ACKNOWLEDGMENTS

M.K. is thankful to CSIR (New Delhi) for an SRF award.

LITERATURE CITED

1. "The Wealth of India," vol. II. CSIR, New Delhi, 1956, p. 86.
2. S. Natarajan, V.V.S. Murti, and T.R. Seshadri, *Phytochemistry*, **9**, 575 (1970).
3. P.A. Gadek and C.J. Quinn, *Phytochemistry*, **24**, 267 (1985) and references therein.
4. T.J. Mabry, K.R. Markham, and M.B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, New York, 1970, p. 52.
5. K.K. Chexal, B.K. Handa, and W. Rahman, *J. Chromatogr.*, **48**, 484 (1970).
6. A. Pelter, R. Warren, K.K. Chexal, B.K. Handa, and W. Rahman, *Tetrahedron*, **27**, 1625 (1971).
7. N. Hameed, M. Ilyas, W. Rahman, and N. Kawano, *Phytochemistry*, **12**, 1497 (1973).

Received 21 October 1985

POLYPHENOLS ISOLATED FROM *PTEROCAULON PURPURASCENS*, I. 6-HYDROXYFLAVONOIDS

S.L. DEBENEDETTI, E.L. NADINIC, M.A. GOMEZ, and J.D. COUSSIO

Instituto de Química y Metabolismo del Fármaco, CONICET, Cátedra de Farmacognosia, Departamento de Farmacología, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Junín 956, 1113 Buenos Aires, Argentina

The genus *Pterocaulon* is widely distributed in northeastern Argentina, southern Brazil, and Paraguay. Various species are used in folk medicine for various applications, as an insecticide and as an agent against snake bites (1-4). In previous papers we described the caffeoylquinic acid content from *Pterocaulon virgatum* DC. (5) and *Pterocaulon purpurascens* Malmé (6) and the isolation of coumarins (7) and flavonoids (8,9) from *P. virgatum*. Continuing our study of the Argentine Compositae with medicinal uses, we now report the isolation and identification of flavonoids from the CH_2Cl_2 extract of *P. purpurascens*. Six flavonoids were isolated and identified as quercetin, isorhamnetin, and the quercetagetin methyl ethers: quercetagetin-3,7,4′-trimethyl ether (10), quercetagetin-3,7-dimethyl ether (11), quercetagetin-3,3′-dimethyl ether (12), and quercetagetin-3,7-dimethyl ether (11). We give further information of the mass spectra which is not detailed in the current literature.

EXPERIMENTAL

PLANT MATERIAL.—Aerial parts of *P. purpurascens* were collected from Chaco, Argentina, in 1983. The herbarium specimens are deposited at the Museo de Botánica "Juan A. Dominguez," Facultad de Farmacia y Bioquímica, U.B.A. (Schultz 1024).

EXTRACTION AND ISOLATION.—Dried and powdered plant material (800 g) was extracted by standard methods, first with petroleum ether (60-80°) and then with CH_2Cl_2. The extracts were concentrated in vacuo to dryness. The CH_2Cl_2 extract (7.52 g) was chromatographed over Polyclar, and the column was eluted with a CH_2Cl_2/C_6H_6 gradient up to 100% CH_2Cl_2 and then with a CH_2Cl_2/MeOH gradient to 100% MeOH. The column fractions gave a mixture of flavonoids that was separated on preparative paper chromatography with 40% HOAc. All the isolated flavonoids were purified on a Sephadex LH20 column eluted with CH_2Cl_2-MeOH (9:1) prior to spectral analysis.

IDENTIFICATION AND SPECTRAL DATA.—The spectra were recorded as follows: uv, Shimadzu model UV-240; ^1H nmr, Perkin-Elmer R12 80 MHz; eims, Varian Mat2 data system 166. The quercetagetin derivatives were identified by their uv and mass spectra. The uv spectra (MeOH) showed peaks and shoulders in Band II corresponding to a dioxygenated B-ring (13), but they also exhibited a shoulder at 238-245 nm which, in our experience, is present in all the flavonoids derived from the 6-hydroxyquercetin and 6-hydroxyluteolin structures. The presence of this substitution was confirmed by the bathochromic shift of Band I of about 30 nm in $AlCl_3$/HCl (14).

The substitution at 3,5,7,3′, and 4′ positions were verified by uv shifts according to standard methods (15).

The identification of the flavonoids was based on comparision of the spectroscopic data (^{1}H nmr, ms, uv) with literature values.

MASS SPECTRA DATA.—Quercetagetin-3,7,4′-trimethyl ether (Oxyayanin B): ms *m/z* (rel. int.) 360 M+ (100), 359 M+-H (51), 345 M+-Me (20), 342 M+-H_2O (9), 331 M+-CHO (4), 317 M+-COMe (18), 182 A_1 (7), 167 A_1-Me (11), 149 A_1-H_2O (10), 148 B_1 (10), 151 B_2 (11), 180 M++ (4).

Quercetagetin-3,7-dimethyl ether.—Ms *m/z* (rel. int.) 346 M+ (100), 345 M+-H (93), 331 M+-Me (2), 328 M+-H_2O (13), 317 M+-CHO (6), 303 M+-COMe (12), 182 A_1 (5), 167 A_1-Me (2), 164 A_1-H_2O (7), 134 B_1 (3), 137 B_2 (15), 173 M++ (18).

Quercetagetin-3,3′-dimethyl ether.—Ms *m/z* (rel. int.) 346 M+ (100), 345 M+-H (29), 331 M+-Me (8), 328 M+-H_2O (38), 317 M+-CHO (27), 303 M+-COMe (17), 168 A_1 (4), 153 A_1-Me (5), 150 A_1-H_2O (14), 148 B_1 (1), 151 B_2 (23), 173 M++ (18).

Quercetagetin-3-methyl ether.—Ms *m/z* (rel. int.) 332 M+ (100), 331 M+-H (60), 317 M+-Me (7), 314 M+-H_2O (21), 303 M+-CHO (18), 289 M+-COMe (30), 168 A_1 (30), 153 A_1-Me (6), 150 A_1-H_2O (10), 134 B_1 (3), 137 B_2 (15), 166 M++ (13).

Full details of the extraction and isolation of the compounds are available on request to the senior author.

ACKNOWLEDGMENTS

The authors would like to thank Dr. A.G. Schultz for the collection and classification of plant material; to Dr. Benjamin Frydman for the determination of ^{1}H-nmr spectra and to Juan C. Oberti from the Department of Organic Chemistry of the National University of Córdoba for mass spectra.

LITERATURE CITED

1. B. Sorarú and A. Bandoni, "Plantas de la Medicina Popular Argentina," Ed. Albatros, Buenos Aires, 1978, p. 41.
2. J. Hyeronimus, *Bol. Acad. Nac. Cienc., Córdoba, Arg.*, **4**, 343 (1882).
3. P. Arenas, "Etnobotánica Lengua Maskoy," FECYC, Buenos Aires, 1981, pp. 332-334.
4. O. Boelcke, "Plantas vasculares de la Argentina, nativas y exóticas," FECYC, Buenos Aires, 1981, p. 265.
5. V. Martino, S. Debenedetti, and J.D. Coussio, *Phytochemistry*, **18**, 2052 (1979).
6. V. Martino, S. Debenedetti, G. Ferraro, and J.D. Coussio, 1986, submitted for publication.
7. S. Debenedetti, G. Ferraro, and J.D. Coussio, *Planta Med.*, **42**, 97 (1981).
8. S. Debenedetti, G. Ferraro, and J.D. Coussio, *Rev. SAFYBI*, **24**, 1902 (1984).
9. S. Debenedetti, G. Ferraro, and J.D. Coussio, *Acta Farm. Bonaerense*, **2**, 1, (1983).
10. T.A. Geissman, "The Chemistry of Flavonoid Compounds," McMillan Co., New York, 1962, p. 428.
11. A. Ulubulen, K. Kerr, and T. Mabry, *Phytochemistry*, **19**, 1761, (1980).
12. E. Rodriguez, N. Carman, P. Chavez, and T. Mabry, *Phytochemistry*, **11**, 1507, (1972).
13. T.J. Mabry, K.R. Markham, and M.B. Thomas, "The Systematic Identification of Flavonoids," Springer Verlag, New York, 1970, p. 44.
14. J.A. Mears and T. Mabry, *Phytochemistry*, **11**, 411, (1972).
15. J. Harborne, T. Mabry, and H. Mabry, "The Flavonoids," Academic Press, New York, 1975, pp. 46-126.

Received 30 January 1986