g) was fractionated into a CHCl₃-soluble part (7.2 g) and a CHCl₃-insoluble residue. The former yielded β -sitosterol (60 mg); quinovic acid (20 mg), mp 299-301°; and rotundic acid (25 mg), mp 268-270°. Part of the CHCl₃-insoluble fraction (25 g) afforded a white material which, after several recrystallizations, gave the saponin (150 mg), mp 220-222°. This saponin, upon hydrolysis with 10% HCl for 4 h followed by the usual work up, gave quinovic acid. The sugar was not identified.

The identification of the compounds was made by direct comparison with authentic samples or by comparison of the physical data with those published in the literature (3-5). Full details of the isolation and identification of the compounds are available on request to the senior author.

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LITERATURE CITED

- 1. M.F. Agra, Ciência e Cultura, 33 (Supplement), 64 (1980).
- M.Z. de Almeida, "Estudo Fitoquímico e Triagem Farmacológica da Casca da Raiz de Guettarda platypoda DC.," M.S. Thesis, Universidade Federal da Paraíba, João Pessoa, Paraíba, Brazil, 1982.
- 3. "The Merck Index," 10th ed., Rahway, NJ: E. Merck & Co., Inc., p. 1168.
- 4. R.F. Raffaut, P.W. Le Quense, and P.C. Ghosh, J. Nat. Prod., 41, 432 (1978).
- 5. T.K. Devon and A.I. Scott, "Handbook of Naturally Occurring Compounds," vol. II. New York: Academic Press, 1972, p. 288; and the references cited therein.

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FLAVONOL 3-0-METHYL ETHERS FROM SOLANUM PUBESCENS

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Besides alkaloids, flavonoids form the other major group of compounds reported from the Solanum genus. The flavonoid pattern in the Solanaceae is mainly based on kaempferol and quercetin with rare occurrence of apigenin and luteolin (1). We recently reported the isolation of a novel myricetin derivative (2), and we now report the isolation of some methyl ethers of quercetin and kaempferol from the leaves of Solanum pubescens Willd. All the methyl ethers were found to be 3-methyl ethers with a free 5-hydroxyl group.

Except for quercetin-3,7,4'-trimethyl ether and quercetin-3,3'-dimethyl ether, which were reported from *Nicotiana tabacum* (3) and *Physalis angulata* (4), respectively, all the other methyl ethers are being reported here for the first time from the Solanaceae.

The isolation of flavonol-methyl ethers was reported only once before from the Solanaceae (5). The current report is thus of taxonomic importance, indicating the possibility of further existence of 3-0-methyl ethers in the Solanaceae. The occurrence of eight methoxylated flavonols from *S. pubescens* may be attributed to the presence of secretory structures as mentioned earlier (6). The observation that the co-occurrence of parent flavonols with their 0-methyl derivatives, as previously known in angiosperms, can also be extended to the Solanaceae based on this investigation. Also, the isolation of the 3-0-glucoside and 3-0-rutinoside of kaempferol is in support of the previous report of abundant occurrence of these glycosides in the Solanaceae.

EXPERIMENTAL

PLANT MATERIAL.—S. pubescens was collected near Nagarjuna Sagar, (Andhra Pradesh), India, in 1983. Vouchers are deposited in the Nagarjuna University Herbarium (No.NUH.NSP001). The powdered, air-dried leaves (2.5 kg) were successively extracted with n-hexane and MeOH.

ISOLATION OF FLAVANOIDS.—The concentrated hexane extract was chromatographed over silica gel eluting with hexane, hexane- C_6H_6 mixtures. The eluates from different fractions on preparative tlc developed with CHCl₃-MeOH (99:1) yielded kaempferol-3,7,4'-trimethyl ether (300 mg, Rf: 0.78),

quercetin-3,7,3',4'-tetramethyl ether (300 mg, Rf: 0.66), quercetin-3,7,3'-trimethyl ether (270 mg, Rf: 0.45), and quercetin-3,7,4'-trimethyl ether (350 mg, Rf: 0.40).

The MeOH extract was separated into phenolic and nonphenolic parts with neutral lead acetate. The phenolic part was chromatographed over silica gel eluting with C₆H₆, C₆H₆-Me₂CO mixtures, and Me₂CO. The eluates from different fractions, on repeated column and preparative tlc yielded with CHCl₃-MeOH (99:1) kaempferol-3,7-dimethyl ether (15 mg, Rf: 0.12), kaempferol-3,4'-dimethyl ether (15 mg, Rf: 0.10), and myricetin-3,7,3',5'-tetramethyl ether (12 mg, Rf: 0.26); with CHCl₃-MeOH (98:2) quercetin-3,3',4'-trimethyl ether (16 mg, Rf: 0.56), and quercetin-3,3'-dimethyl ether (100 mg, Rf: 0.28), with CHCl₃-MeOH (9:1) kaempferol (700 mg, Rf: 0.40), myricetin-3,7,3'-trimethyl ether (120 mg, Rf: 0.35), and quercetin (850 mg, Rf: 0.24); and with CHCl₃-MeOH (7:3) kaempferol-3-0-glucoside (500 mg, Rf: 0.75) and kaempferol-3-0-rutinoside (600 mg, Rf: 0.34).

Full details of the isolation and physical and spectral identification of the compounds are available on request from the senior author.

LITERATURE CITED

- 1. J.B. Harborne and T. Swain, in: "The Biology and Taxonomy of the Solanaceae," Eds. J.G. Hawkes, R.N. Lester, and A.D. Skelding, Ch. 18, London: Academic Press, 1979, pp. 257-268.
- 2. G.N. Krishna Kumari, L. Jagan Mohan Rao, and N.S. Prakasa Rao, Phytochemistry (in press).
- C.N. Yong, H.D. Brahmer, E.L. Murphy, W. Chorney, N. Scully, and S.H. Wender, J. Org. Chem., 25, 2063 (1960).
- 4. J.A. Lopez, J.A. Saenz, D.J. Slatkin, J.E. Knapp, and P.L. Schiff, Phytochemistry, 15, 2028 (1976).
- 5. W.D. Michael and T.J. Mabry, Phytochemistry, 18, 263 (1979).
- 6. E. Wollenweber and V.H. Dietz, Phytochemistry, 20, 869 (1981).

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FLAVONOID GLYCOSIDES FROM ANISOMELES OVATA

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In our earlier communications we have reported the isolation and characterization of terpenoids and steroids (1), acylated flavone glycosides (2,3), and flavones (4,5) from *Anisomeles ovata* R.Br. We now report the isolation of the flavone glucosides and flavanone glucosides listed below. All the compounds were identified by standard spectral and chemical degradative methods.

This is the first report of a flavanone from the Labiatae family. The general trend of chalcones accompanying flavanones was not observed in A. orata where the flavanones prunin (naringenin 7-0- β -D-glucoside), prunin-6"-p-coumarate, prunin-3",6"-di-p-coumarate, were accompanied by the corresponding flavones cosmosiin (apigenin 7-0- β -D-glucoside), terniflorin (apigenin 7-0- β -D-(6"-p-coumaroyl) glucoside, and anisofolin-A [apigenin 7-0- β -D-(3",6"-di-p-coumaroyl) glucoside] (2). This is the second report for prunin-6"-p-coumarate (6) and prunin-3",6"-di-p-coumarate (7) and the third report for terniflorin (8-10) from nature. This is also the first report for cosmosiin with a higher melting point of 242° which is due to an anhydrous form. All the other reported melting points were below 242°.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded with the following instruments: uv, Beckmann DBG; ir, Perkin-Elmer 237; ¹H and ¹³C nmr Perkin-Elmer 90 M Hz, JOELFX 100 and Brucker 270 M Hz.

PLANT MATERIALS.—Aerial parts of A. ovata were collected at a hillside near Mangalagiri, Guntur district Andhra Pradesh, India, in the autumn of 1980. Specimen vouchers are deposited in Nagarjuna University Herbarium (No. NUH. NSP002).

EXTRACTION AND ISOLATION.—Dried aerials parts were worked up by standard procedures (1-5). The compounds obtained from *A. ovata* were cosmosiin hydrate (300 mg), cosmosiin (50 mg), terniflorin (800 mg), prunin (150 mg), prunin-6"-p-coumarate (250 mg) and prunin-3",6"-di-p-coumarate (150 mg). The 13 C-nmr spectrum of prunin-3",6"-di-p-coumarate at 67.89 MHz in DMSO- d_6 showed signals at δ 78.5 (C-2), 42.0 (C-3), 197.0 (C-4), 163-0 (C-5), 96.4 (C-6), 164.8 (C-7), 95.6 (C-8), 162.8 (C-9),