UDC 577.15/17:582.89

TOMASIN—A NEW COUMARIN FROM XANTHOGALUM PURPURASCENS LALLEM

A. I. Sokolova, M. E. Perel'son, and G. K. Nikonov

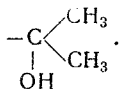
Khimiya Prirodnykh Soedinenii, Vol. 5, No. 5, pp. 359-361, 1969

Continuing our study of the plant [1-4] growing in the Transcaucasus, we have isolated yet another new alkyl coumarin $C_{21}H_{22}O_7$ with mp 104-105° C, $[\alpha]_D^{20}$ +19° (c 1.09; ethanol), readily soluble in organic solvents and insoluble in water, with chemical properties characteristic for the coumarins [5]. The substance contains one labile hydrogen atom. On successive treatment with alkali and acid, the R_f value changes, which shows the presence of an ester grouping in its molecule.

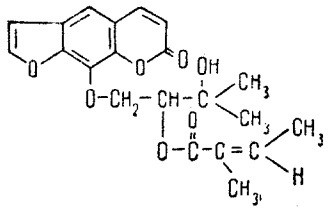
The IR spectrum of the substance (λ_{max} 218, 250, and 301 mμ; log ε 4.50, 4.36, and 4.07, respectively) shows that it belongs to the furocoumarins [5]. The IR spectrum of the lactone (Fig. 1) has the absorption bands of a hydroxyl group (3484 cm^{-1}), the C—H bonds of a furan nucleus (3137 cm^{-1}), the carbonyl of an α-pyrone ring (1716 cm^{-1}), and the skeletal vibrations of aromatic and heteroaromatic rings (1650, 1614, and 1589 cm^{-1}).

From its physicochemical constants, the lactone is a new furocoumarin which we have called tomasin. The structure of tomasin was established definitively on the basis of its NMR spectrum (Fig. 2).

On considering the region from 6 to 8 ppm, it can be seen that tomasin is an 8-monosubstituted psoralen. In fact, the doublets a (δ = 7.71; J = 10 Hz) and e (δ = 6.29; J = 10 Hz) show the presence of protons in positions 4 and 3; the doublets b (δ = 7.61; J = 2.3 Hz) and d (δ = 6.76; J = 2.3 Hz) relate to the protons of a furan ring condensed with a benzene ring. The singlet c (δ = 7.33) can be due only to the proton at C_5 of the psoralen nucleus. Other assignments of this singlet are excluded, since both the signal from H_8 for psoralen derivatives and the signals from H_5 and H_6 for isopsoralen derivatives must be located in a stronger field [6]. The signals g, h, i, each with an intensity of one proton unit, like those observed for ostruthol, are due to the methine and methylene protons of the Ar—O—CH_2—CH(OAc)— grouping. In this case the acyl residue is that of angelic acid, as follows from the presence of the signals f (δ = 6.05; J_1 = 7.5 Hz; J_2 = 1.5 Hz) (1H) and k (δ_1 = 1.95; J = 7.5 Hz; δ_2 = 1.86; J = 1.5 Hz) (6H). The broadened peak j (2.60 ppm) probably relates to the proton of a hydroxy group. The two singlets l with an intensity of 6 proton units are due to the methyl groups of the moiety



Thus, tomasin has the following structure:



Experimental

The IR spectrum was recorded on a UR-10 spectrophotometer, the UV spectrum on an SF-4A spectrophotometer, and the NMR spectrum on a JNM-4H-100 instrument.

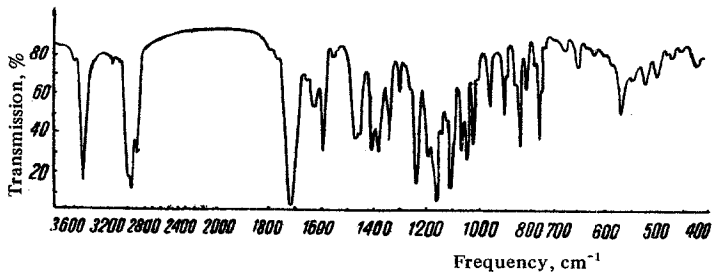


Fig. 1. IR spectrum of tomasin in paraffin oil.

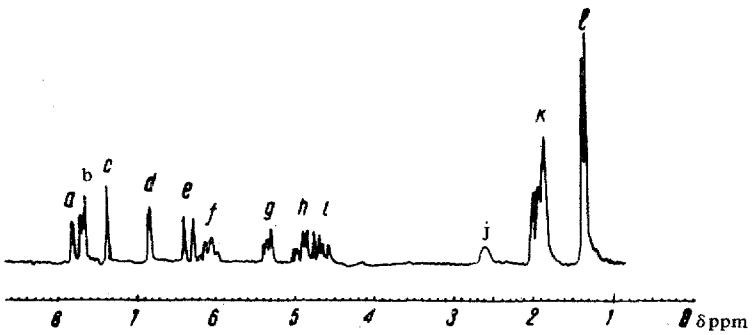


Fig. 2. NMR spectrum of tomasin in deuterochloroform (O-tetramethylsilane).

Isolation of tomasin. Five hundred grams of the dried and comminuted roots was treated three times with 3.2 and 1.7 *l* of ethanol. The combined extract was concentrated in vacuum to 180 ml (125.3 g), diluted with water, and extracted with ether (3 × 250 ml). The ethereal extracts were combined, washed with water, and dried with anhydrous sodium sulfate. The extract was evaporated to dryness, giving a residue (79.2 g) consisting, according to paper chromatography, of a mixture of ten coumarins.

The resulting mixture (50 g) was deposited on a chromatographic column of acid alumina (Brockmann activity II) with a diameter of 8 cm and a height of 20 cm. The column was eluted first with 9 *l* of thiophene-free benzene and then with 2 *l* of a mixture of benzene and chloroform (3 : 1, by volume). Concentration of the benzene-chloroform eluate gave 4.18 g of colorless multifaceted crystals with mp 104–105° C (from benzene).

Found, %: C 65.18, 65.21; H 5.77, 5.76; mol. wt. 389 (Rast). Calculated for $C_{21}H_{22}O_7$, %: C 65.30; H 5.70; mol. wt. 386.

The microanalysis was carried out by E. A. Nikonova.

Conclusions

From the roots of Xanthogalum purpurascens collected in the region of the Arsiansk range, a new furocoumarin has been isolated with the formula $C_{21}H_{22}O_7$, mp 104–105° C, $[\alpha]_D^{20}$ +109° (c 1.09; ethanol), and it has been named tomasin. On the basis of its UV, IR, and NMR spectra it has been established that it is 8-(2'-angeloyloxy-3'-hydroxy-3'-methylbutoxy)furo-3',2':6,7-coumarin.

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27 May 1968

Sechenov Moscow Medical Institute

All-Union Scientific-Research Institute for Medicinal Plants