Qatar Univ. Sci. J. (1993), 13(1): 51 - 52

CONSTITUENTS OF PLANTS GROWING IN QATAR XXIII. FLAVONOIDS OF *FRANCOEURIA CRISPA*

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المكونات الكيميائية لنباتات دولة قطر
الجزء ٢٣ : فلافونيدات الجثجاث

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أسفرت دراسة فلافونيدات نبات الجثجاث عن فصل والتعرف على أربعة فلافونيدات :
كيرستين ، كير ستين ٣ - جليكوزيد ، كيرستين ٧ - جليكوزيد ، كيروستين ٣ - ميثيل أيثر.

Key Words: *Francoeuria crispa,* Compositae, flavonoids, quercetin, quercetin-3-O-glucoside, quercetin-7-O-glucoside, quercetin-3-methyl ether.

ABSTRACT

Investigation of the flavonoid constituents of *Francoeuria crispa,* resulted in the isolation and identification of four flavonoids: quercetin, quercetin-3-O-glucoside, quercetin-7-O-glucoside and quercetin-3-methyl ether.

INTRODUCTION

Francoeuria crispa (Forssk.) Cass. (= *Pulicaria crispa* (Forssk.). Benth and Hook) (Compositae) is a small annual herb which grows wild in Qatar. The plant is used in folk medicine for the treatment of colds, coughs, colic, excessive sweating and as carminative (Ibn Sina, 1971). Flowering branches are also used for preparing sneezing powder and are sternutatory (Boulos, 1983, Rizk and El-Ghazaly, 1994. Previous studies of *F. crispa,* growing in Saudi Arabia resulted in the isolation of β-sitosterol, β-amyrin, choline, quercetin and an unidentified triterpene (Sarg, 1975). Several sesquiterpene lactones (Xantholides, a *pseudo*-guainolide and a secosesquiterpene lactone) have been isolated from *P. crispa,* growing in Egypt (Bohlmann *et al.*, 1979). The present work deals with the investigation of flavonoids of this plant.

EXPERIMENTAL

Plant material:

The plant was collected from Doha in April (during the flowering stage), and was kindly identified by Prof. Dr. G. El-Ghazaly.

Thin-layer Chromatography:

a- Polyamide, developed with benzene-ethyl methyl ketone-methanol (4:3:3); b- Cellulose (Two-dimensional), developed with t-butanol-acetic acid-water (3:1:1) and 15% acetic acid.

Paper Chromatography:

Whatmann 3 MM, developed with 30 % acetic acid.

Detection on TLC and PC was carried out by UV light at 366 nm before and after spraying with Naturstoff reagent (β-amino diethyl ether of diphenyl boric acid, 5% in methanol).

Droplet counter-current chromatography (DCCC):

DCCC apparatus, Buchi model (670) consists of n_c 294 pyrex glass tubes (41 cm long and 2.7 nm i.d.) connected to each other top to bottom with PTFE connections. Solvent: chloroform-methanol-water (7:13:8).

^{1}H-NMR:

The proton NMR spectra were obtained by a Varian EM-390 apparatus, measured at 90 MHz.

MS:

The mass spectra were obtained on a Finningan 4000 instrument, electron impact with direct inlet at 30 eV.

Extraction and Fractionation of the Flavonoids:

About 0.5 Kg. of the defatted powdered plant (leaves and flowers) was extracted with methanol. The solvent free extract was taken with hot water and extracted with chloroform, followed by ethyl acetate. Treatment of the chloroform extract (15 gm.) with hot methanol gave a crystalline precipitate, which was chromatographed on a silica gel column (benzene, benzene-chloroform and chloroform-ethyl acetate mixtures), followed by dry column (polyamide; benzene-ethyl methyl ketone-methanol 8:2:2). Further fractionation was carried out by PC, followed by sephadex LH-20 (quercetin and quercetin-3-O-methyl ether). The ethyl acetate fraction was fractionated by DCCC (quercetin-3-O-glucoside and quercetin-7-O-glucoside.

Quercetin-3-O-methyl ether:

UV (MeOH) nm: 258, 269 sh, 294 sh, 356; (NaOMe) 272, 330 sh, 405; (Al Cl_3) 277, 305 sh, 338, 440; (Al Cl_3+HCl) 268, 277 sh, 299 sh, 400; (NaOAc) 273, 325, 282; (NaOAc+H_3BO_3) 262, 298 sh, 380.

^{1}H-NMR: δ 6.0 (d, H-6), 6.6 (d, H-8), 6.6.-6.8 (m, H-5'), 7.4 (m, H-2' and H-6') and 3.6-3.8 (s, -OCH_3 at C-3).

Quercetin:

Yellow needles, m. p. 316-318°C (methanol), UV (MeOH) nm: 256, 269 sh, 300 sh, 370; (NaOMe) 248, 328 (dec); (Al Cl_3) 272, 301sh, 330, 454; (Al Cl_3+HCl) 268, 300sh, 360, 430, (NaOAc), 260, 276, 330, 394 (dec); (NaOAc+H_3BO_3) 260, 300 sh, 386.

^{1}H-NMR: δ 6.2 (d, H-6), 6.5 (d, H-8), 6.9-7.1 (d, H-5'), and 7.6-7.9 (m, H-2' and H-6').

Quercetin-3-O-glucoside (Isoquercetrin):

Yellow needles, m. p. 216-218°C (methanol), UV (MeOH) nm: 258, 269, 295 sh, 355; (NaOMe) 273, 330 sh, 409; (Al Cl_3) 278, 309sh, 360 sh, 434; (Al Cl_3+HCl) 265, 280sh, 302sh, 369, 405, (NaOAc), 274, 323sh, 379, (NaOAc+H_3BO_3) 267, 295 sh, 379.

Acid hydrolysis (10% H_2SO_4) gave quercetin (m.m.p., UV) and glucose (PC).

Quercetin-7-O-glucoside:

UV (MeOH) 370, 335sh, (NaOMe) 427, 330 sh, (Al Cl_3) 455, 360sh, 320 sh, (Al Cl_3+HCl) 427, 365sh, (NaOAc), 378, 330sh, (NaOAc+H_3BO_3) 383.

Acid hydrolysis afforded quercetin and glucose. MS of quercetin showed M^+ at m/e 302 and fragments at 274, 153, 152, 137, 134, 124 and 123.

RESULTS AND DISCUSSION

The isolation of the flavonoids was carried out by extracting the defatted powdered plant with methanol followed by solvent fractionation using chloroform and ethyl acetate. Investigation of the chloroform fraction revealed the presence of two flavonoids. Successive column chromatographic fractionation using silica gel, followed by dry column on polyamide, then prepative PC and finally Sephadex LH-20 succeeded in the separation of quercetin and quercetin 3-methyl ether. Fractionation of the ethyl acetate fraction by DCCC resulted in the isolation of quercetin-3-O-glucoside and quercetin-7-O-glucoside. The identification of the four isolated flavonoids was carried out by m.p., TLC, PC, UV, ^{1}H-NMR (Mabry *et al.*, 1970) and MS.

The genus *Francoeuria* is close to *Pulicaria.* Previous studies of flavonoids of *Pulicaria* species revealed also the presence of quercetin and quercetin derivatives and glucosides e.g. 3.7-dimethoxy quercetin, 7-methoxy quercetin and a number of quercetin glucosides (e.g. isoquercetin) (Rizk, 1986).

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