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RHAMNETIN-3-*O*-NEOHESPERIDOSIDE, A NEW FLAVONOID FROM THE LEAVES OF *DERRIS TRIFOLIATA*

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Derris trifoliata Lour. (Syn *Derris uliginosa* Benth., Leguminosae) is a large shrub common in the coastal forests of India and the northeastern Himalayas. The whole plant is used as a stimulant, anti-
spasmodic, and counter-irritant (1). The leaves of *D. trifoliata* were studied for flavonoid compounds following standard procedures (2), and the isolation and characterization of two flavonol glycosides, including a new one, are presented here.

The EtOAc-soluble fraction of the hot MeOH concentrate of fresh leaves of *D. trifoliata* yielded a light yellow solid. This was separated into two homogeneous compounds by preparative pc. The flavonoid from the higher band (Rf 0.70) was recrystallized twice from MeOH to yield light yellow needles which responded to flavonoid tests (2). On hydrolysis (2 N HCl) it yielded 3,5,3′,4′-tetrahydroxy-7-methoxy flavone (rhamnetin), D-glucose, and L-rhamnose. Oxidation of the glycoside with H_2O_2 yielded 2-*O*-α-L-rhamnopyranosyl-D-glucopyranose (neohesperidose). The ^{1}H-nmr spectrum of the peracetate of the glycoside gave evidence for a 3,5,7, 3′,4′-penta oxygenated flavone skeleton, one methoxy group, and one β-neohesperidoside moiety (H-1″ appeared as doublet at δ 5.50 with J=8 Hz, H-1‴ at δ 5.25, CH_3 of rhamnose at δ 1.06 as doublet, J=6 Hz, and protons of nine acetyl groups between δ 1.95 and 2.45) pointing to the nature of the glycoside as rhamnetin neohesperidoside. 3-*O*-Glycosylation was inferred from the characteristic uv fluorescence (purple changing to yellow with NH_3) and uv absorption maxima (2) and confirmed by obtaining 3-hydroxy-5,7,3′,4′-tetra methoxy flavone, mp and mmp 190-191° (3). Based on the above data, the glycoside was characterized as 5,3′,4′-trihydroxy-7-methoxy-3-*O*-β-D-(2-*O*-α-L-rhamnopyranosyl)-glucopyranosyl flavone (rhamnetin 3-*O*-β-neohesperidoside), which is a new natural product.

The flavonoid from the lower band (Rf 0.54) was identified as 5,7,3′,4′-tetrahydroxy-3-*O*-β-D-(2-*O*-α-L-rhamnopyranosyl) glucopyranosyl flavone (quercetin 3-*O*-β-neohesperidoside) (4).

The leaves of *D. trifoliata* have, thus, been found to contain the 3-*O*-β-neohesperidosides of rhamnetin and quercetin in the ratio of about 2:1. It is interesting that there is no free aglycone detectable in the leaves, and this is in agreement with the observation that the occurrence of free rhamnetin in plants is very rare (E. Wollenweber, personal communication). Rhamnetin 3-neohesperidoside from *D. trifoliata* is the sixth reported glycoside of this a glycone; five glycosides and two sulfate esters have been reported earlier (5,6).

EXPERIMENTAL

PLANT MATERIAL.—Fresh leaves of *D. trifoliata* were collected from Panjim, Goa, India. A voucher specimen is deposited in the Department of Botany, Bharathidasan University, Tiruchirapalli, India.

EXTRACTION AND ISOLATION.—Fresh leaves (800 g) were extracted with hot MeOH, and the residue was fractionated into petrol (60-80°), Et_2O, and EtOAc soluble components. A

light yellow solid (0.85 g) from the EtOAc fraction, on preparative pc (Whatman No. 3, descending, H_2O saturated phenol, 28°, 17 h), yielded two homogeneous compounds (Rf 0.70, 0.4 g; Rf 0.54, 0.2 g).

RHAMNETIN 3-*O*-NEOHESPERIDOSIDE.—Mp 212-213° (MeOH); $[\alpha]^{28}D$ − 80° (c, 0.12, C_5H_5N); uv λ max (MeOH) 259, 302 (sh), 362 nm; λ max (MeOH+NaOMe) 276, 422; λ max (MeOH+$AlCl_3$), 277, 301 (sh), 335 (sh), 435; λ max (MeOH+$AlCl_3$+HCl) 272, 362 (sh), 404; λ max (MeOH+NaOAc) 262, 367, 418 (sh); λ max (MeOH+NaOAc+H_3BO_3) 262, 385 nm; ir ν max (KBr) 3400 (br), 2953, 2923, 2853, 1651, 1596, 1456, 1377, 1295, 1212, 1157, 1115, 1067, 1046, 1018, 876, and 807 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) of peracetate ($Ac_2O+C_5H_5N$) δ 7.98 (1H, d, J=9 Hz, *H*-6′), 7.94 (1H, s, *H*-2′), 7.38 (1H, d, J=9 Hz, *H*-5′), 6.85 (1H, d, J=2 Hz, *H*-8), 6.62 (1H, d, J=2 Hz, *H*-6), 5.50 (1H, d, J=8 Hz, *H*-$1''_{ax}$), 5.25 (1H, s (br), *H*-$1'''_{eq}$), 3.90 (3H, s, OCH_3-7), 2.45, 2.35, 2.30 (3×3H, 3×s, 3×phenolic $OCOCH_3$), 2.15, 2.10, 2.05, 1.95 (2×3H, 2×6H, 4×s, 6×alcoholic $OCOCH_3$), and 1.06 (3H, d, J=6 Hz, CH_3-6‴).

PAPER CHROMATOGRAPHY.—Rf values (×100, Whatman No. 1, ascending, 28°) are in the order for rhamnetin 3-neohesperidoside and quercetin 3-neohesperidoside: 44, 68 (H_2O), 57, 52 (15% HOAc), 83, 75 (50% HOAc), 47, 50 (*n*-BuOH-HOAc-H_2O, 4:1:5), 70, 54 (phenol), and 66, 63 (*t*-BuOH-HOAc-H_2O, 3:1:1). The latter compound was also identified by its uv, ^1H nmr, and hydrolysis products.

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