Tetrahedron Letters No. 10, pp. 1-4, 1959. Pergamon Press Ltd. Printed in Great Britain.

POSITION OF THE CYCLOPROPANE RING IN AROMADENDRENE

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(Received 29 June 1959)

IN 1953, Birch and Lahey[1] suggested for aromadendrene two alternative structures I and II with the cyclopropane ring in different positions. As aromadendrene on dehydrogenation affords S-guajazulene only, Birch *et al.* in their recent paper,[2] prefer formula I. In view of the speculative character of this argument, we considered it worthwhile to establish a conclusive proof of the position of the three-membered ring in aromadendrene. We, therefore, carried out the degradation of aromadendrene which enabled us to decide definitely in favour of structure I.

Apoaromadendrone (III)[3] on treatment with perphtalic acid and subsequent hydrolysis of the resulting lactone afforded hydroxy acid IV, m.p. 122.5°, $[\alpha]_D^{20}$ + 6.3° (methanol, c, 3.15), I.R. λ_{max} (dioxan): 1736 cm^{-1} (COOH) and 3490 cm^{-1} (OH). Found: C, 69.77; H, 10.14. $C_{14}H_{24}O_3$ requires: C, 69.96; H, 10.07%. The proof that the tertiary carbon atom was oxidized by Bayer-Villiger procedure has been brought forward by subsequent oxidation of substance IV to the known keto acid $C_{14}H_{22}O_3$ (oxime m.p. 168°).[1]

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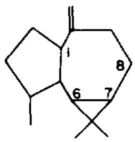
[1] A. J. Birch and F. N. Lahey, Aust. J. Chem. 6, 379 (1953).

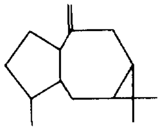
[2] A. J. Birch, J. Grimshaw, R. N. Speake, R. M. Gascoigne and R. O. Hellyer, Tetrahedron Letters No. 3, 15 (1959).

[3] L. H. Briggs and W. F. Short, J. Chem. Soc. 2524 (1928).

The methylester of the acid IV on treatment with phenylmagnesium bromide followed by acetylation of the resulting product with acetic anhydride in pyridine, afforded acetoxy derivative of a diphenylcarbinol, m.p. 119-122°, I.R. λ_{max} ($CHCl_3$): 1721, 1260 cm^{-1} (OAc), 3510, 3600 cm^{-1} (OH), 1496, 1600 cm^{-1} (phenyl) and 1377 cm^{-1} (gem. dimethyl on cycloprogane ring[4]). (Found: C, 80.12; H, 8.76. $C_{28}H_{36}O_3$ requires: C, 79.96; H, 8.63%). The carbinol on dehydratation with acetic acid yielded a liquid olefine (I.R. λ_{max}/CCl_4): 1738, 1244 cm^{-1} (OAc), 1496, 1599 cm^{-1} (phenyl) and 1377 cm^{-1} (gem. dimethyl on cyclopropane ring[4]) which was subsequently ozonized. The product of ozonolysis after



I



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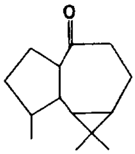

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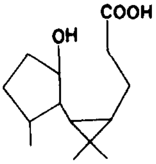

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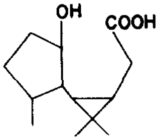

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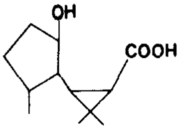

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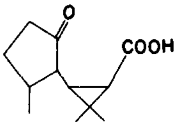
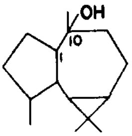


VII



VIII

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[4] M. Horák and J. Plíva, Coll. Czech. Chem. Comm. In press.

oxidation with hydrogen peroxide in alkaline medium afforded hydroxy acid V, m.p. 153.5°, $[\alpha]_D^{20}$ + 7.7° (alcohol, c, 3.31), I.R. λ_{max}/$CHCl_3$): 1672 cm^1, shifted by intermolecular association with hydroxyl group), 3240 cm^{-1} (OH); λ_{max} (dioxan): 1738 cm^{-1} (COOH) and 3492 cm^{-1} (OH). (Found: C, 68.95; H, 9.97. $C_{13}H_{22}O_3$ requires: C, 68.99; H, 9.80%).

The methylester of the acid V submitted to another Barbier-Wieland degradation via the acetoxy diphenylcarbinol (liquid, I.R. λ_{max}/$CHCl_3$): 1728, 1258 cm^{-1} (OAc), 3465, 3595 cm^{-1} (OH), 1495, 1600 cm^{-1} (phenyl) and 1378 cm^{-1} (gem. dimethyl on cyclopropane ring[4]) and unsaturated acetoxy derivative (liquid, I.R. λ_{max}/$CHCl_3$): 1726, 1255 cm^{-1} (OAc), 1497, 1598 cm^{-1} (phenyl), 1619 cm^{-1} (conjugated double bond) and 1378 cm^{-1} (gem. dimethyl on cyclopropane ring[4]) afforded hydroxy acid VI, m.p. 156°, $[\alpha]_D^{20}$ - 20.5° alcohol, c, 1.47), I.R. λ_{max}/$CHCl_3$): 1694 cm^{-1} (COOH); λ_{max}/dioxan): 1726 cm^{-1} (COOH) and 3500 cm^{-1} (OH). (Found: C, 67.79; H, 9.64; H^x, 0.93. $C_{12}H_{20}O_3$ requires: C, 67.89; H, 9.50; H^x, 0.95%). The fact that the three-membered ring in hydroxy acid VI remained untouched came out from the elementary analysis which indicated the normal course of Barbier-Wieland degradation; further the substance did not contain a double bond because it was prepared by ozonolysis and its infra-red spectrum did not exhibit any frequency of ethylenic linkage. The shift of the frequency due to the carbonyl in a carboxyl group (1726 cm^{-1}, dioxan), in comparison with the acid V (1738 cm^{-1}, dioxan) is in accordance with the presence of a cyclopropane ring in α-position to the carboxyl group. The cyclopentane ring of IV, **substituted** with a hydroxyl group, was maintained in the acid VI as follows from the chromic acid oxidation of the latter to the keto acid VII, m.p. 118° (Found: C, 68.39; H, 8.70. $C_{12}H_{18}O_3$ requires: C, 68.54; H, 8.63%) which in view of its infra-red spectrum had a keto group in a five-membered ring (λ_{max}/$CHCl_3$): 1734 cm^{-1}). (2,4-Dinitrophenylhydrazone: yellow needles, m.p. 241°, found: N, 14.43. $C_{18}H_{22}N_4O_6$ requires: N, 14.35%).

The sequence of degradation ractions outlined above, shows unambiguously in aromadendrene the same location of the cyclopropane ring as in formula I. The identical location of the cyclopropane ring may be ascribed also to some other compounds of the aromadendrene type, the relationship of which with aromadendrene had previously been established. To the compounds mentioned above belong alloaromadendrene, isolated recently in this Laboratory from the oil of Perovskia scrophullariaefolia and Eucalyptus globulus which was characterized as the C_1-epimer of aromadendrene[5b] (cf. also[2]). Further compounds of this group are three stereoisomeric alcohols - globulol,[6] ledol[5,7] and viridiflorol[5b] (cf. also[2]) - which possess the same formula VIII and differ only in configuration on the carbon atoms C_1 and/or C_{10}; their relationship to isomeric aromadendrenes was clarified in our preceding communication.[5b]

[5a] L. Dolejš, F. Šorm and M. Souček, Chem. & Ind. 160 (1959);
[b] L. Dolejš, V. Herout, O. Motl, F. Šorm and M. Souček, Chem. & Ind. 566 (1959); L. Dolejš, O. Motl, M. Souček, V. Herout and F. Šorm, Coll. Czech. Chem. Comm. In press.

[6] A. Blumann, A. R. H. Cole, K. J. L. Thieberg and D. E. White, Chem. & Ind. 1426 (1954).

[7] L. Dolejš, M. Souček, M. Horák and F. Šorm, Chem. & Ind. 494 (1958); Chem. Listy 52, 2188 (1958); Coll. Czech. Chem. Comm. 24, 1353 (1959).