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FLAVANONES FROM *CYCLOTRICHIUM NIVEUM*

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Key Word Index—*Cyclotrichium niveum*; Labiatae; whole plant; isosakuranetin; isosakuranetin 7-*O*-rhamnoside; eriodictyol 7-*O*-glucoside; flavones; triterpenes.

Abstract—A new flavanone isosakuranetin 7-*O*-rhamnoside was isolated from *Cyclotrichium niveum* together with known flavanones isosakuranetin and eriodictyol 7-*O*-glucoside, the flavones apigenin, apigenin 7-methyl ether, acacetin 7-*O*-rutinoside and the triterpenoids vergatic acid, oleanolic acid, β-amyrin and sitosterol.

INTRODUCTION

Although isosakuranetin 7-*O*-rutinoside was first isolated from a member of the Labiatae, *Monarda didyma* L. [1, 2] and eriodictyol from *Coleus amboinicus* [3] and its 7-*O*-rutinoside as well as 7-*O*-rhamnosylglucoside from *Mentha longifolia* [4], flavanones are relatively rare in Labiatae. In our chemical investigation of the genus *Salvia* (Labiatae) we have not previously encountered flavanones. In this first chemical investigation of another member of the Labiatae, *Cyclotrichium niveum* Boiss., which is endemic to Turkey, we obtained a new glucoside of a well-known flavanone, isosakuranetin 7-*O*-rhamnoside (**1**) together with isosakuranetin, eriodictyol 7-*O*-glucoside, apigenin and apigenin 7-methyl ether, acacetin 7-*O*-rutinoside and the triterpenoids vergatic acid, oleanolic acid, β-amyrin and -sitosterol. The structures of the known compounds were established by comparing their spectral data to those of known compounds.

RESULTS AND DISCUSSION

Extraction of the whole plant yielded three flavanones, one of which is the new glycoside of isosakuranetin, the 7-*O*-rhamnoside. Its structure was established mainly by spectral data. The UV spectra of **1** indicated 7,4′disubstitution; λ_{max}^{MeOH} nm 324 (sh), 282; + NaOMe 330 (sh) (lower intensity), 282; + $AlCl_3$ 372, 312, 260 (sh); + $AlCl_3$ − HCl 372, 310, 258 (sh); + NaOAc 334 (sh), 283; + NaOAc − H_3BO_3 324 (sh), 282. The colour reactions were brown under UV light, when exposed to ammonia vapour and when sprayed with NA reagent, indicating a flavanone skeleton with a free hydroxyl group at the 5-position. The ^{1}H NMR spectrum of **1** (Table 1) showed ABX system for H-2 and H-3 signals at δ5.48, 3.2 and 2.8 respectively indicating a flavanone nucleus. The rhamnose methyl was at δ1.14 and H-1 of rhamnose at δ5.2. The MS spectrum of the acetylated compound (**1a**) showed fragments at 327 (monoacetylisosakuranetin-H), 273 (three acetylated rhamnose-OH), 214 (273-HOAc), 153 (213-HOAc), 110 (153-COMe). Acetylation of **1** yielded a tetra-acetate (**1a**) in the ^{1}H NMR spectrum of **1a** three acetoxyl groups of the rhamnose moiety at δ2.04, 2.07, 2.09 and one acetoxyl group at δ2.37 indicated that there was only one free aromatic hydroxyl in **1** (Table 1). Acid hydrolysis yielded isosakuranetin (UV, UV shifts, ^{1}H NMR, ^{13}C NMR and MS) and rhamnose (TLC and PC comparison with authentic sample).

Table 1. ^{1}H NMR spectral data of flavanones **1**, **1a** and **1b**

H	**1** (DMSO)	**1a** ($CDCl_3$)	**1b** ($CDCl_3$)
2	5.48 *dd* (3, 13)	5.45 *dd* (3.2, 12.8)	5.40 *dd* (3, 12)
3	3.20 *dd* (13, 13)	3.12 *dd* (12.8, 12.8)	3.22 *dd* (12, 12)
3	2.80 *dd* (3, 13)	2.75 *dd* (3.2, 12.8)	2.72 *dd* (3, 12)
5	12.02 *s*	2.37 *s* (OAc)	12.06 *s*
6	6.12 *d* (1.5)	6.09 *d* (1.5)	5.97 *d* (2.0)
8	6.15 *d* (1.5)	6.12 *d* (1.5)	6.01 *d* (2.0)
2′	7.45 *d* (8.0)	7.35 *d* (8.0)	7.39 *d* (8.2)
3′	6.85 *d* (8.0)	6.92 *d* (8.0)	6.95 *d* (8.2)
4′	3.80 *s* (OMe)	3.83 *s* (OMe)	3.84 *s* (OMe)
5′	6.85 *d* (8.0)	6.92 *d* (8.0)	6.95 *d* (8.2)
6′	7.45 *d* (8.0)	7.35 *d* (8.0)	7.39 *d* (8.2)
rham H-1	5.20 *d* (2)	—	—
rham Me	1.14 *d* (6.1)	—	—
rham H-2; H-5	4.0–5.2 ppm	—	—
OAc	—	2.04 (*s*), 2.07 (*s*), 2.09 (*s*)	—

EXPERIMENTAL

Plant material. Cyclotrichium niveum Boiss. (Labiatae) was collected from eastern Turkey (Sivas) in July 1987 and was identified by one of us (E. Tuzlaci), a voucher is deposited in the Herbarium of the Faculty of Pharmacy, University of Marmara (MARE 1293).

Isolation. The powdered whole plant (500 g) was extracted with Me_2CO in a Soxhlet. The extract was evapd *in vacuo* yielding 11 g of a residue. The residue was fractioned in a silica gel column (4 × 60 cm) eluting with petrol, a gradient of C_6H_6 was added up to 100% followed by $CHCl_3$ and EtOH both to 100%. The compounds were obtained in the following order: β-amyrin (90 mg), sitosterol (400 mg), vergatic acid (1 g), oleanolic acid (2 g), apigenin (34 mg), apigenin 7-methyl ether (43 mg), eriodictyol 7-*O*-glucoside (38 mg), isosakuranetin (125 mg), isosakuranetin 7-*O*-rhamnoside (260 mg), acacetin 7-*O*-rutinoside (15 mg).

Hydrolysis of **1**. Acid hydrolysis was carried out with 2 N HCl (3 hr at 100°) under reflux. Rhamnose was identified by Co-PC (BuOH:–HOAc–H_2O 4:1:5 and pyridine–EtOAc–HOAc–H_2O 36:36:7:21) and on TLC silica gel plates (EtOH–$CHCl_3$ 1:19) and cellulose plates (30% HOAc; 45% HOAc; BuOH–pyridine–H_2O; 15:3:2).

Isosakuranetin 7-O-rhamnoside (**1**). Cream coloured crystals, mp 205°, UV given in the text. ^{1}H NMR given in Table 1.

Isosakuranetin 7-O-rhamnoside tetra-acetate (**1a**). Mp 195°, ^{1}H NMR given in Table 1. MS *m/z* (%), no mass peak was observed, 327 $[\text{isosakuranetin} + 5 \times \text{OAc} - \text{H}]^+$ (2), 273 $[\text{rham} + 3 \times \text{OAc} - \text{H}]^+$ (80), 213 $[273\text{-HOAc}]^+$ (30), 153 $[213 - \text{HOAc}]^+$ (100), 110 $[153 - \text{COMe}]^+$ (76), 151 $[A_1 - H]^+$ (30), 132 $[B_3]^+$ (10), 119 $[B_3 - Me]^+$ (8).

Isosakuranetin (**1b**). Mp 191°, UV, MS and ^{13}C NMR spectral data as the lit., ^{1}H NMR spectrum is given in Table 1.

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TWO FLAVANONES FROM *CITRUS* SPECIES

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Key Word Index—*Citrus*; Rutaceae; flavanones; hiravanone; yukovanol; 3-methylbut-2-enyl.

Abstract—The new flavanones, hiravanone and yukovanol were isolated from root extracts of some *Citrus* species and structures were determined by spectrometric and synthetic methods.

INTRODUCTION

In our phytochemical studies of the root of *Citrus* plants, we have isolated many kind of coumarins, acridones, and flavanones [1]. In a continuation of these studies two new flavanones named hiravanone (**1**) and yukovanol (**5**) were isolated and characterized from roots of *Citrus* species.

RESULTS AND DISCUSSION

Hiravanone (**1**) was obtained from the root extract of several hybrid seedlings resulting from crosses of *C. tamurana* and *C. kinokuni*, as a pale yellow oil, $[\alpha]_D$ 0° ($CHCl_3$). The IR and ^{1}H NMR spectra showed the presence of a conjugated carbonyl, a methoxyl, three hydroxyl, and two 3-methylbut-2-enyl moieties. An observation of a characteristic ABX signals at δ5.31 (*dd*, $J = 3.4$ and 12.8 Hz), 3.05 (*dd*, $J = 12.8$ and 17.2 Hz), and 2.80 (*dd*, $J = 3.4$ and 17.2 Hz) together with the hydrogen-bonded hydroxy proton signal suggested the presence of a flavanone nucleus in the molecule. A remaining 3H-multiplet at δ6.94 was attributable to protons of a 1,3,4-trisubstituted aromatic ring. The appearances of diagnostic mass fragment peaks at *m/z* 288 and 150 produced by a retro-Diels–Alder process at the B-ring in the flavanone skeleton [2], suggested the location of two 3-methylbut-2-enyl moieties on the A-ring and a hydroxyl and a methoxyl group on the C-ring. Based on these spectral