THE STRUCTURE OF GALBANIC ACID

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In an investigation of the roots of Ferula microloba Boiss. (Turkmen SSR), we found six compounds of coumarin nature in them. One of them, with R_f 0.28 [TLC, SiO_2, benzene–chloroform–ethyl acetate (5 : 4 : 1)] is an optically active crystalline substance with mp 92°C, $[\alpha]_D^{21}$ −25.3° (c 0.89; MeOH). The features of its UV spectrum (λ_{max} 217, 325 nm; log ε 4.17, 4.25) show that this compound is a derivative of umbelliferone, and umbelliferone was in fact isolated when the substance was subjected to acid degradation. The IR spectrum showed the absorption bands of the carbonyl of an α-pyrone at 1730 cm^{-1}, of a carboxy group at 2700, 1708, and 1300–1280 cm^{-1}, and of an aromatic nucleus at 1620, 1560, 1510, and 1465 cm^{-1}. The presence of a carboxy group in the substance was shown by the preparation of salts and esters of it.

On the basis of its physicochemical properties and a mixed melting point with an authentic sample [1, 2], the substance isolated was identified as galbanic acid.

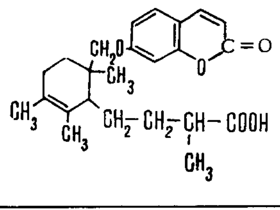
However, the results of combustion, the number of protons in the NMR spectrum, and the corresponding molecular weight (M^+ 398) confirm the composition $C_{24}H_{30}O_5$ proposed previously by certain authors [3, 4] and do not correspond to the composition found by others [5, 6].

According to the NMR spectrum, the molecule of galbanic acid contains methyl groups on tertiary and quaternary carbon atoms (0.85 ppm, J = 7.0 Hz; and 1.08 ppm, respectively), two methyl groups at a double bond (1.38 ppm, J = 1.9 Hz and 1.54 ppm), a carboxy group (9.4 ppm), the methyl group with an ether bond (3.63 and 3.81 ppm, $^2J = 8.5$ Hz), and an umbelliferone residue (6.1–7.7-ppm region) [7]. These facts indicate the presence of five substituents in the molecule of galbanic acid, which again does not agree with the structure proposed previously [5].

In the mass spectrum, peaks with m/e 298 and 297, of low intensity, corresponding to fragments formed by the cleavage of the side chain from the ring in the molecular ion with and without the transfer of one atom of hydrogen to the ring, and also an ion with m/e 100, corresponding to the molecular weight of the side chain without one hydrogen atom, show the presence of a double bond in the ring and not in the alkyl residue of the side chain. The peak of an ion with m/e 85 can be explained by the elimination of a methyl group in the side chain. The latter is most likely where the methyl group is present in the α position to the carboxyl.

In the NMR spectrum of galbanic acid, a triplet at 2.87 ppm ($\Sigma J = 15.1$ Hz) undoubtedly relates to a proton on a carbon atom present in the α position to a double bond. Its multiplicity is due to coupling with two protons, which can occur only if the quaternary methyl group and the $-CH_2-O-Ar$ grouping are present on a homoallyl carbon atom.

Consequently, the following structure is the most probable for galbanic acid:



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The proposed structure of galbanic acid is in harmony with the "isoprene biogenetic rule" [8].

On the basis of this structure, the production of 1,2,5,6-tetramethylnaphthalene [5] can be explained by the formation by the aliphatic chain of a six-membered ring with the elimination of the $-CH_2-O-Ar$ fragment and the migration of the angular methyl group.

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