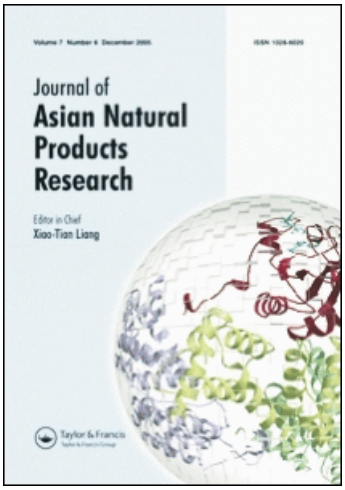

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Diarylheptanoids from *Alpinia officinarum*

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A new diarylheptanoid, along with five known diarylheptanoids, was isolated from the rhizomes of *Alpinia officinarum* (Zingiberaceae). The structure of the new compound was determined to be *trans*,*trans*-1(3′-methoxy-4′-hydroxyphenyl)-7-phenyl-5-ol-4,6-dien-3-heptanone on the basis of spectral and chemical evidence.

Keywords: Diarylheptanoid; *Alpinia officinarum*; Zingiberaceae; *trans*, *trans*-1(3′-Methoxy-4′-hydroxy-phenyl)-7-phenyl-5-ol-4; 6-dien-3-heptanone

1. Introduction

Diarylheptanoids are a group of natural compounds possessing antiplatelet, antioxidant, antiproliferative, anti-emetic, antihepatotoxic and anti-inflammatory activities. These natural products are divided into linear and cyclic diarylheptanoids on the basis of their structure. Sixty-seven linear diarylheptanoids have been found since curcumin was identified in 1815 [1]. Fourteen diarylheptanoids were isolated from the rhizomes of *Alpinia officinarum*, which are used as traditional herbs in China for relieving stomach ache, treating colds, invigorating the circulatory system, and reducing swelling [2]. Here we report the isolation and structure determination of a new diarylheptanoid (**1**), along with five known diarylheptanoids (**2**–**6**) (figure 1) isolated from the rhizomes of *Alpinia officinarum*.

2. Results and discussion

Compound **1** was isolated as colourless crystals with mp 86–88°C. The molecular formula was established to be $C_{20}H_{20}O_4$ by HREI-MS at *m*/*z* 324.1365. Compound **1** was positive to $FeCl_3$ reagent, and therefore it was suggested to have the phenolic hydroxy or enol form of 1,3-diketone. The IR spectrum of **1** showed absorption bands at 3362 and 1641 cm^{-1} assignable to hydroxyl and conjugated C=O groups. The UV spectrum of **1** indicated characteristic absorption band of a δ-phenyldienone structure (λ_{max} MeOH 342 nm, log ε

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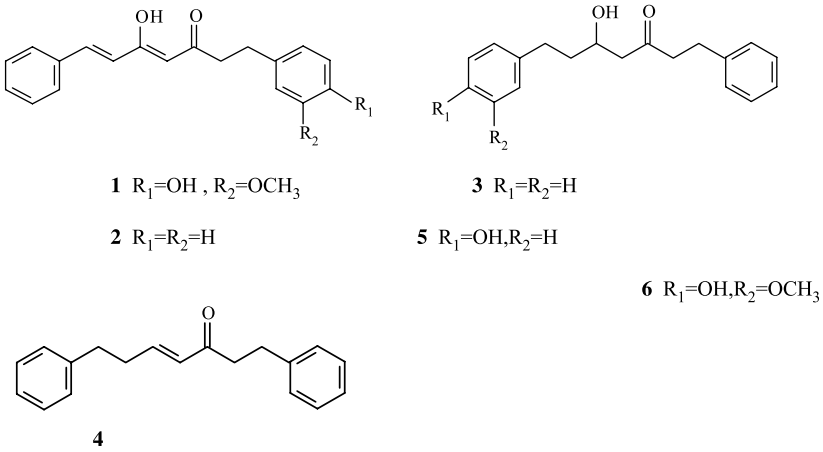

Figure 1. Structures of compounds **1**–**6**.

4.50) [3]. ^{13}C-NMR showed signals for a carbonyl group at δ 201.3 (C-3), an hydroxylated olefinic carbon at δ 177.2 (C-5) and an α-carbon of a β-hydroxy-α,β-unsaturated ketone at δ 101.4 (C-4). The ^{1} H-NMR spectrum of **1** showed a signal at δ 5.88 (s, H-4) and another signal at δ 15.27 (br. disappearing with D_2O, 5-OH). These data support the presence of a β-hydroxy-α,β-unsaturated ketone moiety. Compound **1** exhibited a hydroxy group at δ 7.30 and a methoxy group at δ 3.82 as well as two phenyl moieties. One was non-substituted with proton signals at δ 7.44–7.65 (5H, m). The other showed an ABX system at δ 6.87 (1H, d, $J = 2.0$ Hz), 6.71 (1H, d, $J = 7.5$ Hz) and 6.69 (1H, dd, $J = 7.5$, 2.0 Hz) in the ^{1}H-NMR spectrum. The coupling constants and chemical shifts of the aromatic signals were in accordance with the data reported for compound **6** [4], indicating that another aromatic ring was 3′-methoxy-4′-hydroxy substituted. This was also supported by NOESY correlations (figure 2). The ^{1}H-NMR spectrum also displayed a pair of *trans* olefinic protons (δ 6.73 and 7.60, $J = 15.5$ Hz) and two methylenes (δ 2.88 and 2.78). Therefore, compound **1** was determined to be *trans*,*trans*-1(3′-methoxy-4′-hydroxyphenyl)-7-phenyl-5-ol-4,6-dien-3-heptanone. The structure can also be confirmed by the diagnostic fragment ions in the mass spectrum (figure 3). All the carbon and proton signals of **1** were assigned with the help of HMQC and HMBC spectral data (figure 4).

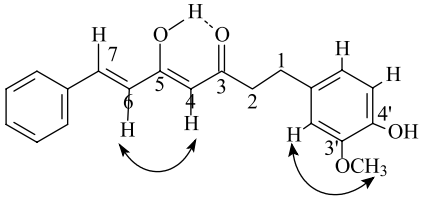

Figure 2. Significant NOESY correlations for **1**.

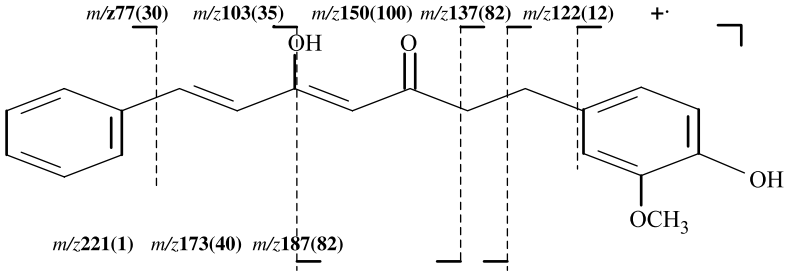

Figure 3. Diagnostic fragment ions of compound **1**.

3. Experimental

3.1 General experimental procedures

Melting points were determined using a Fisher Johns apparatus and are uncorrected. UV spectra were measured on a Philips PYE Unican Pu8800 spectrophotometer. IR spectra were obtained on an IMPACT-400. One- and two-dimensional NMR spectra were recorded on a Bruker ARX 400 spectrometer. The EIMS were obtained on a VG ZAB-2f mass spectrometer. Precoated silica gel plates (Qingdao Haiyang Chem. Co.) were employed for TLC and HPTLC. For column chromatography, silica gel (Qingdao Haiyang Chem. Co.) and Sephadex LH 20 (Pharmacia) were used. The MPLC were performed on a system equipped with a Büchi pump B-688 and Büchi columns with the stationary phase Silica gel 60 (15–40 μm, Qingdao Haiyang Chem. Co.).

3.2 Plant material

The rhizomes of *Alpinia officinarum* were collected from Guangdong province, China, and identified by Professor Shou-Quan Lin (our Institute). A voucher specimen has been deposited at the New Drug Research and Development Center of our Institute.

3.3 Extraction and isolation

The dried rhizomes of *Alpinia. officinarum* (28 kg) were extracted three times with 95% EtOH at room temperature. The extract was dried under reduced pressure to yield a residue (2.2 kg), which was diluted with H_2O and partitioned with petroleum ether, $CHCl_3$, EtOAc and n-butanol, respectively. The petroleum ether part (200 g) was subjected to column chromatography on silica gel (100–200 mesh) and eluted with a gradient of Me_2CO in petroleum ether (100(0–50(50) to give 10 fractions. Fraction 2 was chromatographed on silica gel (200–300 mesh), eluted with petroleum ether–EtOAc (100(0–90(10 gradient) and

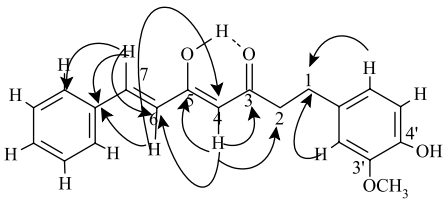

Figure 4. Significant HMBC correlations for **1**.

purified by recrystallization to give compound **2** (10 mg). Fraction 3 was chromatographed using $AgNO_3$ column chromatography with a petroleum ether–EtOAc (100(0–95(5 gradient) system yielding compound **4** (50 mg). Fraction 3 was recrystallized to give compound **3** (8 g). The $CHCl_3$ part was subjected to MPLC and eluted with $CHCl_3$–MeOH (100(0–90(10 gradient) and Sephadex LH-20 to give compounds **1** (15 mg), **5** (20 g) and **6** (15 g).

3.3.1. t*rans,trans*-1(3′-Methoxy-4′-hydroxyphenyl)-7-phenyl-5-ol-4,6-dien-3-heptanone (1). Colourless crystals (petroleum ether); mp 86–88°C; UV (MeOH) λ_{max} (nm): 228 (sh), 290 (sh), 342 (4.50); IR (KBr) ν_{max} (cm^{-1}): 3352, 2993, 2927, 1641, 1516, 1448, 1267, 1124, 700; ^{1}H-NMR [$(CD_3)_2CO$]: 2.86–2.89 (2H, m, H-1), 2.77–2.79 (2H, m, H-2), 5.87 (1H, s, H-4), 6.73 (1H, d, $J = 15.5$ Hz), 7.60 (1H, d, $J = 15.5$ Hz), 6.87 (1H, d, $J = 2.0$ Hz), 6.71 (1H, d, $J = 7.5$ Hz), 6.69 (1H, dd, $J = 2.0, 7.5$ Hz), 7.60–7.70 (2H, m, H-2″, 6″), 7.40–7.50 (3H, m, H-3″, 4″, 5″), 3.82 (3H, s, OCH_3), 15.53 (1H, br, 5-OH, disappeared on addition of D_2O), 7.30 (1H, s, 4′-OH); ^{13}C-NMR [$(CD_3)_2CO$]: 31.2 (C-1), 42.6 (C-2), 201.3 (C-3), 101.4 (C-4), 177.2 (C-5), 123.6 (C-6), 139.7 (C-7), 132.9 (C-1″), 112.5 (C-2′), 147.9 (C-3′), 145.5 (C-4′), 115.4 (C-5′), 121.2 (C-6′), 135.9 (C-1″), 128.5 (C-2″), 129.5 (C-3″), 130.4 (C-4″), 129.5 (C-5″), 128.5 (C-6″), 55.9 (OCH_3); EIMS *m/z* (%): 324 (M^+, 90), 233 (5), 187 (17), 173 (40), 150 (100), 137 (82), 103 (30), 91 (28), 77 (24); HREIMS *m/z* 324.1365 $[M]^+$ (calcd. for $C_{20}H_{20}O_4$, 324.1361).

3.3.2. *trans,trans*-1,7-Diphenyl-5-ol-4,6-dien-3-heptanone (2). Yellow crystals (petroleum ether); mp 66–69°C; EIMS *m/z* (%): 278 (M + , 70), 187 (42), 173 (90), 145 (49), 155 (15), 131 (100), 105 (35), 103 (43), 91 (72); NMR data were identical to literature values [3].

3.3.3. 1,7-Diphenyl-5-ol-3-heptanone (3). White needle-shaped crystals; mp 46–48°C; $[\alpha]_D^{20}$ −18 (*c* 0.05, DCl_3); EIMS *m/z* (%): 282 (M + , 2), 264 (40), 177 (5), 159 (10), 160 (6), 133 (28), 134 (8), 117 (10), 105 (50), 91 (100), 77 (8); NMR data were identical to literature values [4].

3.3.4. 1,7-Diphenyl-4-en-3-heptanone (4). Colourless oil; UV (MeOH) λ_{max} (nm): 223 (3.8); IR (film) ν_{max} (cm^{-1}): 3086, 3028, 2927, 2854, 1905, 1736, 1709, 1496, 1454, 1367, 1286, 1167, 1078, 978, 748, 700; EIMS *m/z* (%): 264 (M + , 15), 159 (75), 105 (10), 91 (100), 77 (8); NMR data were identical to literature values [5].

3.3.5. 7-(4″-Hydroxyphenyl)-1-phenyl-5-ol-3-heptanone (5). Colourless oil; $[\alpha]_D^{20}$ −13.20 (*c* 0.10, $CDCl_3$); UV (MeOH) λ_{max} (nm): 2.14 (3.95), 224 (sh), 278 (3.2); IR (film) ν_{max} (cm^{-1}): 3507, 3456, 2959, 1693, 1602, 1518, 1447, 1426, 1129, 1046, 751, 702; EIMS *m/z* (%): 298 (M + , 10), 280 (56), 175 (15), 159 (5), 147 (50), 33 (56), 120 (45), 107 (100); NMR data were identical to literature values [6].

3.3.6. 7-(4″-Hydroxy-3″-methoxyphenyl)-1-phenyl-5-ol-3-heptanone (6). Colourless oil; $[\alpha]_D^{20}$ −11.06 (*c* 0.10, $CDCl_3$); UV (MeOH) λ_{max} (nm): 213 (3.97), 227 (sh), 281 (3.48); IR

(film) ν_{max} (cm^{-1}): 3400, 2937, 1701, 1602, 1430, 1040, 822, 750, 710; EIMS *m/z* (%): 328 (M + , 45), 310 (15), 205 (5), 177 (19), 150 (27), 138 (100), 137 (72), 105 (45), 91 (55), 77 (25); NMR data were identical to literature values [4].

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