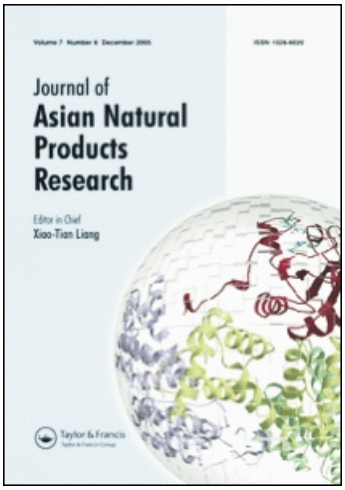

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Novel N-containing rotenoid and *seco*-rotenoid from the root of *Derris elliptica*

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To cite this Article Lu, Hai-Ying and Liang, Jing-Yu(2009) 'Novel N-containing rotenoid and *seco*-rotenoid from the root of *Derris elliptica*', Journal of Asian Natural Products Research, 11: 1, 58 — 62
To link to this Article: DOI: 10.1080/10286020802514002
URL: http://dx.doi.org/10.1080/10286020802514002

Journal of Asian Natural Products Research
Vol. 11, No. 1, January 2009, 58–62

Novel N-containing rotenoid and *seco*-rotenoid from the root of *Derris elliptica*

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(*Received 16 April 2008; final version received 6 September 2008*)

Two new rotenoids, 2-hydroxy-5-aminorotenonone (**1**) and elliptoic acid (**2**), were isolated from the roots of *Derris elliptica* collected in Guangdong Province, China. Their structures were established by extensive spectral analysis. Compound **1** is the first N-containing rotenoid and compound **2** is the third rotenoid with the cleavage of C(12)–C(12a).

Keywords: *Derris elliptica*; rotenoid; 2-hydroxy-5-aminorotenonone; elliptoic acid

1. Introduction

The genus *Derris* (family Legumina) is well known as a rich source of rotenoids. The plants have been used by native fishermen in many tropical countries as fish poisons to stupefy fish prior to capture and the ground root preparations were used as insecticides. Recently, it was reported that rotenoids such as deguelin also displayed antitumor actions, by inhibiting pulmonary adenoma formation and growth with no detectable toxicity [1,2]. *Derris elliptica* is characterized by the presence of active rotenoids. However, until now, there were few chemical investigations of *D. elliptica*. In order to isolate the effective compounds, the plant collected in Guangdong Province was chemically investigated. In this paper, we report the isolation and structural elucidation of two new compounds 2-hydroxy-5-aminorotenonone (**1**) and elliptoic acid (**2**) from *D. elliptica* (Figure 1).

2. Results and discussion

Compound **1**, crystallized as yellow needles, gave an $[M+H]^+$ ion peak at *m/z* 392.1113 in the (+)HRTOF mass spectrum, consistent with the molecular formula $C_{22}H_{17}O_6N$. Careful analysis of the ^1H and ^{13}C NMR spectral data (Table 1) indicated **1** to be a rotenoid similar to rotenonone (**1a**) [3]. They had the same C, D, and E rings with differences in rings A and B. The OCH_3(2) and O(5) observed for rotenonone were replaced by OH and NH, respectively, in **1**.

In the ^1H NMR spectrum of **1**, characteristic signals of the skeleton of rotenoid were observed at δ 8.94 (H-1), 6.92 (H-4), 7.08 (H-10, $J = 8.7$ Hz), 8.07 (H-11, $J = 8.7$ Hz). The signals at δ 3.68 (dd, $J = 15.9$, 9.9 Hz, H-4′a), 3.24 (dd, $J = 16.0$, 7.8 Hz, H-4′b), 5.57 (dd, $J = 8.4$, 9.2 Hz, H-5′), 5.14 (s, H-7′a), 4.98 (s, H-7′b), and 1.78 (s, H-8′) suggested the presence of 2-isopropenyl-2,3-dihydrofuran. It was corroborated by HSQC and HMBC experiments (Table 1, Figure 2). Due to the presence of the HMBC correlations of H-1 and H-4 with C-1a, C-2, C-3, and C-4a; H-10 with C-8 and C-11a; H-11 with C-7a, C-9, and C-12; H-4′ with C-8, C-9, and C-6′; H-7′ with C-5′ and C-8′; and H-8′ with C-5′,

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ISSN 1028-6020 print/ISSN 1477-2213 online

DOI: 10.1080/10286020802514002
http://www.informaworld.com

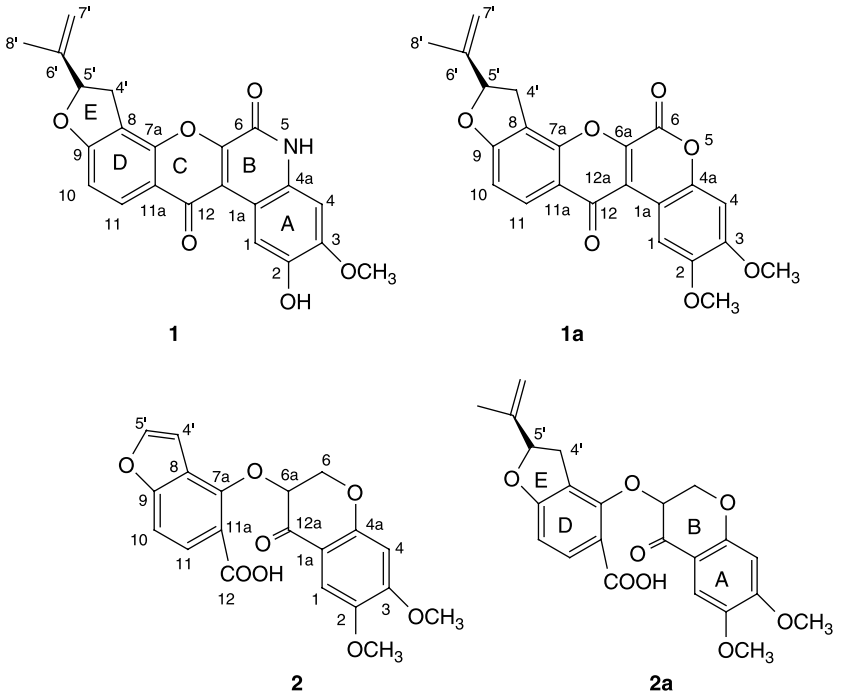

Figure 1. Structures of compounds **1** and **2**.

the skeleton was assigned to be similar to rotenonone. On the basis of the observed HMBC correlations of OH (δ 9.24) with C-1 (δ 111.5), C-2 (δ 143.2), and C-3 (δ 149.6); OMe (δ 3.83) with C-3 (δ 149.6), the OH and OMe groups were placed at C(2) and C(3), respectively. The 5-NH was confirmed by correlations of NH (s, δ 12.4) with C-1a (δ 108.5) and C-6a (δ 146.7). Thus, the structure of **1** was determined to be 2-hydroxy-5-aminorotenonone. It is the first N-containing rotenoid.

Compound **2**, obtained as a white amorphous powder, gave rise to the $[M+H]^+$ ion peak at *m/z* 385.0904 in the (+)HRTOF mass spectrum, consistent with the molecular formula $C_{20}H_{16}O_8$. Careful analysis of the ^1H and ^{13}C NMR spectral data (Table 1) indicated **2** to be a *seco*-rotenoid similar to (−)-rotoic acid (**2a**) and (−)-deguoic acid [4]. The difference of the three compounds was only in ring E. The group of 2-isopropenyl-2,3-dihydrofuran in **2a** was replaced by furan group in **2**.

In the ^1H NMR spectrum of **2**, characteristic signals of the skeleton of C(12)–C(12a) *seco*-rotenoid were observed at δ 7.12 (H-1), 6.69 (H-4), 4.70, 4.80 (H-6), 4.91 (H-6a), 7.44 (H-10), and 7.76 (H-11). The signals at δ 3.75 and 3.87 were assigned to two OMe groups at C-2 and C-3. The signals at δ 6.77 (d, $J = 2.2$ Hz, H-4′), 7.97 (d, $J = 2.2$ Hz, H-5′) suggested that E ring was furan, and the ^1H signal at δ 12.7 (br s, OH) and the ^{13}C signal at δ 166.5 (C-12) suggested the group of COOH (12).

The above assignment was also corroborated by HSQC and HMBC experiments (Table 1, Figure 3). Due to the HMBC correlations of H-1, H-4, H-6, and H-6a with C=O (δ 185.7); H-11 with COOH (δ 166.5), the C=O and COOH were placed at C-12a and C-12, respectively, which indicated the presence of the cleavage of C(12)–C(12a). The furan ring was confirmed by the HMBC correlations of H-4′ and H-5′ with C-8 and C-9. Thus, the structure of **2** was determined to be 12,12a-*seco*-elliptone, and named

Table 1. ^{1}H- (500 MHz) and ^{13}C- (125 MHz) NMR spectral data of **1** and ^{1}H- (300 MHz) and ^{13}C- (75 MHz) NMR spectral data of **2**.

	Compound **1**			Compound **2**		
	δ_C	δ_H	HMBC (position)	δ_C	δ_H	HMBC (position)
1	111.5	8.94 (s)	1a, 2, 3, 4a, 12a	107.0	7.12 (s)	1a, 3, 4a, 12a
1a	108.5			111.4		
2	143.2			144.7		
3	149.6			156.6		
4	98.0	6.92 (s)	1a, 2, 3, 4a	100.4	6.69 (s)	1a, 3, 4a, 12a
4a	129.1			157.6		
6	154.9			69.8	4.70 (dd, J = 12.3, 3.4 Hz) 4.80 (dd, J = 12.4, 5.3 Hz)	4a, 6a, 12a
6a	146.7			78.4	4.91 (dd, J = 5.2, 3.4 Hz)	1a, 6, 12a
7a	151.9			151.2		
8	113.2			122.0		
9	165.2			157.3		
10	108.6	7.08 (d, J = 8.7 Hz)	8, 11a	107.5	7.44 (d, J = 8.7 Hz)	8, 9, 11, 11a
11	127.7	8.07 (d, J = 8.7 Hz)	7a, 9, 12	127.4	7.76 (d, J = 8.7 Hz)	8, 9, 12a
11a	117.6			118.8		
12	176.7			166.5		
12a	119.3			185.7		
4′	30.7	3.68 (dd, J = 15.9, 9.9 Hz) 3.24 (dd, J = 16.0, 7.8 Hz)	8, 9, 6′	104.9	6.77 (d, J = 2.2 Hz)	8, 9
5′	87.5	5.57 (dd, J = 8.4, 9.2 Hz)		146.1	7.97 (d, J = 2.2 Hz)	8, 9, 4′
6′	142.9					
7′	112.4	5.14 (s), 4.98 (s)	5′, 8′			
8′	16.8	1.78 (s)	5′, 6′, 7′			
2-OH		9.24 (s)	1, 2, 3			
2-OMe				56.2	3.75 (s)	2
3-OMe	55.4	3.83 (s)	3	55.9	3.87 (s)	3, 4
5-NH		12.4 (s)	1a, 6a			
12-COOH					12.7 (s)	

DMSO-d_6; δ in ppm, J in Hz.

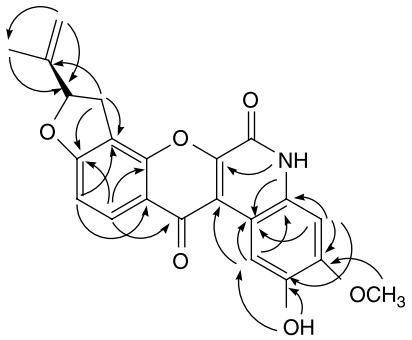

Figure 2. Key HMBC ($^1H \rightarrow {}^{13}C$) correlations of **1**.

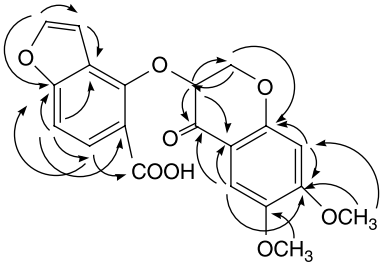

Figure 3. Key HMBC ($^1H \rightarrow {}^{13}C$) correlations of **2**.

elliptoic acid. It is the third rotenoid with the cleavage of C(12)–C(12a).

3. Experimental

3.1 General experimental procedures

Melting points were measured on a XT-4 micro-melting point apparatus, uncorrected. IR spectra were measured on a Shimadzu FTIR-8400s spectrometer, KBr pellets, in cm^{-1}. $[\alpha]_D$ spectra were obtained on a JASCO P-1020 spectrometer. UV spectra were obtained on a Shimadzu 2501 PC spectrometer. The 1D and 2D NMR spectra were recorded on a Bruker AV-300 and AV-500 spectrometers, δ in ppm, J in Hz, Me_4Si as internal standard, in DMSO-d_6. MS spectra were run on an Agilent 1100 Series LC/MSD Trap ESI and Agilent 1100 LC/TOF MSD spectrometer, in *m/z*. All solvents used were of analytical grade (Tianjing Chemical Plant, Tianjing, China). Column chromatography was performed on silica gel H (100–200, 200–300 mesh; Qingdao Marine Chemical Ltd, Qingdao, China), and thin layer chromatography was performed on silica gel GF254 (Yantai Huiyou, Yantai, China).

3.2 Plant material

The roots of *D. elliptica* were collected in Fengshun Prefecture, Guangdong Province (2004), and identified by Prof. Xue-Hua Song, the curator of China Pharmaceutical University (China). A voucher specimen (No. 040816) is deposited in Department of Natural Medicinal Chemistry, China Pharmaceutical University, China.

3.3 Extraction and isolation

The air-dried roots (12 kg) were crushed into small pieces and extracted thrice with 85% EtOH at 80°C. The combined extracts were evaporated *in vacuo*, and the resulting residue was suspended in H_2O and subsequently extracted with petroleum ether, $CHCl_3$, and AcOEt. The AcOEt fraction (158 g) was fractionated by column chromatography (silica gel 100–200 mesh, 1.2 kg, $CHCl_3$/MeOH 1:0–0:1) to afford eight fractions (I–VIII). Fraction II was chromatographed over silica gel, eluting with petroleum ether/AcOEt 2:1 to give compound **1** (3.5 mg), and 1:1 to give compound **2** (69 mg).

3.3.1 2-Hydroxy-5-aminorotenonone (**1**)

Yellow needles; mp > 300°C. ^1H and ^{13}C NMR spectral data: see Table 1. (−)ESI-MS: *m/z* 390 $[M-H]^-$, 375 $[M-H-Me]^-$. (+)HRTOF-MS: *m/z* 392.1113 $[M+H]^+$ (calcd for $C_{22}H_{18}NO_6$, 392.1128).

3.3.2 Elliptoic acid (**2**)

White amorphous powder; mp 259–262°C. $[\alpha]_D^{20}$ −92.9 ($c = 0.034$, pyridine). IR ν_{max} (KBr) 3453, 1694, 1616, 1514, 1470, 1275, 1215, 1084, 752 cm^{-1}. UV (pyridine) λ_{max} 342 nm. ^1H and ^{13}C NMR spectral data:

see Table 1. (+)ESI-MS: *m/z* 385 $[M+H]^+$, 367 $[M+H-H_2O]^+$, 323, 208; (−)ESI-MS: *m/z* 383 $[M-H]^-$, 223. (+)HRTOF-MS: 385.0904 $[M+H]^+$ (calcd for $C_{20}H_{17}O_8$, 385.0917).

Acknowledgements

The authors are grateful to the Research Foundation for University Ph. D. Program, Ministry of Education of China (No. 20070316003) for financial support.

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