

Two New Dichromenes from *Evodia leptia*

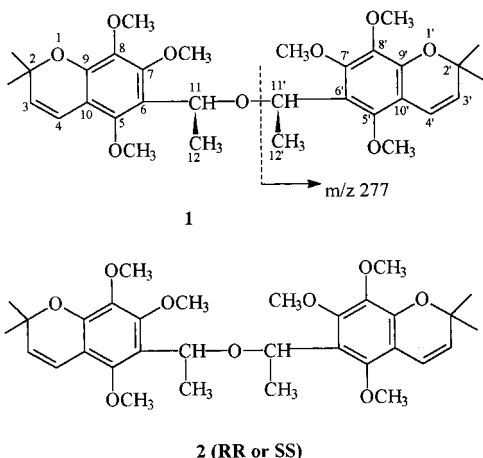
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Two new dichromenes, **1** and **2**, were isolated from the aerial parts of *Evodia leptia*. Their structures were determined by spectroscopic analysis.

Evodia leptia (Spreng) Merr. (Rutaceae), a traditional Chinese herb, is widely used as a folk medicine to treat many diseases.¹ Previous papers have reported the isolation and identification of five chromenes, evodione, isoevodionol, leptol A (**3**), ethylleptol A, and leptene A,¹ from this plant.² Continuing with the chemical studies of *E. leptia*, we report herein the isolation and identification of two new dichromenes **1** and **2**.



Compound **1** was isolated as a colorless oil, and HREIMS indicated $C_{32}H_{42}O_9$ to be its molecular formula (570.2842, requires 570.2829). The 1H NMR spectrum was very similar to that of leptol A (**3**), except that the

H-11 signal in **1** appeared at δ 4.91 and in leptol A it appeared at δ 5.09. The ^{13}C NMR spectra of these two compounds were also very similar, except for some small chemical shift differences. The IR spectrum of **1** demonstrated that this compound had no hydroxyl group. The EIMS of this compound indicated 570 as its molecular weight, which is equal to that of the product of condensation of two molecules of **3** with loss of one

molecule of water. The base ion peak, at m/z 277, is consistent with a fragment arising from cleavage of the oxygen link of a dimer. From the above evidence, we conclude that the planar structure of dichromene A is that shown. In its HMBC spectrum, H-11 is correlated with C-11' and H-11' is correlated with C-11, confirming the dimer structure **1**. Other correlations such as between H-4 and C-5 and C-9, H-11 and C-5 and C-7 and C-6, H-12 and C-6 demonstrate the correct placement of substituents in the aromatic ring.

Compound **2** was obtained as an orange oil, and HREIMS indicated its molecular formula to be $C_{32}H_{42}O_9$ (570.2816, requires 570.2829), the same as **1**. 1H NMR and ^{13}C NMR spectra of **1** and **2** are very similar except for significant chemical shift differences in a few protons and carbons. Using the same method, the planar structure of **2** was shown to be identical to that of **1**, and hence, these compounds are diastereoisomers. Since the optical rotation of **1** is zero, it must be the meso *RS* stereoisomer, while the optically active **2** ($[\alpha]_D^{20} -13.7^\circ$) must be either the *RR* or *SS* enantiomer.

Experimental Section

General Experimental Procedures. 1H and ^{13}C NMR and all 2D spectra were recorded in CD_3COCD_3 solution on a Bruker Am-400 spectrometer at 400 and 100 MHz, respectively, and the solvent signal was used as reference (2.05 ppm for 1H NMR and 29.8 for ^{13}C NMR). Low-resolution EIMS were recorded on a MAT-95 spectrometer, and the HREIMS were obtained on a MAT-77 spectrometer. TLC was performed on silica gel F₂₅₄.

Plant Material. Aerial parts of *E. leptia* (Spreng) Merr. were collected from Hainan province, People's Republic of China, in July 1992. A voucher sample (no. 910042) is deposited in the herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Sciences. A specimen was authenticated by Dr. Xiao-qiang Ma, Department of Phytochemistry, Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

Extraction and Isolation. From the petroleum ether–EtOAc (10:1) part mentioned in a previous paper² we obtained compound **1** (50 mg) using petroleum ether–acetone (15:1) and compound **2** (22 mg) using petroleum ether–EtOAc (10:1) by repeated silica gel CC.

Dichromene A (1): colorless oil; $[\alpha]_D^{25} 0.00^\circ$ (c 0.61, acetone); IR (film) ν_{max} cm^{-1} 2970, 2940, 1732, 1633, 1595, 1471, 1375, 1234, 1132, 1055, 980; 1H NMR (CD_3COCD_3 , 400 MHz) δ 6.48 (1H, d, $J = 9.9$ Hz, H-4), 5.68

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(1H, d, $J = 9.9$ Hz, H-3), 4.91 (1H, q, $J = 6.6$ Hz, H-11), 3.76 (3H, s, CH₃O-8), 3.66 (3H, s, CH₃O-7), 3.54 (3H, s, CH₃O-5), 1.59 (3H, d, $J = 6.6$, CH₃-12), 1.43, 1.39 (each 3H, s, 2 × CH₃-2); ¹³C NMR (CD₃COCD₃, 100 MHz) δ 153.59 (s, C-7), 151.45 (s, C-5), 147.12 (s, C-9), 139.78 (s, C-8), 129.86 (d, C-3), 123.30 (s, C-6), 118.04 (d, C-4), 112.78 (s, C-10), 76.67 (s, C-2), 67.55 (d, C-11), 62.89, 61.40, 60.85 (each q, 3 × CH₃O-8, 7, 5), 27.91, 27.36 (each q, 2 × CH₃-2), 20.43 (q, C-12); HREIMS m/z [M]⁺ 570.2842 (C₃₂H₄₂O₉ requires 570.2829); EIMS m/z [M]⁺ 570 (22), 555 [M - CH₃]⁺ (14), 277 (100).

Dichromene B (2): orange oil; $[\alpha]_D^{20} -13.7^\circ$ (*c* 1.2, acetone); IR (film) ν_{\max} cm⁻¹ 2970, 2930, 1714, 1633, 1593, 1471, 1375, 1234, 1132, 1057, 980; ¹H NMR (CD₃COCD₃, 400 MHz) δ 6.54 (1H, d, $J = 9.9$ Hz, H-4), 5.71 (1H, d, $J = 9.9$ Hz, H-3), 4.91 (1H, q, $J = 6.7$ Hz, H-11), 3.81 (3H, s, CH₃O-8), 3.85 (3H, s, CH₃O-7), 3.71 (3H, s, CH₃O-5), 1.46 (3H, d, $J = 6.7$, CH₃-12), 1.45, 1.43 (each 3H, s, 2 × CH₃-2); ¹³C NMR (CD₃COCD₃, 100 MHz) δ 153.63 (s, C-7), 151.32 (s, C-5), 147.06 (s, C-9), 139.68 (s, C-8), 129.78 (d, C-3), 123.10 (s, C-6), 118.08 (d, C-4), 112.62 (s, C-10), 76.78 (s, C-2), 70.02 (d, C-11), 63.23,

61.69, 60.92 (each q, 3 × CH₃O-8, 7, 5), 27.96, 27.61 (each q, 2 × CH₃-2), 22.06 (q, C-12); HREIMS m/z [M]⁺ 570.2816 (C₃₂H₄₂O₉ requires 570.2829); EIMS m/z [M]⁺ 570 (13), 555 [M - CH₃]⁺ (11), 289 (39), 277 (100), 121 (76).

Leptol A (3): ¹H NMR (CD₃COCD₃, 400 MHz) 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-11), 3.91, 3.81, 3.73 (each 3H, s, 3 × CH₃O-8, 7, 5), 1.51 (3H, d, $J = 6.6$, CH₃-12), 1.45 (6H, s, 2 × CH₃-2); ¹³C NMR (CD₃COCD₃, 100 MHz) δ 152.93 (s, C-7), 150.25 (s, C-5), 146.92 (s, C-9), 139.58 (s, C-8), 130.05 (d, C-3), 124.59 (s, C-6), 117.87 (d, C-4), 112.53 (s, C-10), 76.93 (s, C-2), 63.95 (d, C-11), 63.49, 61.96, 61.04 (each q, 3 × CH₃O-8, 7, 5), 27.89, 27.89 (each q, 2 × CH₃-2), 24.73 (q, C-12).

References and Notes

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- (2) Li, G. L.; Zeng, J. F.; Song, C. Q.; Zhu, D. Y. *Phytochemistry* **1997**, *44*, 1175–1177.

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