FLAVONOIDS OF *STEVIA NEPETIFOLIA*

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In a continuation of our chemical investigation of the genus *Stevia* (Compositae, Eupatorieae) (1), we report the isolation and characterization of eight flavonoids from the leaves of *Stevia nepetifolia* H.B.K. The flavonoid pattern in this plant proved to be similar to that of the previously reported *Stevia rebaudiana* (1) in that the methoxylated flavonoid, centaureidin, and flavonoid glycosides of luteolin and quercetin were found in both species. However, of the isolated glycosides, only luteolin-7-O-glucoside, quercetin-3-O-arabinoside, and quercetin-3-O-glucoside were common to both species.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded using the following instruments: uv, Pye SP8-100; pmr, Brücker 250 MHz; ms, M.S. 3VG Micromass Zab 1F. Adsorbents for tlc were from E. Merck; cc, E. Merck and Gaf (G.B. Ltd.) (PVP). Sephadex LH-20 was from Pharmacia.

PLANT MATERIALS.—Whole plants of *S. nepetifolia* H.B.K. were collected in Mexico, 7.5 m north of San Juan de Estado. A voucher specimen (No. 223) is deposited in the herbarium at the University of Texas at Austin, Austin TX.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—Air-dried leaves of *S. nepetifolia* (185 g) were extracted using standard procedures (2-5). The *n*-hexane and $CHCl_3$ extracts yielded centaureidin (25 mg) (2). The EtOAc extract yielded the following flavonoid glycosides: luteolin-7-O-glucoside (8 mg) (6); quercetin-3-O-arabinoside (16 mg) (7); quercetin-3-O-galactoside (26 mg) (8); quercetin-3-O-glucoside (13 mg) (2); quercetin-3-O-digalactoside (16 mg) (8); and quercetin-3-O-galactosyl rhamnoside (15 mg) (9). All these flavonoids have been previously isolated.

A further flavonoid not previously isolated was identified as quercetagetin-4′-methylether-3-O-arabinoside from the following data. Pc: *t*-BuOH-HOAc-H_2O, 3:1:1 (TBA) 0.4; 15% HOAc (HOAc), 0.25; after hydrolysis: TBA, 0.3 and HOAc 0.05; color: uv, purple; uv/NH_3, brown; Naturstoff Reagenz-A, Carl Roth, Germany (NA), brown. After hydrolysis, color: uv, brown; uv/NH_3, yellow; NA, yellow. Uv λ max (MeOH) 352, 280 sh, 259; + NaOMe 392, ↦ 268; ↦ + $AlCl_3$ 420, 280; + $AlCl_3$HCl 380, 292 sh, 268; + NaOAc 386, 268; + NaOAc/H_3BO_3 356, 268 nm. After hydrolysis, uv λ max (MeOH) 360, 256; + NaOMe 360, 290 sh, 246 (fast decomp.); + $AlCl_3$ 445, 280; + $AlCl_3$/HCl 390, 268; + NaOAc 360, 294 (fast decomp.); + H_3BO_3 360, 260 nm. Pmr 250 MHz ($CDCl_3$ TMS) ϕ 3.89 (3H, *s* for 4′-OCH_3), δ 5.28 (1 H *m*, for H-1′ of arabinose δ 2.9-4.18 (remaining arabinose protons), δ 6.57 (s for C8-H), δ 6.9 (ds*J* 8.4, for C5′H), δ 7.37 (d*J*=2,2, for C2′-H), δ 7.82 (q*J*, o, = 8.4*J*, m, = 2.2 for C6′-H). Tlc confirmed the sugar arabinose.

All flavonoids were identified by standard spectral and hydrolytic data, as well as by authentic sample comparison and color reaction procedures (2-5). Samples were further characterized by their pmr spectra and the data for centaureidin included ms. Original extracts were screened for sulfated compounds using the electrophoresis techniques described in (5).

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

ACKNOWLEDGMENTS

A.R. would like to thank the British Council for a student bursary. We should also like to thank the following for reference samples: Professor J.B. Harborne for quercetin-3-O-galactoside, Professor H. Geiger for luteolin-7-O-glucoside, and Professor T.J. Mabry for quercetin-3-O-glucosode. We should like to thank King's College, London University, for 250 MHz pmr spectra.

LITERATURE CITED

1. A. Rajbhandari and M.F. Roberts, *J. Nat. Prod.*, **46**, 194 (1983).
2. "The Flavonoids." Ed by J.B. Harborne, T.J. Mabry, and H. Mabry, Chapters 1-3. London: Chapman and Hall Ltd, 1975.
4. M.F. Roberts, B.N. Timmerman, and T.J. Mabry, *Phytochemistry*, **19**, 127 (1980).
5. C.A. Williams, J.B. Harborne, and H.T. Clifford, *Phytochemistry*, **12**, 2417 (1973).
6. A. Ulubelen, M. Miski, P. Neumann, and T.J. Mabry, *J. Nat. Prod.*, **42**, 261 (1979).
7. J.B. Harborne, *Arch. Biochem. Biophys.*, **96**, 171 (1962).

8. W. Bienenfeld and H. Katzlmeier, *Arch. Pharmaz.*, **299**, 598 (1966).
9. A. Ulubelen, B.N. Timmermann, and T.J. Mabry, *Phytochemistry*, **19**, 905 (1980).

Received 29 July 1983

CONSTITUENTS OF THE SEA CUCUMBER *CUCUMARIA FRONDOSA*

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Fractionation of extracts of the orange-footed sea cucumber *Cucumaria frondosa* Gunnerus, collected in Passamaquoddy Bay, resulted in the identification of the compounds listed below. Full details of the isolation and identification are available on request from the senior author.

This study was supported by a Natural Sciences and Engineering Research Council Strategic Grant.

Compound	Identified by	Reference
Plastochromanol-8[a]	pmr, ms, uv, ir	(1,2)
4α,14α-Dimethylcholest-9(11)-en-3β-ol[a]	pmr, cmr, ms, ir	(3)
Canthaxanthin	mp, pmr, ms, uv, ir	(4)
3-Octadecyloxy-1,2-propanediol	mp, pmr, ms, ir	(5)
N^5-Acetylornithine[a]	pmr, ms, ir	(6)

[a]Not previously reported from marine sources.

LITERATURE CITED

1. K.T. Whittle, P.J. Dunphy, and J.F. Pennock, *Biochem. J.*, **96**, 17c (1965).
2. H. Mayer, J. Metzger, and D. Isler, *Helv. Chim. Acta*, **50**, 1376 (1967).
3. T. Itoh, T. Ishii, T. Tamura, and T. Matsumoto, *Phytochemistry*, **17**, 971 (1978).
4. F.H. Foppen, *Chromatography Rev.*, **14**, 164 (1971).
5. Aldrich Library of NMR Spectra, Vol. I, Milwaukee, WI: Aldrich Chemical Company, Inc., 1974, p. 144D.
6. a) L. Fowden, *Nature*, **182**, 406 (1958).
   b) A. I. Virtanen and P. Linko, *Acta Chem. Scand.*, **9**, 531 (1955).

Received 29 July 1983

ALCALOÏDES DE *PAPAVER APOKRINOMENON*

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Dans le cadre d'une étude chimiotaxonomique des *Papaver* turcs appartenant à la section *Pilosa*, nous nous sommes intéressés à la composition alcaloïdique de *Papaver apokrinomenon* Fedde. Endémique de l'ouest de la Turquie, ce *Papaver* vivace est très proche botaniquement de *Papaver strictum* dont il se distingue par sa taille plus petite, ses capsules plus grandes et l'aspect de ses feuilles (1,2).

RÉSULTATS ET DISCUSSION

Neuf alcaloïdes ont été isolés des parties aériennes et identifiés.
La composition alcaloïdique du *P. apokrinomenon* le rapproche très fortement du *P. strictum*, aussi bien sur le plan qualitatif que quantitatif (6,7).

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