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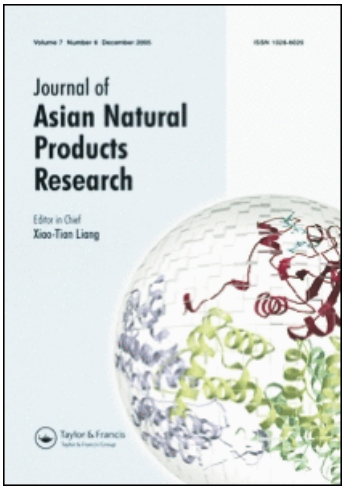

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
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Two Dichromenes from *Evodia lepta*

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To cite this Article Li, Guo-Lin and Zhu, Da-Yuan(1999) 'Two Dichromenes from *Evodia lepta*', Journal of Asian Natural Products Research, 1: 4, 337 — 341
To link to this Article: DOI: 10.1080/10286029908039883
URL: http://dx.doi.org/10.1080/10286029908039883

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JANPR, Vol. 1, pp. 337–341
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TWO DICHROMENES FROM *EVODIA LEPTA*

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(Received 11 March 1999; Revised 12 April 1999; In final form 23 April 1999)

Two new dichromenes, dichromene C and dichromene D, were isolated from the aerial parts of *Evodia lepta*. Their structures were determined by spectroscopic analysis.

Keywords: *Evodia lepta*; Rutaceae; Dichromene; Dichromenes C and D

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INTRODUCTION

In the course of our study of chemical constituents of a traditional Chinese herb, *Evodia lepta* (Spr.) Merr. [1], we isolated 20 chromenes, evodione, alloevodione, isoevodionol (**3**), leptol A (**5**), methylleptol A, ethylleptol A, leptonol, leptol B (**4**), ethylleptol B, methylleptol B, leptenes A, B and leptins A–H as well as 2 dichromenes, dichromenes A and B from the title plant [2–7]. We report herein the isolation and structural elucidation of another 2 new dichromenes, dichromene C (**1**) and D (**2**) after further chemical investigation of the material.

RESULTS AND DISCUSSION

Dichromene C (**1**) was isolated as emerald plates, showed $[M]^+$ at m/z 494.2330 in the HREIMS, corresponding to a formula of $C_{29}H_{34}O_7$ (calcd. 494.2305). Fully decoupled ^{13}C NMR spectrum of **1** exhibited 29 carbon

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signals, consisting of 9 methyls, 6 methines and 14 quaternary carbons. There was no methylene in this compound. Closer inspection of the ^{1}H NMR spectrum of **1** revealed 2 sets of signals (set A and set B). The signals in set A were very similar to those of leptol B (**4**) [3], the main difference being that H-11 resonated at δ 3.97 (1H, q, $J = 6.9$ Hz), and H-1′ in compound **4** resonated at δ 5.10 (1H, q, $J = 6.8$ Hz) as C-11 was attached to olefin group and C-1′ was attached to a hydroxyl group. Because position 3 was substituted in compound **1**, the signal of H-3 disappeared in the ^{1}H NMR spectrum, and the signal of H-4 became a singlet at δ 6.70 rather than a doublet at δ 6.63 in that of isoevodionol (**3**) [8]. The other signals in set B were similar to those of compound **3** except for small chemical shift differences. From the above evidence, we could infer the structure of compound **1** to be a dimer of compounds **3** and **4**. Correlation of H-12 to C-3 observed at the HMBC spectrum of compound **1** demonstrated that C-11 was attached to position 3. The proposed structure was demonstrated by HMQC and HMBC experiments. The signals in ^{1}H and ^{13}C NMR spectra were assigned according to 2D-NMR techniques.

Dichromene D (**2**) was obtained as a colourless oil. The ^{1}H and ^{13}C NMR spectra of this compound also showed 2 sets of signals, one set was very similar to those of compound **4**, and another was very similar to those of leptol A (**5**) [2]. The electron impact (EI) mass spectrum revealed the molecular ion peak at m/z 540, and this molecular weight was equal to that of product of condensation of compounds **4** and **5** and losing a 18 mass unit (H_2O) from m/z 540. From above results, the structure of compound **2** was established as that showed in Fig. 1. The fragment ion peak in the EI-MS spectrum of this compound supported the proposed structure, the fragment ion peak at m/z 247 was the signal of part A, and the basic ion peak at m/z 277 was the signal of part B. In the HMBC spectrum of compound **2**, the correlation peaks between H-11 and C-11′, H-11′ and C-11 also confirmed the proposed structure. The other correlation peaks demonstrated the assignment of substituents on the aromatic ring. The total assignments of ^{1}H and ^{13}C NMR spectra of compound **2** were in accord with its HMQC and HMBC spectra.

EXPERIMENTAL SECTION

General Experimental Procedures

IR spectra were taken with Nicolet Maganm 750 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3COCD_3 solution on a Bruker

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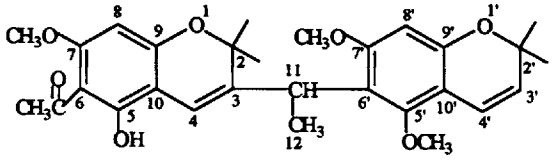

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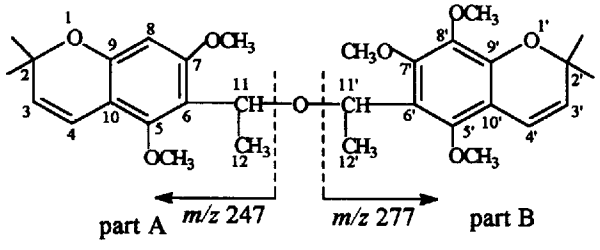

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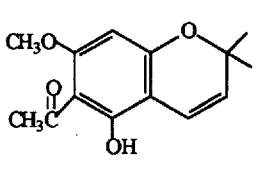

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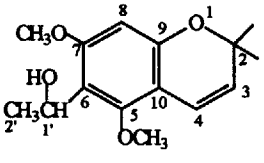

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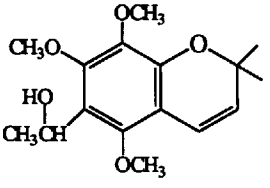

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FIGURE 1

Am-400 spectrometer at 400 and 100 MHz, respectively. The ^1H NMR chemical shifts were referred in $CDCl_3$ to the residual $CHCl_3$ δ 7.24 and in CD_3COCD_3 to the residual CD_3COCD_2H δ 2.05 for ^1H NMR. In ^{13}C NMR spectra, chemical shifts of solvents $CDCl_3$ (δ 77.00) and CD_3COCD_3 (δ 29.8) were used as references. Multiplicity determinations (DEPT) and 2D spectra were obtained using standard Bruker software. Low resolution EIMS was recorded with MAT-95 spectrometer and the HREIMS was obtained at MAT-77 spectrometer. TLC was performed on silica gel F_{254}.

Plant Material

Aerial parts of *E. lepta* (Spr.) Merr. were collected from Hainan province, China, in July, 1992. A voucher sample was deposited in the herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

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The specimen was authenticated by Dr. Xiao-Qiang Ma, Department of Phytochemistry, Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

Extraction and Isolation

The fractions mentioned in a previous paper [2] were repeatedly chromatographed by silica gel chromatography using petrol–EtOAc (12 : 1) to give compound **1** (10 mg) and (20 : 1) to give compound **2** (11 mg).

Dichromene C (**1**) $C_{29}H_{34}O_7$. Green plates. $[\alpha]_D^{20} = +2.94$ (acetone; *c* 0.367). HREIMS *m/z* $[M]^+$ 494.2330 ($C_{29}H_{34}O_7$, calcd. 494.2305). IR ν_{max}^{KBr} cm^{-1}: 2980, 2970, 2920, 1626, 1603, 1425, 1367, 1211, 1128, 1149, 1084. ^1H NMR data, see Table I; ^{13}C NMR data, see Table II. EIMS *m/z* (rel. int.): $[M]^+$ 494 (15), 479 (34), 451 (31), 277 (7), 259 (31), 247 (100), 231 (28).

Dichromene D (**2**) $C_{31}H_{40}O_8$. Oil. $[\alpha]_D^{20} = +0.87$ (acetone; *c* 0.462). HREIMS *m/z* $[M]^+$ 540.2743 ($C_{31}H_{40}O_8$, calcd. 540.2723). IR ν_{max}^{film} cm^{-1}: 2970, 2930, 1730, 1633, 1606, 1470, 1375, 1191, 1134, 1057, 891. ^1H NMR data, see Table I; ^{13}C NMR data, see Table II. EIMS *m/z* (rel. int.): $[M]^+$ 540 (6), 525 (4), 321 (5), 277 (100), 247 (45), 231 (34), 205 (19).

Isoevodionol (**3**) $C_{14}H_{16}O_4$. Prism. ^{13}C NMR ($CDCl_3$). δ 203.17 (C=O), 162.96, 161.80, 160.12, 125.30 (C-3), 115.96 (C-4), 105.66, 102.67, 91.06 (C-8), 78.10 (C-2), 55.53 ($-OCH_3$), 32.95 ($-COCH_3$), 28.32 (CH_3-2).

Leptol B (**4**) $C_{15}H_{20}O_4$. Oil. ^1H NMR ($CDCl_3$): δ 6.45 (1H, *d*, $J = 9.8$ Hz, H-4), 6.21 (1H, *s*, H-8), 5.49 (1H, *d*, $J = 9.8$ Hz, H-3), 5.10 (1H, *q*, $J = 6.8$ Hz, H-1′), 3.80 (*s*, $-OCH_3$), 3.74 (*s*, $-OCH_3$), 1.51 (3H, *d*, $J = 6.8$ Hz, H-2′), 1.41 (*s*, CH_3-2), 1.38 (*s*, CH_3-2).

TABLE I The ^1H NMR spectral data of compounds **1** and **2** (**1**: $CDCl_3$; **2**: CD_3COCD_3)

H	1	2	*H*	1	2
3		5.68 *d* (9.9)	12	1.53 *d* (7.0)	1.54 *q* (6.8)
4	6.70 *s*	6.48 *d* (9.9)	3′	5.46 *d* (9.9)	5.58 *d* (9.7)
8	5.86 *s*	6.16 *s*	4′	6.47 *d* (9.9)	6.46 *d* (9.7)
CH_3O-5		3.54 *s*	CH_3O-5′	3.69 *s*	3.63 *s*
CH_3O-7	3.81 *s*	3.63 *s*	CH_3O-7′	3.68 *s*	3.64 *s*
CH_3O-8′		3.75 *s*	H-8	6.13 *s*	
CH_3CO-6	2.59 *s*		CH_3-2′	1.42 *s*	1.34 *s*
CH_3-2	1.47 *s*	1.44 *s*		1.37 *s*	1.29 *s*
	0.97 *s*	1.41 *s*	11′		5.05 *q* (6.6)
11	3.97 *q* (7.0)	4.84 *q* (6.8)	12′		1.57 *d* (6.6)

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TABLE II The ^{13}C NMR spectral data of compounds **1** and **2** (**1**: $CDCl_3$; **2**: CD_3COCD_3)

C	**1**	**2**	*C*	**1**	**2**
2	81.77	77.49	2′	75.95	77.38
3	138.35	130.56	3′	127.00	128.93
4	112.47	118.80	4′	117.58	118.80
5	161.34	152.15	5′	154.97	158.10
6	104.96*	124.48	6′	118.05	118.80
7	162.26	154.20	7′	159.50	161.00
8	90.84	140.42	8′	96.69	140.42
9	159.29	147.65	9′	153.20	155.74
10	105.78*	113.50	10′	108.00	109.80
11	30.93	68.53	11′		67.73
12	19.05	21.25	12′		21.25
CH_3O-5		63.65	CH_3O-5′	62.49	63.65*
CH_3O-7	55.48	62.16*	CH_3O-7′	55.22	56.99
$\underline{C}H_3CO$-6	33.01		CH_3O-8′		67.71
CH_3-2	26.05	28.83	CH_3-2′	28.04	28.83
	26.15	28.28		27.27	28.28
C=O	203.24				

*Interchangeable assignment.

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Leptol A (**5**) $C_{16}H_{22}O_5$. Oil. ^1H NMR (CD_3COCD_3): δ 6.53 (1H, *d*, $J=10.0$ Hz, H-4), 5.72 (1H, *d*, $J=10.0$ Hz, H-3), 5.09 (1H, *q*, $J=6.6$ Hz, H-1′), 3.91 (*s*, $-OCH_3$), 3.81 (*s*, $-OCH_3$), 3.73 (*s*, $-OCH_3$), 1.51 (3H, *d*, $J=6.6$ Hz, H-2′), 1.45 (*s*, $2\times CH_3$-2). ^{13}C NMR (CD_3COCD_3): δ 152.93, 150.25, 146.92, 139.58, 130.05 (C-3), 124.59 (C-6), 117.87 (C-4), 112.53 (C-10), 76.93 (C-2), 63.95 (C-1′), 63.49 ($-OCH_3$), 61.96 ($-OCH_3$), 61.04 ($-OCH_3$), 27.89 ($2\times CH_3$-2), 24.73 (C-2′).

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