EDULTIN FROM Libanotis seseloides

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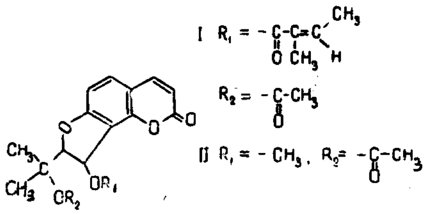
In a study of the chemical composition of the roots and fruit of Libanotis seseloides (Fisch et Mey) Turcz, collected in the Amur region (Malyi Khingan range, surroundings of the village of Birofel'd) we isolated a coumarin with the composition $C_{21}H_{22}O_7$, mp 156-159°C (petroleum ether), 158-160°C (aqueous ethanol), 165-166°C (sublimate), $[\alpha]_D^{27}$ +57.5° (c 1.0; chloroform), identified by its IR [1] and NMR [2] spectra as libanotin (I) [3]. Prokopenko [3] did not show the mutual positions of the acid residues in the molecule of libanotin.



In order to determine the positions of the angelic and acetic acid residues we performed mild alkaline methanolysis of the compound that we had isolated (0.4% NaOH in methanol, 20°C, 15 min). This gave a mixture of substances from which, by TLC on acid alumina [with ethyl acetate–petroleum ether (1 : 2) as the mobile phase] we isolated a substance (II) differing in its R_f value (0.7) from the initial compound (R_f 0.9) but retaining the violet fluorescence in UV light characteristic for dihydrofurocoumarins. A study of the NMR spectrum (Fig. 1) of the product isolated showed that in the alkaline methanolysis of (I) the angelic acid residue present in position 4' was split off and replaced by a methoxy group. The coumarin part of the molecule remained unchanged in methanolysis (H_3 and H_4: 6.14 and 7.58 ppm, doublets, J = 9.8 Hz; H_5 and H_6: 7.28 and 6.71 ppm, doublets, J = 8.4 Hz). In the transition (I) → (II), the signal from $H_{4'}$ (7.08 ppm, doublet, J = 6.5 Hz) [2] shifts upfield, as a result of which, in the 4.70-5.15 ppm region, there are two doublets, one of which is due to $H_{4'}$ and the other to $H_{5'}$. The positions of the signals of the protons of the gem-dimethyl grouping in the spectrum of (II) scarcely change (1.60 and 1.46 ppm, singlets, 3H each), which shows the attachment of the acetoxy group (1.93 ppm) in (II) and consequently indicates an isopropyl residue in (I). The results obtained agree completely with literature data on the greater lability of an acyloxy group in the α position to an aromatic nucleus [4].

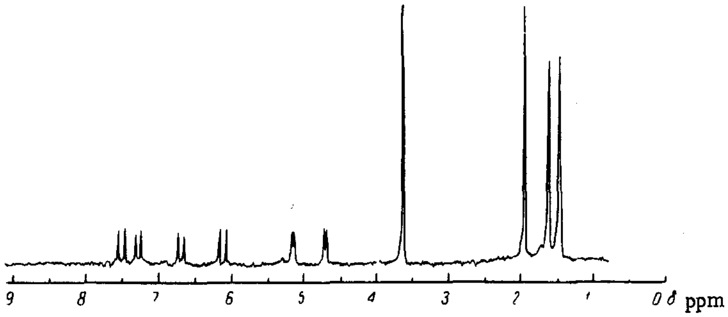


Fig. 1. NMR spectrum of the product of the alkaline saponification of edultin in CCl_4 (NA-100D, 100 MHz, 0 – TMS).

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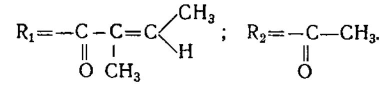
Thus, the product of the alkaline methanolysis of libanotin corresponds to structure (II) and libanotin to (I), where  $R_1{=}-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}{=}C\begin{smallmatrix}CH_3\\ H\end{smallmatrix}$; $R_2{=}-\underset{\underset{O}{\|}}{C}-CH_3$. This structure has been proposed for the dihydrofurocoumarin edultin [5, 6]. A comparison of the published IR spectra of edultin [5], libanotin [1], and the spectrum of the substance that we have isolated showed their identity. Consequently, cnidimin, earlier identified with libanotin [7, 8] must also be identified with edultin. The difference in the melting point of edultin (136-142°C) [5], libanotin (160-161°C) [3], and cnidimin (151-153°C) [8] is apparently due to the capacity of the substance for retaining solvents of crystallization [8].

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