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STEREOCHEMISTRY OF AROMADENDRENE, ALLOAROMADENRENE, GLOBULOL, LEDOL AND VIRIDIFLOROL

L. Dolejš and F. Šorm

Department of Natural Products, Institute of Chemistry,

Czechoslovak Academy of Science, Prague

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IN preceding papers of this series we proved the existence of a new hydrocarbon isomeric with aromadendrene which we called alloaromadendrene. Further, we elucidated the constitution of ledol and viridiflorol and their relationship to globulol and both isomeric aromadendrenes.[1-3] Recently, on the basis of degradation of aromadendrene, we established the location of the cyclopropane ring at compounds of this type.[4] In view of these results, both aromadendrenes are C_1 epimers of formula I, and ledol, viridiflorol and globulol C_1 and/or C_{10} epimers of structure II. Ledol and viridiflorol are derived from alloaromadendrene (the same configuration at C_1), globulol is related to aromadendrene.

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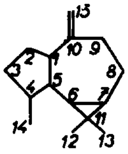
[1] L. Dolejš, M. Souček, M. Horák and F. Šorm, Chem. & Ind. 494 (1958); Chem. listy 52, 2189 (1958); Coll. Czech. Chem. Comm. 24, 1353 (1959).

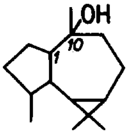
[2] L. Dolejš, F. Šorm and M. Souček, Chem. & Ind. 160 (1959).

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

[4] L. Dolejš and F. Šorm, Tetrahedron Letters 10, 1 (1959).



I



II

As Buchi et al.[5] published, a short time, ago, complete structures of the discussed compounds, we also wish to report our present results which are in full agreement with those of the American authors.

On treatment with perphtalic acid, apoaromadendrone (III) afforded a lactone which on subsequent saponification yielded the hydroxy acid IV.[4] The keto-acid V (cf[6]), derived from the latter compound, on catalytical hydrogenation or on treatment with lithium tri-(t-butoxy)-aluminohydride converts into the isomeric hydroxy acid VI, m.p. 143.5°, $[\alpha]_D^{20}$ + 19.4° (methanol, c = 5.35). It may be assumed that the reagent approaches the carbonyl group of V from the side opposite to the bulky substituent in position α. Hence both hydroxy-acids may be allotted the configuration on C_1 and C_5 in the sense of formulae IV and VI respectively.

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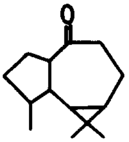
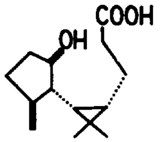
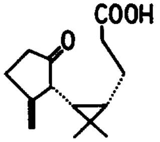
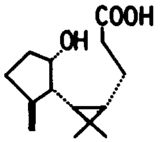
[5] G. Büchi, S. W. Chow, T. Matsuura, T. L. Popper, H. H. Rennhard and M. Schach v. Wittenau, Tetrahedron Letters **6**, 14 (1959).

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


III


IV


V


VI

Further evidence of the configuration was obtained from the results of equilibration of both hydroxy-acids by aluminium isopropoxide at the presence of traces of the keto-acid V. Equilibration of the cis-derivative VI afforded a product which partially crystallized and from which the trans-acid IV was isolated; the acid IV, on the other hand, yielded a product which solidified completely, affording, after crystallization, only the unchanged starting material.

With regard to the above results and to the fact that the peracid-ketone reaction proceeds with retention of configuration of the migrating group,[7,8] the fusion of the five- and seven-membered ring in aromadendrene may be regarded as trans.

Birch and Lahey[6] elucidated the relative configuration of asymmetric

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[7] R. B. Turner, J. Amer. Chem. Soc. **72**, 878 (1950).

[8] T. F. Gallagher and T. H. Kritchevsky, J. Amer. Chem. Soc. **72**, 882 (1950).

carbon atoms C_4 and C_5 from the stability of the keto-acid V in alkaline medium. The configuration of centres of asymmetry of the cyclopropane ring in relationship to the other asymmetric carbon atoms may be deduced from the molecular models of ledol.

As has already been proved,[3] ledol possesses the opposite configuration on C_1 than aromadendrene; thus two alternative structures VII and VIII* with different orientation of the cyclopropane ring come into account for the former.** In the structure VIII, however, the five- and the seven-membered ring approach themselves to a considerable extent and strong interactions between the hydrogen atoms (at C_2, C_3, C_4) and the methyl group at C_{12} and the hydrogen atoms of the seven-membered ring (at C_8 and C_9) take place.

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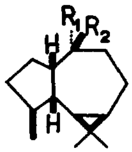
* For structures VII and VIII $R_1 = OH$, $R_2 = CH_3$ or vice versa.

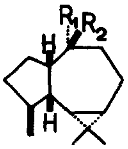
** The a priori possible pseudo-boat conformation of the seven-membered ring (IX) of structures VII and VIII may be, in both cases,

IX

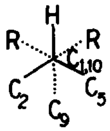
excluded because of the total interference of the C_{10}-substituent (OH or CH_3) with the geminal-methyl group of the cyclopropane ring.



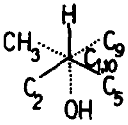
VII



VIII

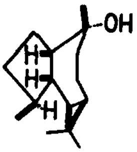


X

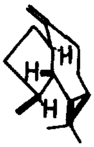


XI

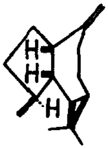
An unambiguous proof, excluding formula VIII, is constituted by the behaviour of ledol at dehydration. On treatment with thionyl chloride in pyridine, ledol afforded only a small amount of a hydrocarbon with a semicyclic double bond; the main product was an isomer with a quaternary double bond.[2] The almost uniform course of dehydratation requires a trans-antiparallel position of the eliminated hydrogen atom and the hydroxyl group. This condition is fulfilled in formula VII (R_1 = OH,



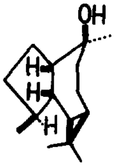
XII



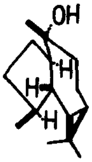
XIII



XIV



XV



XVI

$R_2 = CH_3$) only (<u>cf</u>. XI) contrary to the structure VIII (<u>cf</u>. X*). The resistance of ledol to form esters is also in agreement with the axial character of the hydroxyl group.

On the basis of the above discussed molecular models of ledol which is now formulated as XII, structures XIII and XIV follow for aromadendrene and alloaromadendrene and formula XV for the C_{10} epimer of ledol - the alcohol viridiflorol.[3] The configuration on C_1 in globulol corresponds to that in aromadendrene.[3] The former on dehydration with thionyl chloride in pyridine[2] affords 60 per cent yield of an olefin with a semicyclic double bond; this constitutes the proof of the equatorial character of the hydroxyl group as may be seen in formula XVI.

As the C_7 substituent at all hitherto known absolute configurations of sesquiterpenes and their derivatives is β-oriented[9] the submitted structures may be regarded tentatively as absolute configurations.

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[*] In projection X, R = OH or CH_3.

[9] D. H. R. Barton and J. E. D. Levisalles, <u>J. Chem. Soc.</u> 4518 (1958).