

POLYACETYLENES FROM *LEUCANTHEMUM PALLENS*

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Key Word Index — *Leucanthemum pallens*, Anthemideae; Compositae; polyacetylenes.

Abstract — From the aerial parts of *Leucanthemum pallens*, four acetylenic compounds have been isolated. One of these was not previously described as a naturally occurring compound. All structures were elucidated by spectral methods: ^1H NMR, ^{13}C NMR, IR and UV spectroscopy.

These are results of a systematic study of the composition of *Leucanthemum pallens* (Gay) D.C. of the tribe Anthemideae (Compositae) collected at the end of July in Barbadillo (Salamanca, W. Spain).

From the hexane soluble part of the MeOH extract were isolated, in addition to previously described triterpenes and sterols, the known acetylenes 1,7-Z-hexadecadien-10,12,14-triene **1** [1], 1,6E,8E-hexadecatrien-10,12,14-triene **2** [2-5] and 3E,5E-tridecadien-7,9,11-triinyl acetate **3** [2-5], the new acetylenic alcohol **4**.

The structure of **4** was assigned by spectral data. Its IR spectrum showed absorptions due to an —OH group (3500, 3440, 1070 cm^{-1}), $\text{C}\equiv\text{C}$ (2220, 2180 cm^{-1}), $\text{CH}=\text{CH}$ and $\text{CH}=\text{CH}_2$ bonds (1640, 1590, 995, 955, 915 cm^{-1}). The presence of a $-(\text{C}\equiv\text{C})_3\text{—CH}=\text{CH—}$ chromophor was indicated by the UV absorption peaks at 330, 308, 290, 273, 258, 243, 232 nm.

The ^{13}C NMR spectrum (Table 1) showed the presence of one $\text{Me-C}\equiv\text{C}$ group, five methylenes, one of them olefinic, four methyne, six signals which could be acetylenic carbons and one oxygenated carbon atom.

In the ^1H NMR spectrum, the $\text{Me-C}\equiv\text{C}$ group was shown at 1.98 ppm. At 4.18 ppm was the doublet of triplets assignable to a OH-geminal proton and at 4.97-6.35 ppm were shown the signals characteristic of a *trans* disubstituted double bond and a vinyl group. All these data allowed us to assign the structure 1,8E-hexadecadien-10,12,14-triene-7-ol for **4**. Assignment of each ^{13}C NMR signal of acetylenes **1**, **2** and **4** was made by comparison with the heteronuclear correlation C-H for acetylene **3** (Table 1).

Me-(C≡C)₃-CH₂-CH=CH-(CH₂)₄-CH=CH₂ **1**
Me-(C≡C)₃-CH=CH-CH=CH-(CH₂)₃-CH=CH₂ **2**
Me-(C≡C)₃-CH=CH-CH=CH-CH₂-CH₂-OAc **3**
Me-(C≡C)₃-CH=CH-CHOH-(CH₂)₄-CH=CH₂ **4**

EXPERIMENTAL

UV spectra were recorded in EtOH. ^1H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were measured in CDCl_3 with TMS as int standard.

Collection of plants. *L. pallens* was collected in Barbadillo (Salamanca, Spain) in July 1985. The Plant material was identified by Prof. M. Ladero, from the Botany Department of the Pharmacy Faculty (Salamanca) where a specimen is held (SALAF no. 11773).

Extraction and isolation. The air dried parts (1.7 kg.) were extracted with MeOH. After cooling for 12 hr at -20°C, the MeOH soluble fraction was evaporated *in vacuo* was extracted with *n*-hexane-MeOH-H₂O (3.2:1) and the organic extract (8.2%) by treatment with NaHCO₃ affording 32.5 g (8.1%) of neutral fraction which was separated by CC (silica gel). By repeated chromatography and/or crystallizations, a triterpenic and steroidic series (taraxasterol acetate, 18-*epi*-taraxasterol, dammar-20-en-3 β -ol, stigmast-20(21)-en-20 β -ol and stigmast-22E-en-3 β -ol), and pure samples of **1** (98 mg), **2** (50 mg), **3** (220 mg) and **4** (49 mg) were isolated.

Table 1. ^{13}C NMR chemical shifts of polyacetylenes **1-4** (50.3 MHz, solvent CDCl_3 , int. standard TMS).

Carbon	1	2	3	4
1	114.3	114.8	63.1	114.3
2	139.9	140.2	32.2	138.9
3	33.8	33.2	134.8	33.6
4	29.3	28.1	131.8	28.1
5	28.8	27.1	146.0	25.0
6	27.2	133.1	108.3	36.8
7	133.2	129.6	59.4*	72.0
8	121.9	146.7	65.1*	150.7
9	17.8	106.9	68.3*	108.0
10	59.9*	59.5*	75.2*	59.1*
11	61.0*	65.1*	77.1*	65.0*
12	65.1*	68.1*	78.7*	67.2*
13	65.6*	75.0*	4.6	73.8*
14	73.0*	65.6*		75.2*
15	76.8*	78.5*		78.2*
16	4.8	4.5		4.6
Me-COO-			20.8	
Me-COO-			170.8	

*Six singlets of acetylenic carbons, interchangeable assignments.

1,8E-Hexadecadien-10,12,14-triin-7-ol **4**. Colourless oil eluted with *n*-hexane-AcOEt 8:2. IR ν_{max} cm⁻¹: 3500, 3440, 3080, 2935, 2860, 2220, 2180, 1640, 1590, 1380, 1070, 995, 915. UV λ_{max} nm (ϵ): 330 (4800), 308 (6200), 290 (5100), 273 (4000), 258 (4100), 242 (17900), 232 (17200). ¹H NMR δ ppm (*J* Hz): 1.4 (6H, *m*, H-4, 5 and 6), 1.98 (3H, *s*, H-16), 2.01 (2H, *m*, H-3), 4.18 (1H, *dt*, *J* = 5.5, H-7), 4.97 (2H, *m*, H-1), 5.78 (1H, *m*, H-2), 5.82 (1H, *d*, *J* = 15.8, H-9) and 6.35 (1H, *dd*, *J*₁ = 15.8, *J*₂ = 5.5, H-8). ¹³C NMR: see Table 1.

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SEQUITERPENES FROM *AGERATINA TOMENTELLA*

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Key Word Index—*Ageratina tomentella*; Compositae; Eupatorieae; sesquiterpene lactones; heliangolides; guaianolides; elemanoic acid.

Abstract—An investigation of *Ageratina tomentella* yielded, besides the two known sesquiterpene lactones hiyodorilactone C acetate and 5"-desoxy-3-*epi*-4"-hydroxyprovincialin, two new sesquiterpenes, 11,13-dehydro-8 β -tigloyloxy-eleman-12-oic acid and 8-*epi*-8-[5'-(4"-hydroxytigloyloxy)-tigloyloxy]-rupicolin A. The structures of the new compounds were elucidated by spectroscopic methods.

INTRODUCTION

As a part of our chemosystematic survey of the tribe Eupatorieae [1-7], we investigated the sesquiterpenes of *Ageratina tomentella* (Schrad.) R. M. King & H. Robinson. The results are discussed in this paper.

RESULTS AND DISCUSSION

The dichloromethane extract of leaves of *A. tomentella* afforded the known heliangolide hiyodorilactone C acetate (**1**) [8, 9] as the major constituent. The structure of **1** was easily deduced from its ¹H NMR spectrum. We also include previously unreported ¹³C NMR data for **1** in Table 1. Most of the signals of the second compound (**2**) were nearly identical with those of **1**. One difference between the two compounds appeared to be in the nature of their side chains at C-8. In place of a simple acetate ester at C-8, compound **2** contained a complex C₁₀ diester at C-8. Also, the configuration of the acetate function at C-3 differed in **2** from that of **1**. ¹³C and ¹H NMR data showed that **2** is the known compound 5"-desoxy-3-*epi*-4"-hydroxyprovincialin which was previously isolated from *Piptothrix pubens* [10] and from *P. areolata* [11].

The ¹H NMR spectrum of the new compound **3**, C₂₅H₃₀O₉, showed signals characteristic for the C₁₀ diester 5'-(4"-hydroxytigloyloxy)-tiglate group is a triplet at δ 7.07 (H-3'), a doublet of triplets at 6.64 (H-3''), an AB pair at 4.90 and 4.85 (H-5'a and 5'b), a broadened two proton doublet at 4.30 (H-4''a and 4''b) and another doublet of doublets at 4.46 (H-4'a and H-4'b). Inspection of the other signals in the ¹H NMR spectrum, together with the ¹³C NMR and IR data, indicated that **3** was obviously an α,β -unsaturated lactone (IR band at 1760, 1650 cm⁻¹, ¹³C NMR: δ 124.0 (C-13) and 169.5 (C-12); ¹H NMR: δ 6.29 (1H, *d*, *J* = 3.6 Hz, H-13a) and 5.62 (1H, *d*, *J* = 3.2 Hz, H-13b). Moreover, the ¹H NMR spectrum of **3**, in conjunction with systematic spin decoupling, suggested that **3** was a derivative of rupicolin A (Table 2) [12]. Comparison of the ¹H NMR spectrum of **3** (Table 2) with those of two other derivatives of rupicolin A, 8-*epi*-8-isobutyryl rupicolin A (**4**) [13] and 8-*epi*-8-tiglyl rupicolin A (**5**) [14], showed significant differences among **3**, **4** and **5**, only for the signals due to the side chains at C-8. All other spectral data (see Experimental) supported the assignment of **3** as the new compound, 8-*epi*-8-[5'-(4"-hydroxytigloyloxy)-tigloyloxy]-rupicolin A.

The CIMS of **6** exhibited a [M + 1]⁺ at *m/z* 333 (6%), suggesting a molecular formula of C₂₀H₂₈O₄. The base peak at *m/z* 233 (232 + 1) (C₁₅H₂₀O₂) was formed by loss of the side chain ester + H. This was identified as a tiglate

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