray, A. J. Renfrew, K. H. Overton, and A. Melera, preceding Paper.

[10] N. S. Bhacca and D. H. Williams, " Applications of N.M.R. Spectroscopy in Organic Chemistry," Holden Day, San Francisco, 1964, p. 89.

[11] R. M. Carman, *Austral. J. Chem.*, 1963, **16**, 225.

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(VII) of erythroxytriol Q,[12] an obvious candidate if rimuene were represented by (V), was not available. The most attractive alternative was the diene (VIII), accessible in two antipodal forms either from erythroxydiol Y, by acid-induced isomerisation of the nuclear double bond and conversion of the dihydroxyethyl side-chain into a vinyl group, or by a lengthier route from rosenonolactone.[9] Because of its easier accessibility we chose the former. Our experience with the erythroxydiols [9] led us to suppose that if rimuene were represented by (V), exposure to acidic conditions would transform it into a mixture of double-bond isomers, among them the $\Delta^{5(10)}$-isomer. In the event, when rimuene was dissolved and kept in moist chloroform–hydrogen chloride at 20° for 16 hours, the resulting mixture of hydrocarbons exhibited two peaks of almost equal intensity in the gas chromatogram. One had, on three different columns, the same retention time as rimuene; the other emerged first and was presumed to be the $\Delta^{5(10)}$-isomer. No attempt was made to separate this substance, since the diene (VIII) from erythroxydiol Y gave, under the same acidic conditions, a mixture of different hydrocarbons; the gas chromatogram again exhibited a similar pair of peaks, but these were of longer retention time than in the case of rimuene. Such a difference in gas-chromatographic behaviour might result from different configurations at C-13. Since the diene from erythroxydiol Y has, as previously established,[9] an equatorial vinyl group, the vinyl group of rimuene would necessarily be axial. On this assumption the difference between the two series could be removed by converting the vinyl group of each into methyl, and this was done as follows: Rimuene was osymlated preferentially at the exocyclic double bond, and the mixture of C-15 epimeric diols, without separation, cleaved with sodium periodate in aqueous methanol. The resulting nor-aldehyde, m. p. 80—82°, $[\alpha]_D$ +58° was converted into the hydrocarbon (IX), m. p. 37—38°, $[\alpha]_D$ +55° by reduction of the derived ethylene thioketal with Raney nickel. The diol (X) obtained from erythroxydiol Y by acid isomerisation [9] was converted as above first into the nor-aldehyde, m. p. 68—70°, $[\alpha]_D$ +81° (1H singlet τ 0·62) and then into the nor-hydrocarbon (XI), m. p. 61—63°, $[\alpha]_D$ +116°.

When nor-rimuene (IX) was exposed to chloroformic hydrogen chloride under the conditions previously used with rimuene, the mixture again exhibited two bands on g.l.c. An excellent separation, as evidenced by g.l.c.—monitoring, of the desired $\Delta^{5(10)}$-isomer from this mixture was readily achieved by chromatography in light petroleum on silver nitrate–silica gel. The less strongly retained component (XII) crystallised as needles from methanol and had m. p. 61—63°, $[\alpha]_D$ −112°; $\varepsilon_{205\,m\mu}$ 3600 $\varepsilon_{220\,m\mu}$ 950; n.m.r. signals at τ 9·17 (3H), 9·05 (6H), 9·01 (6H), but no signal in the olefinic proton region (τ 4·0—5·5). The second component was non-crystalline, had in its n.m.r. spectrum a signal at τ 4·6 characteristic of a vinyl proton (mixture of Δ^5- and $\Delta^{1(10)}$-isomers ?), and was not further investigated.

The nor-hydrocarbon from erythroxydiol Y (XI), m. p. 61—63°, $[\alpha]_D$ +116° (see above), also crystallised as needles from methanol. Its u.v., n.m.r., and mass spectra were indistinguishable from those of the above C-19 hydrocarbon from rimuene as was its behaviour on g.l.c. (10% Apiezon L, 10% PEGA, and 5% QFI.) and t.l.c. (silver nitrate–silica gel), either separately or in admixture with the antipodal olefin. Furthermore, on exposure to chloroformic hydrogen chloride, both antipodes gave identical hydrocarbon mixtures.

The conversion by acid of the C-19 hydrocarbon (IX) from rimuene into the $\Delta^{5(10)}$-isomer (XII) still left open a choice between the alternative $\Delta^{5(6)}$- and $\Delta^{1(10)}$-positions for the nuclear double bond of rimuene. The $\Delta^{5(6)}$-position is in fact strongly indicated by three independent strands of evidence and securely established by Ireland's total synthesis.[2] First, as already mentioned, the appearance of one quaternary methyl group at τ 9·38 in rimuene and dihydrorimuene, but not in tetrahydrorimuene, is satisfactorily explained by location of the nuclear double bond at position 5,6, since the methyl group at C-9 is then situated in a shielding zone above the olefinic double bond. Secondly, comparison of the optical rotatory dispersion of the αβ-unsaturated ketone (XIII) obtained from dihydrorimuene by osmylation, oxidation, and dehydration (see Experimental section) with that of methyl dihydrorosonate (XIV) showed correspondence in both the weak negative $n \longrightarrow \pi^*$ and the strong negative $\pi \longrightarrow \pi^*$ Cotton curves (see Experimental section) with regard to sign, position, and magnitude. Finally, comparison of the mass spectra of rimuene, dihydrorimuene, and tetrahydrorimuene proved to be instructive. Thus, $m - 15$ was by far the most abundant ion in the spectrum of rimuene and dihydrorimuene, while this was a comparatively minor peak in tetrahydrorimuene. This suggests the location of more than one methyl group and possibly a *gem*-dimethyl group allylic to an olefinic double bond. More significant, the mass spectra of rimuene and dihydrorimuene but not of tetrahydrorimuene, had major fragments at m/e 136 and 121, corresponding to a retro-Diels–Alder fission of ring B, the charge remaining, as previously observed, on the fragment originating from ring A either before (136) or after (121) loss of an allylic methyl group.

Simultaneously with our preliminary announcement of the constitution and stereochemistry of rimuene there appeared an identical proposal by Corbett and Wyllie.[13] While these authors adduce excellent degradative evidence for the location of the olefinic double bond in rimuene at position 5,6, and the shift of a methyl group from C-10 to C-9, the remainder of the constitution and the relative and absolute stereochemistry are based on acceptance of the reported conversion of rimuene into

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[12] J. D. Connolly, R. McCrindle, R. D. H. Murray, K. H. Overton, and A. Melera, *Tetrahedron Letters*, 1964, 1859; D. Gunn and K. H. Overton, unpublished results.

[13] R. E. Corbett and S. G. Wylie, *Tetrahedron Letters*, 1964, 1903.

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isophyllocladene which, curiously, leads to the same conclusion as our direct correlation with rosenonolactone *via* erythroxydiol Y and Ireland's total synthesis. Our inability to substantiate the rimuene–isophyllocladene interconversion with pure rimuene leads us to suggest that the arguments advanced on this basis by the New Zealand workers should be regarded with some caution.

EXPERIMENTAL

Melting points were taken on a Kofler hot-stage apparatus. Specific rotations refer to chloroform solutions except where otherwise stated. Infrared solution spectra were recorded by Mrs. F. Lawrie, Glasgow, on a Unicam S.P. 100 Mark II Spectrophotometer with a prisms grating monochromator operated with evacuated optics. Nuclear magnetic resonance spectra were obtained on the Varian Associates A-60 and HR-100 and the Perkin-Elmer R 10 spectrometers, using approximately 0·3M-solutions in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were obtained on an AEI MS 9 mass spectrometer by Messrs. T. A. Bruce, H. C. Hill, and A. McCormick. O.r.d.'s were kindly supplied by Professor W. Klyne. Microanalyses are by Mr. J. M. L. Cameron and his staff, Glasgow. Woelm Grade I alumina, deactivated to the appropriate grade according to Brockmann was used for chromatography. Chromatoplates both for analytical and preparative use were made by the method of Stahl, using Kieselgel G (Merck).

Extraction of Rimuene.—The rimuene used in this investigation was obtained by extraction with light petroleum of the leaves (2·5 kg.) of *Dacrydium cupressinum*, dried at 40°. The extractive was chromatographed over alumina (III) and the hydrocarbon fraction distilled through a spinning-band column. The rimuene fraction so obtained, crystallised three times from ethanol (1·22 g.), had m. p. 55—55·5°, $[\alpha]_D$ +56° (*c* 2·30). It showed on g.l.c. one single symmetrical peak (25·5 min. on 10% Apiezon L at 200°) and complete absence of minor contaminants.

Attempts to Convert Rimuene into Isophyllocladene.—The g.l.c. analyses in the following set of experiments were carried out on a 10% Apiezon L column at 200°. Isophyllocladene used for comparison had m. p. 110—112°, $[\alpha]_D$ +23° (*c* 3·00).

Rimuene (5 mg.; m. p. 55—55·5°, $[\alpha]_D$ +56°, single sharp peak on g.l.c., retention time 25·5 min.) was refluxed in 90% formic acid (5 ml.) for 48 hr. The cooled solution was neutralised with sodium carbonate and the hydrocarbons were extracted into ether. G.l.c. of the product showed the complete absence of isophyllocladene (r.t. 37·5 min.) and rimuene (25·5 min.). There were five major peaks (r.t. 19·5—30 min.). The longest-retained component, present in very minor amount had r.t. 34 min.). In a blank experiment, with isophyllocladene, carried out under identical conditions, one major component of the mixture had the retention time of isophyllocladene (37·5 min.), the three other major components preceding it at 29·75, 32, and 34·5 min.).

Conversion of the Diol (X) *into the Nor-hydrocarbon* (XI).—The diol (X), m. p. 127—130°, $[\alpha]_D$ +60° (obtained from acid isomerisation of erythroxydiol X or Y [9]) (53 mg.), and sodium periodate (50 mg.) were kept in aqueous methanol (1 : 4; 15 ml.) for 2 hr. at 20°. The product, obtained by dilution with water and extraction into ether, was chromatographed over silica gel. Elution with benzene–light petroleum (1 : 9) gave the *nor-aldehyde* (45 mg.), needles from aqueous methanol, m. p. 68—70°, $[\alpha]_D$ +81° (*c* 0·58), $\nu_{max.}$ (CCl_4) 1745 cm.$^{-1}$, n.m.r. signals at τ 0·62 (1H, singlet, aldehyde) and 8·89 (3H), 9·02 (6H) and 9·12 (3H) (quaternary methyls) (Found: C, 83·25; H, 11·25. $C_{19}H_{30}O$ requires C, 83·15; H, 11·0%). This aldehyde (45 mg.) in dry ether (10 ml.) was kept with freshly distilled boron trifluoride etherate (0·2 ml.) and ethanedithiol (0·2 ml.) for 3 hr. at 20°. Chromatography of the product over silica gel (20 g.) gave, on elution with benzene–light petroleum (1 : 20), the t.l.c.-pure thioketal (38 mg.). This was reduced by refluxing it together with acetone-deactivated Raney nickel (2 g.) in AnalaR acetone (10 ml.) for 16 hr. The oily product obtained after removal of catalyst and solvent, was chromatographed on silica gel (10 g.) in redistilled AnalaR light petroleum, affording the pure *hydrocarbon* (XI) (24 mg.). It crystallised as needles, m. p. 60—62° (from aqueous methanol), $[\alpha]_D$ +116° (*c* 1·57), n.m.r. signals at τ 9·17 (3H), 9·06 (6H), 9·01 (6H) (Found: C, 87·6; H, 12·25. $C_{19}H_{32}$ requires C, 87·6; H, 12·4%).

Conversion of Rimuene into the Nor-hydrocarbon (XII).—Rimuene (200 mg.) and osmium tetroxide (190 mg. 1·05 mol.) were kept in ether–pyridine (15 ml.; 1 : 2) for 16 hr. at 20°. The mixed osmates were decomposed with saturated sodium hydrogen sulphite solution and the mixture of epimeric diols was extracted into ether. Chromatography over silica gel (15 g.) separated the diols [140 mg.; eluted with ether–light petroleum (1 : 1)] from rimuene and tetraols. The diols were kept in aqueous methanol (1 : 4; 40 ml.) with sodium periodate (125 mg.) for 2 hr. The *nor-aldehyde* (106 mg.) obtained by chromatography over silica gel, crystallised as rods from aqueous methanol, m. p. 80—82°, $[\alpha]_D$ +58° (*c* 0·70), n.m.r. signals at τ 0·53 (1H, singlet, aldehyde) and 8·93 (3H), 9·04 (6H), and 9·33 (3H) (quaternary methyls) (Found: C, 82·5; H, 11·35%).

The aldehyde (97 mg.) was converted into the thioketal with ethanedithiol and boron trifluoride–etherate and the t.l.c.-pure thioketal (82 mg.), obtained by chromatography over silica gel reduced by Raney nickel in refluxing acetone. Chromatography over silica gel in redistilled AnalaR light petroleum afforded the *hydrocarbon* (IX), m. p. 37—38°, $[\alpha]_D$ +55° (*c* 1·11), n.m.r. signals at τ 4·52 (vinyl H), 8·72, 8·92, 8·98, 9·10, 9·33 (3H each; quaternary methyls) (Found: C, 87·5; H, 12·5%).

This hydrocarbon (50 mg.; g.l.c.-pure) was dissolved in dry methanol and dry hydrogen chloride passed through the solution for 5 min. After 16 hr. at 20°, the solvent was removed under reduced pressure, and the residue (two components by g.l.c.; retention times on 10% PEGA at 125°, 9·25 and 11·5 min., 10% Apiezon L at 175°, 16·5 and 19 min., 5% QFI at 125°, 9 and 10·25 min.; nor-rimuene on 10% Apiezon L at 175°, 19 min.) in redistilled light petroleum chromatographed (10-ml. fractions) over silver nitrate–silica gel (3 g.). Fractions 2 and 3 (18 mg.) had retention time on 10% Apiezon L at 175° of 16·5 min. (1 sharp peak) and crystallised on standing. Fraction 4 (8 mg.) was contaminated with the second component (r.t. 19 min., n.m.r. signals at τ 4·6, vinyl proton; mixture of Δ^5- and $\Delta^{1(10)}$-isomers ?). Fractions 2 and 3, cyrstallised from methanol, had m. p. 61—63°, $[\alpha]_D$ −112° (*c* 0·92). Mixed chromatograms of this hydrocarbon with its antipode obtained from erythroxydiol Y were indistinguishable from the single components with the following columns:

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10% Apiezon L at 175°, 16·5 min.; 10% PEGA at 125°, 9·25 min.; 5% QFI at 125°, 9 min.

Treatment with chloroformic hydrogen chloride of the olefin obtained from both sources gave mixtures of two components having the following retention times: 10%, PEGA at 125°, 9·25 and 11·5 min.; 10% Apiezon L at 175°, 16·5 and 19 min.; 5% QFI at 125°, 9 and 10·25 min.

Osymlation of Dihydrorimuene.—Dihydrorimuene (m. p. 30—31°; 40 mg.) dissolved in ether–pyridine (1 : 1; 5 ml.) was kept with osmium tetroxide (38 mg., 1 mol.) at 20° for 16 hr. Decomposition of the osmate with aqueous sodium hydrogen sulphite and filtration of the product through alumina (V; neutral) in ether–benzene (2 : 1) afforded *rimuan*-5,6-*diol*, m. p. 132—133° (Found: C, 77·55; H, 11·2. $C_{20}H_{36}O_2$ requires C, 77·85; H, 11·75%).

Oxidation of Rimuan-5,6-*diol.*—To the diol obtained above (36 mg.) in acetone (2 ml.) cooled to 0° was added Jones reagent (3 drops) and after 2 min. the mixture was diluted with water and extracted into ether. The desired ketol was separated from the otherwise acidic reaction product with sodium hydrogen carbonate and the neutral portion purified by preparative t.l.c., affording 5-*hydroxy*-6-*oxorimuane* (19 mg.), rods from light petroleum, m. p. 140—141°, $\nu_{max.}$ (CCl_4) 1705 cm.$^{-1}$ (H-bonded cyclohexanone) (Found: C, 78·2; H, 11·1. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%).

Rimu-5(10)-*ene*-6-*one.*—The ketol obtained above (11 mg.) in pyridine (1 ml.) containing thionyl chloride (3 drops) was kept in ice for 10 min. Addition of water, extraction into chloroform, and purification by preparative t.l.c. gave *rimu*-5(10)-*ene*-6-*one* (8 mg.), m. p. 101—102°, $\nu_{max.}$ (CCl_4) 1670 cm.$^{-1}$, $\lambda_{max.}$ 250 mμ (ε 10,800); rotatory dispersion (MeOH): $[\phi]_{500}$ −340, $[\phi]_{400}$ −734, $[\phi]_{360}$ −1600, $[\phi]_{325}$ +365, $[\phi]_{323}$ +920, $[\phi]_{263}$ −7300, $[\phi]_{222}$ +15,800, $[\phi]_{210}$ +13,600 (Found: C, 83·0; H, 11·1. $C_{20}H_{32}O$ requires C, 83·25; H, 11·2%).

Methyl Dihydrorosonate.—This substance was prepared by the literature method[14] from rosololactone kindly provided by Professor W. B. Whalley through the courtesy of Professor W. Klyne. It had $\nu_{max.}$ (CCl_4) 1678 cm.$^{-1}$, $\lambda_{max.}$ 251 mμ (ε 10,300) and rotatory dispersion (MeOH): $[\phi]_{400}$ −815, $[\phi]_{348}$ −1790, $[\phi]_{300}$ −2900, $[\phi]_{274}$ −7800, $[\phi]_{258}$ −10,300, $[\phi]_{250}$ −6250, $[\phi]_{223}$ +20,100, $[\phi]_{217}$ +19,200.

One of us (J. D. C.) is indebted to Imperial Chemical Industries Limited for fellowship support. We are grateful to Professor W. Klyne for the o.r.d. data.

Department of Chemistry, The University,
Glasgow W.2. [5/908 *Received, August* 23*rd*, 1965]

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[14] A. Harris, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 1958, 1807.