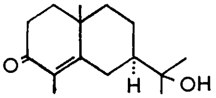
514. *Synthetical Experiments in the Eudalene Group of Bicyclic Sesquiterpenes. Part I. Synthesis of Carissone and γ-Eudesmol.*

By A. R. Pinder and R. A. Williams.

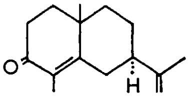
Total syntheses of (+)-carissone and of (+)-γ-eudesmol are described.

The crystalline sesquiterpene keto-alcohol, (+)-carissone, was first isolated from the roots of the Australian shrub *Carissa lanceolata* (R. Brown) by Mohr, Schindler, and Reichstein,[1] and was later found in the essential oil of *Eucalyptus macarthuri*.[2] Barton and Tarlton [3] have shown that the compound must be formulated as (I), by converting it into α- (II) and β-cyperone (III), of known constitution,[4,5] by dehydration. The absolute configuration (I) for (+)-carissone has been established by the transformation of eudesmol (IV) into the (+)-keto-alcohol.[2,6]

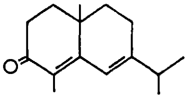
We describe here confirmation of the structure and absolute configuration (I) for (+)-carissone by total synthesis.



(I)



(II)



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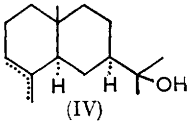
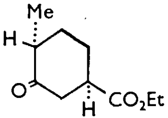


(IV)

The well-known Robinson–Mannich annelation reaction has featured prominently in synthetic approaches to the eudalene group of bicyclic sesquiterpenes.[4,5] We considered the possibility of applying it to ethyl 4-methyl-3-oxocyclohexanecarboxylate (V), which was synthesised from *p*-toluic acid.[7] On conformational grounds this product was assigned the *trans*-configuration. It was first demonstrated that the ethoxycarbonyl group could be transformed into the hydroxyisopropyl group, a requirement in the projected synthesis. The ketonic carbonyl group was protected as the ethylene ketal (VI), which with methylmagnesium iodide afforded the tertiary alcohol (VII). Mild hydrolysis then gave the keto-alcohol (VIII). Unfortunately, however, the keto-ester (V) reacted with 1-diethylaminopentan-3-one methiodide or 2-chloroethyl ethyl ketone to give only very poor yields of the octalone (IX) and the decalone (X), respectively.



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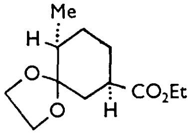

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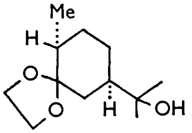

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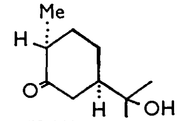

(VIII)

The keto-alcohol (VIII) was also obtainable, as its (+)-form, from (+)-dihydrocarvone, the absolute configuration (XI) of which has been settled.[8] Epoxidation of the ketone, already described [for the (—)-enantiomorph] by Clemo and McQuillin,[9] yielded the epoxy-ketone (XII), together with some of the corresponding diol. Reduction of the former with lithium aluminium hydride gave the diol (XIII), which on oxidation with chromic acid afforded (+)-5-(1-hydroxy-1-methylethyl)-2-methylcyclohexanone (VIII). The

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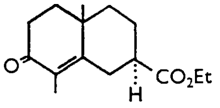
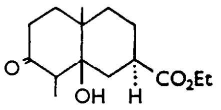
[1] Mohr, Schindler, and Reichstein, *Helv. Chim. Acta*, 1954, **37**, 462.
[2] McQuillin and Parrack, *J.*, 1956, 2973.
[3] Barton and Tarlton, *J.*, 1954, 3492.
[4] McQuillin, *J.*, 1955, 528, and earlier references there cited.
[5] Howe and McQuillin, *J.*, 1955, 2423.
[6] Ayer and Taylor, *J.*, 1955, 3027.
[7] Meldrum and Perkin, *J.*, 1908, **93**, 1416.
[8] Birch, *Ann. Reports*, 1950, **47**, 192.
[9] Clemo and McQuillin, *J.*, 1952, 3839.

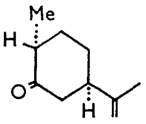
infrared spectra of this product and of racemic ketone (VIII), synthesised as described above, were identical. This identity confirms the expectation that the racemic compound (VIII), and therefore the racemic keto-ester (V), have the *trans*-configuration, and proves that reduction of the epoxy-group in the epoxy-ketone (XII) leads to the tertiary alcohol and not to the isomeric primary alcohol. This direction of cleavage of the epoxide ring was to be expected during reduction under alkaline conditions.[10] The same keto-alcohol (VIII) was also obtainable from (+)-dihydrocarvone ethylene ketal (XIV), which was epoxidised to compound (XV). Reduction then yielded the hydroxy-ketal (XVI), which on mild acid hydrolysis afforded compound (VIII).



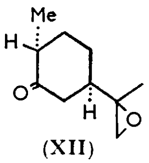
(IX)



(X)

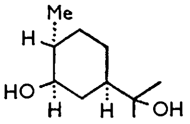


(XI)

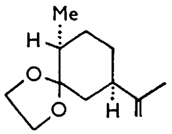


(XII)

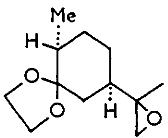
These studies suggested that α-cyperone (II) might be transformed into carissone (I). (+)-α-Cyperone (II), synthesised from (+)-dihydrocarvone by Howe and McQuillin's method,[5] was selectively converted into the 11,12-epoxide (XVII) * by perbenzoic acid.[11] The ultraviolet and infrared spectra of this product showed that the αβ-unsaturated ketone grouping was intact. Reduction of the epoxy-ketone with lithium aluminium hydride



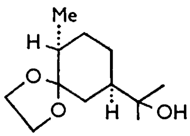
(XIII)



(XIV)



(XV)



(XVI)

yielded 3β-hydroxy-γ-eudesmol (XVIII), the quasi-equatorial conformation[12] being assigned to the 3-hydroxyl group, which arises by reduction of an unhindered keto-group.[13] Oxidation of 3β-hydroxy-γ-eudesmol with activated manganese dioxide[14] yielded (+)-carissone (I), identical with an authentic specimen. Since (II) represents the absolute configuration of (+)-α-cyperone,[5,6] this synthesis confirms that (I) portrays the absolute configuration of (+)-carissone.

McQuillin and Parrack[2] have separated natural eudesmol, long suspected of being a mixture, into α- and β-isomers (IV) and have characterised a third isomer, γ-eudesmol, obtained by careful hydrolysis of selinene dihydrochloride[15] and formulated as (XIX). γ-Eudesmol has recently been found to be a constituent of the essential oil of *Callitropsis araucarioides*.[16] We have confirmed the structure assigned to γ-eudesmol by synthesis. (+)-Carissone (I) was converted into its ethylene–thioketal (XX) with ethanedithiol and the boron trifluoride–ether complex. Desulphurisation with Raney nickel[17] yielded (+)-γ-eudesmol (XIX), the physical properties of which agreed with those of McQuillin and Parrack's product,[2] and with those of natural (+)-γ-eudesmol.[16] The infrared spectra of all three products were identical, except that in the 1640 and 890 cm.$^{-1}$ regions McQuillin

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* Eudesmane numbering according to Cocker and McMurry, *Tetrahedron*, 1960, **8**, 181.

[10] Parker and Isaacs, *Chem. Rev.*, 1959, **59**, 742.

[11] Howe, McQuillin, and Temple, *J.*, 1959, 363.

[12] Klyne, in "Progress in Stereochemistry," Butterworths Scientific Publns., London, 1954, Vol. I, pp. 81—83.

[13] Barton and Holness, *J.*, 1952, 78; Barton, *J.*, 1953, 1027.

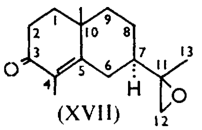
[14] Cf. Sondheimer and Rosenkranz, *Experientia*, 1953, **9**, 62.

[15] Semmler and Risse, *Ber.*, 1912, **45**, 3301; Ruzicka, Wind, and Koolhaas, *Helv. Chim. Acta*, 1931, **14**, 1132.

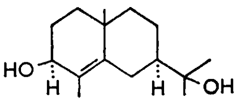
[16] Bates and Hendrickson, *Chem. and Ind.*, 1962, 1759.

[17] Pettit and van Tamelen, *Org. Reactions*, 1962, **12**, 356.

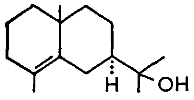
and Parrack's product and natural γ-eudesmol showed weak C=C and =C–H stretching vibration absorptions. Our product showed no band in the latter region, and only a very weak one near 1640 cm.$^{-1}$; in a tetrasubstituted ethylene no =C–H stretching vibration is, of course, possible, and it is often found that the C=C stretching band is absent with this grouping.[18] That such a grouping was present was shown by the ultraviolet absorption ($\lambda_{\text{max.}}$ 203 mμ; ε 6000 in hexane). Catalytic hydrogenation of our product afforded



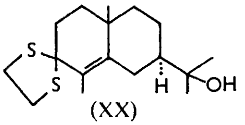
(XVII)



(XVIII)



(XIX)



(XX)

crystalline dihydroeudesmol, in almost theoretical yield, with uptake of one mol. of hydrogen. It seems possible that McQuillin and Parrack's product, and the natural product, were contaminated with material containing a terminal methylene group. Although our product reacted with 3,5-dinitrobenzoyl chloride under the usual conditions, we have not been able to obtain a crystalline 3,5-dinitrobenzoate, described by McQuillin and Parrack.[2]

This synthesis of (+)-γ-eudesmol estabishes its absolute configuration as (XIX).

EXPERIMENTAL

Optical rotations were measured for chloroform solutions.

(±)-*Ethyl* trans-*4-Methyl-3-oxocyclohexanecarboxylate* (V).—The keto-ester was synthesised from *p*-toluic acid by sulphonation, fusion with potassium hydroxide, reduction, esterification, and oxidation; [7] it had b. p. 140—142°/10 mm. (lit.,[7] b. p. 146—148°/25 mm.), $\nu_{\text{max.}}$ (liquid film) 1712 (ketone C=O) and 1721 cm.$^{-1}$ (ester C=O). The 2,4-*dinitrophenylhydrazone* crystallised from ethanol in yellow needles, m. p. 131—131·5° (Found: C, 52·75; H, 5·4; N, 15·4. $C_{16}H_{20}N_4O_6$ requires C, 52·7; H, 5·5; N, 15·4%).

(±)-*Ethyl* trans-*3,3-Ethylenedioxy-4-methylcyclohexanecarboxylate* (VI).—The foregoing keto-ester (1·3 g.), ethylene glycol (0·88 g.), dry benzene (20 c.c.), and a small crystal of toluene-*p*-sulphonic acid were mixed and refluxed in a Dean and Stark apparatus for 4 hr. Benzene (10 c.c.) was added to the cooled mixture, which was washed in turn with water, aqueous sodium carbonate, and water. The dried organic layer was concentrated, leaving the *ethylene ketal* (VI), b. p. 106—108°/0·5 mm. (1·14 g.) (Found: C, 63·1; H, 8·8. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·8%), $\nu_{\text{max.}}$ (liquid film) 1730 (saturated ester C=O) and 1095 cm.$^{-1}$ (cyclic ester); no ketonic C=O band.

(±)-trans-*2,2-Ethylenedioxy-4-(1-hydroxy-1-methylethyl)-1-methylcyclohexane* (VII).—The above ethylene ketal (2·0 g.) in anhydrous ether (20 c.c.) was added gradually, with stirring, to a Grignard reagent prepared from magnesium (0·58 g.), methyl iodide (3·44 g.), and anhydrous ether (60 c.c.). After being allowed to reflux for 2 hr. the system was cooled and decomposed by addition of a solution of ammonium chloride (6·0 g.) in water (50 c.c.). The organic layer was separated, washed with water, and dried; concentration afforded *2,2-ethylenedioxy-4-(1-hydroxy-1-methylethyl)-1-methylcyclohexane*, b. p. 87—88°/0·05 mm. (75%) (Found: C, 67·5; H, 10·3. $C_{12}H_{22}O_3$ requires C, 67·3; H, 10·35%), $\nu_{\text{max.}}$ (liquid film) 3623 (OH) and 1093 cm.$^{-1}$ (cyclic ether) (no carbonyl band). The 3,5-dinitrobenzoate was an oil.

(±)-trans-*5-(1-Hydroxy-1-methylethyl)-2-methylcyclohexanone* (VIII).—The foregoing ketal (0·6 g.) in methanol (10 c.c.) was mixed with water (3 c.c.) and concentrated hydrochloric acid (0·2 c.c.), and the whole refluxed on the water-bath for 2 hr. Water was added, followed by solid sodium hydrogen carbonate, and the product was isolated with ether. Concentration of the dried extract yielded the *keto-alcohol*, b. p. 81—82°/0·05 mm. (0·43 g.) (Found: C, 70·3; H, 10·7. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·7%), $\nu_{\text{max.}}$ (liquid film) 3571 (OH) and 1704 cm.$^{-1}$ (saturated ketone C=O). The 2,4-*dinitrophenylhydrazone* crystallised from ethanol in orange needles, m. p. 136° (Found: C, 54·8; H, 6·35; N, 16·4. $C_{16}H_{22}N_4O_5$ requires C, 54·8; H, 6·3; N, 16·0%).

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[18] Bellamy, "Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, Chapter 3.

Ethyl 9-*Hydroxy*-8,10-*dimethyl*-3-*oxodecalin*-2-*carboxylate* (X).—Ethyl 4-methyl-3-oxocyclohexanecarboxylate (8·0 g.), freshly prepared sodamide (2·04 g.), and dry ether (120 c.c.) were refluxed for 5 hr. under nitrogen with stirring, then cooled to 0° during the gradual addition of 2-chloroethyl ethyl ketone [19] (5·24 g.) in dry ether (20 c.c.). After being stirred overnight at room temperature and refluxed for 4 hr. the mixture was decomposed with ice-cold 2N-hydrochloric acid, and the organic layer was separated, washed with water, and dried (Na_2SO_4). Evaporation of the solvent and distillation of the residue gave, after removal of a fore-run (3·1 g.) of unchanged keto-ester, the *decalin ester* (X) (0·9 g.), b. p. 124—128°/0·05 mm. (Found: C, 67·6; H, 8·9; OEt, 15·9. $C_{15}H_{24}O_4$ requires C, 67·1; H, 9·0; OEt, 16·8%), $\nu_{max.}$ 3717 (OH), 1739 (saturated ester C=O), and 1724 cm.$^{-1}$ (saturated ketone C=O). Reaction with 2,4-dinitrophenylhydrazine gave an oil.

Ethyl 1,2,3,4,5,6,7,10-*Octahydro*-8,10-*dimethyl*-7-*oxo*-2-*naphthoate* (IX).—Ethyl 4-methyl-3-oxocyclohexanecarboxylate (8·0 g.) in dry ether (30 c.c.) was stirred under nitrogen for 4 hr. with a suspension of freshly prepared sodamide (from 2·0 g. of sodium) in ether (120 c.c.). 1-Diethylaminopentan-3-one methiodide [19,20] [from the base (7·85 g.) and an excess of methyl iodide] in dry pyridine (40 c.c.) was added rapidly to the stirred suspension at 0° and stirring was continued for 1½ hr. at this temperature, then for 12 hr. at room temperature and for 5 hr. at the b. p. Water was added, and the ether layer separated and washed in turn with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water. Evaporation of the dried (Na_2SO_4) solution yielded, after a fore-run (3·05 g.) of unchanged keto-ester, a fraction b. p. 120—132°/0·05 mm. (1·05 g.), which was dissolved in methanol (50 c.c.) and treated with concentrated hydrochloric acid (5 c.c.). After being kept for 2 days the solution was diluted with water and extracted with ether. Evaporation of the dried extract gave the *octahydronaphthoate*, b. p. 117—120°/0·05 mm. (0·46 g.) (Found: C, 71·95; H, 8·6. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·9%), $\lambda_{max.}$ (in MeOH) 244 mμ (ε 11,000), $\nu_{max.}$ (liquid film) 1721 (saturated ester C=O), 1664 (conjugated ketone C=O), and 1609 cm.$^{-1}$ (conjugated C=C). The 2,4-*dinitrophenylhydrazone* separated from ethanol in red needles, m. p. 141° (Found: C, 58·8; H, 6·4; N, 13·4. $C_{21}H_{26}N_4O_6$ requires C, 58·6; H, 6·1; N, 13·0%).

(−)-trans-2,2-*Ethylenedioxy*-4-*isopropenyl*-1-*methylcyclohexane* (XIV).—(+)-Dihydrocarvone [21] (12·0 g.), ethylene glycol (9·8 g.), dry benzene (100 c.c.), and a crystal of toluene-*p*-sulphonic acid were refluxed in a Dean and Stark apparatus for 6 hr. The solution was washed with sodium carbonate solution and water, dried (Na_2SO_4), and concentrated. The residual *ethylene ketal* distilled at 69—71°/1·0 mm. (90%) (Found: C, 73·5; H, 10·2. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·3%) and had n_D^{22} 1·4737, $[\alpha]_D^{20}$ −6·1° (*c* 3·3), $\nu_{max.}$ (liquid film) 1642 (C=C), 1093 (cyclic ether), and 891 cm.$^{-1}$ (RR′C=CH_2), no carbonyl absorption.

(+)-trans-4-(1,2-*Epoxy*-1-*methylethyl*)-2,2-*ethylenedioxy*-2-*methylcyclohexane* (XV).—The foregoing ketal (34·7 g.) in dry ether (50 c.c.) was added gradually to a solution of monoperphthalic acid [22] (1·15 mol.) in dry ether at 0°. The solution was kept at 0° for 6 days. The phthalic acid was removed by filtration and the ethereal solution washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and concentrated. The residual *epoxy-ketal* distilled at 74—75°/0·05 mm. (35·2 g.) (Found: C, 67·9; H, 9·5. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%) and had n_D^{19} 1·4771, $[\alpha]_D^{19}$ +11·9° (*c* 6·3), $\nu_{max.}$ (liquid film) 10·93 (cyclic ether) and 1265 cm.$^{-1}$ (epoxide), no C=C band. The product gave no colour with tetranitromethane.

(+)-trans-2,2-*Ethylenedioxy*-4-(1-*hydroxy*-1-*methylethyl*)-1-*methylcyclohexane* (XIV).—The above epoxy-ketal (35·0 g.) in dry ether (40 c.c.) was added gradually, with swirling, to an ice-cold solution of lithium aluminium hydride (4·0 g.) in dry ether (400 c.c.). After 16 hr. at room temperature "Celite" was added, followed by ice–water, with swirling, until decomposition was complete. The ethereal solution was decanted, dried (Na_2SO_4), and evaporated. The residual *hydroxy-ketal* distilled at 84—86°/0·1 mm. (30·7 g.) (Found: C, 67·1; H, 10·2. $C_{12}H_{22}O_3$ requires C, 67·3; H, 10·35%), n_D^{21} 1·4787, $[\alpha]_D^{20}$ +16·3° (*c* 2·15), $\nu_{max.}$ (liquid film) 3610 (OH) and 1093 cm.$^{-1}$ (cyclic ether). The infrared absorption curve was identical with that of the racemic product described above. The 3,5-*dinitrobenzoate* crystallised from light

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[19] McMahon, Roper, Utermohlen, Hasek, Harris, and Brant, *J. Amer. Chem. Soc.*, 1948, **70**, 2971.

[20] Adamson, McQuillin, Robinson, and Simonsen, *J.*, 1937, 1576; cf. Wilds and Shunk, *J. Amer. Chem. Soc.*, 1943, **65**, 469.

[21] Wallach and Schrader, *Annalen*, 1894, **279**, 377; McQuillin, private communication.

[22] Böhme, *Org. Synth.*, 1940, **20**, 70.

petroleum (b. p. 60—80°) in prisms, m. p. 154—155° (Found: C, 55·7; H, 6·0; N, 7·3. $C_{19}H_{24}N_2O_8$ requires C, 55·9; H, 5·9; N, 6·9%).

(+)-trans-5-(1-*Hydroxy*-1-*methylethyl*)-2-*methylcyclohexanone* (VIII).—The foregoing hydroxy-ketal (30·7 g.), methanol (220 c.c.), water (150 c.c.), and concentrated hydrochloric acid (2·7 c.c.) were refluxed on the water-bath for 2 hr. The methanol was removed *in vacuo* and the product isolated with ether. The *alcohol* (VIII) obtained by evaporation of the dried ether extract distilled at 78—80°/0·05 mm. (21·7 g.) (Found: C, 70·2; H, 10·8. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·7%) and had n_D^{20} 1·4756, $[\alpha]_D^{20}$ +16·6° (*c* 6·3). The infrared absorption curve (liquid film) was identical with that of the racemic product obtained as described above. The 2,4-*dinitrophenylhydrazone* crystallised from ethanol in orange-yellow needles, m. p. 131° (Found: C, 54·5; H, 6·45; N, 15·8. $C_{16}H_{22}N_4O_5$ requires C, 54·8; H, 6·3; N, 16·0%), $[\alpha]_D^{20}$ +165·4° (*c* 0·27). Dehydration of this derivative (400 mg.) at 100° with pyridine (10·0 c.c.) and phosphoryl chloride (1·0 c.c.) gave (+)-dihydrocarvone 2,4-dinitrophenylhydrazone,[23] m. p. and mixed m. p. 146° (180 mg.), $[\alpha]_D^{20}$ +74·5° (*c* 0·05), isolated by chloroform extraction.

(+)-trans-5-(1,2-*Epoxy*-1-*methylethyl*)-2-*methylcyclohexanone* (XII).—Epoxidation of (+)-dihydrocarvone was effected with perbenzoic acid essentially as described by Clemo and McQuillin for the (−)-enantiomorph.[9] The epoxy-ketone distilled at 75°/0·2 mm. (75%) and had n_D^{20} 1·4736, $[\alpha]_D^{20}$ +14·9° (*c* 0·9). As observed by the above workers, a small higher-boiling fraction, b. p. 138°/0·25 mm., was obtained, probably the corrresponding diol.

(−)-trans-5-(1-*Hydroxy*-1-*hydroxyethyl*)-2-*methylcyclohexanol* (XIII).—The above epoxy-ketone (3·0 g.) in dry ether (25 c.c.) was added gradually, with swirling, to a solution of lithium aluminium hydride (0·51 g.) in dry ether (50 c.c.). After an hour the solution was refluxed for 2 hr., then cooled to 0° and decomposed with ice–water in the presence of "Celite." The ether was decanted, dried (Na_2SO_4), and evaporated; the residual viscous *diol* distilled at 90—92°/0·05 mm. (2·46 g.). It crystallised in contact with light petroleum (b. p. 60—80°) and separated from a mixture of the same solvent and benzene in long needles, m. p. 103—104° (Found: C, 69·5; H, 11·8. $C_{10}H_{20}O_2$ requires C, 69·7; H, 11·7%), $[\alpha]_D^{20}$ −8·0° (*c* 1·6), $\nu_{max.}$ (in Nujol mull) 3390 cm.$^{-1}$ (OH) (no carbonyl band). The *bis*-3,5-*dinitrobenzoate* crystallised from benzene in plates, m. p. 183—184° (Found: C, 51·7; H, 4·3; N, 9·8. $C_{24}H_{24}N_4O_{12}$ requires C, 51·4; H, 4·3; N, 10·0%).

(+)-trans-5-(1-*Hydroxy*-1-*methylethyl*)-2-*methylcyclohexanone* (VIII).—The foregoing diol (2·0 g.) in glacial acetic acid (60 c.c.) was mixed with a solution of chromic anhydride (1·6 g.) in 80% aqueous acetic acid (20 c.c.) and kept at 60° for 30 min. The *keto-alcohol*, isolated by dilution with water and ether-extraction, distilled at 81—83°/0·1 mm. (1·2 g.), $[\alpha]_D^{20}$ +18·4° (*c* 2·1). The infrared absorption spectrum (liquid film) was identical with that of the racemic keto-alcohol described above.

(+)-11,12-*Epoxy*-11,12-*dihydro*-α-*cyperone* (XVII).—(+)-α-Cyperone[5] (0·86 g.) in dry chloroform (10 c.c.) was epoxidised with perbenzoic acid (0·56 g., 1·02 mol.) in the same solvent (17·5 c.c.), essentially as described by Howe, McQuillin, and Temple.[11] The epoxy-ketone (XVII) distilled at 110—112°/0·1 mm. (0·90 g.) (lit.,[11] b. p. 125°/0·3 mm.) (Found: C, 76·8; H, 9·4. Calc. for $C_{15}H_{22}O_2$: C, 76·9; H, 9·5%), n_D^{20} 1·5247, $[\alpha]_D^{20}$ +110·2° (*c* 1·49) (lit.,[11] n_D^{20} 1·5238, $[\alpha]_D$ +108° [*c* 3·01]), $\lambda_{max.}$ (in hexane) 247 mμ (ε 14,150), $\nu_{max.}$ (liquid film) 1664 (conjugated C=O) and 1615 cm.$^{-1}$ (conjugated C=C) (no epoxide band in the 1250 cm.$^{-1}$ region).[24]

(+)-3β-*Hydroxy*-γ-*eudesmol* (*Eudesm*-4-*ene*-3β,11-*diol*) (XVIII).—A cooled solution of lithium aluminium hydride (0·16 g.) in dry ether (40 c.c.) was added gradually to a stirred solution of the foregoing epoxy-α-cyperone (0·65 g.) in dry ether (20 c.c.), the temperature being kept below 0°. After 24 hr. at 0° the complex was decomposed in the usual way with ice–water in the presence of " Celite." The dried (Na_2SO_4) ethereal solution was evaporated, leaving (+)-3β-*hydroxy*-γ-*eudesmol*, b. p. 120—122°/0·1 mm. (0·60 g.), which solidified readily and crystallised from benzene–light petroleum (b. p. 60—80°) in sheaves of needles, m. p. 129·5—130° (Found: C, 75·3; H, 10·9. $C_{15}H_{26}O_2$ requires C, 75·6; H, 11·0%), $[\alpha]_D^{20}$ +57·6° (*c* 2·9), $\lambda_{max.}$ (in MeOH) 209 mμ (ε 10·070), $\nu_{max.}$ (Nujol mull) 3425 cm.$^{-1}$ (OH) (no carbonyl or C=C bands). The product gave a brown colour with tetranitromethane and decolorised cold, acid permanganate immediately.

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[23] McQuillin and Ord, *J.*, 1959, 2902.

[24] Ref. 18, p. 118.

(+)-*Carissone* (I).—Activated manganese dioxide[25] (2·0 g.), (+)-3β-hydroxy-γ-eudesmol (0·3 g.), and dry chloroform (30 c.c.) were shaken together at room temperature for 20 hr. The solution was filtered and the residue washed with chloroform. The combined filtrate and washings were evaporated, leaving (+)-carissone (0·25 g.), which crystallised readily and separated from ether–light petroleum (b. p. 60—80°) in prisms, m. p. 78—79° (Found: C, 76·15; H, 10·2. Calc. for $C_{15}H_{24}O_2$: C, 76·2; H, 10·2%), $[\alpha]_D^{20}$ +134·4° (*c* 0·6). The m. p. was undepressed by admixture with an authentic specimen of natural (+)-carissone, m. p. 78—79°, kindly supplied by Professor T. Reichstein,[1] and the infrared absorption spectra (Nujol mull) were identical.

(+)-*Carissone Ethylene Thioketal* (XX).—(+)-Carissone (0·33 g.), ethanedithiol (0·22 g.), and methanol (8·0 c.c.) were mixed and cooled to 0°. Freshly distilled boron trifluoride–ether complex[26] (0·2 c.c.) was added, and the mixture was kept at 0° overnight. The methanol was removed *in vacuo* and the residual yellow syrup taken up in ether. The solution was washed with aqueous sodium carbonate and water, dried (Na_2SO_4), and concentrated. The remaining *ethylene thioketal* distilled at 120—123°/0·1 mm. (0·36 g.) and separated from light petroleum (b. p. 40—60°) in needles, m. p. 101—101·5° (Found: C, 65·6; H, 9·15; S, 19·9. $C_{17}H_{28}OS_2$ requires C, 65·4; H, 9·0; S, 20·5%), $[\alpha]_D^{20}$ +100° (*c* 0·88), $\nu_{max.}$ (Nujol mull) 3534 (OH) 1637 cm.$^{-1}$ (C=C) (no carbonyl band). The product gave a yellow colour with tetranitromethane.

(+)-γ-*Eudesmol* (XIX).—The foregoing thioketal (0·44 g), W-2 Raney nickel[27] (8·0 g.), and 90% aqueous ethanol (40 c.c.) were refluxed for 14 hr. The nickel was removed by filtration and the filtrate concentrated *in vacuo*. The residue was dissolved in ether, and the solution dried (Na_2SO_4) and evaporated, leaving (+)-γ-eudesmol (0·26 g.) which distilled at 80—81°/0·05 mm. (Found: C, 81·2; H, 11·7. Calc. for $C_{15}H_{26}O$: C, 81·0; H, 11·8%) and had $[\alpha]_D^{20}$ +59·1° (*c* 1·8), $\lambda_{max.}$ (in hexane) 203 mμ (3 6000), $\nu_{max.}$ (liquid film) 3400 cm.$^{-1}$ (OH), only very weak absorption in the 1640 cm.$^{-1}$ region, and none in the 890 cm.$^{-1}$ region ($R^1R^2C=CR^3R^4$){McQuillin and Parrack[2] record b. p. 80—84°/0·1 mm., $[\alpha]_D$ (in $CHCl_3$) +62·5° (*c* 0·73); Bates and Hendrickson[16] report $[\alpha]_D^{25}$ +66·7°}. The infrared spectra of our product, Dr. McQuillin's, and natural (+)-γ-eudesmol[16] were identical except for the presence in the spectra of the last two of weak bands in the 1640 and 890 cm.$^{-1}$ regions ($C=CH_2$). McQuillin and Parrack[2] also report the formation of a crystalline 3,5-dinitrobenzoate, m. p. 105—106°, but we have not been able to obtain this derivative in a crystalline state, though a reaction occurred with 3,5-dinitrobenzoyl chloride in pyridine. Our product gave a brownish-yellow colour with tetranitromethane and decolorised cold acid permanganate immediately.

A solution of synthetic (+)-γ-eudesmol (0·11 g.) in glacial acetic acid (10 c.c.) was shaken in hydrogen with pre-reduced Adams catalyst at room temperature and pressure (uptake H_2). The catalyst was removed and the filtrate was diluted with much water and extracted with ether. The extract was washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and concentrated, yielding dihydroeudesmol (0·10 g.) which crystallised from ethanol in elongated prisms, m. p. 82·5 alone or mixed with an authentic specimen obtained by the hydrogenation of natural eudesmol.[2] The infrared spectra were identical.

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[25] Mancera, Rosenkranz, and Sondheimer, *J.*, 1953, 2189.
[26] Cook, Ilett, Saunders, and Stacey, *J.*, 1950, 3125.
[27] Mozingo, *Org. Synth.*, 1941, **21**, 15.