Ankara Ecz. Fak. Derg.
32(1)31-35,2003

J. Fac. Pharm, Ankara
32(1)31-35,2003

ANTHRAQUINONES AND FLAVONOIDS FROM *RHEUM RIBES*

RHEUM RIBES BİTKİSİNİN ANTRAKİNONLARI VE FLAVONOİTLERİ

Fatma TOSUN **Çiğdem AKYÜZ KIZILAY**

Department of Pharmacognosy, Faculty of Pharmacy, Gazi University,
06330 Hipodrom, ANKARA- TURKEY

ABSTRACT

The anthraquinones chrysophanol, physcion and emodin, the flavonoids quercetin, 5-desoxyquercetin, quercetin 3-0-rhamnoside, quercetin 3-0-galactoside and auercetin 3-0-rutinoside were isolated from the shoots of Rheum ribes, the only native Rheum species growing in Turkey.
Key words: Rheum ribes; Anthraquinones; Flavonoids

ÖZET

Türkiye'de yabani olarak yetişen tek Rheum türü olan Rheum ribes' in sürgünlerinden krizofanol, fiskiyon ve emodol antrakinonları ile kersetin, 5-dezoksikersetin, kersetin 3-0-ramnozit, kersetin 3-0-galaktozit, kersetin 3-0-rutinozit flavonoitleri izole edilmiştir.
Anahtar kelimeler: Rheum ribes, Antrakinonlar, Flavonoitler

INTRODUCTION

Rheum ribes L. (Polygonaceae), the only native *Rheum* species growing in Turkey (1) is distributed in Sivas, Kars, Erzincan, Tunceli, Elazığ, Muş, Ağrı, Bitlis, Erzurum, Van, Hatay, Kahramanmaraş and Hakkari (2). The plant is known as "Işgın, Uşgun and Uçgun" in Turkey. Its young shoots and petiols are eaten as a vegetable and used to promote digestion, improve appetite (2, 3) treat diarrhoea and as stomachic, antiemetic; young shoot and petiol juice is used against hemorrhoids, measles, smallpox and as cholagogue (4). Roots are used to treat diabetes, hemorrhoids (2), ulcer, diarrhoea and anthelmintic, expectorant; roots and leaves to treat stomach disorders (3). Four anthraquinone derivatives, 2 anthraquinone glucosides, 1 dianthron glucoside and 1 stilbene glucoside ha ve been reported from subterranean parts of the plant (5).

in the current paper, the compounds of the aerial parts of *Rheum ribes* which have not been studied before were reported.

EXPERIMENTAL

Plant material

Rheum ribes used in this study was collected from Yüksekova (Hakkari-Turkey) in June 1998. Voucher specimen is deposited in the Herbarium of Pharmocognosy Department, Faculty of Pharmacy, Gazi University, Ankara, Turkey (GUE No. 2106).

Extraction and isolation

The air-dried powdered shoots of *Rheum ribes* were sequentially extracted at room temperature with petrol, chloroform and methanol. The extracts were separately evaporated under vacuum to dryness.

The petrol and chloroform extracts were subjected to column chromatography eluting gradually with chloroform of increasing polarity with methanol (S4 solvent system). Methanol extract was chromatographed on a silica gel column with S2 solvent system.

General experimental procedures

H NMR spectra were recorded on a Bruker 400 MHz Spectrometer. IR spectra were run in KBr discs on a Perkin Elmer 1330 Spectrophotometer. UV spectra were recorded on a Beckman DU 650 UV-vis Spectrophotometer cabled to Star LC-20 printer recorder. Melting points were determined on a Electrothermal 9200 Digital Melting Points Apparatus and uncorrected. Thin-layer chromatography was performed on silica gel 60 F254 plates (Merck No. 5554) in three solvent systems Si: CHCI3/CH3OH (95:5); S_2: $CHC1_3/CH_30H/H_20$ (65:25:2); S_3: Petrol/EtOAc (90:10). Column chromatography was performed on silica gel (0.040-0,063 mm, Merck No. 9385) column with solvent systems S2 and S4: CHCI3/CH3OH mixtures of increasing polarity (0-10 % CH_3OH). Preparative thin-layer chromatography was carried out using S_2 and S_3 solvent systems on silica gel 60 F254 plates (Merck No. 5744).

RESULTS AND DISCUSSION

This is the first report on the compounds from the aerial parts of *Rheum ribes.* Three anthraquinone and five flavonoid compounds were isolated and identified by comparing their Rf values, melting points and spectral characteristics (IR, 1H NMR and UV) with those of the authentic samples. Column chromatography of petrol extract gave two anthraquinone compounds identified as chrysophanol and physcion. Column chromatography of chloroform

extract afforded three anthraquinone compounds and identified as chrysophanol, physcion and emodin. These compounds were purified by preparative thin-layer chromatography using S_3 solvent system. Chromatographic fractionation of methanol extract yielded five compounds. Further purification of these compounds by preparative thin-layer chromatography in S_2 solvent system afforded quercetin, 5-desoxyquercetin, quercetin 3-0-rhamnoside, quercetin 3-0-galactoside and quercetin 3-0-rutinoside.

Chrysophanol

Mp 196°C; R_f (S_1): 0.91 , (S_3): 0.55; UV X_{max} (CH_3OH) 225, 258, 279, 288, 432, (NaOH) 236, 282, 502 nm. İR v™ 3410 (OH), 1687 (C=0), 1638 (C=0) cm[1].

Physcion

Mp 209°C; R_f (S_1): 0.89, (S_3): 0.44; UV Xmax (CH3OH) 226, 254, 267, 287, 438, (NaOH) 240, 304, 510 nm. İR $v_{TO)t}$ 3415 (OH), 1683 (C=0), 1634 (C=0) cm"[1].

Emodin

Mp 259°C; R_f (S_1): 0.61, (S_3): 0.09; UV X_{imx} (CH_3OH) 223, 254, 267, 290, 440, (NaOH) 237, 285, 520 nm. İR v„ 3395 (OH), 1685 (C=0), 1642 (OO) cm"[1].

Quercetin

Mp 312°C (dec); R_f (S_2): 0.76; UV L, (CH_3OH) 254, 300, 369, (NaOMe) 247, 320 (dec), (AICI3) 271, 302, 331, 460, (AICI3/HCI) 264, 300, 356, 427, (NaOAc) 272, 330 (dec), 388, (NaOAc/H_3B0_3) 261, 300, 387 nm. İR v„ 3420 (O-H), 1690 (C=0) cm"[1]. 'H NMR (5 ppm) 6.24 (İH, d, H-6, J=2.2 Hz), 6.62 (İH, d, H-8, J=2.2 Hz), 7.21 (İH, d, H-5', J=8.1 Hz), 7.74 (2H, dd, H-2' and H-6', J=8.3 Hz), 12.32 (5H, s, Ar-OH).

5-Desoxyquercetin

Mp 330°C (dec); R_f (S_2): 0.68; UV 7^$_{ax}$ (CH_3OH) 248, 262, 307, 319, 362, (NaOMe) 252, 292, 341 (dec), ($AlCl_3$) 268, 281, 318,458, (AICI3/HCI) 263, 274, 322, 423, (NaOAc) 263, 321, 331, 378 (dec), (NaOAc/H_3B0_3) 265, 315, 381 nm. İR v_{max} 3435 (O-H), 1693 (C=0) cm"[1]. ^1H NMR (5 ppm) 6.67 (İH, dd, H-6, J=2.2 Hz), 6.74 (İH, d, H-8, J=2.3 Hz), 7.18 (İH, d, H-5', J=8.2 Hz), 7.34 (İH, d, H-2', J=8.3 Hz), 7.71 (İH, d, H-6', J=8.2 Hz), 8.08 (İH, d, H-5, J=2.4 Hz), 12.87 (4H, s, Ar-OH).

Quercetin 3-O-rhamnoside

Mp 184°C; R_f (S_2): 0.56; UV X_{wx} (CH_3OH) 256, 265, 301, 348, (NaOMe) 270, 326, 395, (AICI3) 274, 304, 333, 420, (AICI3/HCI) 272, 303, 353, 398, (NaOAc) 272, 322, 372, ($NaOAc/H_3B0_3$) 260, 300, 367 nm. İR v„ 3410 (O-H), 1682 (C=0), cm"[1]. [:]H NMR (8 ppm) 1.05 (3H, d, rhamnosyl-CHj, J=10.8 Hz), 3.43-4.12 (4H, m, rhamnosyl protons), 5.03 (İH, d, rhamnosyl-H-1", J=7.6 Hz), 6.21 (İH, d, H-6, J=2.2 Hz), 6.42(1H, d, H-8, J=2.2 Hz), 6.72 (İH, d, H-5', J=8.4 Hz), 7.31(1H, d, H-2', J=8.1 Hz), 7.48 (İH, d, H-6', J=8.1 Hz), 12.76 (4H, s, Ar-**OH).**

Quercetin 3-O-galactoside

Mp 230°C; R_f (S_2): 0.36; UV A_{max} (CH_3OH) 257, 269, 299, 362, (NaOMe) 272, 327, 410, (AICI3) 275, 305, 331, 428 (AICI3/HCI) 268, 299, 366, 395 (NaOAc) 274, 324, 379 ($NaOAc/H_3B0_3$) 261, 298, 376 nm. İR v_{max} 3390 (O-H), 1685 (OO) cm"[1]. [1]H NMR (8 ppm) 3.49-3.78 (6H, m, galactosyl protons), 5.62 (İH, d, galactosyl-H-1", J=7.4 Hz), 6.17 (İH, d, H-6, J=2.3 Hz), 6.49 (İH, d, H-8, J=2.3 Hz), 6.81 (İH, d, H-5', 1=8.2 Hz), 7.42 (İH, d, H-2', J=8.4 Hz), 7.78-7.82 (İH, dd, H-6', 1=8.4 Hz), 12.68 (4H, s, Ar-OH).

Quercetin 3-O-rutinoside

Mp 189°C; RKS2): 0.26; UV X_{imx} (CH_3OH) 257, 268, 297, 357, (NaOMe) 270, 328, 410 (AICI3) 274, 307, 327, 433, (AICI3/HCI) 267, 301, 361, 400, (NaOAc) 273, 323, 395 ($NaOAc/H_3B0_3$) 261, 294, 380 nm. İR v_{max} 3415 (O-H), 1687 (C=0) cm"[1]. [1]*U* NMR (8 ppm) 1.08 (3H, d, rhamnosyl-CH_3, J=10.6 Hz), 3.26-3.81 (10H, m, rhamnosyl and glucosyl protons), 4.28 (İH, d, rhamnosyl-H-1'", J=7.2 Hz), 5.73 (İH, d, glucosyl-H-1", 1=7.3 Hz), 6.18 (İH, d, H-6, J=2.3 Hz), 6.39 (İH, d, H-8,1=2.2 Hz), 6.91 (İH, d, H-5', J=8.3 Hz), 7.36-7.47 (2H, dd, H-6' and H-2', J=8.1 Hz), 12.63 (4H, s, Ar-OH).

REFERENCES

1. **Cullen, J.** *"Rheum* L.", in *Flora of Turkey and the East Aegean Islands,* Vol. 2, Davis, P. H. (Ed.) Edinburgh Universty Press, Edinburgh; 268-269 (1967).

2. **Tuzlacı, E., Meriçli, A. H.** "Some Studies on Işgın *(Rheum ribes)* and its Distribution in Turkey", in *Proceedings of the IX. Symposium on Plant Drugs,* Başer, K.C.H. (Ed). Publication of Anadolu University, No. 641, Eskişehir, 336-341 (1992).

3. **Tabata, M., Sezik, E., Honda, G., Yeşilada, E., Fuki, H., Goto, K., Ikeshiro, Y.** "Traditional Medicine in Turkey III. Folk Medicine in East Anatolia, Van and Bitlis Provinces". *Int. J. Pharmacog.* **32,** 3-12 (1994).

4. **Baytop, T.** Theraphy with Medicinal Plants in Turkey (Past and Present), Publication of the istanbul University, No.3255, İstanbul, 357-358 (1984).

5. **Meriçli, A. H., Tuzlacı,** E. "Constituents *of Rheum ribes". Fitoterapia* **61:** 375 (1990).

Başvuru Tarihi: 06.02.2003

Kabul Tarihi: 19.03.2003