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Flavonoids from *Pulicaria jaubertii* (Asteraceae) from Yemen.

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ABSTRACT

A phytochemical study of the *Pulicaria jaubertii* (Asteraceae) ethyl acetate extract resulted in the isolation, purification and characterization of two dihydroflavonols:, dihydroquercetin 4'methyl ether (1) Taxifolin (3) and one flavonol Quercetin 3 methyl ether (2). The structures were assigned on the basis of UV spectrophotometry as well as 1H and 13C NMR spectroscopy.
Keywords: Asteraceae, *Pulicaria jaubertii*, dihydroflavonols, flavonoids.

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INTRODUCTION

Genus *Pulicaria* belonging to the tribe Inuleae of the Asteraceae family consists of 100 species distributed in Europe, North Africa and Asia and five species of this genus reported from Yemen [1]. Previous phytochemical investigations on several *Pulicaria* species have led to the identification of sesquiterpene lactones [2-3], diterpenes [4] as well as flavonoids [5-6]. Some of these substances such as flavonoids have exhibited many biological activities: antifungal [7], antimicrobial [8], antibacterial [9], antioxidant [10-11], cytotoxic [12] and anti-inflammatory [13] activities.

The antioxidant activity of $CHCl_3$, EtOAc and *n*-butanol extracts of the aerial parts of *Pulicaria jaubertii* [14], as well as the chemical composition of its essential oil [15] have been reported previously. In continuation of our study on species of medicinal plants of the Asteraceae family, here we report the isolation and the structure elucidation of flavonol and dihydroflavonol from ethyl acetate extract of the soluble parts of the aqueous EtOH extract of the leaves of this species. The structures of the isolated compounds were identified on the basis of spectroscopic studies and comparison with literature values.

MATERIALS AND METHODS

Plant material

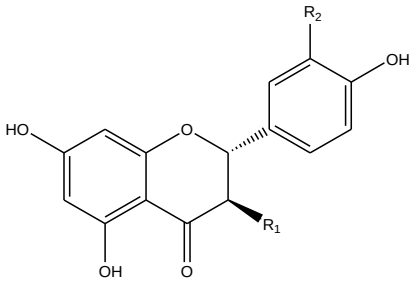
The leaves of *Pulicaria jaubertii* were collected from Aljar region (Hajjah - Yemen) in October 2008. The plant was identified by Pr. Abdellah Amine (Sana'a University). A voucher specimen of the plant material has been deposited at the department of biology (Sana'a University).

Extraction and isolation

Dried and powdered leaves (400 g) of *P. jaubertii* were extracted with 70% MeOH solution three times during 24 hours. The aqueous MeOH extract was concentrated to dryness. The residue was dissolved in water (200 ml). The resulting solution was extracted successively with petroleum ether, $CHCl_3$, EtOAc and *n*-BuOH. The organic layers were dried with Na_2SO_4 to give after concentration the $CHCl_3$ (2 g), EtOAc (2.5 g) and *n*-BuOH (6 g) extracts respectively.

A part of the EtOAc extract (1 g) was chromatographed on preparative plates of silica gel eluted with $CHCl_3$/ MeOH (8.5:0.5) to yield 5 fractions (1–5). Fraction 3 (170 mg) was resubmitted to preparative TLC ($CHCl_3$/MeOH; 9:1) to afford 7 sub-fractions (3-1; 3-7). The sub-fraction 3-2 was purified using Sephadex LH-20 to yield compounds **1**. Fraction 4 was subjected to repeated chromatography on silica gel by thin layer chromatography eluting with ($CHCl_3$/MeOH; 9:1) to offered compounds **2** (8 mg) and **3** (8.2 mg).

RESULTS AND DISCUSSION



Compound	R_1	R_2	C_2-C_3
1 Dihydroquercetin4'methyl ether	OH	OCH_3	Single
2 Quercetin 3 methyl ether	OCH_3	OH	Double
3 Taxifolin	OH	OH	Single

Figure 1: Structures of identified compounds

All compounds (**1-3**) (Fig. 1) were isolated as yellow amorphous powder from the ethyl acetate extract. The UV spectra in methanol of compounds 1 and 3 showed similar behavior with maxima of absorbance at λmax(nm) 289, 328 and 379 (sh) corresponding to π→π* and n→π* transitions, that matched the dihydrofavonol skeletons [16-17]. The ^{1}H NMR spectrum of these compounds exhibited a typical AX system due to H-2 and H-3 of a dihydroflavonol [1**8**] at 4.85 (*d*, *J* 11.6 Hz) and δH 4.44 (*d*, *J* 11.6 Hz) respectively. These assignments were confirmed by the ^{13}C NMR spectrum which showed three C-ring carbon signals at δC85.5 (C-

2), 74.1 (C-3) and 198.5 (C-4) **[19]**. The trans-configuration of the upper dihydroflavonols unit could be deduced from the coupling constant between H2 and H 3 ($^3J_{H2-H3}$=11.6 Hz) in the ^{1}H NMR spectrum.

Compound 1:^{1}H NMR (CD_3OD, 400 MHz) δ (ppm) : 6.87 (1H, d, *J* = 2.0 Hz, H - 2'), 6.86 (1H, dd, *J* = 8.0, 2.0 Hz, H - 6'), 6.70 (1H, d, *J* = 8.0 Hz, H - 5'), 5.99 (1H, d, *J* = 2.0 Hz, H – 8), 5.95 (1H, d, J = 2.0 Hz, H – 6), 4.44 (1H,d, *J* = 11.6 Hz, H - 3), 4.85 (1H,d, *J* = 11.6 Hz, H - 2), 3.71 (3H, s, OCH_3). This compound was identified as 3',5,7-trihydroxy 4'- methoxy dihydroflavonol or dihydroquercetin 4'methyl ether [6, 20].

Compound 2: UV Spectral Data, λ max (nm); MeOH: 256 nm, 358 nm, 294 nm; + NaOH: 270 nm, 407nm, 331 nm; + $AlCl_3$: 264 nm, 396 nm, 300 nm; + $AlCl_3$/HCl: 264 nm, 360 nm; + NaOAc: 264 nm, 369 nm; + NaOAc/H_3BO_3: 262 nm, 380 nm, 297 nm. ^{1}H NMR (CD_3OD, 400 MHz) δ (ppm) : 7.42 (1H, sl, H - 2'), 7.35 (1H, dl, *J* = 8.6, Hz, H - 6'), 6.80 (1H, d, *J* = 8.6 Hz, H - 5'), 6.23 (1H, d, *J* = 2.0 Hz, H – 8), 5.95 (1H, d, *J* = 2.0 Hz, H – 6), 4.44 (1H,sl, H - 8), 6.05 (1H,sl, H - 6), 3.67 (3H, OCH_3). This compound was identified as Quercetin 3 methyl ether [21].

Compound 4:^{1}H NMR (CD_3OD, 400 MHz) δ (ppm) : 6.86 (1H, d, *J* = 1.7Hz, H - 2'), 6.74 (1H, dd, *J* = 1.7 , 8.1 Hz, H - 6'), 6.70 (1H, d, *J* = 8.1 Hz, H - 5'), 5.80 (1H, d, *J* = 1.7 Hz, H – 8), 5.76 (1H, d, *J* = 1.7 Hz, H – 6), 4.39 (1H,d, J = 11.5Hz, H - 3), (H -2 Covered with a signal Solvent). ^{13}C NMR (CD_3OD, 100 MHz) δ (ppm) : 85.47 (C- 2), 74.06 (C- 3), 198.51 (C- 4), 164.88 (C- 5), 98.01 (C- 6), 170.08 (C- 7), 97.01 (C- 8), 165.72 (C- 9), 102.01 (C-10), 130.35 (C- 1'), 121.34 (C- 2'), 146.71 (C- 3'), 147.52 (C- 4'), 116.54 (C- 5'), 116.32 (C- 6').This compound was identified as Taxifolin [22].

CONCLUSION

The present study allowed the isolation and structural determination of two dihydroflavonols named: dihydroquercetin4'methyl ether (1) and Taxifolin (3) together with substituted flavonol Quercetin 3 methyl ether (2). In our Knowledge, this is the first report describing the isolation of all these compounds from *P. jaubertii*.

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