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STRUCTURE OF THE SESQUITERPENIC HYDROCARBON YLANGENE

O.Motl, V.Herout and F.Šorm
Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Science, Prague

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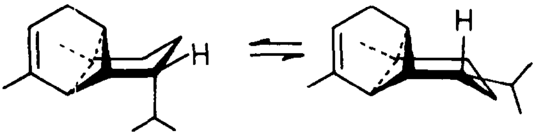
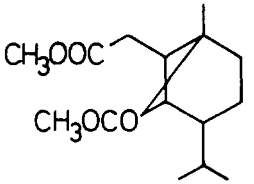
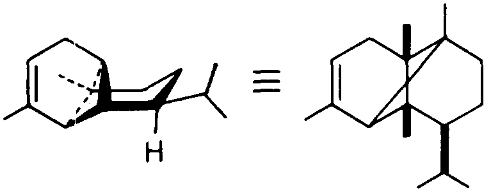
In a preliminary communication /1/ we reported the isolation of pure ylangene and proposed for it three possible structures containing a cyclopropane ring in the molecule. Further investigation of its degradation products led us to the conclusion that the molecule of ylangene contained a four membered ring /I/. The existence of a four membered ring was inferred from the character of the methylketo carboxylic acid II obtained by ozonisation of ylangene; in the IR spectrum of its methyl ester the following maxima were present: γ^{CO} 1704 cm^{-1}, γ^{COOCH_3} 1169 and 1740 cm^{-1}, γ^{CH_3CO} 1353 cm^{-1}. Upon oxidation with perbenzoic acid according to Bayer and Williger this ester afforded the diester III, $C_{16}H_{26}O_4$ /γ^{CO} 1745 cm^{-1}, γ^{OCOCH_3} 1238 cm^{-1}, γ^{COOCH_3} 1166 cm^{-1}, 1436 cm^{-1}/. Alkaline hydrolysis and esterification of III yielded the corresponding hydroxyester IV, $C_{14}H_{24}O_3$ / γ^{COOCH_3} 1740 cm^{-1}, γ^{OH} 3610 cm^{-1}/ which gave upon oxidation with chromium trioxide (according to Jones /2/) the ketoester V. Its IR spectrum showed, in addition to the maximum belonging to the ester group /1745 cm^{-1}/, another maximum at 1772 cm^{-1} due to a carbonyl group of the same intensity, typical for cyclobutanone.

When compared with the IR spectrum of the analogous ketoester /3/ obtained from copaene[x], it differred only in the fine structure and by the position of the maximum for cyclobutanone / the compound prepared from copaene had ν^{CO} 1778 cm^{-1}

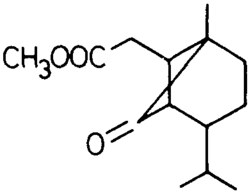




III



VI



V

A detailed study of the NMR spectrum of ylangene[xx] has shown the presence of a methyl group on the quarternary carbon atom / singlet at τ-9.24 /; integration curve proved that the

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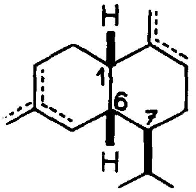
[x] We thank Dr.Sukh Dev, National Chemical Laboratory, Poona, India, for the kind gift of a sample of this substance.

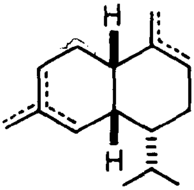
[xx] Our thanks are due to professor Paul de Mayo, University of Western Ontario, London, Canada, for comparing the NMR spectra of copaene and ylangene. We thank also Dr.J.Jonáš from our Institute for the measurement and interpretation of the NMR spectra.

molecule contained three hydrogen atoms in α position to the double bond. Spin decoupling measurements indicated the presence of an isopropyl group. These facts agree with our previous statement /1/ that ylangene is a substance whose structure is based on the cadinane carbon skeleton. This as well as that published earlier, together with the chemical proof of the existence of a four membered ring in ylangene, led us to assign it the structure I; it is a stereoisomer of copaene /3,4/ VI differring from ylangene only by the configuration of the isopropyl group.

From the similarity of mass, IR and NMR spectra of ylangene and copaene, as well as from some chemical evidences, Hunter and Brogden /5/ could conclude recently that the difference between these two hydrocarbons "lies at the ring junction centers". However, this statement was done by "assuming that the configuration at the isopropyl group remains the same". We do not agree with this assumption because in its consequences it would require a substance of trans-decaline type as the precursor of either ylangene or copaene, forbidding the closure of a four membered ring / stereochemical reasons/. We assume that only a substance of the cis-decaline type can be considered as a precursor of <u>both</u> hydrocarbons, for example a substance from the group of the so called muurolenes whose structure has been elucidated recently by Westfelt /6/, or a substance of the amorphane type identified now in our laboratories /7/. The main difference in structures of both groups of substances consists in the very configuration of the isopropyl group; they can be, therefore, schematically represented by formulae VII and VIII.



„Muurolenes"
VII



„Amorphenes"
VIII

In view of the fact that /-/-copaene can be transformed to /-/-cadinene dihydrochloride /3/ and muurolene dihydrochloride /6/ / in the 6:1 ratio /, absolute configuration at C_6 and C_7 for ylangene is also given. However, the transformation to /-/-cadinene dihydrochloride requires a change of configuration at C_1; such a change was observed during the reaction of muurolenes with hydrogen chloride /6/ when /-/-cadinene dihydrochloride was formed simultaneously with muurolene dihydrochloride, in a ratio depending on the reaction conditions /6,8/. The above mentioned reasons led us to assign the structure I to ylangene; we shall try to decide in the near future definitely to which antipode of the isolated ylangenes /9/ this formula should be attributed.

A more detailed study on the structure of ylangene and on the existence of amorphenes will be published in Collection Czech. Chem. Commun.

REFERENCES

1. O.Motl, V.G.Bucharov, V.Herout and F.Šorm, *Chem.and Ind.* /London/ 1759 /1963/.
2. K.Bowden, I.M.Heilbron, E.R.Jones and B.C.L.Weedon, *J.Chem.Soc.* 39 /1946/.
3. V.H.Kapadia, B.A.Nagasampagi, V.G.Naik and Sukh Dev, *Tetrahedron Letters* 1933 /1963/.
4. G.H.Büchi, S.H.Feairheller, P.de Mayo and R.E.Williams, *Proc.Chem.Soc.* 214 /1963/.
5. G.L.K. Hunter and W.B. Brogden Jr., *J.Org.Chem.* **29**,982 /1964/.
6. L.Westfelt, *Acta Chem.Scand.* **18**,572 /1964/.
7. M.Romaňuk, O.Motl, V.Herout and F.Šorm, unpublished.
8. A.Zabža, M.Romaňuk, V.Herout and F.Šorm, *Collection Czech.Chem.Commun.*, in the press.
9. V.Herout and D.I.Dimitrov, *Chem.listy* **46**,432 /1952/; O.Motl, V.Herout and F.Šorm, *Collection Czech.Chem.Commun.* **26**,1656 /1960/; O.Motl and V.Lukeš, ibid. **27**,987 /1962/.