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A New Eudesmanolide and a New Aromatic Derivative from *Carpesium cernuun*

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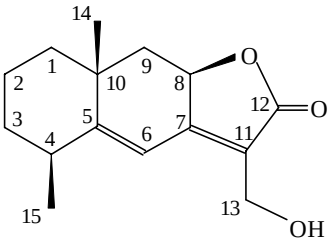
Abstract: A new eudesmanolide and a new aromatic derivative were isolated from the roots of *Carpesium cernuun.* Their structures were elucidated as 13-hydroxy-5,7(11)-eudesmadien-12,8-olide and 3-methyl-8-acetoxy-9,10-diisobutyryloxy-*p*-cymene by spectral methods (EIMS, FAB-MS, 1D and 2D NMR).

Keywords: *Carpesium cernuun*, Compositae, eudesmanolide, aromatic derivatives.

Carpesium cernuun L. has long been used as chinese folk medicine for its anti-inflammatory, pain-relief, and detoxication properties[1]. Up to now, no phytochemical studies of *Carpesium cernuun* has been carried out. Here we report the structure elucidation of a new eudesmanolide **1** and a new aromatic derivative **2**, which were obtained from this plant.



1

Compound **1** was isolated as colorless gum, $[\alpha]_D^{20}$+128.4 (c 0.43, $CHCl_3$). Its EIMS revealed a molecular ion peak *m/z* 248. Together with the support of ^{13}C-NMR and DEPT (**Table 1**), which showed the presence of two CH_3, five CH_2, three CH, five C, the molecular formula was deduced to be $C_{15}H_{20}O_3$. The ^{1}H-NMR and ^{13}C-NMR spectra indicated the presence of a >C=CH– group, a >C=C< group, a >CH-CH_3 unit, a-CH_2OH unit, and an ester carbonyl group. The ^{1}H-^{1}H COSY and HMQC spectra of **1,** showed the following two main moieties: –CH_2-CH_2-CH_2-$CH(CH_3)$– and –CH_2-CH(OC=O)–. The C-C interconnectivity of all the fragments was established through ^{1}H-^{13}C cross peaks (^{3}J) in HMBC experiment: C-1/H-9, H-14; C-2/H-4; C-3/H-15;

C-4/H-6; C-5/H-9, H-14, H-15; C-7/H-9, H-13; C-8/H-6; C-9/H-1, H-14; C-10/H-4, H-6; C-11/H-6; and C-12/H-13. The above information suggested that compound **1** was an eudesmanolide. The stereochemistry of compound **1** was confirmed through ^{1}H-^{1}H NOESY experiment and coupling constant values. The correlation points: 9β-H/14-CH_3, H-6/H-4, and 14-CH_3/15-CH_3 in NOESY spectra of **1** and the J values of H-4: $J_{4,3\beta}$=2.0Hz, $J_{4,3\alpha}$=6.5Hz (**Table 1**) confirmed the α-configuration of H-4, as well as the β-configurations of 14-CH_3 and 15-CH_3. The α-configuration of H-8 was given from $J_{8,9\beta}$=13.0Hz, $J_{8,9\alpha}$=6.0Hz (**Table 1**)[2]. Hence, the structure of compound **1** was confirmed as 13-hydroxy-8(αH)-eudesma-5,7(11)-dien-8,12-olide. Its ^{1}H- and ^{13}C-NMR spectral data were assigned by the use of HMQC and HMBC experiments.

Table 1 ^{1}HNMR (400 MHz), ^{13}CNMR (100 MHz) and DEPT data of **1** ($CDCl_3$, TMS, δ, ppm)

No.	^{1}H(α/β)	^{13}C	DEPT
1	1.60(m) / 1.68(br.dd, 13.0, 4.0)	39.7	CH_2
2	1.56(m) / 1.95(m)	29.5	CH_2
3	1.56(m) / 1.74(m)	34.0	CH_2
4	2.78(ddq, 7.5, 6.5, 2.0)	40.6	CH
5	-	163.5	C
6	6.36(s)	112.7	CH
7	-	158.8	C
8	4.80(dd, 13.0, 6.0)	76.4	CH
9	2.18(dd, 13.0, 6.0) / 1.54(t, 13.0, 13.0)	43.2	CH_2
10	-	38.6	C
11	-	118.4	C
12	-	174.4	C
13	4.44(br.s)	55.4	CH_2
14	1.32(s)	18.0	CH_3
15	1.29(d, 7.5)	20.6	CH_3

Signal multiplicity and coupling constants (Hz) are in parentheses.

Compound **2** was obtained as colorless crystals from acetone, mp 92-94°C. The FAB-MS gave the quasi-molecular ion peak *m/z* 385 $[M+Li]^+$, 401 $[M+Na]^+$, and 379 $[M+1]^+$. Together with ^{13}C-NMR and DEPT (**Table 2**) (seven CH_3, two CH_2, five CH, seven C), the molecular formula of **2** was deduced as $C_{21}H_{30}O_6$. There were three signals at δ 7.29 (d, 1H, J=8Hz), 7.08 (dd, 1H, J=8Hz, 2Hz), 6.90 (d, 1H, J=2Hz) in the downfield region of ^{1}H-NMR spectrum of **2**. The chemical shift and the coupling constant values of these signals revealed that **2** was a 1,2,4-trisubstitued benzene. In ^{1}H- and ^{13}C- NMR spectra, there were signals of a glyceryl, a acetyl and double overlapped isobutanoyl (**Table 2**), along with the cross peaks (J^3) between carbonyl of isobutanoyl and H-9a, 9b, H-10a, 10b of the glyceryl in HMBC experiments, revealed the presence of a glyceryl-2-acetate-1,3-diisobutyrate[3]. In addition, there were two methyls δ 2.38 (3H, s) and δ 2.35 (3H, s) in the upfield region, so these substitutions were confirmed. Furthermore, through HMBC experiment the relative location of the three substituting groups was established. In HMBC spectra, the ^{1}H-^{13}C correlation points (^{3}J): C-1/H-5 and C-7/H-2, H-6 due to 7-CH_3 at C-1; C-3/H-5 and C-11/H-2 due

to another methyl group at C-3; C-8/H-5 and C-4/H-2, H-6, H-9, H-10 due to the glyceryl-2-acetate-1,3-diisobutyrate at C-4 supported the structure of compound **2** as 3-methyl-8- acetoxy-9,10-diisobutyryloxy-*p*-cymene. Its ^{1}H- and ^{13}C-NMR data were assigned by the use of HMQC and HMBC experiments.

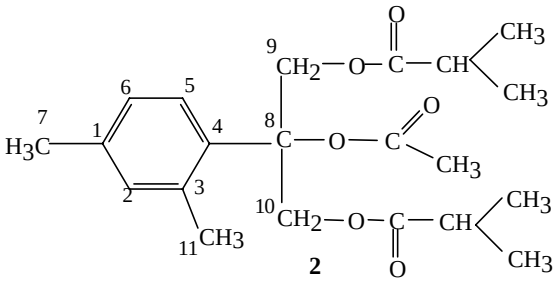


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Table 2 ^{1}HNMR (400 MHz), ^{13}CNMR (100 MHz) and DEPT data of **2** ($CDCl_3$, TMS, δ, ppm)

No.	^{1}H	^{13}C	DEPT
1	-	140.0	C
2	6.90 (d, 2.0)	124.8	CH
3	-	147.8	C
4	-	125.8	C
5	7.29 (d, 8.0)	127.6	CH
6	7.08 (dd, 8.0, 2.0)	126.9	CH
7	2.35 (s)	21.2	CH_3
8	-	80.8	C
9	4.87 (d, 11.4) / 4.75 (d, 11.4)	62.7	CH_2
10	4.87 (d, 11.4) / 4.75 (d, 11.4)	62.7	CH_2
11	2.38 (s)	20.8	CH_3
isobutanoyl	-	176.0	C
	2.55 (m)	33.9	CH
	1.12 (d, 7.2)	18.8	CH_3
	1.12 (d, 7.2)	18.8	CH_3
isobutanoyl	-	176.0	C
	2.55 (m)	33.9	CH
	1.12 (d, 7.2)	18.8	CH_3
	1.12 (d, 7.2)	18.8	CH_3
acetyl	-	169.3	C
	1.99 (s)	21.2	CH_3

Signal multiplicity and coupling constants (Hz) are in parentheses.

Acknowledgment

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