^{1}H NMR (90 MHz, $CDCl_3$): δ 1.60 (*s*, 6H), 1.67 (*s*, 3H) and 1.75 (*s*, 3H) due to 4 × Me groups; 1.90–2.20 (*m*, 8H) due to 4 × allylic CH_2 groups; 3.45 (*br d*, J = 7 Hz, 2H: H-1'); 5.19 (*m*, 2H: H-6' and H-10'); 5.45 (*br t*, J = 7 Hz, 1H: H-2'); 6.85 (*br s*, 1H: H-2); 7.0–7.5 (complex *m*, 3H: H-5, H-6 and H-7); 7.6–7.7 (*m*, 1H: H-4) and 7.95 (*br s*, 1H: N–H); CI-MS (CH_4) *m/z* (rel. int.): 321 $[M]^+$ (16); 184 $[M - C_{10}H_{17}]^+$ (10.5); 158 $[184 - CN]^+$ (5.3) and 130 $[M - C_{14}H_{23}]^+$ (100) and ^{13}C NMR resonances as shown in Table 1.

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Table 1. Tentative assignment of ^{13}C NMR (15.08 MHz, $CDCl_3$) spectral data for 3-farnesylindole (1)

Chemical shift (δ)	Assignment
136.1	C-8
135.2	C-7'
134.6	C-3'
130.7	C-11'
127.1	C-9
124.0	C-10'
123.8	C-2
122.5	C-6
121.4	C-5
120.7	C-2'
118.7 (*br*)	C-4 and C-6
110.4 (*br*)	C-3 and C-7
38.7 (*br*)	C-4' and C-8'
25.6 (*br*)	C-12'
25.6 (*br*), 24.5 and 22.7	C-9', C-5' and C-1'
16.5	C-3'Me
14.9 (*br*)	C-7'Me and C-11'Me

br = Broad signal.

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TWO GUAIANOLIDES FROM *CENTAUREA COLLINA*

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Key Word Index—*Centaurea collina*; Compositae; sesquiterpene lactones; guaianolides.

Abstract—Two guaianolides isolated from the aerial parts of *Centaurea collina* were identified as 3β-hydroxy-8α-epoxymethylacriloiloxy-4(15),10(14),11(13)-trien-(1αH),(5αH)-guaian-6,12-olide and its 11β,13-dihydro derivative by spectroscopic methods.

INTRODUCTION

Many sesquiterpene lactones have been reported from the large genus *Centaurea* (Compositae, Cynareae) with approximately 700 species [1]. In the present paper we report the isolation and structure elucidation of two guaianolides from *C. Collina*, one of them being new. In previous work [2–4] several flavonoids were reported from this plant.

RESULTS AND DISCUSSION

From the methanolic extract of the aerial parts of *C. collina*, two sesquiterpene lactones were isolated.

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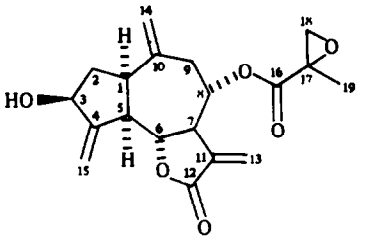
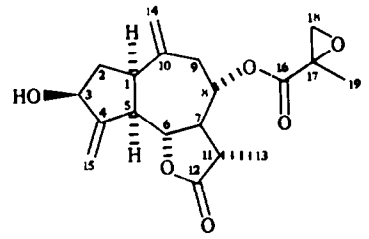


1



2

Compound (1) was non-crystalline; its IR spectrum showed bands characteristic of a γ-lactone (1750 cm^{-1}), a hydroxyl group (3500–3200 cm^{-1}) and a double bond (1650 cm^{-1}). The high resolution mass spectrum showed a $[M]^+$ at *m/z* 346.1421 corresponding to $C_{19}H_{22}O_6$, with fragments at *m/z* 262 and 244 which suggested the presence of a C_4 ester side chain. The ^1H NMR data (Table 1) established that the side chain was a epoxymethylacrylic acid residue (singlet at δ 1.34 and two doublets typical of an AB system at δ 3.57 and 3.78 (J = 11.7 Hz). The exocyclic methylene conjugated with a carbonyl lactone was easily recognizable in the two one-proton-doublets at δ 5.91 and 6.14 (J = 3.0 Hz). Two pairs of broad singlets (δ 5.30, 5.40 and δ 4.81, 5.07) were attributed to the hydrogens of an exocyclic methylene group attached to C-4 and C-10, respectively. The lactonic proton (H-6) appeared as a triplet at δ 4.22, the coupling constant of which (J = 9.0 Hz) indicated its *trans*-diaxial disposition to the hydrogens at C-5 and C-7. The H-8 proton gave a doublet triplet at δ 5.05 (J = 9.0 and 4.0 Hz) the coupling of which indicated the α-orientation for the ester group. The chemical shifts (δ 4.49) and coupling constant (*t*, J = 7.5 Hz) for H-3 indicated a β-orientation for the 3-hydroxyl group [5]. These signals, as were all the remaining signals of the ^1H NMR spectrum, were assigned by spin decoupling. According to the above data, the structure (1) was assigned to this compound which has been recently isolated from *C. solstitialis* [6].

Compound (2) ($C_{19}H_{24}O_6$, $[M]^+$ 348.1609) was non-crystalline. In the IR spectrum, absorption for a hydroxyl group was observed at 3550–3200 cm^{-1}, for a γ-lactone at 1770 cm^{-1}, for an ester at 1740 cm^{-1} and for a double bond at 1640 cm^{-1}. As in 1, the presence of an epoxymethylacrylic ester was revealed by ions at *m/z* 264 and 246 in the mass spectrum and the signals at δ 1.35(*s*), 3.57 and 3.78 (AB system, J = 11.2 Hz) in the ^1H NMR spectrum (Table 1). The $[M]^+$ at *m/z* 348 is two mass units greater than that of 1 and this difference is maintained in the most significant fragment ions (*m/z* 264 and 246). In the ^1H NMR spectrum of 2, the signal corresponding to the conjugated exocyclic methylene does not appear, although a doublet is observed at δ 1.30 ($J_{11,13}$ = 7.0 Hz) which may be attributed to a C-11 methyl group. The α-orientation of this methyl group is inferred from the coupling constant ($J_{7,11}$ = 9.0 Hz) [7, 8]. The signals corresponding to H-14, H-15, H-3, H-6, H-8 (Table 1) and spin decoupling experiments allowed us to assign the structure (2) for this compound.

Table 1. ^1H NMR spectral data for compounds 1 and 2

	1	2
H-1	2.91 *q*	2.91 *q*
H-2	1.68 *dt*	1.70 *ddd*
H-2′	2.11 *ddd*	2.20 *m*
H-3	4.49 *t*	4.53 *tt*
H-5	2.72 *t*	2.77 *t*
H-6	4.22 *t*	4.14 *t*
H-7	3.06 *tt*	2.24 *q*
H-8	5.05 *dt*	5.00 *dt*
H-9	2.30 *dd*	2.23 *dd*
H-9′	2.60 *dd*	2.70 *dd*
H-11	—	2.54 *dq*
H-13	5.91 *d*	1.30 *d*
H-13′	6.14 d	—
H-14	4.81 *s*	4.96 *s*
H-14′	5.07 *s*	5.12 *s*
H-15	5.30 *s*	5.30 *t*
H-15′	5.40 *s*	5.40 *t*
H-18	3.57 *d*	3.57 *d*
H-18′	3.78 *d*	3.78 *d*
H-19	1.34 *s*	1.35 *s*

Coupling constants (Hz): 1, $J_{1,2} = J_{1,2'} = J_{1,5} = 9$; $J_{2,2'} = 13$; $J_{2,3} = J_{2',3} = 7.5$; $J_{5,6} = J_{6,7} = J_{7,8} = 9$; $J_{8,9} = J_{8,9'} = 4$; $J_{9,9'} = 15$; $J_{7,13} = J_{7,13'} = 3$; $J_{18,18'} = 11.7$. 2, $J_{1,2} = J_{1,2'} = J_{1,5} = 9$; $J_{2,2'} = 13.5$; $J_{2,3} = J_{2',3} = 7$; $J_{5,6} = J_{6,7} = J_{7,8} = J_{7,11} = 9$; $J_{8,9} = J_{8,9'} = 4$; $J_{9,9'} = 14$; $J_{11,13} = 7$; $J_{3,15} = J_{5,15} = 1.8$; $J_{18,18'} = 11.2$.

Further characterization of the guaianolides (1) and (2) was obtained by ^{13}C NMR spectroscopy. The data (Table 2) were interpreted on the basis of previous assignments [9, 10] and distortionless enhancement by polarization transfer (DEPT) experiments. Although some resonances were not assigned without ambiguity, it is clear that (1) and (2) possess the same relative stereochemistry C-1,3,5–8.

EXPERIMENTAL

MS were recorded at 70 eV. NMR spectra were measured at 200 MHz for ^1H and 50 MHz for ^{13}C. *C. collina* L. was collected at the Enguera-Ayora road (Valencia). A voucher specimen is deposited at the Botanic Department Herbarium, Faculty of Biological Sciences, University of Valencia. Aerial parts (3.6 kg) were extd exhaustively firstly with hexane and afterwards with

Table 2. ^{13}C NMR spectral data for compounds 1 and 2

	1	2
C-1	45.3[a]	44.5
C-2	38.3[b]	38.7[b]
C-3	73.2	73.3
C-4	151.8	152.4
C-5	51.5	52.2[a]
C-6	78.1[c]	78.7[c]
C-7	46.9[a]	51.0[a]
C-8	75.2[c]	77.7[c]
C-9	35.6[b]	39.0[b]
C-10	141.6	141.8
C-11	136.8	41.3
C-12	169.5	178.4
C-13	123.6	15.2
C-14	118.1	117.5
C-15	113.8	112.8
C-16	174.8	175.0
C-17	76.0	75.9
C-18	68.1	68.0
C-19	21.6	21.8

[a,b,c] Chemical shifts denoted by the same letter in each column may be interchanged.

MeOH. The MeOH extract was reduced *in vacuo* to *ca* 1 l diluted with H_2O (2 l) and re-extd with Et_2O. Evapn of solvent yielded 56 g of crude syrup which was chromatographed on silica gel. Elution of the column with mixtures of increasing polarity (hexane–CH_2Cl_2–EtOAc) and repeated CC of the fractions eluted with CH_2Cl_2–EtOAc (9:1 l) afforded 1 (30 mg) and 2 (15 mg).

Compound (1). Non-crystalline. IR ν_{max} cm^{-1}: 3500–3200, 2930, 1750, 1650, 1460, 1270, 1140, 1070, 990 and 930. MS *m/z* (rel. int.): 346.1421 $[M]^+$ (0.6) ($C_{19}H_{22}O_6$ requires 346.1410) 262 (6.0) 244 (39.3) and 226 (15.6).

Compound (2). Non-crystalline. IR ν_{max} cm^{-1}: 3550–3200, 2930, 1770, 1740, 1640, 1460, 1380, 1190, 1140, 1060, 1010 and 910. MS *m/z* (rel. int.) 348.1609 $[M]^+$ (0.5) ($C_{19}H_{24}O_6$ requires 348.1509) 264 (4.6), 246 (33.6) and 228 (13.8).

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