SOME FLAVONOL GLYCOSIDES OF Equisetum arvense

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The isolation of saponaretin and of apigenin and its 5-glucoside from the herb Equisetum arvense L. (field horsetail) has been reported previously [1, 2]. Continuing investigations of the ether-soluble fraction of the methanolic extract treated as described previously [1], by chromatography on polyamide we have isolated kaempferol and quercetin, which were identified by their IR and UV spectra and also by a chromatographic comparison with authentic samples.

When the aqueous residue from the first fractions of the eluate was chromatographed, compound (I) was obtained with mp 222-224°C (aqueous methanol), λ_{max} (methanol) 268, 350 nm (log ε 4.31, 4.25); ν_{CO} 1660 cm^{-1}. The acid hydrolysis of this compound yielded kaempferol (46%) and D-glucose in a ratio of 1:2. From the nature of the bathochromic shifts of the absorption bands in the UV spectra in the presence of diagnostic additives it was established that there are free hydroxy groups in positions 4', 5, and 7 of the glycoside, and the stronger bathochromic shift (57 nm) of band I on the addition of $AlCl_3$ to the aglycone as compared with the glycoside shows the addition of a biose residue to position 3.

In the PMR spectrum of the TMS ether of compound (I) (100 MHz, CCl_4, HMDS) doublets at δ 6.21 ppm (1 H) and 6.53 ppm (1 H) with J = Hz belong to the H-6 and H-8 protons, respectively. Doublets at δ 6.78 ppm (2 H) and 7.82 ppm (2 H) correspond to the H-3', H-5' and the H-2', H-6' protons (J = 8 Hz, ortho position). A doublet at δ 5.80 ppm (1 H, J = 6 Hz) is the signal of the anomeric proton of β-glucose attached at the 3-OH group, and a doublet at δ 4.82 ppm (1 H, J = 6 Hz) relates to the anomeric proton of the second β-glucose molecule in the biose. A complex multiplet in the 3.14-3.74 ppm region corresponds to the 12 protons of the biose [3].

On the basis of the information obtained and also of a comparison with a sample kindly given to us by Dr. Salleh, compound (I) was identified as kaempferol 3-sophoroside [4].

From the ethyl acetate extract, by elution with a mixture of chloroform and methanol (9:1), compound (II) was obtained in the form of small light yellow needles with mp 226-228°C (methanol), λ_{max} (CH_3OH) 257, 362 nm (log ε 4.40, 4.33), ν_{CO} 1665 cm^{-1}; on acid hydrolysis it gave quercetin and D-glucose in equimolar amounts.

On the basis of its physicochemical constants, the results of IR and UV spectroscopy, and a chromatographic comparison with an authentic sample [5], compound (II) was identified as quercetin 3-O-β-D-glucopyranoside (isoquercitrin).

Quercetin 3-glucoside has been found previously in Equisetum arvense L. [6], and kaempferol 3-sophoroside in other species of horsetail [4]. The PMR spectrum of the TMS ether of kaempferol 3-sophoroside was taken in VILR [All-Union Scientific-Research Institute of Medicinal Plants].

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