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(13*E*,15*E*,18*Z*,20*Z*)-1-Hydroxypentacosa-13,15,18,20-tetraen-11-yn-4-one 1-acetate, from the venom of a Brazilian *Crematogaster* ant

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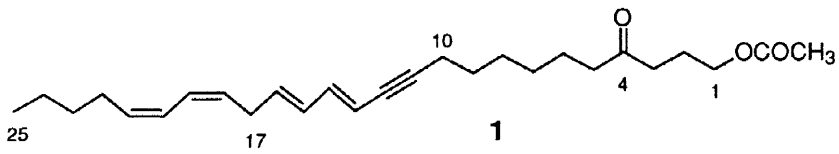
Abstract

(13*E*,15*E*,18*Z*,20*Z*)-1-hydroxypentacosa-13,15,18,20-tetraen-11-yn-4-one 1-acetate, a new polyfunctionalized long chain derivative, was isolated from the venom of an as yet undetermined *Crematogaster* ant species from Brazil, and its structure established by a detailed high-field 1D and 2D NMR study.

Keywords: Insects; NMR; lipids; polyene.

Ants of the genus *Crematogaster* possess a peculiar defensive mechanism which requires a cooperation between the poison and the Dufour glands. In most of the species examined so far, the Dufour gland contains complex mixtures of long-chain derivatives bearing a (*E*,*E*)-cross-conjugated dienone linked to a primary acetate function [1-4]. When the venom is emitted, these compounds are transformed into highly electrophilic and toxic 4-oxo-2,5-dienals by an esterase and an oxidase stored in the poison gland [2]. We have now undertaken the study of Brazilian *Crematogaster* ants, to determine whether the characteristic compounds already evidenced in European [1-3] and New Guinean [4] species are also present in American species, and to further investigate whether the composition of the Dufour gland secretion could be used for taxonomic purposes in this ant genus. We report here our first result along these lines.

The venom of the ants (200 specimens of an as yet undetermined species, collected at Pentecoste, Ceará, Brazil) was obtained in the usual manner [1] and stored in MeOH. A GC-MS analysis [Finnigan ITD 800 coupled to a Tracor GC equipped with a 12 m SE 54 capillary column, programmed from 180 °C (1 min) to 295 °C at 7 °C/min] showed the presence of one major peak displaying a $M^{+\cdot}$ at *m/z* 412 in EIMS and a $(M+H)^+$ at *m/z* 413 in CIMS (NH_3). Flash chromatography of 4.5 mg of this material (SiO_2, hexane-acetone, from 95:5 to 80:20) afforded 400 μg of the major compound, which proved to be unstable and light-sensitive. Its HREIMS displayed a $M^{+\cdot}$ at *m/z* 412.2982 (calc. for $C_{27}H_{40}O_3$: 412.2977), indicating the presence in the molecule of 8 degrees of unsaturation and three oxygen atoms. The latter were located in a ketone and an ester functions (IR: ν_{CO} at 1717 and 1740 cm^{-1}, respectively). The UV spectrum [λ_{max} (MeOH) 240, 269 and 278 nm (ε 32300, 27000 and 17000)] suggested the presence of a conjugated dienyne [5]. The connectivity pattern of the molecule was inferred from a 1D and 2D NMR study (^1H, COSY, HMQC and HMBC), which allowed us to identify **1** as (13*E*,15*E*,18*Z*,20*Z*)-1-hydroxypentacosa-13,15,18,20-tetraen-11-yn-4-one 1-acetate.



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The complete assignment of the H and C atoms of the molecule is reported in Table 1. The ^1H-^1H COSY spectrum allowed us to determine the presence of three separate spin systems (H_2C-1 to H_2C-3; H_2C-5 to

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H_2C-10 and HC-13 to H_3C-25). Particularly noteworthy was the homopropargylic coupling (2.0 Hz) between H_2C-10 and HC-13, which permitted to connect these two carbon atoms through an acetylene function [5]. The HMBC correlations between H-10 and the two acetylenic carbon atoms C-11 and C-12 (see Table 1) fully confirmed this assignment. HMBC correlations between H-3 and C-4 and between H-5 and C-4 led to the complete structure of **1**. The ^1H and ^{13}C NMR data of HC-18 to HC-20 and of H_2C-10 to HC-16 of **1** are in complete agreement with those reported for the corresponding atoms of (5*Z*,7*Z*)-dodecadien-1-ol [6] and (7*E*,9*E*,13*E*,15*Z*)-14,16-dibromohexadeca-7,9,13,15-tetraen-5-ynoic acid [5], respectively. The structure of **1** is also supported by a diagnostic fragment ion in HREIMS at *m/z* 213 (calc. for $C_{16}H_{21}$: 213.1643; found: 213.1641), corresponding to the cleavage between H_2C-9 and the propargylic H_2C-10.

Table 1. NMR data of **1** ($CDCl_3$, δ, *J* in Hz)

Position	δC[a]	δH[b]	HMBC (H to C)[c]
1	64.0	4.05, 2H, t, 7.0	C-2, C-3
2	23.0	1.88, 2H, quint, 7.0	C-1, C-3, C-4
3	39.5	2.45, 2H, t, 7.0	C-1, C-2, C-4
4	210.0	-	
5	42.5	2.38, 2H, t, 7.0	C-4, C-6, C-7
6	24.0	1.56, 2H, quint, 7.0	C-5
7	30.3	1.29, 2H, m	
8	29.5	1.34, 2H, m	
9	28.5	1.51, 2H, quint, 7.0	C-11
10	20.3	2.28, td, 7.0, 2.0	C-9, C-11, C-12
11	92.5	-	
12	80.0	-	
13	110.0	5.48, 1H, bd, 15.5	
14	140.5	6.45, 1H, dd, 15.5, 10.5	
15	130.0	6.05, 1H, dd, 15.5, 10.5	
16	134.0	5.70, 1H, dt, 15.5, 7.0	
17	31.0	2.95, 2H, bt, 7.0	C-15, C-16, C-18, C-19
18	128.0	5.40, 1H, dt, 10.5, 7.0	
19	124.5	6.28, 1H, t, 10.5	
20	123.5	6.20, 1H, t, 10.5	
21	133.0	5.44, 1H, dt, 10.5, 7.0	
22	27.7	2.15, 2H, quart, 7.0	C-20, C-21, C-23
23	30.5	1.38, 2H, quint, 7.0	C-21, C-22
24	22.5	1.29, 2H, m	C-23
25	14.3	0.88, 3H, t, 7.0	C-23, C-24
COO	172.0	-	
CH_3	21.0	2.03, 3H, s	COO

[a]Assignments by HMQC and/or HMBC
[b]600 MHz, Varian Unity 600
[c]Optimized for $^nJ_{CH}$ = 5 and 10 Hz

The structure of **1** is intriguing as it departs from the usual pattern of cross-conjugated dienones and furan derivatives found in the venom of the other species of *Crematogaster* ants examined so far [1-4]. The study of other South American species of this genus is currently under way in our laboratories.

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