FLAVONOIDS OF Atraphaxis pyrifolia AND spinosa II

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In an investigation of the extractive substances of phenolic nature by chromatography on a column of polyamide sorbent and by preparative chromatography on paper, we isolated from the leaves of Atraphaxis pyrifolia Bge substances with mp 179-181°C and 193-195°C, and from the leaves of Atraphaxis spinosa L. a substance with mp 166-168°C.

Substance (1), $C_{21}H_{20}O_{11}$, mp 179-181°C, was identified on the basis of its hydrolysis products, UV and IR spectra, and specific and molecular rotations as 7-O-methylluteolin 4'-β-L-rhamnopyranoside [1].

Substance (2) formed pale yellow needles with mp 193-195°C (from aqueous ethanol), $[\alpha]_D^{20} - 56.1°$ (c 0.24; methanol); UV spectrum: λ_{max} 370, 275 nm (ethanol), 390, 278 nm (zirconyl chloride). The reduced shift with zirconyl chloride is apparently due to the steric influence of a substituent in the C-6 position [2].

The aglycone of substance (2), $C_{15}H_{20}O_6$, mp 238-240°C (48%), as shown by UV spectroscopy [λ_{max} 335 and 275 nm (ethanol), 360 and 280 nm (sodium acetate), 380 and 280 nm (sodium ethoxide), and 355 and 280 nm (zirconyl chloride)], contains free hydroxy groups at C-5, C-7, and C-4'. p-Hydroxybenzoic acid was found in an alkaline melt of the substance by paper chromatography.

It was established by IR spectroscopy that in substance (2) there are two absorption bands in the 1010-1100 cm^{-1} region (furanose form of a carbohydrate) and a band at 840 cm^{-1} (α configuration of a glycosidic bond). On comparing the molecular rotations of the glycoside isolated with those of the corresponding phenylrhamnosides [3], it was seen that the L-rhamnose is attached by an α-glycosidic bond and is in the furanose form.

Both the glycoside and the aglycone rapidly decomposed on heating with sodium acetate in an aqueous medium. Such properties are probably explained by the presence in the molecule of a 5,6-dihydroxy grouping, which is readily oxidized even in a weakly alkaline medium.

Substance (3), mp 166-168°C (from aqueous ethanol), $[\alpha]_D^{22} - 50.5°$ (c 0.1; methanol) gave on acid hydrolysis an aglycone (50%) with mp 306-308°C, identified as 7-O-methylluteolin, and D-glucose.

On studying the product of stepwise hydrolysis (0.1% HCl in 50% methanol, 100°C), we established by paper chromatography that the glycoside is cleaved into the aglycone and a biose in the first five minutes.

The UV spectra of the substance with additives shows that the carbohydrate moiety is present in the C-4' position. The results of a comparison of the intensity of the absorption of the corresponding maxima in the spectra of the aglycone and of glycosides show that the glycoside obtained is a bioside [1, 4].

A positive reaction with aniline phthalate characterizes the linkage of the sugars in the biose as 1-6.

IR spectroscopy, and also a comparison of the $[M]_D$ of the glycoside with [M] of phenyl β-D-glucopyranoside permits the statement that the D-glucose is in the form of β-D-glucopyranose [3].

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Thus, the above facts make it possible to characterize substance (2) as 4',5,6,7-tetrahydroxyflavone 4',7-di-α-L-rhamnofuranoside and substance (3) as 7-O-methylluteolin 4'-O-β-D-glucofuranosyl-(1→6)-D-glucopyranoside. This is the first isolation of both substances.

LITERATURE CITED

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