The Structure of Metrosiderene.

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(—)-Metrosiderene, one of the sesquiterpenes present in the essential oils of *Metrosideros umbellata* and *Dacrydium biforme,* is shown to be a mixture of the isomers (I) and (II).

THE essential oil of *Metrosideros umbellata,* a tree endemic to New Zealand, was examined by Gardner (*J. Soc. Chem. Ind.,* 1931, **50**, 142T), who made a preliminary study of the dextrorotatory sesquiterpene fraction. By a precise fractionation Corbett and Hanger (*J. Sci. Food Agric.,* 1953, **4**, 508) isolated (+)-aromadendrene, (+)-cadinene, and a third sesquiterpene, to which the name (—)-metrosiderene is assigned.

This communication deals with metrosiderene. This has also been isolated from the essential oil of *Dacrydium biforme* (Corbett and Wong, unpublished work), the identity being established by comparison of their physical constants (see Table) and by the identity of their infra-red spectra.

B. p.	n_D^{20}	d_4^{20}	$[\alpha]_D^{20}$	$[R_L]_D$	Source
98°/3 mm.	1·5041	0·9155	−8·05°	66·1	*M. umbellata*
100°/4 mm.	1·5050	0·9148	−2·00	66·13	*D. biforme*

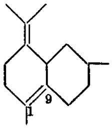
Analysis confirms the molecular formula $C_{15}H_{24}$. The sesquiterpene yields a dimeric crystalline nitrosate, by which it may be identified, and which is of unusual structure as it has the formula $C_{30}H_{48}O_{12}N_6$.

The molecular refraction is in agreement with that for a dicyclic sesquiterpene; this was confirmed by the preparation of an oily monohydrochloride which is unsaturated (nitromethane), and by consumption of 1·85 mols. of hydrogen in presence of Adams's platinum oxide. Further the sesquiterpene absorbed *ca.* 2 atoms of oxygen from perbenzoic acid. On dehydrogenation with selenium it yielded cadalene, and the infra-red spectrum of tetrahydrometrosiderene is identical with that of tetrahydro*iso*zingiberene, which Sorm *et al.* (*Chem. Listy,* 1952, **46**, 410) have shown to be a stereoisomer of cadinane. Stereochemically metrosiderene must be related to calacorene and *iso*zingiberene rather than to the various isomers of cadinene (Sorm *et al., loc. cit.*).

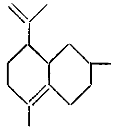
Quantitative ozonolysis of the sesquiterpene of $[\alpha]_D^{20}$ −2·0° gave acetone (0·30 mol.), formaldehyde (0·30 mol.) and formic acid (0·28 mol.), indicating the presence of 30% of a hydrocarbon containing an *iso*propylidene group and 58% of one with an *iso*propenyl group. Sorm *et al.* (*Coll. Czech. Chem. Comm.,* 1950, **15**, 82) have shown that such a mixture of isomers cannot be readily separated, even by repeated chromatography on very active alumina.

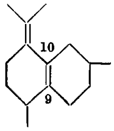
When the sesquiterpene was hydrogenated with palladized barium sulphate as catalyst, the hydrogen consumption ceased after 0·7 mol. had been consumed. This evidently represents the saturation of the methylene bond, for this partially reduced sesquiterpene gave neither formaldehyde nor formic acid on quantitative ozonolysis, but the yield of acetone was not significantly altered (0·27 mol.). The somewhat lower value for the methylenic determination by ozonolysis is probably due to the loss of small amounts of the rather volatile formaldehyde and formic acid.

The infra-red spectrum of metrosiderene shows a very strong band at 888 cm.$^{-1}$ which is characteristic of the methylenic structure. There are no strong bands in the regions 780—810 and 1655—1685 cm.$^{-1}$, characteristic of the C–H deformation and double-bond stretching vibrations respectively, of a trisubstituted double bond in a cyclic olefin, *e.g.*, α-pinene. Furthermore there are no strong bands in the regions characteristic of the group –CH:CH– (Herout and Pliva, *Coll. Czech. Chem. Comm.*, 1949, **15**, 160). The second double bond is thus probably tetrasubstituted, *i.e.*, in position 1 : 9 or 9 : 10, as in formulæ (I—II) and (III—IV) respectively. This is also in agreement with the fact that only one double bond is readily hydrogenated, and that only a monohydrochloride can be prepared. Formulæ (III—IV) for metrosiderene are excluded since the ultra-violet spectrum of the sesquiterpene showed no absorption band.

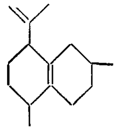


(I)


(II)



(III)


(IV)

Structures (I—II) representing metrosiderene have been confirmed by ozonolysis of the partially reduced (palladium) product. When the neutral product was oxidised with sodium hypoiodite, it gave iodoform, which must be derived from the methyl ketone formed by fission of the 1 : 9-double bond.

EXPERIMENTAL

(–)-*Metrosiderene*.—The sesquiterpenes from *M. umbellata* and from *D. biforme* were distilled separately through a Lecky and Ewell column (*Ind. Eng. Chem. Anal.*, 1940, **12**, 544) of 48 plates, and the distillate was collected in 3-c.c. portions. The fractions of *sesquiterpene* with the physical constants listed on p. 1179 were isolated (Found : C, 88·3; H, 11·7. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%). To ensure that the fractions were homogeneous, the infra-red spectra of successive distillates were measured. The *nitrosate* was prepared by standard procedure in good yield, and had m. p. 122° after repeated crystallisation from chloroform–methanol (Found : C, 52·1; H, 6·8; N, 11·9%; *M*, by the micro-isopiestic method, 672, 680. $C_{30}H_{48}O_{12}N_6$ requires C, 52·6; H, 7·0; N, 12·3%; *M*, 684). The *monohydrochloride* was prepared by saturating a solution of the sesquiterpene in dry ether with hydrogen chloride : removal of the solvent gave a colourless liquid, n_D^{20} 1·5110, d_4^{20} 1·019 (Found : Cl, 15·22. $C_{15}H_{25}Cl$ requires Cl, 14·8%). No crystalline derivatives were obtained in attempted preparations of the nitrosochloride and nitrosite.

When a chloroform solution of perbenzoic acid and (–)-metrosiderene, $[\alpha]_D^{20}$ –8·05°, was kept at 0° until the iodine titre was constant, the oxygen absorption corresponded to 2·14 double bonds in the molecule. (–)-Metrosiderene, $[\alpha]_D^{20}$ –2·0°, gave an oxygen absorption corresponding to 1·90 double bonds.

Hydrogenation of (–)-*Metrosiderene*.—(*a*) A solution of (–)-metrosiderene (1·3 g.) in glacial acetic acid (30 c.c.) was shaken with hydrogen in the presence of Adams's catalyst (300 mg.) at atmospheric pressure. Hydrogen equivalent to 0·7 double bond was consumed in 10 min., and thereafter the rate rapidly diminished, and it ceased with the consumption of hydrogen equivalent to 1·85 double bonds after 4 hr. Distillation of the product over sodium gave *tetrahydrometrosiderene* (900 mg.), b. p. 134—135°/13 mm., n_D^{20} 1·4810, d_4^{20} 0·8920 (Found : C, 86·8; H, 13·1. $C_{15}H_{28}$ requires C, 86·5; H, 13·5%).

(*b*) (–)-Metrosiderene (4·2 g.) in ethanol (30 c.c.) was shaken with hydrogen in the presence of palladized barium sulphate. Hydrogen equivalent to 0·7 double bond was consumed before reduction ceased. Distillation of this product gave a fraction (A) (4·1 g.), b. p. 123—139°/13 mm.

Dehydrogenation of (–)-*Metrosiderene*.—(–)-Metrosiderene (4 g.) and finely powdered selenium (6 g.) were heated to 200° and the temperature then gradually raised to 280° and held there for 20 hr. Extraction with ether and distillation of the product yielded a blue liquid (3·2 g.), which was treated by Sherndal's method (*J. Amer. Chem. Soc.*, 1915, **37**, 167) for the isolation of azulene, but only a small quantity (50 mg.) was obtained. Distillation of the oil remaining from the azulene extraction gave two fractions, (*a*) b. p. 100°/3 mm., n_D^{20} 1·5100 (1·2 g. of unchanged oil), and (*b*) b. p. 115—122°/2 mm., n_D^{20} 1·5415 (1·7 g. of a colourless oil). Treatment of fraction (*b*) with saturated ethanolic picric acid gave a quantitative yield of cadalene picrate, m. p. and mixed m. p. 115° (from ethanol).

iso*Propylidene Determination.*—(−)-Metrosiderene, $[\alpha]_D^{20}$ −2·0° (117·9 mg.), was ozonised according to the method of Sorm *et al.* (*Coll. Czech. Chem. Comm.*, 1950, **15**, 92). Acetone (0·30 mol.) was found. A similar determination with (−)-metrosiderene of $[\alpha]_D^{20}$ −8·05° gave acetone (0·29 mol.).

Methylene Determination.—(−)-Metrosiderene, $[\alpha]_D^{20}$ −8·05° (117·5 mg.), was ozonised in carbon tetrachloride (30 c.c.), and the formaldehyde and formic acid were determined by the method of Sorm *et al.* (*loc. cit.*). Formaldehyde (0·29 mol.) and formic acid (0·22 mol.) were found. A similar series of determinations with (−)-metrosiderene of $[\alpha]_D^{20}$ −2·0° gave formaldehyde (0·30 mol.) and formic acid (0·28 mol.).

Ozonolysis of Partially Reduced (−)-*Metrosiderene.*—Ozonised oxygen was passed through a solution of partially reduced (−)-metrosiderene (A) (4·1 g.) in carbon tetrachloride (50 c.c.) for 6 hr. The viscous ozonide was decomposed by refluxing distilled water (150 c.c.) in 30 min., and the mixture was then steam-distilled to give 250 c.c. of distillate. Acetone, identified as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 124—125°, was identified in this distillate. The neutral (2·5 g.) and the acid (1·0 g.) fraction from the ozonolysis were isolated in the usual manner. Oxidation of the neutral fraction (70 mg.) with sodium hypoiodite gave iodoform, m. p. and mixed m. p. 118°.

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