NOTE

FLAVONOID AGLYCONES FROM Ballota saxatilis subsp. saxatilis

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ABSTRACT

From the aerial parts of Ballota saxatilis subsp. saxatilis, the three flavone aglycones 6-hydroxy apigenol 7,4’-dimethyl ether (ladanein) (1), kaempferol 3,7,4’-trimethyl ether (2), and quercetin 3,7,3',4'-tetramethyl ether (retusin) (3), have been isolated and identified. The flavonoids were identified as apigenol 7,4’-dimethyl ether (1), kaempferol 3,7,4’-trimethyl ether (2), and quercetin 3,7,3',4'-tetramethyl ether (3) by UV, MS and 1H-NMR data.

INTRODUCTION

Ballota species have been known since the Dioscorides and infusions of the plant are used in Turkish folk medicine in cases of whooping cough and as an antiulcer, antispasmodic and sedative (Meriçli et al., 1988). The genus Ballota (Lamiaceae) consists of about 33 species growing mainly in the Mediterranean region. In Turkey, the genus Ballota is represented by eleven species, and six subspecies, ten of which are endemic (Davis, 1972; Ferreres et al., 1986). Ballota saxatilis subsp. saxatilis Sieber ex J. & C. Presl. is distributed in Central Anatolia and has not been investigated before.

In this research, from the aerial parts of Ballota saxatilis subsp. saxatilis, one flavone and two flavonol were isolated. The flavonoids were identified as apigenol 7,4’-dimethyl ether (1), kaempferol 3,7,4’-trimethyl ether (2), and quercetin 3,7,3',4'-tetramethyl ether (3) by UV, MS and 1H-NMR data.

MATERIALS AND METHODS

General Experimental Procedures
UV spectra (in MeOH) were recorded using a Varian DMS 90 instrument. EIMS spectra were recorded using a VG ZAB spectrometer. 1H-NMR spectra in CDCl3 were recorded at 300 MHz on a Bruker 300 spectrometer. Melting points were recorded on a Dupont 910 DSC instrument.

Plant Material
Ballota saxatilis subsp. saxatilis Sieber ex J. & C. Presl. was collected in 1994 from flowering plants near Ermenek (Turkey) and identified by Prof. Dr. Mehmet Koyuncu. Voucher specimens are kept in the Herbarium of Ankara University, Faculty of Pharmacy (AEF. No. 18676, 18706).

Isolation of Flavonoids
Air-dried and powdered aerial parts of the plant (1.2 kg) were extracted with Me2CO (10 L) at room temperature for 1 week. Solvent was evaporated, the residue extracted with EtOAc and the extract washed with H2O and dried. The extract was concentrated to dryness in vacuo to afford a syrup residue (60 g). From this residue, 25 g were subjected to CC on SiO2 200 mesh (200 g) and eluted with light petroleum and with an increasing amount of EtOAc until 80:20 (v/v). The fractions collected were 50 ml each. Similar fractions were combined and they were chromatographed on a PTLC (Kieselgel 60 PF 254) using Me2O: light
petroleum (98:2) to afford three flavonoid aglycones: ladanein 1 (500 mg), kaempferol-3,7,4’-trimethyl ether 2 (40 mg), and retusin 3 (30 mg).

Ladanein (6-hydroxy apigenol 7,4’-dimethyl ether) (1)
Yellow needles, m.p. 207°C (lit. 205°C) (Barberan et al., 1985). UV \( \lambda_{\text{max}} \) (MeOH) 330, 284, 214; (+NaOMe) 398, 318, 214; (+AlCl\(_3\)) 358, 300, 210; (+AlCl\(_3\)/HCl) 355, 300, 214, 210; (+NaOAc) 330, 300, 210; (NaOAc/H\(_3\)BO\(_3\)) 334, 300, 210; EIMS \( m/z \) (% rel.int) 314.2 (M\(^+\), 100), 296.1 [(M-CH\(_3\)]\(^+\), 52], 285.1 [(M\(^+\)-CH\(_3\)]\(^+\), 13], 268.1 (61), 240.1 (3), 182 (6), 152.0 (9). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \( 3.89 \) (3H, s, OCH\(_3\)), \( 4.0 \) (3H, s, OCH\(_3\)), \( 6.59 \) (2H, s, H-3 and H-8), \( 7.15 \) [2H, dd (J = 2 and 8 Hz) H-3’ and H-5’], 8.0 [2H, dd (J = 2 and 8 Hz) H-2’ and H-6’], 12.59 (1H, brs, 5-OH).

Kaempferol 3,7,4’-trimethyl ether (2)
Yellow needles, m.p. 143°C (lit 145–147°C) (Imre et al., 1988; Jaipetch et al., 1983). UV \( \lambda_{\text{max}} \) (MeOH) 345, 226, 210; (+NaOMe) 355, 280, 210; (+AlCl\(_3\)) 394, 344, 300, 274, 210; (+AlCl\(_3\)/HCl) 394, 344, 300, 274, 210; (+NaOAc) 345, 264, 210; (+NaOAc/H\(_3\)BO\(_3\)) 345, 264, 210; EIMS \( m/z \) (% rel.int): 328.1 (M\(^+\), 100), 314 [M-CH\(_3\)]\(^+\), 179 (10), 165 (24), 150 (15). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \( 3.85 \) (3H, s, OCH\(_3\)), \( 3.89 \) (3H, s, OCH\(_3\)), \( 3.91 \) (3H, s, OCH\(_3\)), \( 6.34 \) [1H, d (J = 8Hz) H-6], 6.47 [1H, d (J = 2Hz) H-8], 7.03 [2H, dd (J = 2.5 and 8.5 Hz) H-3’ and H-5’], 8.09 [2H, dd (J = 2.5 and 8.5 Hz) H-2’ and H-6’], 11.57 (1H, brs, 5=OH).

Retusin (Quercetin 3,7,3’,4’-tetramethyl ether) (3)
Yellow needles, m.p. 153°C (lit. 160–161°C) (Jaipetch et al., 1983) UV \( \lambda_{\text{max}} \) (MeOH) 337, 210; (+NaOMe) 320, 210; (+AlCl\(_3\)) 384, 356, 300, 276; (+AlCl\(_3\)/HCl) 285, 356, 300, 276; (+NaOAc) 337, 270, 210; (+NaOAc/H\(_3\)BO\(_3\)) 337, 270, 210; EIMS \( m/z \) (% rel.int): 358 (M\(^+\), 100), 343 [(M-CH\(_3\)]\(^+\), 179 (10), 165 (24), 150 (15). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \( 3.81 \) (3H, s, OCH\(_3\)), \( 3.87 \) (3H, s, OCH\(_3\)), \( 3.88 \) (3H, s, OCH\(_3\)), \( 3.93 \) (3H, s, OCH\(_3\)), 6.43 (2H, s, H-8), 7.65 [1H, d (J = 8Hz) H-5’], 7.73 [1H, dd (J = 2.5 and 8.5 Hz) H-6’], 8.06 [1H, d (J = 2.5 Hz) H-2’], 12.59 (1H, s, 5-OH).

RESULTS AND DISCUSSION
Chromatography of the plant afforded one flavone and two flavonols, namely, ladanein 1, kaempferol-3,7,4’-trimethyl ether 2 and retusin 3. The identity of the isolated flavonoids was confirmed through interpretation of their physical and spectral characters, namely, m.p., UV, MS and \(^1\)H-NMR and comparison with the reported data (Barberan et al., 1985; Collado et al., 1985; Imre et al., 1984; Jaipetch et al., 1983).

To our knowledge, this is the first report on the isolation of kaempferol 3,7,4’-trimethyl ether 2 and retusin 3 from the genus Ballota. Ladanein 1 was previously...
isolated and identified from *Ballota hirsuta* (Ferreres et al., 1986).

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REFERENCES


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