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ANTHRAQUINONE PIGMENTS FROM *RUMEX CRISTATUS*

RUMEX CRISTASUS ANTRAKİNON PİGMENTLERİ

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The anthraquinones in the roots of Rumex cristatus which grows wild in Turkey were examined. Six anthraquinone derivatives were isolated from this plant. Majors constituents such as emodin, physcion, chrysophanol and minors constituents such as rhein, aloe-emodin and ϖ-hydroxyemodin. One of them, ϖ-hydroxyemodin, have been detected for the first time in genus Rumex..

Bu çalışmada Turkiye'de yabani olarak yetişen Rumex cristatus kökünün antrakinonları incelendi. Bitkilden 6 antrakinon bileşiği izole edildi. Major alanlar emodin, physcion, chrysophalno, minörü olanlar rehein, aloe-emodin ve ϖ-hidroksiemodin olarak teşhis edildi. Bunlardan ϖ-hidroksiemodin'in Rumex türünde ilk defa bulunduğu saptandı.

Keywords: *Rumex cristatus; Anthraquinone; Citreorosein*

Anahtar Kelimeler: *Rumex cristatus; Antrakinon; Citreorosein*

Introduction

Rumex is one of several genera which are characterized mainly by the presence of anthraquinone derivatives and found widespread all over the world. It is represented in Turkey by 28 wild growing species [1, 2]. However there are only a few works on the anthraquinones of these species, mainly on the major pigments [3-5]. In the present work, we have examined the minor as well as the major pigments of the roots of *Rumex cristatus,* one of the Turkish *Rumex* species. We isolated emodin, physcion, chrysophanol as major pigments and as a minor pigment ϖ-hydroxyemodin which is new for the genus *Rumex.* Rhein and aloe-emodin were identified by tlc only.

Material and methods

General procedure

Melting points were determined on a melting point microscope (Reichert) and were uncorrected. The IR and UV spectra were recorded on Perkin- Elmer 577 and Shimadzu 160 A Spectrophotometer. The EIMS and NMR were taken with Kratos MS 30 and Bruker 80 MHz apparatus, respectively. Silicagel Merck (0,063-0,200mm) and Ultramid B-12 were used for column chromatography. Kieselgel 60, Kieselgel F_{254}, Polyamid 11 F_{254} Merck precoated plates were used for tlc. The following solvent systems were used: for silicagel; System 1: petrol (bp40-60^0)/EtOAc/AcOH (75:24:1); System 2: $CHC1_3$/MeOH (5:1); System 3: petrol (bp40-60^0)/EtOAc (2: 1). For polyamid; System 4: MeOH.

Plant material

The roots of *Rumex cristatus* were collected near Tekirdag, European Turkey. A voucher specimen is deposited at the herbarium of Faculty of Pharmacy, University of istanbul (ISTE 59282).

Isolation of aglycons

The coarsely powdered roots (180g) were extracted exhaustively with ether in a soxhlet apparatus. This extract was shaken with 5% aqueous Na_2C0_3 solution. Then, the separated aqueous layer was acidified and reextracted with ether (extract-1). Na_2C0_3 insoluble anthraquinones remained in the second ether extract (extract-II). After evaporation of ether the residues of both extracts were chromatographed on silicagel columns (with solvent system 3).

Compound **1**, directly and **2** after rechromatography on silicagel column were obtained from the corresponding eluates of extract-II with solvent system 3. The compound **3** and **4** were isolated from the eluates of extract-I after preparative tlc with solvent system 1. All the compounds were crystallized in MeOH. Compounds **1, 3** and **4** were identified by comparison (mp, tlc, IR) with authentic samples.

ϖ-Hydroxy emodin (compound 2)

Orange needles, mp.285-288 ^{0}C; UV λ_{max} (MeOH) (logε) 221(4,36), 266 (4,02), 283 (4,01), 436 (3,76) nm; IR V_{max} (KBr) 1670, 1626 cm^{-1}; ^{1}H-NMR ($CDC1_3$) δ 7,74 (1H, s, 2-H), 7,32 (1H, s, 4-H), 7,28 (1H, d, 5-H), 6,63 (1H, d, 7-H), 4,68 (2H, s, $C\underline{H}_2$0H).

EIMZ m/z (rel. int); 286 M$^+$ (100), 270 (49), 257 (50).

Synthesis of 2

The conversion of emodin to its (ϖ-hydroxy derivative was carried out as follows: bromination of **1** triacetate with N-bromosucsinimide in the presence of benzoylperoxide in $CC1_4$; acetylation of ϖ-bromo derivative with silver acetate and acetic acid anhydride; hydrolysis of the acetyl product in H_2SO_4/MeOH; after purification by chromatography and crystallisation in MeOH compound **2** afforded orange needles. Synthetic compound was identical with the natural compound **2** (mp, tlc, IR).

The compounds **5** and **6** were obtained from the fractions of extract-I in very small amounts and therefore could be identified only by tlc comparison with authentic samples (in solvent systems 1,2,4) as aloe-emodin and rhein, respectively.

Result and Discussion

The ether extract of the roots of *Rumex cristatus* was fractioned with Na_2C0_3 (5%) solution. From the Na_2C0_3 soluble fraction major **1** and minor **2** pigments were isolated by column chromatography. Compound **1** was identified by comparison with an authentic sample as emodin. Compound **2**, orange needles, mp.285-288 ^{0}C, showed no similarity with the known *Rumex* anthraquinones. The EIMS displayed [M]$^+$ at 286 *m/z*, calculating for $C_{15}H_{I8}0_6$ and IR spectrum showed free and chelated carbonyl absorption at 1670 and 1626 cm^{-1}. ^{1}H-NMR spectrum of compound **2** revealed the presence of a hydroxymethyl group (δ, 4.68; $C\underline{H}_2OH$) and four isolated aromatic protons. All these data indicated that compound **2** is a "trihydroxy hydroxymethylanthraquinone" and probably 1, 6, 8- trihydroxy -3- hydroxymethyl-anthraquinone (citreorosein) (6). To confirm this, citreorosein was prepared from emodin and the compound **2** was shown to be identical with the synthetic product. This is the first report on the occurrence of citreorosein in the genus *Rumex.*

Na_2C0_3-insoluble part of the ether extract afforded two major (**3, 4**) and two minor pigments (**5, 6**) by cc and tlc. The major pigments were identified by comparison with authentic samples as phycion and chrysophanic acid. Compound **5** and **6** were only in trace amounts and were identified by tlc (in solvent systems 1, 2, 4) as aloe-emodin and rhein.

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