A CHEMICAL STUDY OF SOME SPECIES OF Campanula

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We have investigated the epigeal part of Campanula alliariifolia Willd and C. letschchumensis Kem-Nath. growing in the environs of the village of Kakhuri (Lower Svanetia, Georgian SSR) [1]. The air-dry residue, 2.5 kg of the flowers and leaves of each species separately, was treated with chloroform in apparatuses of the Soxhlet type and was then exhaustively extracted with ethanol. The ethanolic solutions were dried under vacuum and the residue was treated with water and with chloroform and was left in the cold for several weeks. The white curdy precipitate that had deposited (0.45% in each case) was carefully washed with cold water and was repeatedly crystallized from aqueous ethanol, giving substance (I).

Substance (I), $C_{16}H_{18}O_{10}$, forms silvery-white silky needles with mp 222-223°C (from 50% ethanol) readily soluble in hot water and less readily in strong alcohol, and insoluble in $CHCl_3$. The results of two-dimensional chromatography on paper in the BAW (4 : 1 : 5), 5% CH_3COOH, and water-saturated C_6H_5OH systems showed that it contained a single substance with R_f 0.56, 0.72, and 0.85, respectively. In UV light it had a dull blue-violet fluorescence which disappeared under the action of NH_3. The substance reacts with Fehling's solution, which shows its glycosidic nature. Hydrolysis with 10% H_2SO_4 for 6 h formed the aglycone and D-glucose. The melting point of the osazone was 204-206°C. In the UV region, the spectrum of substance (I) is characteristic for trisubstituted hydroxycoumarins: a first fairly strong band at 304 nm and a second considerably weaker band at 255 nm [2]. Acetyl derivative with mp 203-206°C. The IR spectra shows absorption bands at (cm^{-1}) 840 (para-substituted aromatic nucleus), 1005, 1056, 1082 (pyranose form of a glucose residue), 1730 (C =O of an α-pyrone), and 3628 (OH group) [3].

The aglycone, $C_{10}H_8O_5$, consisted of crystals in the form of yellowish plates with mp 227-228°C (from aqueous ethanol, 1 : 1) [4], sparingly soluble in cold water; R_f 0.78 [BAW (4 : 1 : 5)]; 0.38 (5% CH_3COOH); 0.98 (water-saturated C_6H_5OH). In UV light it acquired a green-blue fluorescence changing to golden yellow on contact with gaseous NH_3. With 3% $FeCl_3$ solution it gave a blue-green color and on fusion with alkali it turned blood red and decomposed completely. The UV spectrum showed a fairly strong band at 345 nm and a second scarcely detectable (shoulder) at 280 nm; $\lambda_{max} > 300$ nm shows the presence of a double bond – the $C_3=C_4$ of a pyrone ring in a condensed system with an aromatic nucleus; the latter is hydroxylated, as is confirmed by the bathochromic effect found on comparing the absorption bands of the aglycone, the glycoside, and the coumarin and also from the shifts with additives: $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 363 ($\Delta\lambda$ + 18 nm) 265 nm, and $\lambda_{max}^{C_2H_5ONa}$ 418 ($\Delta\lambda$ + 73 nm) 335 nm. IR spectrum, cm^{-1}: 1375, 1462 (deformation vibrations of a $\gtrdot$CH- group), 1278, 1290, 1470 ($\gtrdot$C–OH), 1508, 1574, 1610 (stretching vibrations $>C=C<$ of an aromatic system), 1680 (strong absorption of a carbonyl group conjugated with $>C=C<$) and 2836 ($-OCH_3$) [5].

The substance gave no depression of the melting point with an authentic sample of isofraxoside kindly given to us by Dr. V. Plouvier (France).

The results obtained permit the substance isolated to be characterized as fraxetol 7-O-D-glucopyranoside or isofraxoside [2].

Substance (III) was obtained from the acidified ethyl acetate extract (pH 2-3) of the mother liquors of both species by chromatography on a column of polyamide: $C_9H_8O_4$, mp 195°C, R_f 0.82 [BAW (4 : 1 : 5)]; 0.31 (0.1 N HCl); and 0.28 (2% CH_3COOH); UV spectrum, nm: $\lambda_{max}^{C_2H_5OH}$ 328, 299, 235. The melting point of the

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acetyl derivative was 196-197°C. From the results of alkaline degradation, IR spectroscopy, and a mixed melting point, the substance was identified as caffeic acid [6].

Substances (IV) and (V) were detected in the total flavonoid glycosides of the species studied and their hydrolyzates; they were characterized by their physicochemical properties as kaempferol and quercetin.

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