Pergamon

Tetrahedron Letters 42 (2001) 7907–7909

TETRAHEDRON LETTERS

A new propentdyopent derivative, rollipyrrole, from *Rollinia mucosa* Baill.

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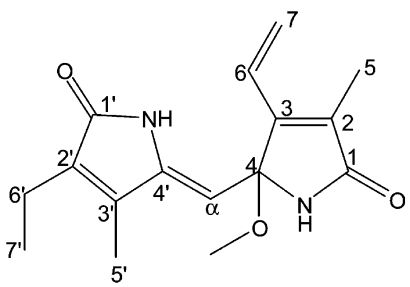
Received 11 May 2001; revised 22 August 2001; accepted 30 August 2001

Abstract—Rollipyrrole **1**, a novel pyrromethenone derivative was isolated from the leaves of *Rollinia mucosa* in the continuing research into Formosan annonaceous plants. This type of compound was isolated from plants for the first time and the structure of **1** was elucidated mainly on the basis of 1D and 2D NMR spectroscopic data. © 2001 Elsevier Science Ltd. All rights reserved.

In our previous study of *Rollinia mucosa*,[1–3] a series of compounds have been isolated and most of them are alkaloids and acetogenins. Further study of this plant led to the isolation of a new propentdyopent derivative, rollipyrrole **1**. Propentdyopents were regarded as the photo-oxidation by-products of pyrromethenones.[4] Interestingly, the pyrromethenones are rarely isolated from the plants but commonly found in animals such as bilirubin.[4,5] The elucidated precursor **2** also possessed a different substitution pattern from those known pyrromethenones. The detailed spectral assignment is reported herein.



rollipyrrole **1**

Rollipyrrole **1** was obtained as a yellow amorphous powder. The HREIMS revealed a $[M]^+$ at m/z 288.1476 (calcd 288.1475) corresponding to the molecular formula $C_{16}H_{20}N_2O_3$. The base peak at m/z 256 (M-32) revealed elimination of the MeOH fragment. The UV spectrum showed a single absorption at 266 nm. The IR spectrum of **1** showed absorption bands at 3200, 1703, and 1657 cm^{-1}, indicating the presence of two NH and two carbonyl groups on lactam rings, which were confirmed by the ^{13}C NMR signals at δ 171.6 and 172.4. The ^1H NMR spectrum showed two broad singlets at δ 9.48 and 9.88 (each 1H), which were assigned as the NH groups. In the olefinic region, four signals at δ 6.60, 5.87, 5.42, and 5.15 were observed; the first three signals are coupled and elucidated as a mono-substituted ethylene. In the aliphatic region, the NMR showed five signals, three signals at δ 3.08 (s, 3H), 2.05 (s, 3H), and 1.79 (s, 3H), which were assigned as a methoxy and two methyl groups, respectively. Two coupled signals at δ 1.05 (t, 3H) and 2.32 (q, 2H) were then assigned as an ethyl group. In the ^{13}C and DEPT spectra, the ^{13}C signals comprised of four methyls, two methylenes, two methines, and eight quaternary carbons. Full characterization of the structure was accomplished by examination of HMQC, HMBC, and NOESY spectra (Table 1).

The dipyrrole unit was identified by the HMBC spectrum. The unit can be divided into two segments (Table 1). In segment I, the olefinic methine proton H-6 showed cross-peaks with two aromatic quaternary carbons C-2 and C-3, an olefinic methylene carbon C-7, and one methine carbon C-4.

Furthermore, the methyl protons H-5 showed correlations with C-2 and carbonyl C-1, and the methoxy protons showed a correlation to C-4. These correlations revealed segment I as a non-conjugated lactam substituted by a methoxy and two alkyl chains. In segment II, the methylene protons H-6′ exhibited couplings with

Keywords: Annonaceae; propentdyopent; *Rollinia mucosa* Baill.; rollipyrrole.

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PII: S0040-4039(01)01621-5

Table 1. The 1D and 2D NMR data of rollipyrrole **1**

Atom	δ_H, multiplicity, J	δ_C	HMBC	NOESY	Segments
1		172.4			
2		133.4			
3		147.6			
4		92.3			
5	2.05 (3H, *s*)	8.70	C_1, C_2, C_3	H_6	
6	6.60 (1H, *ddd*, J=0.8, 11.2, 18.0 Hz,)	126.7	C_2, C_3, C_4	H_5, $H_{7a,7b}$	
7	H_{7a} 5.42 (1H, *dd*, J=0.8, 11.2 Hz) H_{7b} 5.87 (1H, *dd*, J= 0.8, 18.0 Hz)	121.6	C_3, C_6	H_6	
1′		171.6			
2′		135.0			
3′		140.5			
4′		140.8			
5′	1.79 (3H, *s*)	9.28	$C_{2'}$, $C_{3'}$, $C_{4'}$	$H_{6'}$, $H_{7'}$	
6′	1.05 (3H, *t*, J=7.6 Hz)	17.0	$C_{1'}$, $C_{2'}$, $C_{3'}$, $C_{7'}$	$H_{5'}$, $H_{7'}$	
7′	2.32 (2H, *q*, J=7.6 Hz)	13.3	$C_{2'}$, $C_{6'}$	$H_{5'}$, $H_{6'}$	
α	5.15 (1H, *s*)	106.2	C_4, $C_{4'}$	$H_{5'}$	
Ome	3.09 (3H, *s*)	49.3	C_4		

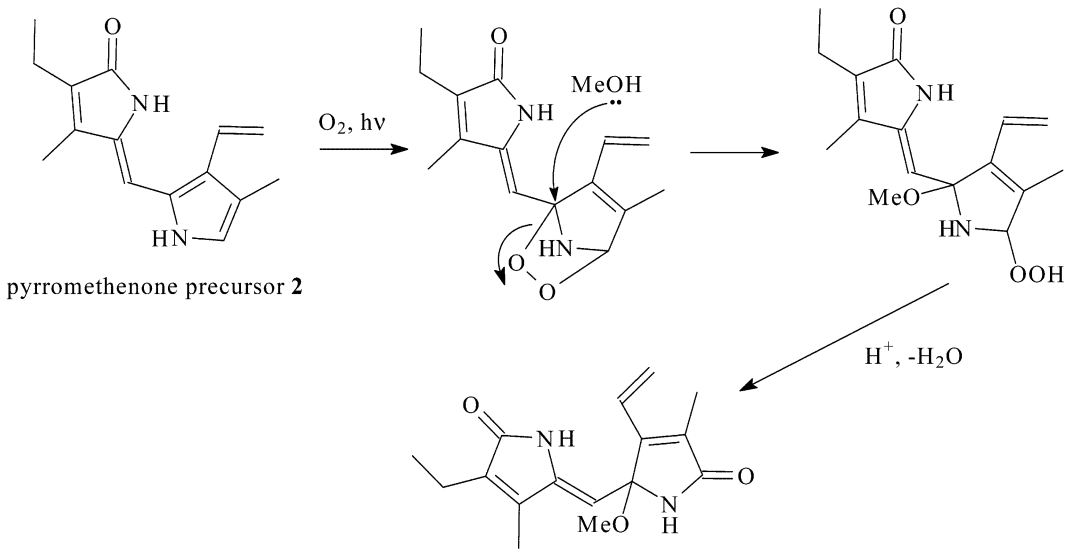
The ^1H and ^{13}C spectrum were recorded at 400 and 100 MHz, respectively, using pyridine-d_5 as solvent.

two aromatic quarternary carbons C-2′ and C-3′, the methyl C-7′, and a carbonyl carbon C-1′. The methyl H-5′ showed correlations with C-2′, C-3′, and C-4′. The segment II represents a conjugated lactam. From these observations, the structure of the two segments were clearly elucidated and then connected by the correlation of H-α with C-4 and C-4′. The interpretation of the NOESY data led to the assignment of its configuration. The strong correlation between proton H-α and H-5′ revealed the *Z*-form configuration of C_α=$C_{1'}$. An optical rotatory value of zero revealed **1** to be racemic.

Based on the surveys of previous studies,[4,5] this type of compound maybe produced from the auto-oxidation of pyrromethenone precursor **2** followed by nucleophilic attack by methanol (Scheme 1). In the addition step to peroxide–pyrromethenones, the stereoselectivity is random which led to a racemic product. Though the precursor **2** was not isolated, the hypothesis is reasonable with literature support.[4,5] These observations raised the possibility that **1** was an isolation artifact, but pyrromethenone itself is unstable under mild irradiation; it should be noted that the occurrence of **1** is still possible in a natural environment.

Acknowledgements

This research was supported by the National Science Council of the Republic of China (Grant No. NSC 89-2113-M-037-026).



Scheme 1. Hypothetic tautomerization from precursor **2** to **1**.

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