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*.

REFERENCES

1. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, p. 272. Springer-Verlag, New York.
2. Horowitz, R. M. (1957) *J. Am. Chem. Soc.* **79**, 6561.
3. Jurd, L. and Horowitz, R. M. (1957) *J. Org. Chem.* **22**, 1618.
4. Arthur, H. R. and Tam, S. W. (1960) *J. Chem. Soc.* 3197.
5. Geissman, T. (1962) *The Chemistry of Flavonoid Compounds*, p. 117. Pergamon, Oxford.
6. Farkas, L., Hoerhammer, L., Wagner, H. and Gurniak, R. (1964) *Ber*, **97**, 610.

Phytochemistry, 1977, Vol. 16, pp. 1108–1109. Pergamon Press. Printed in England.

BRACTEATIN FROM THE MOSS *FUNARIA HYGROMETRICA*

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(*Received* 24 *December* 1976)

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).

Acknowledgements—The authors wish to thank Miss Tiqva Cohen and Mrs. Sima Fundaminsky for spectroscopic measurements, and Prof. C. C. Heyn for her constant interest of the work.

REFERENCES

1. Harborne, J. B., Mabry, T. J. and Mabry, H. (eds.) (1975) *The Flavonoids*. Chapman and Hall, London.
2. Nilsson, E. and Bendz, G. (1973) *Flavonoids in Bryophytes*. In: *Chemistry in Botanical Classification, Nobel Symposium 25*, Bendz, G. and Santesson, J., eds. Academic Press, New York.
3. Harborne, J. B. (1963) *Phytochemistry* **2**, 327.
4. Hänsel, R. and Langhammer, L. (1963) *Arch. Pharmaz.* **296**, 619.

Phytochemistry, 1977, Vol. 16, p. 1109. Pergamon Press. Printed in England.

A NEW WOGONIN DERIVATIVE FROM *GARDENIA* GUM

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(*Received* 3 *October* 1976)

Key Word Index—*Gardenia lucida*; *G. gummifera*; Rubiaceae; 5,7,3′,5′-tetrahydroxy-8,4′-dimethoxyflavone.

Previously, sixteen flavones have been isolated from the gum [1–6]. In continuation of our work [3–6] on the flavonoids of *Gardenia* gum, another new flavone has been isolated from the C_6H_6 and H_2O insoluble portion of the alcoholic extract of the gum. The structure 5,7,3′,5′-tetrahydroxy-8,4′-dimethoxyflavone assigned to it has been confirmed by synthesis.

EXPERIMENTAL

Extraction and isolation. The extraction procedure has been described earlier [6]. PC (Whatman 3 mm) of H_2O insoluble portion using 50% HOAc gave 3 yellow bands, B_1, B_2 and B_3. Band B_1 resolved into two bands on TLC (Si gel, C_6H_6–MeOH–AcOH, 45:3:2). The upper band furnished two known flavones **A** and **B** [5]. The lower band also resolved into two compounds **C** and **D**. Compound **C** has earlier been identified [5]. Bands B_2 and B_3 yielded seven compounds [5, 6].

Identification. Compound **D** crystallized as yellow needles. mp 254–56°; R_f 0.89 (BAW, 4:1:5); 0.88. (PhOH–H_2O, 3:1); 0.22 (15% aq. AcOH); (Found: C, 58.8; H, 4.4. $C_{17}H_{14}O_8$ requires C, 59.0; H, 4.1%); λ_{max}^{MeOH} nm (log ε): 275 (4.03), 327 (3.88); $AlCl_3$, 285, 310, 350; $AlCl_3$–HCl, 285, 305, 345; NaOAc, 285, 340, 355; NaOAc–H_3BO_3, 280, 305, 330; ν_{max}^{KBr}: 3448, 2950, 1650, 1587, 1495, 1013 and 963 cm^{-1}. Comparison of its R_f values on PC and TLC with other compounds isolated from the gum indicated it to be a tetrahydroxyflavone. It gave a positive Gibb's and a negative gossypetone test. Methylation with CH_2N_2 gave a partial methyl ether, mp 215–16°; λ_{max}^{MeOH} nm: 275, 325, identical with 5-hydroxy-7,8,3′,4′,5′-pentamethoxyflavone [3] (mmp, co-TLC, UV and IR). Compound **D** could therefore be 5,7,3′,5′-tetrahydroxy-8,4′-dimethoxyflavone.

Synthesis of 2-(3′,5′-Dibenzyloxy-4′-methoxybenzoyloxy)-4-benzyloxy-3,6-dimethoxyacetophenone. A mixture of 2-hydroxy-4-benzyloxy-3,6-dimethoxyacetophenone [7] (700 mg), 3,5-benzyloxy-4-methoxybenzoyl chloride [8] (1.75 g) and C_5H_5N (5 ml) was heated on a steam bath for 3 hr. The cooled reaction mixture was treated with ice-HCl (1:1) and then extracted with EtOAc. The organic layer was washed with H_2O, dried (Na_2SO_4) and concd. The brown semi-solid ester was purified by passing a soln of it in EtOAc–C_6H_6 (1:1) through a column of neutral alumina and crystallized from EtOAc–petrol as colourless needles (900 mg), mp 132–33°; (Found: C, 72.5; H, 5.8. $C_{39}H_{36}O_9$ requires C, 72.2; H, 5.6%); ν_{max}^{KBr}: 1727, 1672, 1600 and 1493 cm^{-1}.

Synthesis of 2-Hydroxy-4,3′,5′-tribenzyloxy-3,6,4′-trimethoxydibenzoylmethane. The above ester (700 mg) in dry C_5H_5N (7 ml) was treated with powdered KOH (1.8 g) and the mixture shaken vigorously for 2 hr with occasional warming. The reaction mixture was worked up as above. The diketone crystallized from EtOAc–petrol as yellow needles (500 mg), mp 202–4°; (Found: C, 71.9; H, 5.7. $C_{39}H_{36}O_9$ requires C, 72.2; H, 5.6%); ν_{max}^{KBr} 2994, 1613, 1582 and 1534 cm^{-1}.

Synthesis of 7,3′,5′-Tribenzyloxy-5,8,4′-trimethoxyflavone. The above diketone (400 mg) was gently refluxed with glacial HOAc (8 ml) and fused NaOAc (1.2 g) in an oil bath for 3 hr. The resulting flavone crystallized from EtOAc as colourless shining needles (280 mg), mp 192°; (Found: C, 74.3; H, 5.8. $C_{39}H_{34}O_8$ requires C, 74.3; H, 5.4%); λ_{max}^{MeOH} nm (log ε): 275 (4.2), 330 (4.0); ν_{max}^{KBr} 1639, 1595, 1493 and 1418 cm^{-1}.

Synthesis of 7,3′,5′-Trihydroxy-5,8,4′-trimethoxyflavone. The above flavone (200 mg) in EtOAc (20 ml) was stirred in an atmosphere of H_2 in the presence of Pd-C (25 mg; 10%) for 3 hr. The hydroxyflavone crystallized as yellow cubes (80 mg), mp 264–66°; (Found: C, 59.8; H, 4.30. $C_{18}H_{16}O_8$ requires C, 60.0; H, 4.4%); λ_{max}^{MeOH} nm (log ε): 270 (4.4), 330 (4.3); NaOAc, 280; λ_{max}^{KBr} 3125, 1639, 1577 and 1511 cm^{-1}.

Synthesis of 5,7,3′,5′-Tetrahydroxy-8,4′-dimethoxyflavone. A mixture of the hydroxyflavone (50 mg), dry $AlCl_3$ (95 mg) and CH_3CN (5 ml) was refluxed on a steam bath for 3 hr. CH_3CN was distilled off and the $AlCl_3$ complex was decomposed with ice-HCl (1:1). The crude flavone was purified by preparative TLC (Si gel; $C_6H_5CH_3$–HCOOEt–HCOOH, 5:4:1). It crystallized from EtOH as yellow needles (20 mg), mp 255–57°; (Found C, 58.8; H, 4.4. $C_{17}H_{14}O_8$ requires C, 59.0; H, 4.1%). It was identical (mmp, co-TLC, UV and IR) with the natural sample.

REFERENCES

1. Stenhouse, J. and Groves, C. E. (1877) *J. Chem. Soc.* **32**, 551.
2. Rama Rao, A. V., Venkataraman, K., Chakrabarti, P., Sanyal, A. K. and Bose, P. K. (1970) *Indian J. Chem.* **8**, 398.
3. Krishnamurti, M., Seshadri, T. R. and Sharma, N. D. (1972) *Indian J. Chem.* **10**, 23.
4. Gupta, S. R., Seshadri, T. R., Sharma, C. S. and Sharma, N. D. (1975) *Indian J. Chem.* **13**, 785.
5. Chhabra, S. C., Gupta, S. R., Seshadri, T. R. and Sharma, N. D. (1976) *Indian J. Chem.* **14B**, 651.
6. Chhabra, S. C., Gupta, S. R. and Sharma, N. D. (1976) *Phytochemistry* **16**, 399.
7. Geissman, T. A. and Halsall, T. G. (1951) *J. Am. Chem. Soc.* **73**, 1282.
8. Schopf, C. and Winterhalder, L. (1940) *Ann.* **544**, 62.