7-O-METHYLHERBACETIN 3-RHAMNOSIDE FROM Atraphaxis pyrifolia

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From the leaves of Atraphaxis pyrifolia, by extraction with acetone followed by separation on silica gel [chromoform–methanol (48:1, 24:1, and 12:1)] and purification on polyamide, we have isolated a new flavonoid glycoside with mp 154-156°C (from 50% aqueous methanol; Kofler block); $[\alpha]_D^{22}$ −120.8° (c 2.4; methanol), R_f 0.85 [BAW (4:1:5.1)], 0.75 (25% acetic acid), 0.70 [TLC, Silufol, chloroform–methyl ethyl ketone–methanol (12:1:2)], λ_{max} (absolute ethanol): 266 nm (4.19), 3.52 (4.16).

By UV spectroscopy with ionizing and complex-forming reagents free hydroxy groups were found in positions 4' and 5 for the glycosides and 3, 4', and 5 for the aglycone. By acetylation (acetic anhydride in pyridine) we obtained the glycoside acetate with mp 118-120°C (from ethanol), $[\alpha]_D^{24}$ −94.5° (c 0.77; chloroform) and the aglycone acetate with mp 207-209°C (from ethanol). The NMR spectrum of the glycoside acetate (Varian HA-100, $CDCl_3$) showed the signals of the following protons: H-2', H-6' (δ 7.78-7.72 ppm, d, 2 H, J = 9 Hz), H-3', H-5' (δ 7.20 ppm, d, 2 H, J = 9 Hz), H-6 (6.64 ppm, s, 1 H), $-OCH_3$ group (3.83 ppm s), three aromatic acetyl groups at δ 2.22 (s, 3 H), 2.28 (s, 3 H), and 2.34 ppm (s, 3 H), and three aliphatic acetyl groups at δ 1.88 and 2.05 ppm with an intensity ratio of 2:1. The sugar protons appeared at δ 0.80-0.86 ppm (CH_3 group of rhamnose, d, J = 6 Hz), 4.82 ppm (C_4–H, t, J = 9 Hz), 5.15 ppm (C_3–H, d.d, J_1 = 9 Hz, J_2 = 4 Hz), 5.48 ppm (C_2–H, weakly resolved doublet), and 5.56 ppm (C_1–H, weakly resolved doublet).

Adsorption bands in the 840, 1036, 1060, and 1095 cm^{-1} regions in the differential IR spectrum of the glycoside, the results of polarimetric analysis ($[M]_D \cdot K_{Pgl} = -279°$), and also the presence of a weakly resolved doublet at δ 5.56 ppm in the NMR spectrum of its acetate shows an α bond and the pyranose form of the sugar [1]. The position of the signal of the methyl group of the rhamnose, and also the IR spectra of the glycoside and its aglycone with zirconium chloride show the attachment of the rhamnose in position 3 of the flavonoid [2, 3]. As can be seen from the NMR spectrum of the acetate of the glycoside, one of the substituents is a methoxy group. The absence of a shift with sodium acetate in the UV spectrum of the glycoside and of the aglycone, and also the results of alkaline cleavage (formation of p-hydroxybenzoic acid as the only chromatographically detectable product) shows its position at C_7. Demethylation of the aglycone with hydriodic acid gave a flavonol with mp 280°C coinciding in its color reactions, chromatographic behavior, and spectral characteristics with herbacetin [4]. The chemical characteristics and UV, IR, and NMR spectroscopy show that the glycoside isolated from the leaves of Atraphaxis pyrifolia can be characterized as 3,4',5,8-tetrahydroxy-7-methoxyflavone 3-O-α-L-rhamnopyranoside and its aglycone as 3,4',5,8-tetrahydroxy-7-methoxyflavone (7-methoxyherbacetin).

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