POLYPHENOLIC COMPOUNDS OF GERANIUM COLLINUM. IV

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Khimiya Prirodnykh Soedinenii, Vol. 6, No. 4, pp. 496–497, 1970

UDC 547.972.982.973

Continuing an investigation of the leaves of Geranium collinum Steph. (upland geranium), by preparative paper chromatography of the first fractions obtained in the elution of the combined flavone monoglycosides from Kapron with methanol we have isolated 3, 7, 8, 4'-tetrahydroxyflavone 3-β-D-glucopyranoside with mp 230–232° C, $[\alpha]_D$ −70° (c 0.5, methanol), R_f 0.77 in BAW (4 : 1 : 5), 0.30 in 15% acetic acid, λ_{max} 267 and 356 mμ, not previously described in the literature. The position of the substituent was shown by the absence of a shift of the long-wave maximum in the UV spectrum on the addition of aluminum chloride [2, 3].

An aqueous methanolic extract of the leaves was repeatedly treated with ethyl acetate. The resulting solution was concentrated and distributed in an ethyl acetate–water system. On standing, the aqueous solution deposited a light-yellow amorphous precipitate, which on recrystallization from water gave a substance $C_{34}H_{26}O_{22} \cdot 6H_2O$ in the form of yellow plates with $[\alpha]_D$ −164.5° (c 1, methanol), R_f 0.23 in BAW (4 : 1 : 5), 0.28 in 15% acetic acid, and 0.08 in water. Acid hydrolysis led to the formation of glucose and ellagic and gallic acids in a ratio of 1 : 1 : 2. With ammonium ferric alum the substance gave a blue color, while with o-toluidine or aniline phthalate it gave no color, which shows the possibility of substitution of the hydroxyl groups on the first and second carbon atoms of the glucose [4].

On acid hydrolysis with water, ellagic acid was split out first with the formation of digalloylglucose [R_f 0.23 in BAW (4 : 1 : 5), 0.53 in 15% CH_3COOH, and 0.34 in water] which was again not shown up by o-toluidine or aniline phthalate, and this was then hydrolyzed to gallic acid and glucose with the intermediate formation of monogalloylglucose, giving a pronounced qualitative reaction with o-toluidine.

Methylation (diazomethane, and then methyl iodide and silver oxide) led to a tridecamethyl derivative with mp 172–174° C, $[\alpha]_D$ −12.2° (c 0.5, methanol), % OCH_3: 38.9. On alkaline hydrolysis an amount of alkali corresponding to four ester bonds was consumed with the formation of a glucose derivative not revealed with o-toluidine, consequently, methylated at the semiacetal hydroxyl, and (+)-hexamethoxydiphenic acid with $[\alpha]_D$ +117.2° (0.1 N NaOH, c 0.256).

Periodate oxidation showed the presence of two glycol units, thus proving that the gallic and hexahydroxydiphenic acids were attached to the C_2, C_3, C_4, and C_6 atoms of the glucose and that the sugar was present in the pyranose form [4, 5]. Since the digalloylglucose obtained in the hydrolysis of the tannin substance is not revealed by 0-toluidine, the gallic acid is attached to the C_2 hydroxyl of the glucose.

A comparison of the rate of acid hydrolysis with literature information for 3, 6-[(+)-hexahydroxydiphenoyl]-glucose and 4, 6-[(−)-hexahydroxydiphenoyl]glucose showed that in the substance studied the (+)-hexahydroxydiphenic acid is attached to carbon atoms 4 and 6 of the sugar [6]. Thus, the substance studied is 2, 3-digalloyl-4, 6-[(+)-hexahydroxydiphenoyl]-β-D-glucose, not previously described in the literature, and we have called it "collinin."

The identification was confirmed by isolating from an aqueous solution, by preparative paper and column chromatography on cellulose, 2, 3-digalloylglucose, 2-galloyl-β-D-glucose, and 3-galloylglucose. On a chromatogram, 2, 3-digalloylglucose coincided with the digalloylglucose formed by the hydrolysis of the tannin substance; it was not revealed by o-toluidine, but was hydrolyzed with the intermediate formation of 3-galloylglucose. The alkaline hydrolysis of the permethylated product showed the presence of two ester bonds and the absence of a galloyl substituent on carbon atom 1 of the glucose, and periodate oxidation showed the presence of one glycol unit. The 2-galloyl-β-D-glucose [R_f 0.28 in BAW (4 : 1 : 5), 0.76 in 15% HOAc, and 0.70 in water] and the 3-galloylglucose [R_f 0.17 in BAW (4 : 1 : 5), 0.88 in 15% HOAc, and 0.76 in water] were identified on the basis that in the former a reaction with o-toluidine was absent and in the latter there was a pronounced reaction, and by the constants of their acetyl derivatives [7, 8].

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4 February 1970

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