PRIMFLASIN – A NEW FLAVONOL GLYCOSIDE FROM Primula algida

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From a methanolic extract of the flowers of Primula algida Ad. (violet primrose), by chromatography on a polyamide sorbent we have isolated a flavonoid glycoside (0.25%) with the composition $C_{31}H_{36}O_{19} \cdot 2H_2O$, mp 207-211°C (Kofler block), $[\alpha]_D^{21}$ −52.5° (c 0.5; methanol), R_f 0.52 (15% solution of acetic acid), 0.65 [ethyl acetate–formic acid–water (10:2:3)], UV spectrum: λ_{max} 269, 336 nm. The substituents in the glycoside are located at positions 4',5, and 7 and are free hydroxy groups (UV spectroscopy).

The NMR spectrum of the silylated glycoside (Fig. 1) has a doublet at δ 7.96 ppm (J=9 Hz, 2H) corresponding to the H-2' and H-6' protons; a doublet at 6.84 ppm (J=9 Hz, 2H), H-3' and H-5'; a doublet at 6.4 ppm (J=2.5 Hz, 1H), H-8; a doublet at 6.10 ppm (J=2.5 Hz, 1H), H-6; a doublet at 5.60 ppm (J=7Hz, 1H), due to the anomeric proton of β-glucose in position 3 of the flavonol; and doublet at 4.50 and 4.36 ppm (J=6 Hz), which are the signals of two molecules of α-L-arabinose attached to the glucose. The signals of the protons of the carbohydrate moiety are in the 3.10-4.00 ppm region [1].

The hydrolysis of primflasin with 5% sulfuric acid gave an aglycone $C_{15}H_{10}O_6$ with mp 276-278°C, R_f 0.35 (60% solution of acetic acid). The constants of the aglycone agreed with those for kaempferol, as was confirmed by the results of a direct comparison with an authentic sample.

The hydrolyzate after the separation of the aglycone was found by paper chromatography to contain D-glucose and L-arabinose.

The oxidation of primflasin with hydrogen peroxide and subsequent treatment with ammonia solution gave a triose with R_f 0.09 [butanol–acetone–water (2:7:1)], 0.09 [butanol–ethanol–water (40:11:19)], and 0.36 [butanol–pyridine–water (6:4:3)], taking the R_f value of rhamnose as 1 [2]. The acid hydrolysis of the triose formed D-glucose and L-arabinose.

Exhaustive methylation of primflasin with subsequent methanolysis gave the methyl glycosides of 2,3,6-tri-O-methyl-D-glucose and of 2,3,4-tri-O-methyl-L-arabinose, these being identified by the GLC method.

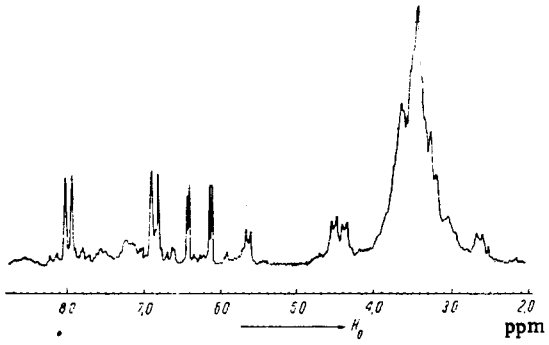

Fig. 1. NMR spectrum of silylated primflasin.

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The formation of these products shows that the arabinose in the pyranose form is the terminal sugar [3]. The glucose is attached directly to the aglycone, since in the NMR spectrum of the silylated glycoside the chemical shift of the anomeric proton of the glucose corresponds to literature figures [1] for β-glucose in position 3.

The second molecule of arabinose can be located only between the glucose and arabinose in the chain: If the chain were branched, we should not have obtained the methyl glycoside of 2,3,6-tri-O-methyl-D-glucose.

It was impossible to separate the 2,3,4-tri-O-methyl-L-arabinose and the 3,5-di-O-methyl-L-arabinose by the GLC method because their relative retention times almost coincide [4].

On the basis of what has been said above the structure of primflasin has been determined as kaempferol 3-[O-α-L-arabopyranosyl-(1 → 2)-O-α-L-arabofuranosyl-(1 → 4)-β-D-glucopyranoside].

LITERATURE CITED

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