

Quercetine, a Major Flavonol Aglycon from *Tanacetum balsamita* L.

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Abstract

From the aerial parts of *Tanacetum balsamita* L. (Compositae) a flavonol aglycon was isolated using chromatographic techniques. The structure of this compound was determined using spectroscopic methods (UV, H-NMR and MS) as 3',4',5,7-Tetrahydroxy flavonol (Quercetin).

Keywords: *Tanacetum balsamita* L.; Compositae; Flavonol aglycon; Quercetin.

Introduction

The genus *Tanacetum* (Compositae) consists of 26 species in Iran one of which is *Tanacetum balsamita* L. (1). *T. balsamita*, locally named Shaheparam, is an aromatic species which grows widely in Azerbaijan province. It has been used in Iranian folk medicine as a tranquilizer and cardiac tonic (2).

Some of the medicinal *Tanacetum* species such as *T. parthenium* and *T. vulgare* are known to be rich in flavonoids (3) but the flavonoid compositions of *T. balsamita* have not been the subject of much study (4, 5).

As part of our phytochemical research on pharmacologically active phenolic constituents of Iranian medicinal plants, the isolation and identification of a flavonol aglycon (compound 1) from aerial parts of *T. balsamita* are described here.

Experimental

Materials

Aerial parts of *T. balsamita* were collected from Tabriz in June 1999. Voucher specimens were deposited in the Herbarium of Department of Pharmacognosy, Faculty of Pharmacy, Tehran University of Medical Sciences.

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Methods

Extraction and purification

Dried and ground plant materials (500g) were extracted with 90% MeOH and then concentrated *in vacuo*. The residue was diluted with water and extracted with n-Hexane, CH₂Cl₂, CHCl₃ and EtOAc, successively. The EtOAc concentrated fraction (3.5g) was rich in flavonoids, so this fraction was chromatographed on Silica gel PTLC with EtOAc-CH₃COOH-HCOOH-H₂O (100:11:11:26) as the best developing solvent and AlCl₃ (5%) in MeOH under UV 366nm as visualizer. Finally, the most abundant constituent (compound 1, R_f=0.48, 15mg) (Figure 1) was isolated as pale yellow amorphous powder. The structure of this compound was established according to combined spectra data.

Spectroscopic data

UV λ_{\max} (in MeOH): 260, 275sh, 380nm; + AlCl₃: 265, 455nm; + AlCl₃ + HCl: 265, 425nm; + NaOAc: 275, 380nm (degradation); +

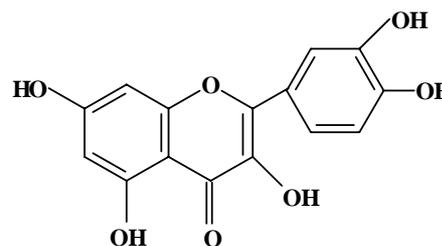


Figure 1. Compound 1 (3',4',5,7-Tetrahydroxy flavonol)

NaOAc + H₃BO₃: 260, 395nm; + NaOMe: rapid degradation.

¹H-NMR (400MHz, in DMSO-d₆): δ 7.78 (1H, d, *J*=1.8Hz, H-2'), 7.65 (1H, dd, *J*=9, 1.8Hz, H-6'), 6.95 (1H, d, *J*=9Hz, H-5'), 6.41 (1H, d, *J*=2Hz, H-8), 6.26 (1H, d, *J*=2Hz, H-6).

EI-MS 70eV, *m/z*: 302 (M⁺, 100%), 301 (46%), 285 (4%), 284 (3%), 274 (6%), 273 (9%), 153 (5%), 152 (10%), 150 (4%), 137 (6%), 136 (17%).

Results and Discussion

Compound 1 developed a magenta color with Mg/HCl and exhibited UV absorption bands of flavonoids. The UV spectrum of the compound in MeOH showed two major absorption bands at 260nm (band II) and 380nm (band I) which are typical for flavonols. The presence of a shoulder in band II (275nm) was an evidence of the 3',4'-*ortho*-dihydroxy system. Also, this system in the B-ring of the compound was indicated by the hypsochromic shift (-30nm, band I) by the AlCl₃/HCl as compared to the band position in AlCl₃ and by the bathochromic shift (+15 nm, band I) in NaOAc/H₃BO₃. The presence of a free hydroxyl group at 5 or 3 position and/or both of them was exhibited by the bathochromic shift (+75nm, band I) in AlCl₃. The bathochromic shift (+15nm, band II) soon after the addition of NaOAc showed a free 7-OH group. The UV spectrum rapid degradation after the addition of NaOMe was an evidence of the presence of free hydroxyl groups at 3,3' and 4' positions (6).

The ¹H-NMR spectrum also confirmed flavonol structure and displayed the presence of H-6, H-8, H-2', H-5' and H-6' protons. The PMR spectrum of the compound in DMSO-d₆ showed two distinctive resonance groups. It displayed two doublets at δ 7.78 (1H, *J*=1.8Hz) and δ 6.95 (1H, *J*=9Hz) and one doublet of doublets at δ 7.65 (1H, *J*=9, 1.8Hz), characteristic of a 1,2,4-trisubstituted benzene ring (the ABC system with *ortho* and *meta* coupling, the B-ring of the flavonol) and two

doublets at δ 6.41 (1H, *J*=2Hz) and δ 6.26 (1H, *J*=2Hz), characteristic of a 1,2,3,5-tetrasubstituted benzene ring (the AB system with *meta* coupling, the A-ring of the flavonol). The combination of the substitution patterns of the A and B rings suggested that the compound could be 3',4',5,7-Tetrahydroxy flavonol (6, 7).

The EI-MS spectrum of the compound was in agreement with the assigned structure. It revealed the empirical formula C₁₅H₁₀O₇ with the molecular ion peak at *m/z* 302 (M⁺, base peak) and ion peaks at *m/z* 153 (A₁+H)⁺ and *m/z* 150 (B₁)⁺ due to the retro-Diel's-Alder type fragmentation and fragment *m/z* 137 (B₂)⁺ (Figure 2) (6).

The UV, ¹H-NMR and EI-MS data led to the identification of the compound 1 as 3',4',5,7-Tetrahydroxy flavonol or Quercetin (Figure 1).

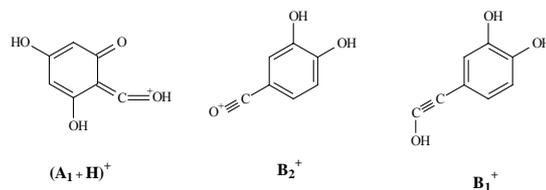


Figure 2. Fragments (A₁+H)⁺, (B₁)⁺ and (B₂)⁺

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