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ANTHRAQUINONES OF GALIUM DASYPODUM

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In alcoholic extracts of fresh roots of Galium dasypodum Klok., family Rubiaceae, by paper chromatography in various mixtures of solvents we have established the presence of not less than ten substances of an anthraquinone nature.

The raw material for the investigation was collected in the period of full flowering of the plant at the Pokatilovka regional station, Khar'kov region. The compounds studied were isolated by the extraction of the roots with ethanol, evaporation of the extract in vacuum, dissolution of the residue in the minimum amount of water, and repeated treatment of the solution with ether.

When the ethereal extract was chromatographed on paper (petroleum ether saturated with 97% methanol), six anthraquinone compounds were detected with R_f (I) 0.74, (II) 0.49, (III) 0.35, (IV) 0.12, (V) 0.06 and (VI) 0.04. By separating the ethereal extract on a column of Kapron (with the eluants petroleum-ether; petroleum ether saturated with ethanol; ether; ethanol; and acetone) we obtained the individual crystalline substances I–IV and VI. These substances and also their conversion products, were identified by means of their physicochemical properties, color reactions, UV and IR spectra, and mixed melting points with known anthraquinones.

Substance I is 2-ethoxymethyl-1,3-dihydroxyanthraquinone(ibericin) [1], $C_{17}H_{14}O_5$, with mp 180–181° C (from benzene), substance II is rubiadin, $C_{15}H_{10}O_4$, with mp 302° C (from ethanol), substance III is rubiadin 1-methyl ether, $C_{16}H_{12}O_4$, with mp 302° C (from ethanol), substance IV is lucidin $C_{15}H_{10}O_5$, with mp 330° C (from dioxane), and substance VI is alizarin, $C_{14}H_8O_4$, with mp 279–280° C (from toluene), 289–290° C (sublimate).

The paper chromatography of the aqueous residue in the ethyl acetate—formic acid—water (10 : 2 : 3) system yielded four substances of an anthraquinone nature (VII–X) which were obtained in the individual state by separation on a column of Kapron (eluants—water and mixtures of water and ethanol). The structures of compounds VII, VIII, and IX have not yet been established.

Substance VII, with R_f 0.72, has mp 227–229° C (from ethanol), VIII with R_f 0.67 has mp 248–250° C (from aqueous ethanol), IX with R_f 0.39 has mp 198–200° C (from aqueous methanol), and X, with R_f 0.31 has mp 223–225° C (from aqueous acetone).

Substance IX is probably a new compound. On hydrolysis with 20% aqueous sulfuric acid, it is cleaved into the aglycone (IV), D-glucose, and D-xylose, and with 20% aqueous ethanolic sulfuric acid into the aglycone (I), D-glucose, and D-xylose. To determine the sequence of addition of sugars to the aglycone, enzymatic hydrolysis was carried out with rhamnodiastase and primeverase, which gave primeverose and lucidin. Stepwise hydrolysis with 0.8% aqueous sulfuric acid led to the formation of a monoside $C_{21}H_{20}O_{10}$ with mp 228–230° C (from ethanol) and D-xylose.

On the basis of the results obtained, it may be assumed that compound IX is lucidin primeveroside. Its definitive structure is being determined.

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VISNADIN—A NEW COMPONENT OF THE PLANT GENUS PHLOJODICARPUS

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It is known that the roots of P. sibiricus (Steph.) K. Pol. and P. villosus Turcz., family Umbelliferae, contain a considerable amount of coumarins from which an acylated pyranocoumarin, dihydrosamidin, has been isolated [1].

Continuing the study of these plants, we have isolated from the roots a second lactone of the coumarin group with the composition $C_{21}H_{24}O_7$ (I), mp 85–86° C (n-hexane) $[\alpha]_D^{21}$ +48° (c 3.33; dioxane; l 2 dm). On paper chromatography and thin-layer chromatography, compound I forms a spot with the same R_f value as dihydrosamidin.

On the basis of its physicochemical constants, IR spectrum, and the products of alkaline cleavage, compound I has been identified as 4'-acetoxy-2',2'-dimethyl-3'-(1"-methylbutyryloxy)-3',4'-dihydropyrano-5',6':7,8-coumarin (visnadin). Until recently, the only source of this coumarin has been the fruit of Ammi visnaga, family Umbelliferae [2,3]. We have found visnadin for the first time among the wild-growing plants of the USSR.

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THE STRUCTURE OF AGASYLLIN

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We have previously [1] reported the isolation from the fruit of Agasyllis latifolia (M. B.) Boiss, family Umbelliferae, of a new alkylcoumarin—agasyllin, $C_{19}H_{20}O_5$, with mp 78–80° C $[\alpha]_D^{24}$ −44° (chloroform, c 0.91; l 2 dm).

When agasyllin is saponified with 5% methanolic caustic potash, a hydroxylactone $C_{14}H_{14}O_4$ is formed with mp 177–178° C, $[\alpha]_D^{22}$ −13.4° (chloroform; c 0.56; l 2 dm); monoacetate $C_{16}H_{16}O_5$ with mp 137–138° C, which, on the basis of its physicochemical constants and NMR spectra has been identified as (−)-3'-hydroxy-3',4'-dihydropyrano[5',6':7,6]coumarin—a known product of the alkaline saponification of decursin [2].

In the NMR spectrum of agasyllin (spectrum taken on a JNM-4-H-100 spectrometer at 100 MHz with a solution of the substance in carbon tetrachloride), in the weak-field region there are signals characteristic for 6,7-substituted coumarins. Signals at δ = 7.46, 7.08, 6.65, and 6.10 ppm are due, respectively, to the C_4, C_5, C_8, and C_3 protons of the coumarin nucleus [3]. In addition, there are peaks at δ = 1.37 ppm (6 H) (protons of a gem-dimethyl grouping) and at δ = 1.94 and 1.83 ppm (6 H) (protons of two methyl groups in the acid residue). An octet in the δ = 2.4–3.3 ppm region relates to the nonequivalent methylene protons at C'_4, leading to splitting because of spin-spin coupling with the methine proton at C'_3, the resonance signal of the latter appearing at δ = 5.07 ppm. As compared with the spectrum of the hydroxylactone, the signal of this proton in the spectrum of agasyllin has been displaced into the weak-field region by 1.19 ppm. This phenomenon characterizes agasyllin as the ester of a secondary alcohol [4] and, moreover, shows that it belongs to the group of dihydropyranocoumarins [5]. Since the vinyl protons of angelates, tiglates, and esters of the coumarins with senecioic acid may differ from one another [6–8] and the corresponding proton of agasyllin gives a signal at δ = 6.1 ppm, we have identified the acid residue as angeloyl.

Thus, agasyllin is (−)-3-angeloyloxy-3',4'-dihydropyrano-5',6':7,6-coumarin. In its NMR spectrum and the results of alkaline hydrolysis, agasyllin is identical with an acylcoumarin which has been isolated in the form of an oil from the roots of Seseli Libanotis (L.) Koch., family Umbelliferae [9].

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