Pergamon

PII: S0031-9422(96)00840-0

Phytochemistry, Vol. 45, No. 3, pp. 533–535, 1997

0031-9422/97 $17.00+0.00

CARVOTACETONE DERIVATIVES FROM THE EGYPTIAN PLANT *SPHAERANTHUS SUAVEOLENS*

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(*Received in revised form* 4 *November* 1996)

Key Word Index—*Sphaeranthus suaveolens*; Asteraceae; monoterpenes; carvotacetone derivatives.

Abstract—Extraction of the aerial parts of *Sphaeranthus suaveolens* afforded three new carvotacetone derivatives, together with four known compounds. The structures were elucidated by spectroscopic analysis. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The genus *Sphaeranthus* (tribe Inuleae, family Asteraceae) is distributed mainly in the tropical and subtropical areas of Africa, Asia and Australia. Few of its 40 or so species have been chemically studied. The main compounds reported so far are thiophenaecetylenes, inositol esters, sesquiterpene lactones and carvotacetone derivatives [1–6]. The importance of this genus stems from the wide use of its members in folk medicine in the treatment of skin infections, glandular swellings, bronchitis, jaundice and nervous depression [6, 7]. We have studied an Egyptian collection of *Sphaeranthus suaveolens* D. C.

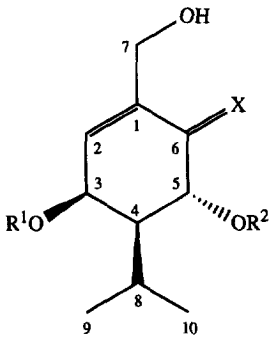
RESULTS AND DISCUSSION

The aerial parts of *Sphaeranthus suaveolens* afforded, in addition to 4-[5-(1,3-pentadinynyl)-2-thienyl]-3-butyne-1,2-diol [8], thymohydrochinone-2-*O*-β-glucopyranoside [1], five carvotacetone derivatives **1**, **2** [1], **3** [1, 2, 9] **4** and **5**. The main constituent was the carvotacetone **3**.

The ^{1}H and ^{13}C NMR spectral data of **1** (Tables 1 and 2) showed the presence of a carvotacetone derivative with an acetoxy group. The ^{1}H NMR spectral data were similar to those of 3β,5α,7-trihydroxycarvotacetone isolated previously from *S. bullatus* [1]. However, H-3 was shifted more downfield (δ 5.60) in **1**, and together with a new methyl signal characteristic for an acetate group (δ 2.09) led to the 3-*O*-acetyl derivative of the trihydroxycarvotacetone [1]. The stereochemistry of **1** was deduced from the coupling constants.

The molecular formula of **4** was established by high resolution FAB-mass spectrometry which revealed a molecular ion peak at *m/z* 341.3721; calculated for $C_{17}H_{25}O_7$ $[M+H]^+$, 341.3775. The ^{1}H and ^{13}C NMR spectra of compound **4** (Tables 1 and 2) were in part very similar to those of the corresponding main compound 5α-acetoxy-3β-tigloyloxy-7-hydroxycarvotacetone (**3**) [1, 2, 8]. The spectra indicated by typical signals that the tiglate residue was replaced by a (2α-hydroxyethyl)acrylate group.

The molecular formula of **5** was found to be $C_{22}H_{32}O_7$ by high-resolution FAB-mass spectrometry ($[M+H]^+$, m/z = 409). The loss of a molecule of acetic acid led to peak at *m/z* 349 (100%). The presence



	R^1	R^2	X
1	Ac	H	=O
2	H	Tig	=O
3	Tig	Ac	=O
4	(2–OH-Et) Acr	Ac	=O
5	Tig	Ac	α–OTig, H

Table 1. ^{1}H NMR spectral data of compounds **1**, **4** and **5** (400 MHz, $CDCl_3$, δ-values)

H	1	4	5	Multiplicity
2	6.96	6.99	6.07	*dt*
3	5.60 *d*	5.67 *d*	5.50 *dd*	
4	2.07	2.47	2.32	*ddd*
5	4.56	5.89	4.56	*d*
6	—	—	5.74	*d*
7	4.35 *br s*	4.33 *dt*	4.08 *dt*	
		4.28	4.04	
8	2.18	2.04	2.04	*dqq*
9	1.10	1.03	1.00	*d*
10	1.08	0.99	0.94	*d*
OCOR^1	2.09 *s*	6.29 *br s*	6.80 *br q* (2H)	
	—	5.91 *br d*	1.81 *br s* (6H)	
	—	4.71 *dq*	1.77 *br s* (6H)	
	—	1.44	—	*d*
OCOR^2	—	2.12	2.05	*s*

J [Hz]: 2,3 = 7; 2,7 = 2,7′ = 1; 3,4 = 3.5; 4,5 = 12; 4,8 = 4; 8,9 = 8,10 = 7; (compound **5**: 5,6 = 3.5); OTig: 3,4 = 7, (2-OH-Et)Acr: 3,4 = 1; 4,5 = 6.5.

Table 2. ^{13}C NMR spectral data of compounds **1** and **3–5** (100 MHz $CDCl_3$, δ-values)

C	1	3	4*	5*†‡	Multiplicity§
1	138.14	139.29	139.62	139.65	*s*
2	139.39	138.81	138.56	124.59	*d*
3	71.72	67.53	67.41	69.20	*d*
4	48.75	46.22	46.82	40.19	*d*
5	67.44	73.06	73.84	68.87	*d*
6	201.62 (*s*)	195.46 (*s*)	194.95 (*s*)	65.87 (*d*)	
7	60.33	60.62	60.46	63.02	*t*
8	27.81	27.80	27.83	26.68	*d*
9	19.73	19.70	19.67	20.11	*q*
10	19.73	19.64	19.60	19.98	*q*
OR^1	Ac	Tig	(2-OH-Et)Acr	Tig	
C-1′	170.09	167.05	165.76	166.98	*s*
C-2′	21.06 (*q*)	127.97 (*s*)	143.41 (*s*)	128.32 (*s*)	
C-3′	—	138.20 (*d*)	124.79 (*t*)	138.20 (*d*)	
C-4′	—	12.16 (*q*)	66.55 (*d*)	11.92 (*q*)	
C-5′	—	14.54	21.45	14.45	*q*
OR^2	H	Ac	Ac	Ac	
C-1″	—	170.08	169.96	170.42	*s*
C-2″	—	21.07	21.04	21.30	*q*

* ^{13}C assignment based on HMQC experiments.
† Assignment based on COLOC experiments
‡ 6-OTig: 167.88, 128.21, 12.10, 14.42.
§ Multiplicity was determined using DEPT experiments.

of two tigloyloxy groups was deduced from the two fragments at *m/z* 249 $[349-C_5H_8O_2+H]^+$ (20%) and 149 $[249-C_5H_8O_2+H]^+$ (90%). The ^{1}H NMR spectrum of **5** (Table 1) revealed the presence of an acetate (δ 2.05, 3H, *s*) and two tiglates (δ 6.80, 2H, *qq*; 1.81, 6H, *br s* and 1.77, 6H, *br s*). Comparison of the IR and ^{13}C NMR spectral data with those of **3** showed the absence of the α,β-unsaturated ketone. Instead, an additional carbon signal was observed in the oxygenated area of δ 65.87 (*d*). A new proton signal appeared at δ 5.74 (1H, *d*, *J* = 3.5 Hz) and showed a coupling with H-5 (δ 4.56, 1H, *dd*, *J* = 12, 3.5 Hz). Furthermore, the olefinic proton signal, H-2, was shifted upfield at δ 6.07 due to the absence of the keto group at C-6. The ^{1}H–^{1}H COSY spectrum allowed the assignment of all proton signals while the ^{13}C NMR

signals were assigned by HMQC and DEPT experiments. The relative positions of the ester groups was finally proved by COLOC experiments, which showed connections between C-1 of 3-OTig at δ 166.98, C-1 of 6-OTig at δ 167.88 and C-1 of 5-OAc at δ 170.42 with H-3, H-6 and H-5 of the terpene part, respectively. The stereochemistry was confirmed by the coupling constants as well as a NOE between H-5 and H-6.

EXPERIMENTAL

Material, extraction and isolation. S. suaveolens was collected from the River Nile Bank, El-Minia, Egypt, in April 1990; voucher specimens are deposited in the Botany department, Faculty of Science, El-Minia University. The aerial parts of the plant (2 kg) were air-dried, ground and extracted with Et_2O–petrol–MeOH (1:1:1) at room temp. The extract was separated as previously reported [10] by CC (silica gel) eluted with petrol, Et_2O and MeOH with increasing polarity. The resultant frs were prefractionated by CC on Sephedex LH-20. The final separation and purification were carried by TLC as well as in part by HPLC (MeOH–H_2O). The known compounds were identified by comparison of their ^1H,^{13}C NMR, mass spectra with those which have been reported in the literature.

3β-Acetoxy-5α,7-dihydroxycarvotacetone (**1**). Gum; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3610, 3500 (OH), 1735 (OAc), 1690 (C=CC=O); positive ion FAB-MS *m/z* (rel. int.): 243 $[M+H]^+$ (6), 225 $[M+H_2O+H]^+$ (8), 183 $[M-HOAc+H]^+$ (20), 165 [225−HOAc] (20), 154 (100), 136 (70), 123 (19); $[\alpha]_D$-229 ($CHCl_3$; *c* 2.1594).

3β-Acetoxy-5α-(2α-hydroxyethyl)acryloyloxy-7-hydroxycarvotacetone (**4**). Oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3500 (OH), 1735 (OAc), 1720 (C=CCO$_2$R) 1690 (C=CC=O); HRFAB-MS $[M+H]^+$ 341.3721 (calcd for $C_{17}H_{25}O_7$: 341.3775), positive ion FAB-MS *m/z* (rel. int.): 341 $[M+H]^+$ (30), 281 $[M-R^1CO_2H+H]^+$ (5), 225 $[M-R^2CO_2H+H]^+$ (57), 185 (100), 165 (53), 149 (35), 123 (54);); $[\alpha]_D$-117($CHCl_3$; *c* 1.1681).

3β,6α-Ditigloyloxy-5α,7-dihydroxy-8,9-dihydrolimonene (**5**). Oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1730 (OAc), 1720 (C=CCO$_2$R); HRFAB-MS $[M+H]^+$ 409.4448 (calcd for $C_{22}H_{33}O_7$: 409.4957); positive ion FAB-MS *m/z* (rel. int.): 409 $[M+H]^+$ (5), 349 $[M-HOAc+H]^+$ (100), 309 $[M-R^1CO_2H+H]^+$ (65), 259 $[349-C_5H_8O_2+H]^+$, 149 $[349-2(C_5H_8O_2)+H]^+$ (90), 137 (52), 121 (15); $[\alpha]_D$-274 ($CHCl_3$; *c* 1.987).

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