COUMARINS OF THE ROOTS OF Libanotis transcaucasica

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The coumarin libanotin has previously been isolated from the seeds of L. transcaucasica Schischk [1]. The present paper gives the results of an investigation of the coumarin composition of the roots of this plant growing in the Georgian SSR.

We extracted the raw material with methanol, evaporated off the solvent, dissolved the residue in water, and extracted the coumarins with ether. The combined coumarins obtained from the ethereal extract were chromatographed on a column of silica gel. Elution was performed successively with petroleum ether, benzene, and diethyl ether. Three individual coumarins were isolated: (I), $C_{15}H_{16}O_3$, mp 83-84°C; (II), $C_{21}H_{22}O_7$, mp 161-163°C; and (III), $C_{23}H_{20}O_6$, mp 212-213°C, $[\alpha]^{20}_{D}$ $-220°$ (c 1.0; ethyl acetate).

On the basis of their elementary compositions, physicochemical constants, NMR and IR spectra, and mixed melting points, substances (I) and (II) were identified as osthole and libanotin, respectively.

Coumarin (III), according to its UV spectrum [$\lambda_{\max}$ 225, 260, 317 nm (log ε 4.52; 4.02; 4.69)], must be asigned to the group of dihydrofuro- or dihydropyranocoumarins. Its IR spectrum contains absorption bands at (cm^{-1}) 1700-1720 (carbonyl of a coumarin nucleus), 1620, 1580 (aromatic nucleus), and 3250-3450 (hydroxy group). The broadened carbonyl band and its position, and also absorption in the 1240 cm^{-1} region, show the presence of an ester group in the substance. The saponification of (III) gave a hydroxycoumarin and an acid. The hydroxycoumarin was identical in its composition, $C_{14}H_{14}O_4$, mp 185-192°C, $[\alpha]^{25}_{D}$ $-25.4°$ (c 1.0; chloroform), and IR spectrum with nodakenetin; the acid, according to its composition, $C_9H_8O_3$, mp of 206°C, and IR spectrum, was identical with p-hydroxycinnamic acid.

The NMR spectrum of (III) (taken in deuteropyridine on a JNM-100/100-4H instrument) had the signals of the protons of a linear dihydrofurocoumarin: doublets at 7.48 and 6.13 ppm, J = 10 Hz (H−4 and H−3); singlets at 7.20 and 6.70 ppm (H−5 and H−8); doublet at 3.10 ppm, J = 8 Hz (H−4'); triplet at 5.02 ppm, J = 8 Hz (H−5'); and singlet at 1.56 ppm (6H; gem-dimethyl groups). In addition to this there were signals of the protons of p-hydroxy-trans-cinnamic acid: doublets at 6.91 and 7.27 ppm, J = 8 Hz (H−3, H−5, and H−2, H−6); and at 7.40 and 6.28 ppm, J = 15.5 Hz (Hα and Hβ).

These facts, and also the presence in the mass spectrum of peaks with m/e 392 and 245 permit the conclusion that substance (III) is an ester of p-hydroxy-trans-cinnamic acid and nodakenetin and is identical with the secorin recently isolated from Seseli coronatum [2].

LITERATURE CITED

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