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QUERCETAGETIN 3,3'-DIMETHYL ETHER, A NEW FLAVONOID FROM *PARTHENIUM TOMENTOSUM*

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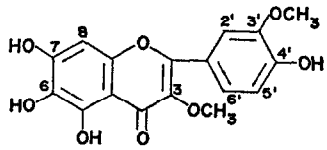
In connection with our intensive biochemical investigation of the genus *Parthenium*,[1] we wish to report the isolation and structure determination of quercetagetin 3,3'-dimethyl ether, a new flavonol, from *Parthenium tomentosum* L. The NMR spectrum of the trimethylsilyl ether of the flavonol indicated that the new compound was a dimethyl ether of quercetagetin: singlets for 2 methoxyl groups at 3·95 and 3·91; aromatic proton signals at 7·75 ($J = 2{\cdot}5$ Hz) and 7·69 ($J = 9$ Hz, 2·5 Hz) for H-2' and H-6'; a doublet at 6·9 ($J = 9$ Hz) for H-5' and a one proton singlet at 6·62 for H-8, demethylation with pyridinium hydrobromide gave quercetagetin, thus confirming the oxygenation pattern. In benzene-d_6[2] the methoxyl signal at 3·95 shifted upfield to 3·30 (+0·65 ppm), indicating that the methoxyl group was either at the 3',4' or 7 position; however, the presence of a free 4' hydroxyl group was evident from the purple to yellow color test in UV alone and with NH_3. Since the flavonol is deep purple when viewed as a chromatographic spot in the UV, the position 3 must be substituted by one of the two methoxyl groups; thus the NMR signal at 3·91 can be assigned to this group and, as expected, this signal did not show any significant shift in benzene-d_6. The presence of four hydroxyl groups in the new natural product prior to trimethylsilylation was evidenced by four distinct trimethylsilyl ether signals which were observed when the spectrum was recorded in benzene-d_6; one signal exhibited a negative shift of −0·19 ppm as expected for a 5-OTMS group.[2]

The presence of substituted oxygen functions at the 3 and 3' positions and hydroxyl groups at positions 4',5,6 and 7 was verified by UV spectral analysis:[3] (1) In presence of NaOMe and NaOAc band I exhibited a bathochromic shift of 45 nm with an increase in intensity typical for 4'-hydroxyl group; slow decomposition occurred with both of these reagents as expected for 5,6,7-hydroxylation pattern. (2) A free hydroxyl group at C_7 was indicated by a band II bathochromic shift of 8 nm in the presence of NaOAc. (3) With added $AlCl_3$–HCl, a band I bathochromic shift of 26 nm confirmed the presence of a 6-oxygen substituent.[4] (4) Substitution of the oxygen function at 3' was confirmed by the absence of band I shift with H_3BO_3–NaOAc.

The MS of the natural product supports the proposed structure: parent peak at 346 *m/e* and a comparable peak at 345 for the expected loss of a proton from the 6-hydroxyl group.[5]

Thus, the new flavonol is quercetagetin 3,3'-dimethyl ether (I).

[1] E. RODRÍQUEZ, H. YOSHIOKA and T. J. MABRY, *Phytochem.* **10**, 1145 (1971); and references cited therein.
[2] E. RODRÍGUEZ, N. J. CARMAN and T. J. MABRY, *Phytochem.* **11**, 409 (1972).
[3] T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, *The Systematic Identification of Flavonoids*, Springer-Verlag, Heidelberg–New York (1970).
[4] J. A. MEARS and T. J. MABRY, *Phytochem.* **11**, 411 (1972).
[5] J. H. BOWIE and D. W. CAMERON, *Austral. J. Chem.* **19**, 1627 (1966).



(I)

EXPERIMENTAL

Two-dimensional chromatographs on Whatman 3MM paper were developed first in TBA (*t*-BuOH–HOAc–H_2O, 3 : 1 : 1) and then in 15% HOAc. The NMR spectra were recorded in CCl_4 and benzene-d_6 using tetramethylsilane as an internal standard; UV spectra were recorded using standard procedures.[3]

Air-dried and ground leaf material of *Parthenium tomentosum* L. (collected 31 miles N. of Oaxaca, Oaxaca, México; Rodríguez and Whiffin No. 48*) was extracted with 85% aq. MeOH and the extract was filtered and concentrated. The aqueous solution which remained was extracted repeatedly with EtOAc, and these extracts were combined and evaporated to dryness. The reddish syrup (700 mg) was chromatographed over polyamide (30 g packed in $CHCl_3$); the column was eluted with $CHCl_3$–MeCOEt–MeOH (5 : 1 : 2). The first few fractions contained mostly phenolic acids and the final fractions yielded a mixture of flavonoids which are currently under investigation. The middle fractions afforded 12 mg of the new flavonol quercetagetin 3,3′-dimethyl ether; the material crystallized from benzene–acetone, m.p. (uncorrected) 214–215°: R_f (TBA) 61; (HOAc) 19; UV λ_{max} (MeOH): 255sh, 276 348 nm; λ_{max} (NaOMe): 260, 393 nm (slow dec.); λ_{max} ($AlCl_3$): 276, 295sh, 345, 434 nm; λ_{max} ($AlCl_3$–HCl): 263, 290, 374 nm; λ_{max} (NaOAc): 263, 365 nm (slow dec.); λ_{max} (NaOAc–H_3BO_3): 270sh, 285, 352 nm. MS measurement showed a parent peak at 346 ($C_{17}H_{14}O_8$ required 346), a large fragment at 345 (60% intensity of parent ion) and a small fragment at 403 (15% intensity of parent peak) for the loss of the C-3(CH_3CO) group.[5]

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* The voucher specimen is deposited in the University of Texas at Austin Herbarium.

Key Word Index—Parthenium tomentosum; Compositae; quercetagetin 3,3′-dimethyl ether.

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EBENACEAE

STEROIDS AND TRITERPENOIDS OF *DIOSPYROS MONTANA*

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Plant. Diospyros montana Roxb. *Uses.* Medicinal.[1,2] *Previous work.* Bark.[3] On sister species.[3–5]

[1] ANON, *The Wealth of India, Raw Materials*, Vol. 3, p. 84, CSIR, New Delhi, India (1952).
[2] R. N. CHOPRA, S. L. NAYAR and I. C. CHOPRA, *Glossary of Indian Medicinal Plants*, p. 98, CSIR, New Delhi, India (1956).
[3] R. S. KAPIL and M. M. DHAR, *J. Sci. Industr. Res.* **20B**, 498 (1961); and references cited therein.
[4] A. V. B. SANKARAN and G. S. SIDHU, *Phytochem.* **10**, 458 (1971).
[5] P. S. MISRA, G. MISRA, S. K. NIGAM and C. R. MITRA, *Phytochem.* **10**, 904 (1971); and references cited therein.