

O-METHOXYLATED C-GLYCOSYLFLAVONES FROM
JUSTICIA PECTORALIS

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Species of *Justicia* (Acanthaceae) are known to contain lignans (1-5). C-Glycosylflavones have been reported from the following genera: *Ecbolium* (6), *Yeatesia* (7), and *Siphonoglossa* (8) but not from the genus *Justicia*. Isolation and identification of C-glycosylflavones from *Justicia pectoralis* Jacq. are reported here. Their chemotaxonomic significance is discussed.

EXPERIMENTAL

PLANT MATERIAL.—*J. pectoralis* was collected in Guadeloupe, French West Indies, and identified at the National Herbarium of the Museum d'Histoire Naturelle in Paris (Quentin No. 117, Stéllé No. 345). A voucher specimen is on deposit in the Herbarium of the Faculté des Sciences Pharmaceutiques, Université Toulouse III, France.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—Dried whole plants, including leaves, stems, and roots (1 kg), were extracted at 50° repeatedly with 95% EtOH followed by extraction with 60% aqueous EtOH. The combined extracts were concentrated in vacuo, and the aqueous syrup was partitioned successively with CHCl₃, EtOAc, and *n*-BuOH. The *n*-BuOH concentrate was subjected to cc on Amberlite XAD₄ with MeOH/H₂O mixtures of decreasing polarity. The MeOH-H₂O (60:40 and 70:30) fractions furnished four flavonoids that were further separated by cc on Sephadex LH-20 with H₂O then MeOH as eluents. Flavonoids were purified by repeated preparative tlc on cellulose in three solvent systems: *n*-BuOH-HOAc-H₂O (4:1:5, upper phase) (BAW); 5% HOAc; and CHCl₃-MeOH-*n*-PrOH-H₂O (60:30:20:5). The bands corresponding to flavonoids were scraped off and eluted with MeOH. Final purification of compounds was made on Sephadex LH-20 columns with MeOH as eluent. The compounds obtained were swertisin (22 mg), 2''-O-rhamnosylswertisin (40 mg), swertiajaponin (19 mg), and 2''-O-rhamnosylswertiajaponin (10 mg).

IDENTIFICATIONS.—All the flavonoids and their hydrolysis products were identified by their chromatographic properties and spectral data: uv, ms of the free compounds measured from desorption/chemical ionization mass spectrometry

(dcims) and of the permethylated Et₂O derivatives measured from eims, and ¹H nmr of acetylated derivatives (9-14). The structure of 2''-O-rhamnosylswertisin was further clarified by ¹³C nmr (15). Swertisin was also identified by direct comparison on tlc of the free compound and permethylated derivative with authentic samples (16). Full details of the isolation and identification of the compounds are available on request to the senior author.

DISCUSSION

Swertisin (16-20) and swertiajaponin (17, 18, 21) have been found in many sources, whereas 2''-O-rhamnosylswertisin has been isolated only from *Gemmingia chinensis* (15) and 2''-O-rhamnosylswertiajaponin only from *Securigera coronilla* (22). Thus, these compounds are reported for the first time in the Acanthaceae. Embinin, an O-methoxylated C-glycosylflavone, which differs from 2''-O-rhamnosylswertisin only by a methoxyl group at the 4' position, has been identified as a major compound in the stem and the leaves of *Siphonoglossa sessilis* (Jacq.) Oerst. (Acanthaceae) (8). This is the only previous report of the presence of O-methoxylated C-glycosylflavones in the Acanthaceae. The systematic position of the genus *Siphonoglossa*, on the basis of the pollen morphology, is in dispute; Lindau (23) places it in the tribe Odontonemae, whereas Henrickson and Hilsenbeck (24) place it in the tribe Justiceae. The presence of O-methoxylated C-glycosylflavones in *J. pectoralis* (tribe Justiceae) and in *S. sessilis* lends support to the view that *Siphonoglossa* also belongs in the tribe Justiceae.

LITERATURE CITED

1. M. Okigawa, T. Maeda, and N. Kawano, *Tetrahedron*, **26**, 4301 (1970).

2. A.A. Olaniyi and J.W. Powell, *J. Nat. Prod.*, **43**, 482 (1980).
3. S. Ghosal, S. Banerjee, and D.K. Jaiswal, *Phytochemistry*, **19**, 332 (1980).
4. S. Ghosal and S. Banerjee, *Chem. Ind.*, **23**, 854 (1979).
5. K. Munakata, S. Maruno, and K. Ohta, *Tetrahedron Lett.*, 4167 (1965).
6. A.G. Ramachandran Nair, P. Ramesh, and S. Sankara Subramanian, *Phytochemistry*, **14**, 1644 (1975).
7. R.A. Hilsenbeck, S.J. Wright, and T.J. Mabry, *J. Nat. Prod.*, **47**, 312 (1984).
8. R.A. Hilsenbeck and T.J. Mabry, *Phytochemistry*, **22**, 2215 (1983).
9. J. Chopin and M.L. Bouillant, in: "The Flavonoids." Ed. by J.B. Harborne, T.J. Mabry, and H. Mabry, Academic Press, New York, 1975, Chapter 12.
10. R.M. Horowitz and B. Gentili, *Chem. Ind.*, 498 (1964).
11. T.J. Mabry, K.R. Markham, and M.B. Thomas, "The Systematic Identification of Flavonoids," Springer, New York, 1970.
12. M.L. Bouillant, A. Besset, J.F. Bonvin, and J. Chopin, *Phytochemistry*, **17**, 527 (1978).
13. K.R. Markham and V.N. Chari, in: "The Flavonoids, Advances in Research." Ed. by J.B. Harborne and T.J. Mabry, Chapman and Hall, New York, 1982, Chapters 2 and 8.
14. B. Gentili and R.M. Horowitz, *J. Org. Chem.*, **33**, 1571 (1968).
15. S. Shirane, S. Ohya, T. Matsuo, R. Hirose, D. Koga, A. Ide, and K. Yagishita, *Agric. Biol. Chem.*, **46**, 2595 (1982).
16. A. Bakhtiar, J. Gleye, C. Moulis, and I. Fourasté, "Abstract of Papers," Proceedings of the Second International Symposium on Plant Flavonoids in Biology and Medicine," Strasbourg, France, Aug. 31-Sept. 3, 1987, Abstract A20.
17. K. Komatsu and T. Tomimori, *Tetrahedron Lett.*, 1611 (1966).
18. R. Hirose, Y. Kazura, D. Koga, A. Ide, and K. Yagishita, *Agric. Biol. Chem.*, **45**, 551 (1981).
19. J.W. Wallace and G. Morris, *Phytochemistry*, **17**, 1809 (1978).
20. S. Asen, R.N. Stewart, K.H. Norris, and D.R. Massie, *Phytochemistry*, **9**, 619 (1970).
21. M. Komatsu, T. Tomimori, and Y. Makiguchi, *Chem. Pharm. Bull.*, **15**, 1567 (1967).
22. M. Jay, B. Voirin, A. Hasan, J.F. Gonnet, and M.R. Viricel, *Biochem. Syst. Ecol.*, **8**, 127 (1980).
23. G. Lindau, *Nat. Pflanzen Fam.*, **IV**, 274 (1895).
24. J. Henrickson and R.A. Hilsenbeck, *Brittonia*, **31**, 373 (1979).

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