OXYTROSIDE FROM Oxytropis myriophylla

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In an investigation of the epigeal part of Oxytropis myriophylla (Pall.) DC., family Fabaceae, Leguminosae, collected in the flowering phase in the Buryat ASSR we have found six flavonol glycosides, two of which have been assigned to kaempferol derivatives and four to quercetin derivatives [1].

A flavonol diglycoside was isolated from the combined flavonoids. It was identified by means of color reactions, a study of the products of complete and stepwise acid, alkaline, and enzymatic hydrolysis, from the melting points of the pure substances and their acetyl derivatives, and by IR and UV spectroscopy. The results of a comparison of the intensities of the absorption maxima in the bands of the UV spectra showed that the substance under investigation was a trioside [2] with the composition $C_{33}H_{40}O_{19}$, mp 195-197°C $[\alpha]_D^{20}$ −136.5° (c 0.5; ethanol), λ_{max} 267, 350 nm. The aglycone of the glycoside was kaempferol, with mp 275-277°C. The yield of the aglycone on complete acid hydrolysis was 38.7%, and the sugar components were D-glucose and L-rhamnose in a ratio of 1:2 (densitometrically). On analysis of the UV spectra of the glycoside in neutral solution using ionizing and complex-forming reagents, free hydroxy groups were found in positions 4' and 5, and substituted hydroxy groups at C_3 and C_7. The mode of attachment of the sugars was also established by an analysis of the intermediate hydrolysis products. On alkaline and stepwise acid hydrolysis of the glycoside, four intermediate substances were formed: the aglycone kaempferol and glycosides A, B, and C. The hydrolysis products were isolated preparatively and analyzed.

Substance A, mp 220-222°C, $[\alpha]_D^{20}$ −27° (c 0.1; ethanol), λ_{max} 260, 360 nm. On acid hydrolysis, the aglycone kaempferol and the sugars D-glucose and L-rhamnose (1:1) were found. According to UV spectroscopy, free OH groups were present in positions 4', 5, and 7. The sugar components were attached at C_3. To determine the order of arrangement of the monoses in the biose, hydrolysis was carried out by Fox's method [3]. The aglycone kaempferol, the monoglycoside astragalin, and rhamnose were detected and identified, which showed that substance A was kaempferol 3-rutinoside.

Substance B, mp 175-177°C, $[\alpha]_D^{20}$ −97° (c 0.1; ethanol), λ_{max} 262, 357 nm. Hydrolysis gave the aglycone kaempferol and the sugar glucose. The position of attachment of the sugar was determined by UV spectroscopy and comparison with an authentic sample and the glycoside itself was identified as kaempferol 3-O-glucoside (astragalin).

Substance C, mp 233-235°C, $[\alpha]_D^{20}$ −112° (c 0.5; methanol), λ_{max} 260, 365 nm. Hydrolysis gave kaempferol and rhamnose, and the glycoside was identified as kaempferol 7-O-rhamnoside (rhamnorobin).

To determine the sizes of the oxide rings of the carbohydrate components and the configurations of the glycosidic bonds between the aglycone and the sugars in the glycosides, we compared their molecular rotations with those of the corresponding phenyl glycosides [4] and performed enzymatic hydrolysis with specific enzymes [3, 5, 6]. It was found that the rhamnose at C_7 has the α configuration of the bond and a pyranose ring, and glycoside C can be characterized as kaempferol 7-O-α-L-rhamnopyranoside. The rutinoside in position 3 is attached to the aglycone by a β bond, and the monoses have a 6→1 linkage (both monoses being pyranoses).

On the basis of the results of the investigations, the glycoside isolated can be characterized as kaempferol 7-O-α-L-rhamnopyranoside-3-O-[O-β-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside] or oxytroside. Oxytrioside was first isolated from Komarov's oxytropis by M. A. Baimukhambetov [7], but he did not determine the sizes of the oxide rings or the configuration of the glycosidic bonds. The isolation of oxytroside from Oxytropis myriophylla is the second case of its being found in representatives of the genus Oxytropis.

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LITERATURE CITED

1. Be tkhi Tkhuan' and K. F. Blinova, Rast Res., 10, No. 1, 72 (1974).
2. N. P. Maksyutina and V. I. Litvinenko, in: Phenolic Compounds and Their Functions [in Russian], Moscow (1968), p. 7.
3. D. W. Fox, W. L. Savage and S. H. Wender, J. Am. Chem. Soc., 75, No. 10, 2504 (1953).
4. I. P. Kovalev and V. I. Litvinenko, Khim. Prirodn. Soedin., 233 (1965).
5. P. I. Gvozdyak and V. I. Litvinenko, Med. Prom. SSSR, 5, 16 (1964).
6. B. V. Chandler and K. A. Harper, Austr. J. Chem., 14, No. 4, 586 (1961).
7. M. A. Baimukhambetov, "A photochemical investigation of Komarov's oxytropis – Oxytropis komarovli Vass.," Author's Abstract of Candidate's Dissertation, Leningrad (1972).

FLAVONOIDS OF Fraxinus raibocarpa

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The leaves and bark of Fraxinus raibocarpa Rgl., family Oleaceae, collected in the Pamir-Alai at the beginning of fruit-bearing were extracted with methanol. After the elimination of the bulk of the solvent, colorless crystals deposited from the methanolic extract with composition $C_6H_{14}O_6$, mp 166-167°C (yield 1%), which were identified as D-mannitol by their IR spectrum and a comparison with an authentic sample.

The residue from the evaporation of a methanolic extract of the leaves was dissolved in hot water and the solution was extracted with chloroform and with ethyl acetate. The ethyl acetate extract was isolated on polyamide in gradient chloroform–methanol and water–ethanol systems and yielded two flavonoid compounds: quercetin 3-O-β-D-glucopyranoside (isoquercitrin) $C_{21}H_{20}O_{12} \cdot 2H_2O$, mp 228-230°C, $[\alpha]_D^{20} -20.5°$ (c 0.6; MeOH) and rutin $C_{27}H_{30}O_{16} \cdot 2H_2O$, mp 187-189°C, $[\alpha]_D^{20} -11.5°$ (c 0.7; MeOH). An extract of the bark under similar conditions yielded the flavonoids kaempferol 3-O-β-D-glucopyranoside (astragalin) $C_{21}H_{20}O_{11}$, mp 172-176°C, $[\alpha]_D^{20} -18.7°$ (c 0.6; MeOH), and kaempferol $C_{15}H_{10}O_6$, mp 272-275°C. The substances obtained were identified by their UV and NMR spectra, the products of acid hydrolysis, and the results of comparison with authentic samples. It was shown by paper chromatography that the flavonoid composition of the leaves and the bark were similar, consisting of the four substances mentioned, but the compounds isolated were predominant in these organs of the plant.

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