METHYL GALBANATE – NEW TERPENOID COUMARIN FROM Ferula microloba

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Continuing a study of the roots of *Ferula microloba* Boiss. [1, 2], from a CCl_4 extract by chromatography by silica gel we have isolated a new substance of coumarin nature with R_f 0.63 [TLC, benzene–chloroform–ethyl acetate (5:4:1)], composition $C_{25}H_{32}O_5$, M^+ 412 (8%), bp 252°C, n_D^{18} 1.5330, d_4^{20} 1.0660, $[\alpha]_D^{18}$ $-25.8°$ (c 1.16; MeOH).

The UV spectrum [λ_{max}^{EtOH} 217, 244, 254, 294, 325 nm (log ε 4.17; 3.60; 3.44; 4.07; 4.27)] is characteristic for 7-O-alkylcoumarins. The IR spectrum shows the presence of an aromatic nucleus (1620, 1560, 1510, 1470 cm^{-1}) and of two carbonyl groups, of an α-pyrone, and of an ester grouping, at 1740-1720 cm^{-1}.

The NMR spectrum of the galbanic acid that we isolated previously [1, 2] is extremely close to a spectrum of this compound (Varian, HA-100D, $CDCl_3$, 0 – HMDS) but differs by the presence of a three-proton singlet at 3.58 ppm ($-OCH_3$) and by the absence of the signal of a carboxy group at 9.4 ppm. Consequently, this compound is the methyl ester of galbanic acid.

The nature of the ester grouping is confirmed by the presence in the mass spectrum of ions with $M^+ - OCH_3$ (m/e 381; 6.4%) and $\overset{+}{O}=C-OCH_3$ (m/e 59; 24%), which are typical of the decomposition of methyl esters of carboxylic acids with a long chain [3].

The peaks of ions with m/e 251 (79%) and 237 (42%) relate to the terpene part of the molecule and are shifted by 14 units into the region of high masses in comparison with the same fragments of galbanic acid. The ions with m/e 163 (100%), 162 (32%), and 161 (22%) relate to the coumarin part of the molecule and arise through the cleavage of the ether bond with and without the transfer of one or two hydrogen atoms from the terpene part of the molecule to the coumarin part, which is characteristic for umbelliferone derivatires [4].

On the alkaline hydrolysis of the substance, we isolated a compound with the composition $C_{24}H_{30}O_5$, mp 92°C, which was identified by a mixed melting point with an authentic sample of galbanic acid.

Methyl galbanate was obtained by independent synthesis, and its UV, IR, NMR, and mass spectra were identidal with those of the natural compound. This is the first time that methyl galbanate has been found in plants.

LITERATURE CITED

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