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A NEW ROTENOID FROM *DERRIS MALACCENSIS*

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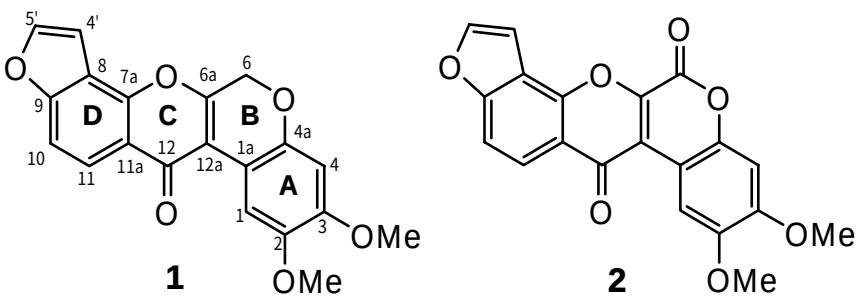
Abstract – A new rotenoid named 6-oxo-dehydroelliptone (**2**) was isolated from the roots of *Derris malaccensis* Prain, along with six known compounds. The isolation of dehydroelliptone (**1**) from a natural source and its unequivocal ^{1}H and ^{13}C NMR assignments were reported for the first time.

The genus *Derris* (Leguminosae) contains about 50 species widely found in the tropical areas of Africa and Asia.[1, 2] The roots of plants in this genus have been reported to be a rich source of rotenoids, a subclass of isoflavonoids known to possess several biological activities, including insecticidal, antiplasmodial, cancer chemopreventive and anti-*Helicobacter pylori* properties.[3]

Derris malaccensis Prain is a climber known in Thailand as "Haang-lai-khao," with its roots locally used as insecticidal and piscicidal agents.[4] Previous chemical investigations of the stems and the roots of this plant revealed the presence of several rotenoids.[5-8] In this paper, we report the isolation and characterization of a new rotenoid (**2**), as well as 6 known compounds, i.e. dehydroelliptone (**1**),[9-13] 12a-hydroxyelliptone,[5] 12-deoxo-12α-acetoxyelliptone,[5] elliptone,[6] tephrosin,[6] and deguelin.[6] Although **1** was earlier synthesized[9-13] and reportedly detected in *Derris elliptica*,[14] its isolation and NMR properties were not known. This study is the first report of the isolation of **1** from a natural source. Moreover, ^{1}H and ^{13}C NMR assignments have been obtained for **1** for the first time (Table 1) through interpretation of the NOESY and HMBC spectra (Figure 1).



Compound **2** was isolated as a new rotenoid. It had the molecular formula $C_{20}H_{12}O_7$, as indicated from its $[M+H]^+$ ion at *m/z* 365.0654 (calcd for $C_{20}H_{13}O_7$, 365.0656) in the HRESIMS. In the EIMS, two prominent ions, $[M]^+$ and $[M-CH_3]^+$, were found at *m/z* 364 (100%) and 349 (18%). UV absorptions at 226, 280 and 290 nm were indicative of a dehydrorotenoid skeleton, whereas IR bands for a lactone carbonyl and a conjugated ketone were observed at 1739 and 1645 cm^{-1}, respectively.

The ^{1}H NMR spectrum of **2** resembled that of **1**, showing signals for two methoxy groups at δ 4.01 and 4.08, and six aromatic and olefinic protons at δ 9.06 (s, H-1), 8.28 (d, *J* = 8.9 Hz, H-11), 7.84 (d, *J* = 1.4 Hz, H-5′), 7.68 (d, *J* = 8.9 Hz, H-10), 7.40 (d, *J* = 1.4 Hz, H-4′) and 6.96 (s, H-4) (Table 1).

Table 1. ^{1}H and ^{13}C NMR data for compounds **1** and **2** in $CDCl_3$

Position	**^{1}H**		**^{13}C**	
	1	**2**	**1**	**2**
1	8.45 (1H, s)	9.06 (1H, s)	110.1	108.3
1a	-	-	110.4	107.9
2	-	-	144.1	147.1
3	-	-	149.1	151.5
4	6.54 (1H, s)	6.96 (1H, s)	100.4	99.7
4a	-	-	146.4	145.5
6	5.08 (2H, s)	-	64.8	156.0
6a	-	-	156.1	142.2
7a	-	-	149.4	150.2
8	-	-	116.9	117.5
9	-	-	158.0	159.1
10	7.54 (1H, d, *J* = 8.7 Hz)	7.68 (1H, d, *J* = 8.9 Hz)	110.4	111.4
11	8.19 (1H, d, *J* = 8.7 Hz)	8.28 (1H, d, *J* = 8.9 Hz)	122.2	122.2
11a	-	-	120.1	119.7
12	-	-	174.6	177.1
12a	-	-	112.5	122.1
4′	7.07 (1H, d, *J* = 1.5 Hz)	7.40 (1H, d, *J* = 1.4 Hz)	104.0	104.9
5′	7.72 (1H, d, *J* = 1.5 Hz)	7.84 (1H, d, *J* = 1.4 Hz)	145.9	146.4
MeO-2	3.95 (3H, s)	4.08 s (3H)	56.3	56.4
MeO-3	3.85 (3H, s)	4.01 s (3H)	55.9	56.3

However, it was noted that in **2** these protons each appeared at a more downfield position than their corresponding protons in **1**, and no signals for the C-6 methylene protons were observed for **2**. Comparison of the molecular formula of **2** with that of **1** indicated that **2** had one oxygen atom more, but two hydrogen atoms less than **1**. The aforementioned data suggested the presence of a carbonyl functionality for **2**, which could be placed only at C-6. In support of this, H-1 of **2** was found to resonate at a very downfield position (δ 9.06), similar to that of 6-oxo-6a,12a-dehydrodeguelin, a 6-keto dehydrorotenoid previously isolated from *Lonchocarpus utilis* and *L. urucu*.[15] The proposed structure of **2** was further supported by the signals of C-6 appearing as a lactone carbon at δ 156.0 and C-6a at a more upfield position at δ 142.2 in the ^{13}C NMR spectrum. The remaining carbon signals were similar to those in **1**. It should be noted that rings B, C and D of **2** constituted a tricyclic system consisting of a

pyran-2-one ring fused to a chrome-4-one moiety. Similar observations have been reported for this type of tricyclic structure such as salviamone, an anthracene-related compound, of which the lactone carbon and the α-carbon each were found to resonate at a rather highfield position.[16] In addition, the NOSEY and HMBC correlations obtained for **2** (Figure 1) were consistent with the proposed structure. Thus, the structure of **2** was determined as 6-oxo-dehydroelliptone. To our best knowledge, structure **2** was hitherto unknown. It should be mentioned that in both **1** and **2**, there were no HMBC correlations for the connection of rings D and B. Several dehydrorotenoids and their 6-oxo analogues have been previously identified from the families Leguminosae, Nyctaginaceae, Euphorbiaceae, Stemonaceae and Asclepiadaceae.[3,17-21]

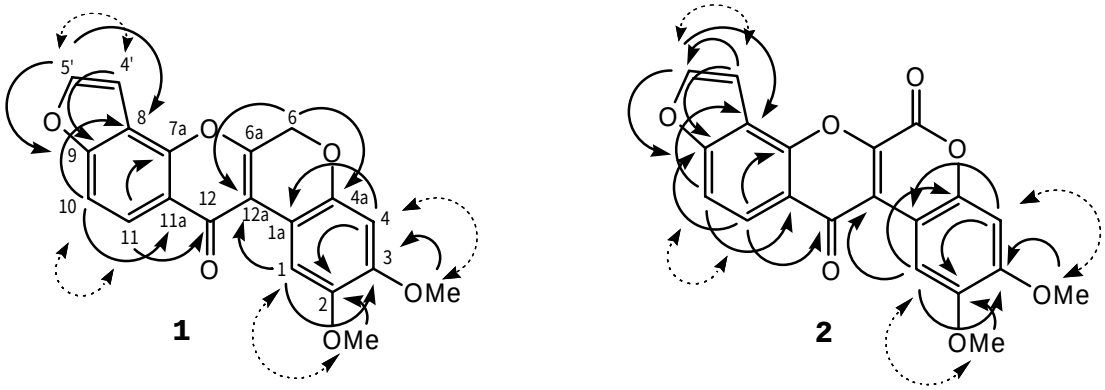


Figure 1 NOESY (◄- - - -►) and HMBC (⟵⟶) correlations observed for **1** and **2**.

EXPERIMENTAL

UV spectra were obtained on a Shimadzu UV-160A spectrophotometer, and IR spectra on a FT-IR Perkin-Elmer spectrometer. HRESIMS were measured with a Bruker microTOF mass spectrometer, and EIMS were recorded on a Thermo-Finnigan polarisQ mass spectrometer. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra were obtained with a Bruker AV-500 NMR spectrometer. HPLC was carried out on a Shimadzu LC-8A liquid chromatograph.

***Extraction and Isolation**:* The roots of *D. malaccensis* were purchased from a drugstore in Bangkok, Thailand, in April 2005, and a voucher specimen (KL-042548) has been on deposit at the Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University. The plant material (4 kg) were extracted with MeOH (10 L). The MeOH extract (41 g) was chromatographed on silica gel (hexane-EtOAc-MeOH gradient) to give 17 fractions. Fraction VIII (1.9 g) was re-chromatographed on silica gel (hexane-EtOAc-MeOH gradient) to give 4 fractions (A-D). Fraction A (780 mg) was further separated on Sephadex LH-20 (MeOH) to give 12-deoxo-12a-acetoxyelliptone (240 mg). Separation of fraction XII (450 mg) by HPLC (ODS, H_2O-CH_3CN 1:1) afforded **2** (4 mg), **1** (52 mg), tephrosin (236 mg), 12a-hydroxyelliptone (45 mg) and deguelin (7 mg). Fraction XIV (3 g) was separated by HPLC (ODS, H_2O-MeCN 4:6) to give elliptone (25 mg).

6-Oxo-dehydroelliptone (**2**): yellow amorphous solid; UV (MeOH) λ_{max} (log ε): 226 (3.5), 280 (3.2) and 290 (3.2) nm; IR (film) ν_{max}: 1739, 1645 and 1464 cm^{-1}; EIMS: *m/z* (rel. int.) 364 (M^+, 100), 349 (18), 321 (43), 293 (19), 278 (16), 194 (12); HRESIMS: $[M+H]^+$ at *m/z* 365.0654 (calcd for $C_{20}H_{13}O_7$, 365.0656); ^1H and ^{13}C NMR: see Table 1.

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REFERENCES

1. W. C. Evans, Trease and Evans Pharmacognosy, WB Saunders, Edinburgh, 2002, pp. 510-511.
2. R. N. Chopra, R. L. Badhwar, and S. Ghosh, Poisonous Plants of India, Vol. I, Indian Council of Agricultural Research, New Delhi, 1965, p. 319-320.
3. N. C. Veitch, *Nat. Prod. Rep.*, 2007, **24**, 417.
4. V. Vudhidhammavej, Encyclopaedia of herbs: principles of Thai traditional pharmacy, Odeon Store, Bangkok, 1997, p. 488-489.
5. N. Thasana, M. Chuankamnerdkarn, and S. Ruchirawat, *Heterocycles*, 2001, **55**, 1121.
6. J. Takashima, N. Chiba, K. Yoneda, and A. Ohsaki, *J. Nat. Prod.*, 2002, **65**, 611.
7. C. M. R. Gomes, O. R. Gottlieb, G. B. M. Bettolo, F. D. Monache, and R. M. Polhill, *Biochem. Syst. Ecol.*, 1981, **9**, 129.
8. A. Sae-Yun, C. Ovatlarnporn, A. Itharat, and R. Wiwattanapatapee, *J. Chromatogr. A*, 2006, **1125**, 172.
9. S. H. Harper, *J. Chem. Soc.*, 1939, 1099.
10. S. H. Harper, *J. Chem. Soc*., 1939, 1424.
11. H. Fukami, G. Sakata, and M. Nakajima, *Agr. Biol. Chem. (Tokyo)*, 1965, **29**, 82.
12. V. Chandrashekar, M. Krishnamurti, and T. R. Seshadri, *Curr. Sci.*, 1965, **16**, 479.
13. V. Chandrashekar, M. Krishnamurti, and T. R. Seshadri, *Tetrahedron*, 1967, **23**, 2505.
14. X.-N. Zeng, J. Coll, S.-X. Zhang, X.-Q. Liu, and F. Camps, *Sepu*, 2002, **20**, 144. (CA 137:151907z).
15. N. Fang and J. E. Casida, *J. Agric. Food Chem.*, 1999, **47**, 2130.
16. M.-J. Don, C.-C. Shen, W.-J. Syu, Y.-H. Ding, and C.-M. Sun, *Phytochemistry*, 2006, **67**, 497.
17. P. M. Dewick, 'The flavonoids-advances in research since 1986: Isoflavonoids.', ed. by J. B. Harborne, Chapman & Hall, London, 1994, p. 159–166.
18. D. M. X. Donnelly and G. M. Boland, *Nat. Prod. Rep.*, 1995, **12**, 321.
19. G. M. Boland and D. M. X. Donnelly, *Nat. Prod. Rep.*, 1998, **15**, 241.
20. J. Reynaud, D. Guilet, R. Terreux, M. Lussignol, and N. Walchshofer, *Nat. Prod. Rep.*, 2005, **22**, 504.
21. Z. Mackova, R. Koblovska, and O. Lapcik, *Phytochemistry*, 2006, **67**, 849.