Tetrahedron Letters, No. 3, pp. 15-18, 1959. Pergamon Press Ltd.
Printed in Great Britain.

AROMADENDRENE AND VIRIDIFLOROL

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(Received 3 April 1959)

FORMULA (I) advanced [1] as a possibility for aromadendrene is more likely to be correct than the alternative with the *cyclo*propane ring terminating at the 6-position since dehydrogenation gives only S-guaiazulene. Ozonolysis of aromadendrene from *Metrosideros scandens* [2] gave α-apoaromadendrone, isomerised by alkali to the well known apoaromadendrone, and it was assumed that this hydrocarbon and the aromadendrene from *Eucalyptus nova-anglica* and other sources were identical and therefore had a *trans*-9,10-ring junction. Failure to obtain α-apoaromadendrone from the latter hydrocarbon in the Manchester and several other laboratories indicates

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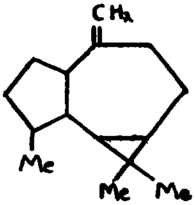
[1] A.J. Birch and F.N. Lahey, *Aust. J. Chem.* **6**, 379 (1953).

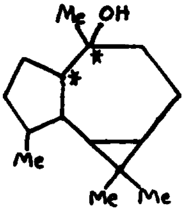
[2] A.J.Birch, *J. Chem. Soc.* 715 (1953).

that the *M. scandens* hydrocarbon (α-aromadendrene) is a stereoisomer with a *trans*-9,10-ring junction and that the authentic aromadendrene has the *cis*-ring junction.

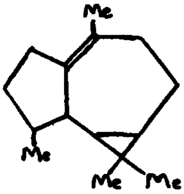
Globulol has been shown [3] to be a stereoisomer of (II) related stereochemically to aromadendrene; we have found that viridiflorol [4] (identical with himbaccol [5])



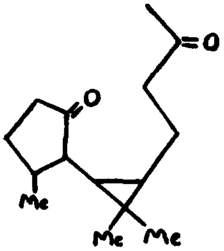
I



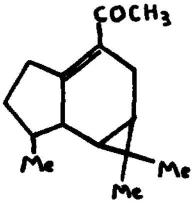
II



III



IV



V

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[3] A. Blumann, A.R.H. Cole, K.J.L. Thiaberg and D.E. White, *Chem. and Ind.* 1426, (1954).

[4] T.G.H. Jones and W.L. Haenke, *J. Roy. Soc. Queensland* **49**, 95 (1938).

[5] A.J. Birch and K.M.C. Mostyn, *Aust. J. Chem.* **8**, 550 (1955).

yields some α-aromadendrene on pyrolysis of its phenylurethane. The product ($C=CH_2$ bands at 3085; 1638; 890 cm^{-1}) on ozonolysis gave α-apoaromadendrone, m.p. 71-72°; $[\alpha]_D^{23}$ -14°, isomerised by base to apoaromadendrone, m.p. and mixed m.p. 83-84°; $[\alpha]_D^{23}$ +3°. Dehydration of viridiflorol by alcoholic sulphuric acid produced some ledene identified as the glycol,[6] m.p. and mixed m.p. 150-151°; $[\alpha]_D^{20}$ -15.5°. Lead tetraacetate fission of the glycol gave a diketone (IV) (carbonyl bands at 1740 and 1715 cm^{-1}, bis-2,4-dinitrophenylhydrazone, m.p. 115-118°) also obtained by chromic acid oxidation of viridiflorol. The diketone was cyclised by alkali to an αβ-unsaturated ketone probably (V) (acetyl ν_{max} 1356 cm^{-1}) contaminated with its βγ-isomer ($\lambda_{max.}^{alc.}$ 241mμ; ν_{max} 1710 and 1688 cm^{-1}). This supports the formula (III) advanced for ledene[7] and the suggestion that ledol and palustrol [8] are probably stereoisomers of (II).[7] Therefore in all probability ledol, palustrol,

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[6] N.P. Kyrialov, Zhur. Obshcheĭ Khim. 21, 2077 (1951); Chem. Abs. 46, 6633 (1952)

[7] L. Dolejs, F. Sorm and M. Soucek, Chem. and Ind. 160 (1959).

[8] N.P. Kyrialov, Zhur. Obshcheĭ Khim. 24, 1271 (1954); Chem. Abs. 49, 13944 (1955).

viridiflorol and globulol are the four possible diastereoisomers of (II) differing at the asterisked positions. Professor F. Šorm (Prague), to whom we are indebted for a specimen of ledeneglycol, has informed us that he and his co-workers have reached similar conclusions.

We have confirmed the observation of Kyrialov [9] that ledeneglycol on acid treatment followed by dehydrogenation yields 1,6-dimethyl-4-isopropylnapth-5-ol the picrate of which was identical with an authentic specimen prepared from guaiol.[10] The weight of evidence in favour of structure (II) for viridiflorol is so great that the mechanism of this rearrangement must be more complex than Šorm originally proposed.[11]

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[9] N.P. Kyrialov, *Sbornik Statei Obshcheĭ Khim.* **2**, 1617 (1953); *Chem. Abs.* **49**, 5389 (1955).

[10] Pl.A. Plattner and G. Magyar, *Helv.Chim. Acta*, **24**, 191; 1163 (1941).

[11] L. Dolejs, M. Soucek, M. Horak and F. Sorm, *Chem. and Ind.* 494 (1958); *Chem. Listy*, **52**, 2188 (1958).