QUERCETIN 3,7,3',4'-TETRAMETHYL ETHER FROM GERMANIUM MACRORHIZUM

RUKA NAKASHIMA, MASAHARU YOSHIKAWA and TERUO MATSUURA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

(Received 11 January 1973. Accepted 24 January 1973)

Key Word Index—Geranum macrorluzum; Geraniaceae; Zdravets oil, quercetin 3,7,3',4'-tetramethyl ether.

Plant. Germanium macrorhizum L. Source. From the extract of Geranium macrorhizum L. (zdravets oil), which was supplied by P. Robert & Cie, Grasse, France. Previous work. Bulgarian zdravets oil was first studied by Wienhaus and Scholz¹ who isolated a sesquiterpene, germacrone whose structure was established by Šorm's group.²

The rare naturally occurring flavonol quercetin 3,7,3',4'-tetramethyl ether was isolated from the cactus, *Ariocarpus Retusus* by Dominguez *et al.*³ and from *Aframomum giganteum* K. Schum. by Vidari *et al.*⁴ We now report its isolation from the precipitate deposited by Zdravets oil as light yellow crystals m.p. 155° (165–167°),³ yield 0.4%. IR, NMR, UV and MS and elemental analysis were identical with that of the authentic quercetin tetramethyl ether,⁵ and its acetyl derivative was also identical with authentic sample.⁶

Spectral data. 3,7,3',4'-Tetramethyl quercetin; IR (KBr disc). 1657, 1607, 1594, 1515, 1499, 1153, 1025, 1005, 950, 821, 800, 770, 700 cm⁻¹. NMR.*(CDCl₃–CCl₄)3·86, (s, 6H)3·75(s, 6H) 6·36 (q, 2H) 6·97 (d, 1H), 7·66 (m, 2H), 12·59 (s, 1H), (s, ppm); UV λ_{max} (EtOH). 350, 270, 255 nm (Found: C, 63·57, 63·41; H, 4·99, 5·16. Calc. for C₁₉H₁₈O₇; C, 63·68; H, 5·06%). 5-Acetyl-3,7,3',4'-tetramethyl quercetin. m.p. 170° (167–169°). Fix (KBr disc). 1770, 1640, 1610, 1518, 1160, 1149, 1080, 998, 906, 818 cm⁻¹. NMR (CDCl₃). 2·47 (s, 3H), 3·85 (s, 3H), 3·98 (s, 3H), 4·00 (s, 6H), 6·75 (q, 2H), 7·08 (s, 1H), 7·69 (s, 2H) (s ppm).

- * The NMR spectra were measured by Varian T-60 NMR spectrometer.
- ¹ WIENHAUS, H. and SCHOLZ, H. (1929) Ber. Schimmel Jubileums Ausgabe 280.
- ² OGNJANOV, L., IVANOV, D, HEROUT, V., HORÁK, H, PLIVA, J. and ŠORM, F. (1958) Coll. Czech. Chem. Commun 23, 2033.
- ³ Dominguez, X. A, Ramirez, R. H, O.-L., Ugaz, Garcia, D. J., and Ketcham, R. (1968) *Planta Med.* 16, 182.
- ⁴ VIDARI, G., FINZI, V. and DE BERNARDI, M. (1971) Phytochemistry 10, 3335.
- ⁵ Gomm, A. S. and Nierenstein, M. (1931) J Am Chem Soc. 53, 4408.
- ⁶ HERZIG, J. (1891) Monatsh. Chem 12, 172; (1893) ibid. 14, 53.
- WILSON, R. G., BOWIE, J. H. and WILLIAMS, D. H. (1968) Tetrahedron 24, 1407.