Phytochemistry, Vol 28, No 4, pp 1263 1264, 1989
Printed in Great Britain

0031 9422/89 $3 00+0 00
Pergamon Press plc

TWO SESQUITERPENE FUCOPYRANOSIDES FROM *CARTHAMUS MAREOTICUS*

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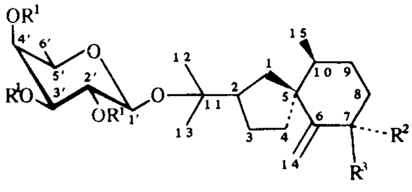
(*Received in revised form* 28 *September* 1988)

Key Word Index—*Carthamus mareoticus*, Compositae, sesquiterpene, fucopyranosides

Abstract—The aerial part of *Carthamus mareoticus* afforded, in addition to known triterpenes, two new epimeric fucopyranosides of a sesquiterpene alcohol The structures were elucidated by spectroscopic methods.

INTRODUCTION

The genus *Carthamus* has *ca* 20 species in the Mediterranian, and in southwest and central Asia; it is placed in the tribe Cynareae, subtribe Centaureinae The chemistry of the roots resembles that of the large genus *Centaurea* [1], but so far the few reports on the aerial parts do not show such similarities. In addition to flavones, some fucopyranosides of sesquiterpene alcohols have been isolated [2–4] and various other compounds are present in the best investigated species *Carthamus tinctorius* [5]. However, no guaianolides, widespread in the genus *Centaurea*, have been reported. We now have studied the polar fraction of *Carthamus mareoticus* Del. [= *Carduncellus mareoticus* (Del) Hanelt] The results are discussed in this paper



	1	2	3	4
R^1	H	H	Ac	Ac
R^2	H	OH	H	OAc
R^3	OH	H	OAc	H

RESULTS AND DISCUSSION

The alcoholic extract of the aerial parts afforded stigmasterol, traxasterol, β-sitosterol β-D-glucoside, and two glycosides which turned out to be the β-fucopyranosides **1** and **2** Acetylation gave the tetraacetates **3** and **4**. The ^{1}H NMR spectra of **1** and **2** (Table 1) indicated the presence of glycosides, and were in part similar to that of the β-fucopyranoside of hinesol [2]. The corresponding tetra acetates **3** and **4** clearly showed that the compounds are epimeric allyl acetates which differed from the hinesol glycoside by the replacement of the olefinic methyl group by an exomethylene group, and the presence of an additional oxygen function in the α-position to the exomethylene group as could be established by spin decoupling. Further inspection of a model showed that the observed couplings required that compound **1** had a 7β-hydroxy group while **2** was the 7α-epimer In agreement with this assumption, in the tetraacetate **3** the coupling of H-7 and H-8 indicated a chair conformation with an axial C-10 methyl group while in the case of **4** no clear chair conformation is present with an equatorial C-10 methyl group NOEs between H-7 and H-1β, between H-14 and H-7 as well as between H-14′ and H-1β further confirmed this assignment The ^{13}C NMR data of **1** and **2**

Table 1 ^{1}H NMR data of compounds **1–4** ($CDCl_3$, 400 MHz)

H	**1**	**2**	**3***	**4**†
7	4 19 *dd*	4.28 *br*	5 26 *dd*	5 22 *dd*
10	1.70 *m*	1 60 *m*	1 74 *ddq*	1 53 *ddq*
12	1 24 *s*	1 22 *s*	1 21 *s*	1 18 *s*
13	1 21 *s*	1 15 *s*	1 14 *s*	1 10 *s*
14	5 12 *br s*	5 05 *br s*	4 93 *br s*	4 90 *br s*
14′	4 86 *br s*	4.83 *br s*	4 75 *br s*	4 84 *br s*
15	0.81 *d*	0 88 *d*	0 84 *d*	0 87 *d*
1′	4 37 *d*	4 33 *d*	4 61 *d*	4 60 *d*
2′	3 52 *dd*	3 58 *m*	5 14 *dd*	5.13 *dd*
3′	3 56 *m*	3 58 *m*	5 02 *dd*	5 01 *dd*
4′	3 71 *br d*	3 71 *br s*	5 21 *dd*	5 21 *br d*
5′	3 58 *br q*	3 54 *br q*	3 76 *dq*	3 76 *dq*
6′	1 29 *d*	1.30 *d*	1 19 *d*	1 19 *d*

J(Hz) 10, 15 = 7, 1′, 2′ = 7 5, 2′, 3′ = 10, 3′, 4′ = 3 5, 4′, 5′ = 1, 5′, 6′ = 6 5, compounds **1** and **3** 7, 8 = 11, 7, 8′ = 4, 9, 10 = 3, 9′, 10 = 5, compounds **2** and **4** 7, 8 = 3.5, 7, 8′ = 7.5, 9, 10 = 11

*OAc 2 17, 2 11, 2 02, 1 97 *s* H-1α 1 70 *dd*(*br*) (7, 13) H-1β 1.52 *dd* (13, 13)

†OAc 2 17, 2.07, 2 04, 1 97 *s* H-1α 1.79 *br dd* (8, 13.5) H-1β 1 29 *dd* (11, 13 5)

Table 2 ^{13}C NMR data of compounds **1** and **2** ($CDCl_3$, 100 6 MHz)

C	**1**	**2**	C	**1**	**2**
1	32 3	31 1	12	25 8	26.5
2	47 2	50 9	13	24 2	24 2
3	25 2	26 3	14	155 4	158 7
4	36 2	36 3	15	14 9	16 1
5	53 1	52 0	1′	97 2	97 2
6	104 1	101 4	2′	73 9	73 8
7	71 1	70 9	3′	72 1	72 0
8	27 5	30 5	4′	71.6	71 6
9	34 4	33 4	5′	70 2	70 1
10	35 1	39 8	6′	16 5	16 6
11	79 2	78 2			

(Table 2) also supported the proposed structure. The glycosides **1** and **2** are most probably formed by an allylic oxidation of hinesol β-fucopyranoside [2] The isolation of a fucopyranoside of a sesquiterpene alcohol may be of chemotaxonomic relevance as already these compounds have been detected in four different species

EXPERIMENTAL

^{1}H NMR, 400 MHz, TMS as internal standard, MS 70 eV The air-dried aerial parts (950 g), collected near Alexandria, Egypt, were extracted with 95% EtOH at room temp The resulting extract was separated by CC (silica gel) and further by repeated TLC (silica gel GF 254) Known compounds were identified by comparison of mp, IR, and ^{1}H NMR spectra with those of authentic materials Finally, 80 mg taraxasterol, 60 mg stigmasterol, 170 mg β-sitosterol β-D-glycoside, and 100 mg of a mixture of **1** and **2** were obtained HPLC of 30 mg of the mixture (RP 8, MeOH–H_2O, 7 3) afforded 15 mg **1** (*R*$_t$ 9 9 min) and 15 mg **2** (*R*$_t$ 12 3 min). Acetylation of **1** and **2** using Ac_2O and dimethyl aminopyridine at 20° for 1 hr gave the tetraacetates **3** and **4** Compound **1** and its 7α-epimer **2**, colourless gum, IR ν_{max}^{nujol} cm^{-1} 3400–3600 (OH), MS *m/z* (rel int) 384 $[M]^+$ (0 1) ($C_{21}H_{36}O_6$), 366 $[M-H_2O]^+$ (0 25), 308 $[C_{18}H_{28}O_4]^+$ (1 6), 220 $[C_{15}H_{24}O]^+$ (25), 203 $[C_{15}H_{23}]^+$ (86), 147 (54), 75 (100)

Acknowledgement—We thank Professor Boulos (Department of Botany, University of Cairo) for identification of the plant material

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Phytochemistry, Vol 28, No 4, pp 1264 1267, 1989
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0031 9422/89 $3 00+0 00
Pergamon Press plc

SESQUITERPENE LACTONES AND AN ELEMANE DERIVATIVE FROM *ONOPORDON CORYMBOSUM*

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(*Received in revised form* 29 *September* 1988)

Key Word Index - *Onopordon corymbosum*, Compositae, sesquiterpene lactones, elemanolides, ^{13}C NMR

Abstract—The aerial parts of *Onopordon corymbosum* afforded dehydromelitensin, its 8-(4-hydroxymethacryloil)-derivative and a related ester. The ^{13}C NMR of several natural and synthetic elemanolides are discussed

INTRODUCTION

From the genus *Onopordon* (Compositae, tribe Cynareae) several species have been investigated chemically Flavonoids [1] and sesquiterpene lactones [2] are the most characteristic isolated constituents In the present paper we report the isolation and structure elucidation of two elemanolides and an elemane derivative from the hitherto unstudied *Onopordon corymbosum* Willk The ^{13}C NMR spectral data for several natural and synthetic elemanolides are given also

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