

# TODDACOUMAQUINONE, A UNIQUE COUMARIN-NAPHTHOQUINONE DIMER, FROM *TODDALIA ASIATICA* (L.) LAM. (*T. ACULEATA* PERS.)

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The spectroscopic structural elucidation of toddacoumaquinone (2), a unique coumarin-naphthoquinone dimer, isolated from *Toddalia asiatica* (L.) Lam. (*T. aculeata* Pers.) is described.

**KEYWORDS** coumarin-naphthoquinone dimer; structural establishment; 2D-NMR; *Toddalia asiatica* (*T. aculeata*); Rutaceae

Recently we<sup>1)</sup> described the structural determination of toddacoumalone (1), a novel mixed dimer of coumarin and quinolone which had been reported as unknown I,<sup>2)</sup> from *Toddalia asiatica* (L.) Lam. (*T. aculeata* Pers.). In this paper we present the structural elucidation of unknown II,<sup>2)</sup> a unique coumarin-naphthoquinone dimer designated as toddacoumaquinone (2), by spectroscopic means.

Toddacoumaquinone (2) was isolated as orange prisms, mp 278–281 °C (AcOEt), in 0.015 % yield in a racemic form.<sup>3)</sup> The molecular formula of C<sub>23</sub>H<sub>18</sub>O<sub>7</sub> (M<sup>+</sup> 406.1052. Calcd 406.1052) was confirmed by high resolution mass spectrometry. The spectral data [ $\nu_{\max}$  (KBr): 1730 and 1620 cm<sup>-1</sup>;  $\lambda_{\max}$  (MeOH): 201 (log  $\epsilon$  4.76), 224sh (4.39), 249sh (4.40), 256 (4.43), 283 (4.36) and 327 (4.20) nm; NMR (see Table I)] indicated the presence of a 8-substituted 5, 7-dimethoxycoumarin moiety in 2 like 1.<sup>1)</sup>

On the other hand, a *p*-naphthoquinone<sup>4)</sup> unit in the molecule was deduced by additional carbonyl bands ( $\nu_{\max}$ : 1683 and 1650 cm<sup>-1</sup>) in the IR spectrum, the lowest frequency  $\pi$ – $\pi^*$  transition of the UV absorption at 327 nm and the two lowest field shifted signals due to carbonyl functions at around 180 ppm in the <sup>13</sup>C-NMR spectrum. The following facts allowed us to extend the unit to an 8-substituted 2-methoxy-6-methylnaphthoquinone: 1. Two 3H singlets attributable to methyl and methoxy groups appeared at  $\delta$  2.50 and 3.80 in the <sup>1</sup>H-NMR spectrum. 2. The NOE enhancements were observed between the methoxy group and a quinoid proton ( $\delta$  6.10) and between the methyl group and a pair of *meta* coupled aromatic protons ( $\delta$  7.29 and 8.00). 3. Two carbons at ring junction, 4'a-C and 8'a-C, showed three independent bond correlations to the quinoid and to the aromatic protons in the COLOC experiments (see Table I).

Thus, toddacoumaquinone should be a biaryl compound consisting of a coumarin and a naphthoquinone, the structure of which could be depicted as 2. It could be reasonable that 2 would be synthesized in a plant body through [4+2] cycloaddition reaction between the coumarin diene (3) and a *p*-benzoquinone derivative because of the coexistence<sup>1, 2)</sup> of formal Diels-Alder dimeric products derived from 3. The synthetic work of 2 based on this biogenetic consideration is now in progress.

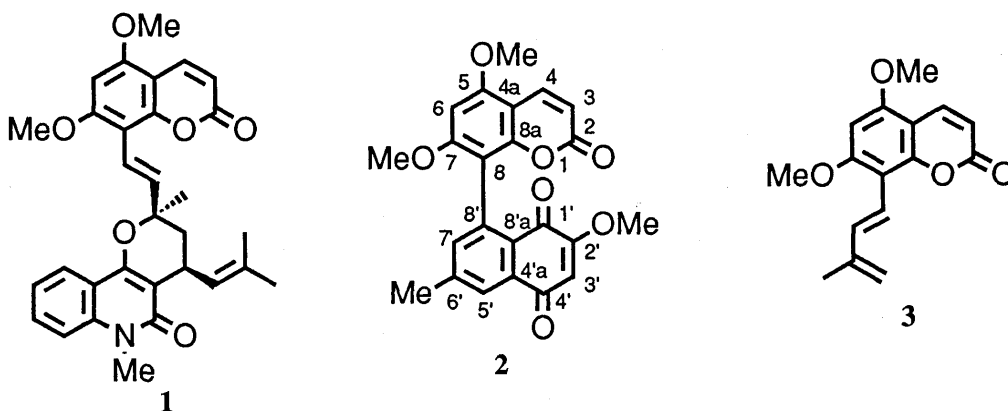


Table I. NMR Data<sup>a</sup> of Toddacoumaquinone (2)

C# <sup>b</sup>	$\delta_H$	NOE	$\delta_C$	COLOC	
				J=8Hz	J=4Hz
2	—		161.34	4-H(3)	4-H(3), 3-H(2)
3	6.10(d, J=9.6Hz)	4-H	110.95		
4	8.03(d, J=9.6Hz)		138.82		
4a	—		103.89	3-H(3), 6-H(3)	
5	—		156.72	5-OMe(3), 6-H(2)	5-OMe(3), 6-H(2)
6	6.41 (s)	5-OMe, 7-OMe	90.45		
7	—		160.33	7-OMe(3), 6-H(2)	7-OMe(3), 6-H(2)
8	—		110.30	6-H(3), 7'-H(3)	6-H(3), 7'-H(3)
8a	—		152.78	4-H(3)	4-H(3)
5-OMe	3.99(s)	4-H, 6-H	56.03		
7-OMe	3.77(s)	6-H	56.13		
1'	—		185.21		5'-H(4)
2'	—		160.64	2'-OMe(3), 3'-H(2)	2'-OMe(3), 3'-H(2)
3'	6.10(s)	2'-OMe	108.60		2'-OMe(4)
4'	—		179.73	3'-H(2)	
4'a	—		133.50	3'-H(3)	3'-H(3)
5'	8.00(d, J=1.1Hz)	6'-Me	127.40	6'-Me(3)	6'-Me(3)
6'	—		144.77	6'-Me(2)	6'-Me(2)
7'	7.29(d, J=1.1Hz)	6'-Me	138.63	6'-Me(3)	6'-Me(3)
8'	—		133.14		6-H(4)
8'a	—		127.11	5'-H(3), 7'-H(3)	
2'-OMe	3.80(s)	3'-H	56.29		
6'-Me	2.50(s)	5'-H, 7'-H	21.86	5'-H(3), 7'-H(3)	5'-H(3), 7'-H(3)

<sup>a</sup> <sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>) are reported downfield from internal TMS at 0.00 ppm. <sup>13</sup>C-NMR assignments are related to internal CDCl<sub>3</sub> at 77.00 ppm. <sup>1</sup>H- and <sup>13</sup>C-NMR assignments are based on H-C COSY, DEPT and COLOC experiments. For the COLOC experiments the number in parentheses denotes the number of bonds involved in the correlation. <sup>b</sup> The number is arbitrarily shown in each structure.

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## REFERENCES AND NOTES

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