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AN AROMATIC COMPOUND from *CENTAUREA PTOSIMOPAPPOIDES*

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SUMMARY

Centaurea ptosimopappoides was previously investigated by our group and the presence of two new triterpenes were reported. The rare occurrence of this type compounds in the plants prompted us to further investigation of *Centaurea ptosimopappoides*. In this work we report the isolation and structure determination of an aromatic glycoside which was found in the genus *Centaurea* for the first time. The structure of the compound was determined by spectral methods.

ÖZET

Centaurea ptosimopappoides bitkisi daha önce grubumuz tarafından çalışılmış ve iki yeni triterpen bileşiğinin moleküler yapıları açıklanmıştır. Bu tip bileşiklerin bitkilerde ender bulunması nedeniyle *Centaurea ptosimopappoides* türünü kimyasal bakımdan tekrar inceledik. Bu çalışmamızda aromatik glikozit yapısındaki bir bileşik elde ettik. Bu bileşik bir *Centaurea* türünden ilk kez elde edilmektedir. Bileşiğin yapı tayininde spektroskopik yöntemlerden yararlanılmıştır.

Key words: *Centaurea ptosimopappoides;* Compositae; aromatic glycoside.

INTRODUCTION

The genus *Centaurea* contains various types of compounds, therefore its has been the subject of many chemical investigations. Sesquiterpene lactones,

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acetylenes, flavonoids and coumarins are the main secondary metabolites of this genus. In a part of our continuing research on the chemistry of *Centaurea* species, we have studied *Centaurea ptosimopappoides* Wagenitz, a plant endemic to Turkey, which is widely distributed in the southern part of Anatolia. Previous investigation with the roots of this species, we reported the presence of two new triterpenoids of which one was a baccharane type triterpene, occurs rare in nature (2), and the other was a new derivative of hopane type triterpene (3). In addition, from the aerial parts several sesquiterpene lactones, a coumarin and sterols were also isolated (1). In this present work, we describe the isolation and identification of a phenylpropane glycoside (**1**) from the aerial parts of *Centaurea ptosimopappoides*. The structure of the compound was determined by spectroscopic methods including 2D NMR techniques.

RESULTS AND DISCUSSION

Compound 1, isolated as white crystalls, was assigned the molecular formula $C_{17}H_{24}O_9$ by EIMS spectroscopy which showed a molecular ion peak at *m/z* 372 and a base peak at *m/z* 210 [M^+-OGlc] was due to the aglycone unit.

The IR spectrum showed strong absorptions of hydroxy group(s) (3563 cm^{-1}), aromaticity (1647, 1588, 1509 cm^{-1}) and C-O absorptions (1239, 1110, 1028 cm^{-1}). The 200 MHz ^1H NMR spectrum (Table 1) in CD_3OD showed a broad singlet at δ 6.74 (H-2 and H-3) for two equivalent protons of a tetrasubstituted aromatic ring, two ethylenic protons at δ 6.54 (dd, J=1 and 16 Hz, H-7) and 6.32 (dt, J=6 and 16 Hz, H-8) and a methylene group protons at δ 4.21 (2H, dd, J=1 and 16 Hz, H-$9_{a,b}$). The spectrum also showed signals of a sugar moiety. The sugar part was identified after acid hydrolysis of **1** as glucose by TLC. The anomeric proton appeared at δ 4.84 as a doublet and the coupling constant of this proton (J=7.4 Hz) was indicative for the orientation of the glycosidic linkage to be β. The ^{13}C NMR (APT) spectrum exhibited 17 signals due to methoxyl, an oxymethylene, two ethylenic and six aromatic carbon atoms, and six signals for a β-D-glucopyranosyl moiety (Table 1). The proton-bearing carbons were deduced by a HETCOR spectrum and all of the multiplicities were assigned by DEPT spectra. The propenoxy group was determined by ^1H-^1H COSY and spin-decoupling experiments. The two ethylenic protons (H-7 and H-8) were correlated with each other with coupling constant J= 16 Hz, and correlated with each proton of the oxymethylene group (H-$9_{a,b}$) with coupling constants

Table 1: ^1H and ^{13}C NMR spectral data of compound **1** (200 MHz)*

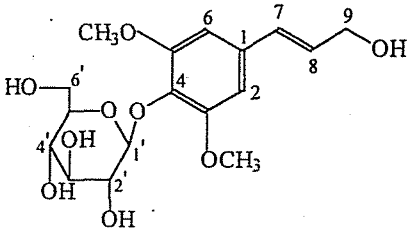
H	1†	1a††	^{13}C**	1†	1a††
2,6	6.74 s	6.60 s	1	135.3 s	133.6 s
7	6.54 d (16)	6.56 d (16)	2,6	105.4 d	104.0 d
8	6.32 dt (6, 16)	6.21 dt (6.5, 16)	3,5	154.3 s	153.1 s
$9_{a,b}$	4.21 dd (1, 6)	4.71 dd (1.2, 6)	4	137.2 s	135.6 s
OCH_3	3.84x2	3.83x2	7	131.3 d	133.1 d
Glucosyl			8	130.0 d	123.3 d
1'	4.84 d (7.4)	5.06 d (7.8)	9	63.5 t	64.9 t
2'	3.30 m	ca 5.24 m	OCH_3	57.0 q	56.3 q
3'	ca 3.41 m	ca 5.24 m	Glucosyl		
4'	ca 3.44 m	ca 5.24 m	1'	104.9 d	101.2 d
5'	3.21 m	3.69 m	2'	75.7 d	68.5 d
6_a	3.65 dd (5, 12)	4.25 dd (5, 12)	3'	78.3 d	72.0 d
6_b	3.78 dd (2.5, 12)	4.11 dd (2.5, 12)	4'	71.3 d	73.2 d
OAc			5'	77.8 d	72.0 d
			6	62.5 t	62.3 t
			OAc		20.7x2
					21.0x2
					21.8
					169.4x2
					170.4
					170.6x2

* J values (Hz) in parenthesis, TMS as internal standard.
** multiplicities were assigned by DEPT spectra.
† in $CDCl_3$
†† in CD_3OD.

J= 1 and *J*= 2 Hz, respectively. The coupling constant between H-7 and H-8 (*J*= 16 Hz) indicated the *trans*-orientation of the ethylenic protons. The chemical shifts of C-7 (δ_c 131.3), C-8 (δ_c 130.0) and C-9 (δ_c 63.5), as seen in ^{13}C NMR spectrum, indicated that C-7 was linked to the aromatic ring.

The location of the glucosyl moiety was deduced by acetylation of compound **1.** After acetylation with Ac_2O-pyridine in room temperature, pentaacetyl derivative of **1** was obtained. Acetylated derivative **(1a)** gave a better resolved ^1H and ^{13}C NMR spectra in $CDCl_3$ (Table 1). The ^1H NMR spectrum showed 5 acetoxymethyl singlets and moreover, oxymethylene proton signal (H_2-9) were shifted from δ 4.21 to 4.71 indicating that the free hydroxy group located to C-9.

Consequently, compound **1** was characterized as *3,5-dimethoxycinnamyl alcohol-4-O-β-Dglucopyranoside* (syringin). Although this compound was previously reported by Sano, K. and co-workers from *Kalopanax pictus* (2), this is the first report the presence of syringin in a *Centaurea* species.



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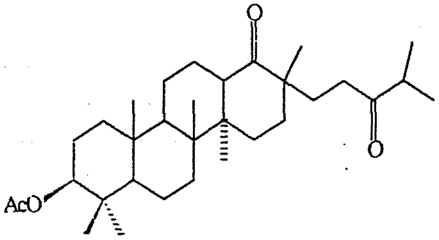

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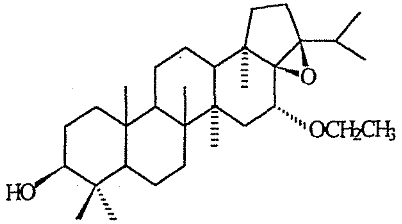

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EXPERIMENTAL

General Experimental Procedures- ^1H (200 MHz) and ^{13}C (50.32 MHz) NMR spectra were recorded with a Bruker AC L instrument and chemical shifts are given on the δ (ppm) scale, TMS as an internal standard; IR spectra were measured with Perkin Elmer 1615 FT apparatus; MS were run with VG Zabspec GC-MS Instrument.

Plant Material- *Centaurea ptosimopappoides* Wagenitz was collected from Adana (Karsantı) in July 1991. A voucher speciemen is deposited in the Herbarium of Faculty of Pharmacy, University of Istanbul (ISTE 43290).

Extraction and isolation- The aerial parts (900 g) were macerated with EtOH for 48 hours and evaporated *in vacuo* to a small volume. The crude extract (22 g) was chromatographed on a silica gel column (300 g, 70-230 mesh) and eluted with petrol ether and gradient of petrol ether-Et_2O (0-100%) followed by EtOH. The similar fractions were combined and five fractions were obtained. Each fraction was rechromatographed on small columns. Compound **1** was obtained from fraction 5 and purified by repeated preparative TLC. The yield was 18 mg.

3,5-dimethoxycinnamylalcohol-4-O-β-D-glucopyranosid (syringin): Colorless needles from MeOH, mp 190°C [lit(2) 192-193]; IR, 3852, 3563, 3022, 2987, 2840, 1647, 1588, 1509, 1458, 1419, 1350, 1193, 1186, 1110, 1076, 985, 965, 843, 784 cm^{-1}; EIMS *m/z* (rel. int.) 372 [M^+, $C_{17}H_{24}O_9$] (2), 210 [M^+-glucose] (94), 194 (16), 182 (14), 168 (36), 162 (100), 149 (29), 71 (21), 69 (19).

Acetylation of 1: 5 mg of **1** was acetylated with 2 ml of Ac_2O-pyridine (1:1) at room temperature for 4 hrs, **1a** was obtained. EIMS *m/z* 582 [M^+, $C_{27}H_{34}O_{14}$] (4), 511 (7), 331 (64), 271 (13), 252 (51), 169 (100), 149 (25), 97 (26), 81 (22), 69 (9).

Hydrolysis of 1: 5 mg of **1** was treated with 2 ml of 2N HCl under reflux. Sugar part was identified as glucose on TLC silica gel plates (EtOAc-H_2O-MeOH-AcOH/13:3:3:4) by comparison with standart sugar samples after treating with anilinphthalate reagent.

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