STUDY OF THE CONFORMATIONS OF THE SESQUITERPENE ALCOHOL δ-CADINOL BY THE METHOD OF ATOM–ATOM POTENTIALS

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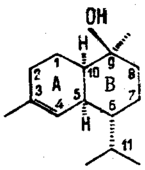
The sesquiterpene alcohol δ-cadinol, $C_{15}H_{26}O$, has been known now for more than 50 years. Several groups of workers have studied its structure and they have obtained contradictory results [1]. The structure and configuration of δ-cadinol generally accepted at the present time are represented by formula (I).



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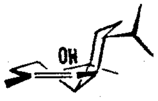

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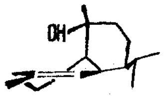

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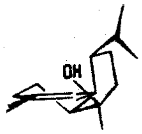

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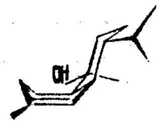

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In our opinion, the contradictory results obtained previously by various workers are due to the conformational mobility of the skeleton of the molecule. Rezvukhin et al., [2] studied the conformation of (I) in solution by the PMR method using the shift reagent $Eu(DPM)_3$. As a result of an analysis of the shifts in the PMR spectra, preference was given to the "non-steroid-like" conformation 1. Later [3], Rezvukhin studied the ^{13}C NMR spectrum. The fact that the C(1), C(5), C(8), and C(11) chemical shifts for conformations 1 and 2 calculated by a simple additive scheme did not correspond to the experimental values led these authors to consider conformation 3. This conformation, having the twist form of ring B, was considered to explain the features of the ^{13}C NMR spectrum of δ-cadinol most completely.

We have made a conformational calculation of the δ-cadinol molecule in the free state by the method of atom–atom potentials. The following interactions were considered:

$$U = U_{bd} + U_{ang} + U_{nev} + U_{tors},$$

where U_{bd} is the energy of deformation of the bond, U_{ang} is the energy of deformation of the valence angle, U_{nev} is the energy of the nonvalent interactions in the 6-exp form, and U_{tors} is the torsional potential. We made use of V. G. Dashevskii's parameters [4].

The search for the minimum strain energy U of the molecule was carried out by the method of fastest descent with respect to the Cartesian coordinates of all the atoms, using the analytical expression for the first derivatives. The search was terminated at $\delta U = 0.01$ kcal/mole.

The calculation was performed for various initial conformations of ring A (half-chair, boat, half-boat) and ring B (chair, boat). As a result, the most stable conformation proved to be 1: (0 kcal/mole). The "steroid-like" conformation 2 had a strain energy of +5.7 kcal/mole, and conformation 3, one of +8.1 kcal/mole, relative to the strain energy of conformation 1. Conformation 4, having ring A in the boat form, is fairly highly strained (+8.2 kcal/mole). The other conformations are still more strained.

Thus, the strain of conformations 2-4 of the δ-cadinol molecule in the free state is not very large, and in the condensed state the ratio of the energies must decrease.

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GLYCOSIDES OF *Caltha polypetala*

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A number of plants of the genus *Caltha* have been investigated previously for their saponin content. The majority of species studied contained triterpene glycosides [1, 2]. A saponin of steroid nature was found in one of them [3].

We have investigated the hypogeal organs of *Caltha polypetala* Hochst. (great marsh marigold) collected in June in Bakuriani (Georgian SSR). By TLC on silica gel we detected no less than 7 glycosides of triterpene nature in a methanolic extract, and we have called them in order of increasing polarity polypetalosides A, B, C, D, E, F, and G. After appropriate purification, and also repeated partition chromatography on a column of silica gel, from the total glycosides we isolated two individual components: polypetaloside C with mp 220-222°C, $[\alpha]_D^{20}$ +21° (c 1.1; methanol), and polypetaloside G with mp 200-202°C, $[\alpha]_D^{20}$ 0° (c 1.5; methanol).

The complete acid hydrolysis of both glycosides yielded a crystalline genin with mp 326-328°C; $[\alpha]_D^{20}$ +79.2° (c 1.1; pyridine), identified as hederagenin [4], while the carbohydrate moieties were each found to include D-glucose, L-arabinose, and L-rhamnose. A rough comparison of the glycosides that we have obtained with kalopanax saponin B [5] and leontoside D [6], which have the same aglycone and set of monosaccharides, did not confirm their identity.

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