Thus, the greatest amount of water-soluble pectins accumulates in the ripe fruit of the mountain ash, and the greatest amount of protopectin in the green fruit.

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SECROLIN — A NEW DIHYDROFUROCOUMARIN FROM *Seseli mucronatum*

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UDC 547.9:582.89

By chromatography on silica gel in the petroleum ether—ethyl acetate system with a rising gradient of the latter, the roots of *Seseli mucronatum* (Schrenk) M. Pimen et Sdobn., collected in the Dzhety-Oguz gorge (environs of Przheval'sk) have yielded an amorphous substance $C_{18}H_{18}O_5S$, M^+ 346, mp 78-82°C, $[\alpha]_D^{20}$ +233.5° (c 2.36; $CHCl_3$), which we have called secrolin.

The UV spectrum of secrolin in ethanol [λ_{max}, nm: 217 (infl.), 263 (infl.), 278, 328 (log ε 4.22, 4.15, 4.27, 4.07); λ_{min}, nm: 240, 305 (log ε 3.71, 3.95)] showed that it was a derivative of 7-hydroxycoumarin.

It follows from the PMR spectrum (Varian HA-100D, $CDCl_3$, 0 — HMDS, 20°C) that the compound isolated was an ester of an angular dihydrofurocoumarin [6.04 and 7.48 ppm, 1 H each, d, J = 9.5 Hz (H_3, H_4); 7.18 and 6.22 ppm, 1 H each, d, J = 8.5 Hz (H_5, H_6); 5.19 ppm, 1 H, t, J = 9.5 Hz ($O-\underline{CH}-CH_2$); 3.32 ppm, 2 H, d, J = 9.5 Hz ($CH-\underline{CH_2}-Ar$); 1.47 and 1.57 ppm, 3 H each, s ($O-C(CH_3)_2$] — columbianetin [1] (zosimol [2]).

The IR spectrum (Fig. 1) contained absorption bands of an α-pyrone C=O, of an ester group, and of the —C=C— bonds of a coumarin nucleus. In this compound, the esterifying component was methylthioacrylic acid [2.26 ppm, 3 H, s ($-S-CH_3$); 7.44 and 5.48 ppm, 1 H each, d, J = 16 Hz (Hα and Hβ)] with the trans arrangement of the olefinic protons, while compounds consisting of esters of cis-methylthioacrylic acid have been found previously [3, 4].

In addition to secrolin, the sample of *S. mucronatum* investigated contained borneol trans-p-hydroxycinnamate [5], ostruthin, mp 118-119°C, and columbianadin (zosimin), mp 120-121°C, and differed from a sample of *S. mucronatum* collected in the valley of the R. Usek (Kazakhstan) [6], which contained anomalin, pteryxin, and ostruthin.

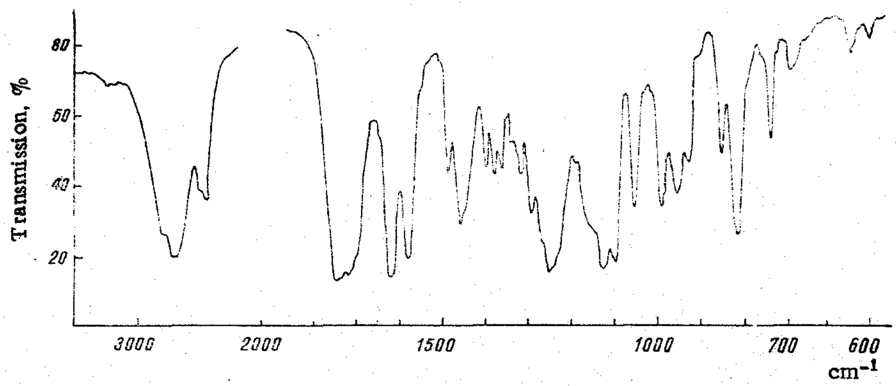

Fig. 1. IR spectrum of secrolin.

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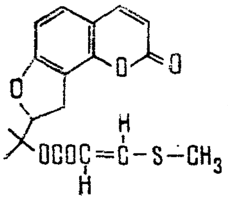
Thus, secrolin is columbianetin (zosimol) trans-methylthioacrylate:



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DEHYDRATION IN TERPENOID COUMARINS

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Continuing a study of the reaction of trifluoroacetic acid (TFA) with terpenoid coumarins of the iresane series [1], we have investigated coumarins of the samarcandin series containing methyl and hydroxy groups in the C-2 position: samarcandin (I) [2], samarcandone (II) [2], nevskin (III) [3, 4], nevskone (IV) [3, 4], ferucrin (V) [5], and ferucrinone (VI).

A study of the end products showed that during the reaction compounds with double bonds in the rings were formed. Thus, the reaction of TFA with (IV) [3, 4] led to conferone (VII) [6]. This transformation is well shown in the ^{1}H NMR spectrum, in which the signals of the protons of the initial product have disappeared and the signals of the protons of (VII) have appeared (Fig. 1). Conferone is also formed by the reaction of TFA with (II) [2], which confirms the equatorial orientation of the substituent at C-1 in compounds (II) and (IV) [3-7].

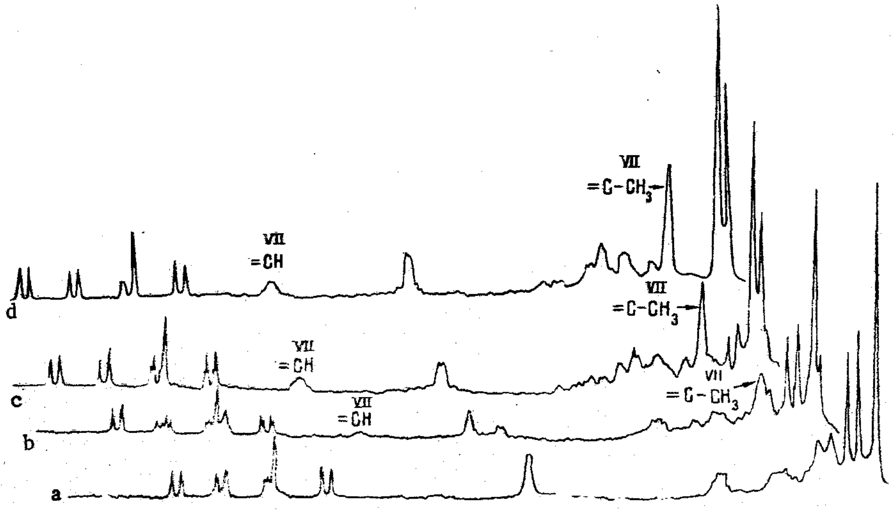

Fig. 1. ^{1}H NMR spectrum of samarcandone (a, b, c) and conferone (d) in trifluoroacetic acid. Spectrum (c) was recorded three hours after the sample had been dissolved.

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