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A new dimeric 9,10-dihydrophenanthrenoid from the rhizome of *Juncus acutus*

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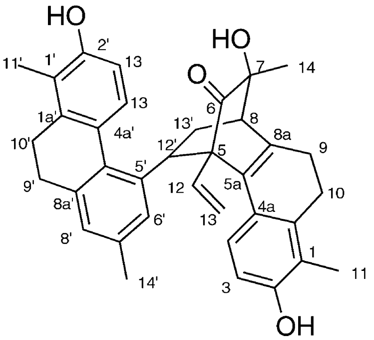
Abstract—In a study of the allelochemical interaction between the wetland plant *Juncus acutus* and microalgae an unusual dimeric 9,10-dihydrophenanthrenoid has been isolated. The structure has been determined on the basis of its spectroscopic properties. © 2002 Elsevier Science Ltd. All rights reserved.

9,10-Dihydrophenanthrenoids form a rather uncommon class of metabolites originated or from stilbenic precursors[1] or by coupling of two phenylethane units.[2]

Many of such compounds have been isolated from the aerial part of two Juncaceae, *Juncus effusus*[3] and *Juncus acutus*,[4] and in vitro assays have evidenced their antialgal activity.[5] This property might justify the allelopathic interaction of these plants with microalgae.

In pursuing the study of *J. acutus* we have isolated from the rhizome of the plant an unusual dimeric 9,10-dihydrophenanthrenoid, which was assigned the heptacyclic structure **1**. The elemental analysis[†] and the presence of 36 carbon signals in the ^{13}C NMR spectrum (Table 1) justified the molecular formula $C_{36}H_{36}O_4$. The EIMS spectrum lacked the molecular peak and showed the fragments at *m*/*z* 250 (65) and 282 (15%) attributable to a retro Diels–Alder of the cyclohexene ring.

In the IR spectrum were present hydroxyl absorptions at 3806 and 3691, and one carbonyl absorption at 1730 cm^{-1}. The UV spectrum exhibited a maximum at 280 nm.



1

The ^{1}H NMR spectrum showed in the aromatic region two coupled doublets at δ 6.77 and 6.43, two coupled doublets at δ 7.23 and 6.70, and two singlets at δ 6.99 and 6.80.

Besides three olefinic double doublets at δ 5.74, 4.86 and 4.41 belonging to a vinyl group, a double doublet at δ 4.22, two multiplets of a methylene group at δ 3.16 and 1.83, and four methyls as singlets at δ 2.22, 2.18, 1.91, and 1.43 respectively were detectable in the aliphatic region. All the remaining protons were present as overlapped signals in the 3.1–2.3 ppm range.

The ^{13}C NMR spectrum and the DEPT experiment indicated the presence of a carbonyl carbon, sixteen quaternary carbons, nine methines, six methylenes and four methyls.

The rough structure was defined on the basis of COSY, HMQC and HMBC experiments (Table 1). Both the A

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[†] Elemental analysis: Found: C, 81.08; H, 6.77; Calcd: C, 81.17; H, 6.81%.

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Table 1. NMR data of compound **1**

C	Dept	δ ^{13}C	δ ^{1}H	HMBC	C	Dept	δ ^{13}C	δ ^{1}H	HMBC
1	C	122.6			1′	C	123.0		
2	C	155.9			2′	C	155.8		
3	CH	112.4	6.43 d (9.0)	C-1 C-2 C-4a	3′	CH	113.3	6.70 d (8.5)	C-1′ C-2′ C-4a′
4	CH	126.1	6.77 d (9.0)	C-2 C-1a C-5a	4′	CH	127.9	7.23 d (8.5)	C-2′ C-1a′ C-5a’
5	C	63.3			5′	C	141.7		
6	C	209.8			6′	CH	129.3	6.99 s	C-8′ C-12′ C-14′ C-5a′
7	C	72.5			7′	C	137.1		
8	CH	51.0	2.96 brs	C-6 C-7 C-5a C-8a C-12′ C-13′	8′	CH	127.1	6.80 s	C-6′ C-9′ C-14′ C-5a′
9	CH_2	29.9	2.38 m 2.58 m	C-10 C-5a C-8a	9′	CH_2	32.5	2.42 m 2.67 m	C-10′ C-5a′ C-8a′
10	CH_2	26.4	2.28 m 2.98 m	C-9 C-1a C-4a C-8a	10′	CH_2	27.4	2.50 m 2.98 m	C-1′ C-9′ C-4a′ C-8a′
11	CH_3	12.3	2.18 s	C-1 C-2 C-1a	11′	CH_3	12.5	2.22 s	C-1′ C-2′ C-1a′
12	CH	138.4	5.74 dd (12.0 18.5)	C-5 C-6 C-5a C-12′	12′	CH	39.8	4.22 dd (9.2 7.7)	C-5 C-6 C-8 C-5′ C-6′ C-5a′ C-13′
13	CH_2	117.1	4.41 dd (1.5 18.5) 4.86 dd (1.5 12.0)	C-5 C-6 C-12	13′	CH_2	36.0	1.83 m 3.16 m	C-5 C-5′ C-7 C-8 C-12′
14	CH_3	26.4	1.43 s	C-6 C-7 C-8	14′	CH_3	21.6	1.91 s	C-6′ C-7′ C-8′
1a	C	140.1			1a′	C	139.2		
4a	C	126.0			4a′	C	127.7		
5a	C	132.1			5a′	C	135.2		
8a	C	142.1			8a′	C	143.4		

s = singlet, brs = broad singlet, d = doublet, dd = double doublet, m = multiplet; the couplings (Hz) are reported in brackets.

and A′ rings of the two 9,10-dihydrophenanthrene moieties constituting the dimer had a methyl at the 1 position and a hydroxyl at the 2 one. The protons at δ 6.43 and 6.77 were attributed to the H-3 and H-4 owing to the heterocorrelations with the C-2 carbon as well as the protons at δ 6.70 and 7.23 were attribute to H-3′ and H-4′ on the basis of the heterocorrelations with the C-2′ carbon. The H-4 proton gave also a cross peak with the C-5a carbon and, to this carbon, were also correlated the vinylic H-12 proton at δ 5.74, and the aliphatic methines H-8 at δ 2.96 and H-12′ at δ 4.22. All these protons were also correlated to the C-6 carbonyl carbon. Beside the already reported correlations, the H-12′ proton was also heterocorrelated to the C-5 and C-8 carbons of the first unit and to the C-5′, C-6′, C-5a′ and C-13′ carbons of the second one. Finally the C-5a′ carbon gave a cross peak with the H-4′ proton.

The relative configuration of **1** was attributed on the basis of the chemical shifts of the H-13′ protons and ROESY experiments (Fig. 1).

In the hypothesis of a *S* configuration at C-5 and a *R* one at C-8, the *R* configuration at C-7 was supported by the NOE interaction of the H-14 methyl with one of the H-9 protons. The 1,3 spatial interaction[6] of the *exo* H-13′ proton with the hydroxyl group at C-7 caused its downfield shift at δ 3.16.

Both the *exo* H-13′ proton and the H-12′ proton gave NOE with the H-4′ proton thus justifying their *cis* relation. Consequently, the 9,10-dihydrophenanthrene moiety at C-12′ was *endo*-oriented according to the C-12′ *S* configuration. In conclusion, the absolute configuration of **1** should be 5*S*,7*R*,8*R*,12′*S* or the enantiomeric one.

Compound **1** may be considered to derive by the coupling of 2-hydroxy-1,7-dimethyl-5-vinyl-9,10-dihydrophenanthrene (**2**) with 2,6-dihydroxy-1,7-dimethyl-5-vinyl-9,10-dihydrophenanthrene (**3**), both metabolites isolated

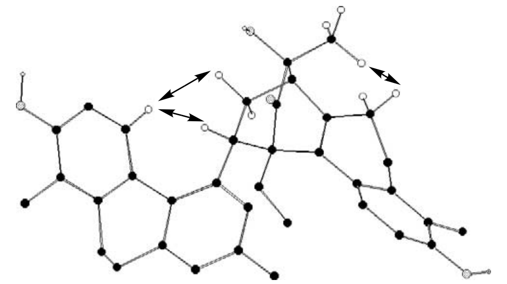

Figure 1. Selected NOE interactions.

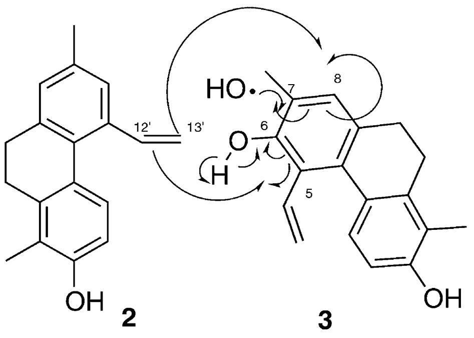

Figure 2. Coupling of **2** and **3** to give **1**.

from the plant. A possible mechanism might consist (Fig. 2) in the loss of the hydrogen from the hydroxyl group at C-6 of **2** with formation of the carbonyl function and the linkage between the C-5 and the C-12′ of **1**. The consequent linkage of the C-13′ with the C-8 and the formal introduction of a hydroxyl radical at C-7 should complete the process.

Compound **1** was tested against *Selenastrum capricornutum*[5] to evaluate its antialgal activity. The toxicity value, reported as IC_{50}, the inhibiting concentration that affect 50% of the population, was 10.3 μM.

Acknowledgements

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