

## Spartidienedione, a New Sesquiterpene with a Novel Carbon Skeleton from *Baccharis spartioides*

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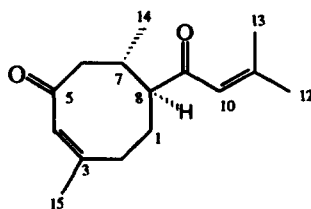
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**Abstract:** Spartidienedione, a new sesquiterpene possessing a novel carbon skeleton, was isolated from the aerial part of *Baccharis spartioides* and its structure established by spectroscopical methods.

The most usual type of secondary metabolites isolated from the chemically well-investigated genus *Baccharis* (*Compositae*, tribe *Astereae*) is that constituted by clerodane-type diterpenes<sup>1)</sup>. However, other types of compounds are also widespread in this genus, sesquiterpenes with different kinds of skeletons being one of them<sup>2)</sup>. In this paper we wish to report on the isolation and chemical characterization of a sesquiterpene possessing a new regular carbon skeleton which was obtained from *Baccharis spartioides*, collected in northern Chile.

Compound **1** was isolated from non-polar fractions as an oil  $[\alpha]_D^{25} = -37.4$  (c 1.63, CHCl<sub>3</sub>). The molecular formula was established as C<sub>15</sub>H<sub>22</sub>O<sub>2</sub> on the basis of its HRMS M<sup>+</sup> at m/z 234.1616 (calc. 234.1619). Bands at 1640 and 1650 cm<sup>-1</sup> in the I.R. spectrum together with the maximum at  $\lambda=231$  nm



( $\epsilon=24.000$ ) in the U.V. spectrum showed the presence of two unsaturated carbonyl groups. The fragmentation in the E.I.M.S. at m/z 83 and m/z 151 divided the molecule into two fragments (C<sub>5</sub>H<sub>7</sub>O)<sup>+</sup> and (C<sub>10</sub>H<sub>15</sub>O)<sup>+</sup> having an acyclic and a cyclic  $\alpha,\beta$ -unsaturated carbonyl system, respectively. The <sup>1</sup>H-<sup>1</sup>H COSY<sup>3)</sup> spectrum of **1** showed the presence of three separate directly-coupled proton spin systems, which simplifies its analysis. Two

of them were isolated  $\alpha,\beta$ -unsaturated carbonyl moieties, in accordance with their chemical shift values and with the long-range correlations observed in the  $^1\text{H}$ - $^1\text{H}$  COSY map. Thus, the vinylic proton signal at  $\delta$  5.80 was long-range correlated with the methyl group at  $\delta$  1.92, while a second vinylic proton signal at  $\delta$  6.08 was long-range correlated with the two methyl groups at  $\delta$  2.10 and 1.85. These correlations define the two fragments A and B as  $-\text{CO}-\text{CH}=\text{C}(\text{Me})-$  and  $-\text{CO}-\text{CH}=\text{C}(\text{Me})_2$ , respectively. The third fragment C was established as  $\blacksquare-\text{CH}_2-\text{CH}(\text{Me})-\text{CH}(\blacksquare)-\text{CH}_2-\text{CH}_2-\blacksquare$  following the connectivities observed in the COSY map from the proton  $\alpha$ -methine to the secondary methyl group. The methyl, methylene and methine carbons were identified by the DEPT technique and their assignments were carried out through the observed correlations of the proton signal assigned to carbons in the  $^1\text{H}$ - $^{13}\text{C}$  COSY spectrum. The remaining quaternary carbons were identified by the correlations observed in the HMBC ( $J=10$  Hz) spectrum. Thus, the olefinic signal from B at  $\delta$  155.7 showed long-range correlations with the methyl group signals at  $\delta$  2.10 and 1.85, whereas that from A at  $\delta$  161.7 was correlated with the proton signal at  $\delta$  1.92. On the other hand, the signals from the carbonyl groups were overlapped at 200.9 ppm and the spectrum showed long-range correlations with both the (fragment) A proton signal at  $\delta$  6.08 and with the C proton signals at  $\delta$  2.76, 2.17, 1.97 and 1.81, which implies that these fragments are linked through the fragment C methine carbon at  $\delta$  49.8 and the fragment B carbonyl group.

Table I. NMR spectroscopical data of compound 1 in  $\text{CDCl}_3$ \*

N <sup>o</sup>	$^1\text{H}$ $\delta$ , m.	$^{13}\text{C}$ ppm,m.	HMBC	ROESY	N <sup>o</sup>	$^1\text{H}$ $\delta$ , m.	$^{13}\text{C}$ ppm,m.	HMBC	ROESY
1 $\alpha$	1.81 m	23.5 t	8	2, 14	8	2.17 ddd	49.8 d	6, 7, 1, 14	---
1 $\beta$	1.97 m			14	9	---	200.9 s	10, 8, 7, 1	---
2	2.29 m	30.8 t	---	1	10	6.08 s	124.2 d	12, 13	12, 7, 6
3	---	161.7 s	15	---	11	---	155.7 s	12, 13	---
4	5.80 s	127.2 d	15	15	12	1.85 s	28.1 q	10, 13	10,13
5	---	200.9 s	6	---	13	2.10 s	21.1 q	12, 10	6, 7, 12, 14, 15
6 $\alpha$	2.31 dd	49.5 t	8, 7, 4, 14	10, 14, 13	14	0.85 d	17.1 q	8, 7, 6	6 $\alpha$ , 7, 1, 13
6 $\beta$	2.39 dd			10, 13	15	1.92 s	24.5 q	4	4, 14
7	2.76 m	28.2 d	6, 1	10, 14, 13					

\* Recorded on Bruker AC-200 and AMX-400 spectrometers.

The application of the 2D-INADEQUATE technique (Fig. 1) afforded us the possibility to connect the three different carbon fragments of the molecule as shown in 1. Thus, the link between fragments B and C at C-8 was confirmed by the observed  $^{13}\text{C}$ - $^{13}\text{C}$  correlations between its carbon signal at  $\delta$  49.8 ppm and C-9 at  $\delta$  200.9 ppm. Moreover, the links between fragments A and C were found to be established through the fragment carbon terminals. Thus, the quaternary olefinic carbon C-3 ( $\delta$  161.7 ppm) from A was connected to the methylene carbon C-2 ( $\delta$  30.8 ppm), which proved to be allylic on the basis of its NMR spectral data. Also, the methylene carbon C-6 ( $\delta$  49.5 ppm) was connected to the carbonyl group C-5 ( $\delta$  200.9 ppm). Besides, the INADEQUATE experiment confirmed all the carbon assignments previously made by using the direct and long-range COSY (HETCOR) sequences.

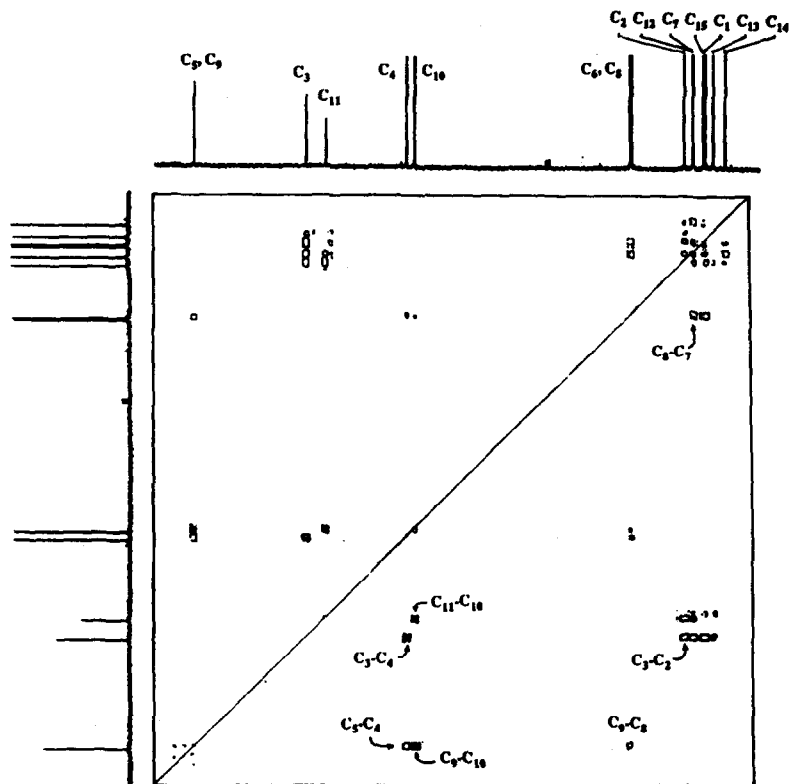


Figure 1. Symmetrized 2D-INADEQUATE (50 MHz) drawing of compound 1.

The relative configurations at carbons C-8 and C-7 were established on the basis of the ROESY experiment<sup>3</sup>), which showed a ROE connectivity between H-10 and the proton signals from H-6, Me-12 and H-7, whereas the secondary methyl group Me-14 showed ROE connectivities with H-1, H-6 and H-8. A weak connectivity was also observed between H-8 and H-7. This result was in agreement with that obtained by a conformational analysis performed by MMX molecular mechanics calculations<sup>4</sup>), revealing two energy minima conformers 1A and 1B (Fig. 2) in agreement with the experimental observations.

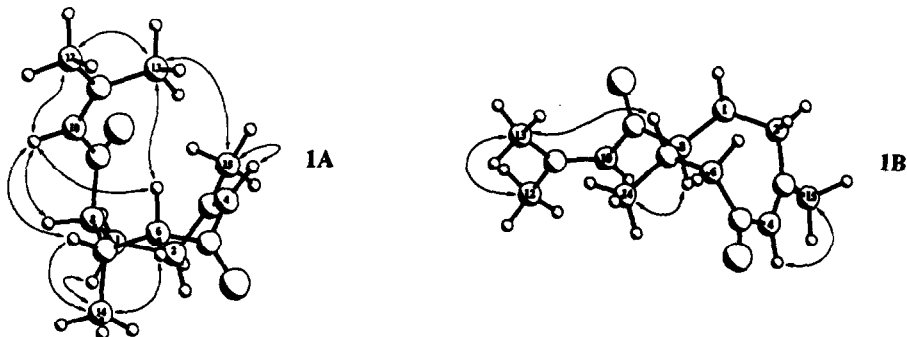
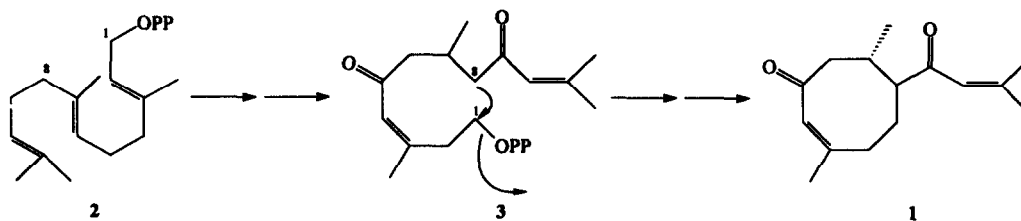


Figure 2. Energy minima conformers (1A and 1B) of compound 1 showing the observed ROE connectivities

To our knowledge, the structure of spartdienedione is unique among the sesquiterpenoids from natural sources<sup>5</sup>). This unprecedented carbon skeleton could be hypothetically derived from a linear precursor by an unusual cyclization between carbons C-1 and C-8 of the intermediate 3 (Scheme 1).



Scheme 1

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