EXPERIMENTAL

Compound I. Yellow amorphous (MeOH), mp 154–157° (dec.). UV λ_{max}^{MeOH} (nm): 225(*sh*), 310(*sh*), 371; $\lambda_{max}^{MeOH+NaOAc}$: 283, 336(*sh*), 407; $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$: 286, 379, 420, 445, 470(*sh*); $\lambda_{max}^{MeOH+AlCl_3}$: 234(*sh*), 320(*sh*), 385(*sh*), 422; $\lambda_{max}^{MeOH+AlCl_3+HCl}$: 235(*sh*), 320(*sh*), 385(*sh*), 422. NMR (DMSO-d_6) δ: 8.20 (1H, *d*, *J* 9 Hz), 7.82 (2H, *d*, *J* 9 Hz), 7.80 (2H, *s*), 6.86 (2H, *d*, *J* 9 Hz), 6.50 (1H, *d*, *J* 9 Hz), 4.70 (1H, *d*, *J* 9 Hz), 4.20–3.00 (6H, *m*). The partial methyl ether (from CH_2N_2 treatment) was oxidized with $FeCl_3$ and the product methylated with MeI to give a mixture of isoliquiritigenin and liquiritigenin permethyl ethers (as pale yellow oils). NMR of the product ($CDCl_3$) δ: (1) trimethylisoliquiritigenin portion 7.86 (H-6′, *d*, *J* 9 Hz), 7.64 (H-β, *d*, *J* 18 Hz), 7.42 (H-2 and 6, *d*, *J* 9 Hz), 6.96 (H-3 and 5, *d*, *J* 9 Hz), 6.84 (H-α, *d*, *J* 18 Hz), 6.50 (H-3′ and 5′, *m*). (2) dimethylliquiritigenin portion 7.84(H-5, *d*, *J* 9 Hz), 7.44(H-2′ and 6′, *d*, *J* 9 Hz), 6.92(H-3′ and 5′, *d*, *J* 9 Hz), 6.50(H-6 and 8, *m*), 5.44(H-2, *dd*, *J* 5 and 12 Hz), 2.94(H-3 *trans*, *d*, *J* 12 Hz), 2.88(H-3 *cis*, *d*, *J* 5 Hz). The chalcone methyl ether (1) was compared by TLC in $CHCl_3$–MeOH (6:1) with material prepared from 2′-hydroxy-4′,4-dimethoxy-3′-C-β-glucosylchalcone. *Pentaacetate* (prepared with $(AcO)_2O$ and a drop of H_2SO_4) triangular needles (MeOH), mp 111–112° (93–95° softness), M^+ 712. NMR (CD_2Cl_2) δ: 7.62(H-6′, *d*, *J* 9 Hz), 7.56(H-2 and 6, *d*, *J* 9 Hz), 7.52(H-β, *d*, *J* 18 Hz), 7.08(H-3 and 5, *d*, *J* 9 Hz), 7.04(H-5′, *d*, *J* 9 Hz), 7.02(H-α, *d*, *J* 18 Hz), 5.60–3.40(glucosyl 7H, *m*), 2.26, 2.14, 2.12(3 aromatic OAc), 1.88, 1.84, 1.64 (4 aliphatic OAc) (See Fig. 1).

Compound II. Pale yellow amorphous powder (MeOH), mp 229–230° (dec.). UV λ_{max}^{MeOH} (nm): 272, 331; $\lambda_{max}^{MeOH+NaOAc}$: 280, 300(*sh*), 350; $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$: 273, 328; $\lambda_{max}^{MeOH+AlCl_3}$: 278, 304, 346, 390(*sh*); $\lambda_{max}^{MeOH+AlCl_3+HCl}$: 278, 303, 244, 380(*sh*). NMR (TMS Et_2O in CCl_4) δ:7.77(2H, *d*, *J* 8.5 Hz), 6.78(2H, *d*, *J* 8.5 Hz), 6.25(1H, *s*), 4.55(1H, *d*, *J* 9 Hz), 4.35(1H, *d*, *J* 3.5 Hz), 4.40–3.10(12H, *m*). IR ν_{max}^{KBr} (cm^{-1}): 3450–3250, 1645, 1625, 1570, 1510, 1470, 1435, 1360, 1285, 1250, 1215, 1180, 1110, 1080, 1050, 1005, 960, 930, 895, 825. Chromatography of II. PC in 15% HOAc vitexin (0.38), 6,8-di-*C*-glucosylapigenin (0.53), compound II (0.41); in BAW vitexin (0.54), 6,8-di-*C*-glycosylapigenin (0.22), compound II (0.24). TLC EtOAc–pyridine–H_2O–MeOH (80:20:10:5) vitexin (0.54), 6,8-di-*C*-glucosylapigenin (0.11), compound II (0.23). *Deca-acetate* (prepared with $(AcO)_2O$ and a drop of H_2SO_4) triangular (MeOH), mp 171–173°. NMR (CD_2Cl_2) δ: 8.15(H-2′ and 6′, *d*, *J* 8.5 Hz), 7.45(H-3′ and 5′, *d*, *J* 8.5 Hz), 6.70(H-3, *s*), 6.20–3.40(glucosyl 14H, *m*), 2.46, 2.44, 2.30 (3 aromatic OAc), 2.04, 2.00, 1.98, 1.94, 1.88, 1.84, 1.74 (7 aliphatic OAc).

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FLAVONOIDS FROM THE LEAVES OF *CASSIA OCCIDENTALIS*

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Key Word Index—*Cassia occidentalis*; Leguminosae; matteucinol 7-rhamnoside; jaceidin 7-rhamnoside; flavonoids.

From the ethanolic extract of the leaves of *Cassia occidentalis* two flavonoid glycosides A and B have been isolated. Homogeneity and purity of both compounds were established by paper and thin layer chromatography.

Compound A, mp 170°(d), molecular formula $C_{24}H_{28}O_9$, gave all the characteristic colour reactions of flavonoids and was found to be glycosidic in nature. On acid hydrolysis, it gave rhamnose (PC, osazone) and an aglycone mp 186°, $C_{18}H_{18}O_5$, which showed colour reactions characteristic of flavanones. The compound analysed for two hydroxyl groups (acetate, IR 3355 cm^{-1}) two C-methyl groups (NMR signal at 7.60 τ corresponding to 6-protons of two CH—Me [1]) and one methoxyl group (Zeisel, IR 2865 cm^{-1}, 1185 cm^{-1}, NMR signal at 6.2 τ corresponding to 3-protons of one —OMe group. Spectral studies of the aglycone (λ_{max} 290 nm, 325 nm) indicated the presence of free hydroxyl groups at positions -5 and -7 (bathochromic shifts with aluminium chloride [2] and fused sodium acetate [3] respectively). On permanganate oxidation the aglycone gave anisic acid as one of the oxidation products which fixed the

methoxyl group at position-4'. On alkali degradation the aglycone gave 2,4-dimethylphloroglucinol and anisic acid. Thus, there are hydroxyl groups at 5 and 7, methyl groups at 6 and 8 in the ring A and the methoxyl group at position-4' in the ring B. Thus the aglycone is 5,7-dihydroxy-4'-methoxy-6,8-dimethylflavanone.

That the rhamnose was attached to the 7-hydroxyl was established by the spectral shift with $AlCl_3$ but not with NaOAc. Rhamnose is in the pyranose form since periodate oxidation gave two moles of periodate per mole of the glycoside consumed and one mole of formic acid was produced. The glycoside was hydrolysed by takadiastase but not by emulsin showing the presence of an α-linkage.

Compound A is thus matteucinol 7-rhamnoside, a glycoside which has not been reported earlier from any plant source. However, its aglycone, 5,7-dihydroxy-4'-methoxy-6,8-dimethyl-flavanone (matteucinol) has been reported earlier by Arthur and Tam from the leaves of *Rhododendron simsii* [4].

Compound B, mp 200°(d), $C_{24}H_{26}O_{12}$, was found to be glycosidic in nature. On acid hydrolysis, it gave rhamnose (PC, TLC and phenylosazone) and an aglycone, mp 127°, $C_{18}H_{16}O_8$, which showed colour reactions characteristic of flavones.

The aglycone (λ_{max} 256 nm and 351 nm) analysed for the presence of three phenolic hydroxyls (acetate, IR 3430 cm^{-}) and three methoxyls (Zeisel, IR 2860 cm^{-1} and 1180 cm^{-1}). Spectral studies revealed the presence of one methoxyl group at position-3 (hypsochromic shift in band 1 in comparison to flavonols [5]) and two free hydroxyls at position 5 and 7 (bathochromic shifts with $AlCl_3$ and NaOAc respectively). The methyl ether of the aglycone gave veratric acid whereas the aglycone gave vanillic acid on oxidation with neutral $KMnO_4$. Thus, there is a hydroxyl group at position-4' and a methoxyl group at position-3'. Alkali degradation of the aglycone and its methyl ether established the presence of a methoxyl group at position-6. Thus the aglycone is 5,7,4'-trihydroxy-3,6,3'-trimethoxyflavone (jaceidin).

The sugar linkage has been shown to be with the 7-hydroxyl group by the study of spectral shifts. That rhamnose is present in the pyranose form has been proved by periodate oxidation and nature of the glycosidic linkage as α-has been confirmed by hydrolysis with diastase. Compound B is thus jaceidin 7-rhamnoside.

This glycoside has not been reported earlier from any plant source, but the 7-glucoside of jaceidin was reported earlier by Wagner *et al.* [6] from *Centaurea jacea*.

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BRACTEATIN FROM THE MOSS *FUNARIA HYGROMETRICA*

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Key Word Index—*Funaria hygrometrica*; mosses; bracteatin; aurone.

Bracteatin (4,6,3',4',5'-pentahydroxyaurone) was isolated from the sporophytes of *F. hygrometrica*; it was not detected in the leaves. This is the first report of the higher plant pigment [1] in mosses. Quantitative comparison of the pigment was determined by comparing size and intensity of spots on filter paper. Variation in the content of braceatin was observed during developmental stages of the sporophytes; shortly after meiosis (March–April) the amount was the greatest. Colour change of capsules [2] from yellow–orange to brown was accompanied by a significant reduction in the quantity of pigment.

EXPERIMENTAL

Plant source. Funaria hygrometrica Hedw. collected in Israel and voucher specimens deposited in the Herbarium of the Department of Botany, Hebrew University of Jerusalem.

Isolation and identification. Air dried sporophytes (0.5–10 g dry wt.) were immersed in hot H_2O for 10 min; EtOH was added to make a 70% ethanolic solution, and left at room temp. for 20 hr. Fresh material was extracted with 95% EtOH. The yellowish extract was concentrated and separation was carried out on Whatman No. 3 paper using Forestal (HOAc–conc HCl–H_2O, 30:3:10), 50% HOAc or BAW (*n*-BuOH–HOAc–H_2O, 4:1:5 upper layer). The yellow bands of bracteatin were extracted from the wet paper with EtOH. Slow evaporation of EtOH offered an orange–red powder, crystallizing as golden-brown needles from aq. MeOH. The identity with bracteatin was confirmed by PC, TLC (cellulose plates), UV [3], IR [4] and MS, using bracteatin isolated from *Helichrysum bracteatum* cv as reference compound. MS (probe) 70 eV *m/e* (rel. int.): 302 M^+ (100) 301(21), 285(9), 274 (M^+—CO; 7), 217(10), 166(6), 153(A^+; 26).

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