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ON TERPENES CXCI[+]

THE STRUCTURE OF BULGARENE DIHYDROBROMIDE

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In our previous paper[1] we have dealt with the determination of the constitution and the steric arrangement of /-/-ε-bulgarene, a sesquiterpenic hydrocarbon isolated from the essential oil of Mentha piperita of Bulgarian origin. Taking into account the chemical processes and the results of physical measurements, we suggested the formula I for /-/-ε-bulgarene. This study was aimed at confirming the suggested structure of /-/-ε-bulgarene by means of X-ray analysis of bulgarene dihydrobromide whose preparation was described in our previous report[1].

Bulgarene dihydrobromide crystallizes in the orthorhombic system with the lattice parameters a = 6,86 b = 13,55 and c = 17,73 Å. The space group is $P\,2_1 2_1 2_1$ and the elementary cell contains 4 molecules. Fig. 1 showing the steric configuration of atoms in the molecule of bulgarene dihydrobromide presents the results of the three-dimensional Fourier's function of electron densities.

[+] Part CXC: Collect.Czechoslov.Chem.Commun. in press

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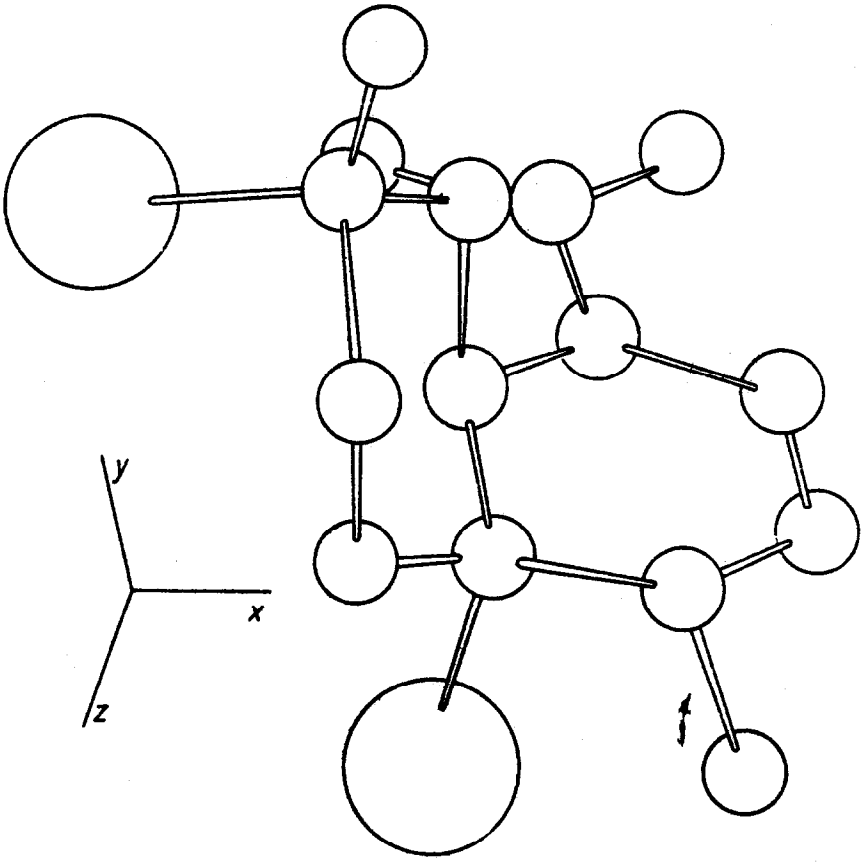
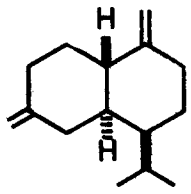


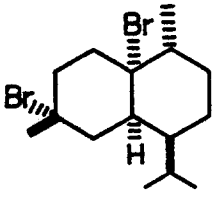
Fig.1.

X-ray analysis has now shown that the molecule of bulgarene dihydrobromide contains one atom of bromine bound to $C_{(4)}$ as we anticipated; however, the second atom of bromine is bound to $C_{(1)}$, contrary to our expectations. On the other hand, both the PMR spectrum of the original hydrocarbon and the presence of diketone III in the products of the ozonization of /-/-ε-bulgarene[1] suggest that the molecule of /-/-ε-bulgarene does not contain a double bond between $C_{(1)}$ and $C_{(10)}$. The action of hydrobromic acid on the exocyclic double

bond originating from $C_{(10)}$ of the mentioned hydrocarbon evidently takes a more complicated course and one of the asymmetric carbons, i.e. $C_{(1)}$, also participates in the reaction. The results of X-ray analysis of bulgarene dihydrobromide provide unambiguous proof for the suggested formula I for /-/-ε-bulgarene, with the exception of the configuration on $C_{(1)}$.



I



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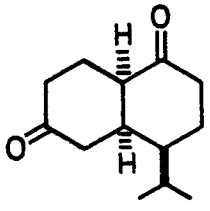

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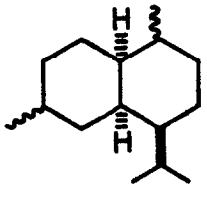
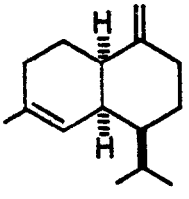


IV



V

The structures of diketone III and bulgarene dihydrobromide /II/, in which the carbon rings are cis-fused, might lead one to the conclusion that the carbon rings in the original hydrocarbon are also cis-annelated and that

/-/-ε- bulgarene should, therefore, belong to the amorphane series (IV)[1]. However, we think that this is not the case as the dihydrochloride prepared from /-/-γ-amorphene (V)[3] is different from bulgarene dihydrochloride[1] and because the hydrogenation products prepared from /-/-γ-amorphene[3] and /-/-ε-bulgarene[1] differ considerably in their infra-red spectra and physical constants. The structure of /-/-ε-bulgarene is hence as shown in formula I[1].

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