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FLAVONOIDS OF *TANACETUM PRAETERITUM* SUBSP. PRAETERITUM

N. GÖREN*

SUMMARY

A further investigation on *Tanacetum praeteritum* subsp. *praeteritum* which is endemic in Turkey afforded five known flavonoids: apigenin, 6-hydroxyapigenin 6-methyl ether, luteolin, 6-methoxy luteolin and quercetagetin 3,7-dimethyl ether (tomentin). Their structures were identified by UV, ^{1}H NMR, EIMS and comparision on TLC with authentic compounds.

This is the first report on the flavonoids of *Tanacetum praeteritum* subsp. *praeteritum.*

ÖZET

Türkiye'de yetişen *Tanacetum* türlerinin kimyasal yapılarının araştırılması ile ilgili proje kapsamında son olarak *Tanacetum praeteritum* subsp. *praeteritum* bitkisinin kimyasal yapısı araştırılmış ve bu bitkiden eudesmanolide yapısında seskiterpen laktonlar elde edilmiştir [1]. Polar fraksiyonlarla yapılan bu çalışmada ise aynı bitkiden 5 bilinen flavonoidal madde, apigenin (**1**) [2], 6-

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(*) TUBITAK, Marmara Research Center, Institute For Basic Sciences, Department of Chemistry, 41470 Gebze-Kocaeli, Turkey.

hidroksiapigenin 6-metil eter (**2**) [3], luteolin (**3**) [4], 6-hidroksiluteolin 6-metil eter (**4**) [5] ve kersetagetin 3, 7-dimetil eter (tomentin) (**5**) [6] elde edilmiştir. Flavonoidlerin yapıları ^{1}H NMR, UV ve EIMS gibi spektral yöntemlerin yanı sıra İTK'de bilinen maddelerle yapılan kıyaslamalarla tayin edilmişlerdir. *Tanacetum praeteritum* subsp. *praeteritum* türünün flavonları ilk defa tarafımızdan incelenmiştir.

INTRODUCTION

Tanacetum species are wide spread and important medicinal plants found throughout the world. *Tanacetum praeteritum* subsp. *praeteritum* which grows on rocks and limestone slopes 1200-2000 m is one of the endemic *Tanacetum* species in Turkey. In a previous work with this plant we have isolated 15 eudesmaolide type of sesquiterpene lactones [1]. In this study the author wishes to report the flavonoids of this species. The aerial part of *Tanacetum praeteritum* subsp. *praeteritum* afforded the flavonoids: apigenin (**1**) [2], 6-hydroxyapigenin 6-methyl ether (**2**) [3], luteolin (**3**) [4], 6-hydroxy luteolin 6-methyl ether (**4**) [5], quercetagenin 3,7-dimethyl ether (tomentin) (**5**) [6].

EXPERIMENTAL

General: CC was carried out on Kieselgel 60 (0.063-0.200 mm, Merck) and Sephadex LH-20 (Pharmacia), TLC was performed on precoated silica gel 60 F_{254}, 0.2 mm plates (Merck), spots were detected under UV and spraying acidified ceric sulphate following by heating and also detected by exposuring NH_3 vapurs and spraying NA reagent. ^{1}H NMR were recorded on the Bruker AC-200L spectrometer with $CDCl_3$ as solvent and TMS as int. standard operating at 200 MHz. EIMS and HRMS spectra were recorded on the VG Zabspec instrument at TUBITAK.

Plant Material: *Tanacetum praeteritum* (Horwood) Heywood subsp. *praeteritum* was collected from the south-west part of Turkey (Fethiye). A voucher specimen (ISTE 64370) is deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul, Turkey.

Extraction and Isolation: Dried and powdered aerial parts (4.9 kg) were extracted with petrol (40-60°), $CHCl_3$ and EtOH respectively. The extracts were

combined and treated with MeOH. The residue was applied to a silica gel column and eluted with petrol, a gradient of Et_2O being added up to 100% followed by MeOH. The fractions from CC were further separated by preparative TLC and/or Sephadex LH-20. Thus 15 mg **1,** 400 mg **2,** 20 mg **3,** 330 mg **4** and 35 mg **5** were obtained from the most polar fraction.

Apigenin (1): Yellow, amorphous compound ^{1}H NMR given in Table 1. UV given in the Table 2. EIMS *m/z* (rel. int.): 270 ($C_{15}H_{10}O_5$) [M^+] (73), 242 [M-CO]$^+$ (14), 153 [$C_7H_5O_4$]$^+$ (47), 124 [$C_6H_4O_3$]$^+$ (45), 121 [$C_7H_5O_2$]$^+$ (88), 118 [C_8H_6O]$^+$ (32), 99 (94), 87 (93), 73 (85), 57 (100).

6-Hydroxyapigenin 6-methyl ether (2): Yellow, amorphous compound. ^{1}H NMR given in the Table 1. UV given in the Table 2. EIMS *m/z* (rel. int.): 301 [M+1]$^+$ (86), 300 ($C_{16}H_{12}O_6$) [$M]^+$ (85.5), 285 [301-CH_3]$^+$ (76), 272 [M-CO]$^+$ (39), 271 [M-1-CO]$^+$ (51), 257 [272-CH_3]$^+$ (66), 167 [$C_7H_3O_5$]$^+$ (44), 139 [$C_6H_3O_4$]$^+$ (43), 119 (56), 105 (53), 69 (100).

Luteolin (3): Yellow, amorphous compound. ^{1}H NMR given in the Table 1. UV given in the Table 2. HRMS *m/z* (rel. int.): 286.0409 ($C_{15}H_{10}O_6$) [$M]^+$ (100), 258 [M-CO]$^+$ (32), 153 [$C_6H_5O_4$]$^+$ (66), 137 [$C_7H_5O_3$]$^+$, 134 [$C_8H_6O_2$]$^+$ (41), 124 [$C_6H_4O_3$]$^+$ (22), 69 (59).

Table 1: ^{1}H NMR data of compounds **1-5** (CDCl3+CD3OD, 200 MHz, TMS as internal standard)

	1	2	3	4	5
H-3	6.53 s	6.53 s	6.53 s	6.51 s	–
H-6	6.28 dd	–	6.24 d	–	–
H-8	6.45 dd	6.53 s	6.50 d	6.55 s	6.40 s
H-2'	7.80 dd	7.80 dd	7.49 d	7.38 d	7.76 d
H-3'	6.95 dd	6.92 dd	–	–	–
H-5'	6.95 dd	6.92 dd	6.88 d	6.93 d	6.84 d
H-6'	7.80 dd	7.80 dd	7.46 dd	7.36 dd	7.66 dd
OCH_3	–	3.83 s	–	3.93 s	3.94 s
OCH_3	–	–	–	–	3.79 s

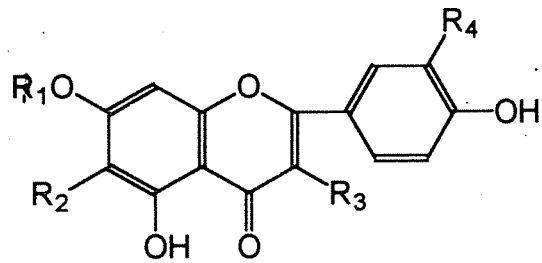
J (Hz): **1-4:** 6,8 = 2', 6' = 3', 5' = 2, 2', 3' = 5', 6' = 8.5

Table 2: UV spectral data of compounds **2-4.**

	2	3	4	5
MeOH	329 274	345 263 sh	347 274	352 285 sh
NaOMe	382 321 272	410 330 274	400 330 264	400 262
$AlCl_3$	356 299 sh 275	390 360 sh 274	424 328 272	440 340 295 sh 281
$AlCl_3$ + HCl	347 299 275	355 274	364 294 283	381 360 274
NaOAc	350 305 274	360 374	381 320 271	400 360 274
NaOAc + H_3BO_3	332 274	375 274	371 273	380 280 sh 265

6-Hydroxyluteolin 6-methyl ether (4): Yellow, amorphous compound. ^{1}H NMR given in Table 1. UV given in the Table 2. EIMS *m/z* (rel. int.): 316 ($C_{16}H_{12}O_7$) $[M]^+$ (63), 301 $[M\text{-}CH_3]^+$ (39), 273 $[301\text{-}CO]^+$ (24), 183 $[C_8H_7O_5]^+$ (13), 167 $[C_7H_3O_5]^+$ (23), 137 $[C_7H_5O_3]^+$ (35), 129 (45), 97 (52), 83 (58), 69 (75).

***Quercetagetin 3, 7- dimethyl ether (tomentin)* (5):** Yellow, amorphous compound. ^{1}H NMR given in the Table 1. UV given in the Table 2. EIMS *m/z* (rel. int.): 347 $[M+1]^+$ (42), 346 $[C_{17}H_{14}O_8]^+$ $[M]^+$ (47), 332 $[347\text{-}CH_3]^+$ (78), 304 $[332\text{-}CO]^+$ (61), 183 $[C_8H_7O_5]^+$ (42), 167 $[C_7H_3O_5]^+$ (73), 153 (57), 150 (76), 135 (100), 121 (99), 105 (72), 80 (60), 69 (64), 57 (79).



1 : $R_1=R_2=R_3=R_4=H$
2 : $R_1=R_3=R_4=H$ $R_2=OCH_3$
3 : $R_1=R_2=R_3=H$ $R_4=OH$
4 : $R_1=R_3=H$ $R_2=OCH_3$ $R_4=OH$
5 : $R_1=CH_3$ $R_2=R_4=OH$ $R_3=OCH_3$

Şekil 1

RESULTS AND DISCUSSION

Compound **1** was purple under UV light (366 nm) on cellulose plates and turned to yellow after exposure NH_3 vapours and gave again yellow colour with NA reagent. ^1H NMR spectrum (Table 1) and UV spectral data (Table 2) of **1** indicated apigenin. EIMS spectrum of the compound confirmed the structure (see experimental).

The compound **2** was purple under UV light (366 nm). Its colour was also purple with NH_3 vapours and NA reagent. ^1H NMR (Table 1) and UV spectral data (Table 2) indicated 6-hydroxyapigenin 6-methyl ether. Its EIMS spectrum confirmed the structure.

The compound **3** was purple under UV light and its colour turned to yellow with NH_3 vapours and to pale orange with NA reagent. ^1H NMR (Table 1), UV (Table 2) and HRMS spectral (See Experimental) indicated that it was luteolin.

The compound **4** was purple under UV light and didn't change its colour with NH_3 vapours and NA reagents. According to its ^1H NMR (Table 1), UV (Table 2) and EIMS (See Experimental) data it was 6-methoxy luteolin.

The compound **5** was purple under UV light and with NH_3 vapours. Its colour turned to red-brown with NA reagent. Its structure was decided as quercetagenin 3, 7-dimethyl ether (tomentin) by means of its ^1H NMR (Table 1), UV spectra (Table 2) and EIMS spectrum (See exper Table 1).

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