nm $\Delta\varepsilon_{290} = +0.19$, $\Delta\varepsilon_{230} = +0.50$ ^{1}H NMR and ^{13}C NMR see Tables 1 and 2

1,5-*Dioxo-2-oxa*-3(S),9(R)-*diacetyl*-4(R)-8(R)-*dimethylhexahydroindane* (**1b**) Colourless oil (200 mg) $C_{14}H_{18}O_7$. $[\alpha]_D^{25} = +21.35°$ ($CHCl_3$, *c*2.13) IR ν_{max}^{film} cm^{-1}: 3500 (w), 1810, 1790, 1750, 1720, 1375, 1220, 1180, 1150, 1000. CD (MeOH) nm $\Delta\varepsilon_{290} = +0.27$, $\Delta\varepsilon_{230} = +0.45$. ^{1}H NMR and ^{13}C NMR: see Tables 1 and 2

1,5-*Dioxo-2-oxa*-3(R),9(R)-*diacetyl*-4(R),8(S)-*dimethylhexahydroindane* (**2a**) Colourless oil. (24 mg) $C_{14}H_{18}O_7$ $[\alpha]_D^{25} = +34.8°$ ($CHCl_3$; *c*2.4) IR ν_{max}^{film} cm^{-1}. 3450 (w), 1820, 1790, 1760, 1730, 1470, 1390, 1250, 1200, 1130, 1000 CD (MeOH) nm· $\Delta\varepsilon_{290} = +0.64$, $\Delta\varepsilon_{230} = +1.39$. ^{1}H NMR and ^{13}C NMR see Tables 1 and 2

1,5-*Dioxo-2-oxa*-3(S),9(R)-*diacetyl*-4(R),8(S)-*dimethylhexahydroindane* (**2b**) Colourless oil (40 mg) $C_{14}H_{18}O_7$. $[\alpha]_D^{25} = +17.47°$ ($CHCl_3$, *c*1.75). IR ν_{max}^{film} cm^{-1}: 3500 (w), 1800, 1770, 1760, 1720, 1480, 1390, 1220, 1180, 990, CD (MeOH) nm $\Delta\varepsilon_{290}$ +0.15, $\Delta\varepsilon_{230}$ +0.51 ^{1}H NMR and ^{13}C NMR see Tables 1 and 2

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A SESQUITERPENE-COUMARIN ETHER AND AN ACETYLENIC COMPOUND FROM *TANACETUM HETEROTOMUM*

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Key Word Index—*Tanacetum heterotomum*, Compositae, sesquiterpene-coumarin ethers, acetylenic compounds, spiroketal-enoletherpolyines

Abstract—The aerial parts of *Tanacetum heterotomum* afforded in addition to known compounds, a new spiroketalenoletherpolyine and a new sesquiterpene-coumarin ether. The structures were elucidated by spectral methods.

INTRODUCTION

Tanecetum species have been investigated for their sesquiterpene lactones and other compounds. Since *Tanacetum heterotomum* Bornm. is an endemic plant in Turkey, it was investigated in order to find its compounds.

RESULTS AND DISCUSSION

The aerial parts of *T. heterotomum* contain known compounds, taraxasterol, lupeyl acetate, epifriedenol, isofraxidin [1], 6,7,8-trimethoxycoumarin, 6′,7′-dimethoxyfeselol (**1**) [2], a C_{14} acetylenic compound (**2**) [3], and two new compounds, a spiroketalenoletherpolyine (**3**) and a sesquiterpene-coumarin ether (**4**). The structures of the compounds were established by spectral methods.

The IR spectrum of **3** showed an acetylene band at 2160 cm^{-1}, an ester band at 1740 and 1260 cm^{-1} and unsaturation at 1680 cm^{-1}. The high resolution mass spectrum gave a molecular peak at *m/z* 300.136 ($C_{18}H_{20}O_4$). Although the ^{1}H NMR spectrum of **3** was very close to that of spiroketalenoletherpolyine (**5**) previously found in *Tanacetum parthenium* [4], they were not identical (Table 1) To understand the differences,

Table 1 ^{1}H NMR spectrum of compounds **3** and **5** (400 MHz, $CDCl_3$)

H	3	5
1β	4 25 *dd*	4 38 *dd*
1α	4 29 *dd*	4 04 *ddd*
2α	5 38 *dddd*	5 49 *dddd*
3β	2 35 *dd*	2 74 *dd*
3α	2 41 *dd*	2 28 *ddd*
5	6 12 *dd*	6 21 *dd*
6	6 29 *d*	6 27 *d*
8	4 54 *br s*	4 67 *br s*
13	1.97 *d*	2 00 *d*
OCOR	2 50 *d*	2 21 *d*
	2 22 *tqq*	2 10 *tqq*
	1 02 *d*	
		0 97 *d*
	1 01 *d*	

J(Hz) Compound **3** 1α,1β = 10, 1β,2α = 2 5, 1α,2α = 5, 2α,3α = 6, 2α,3β = 6, 3α,3β = 14, 5,6 = 5 5, 5,8 = 0 6, 8,13 = 1, isoval 2,3 = 3,4 = 3,5 = 7

Compound **5** 5,6 = 5 5, 5,8 = 8,13 = 1, isoval 2″,3″ = 3″,4″ = 3″,5″ = 7

Table 2 NOE experiment with compound **3** (400 MHz, $CDCl_3$)

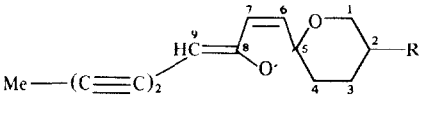
Irradiated protons	Affected protons
H-5	H-1 (8%)
H-2	H-3 (6%), H-1 (8%)
H-6	H-8 (15%)
H-1	H-2 (10%)

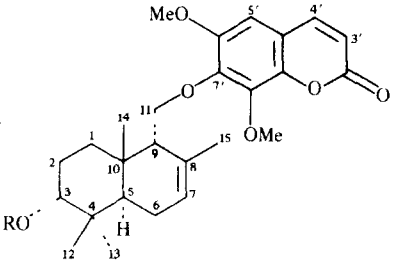
NOE experiments were performed (Table 2) The irradiation of H-1α caused NOE with H-2, the irradiation of H-2 enhanced H-3α and H-1α. Thus the NOE experiments confirmed that the ester group has the β-configuration, while it was α in compound **5**.

The IR spectrum of **4** showed a ketone band at 1719 cm^{-1}, ester bands at 1740 (sh), 1280 cm^{-1}, and the aromatic bands at 3030, 1560, 1510, 1480, 750 cm^{-1}. The high resolution mass spectrum of **4** gave a molecular ion peak at *m/z* 540 272 ($C_{31}H_{40}O_8$). The ^{1}H NMR spectrum exhibited methyl singlets at δ1 22 (H-12), 1.17 (H-13), 1 20 (H-14) and 2 08 (H-15) A double doublet at δ4 64 for H-3 indicated an ester group and a broadened singlet at δ5.89 revealed the olefinic proton at C-7 The typical coumarin ring doublets were observed at δ7 61 (H-4′) and 6.36 (H-3′). A singlet at δ6.68 (H-5′) and two methoxyl singlets at δ3 99 and 3 94 showed the presence of two methoxyl groups on a coumarin ring. These signals indicated an isofraxidin moiety The two double doublets at δ4.38 and 4 25 indicated the C-11 protons and the signals at δ0.97 (*d*, H-5″ and H-4″), 2.23 (*d*, H-2″), 2 14 (*tqq*, H-3″) an isovalerate moiety as the ester group The protons were assigned by spin-decoupling experiments The double doublet at δ4.64 (H-3) collapsed to a doublet when H-2 was irradiated The irradiation of H-9 at δ2 04 converted the double doublet at δ4.38 and 4.25 (H-11 and H-11′) to doublets and the irradiation of H-2 at δ1 8 and H-1 at δ2 4 collapsed the triple doublet at δ1 45 (H-2′) to a double doublet

EXPERIMENTAL

Tanacetum heterotomum was collected from central Turkey (Sivas) A voucher (185 225) is deposited in the Herbarium of Faculty of Science and Literature, University of Cumhuriyet (Sivas, Turkey) Dried and powdered aerial parts of *Tanacetum heterotomum* (2 5 kg) were extracted with Et_2O–petrol (1 2) and the extract was treated with MeOH to remove long chain saturated hydrocarbons, the residue was roughly separated by CC (silica gel), then the fractions were further separated by TLC Thus 10 mg taraxesterol, 35 mg lupeyl acetate, 30 mg epifriedelinol, 6 mg isofraxidin, 8 mg 6,7,8-trimethoxycoumarin, 5 mg **1**, 8 mg **2**, 6 mg **3**, 25 mg **4** were obtained





2 R = βOAc
3 R = βO*i*Val
5 R = αO*i*Val

1 R = H
4 R = *i*Val

Table 3. ^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$)

H	
1	2.4 *m*
2	1.8 *ddd*
2′	1.45 *ddd*
3	4.635 *dd*
7	5.885 *br s*
9	2.04 *br t*
11	4.38 *dd*
11′	4.25 *dd*
12	1 22 *s*
13	1.17 *s*
14	1.20 *s*
15	2.075 *d*
3′	6 36 *d*
4′	7.605 *d*
5′	6.68 *s*
OMe	3.985 *s*
OMe	3.94 *s*
OCOR	0 97 *d*
	1.21 *d*
	2.23 *d*
	2.14 *tqq*

J(Hz): 1,2′ = 3 5, 1,2 = 7 5; 2,2′ = 13; 2′,3 = 13; 2,3 = 5, 11,11′ = 10; 9,11 and 11′($W_{1/2}$) = 4, 3′,4′ = 10, Oival. 2″,3″ = 3″,4″ = 3″,5″ = 4″,5″ = 7

2β-Isovaleryloxy-8Z-C_{13} spiroketalenol ether (**3**). Amorphous, colourless compound. IR $\nu_{max}^{CHCl_3}$ cm^{-1} 2160, 1740, 1260, 1680 ^{1}H NMR given in Table 1. MS *m/z* (rel. int.): 300 136 $[M]^+$ ($C_{18}H_{20}O_4$) (58), 198 $[M-C_4H_9CO_2H]^+$ (65), 185 (50), 169 (46), 85 $[C_4H_9CO]^+$ (86), 57 $[85-CO]^+$ (100)

6-Oxo-drimenol-3α-isovalerate-isofraxidin-ether (**4**). Amorphous, colourless compound IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3030, 2940, 2840, 1730, 1710, 1600, 1560, 1510, 1480, 1450, 1360, 1280, 1120, 1040, 750 ^{1}H NMR given in Table 3 MS *m/z* (rel int.): 540 272 $[M]^+$ ($C_{31}H_{40}O_8$) (2.8), 439 $[M-OCOC_4H_9]^+$ (1.3), 319 $[M-a]^+$ (2.3), 222 [a + 1] (100), 199 (28), 85 (58), 69 (57), 57 (68), 55 (66).

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