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FLAVONOIDS FROM *PASSIFLORA PALMERI*

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As a part of our continuing study of the genus *Passiflora* (1-8), we report here 17 known flavonoids and one new flavone from *Passiflora palmeri* Rose, a member of the subgenus *Dysosmia*. The known flavonoids found were: quercetin 7,3′-dimethyl ether, isoscoparin (9), isovitexin, apigenin 7-glucoside, chrysoeriol, vitexin, isoscutellarein 8-methyl ether (10), quercetin, isorhamnetin, luteolin, isoorientin (11), luteolin 7-glucoside, 6-methoxykaempferol (12), selgin (13), vicenin-2 (14), 2″-O-glucosylvitexin (15), and 2″-O-rhamnosylvitexin (16). The new flavone isolated was tricetin 4′-methyl ether.

IDENTIFICATION OF TRICETIN 4′-METHYL ETHER.—The uv spectrum of this new flavone in MeOH with added NaOMe showed a 42 nm bathochromic shift of Band I, with a lower intensity relative to the Band I at 350 nm in the MeOH spectrum; this result indicated that the 4′-OH was substituted. The color reactions (purple with and without NH_3 under uv light, and yellow when sprayed with Naturstoffreagenz-A, Carl Roth, Germany) were in accord with this conclusion. The lack of a significant shift in Band I in the $AlCl_3$/HCl spectrum (389 nm) relative to Band I in the $AlCl_3$ spectrum (390 nm), as well as the lack of a shift in Band I in the NaOAc/H_3BO_3 spectrum relative to Band I in the MeOH spectrum confirmed the absence of a 3′,4′-di-OH group. The presence of Band III at 325 nm in the NaOMe spectrum and a 6-nm shift in Band II in the NaOAc spectrum relative to Band II in the MeOH spectrum indicated a free 7-OH group. Confirming information about this compound was obtained from the pmr spectrum of its partially derivatized (5-OH free; s, δ12.74) TMSi ether. A symmetrical trisubstituted B-ring was apparent from the two-proton singlet at δ7.04 (H-2′ and H-6′). This signal, in combination with the methoxyl resonance at 3.88 (s, 3H) and the uv data, indicated that the B-ring is 3′,5′-dihydroxyl, 4′-methoxyl substituted. The two *meta* coupled doublets (J=2.5 Hz) at 6.42 and 6.3 are typical for H-8 and H-6, respectively, in a partially derivatized flavonoid, while the remaining signal in the spectrum, a one-proton singlet at 6.55, is assignable to H-3. Further support for the structure was provided by ms. The molecular ion (*m/z* 316) was the base peak in the spectrum. Other peaks were noted at 301 (M-15, 20%) and 273 (M-43, 8%). Finally, the A-ring and B-ring substitution patterns were confirmed by the occurrence of the appropriate A_1+1 (*m/z* 153, 25%) and B_1 (*m/z* 164, 10%) fragments.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded on the following instruments: uv, Varian Techtron model 635; pmr, NT-200 MHz; ms, DuPont 21-491 and AEI 902. Adsorbants for tlc and cc were from E. Merck. Sephadex LH-20 was from Pharmacia.

PLANT MATERIAL.—*P. palmeri* was collected in Baja California Sur, Mexico, 8 km south of Mulege in March 1982 by S. McCormick, J. Ger-

shenzon, and M. Warnock, *s.n.* A voucher is deposited in the Herbarium of the University of Texas at Austin.

EXTRACTION AND ISOLATION.—Dried leaf material of *P. palmeri* (270 g) was worked up using standard procedures (1-5). The EtOAc concentrate (5.6 g) was chromatographed on a Polyclar column (5 x 50 cm). Elution was initiated with CH_2Cl_2-MeOH-MeEtCO-Me_2CO (4:2:0.5:0.1), and the polarity was increased by decreasing the amount of CH_2Cl_2. The compounds obtained from the Polyclar column were cleaned over Sephadex LH-20. However, the C-glycosylflavonoid mixtures were first separated over microcrystalline cellulose before cleaning on Sephadex LH-20. The flavonoids were obtained in the following order from the Polyclar column: quercetin 7,3′-dimethyl ether (10 mg), isoscoparin (20 mg), isovitexin (10 mg), apigenin 7-glucoside (15 mg), chrysoeriol (200 mg), vitexin (22 mg), isoscutellarein 8-methyl ether (6 mg), quercetin (5 mg), isorhamnetin (20 mg), luteolin (15 mg), isoorientin (4 mg), luteolin 7-glucoside (10 mg), 6-methoxykaempferol (10 mg), selgin (10 mg), vicenin-2 (10 mg), 2″-O-glucosylvitexin (15 mg), 2″-O-rhamnosylvitexin (15 mg), and the new compound tricetin 4′methyl ether (8 mg).

IDENTIFICATION OF FLAVONOIDS.—All the known flavonoids were identified by uv, ms, pmr, color reactions (17) and, except for quercetin 7,3′-dimethyl ether, isoscutellarein 8-methyl ether, and selgin, authentic sample comparison. In addition, the apigenin and luteolin 7-glucosides gave the expected hydrolytic products. Vicenin-2 was also confirmed by cochromatography by hplc on a Lichosorb RP 18 (10 μm) column with an isocratic solvent mixture of MeOH-H_2O-HOAc (30:65:5) separating vicenins 1, 2, and 3. The flow rate was 1.5 ml/min.

Permethyl derivatives of 2″-O-glucosylvitexin and 2″-O-rhamnosylvitexin gave the following ms peaks respectively: 734 (M^+, 10%); 544 (SO_j, 34%); 515 (SO, 95%); 499 (S, 33%); 341 (j, 100%); and 704 (M^+, 15%), 544 (SO_j, 26%); 515 (SO, 71%); 499 (S, 8%); and 341 (j, 100%) (18).

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LITERATURE CITED

1. A. Ulubelen and T.J. Mabry, *J. Nat. Prod.*, **43**, 162 (1980).
2. A. Ulubelen, H. Ayyildiz, and T.J. Mabry, *J. Nat. Prod.*, **44**, 368 (1981).
3. S. McCormick and T.J. Mabry, *J. Nat. Prod.*, **44**, 623 (1981).
4. E. Ayanoglu, A. Ulubelen, T.J. Mabry, G. Dellamonica, and J. Chopin, *Phytochemistry*, **21**, 799 (1982).
5. A. Ulubelen, R.R. Kerr, and T.J. Mabry, *Phytochemistry*, **21**, 1145 (1982).
6. A. Ulubelen, G. Topcu, T.J. Mabry, G. Dellamonica, and J. Chopin, *J. Nat. Prod.*, **45**, 103 (1982).
7. A. Ulubelen, S. Oksuz, T.J. Mabry, G. Dellamonica, and J. Chopin, *J. Nat. Prod.*, **45**, 783 (1982).
8. A. Ulubelen and T.J. Mabry, *J. Nat. Prod.*, **46**, 597 (1983).
9. J.W. Wallace, T.J. Mabry, and R.E. Alston, *Phytochemistry*, **8**, 93 (1969).
10. S.R. Gupta, T.R. Seshadri, C.S. Sharma, and N.D. Sharma, *Indian J. Chem.*, **13**, 785 (1975).
11. L. Horhammer, H. Wagner, and F. Gloggengiesser, *Arch. Pharm.*, **291**, 126 (1958).
12. E. Rodriguez, N.J. Carman, G. Vander Velde, J.H. McReynolds, T.J. Mabry, M.A. Irwin, and T.A. Geissman, *Phytochemistry*, **11**, 3509 (1972).
13. B. Voirin, M. Jay, and M. Hauteville, *Phytochemistry*, **15**, 840 (1976).
14. J. Chopin, B. Roux, M.L. Bouillant, A. Durix, A. D'Arcy, T.J. Mabry, and Y.H. Yoshioka, *C.R. Acad. Sci. Ser. C.*, **268**, 980 (1969).
15. N. Morita, M. Arisawa, and A. Yoshikawa, *J. Pharm. Soc. J.*, **96**, 1180 (1976).
16. J. Chopin, G. Dellamonica, M.L. Bouillant, A. Besset, G. Popocivi, and G. Weissenbock, *Phytochemistry*, **16**, 2041 (1977).
17. T.J. Mabry, K.R. Markham, and M.B. Thomas, "Systematic Identification of Flavonoids," New York: Springer-Verlag, 1970.
18. M.L. Bouillant, A. Besset, J. Favre-Bonvin, and J. Chopin, *Phytochemistry*, **17**, 527 (1978).

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