ANTHRAQUINONES OF GALIUM DASYPODUM

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 2, p. 118, 1969

In alcoholic extracts of fresh roots of <u>Galium dasypodum</u> 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 1–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.

REFERENCE

1. V. A. Stikhin, A. I. Ban'kovskii, and M. E. Perel'son, KhPS [Chemistry of Natural Compounds], 3, 276, 1967.

24 October 1968

Khar'kov Pharmaceutical Institute

UDC 577.15/17.582.89

VISNADIN-A NEW COMPONENT OF THE PLANT GENUS PHLOJODICARPUS

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 2, pp. 118-119, 1969

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