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JATROWEDIONE, A LATHYRANE DITERPENE FROM *JATROPHA WEDDELLIANA*

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Key Word Index—*Jatropha weddelliana*; Euphorbiaceae; diterpene; lathyrane; jatrowedione; pantanal.

Abstract—3-Acetylaleuritolic acid, sitosterol and a novel lathyrane diterpene, jatrowedione, have been isolated from the roots of *Jatropha weddelliana*. The elucidation of the structure of the latter was accomplished by detailed NMR investigation, and the relative configuration was established by difference NOE experiments.

INTRODUCTION

Jatropha weddelliana is a shrub found in calcimorphic and dry soils of the highlands bearing the 'pantanal' of Mato Grosso do Sul, Brazil [1]. This plant was chosen for investigation because previous studies with plants of the genus *Jatropha* led to the isolation of biologically active compounds [2–4]. In the present report we describe the isolation and structure elucidation of jatrowedione, a novel lathyrane diterpene present in the roots of *J. weddelliana*.

RESULTS AND DISCUSSION

Jatrowedione (**1**) was obtained from the extract of the stems of *J. weddelliana* as a dextrorotatory powder. The molecular formula $C_{20}H_{28}O_3$ was deduced from the NMR data and the molecular ion ($[M+1]^+$ at m/z 317) in the FAB-mass spectrum. The IR spectrum indicated the presence of carbonyl groups (1702 cm^{-1}, broad) and no hydroxyl. The ^{13}C NMR and DEPT spectra presented twenty carbon signals, including characteristic signals due a trisubstituted double bond (δ_c 140.5 and 156.0), two carbonyls (δ_c 211.9 and 210.5), a trisubstituted epoxide (δ_c 79.2 and 73.6), five methyls, three methylenes, five methines and a quaternary carbon. Signals at δ 0.69 and 0.23 (1 H each) in the ^1H NMR spectrum suggested the presence of a cyclopropane moiety in the molecule. The unambiguous assignment of the protonated carbons was obtained by the HETCOR measurements (Table 1) and decoupling experiments,

Table 1. NMR data of compounds **1** and **2** [5]

	1*		2+
Position	H	C	C
1	7.51 *s*	156.0 *d*	152.7 *d*
2		140.5 *s*	142.7 *s*
3		211.9 *s*	203.4 *s*
4	4.28 *d*(J=2.1 Hz)	47.6 *d*	62.4 *d*
5	4.93 *d*(J=2.1 Hz)	79.2 *d*	57.7 *d*
6		73.6 *s*	58.6 *s*
7	2.17 *m* and 1.85 *m*	41.3 *t*	41.0 *t*
8	1.68 *m*	18.9 *t*	18.4 *t*
9	0.29 *br q*	28.6 *d*	29.1 *d*
10		16.0 *s*	16.5 *s*
11	0.69 *td*	19.9 *d*	18.7 *d*
12	2.04 *m*	28.3 *t*	24.3 *t*
13	3.40 *m*	43.8 *d*	37.6 *d*
14		210.5 *s*	214.0 *s*
15	5.28 *br q*	51.5 *d*	86.4 *s*
16	1.68 *s*	10.1 *q*	10.2 *q*
17	1.77 *s*	26.0 *q*	18.3 *q*
18	1.00 *s*	28.9 *q*	28.2 *q*
19	0.92 *s*	15.0 *q*	15.4 *q*
20	1.34 *d* (J=6.8 Hz)	13.4 *q*	14.6 *q*

* In pyridine-d_5
\+ In $CDCl_3$-DMSO (9:1)

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Table 2. Long-Range NMR connectivities of compound **1**

H-C*		C-H+	
Irradiated proton	Connected carbons	Carbon	Connected protons
H-1	C-2, C-3, C-15, Me-16	C-1	H-15, Me-16
H-4	C3,C-5,C-6, C-14,C-15	C-2	H-15, Me-16
H-5	C-3, C-6	C-3	H-1
H-9	C-10, Me-19	C-5	H-4, Me-17
H-11	C-10, Me-18, Me-19	C-6	Me-17
H-13	C-11, C-14, Me-20	C-10	Me-18, Me-19
H-15	C-1, C-2, C-14	C-14	H-12
Me-17	C-5, C-6	Me-18	Me-19
Me-18	C-9, C-10	Me-19	Me-18
Me-19	C-10, Me-18		
Me-20	C-12, C-13, C-14		

* Selective INEPT experiments
\+ Long-Range HETCOR

while that of quaternary carbons came from the long-range HETCOR spectrum and selective INEPT experiments (Table 2). Together, the above data suggested a lathyrane gross structure for **1**. Many members of this class of diterpenes have been isolated from *Jatropha* spp [5], and the comparison (Table 1) of ^{13}C NMR data with those of jatrogrossidione, (**2**) [6] was particularly significant. The main differences were found for the C-15 signal (δ 51.5 *d* for **1**; δ 86.4 *s* for **2**) suggesting that in **1** the hydroxyl group was lacking. Accordingly, the signals of the neighboring carbons (C-1, C-4 and C-14) were shifted. Nevertheless, the other relevant differences (see δ_C values for C-5, C-6 and Me-17) between the ^{13}C NMR spectra of **1** and **2**, could not be ascribed to the absence of OH, but to a different stereochemistry in the epoxide ring, that was confirmed by a series of difference NOE experiments. For both compounds the irradiation of the signal of H-9 enhanced those of H-11 and Me-18, and on irradiation of H-11 the NOE effects were observed on H-9, Me-18 and Me-20. However, by contrast to the observation for compound **2**, the irradiation of H-5 of **1** enhanced the signals of H-4, H-15 and Me-17, while **no effect** was observed on H-9 and H-11. Furthermore, the irradiation of H-15, H-13 and H-4 (see Fig. 1) confirmed that these protons were on the same side of the molecule with respect to H-5. Together, these experiments established a *cis*-fusion of the epoxide ring, and the relative configuration depicted in **1**.

Sitosterol and 3-acetyl aleuritolic acid [7] were isolated from the hexane extract of the roots.

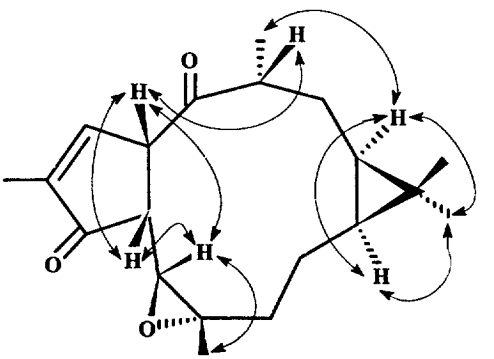


Fig. 1. NOE effects of compound **1**.

EXPERIMENTAL

Plant material

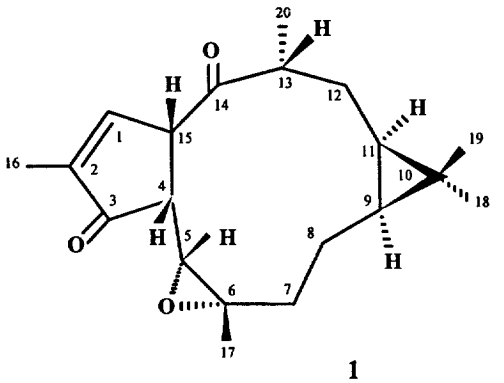
Jatropha weddelliana Bail was collected in Corumbá (Mato Grosso do Sul, Brazil) and identified by G. A. Damasceno Jr. (DAM/CEUC/UFMS). A voucher specimen is deposited in the herbarium of the Centro Universitario de Corumbá/UFMS under number 1722.

Extraction and isolation

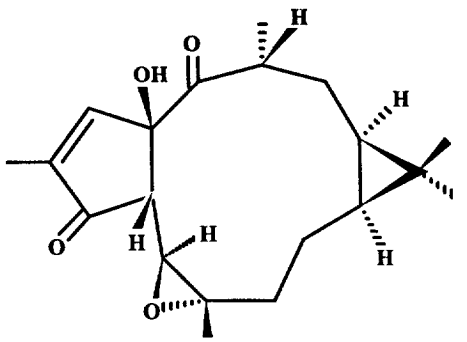
The powdered roots (2.3 Kg) were exhaustively extracted with cold hexane and CH_2Cl_2. CC of the hexane extract (42 g) (silica gel; hexane with increasing amounts of Me_2CO) yielded fatty acids, sitosterol and 3-acetyl aleuritolic acid. Repeated CC (silica gel; hexane with increasing amounts of Me_2CO) of the CH_2Cl_2 extract (73,4 g) afforded a solid, which was washed with Et_2O and Me_2CO, successively. The insoluble material gave, by crystallization with pyridine, pure compound **1** (150 mg).

Jatrowedione (**1**)

$C_{20}H_{28}O_3$. FAB-MS $[M+1]^+$ at *m/z* 317. Mp 235°C (sub.); $[\alpha]_D$ + 76.8 (1.0; pyridine); IR νKBrmax cm^{-1}: 1702. NMR data see Tables 1 and 2.



1



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