FLAVONOIDS OF *PAPAVER ANGRENICUM* PLANT

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Abstract. *The composition of flavonoids of the plant Papaver angrenicum, growing in the Ertosh district of the Angren district of the Tashkent region, was studied. We studied the composition of flavonoids in the plant Papaver angrenicum, growing in Uzbekistan, for the first time. A flow diagram for the extraction of flavonoids from plants of the Papaveraceae family has been developed. For the first time, the flavonoid apigenin was isolated from a plant composition and its structure was proven based on mass, IR, and NMR spectroscopy data.*

Keywords: *flavanoids, apigenin, Papaver angrenicum, Mass, IR, NMR spectroscopy*

Introduction

Papaver angrenicum (angren poppy) is a perennial herbaceous plant belonging to the *Papaveraceae* family. It germinates in April and blooms in June-August. The general appearance of its stems and leaves is light green, and the upper part of the plant is covered with needle-like hairs, forming a small grass. The roots form numerous rhizomes and their upper parts are thickly covered with bands of dead leaves [1]. The bunch of leaves at the root neck has leaf bands of medium length. The lower side of the leaf plates is covered with thick needle-like hairs, the hairs on the upper side are sparser. The leaves are finely cut three times, the side parts are long ovate and not cut, the upper part is sharpened, divided into 2 and 3 parts [2].

Inflorescences are simple erect thin 20-25 cm tall covered with sparse long hairs, the upper part is covered with pale yellow hairs. The bud is 9-10 mm long, ovoid or spherical, covered with yellow hairs. The flower crown is pale pink and round, 17-25 mm long. The pod is 10-12 mm long, 4-5 mm wide and covered with very thick white hairs. The flange of the capsule is bulging, consisting of 5-6 rays, the membranous rays are almost invisible [3].

This plant is found in alpine and subalpine meadows. Its distribution in Uzbekistan is mainly found in the territory of the village of Ertash, located above the Angren river in the Tashkent region, and in the Guralash mountains of the Zomin State Reserve, Zomin district, Jizzakh region. It is also found in Western Tien-Shan and Pamir-Aloy, Turkestan and Aloy ranges of Central Asia. [4]

Materials and methods

We collected 1 kg (per plant dry weight) of *Papaver angrenicum* plant growing near Ertash village, Ohangaron district, Tashkent region on June 25-26, 2020. We studied this plant for the first time in October 2004 at the Alkaloid Laboratory of the "Institute of Chemistry of Plant Substances" named after Academician Sabir Yunusovich Yunusov, and the sum of alkaloids was isolated. As a result, it was determined that the plant contains 0.19% alkaloid [5].

Continuing our scientific research, we decided to study the composition of flavonoids of the *Papaver angrenicum* plant growing in the Ertash area of Angren district of Tashkent region. The analysis of the literature showed that the flavonoid content of the *Papaver angrenicum* plant growing in the territory of Uzbekistan has not been studied at all.

In order to search for new physiologically active compounds, the phenolic composition of the above-ground and underground parts of *Papaver angrenicum* was studied. A general block

scheme was developed for the extraction and isolation of flavonoids from this plant belonging to the *Papaveraceae* family. Using column chromatography (h=165, d=4.5 cm), several fractions with different phenol compounds were obtained from the chloroform fraction of the aqueous-alcoholic extract. These fractions were then rechromatographed on a column with Sephadex LH-20 adsorbent, and the pure flavanoid substance was isolated. ^{1}H NMR spectra were recorded on a UNITY 400 Plus spectrometer with an operating frequency of 400 MHz (Varian, USA). GMDS internal standard. Chemical shifts are given in parts per million (ppm). Spin-spin interaction constants are in hertz (Gs).

The melting points of the isolated compounds were determined in glass capillaries using an electrothermal device "MEL-TEMP" (USA).

Quantitative HPLC analysis was performed on an Agilent 1100 series liquid chromatograph (Agilent Technologies Inc., USA) equipped with a G1311A 4-gradient pump, G1322A degasser, gradient mixer, G1314A variable wavelength detector (VWD27) and loop. injector (Rheodyne, USA) with 100 µl loop.

Thin layer chromatography (TLC) was performed on glass plates fixed with Silufol UV-254 (Czech Republic), silica gel 60 F254 from Merck (Germany) and thin layer silica gel L-50/40 MKM. Czechoslovakia). The following solvent systems were used for LUQX: I - chloroform; II – chloroform-methanol (9:1); Substances that produce spots on the HCV: 254 nm or 365 nm ultraviolet rays; iodine and ammonia vapors; 1% alcohol solution of aluminum chloride; 1% solution of vanillin in a 5% alcohol solution of sulfuric acid; A mixture of 1% aqueous solutions of $FeCl_3$ $K_3[Fe(CN)_6]$ (1:1); an acid solution of aniline phthalate.

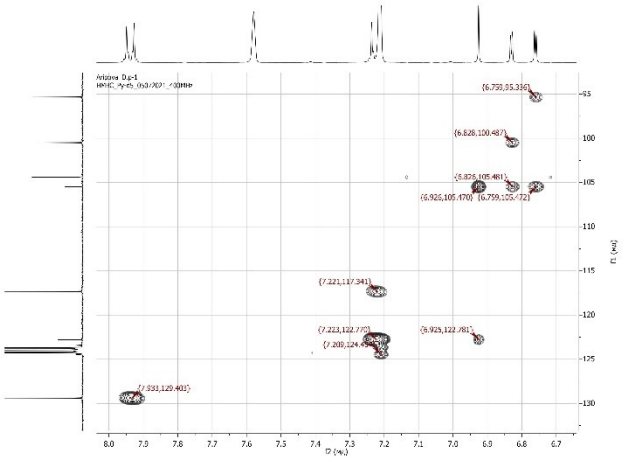
Silica gel 150/200, KSC from Tianjin Sinomed Pharmaceutical (China) and Sephadex LH-20 sorbent from GE Healthcare Bio-Sciences AB (Sweden) were used for column chromatography.

20 g of the chloroform fraction was chromatographed on a silica gel column using chloroform as the eluent. Fractions 3-7 with chloroform were combined (9mg), this fraction was rechromatographed on Sephadex LH-20 sorbent and 6mg of pure substance Rf=0.6 (Sistema chloroform-methanol 9:1) was isolated.

Results

In order to prove the structure of the isolated flavonoid, its liquefaction temperature, mass and NMR spectrum data were studied.

Apigenin is a $C_{15}H_{10}O_5$ substance with a melting temperature of 347-348°C and a molecular mass of M+ 270. In the ^{1}H spectrum of apigenin, signals related to hydrogen atoms located in 5 aromatic rings are shown in Fig. 1. Apigenin HMBC spectrum can be observed. 1 of them is in the form of a singlet and appears in the area of 6.93 m.u.s. The remaining 4 doublet signals at 6.76, 6.83, 7.94, 7.23 m.u. belong to the hydrogens of carbon atoms 6, 8, 2' and 6', 3' and 5, respectively. 13.79 m.u. the singlet signal broadened in the field belongs to the hydrogen atoms of the 5-OH group, and there



is no spin-spin interaction. The ^{1}H, ^{13}C NMR and additional experimental HMBC spectroscopy data of apigenin are presented in the table.

^{1}H, ^{13}C NMR and additional experimental HMBC spectroscopy data of apigenin (α-Py-d5 (150.35), d, m.u., 400MHz).

Table

Atom C	δ_C	δ_H (J/Hz)	HMBC (H→C)
2	164.99		
3	104.40	6.93, c	2, 4, 1`, 10
4	183.24		
5	163.67		
6	100.49	6.76, d (2.1)	5, 7, 8, 10
7	166.37		
8	95.33	6.83, d (2.1)	7, 9, 6, 10
9	158.99		
10	105.47		
1`	122.79		
2`	129.39	7.94, d (8.8)	4`, 2
3`	117.33	7.23, d (8.8)	4`, 1`
4`	163.18		
5`	117.33	7.23, d (8.8)	4`, 1`
6`	129.39	7.94, d (8.8)	4`, 2
5-OH	-	13.79, u.c.	

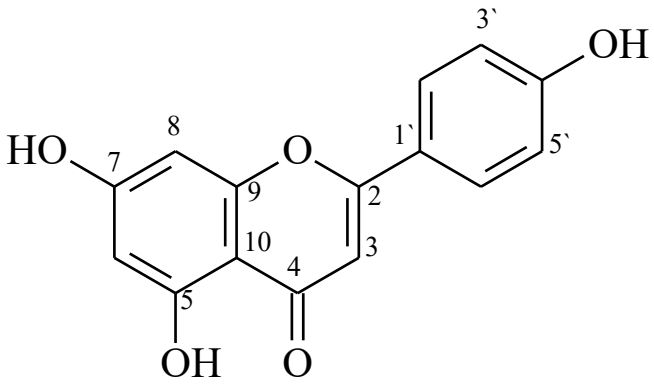


Figure 2: Structure of Apigenin

For the first time, apigenin flavonoid was isolated from the plant composition and its structure was proved based on NMR spectroscopy and additional experimental HMBC data. (Figure 2)

Apigenin is one of the most common flavone aglycones and is a natural antioxidant with anti-inflammatory and anticarcinogenic properties [6]. In plants, it is usually formed as a result of oxidation of naringenin under the influence of flavanone synthase enzyme [7]. Chamomile (*Matricaria recutita*) and tansy (*Tanacetum parthenium*) are found in fruits and vegetables, as well as medicinal plants[8]. It is especially abundant in parsley, celery and lemon[9-10].

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