DUMORTENOLS, NOVEL SKELETAL SESQUITERPENOIDS FROM THE ARGENTINIAN LIVERWORT *DUMORTIERA HIRSUTA*

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The diethyl ether extract of the Argentina liverwort *Dumortiera hirsuta* yielded a sesquiterpenoid with a novel carbon skeleton. The structure was established by extensive 2D NMR techniques and X-ray crystallographic analysis. It was shown to be 3,4,11-trimethyl-7-methylenebicyclo [6. 3. 0] undec-2-en-11α-ol.

KEY WORDS liverwort; Marchantiales; *Dumortiera hirsuta*; sesquiterpene; chemosystematics

The thallic liverwort *Dumortiera hirsuta* belongs to the Marchantiales and grows on moist rocks. Classification of the liverworts is extremely difficult morphologically, and thus study of their chemical constituents is invaluable in making interpretations of index compounds. For this reason we have been investigating the chemosystematics of liverworts. Many species of liverworts have oil bodies in the cell and produce mono-, sesqui-, and diterpenoids with a variety of carbon skeletons and aromatic compounds as major constituents of those species[1)] some of which are peculiar constituents of the liverworts. The viewpoint of natural product chemistry of liverworts thus is of considerable interest. A previous phytochemical study of Japanese *D. hirsuta* led to the isolation of (4*S*, 6*R*)-2,7,10-bisabolatrien-4-ol, (4*S*, 7*R*)-germacra-1(10)*E*, 5*E*-dien-11-ol, 1(10)*E*-lepidozen-5-ol, marchantin C, isomarchantin C, riccardin C, and lunularine.[2)] Even when the same species are investigated, liverwort constituents are often different. In order to compare the constituents of Japanese and Argentinian *D. hirsuta*, the latter species was investigated. Here we report on the isolation and structure elucidation of a novel sesquiterpene alcohol from Argentinian *D. hirsuta*.

D. hirsuta (453 g) was collected in February 1994 at San Javier, Tucumán province, Argentina. A voucher specimen is deposited at the Universidad Nacional de Tucumán. *D. hirsuta* was extracted with diethyl ether for 30 days. The ether extract (4.0 g) of this species was chromatographed repeatedly on silica gel and preparative HPLC to give a novel sesquiterpene alcohol **1** (2.8 mg).

The EI-mass spectrum of **1** showed a molecular ion peak at *m/z* 220 and a base peak at *m/z* 107. The ^{1}H NMR spectrum (Table 1) exhibited the presence of three methyl groups, a trisubstituted double bond, and an exocyclic methylene. The ^{13}C NMR spectrum of **1** not only demonstrated the presence of 15 carbon signals, including four down field-shifted signals, but also showed an oxygenated carbon signal. The gross structure

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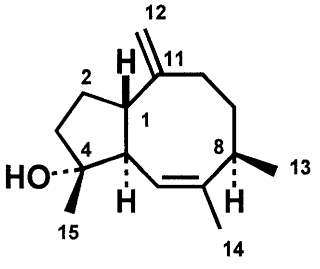
of **1** was proved by extensive 2D NMR experiments involving the analyses of its COSY, HSQC, HMBC, and NOESY spectra. The stereochemical assignments at the centers C-1, C-4, C-5, and C-8 of **1** were inferred from the latter spectrum. The above data were clarified by an X-ray crystallographic analysis[3)] on crystals of **1** obtained from methanol solution. Accordingly, the structure of **1** was elucidated as shown.

Table 1. NMR Data for **1**^{a}

No.	^{1}H	^{13}C
1	2.12 (dddd, *J*=10, 12.5, 12.5 Hz)	53.6
2	1.59 (dddd, *J*= 5, 7.5, 12.5, 15 Hz)	25.3
	1.92 (dddd, *J*= 7.5, 10, 12.5, 12.5 Hz)	
3	1.72 (ddd, *J*= 7.5, 7.5, 12.5 Hz)	40.6
	1.84 (ddd, *J*=5, 12.5, 12.5 Hz)	
4		80.1
5	2.48 (dd, *J*=7.5, 12.5 Hz)	55.6
6	5.48 (d, *J*=7.5 Hz)	122.4
7		141.3
8	2.70 (ddddd, *J*=5, 7, 7, 7, 12.5 Hz)	32.3
9	1.35 (dddd, *J*=5, 7.5, 12.5, 12.5 Hz)	36.8
	1.51 (dddd, *J*=5, 5, 12.5, 12.5 Hz)	
10	1.75 (dddd, *J*=1, 5, 12.5, 12.5 Hz)	33.4
	2.21 (ddd, *J*=5, 7.5, 12.5 Hz)	
11		152.4
12	4.83 (d, *J*=1 Hz)	109.1
	4.94 (s)	
13	0.99 (d, *J*=7 Hz)	18.7
14	1.63 (br s)	18.7
15	1.34 (s)	25.5

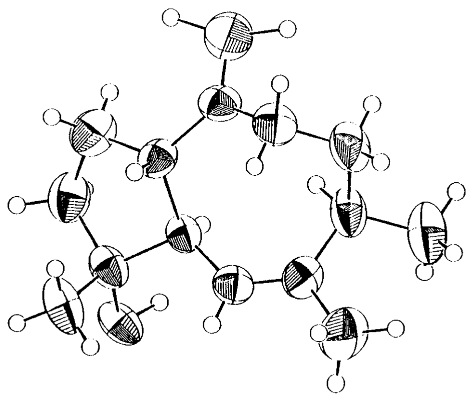
[a)] Spectra were recorded at 150 MHz for ^{13}C and 600 MHz for ^{1}H in CDCl$_3$. Assignments were confirmed by HSQC and MHBC spectra.

It is intriguing to note that compound **1** has a unique carbon skeleton, while many naturally occurring compounds with a bicyclic five-seven-membered ring system such as guaiane-type sesquiterpene derivatives have been reported.

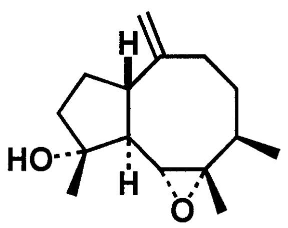


1

Further purification of the extract by preparative HPLC yielded **2** (1.2 mg) with NMR spectra similar to those of **1**. Comparison of ^{1}H and ^{13}C NMR spectral data of **1** and **2**[4)] suggested that **2** was the derivative of **1**, with the replacement of a double bond by an epoxy ring. This was inferred from two signals at δ 61.1 and 64.5 due to an oxygenated carbon and the lack of the trisubstituted double bond signal in its ^{13}C NMR spectrum. The configuration of the epoxy ring was deduced by a coupling constant



ORTEP drawing of **1**.

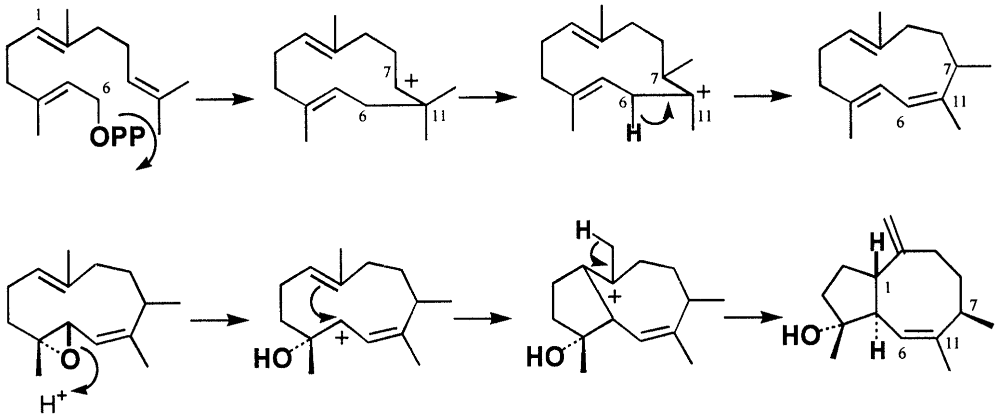


2

(J=10 Hz) in its ^{1}H NMR spectrum. Observation of NOE between H-15 and H-6 of **2** using the difference spectrum provided further evidence for the α-configuration of the epoxy ring. The structure of **2** was tentatively assigned as shown. The attempt to establish the structure of **2** was thwarted by lack of material.

Although the present work reports the isolation of **1** and **2** from the Argentinian species, these compounds were not present in the Japanese species. We propose the name "dumortane" for the new type of skeleton.

The biogenesis of compound **1** was presumably derived from the cyclization of *trans*-farnesylpyrophosphate with the migration of the methyl group as shown in the Figure.



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3) Compound **1** was crystallized in trigonal space group R3 with cell dimensions a=23.37(1) Å, b=23.37(1) Å, c=6.707 Å, V=3171.510010(5) Å^3, Z=9, R=0.063, total measurement 3866 reflections and crystal size 0.5, 0.1 and 0.1 mm. The crystal structure was solved by the CRYSTAN SIR 92 program.

4) ^{1}H NMR (600 MHz in CDCl$_3$): δ 1.02 (d, 3H, J=6.6 Hz), 1.19 (s, 3H), 1.44 (s, 3H), 2.73 (d, 1H, J=10 Hz), 4.86 (br s, 1H), 4.99 (br s, 1H). ^{13}C NMR (100 MHz in CDCl$_3$): δ 16.7, 16.8, 25.9, 27.4, 33.4, 33.7, 36.9, 41.1, 49.8, 57.3, 61.1, 64.5, 80.3, 110.4, 152.0.

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