THE STRUCTURE OF THERMOPSOSIDE – A NEW FLAVONOID FROM Thermopsis alterniflora

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We have previously reported the isolation from the herb Thermopsis alterniflora Rg. et Schmalh. of three flavonoids, one of which was identified as genistin [1]. In the present paper we give the results of a chemical investigation of flavonoid (II), which we have called thermopsoside.

Thermopsoside has the composition $C_{22}H_{22}O_{11}$, mp 176-179°C (from methanol), $[\alpha]_D^{25}$ −34.6° (c 0.65; DMFA), mol. wt. 462, R_f 0.53 in the BAW (4:1:2) system. It dissolves readily in pyridine, dimethyl sulfoxide, formamide, and dioxane, and sparingly in ethanol, water, n-butanol, and ethyl acetate, and is insoluble in acetone, chloroform, benzene, and carbon tetrachloride. It gives a positive reaction with magnesium and hydrochloric acid, and the pigment so obtained does not pass into octanol, which shows its glycosidic nature [2]. Its IR spectrum has maxima with λ_{max} 253 and 347 nm (log ε 4.1, 4.21), which shows that thermopsoside is a derivative of 3',4',5,7-tetrahydroxyflavone. In the IR spectrum there are absorption bands at (cm^{-1}) 1665 (C=O of a γ-pyrone), 1450, 1510, 1615 (aromatic nucleus) and 2880-2950 ($-OCH_3$), and a broad band at 3300-3480 (hydroxy groups). Bands at 905 and 950 and also at 1009, 1050, and 1087 cm^{-1} show the presence of a β-glycosidic linkage and the pyranose form of the sugar residue. This is confirmed by its enzymatic cleavage with β-glucosidase and by the calculated value of $[M]_D \cdot K_P$ according to Klyne [3].

On hydrolysis by 15% H_2SO_4 with heating for 2 h, we obtained D-glucose, which was identified by paper chromatography and by GLC in the form of the silyl ether [4], and the aglycone, $C_{16}H_{12}O_6$, with mp 332-335°C (60% of the initial glucoside). On the basis of the compositions and optical densities of the glucoside and the aglycone, it may be concluded that thermopsoside is a monoside. The glucoside gives bathochromic shifts of the long-wave maximum in the presence of sodium methoxide (54 nm) and zirconyl nitrate (47 nm), the latter being eliminated in the presence of citric acid, which is characteristic for the presence of free hydroxy groups in the 5 and 4' positions [5]. In the case of the aglycone, a bathochromic shift appears in the presence of sodium acetate (10 nm), from which it follows that the glucose residue is present in position 7.

We used the method of NMR spectroscopy to determine the position of the methoxy group [6]. In the spectrum of thermopsoside taken at 60 MHz (solution of the substance in DMSO, δ scale from the signal of HMDS taken as 0), there are a broadened singlet at 7.68 ppm (2 H) (the H-2' and H-6' protons), a doublet at 7.17 ppm, J 8.5 Hz (1 H) (the H-5' proton), a singlet at 6.96 ppm (H-3), and doublets at 6.69 and 6.42 ppm, J 1.5 Hz (H-6 and H-8).

A singlet at 13.12 ppm and a broadened signal at 10.38 ppm correspond to the protons of hydroxy groups located, respectively, at C-5 and C-4'. In the spectrum taken in deuteropyridine, a three-proton singlet is found at 3.66 ppm ($Ar-OCH_3$) and multiplets at 5.58 ppm (β-anomeric proton of glucose) [7, 8] and at 4.14 ppm (6 H, the protons of one molecule of glucose).

On the basis of the above facts, it may be concluded that thermopsoside has the structure of 7-O-β-D-glucopyranosyl-4',5-dihydroxy-3'-methoxyflavone. This is the first time that the aglycone concerned (chrysoeriol) [9] has been isolated in the form of a glucoside.

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