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Two New Diarylheptanoids from the Rhizomes of *Zingiber officinale*

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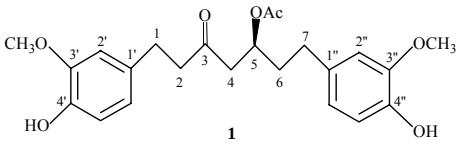
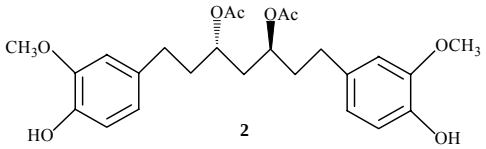
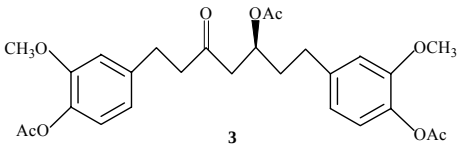
Abstract: Two new diaryheptanoids, (5S)-5-acetoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)-3-heptanone (**1**) and (3S,5S)-3,5-diacetoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)heptane (**2**) were isolated from the rhizomes of *Zingiber officinale*. Their structures were elucidated by spectral methods.

Keywords: *Zingiber officinale*, diarylheptanoid, (5S)-5-acetoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)-3-heptanone, (3S,5S)-3,5-diacetoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)heptane.

Ginger, the rhizome of *Zingiber officinale* Roscoe (Zingiberaceae) is one of the most popular spices and has been frequently used in Chinese traditional medicines both in fresh and dried forms[1]. Numerous chemical investigations of this material have led to the isolation and identification of a large number of biologically active compounds, such as gingerols, shogaol and zingerone[2]. As a part of our ongoing program on finding biologically active components from Chinese herbs[3] we found two previously unknown diarylheptanoids **1** and **2,** besides 21 known gingerol-related constituents from the ethanol extract of the rhizomes of *Zingiber officinale*. We report herein the structural elucidation of these two new compounds.







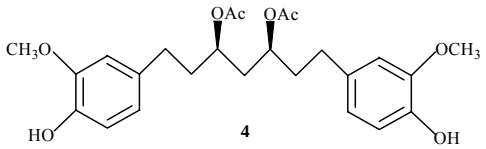


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Table 1 ^{1}H (400 MHz) and ^{13}C (100.5 MHz) NMR spectral data for **1** and **2**[a]

Compound		**1**			**2**
Position	δ_C	δ_H	HMBC correlations	δ_C	δ_H
1	29.29	2.80	C-1/H-2, H-2′	31.18	2.52, 2.54
2	45.15	2.69	C-2/H-1	36.66	1.84
3	206.86		C-3/H-1, H-2, H-4a,b	69.72	5.00
4	47.36	2.54, 2.70		38.55	1.76, 1.92
5	69.97	5.26	C-5/H-4a,b, H-6, H-7	69.72	5.00
6	36.01	1.86	C-6/H-4a,b, H-7	36.66	1.84
7	31.27	2.57	C-7/ H-5, H-6, H-2″	31.18	2.52, 2.54
3-OAc				170.75, 21.09	2.01
5-OAc	170.41, 21.04	2.00	C=O/H-5	170.75, 21.09	2.02
1′	132.77		C-1'/H-1, H-5′	133.20	
2′	111.10	6.66	C-2'/H-1, H-6′	110.85	6.67
3′	146.44		C-3'/H-2′, H-5′	146.33	
4′	143.90		C-4'/H-2′, H-5′, H-6′	143.72	
5′	114.34	6.82	C-5'/H-6′	114.20	6.62
6′	120.79	6.65	C-6'/H-1, H-2′	120.79	6.81
3′-OMe	55.90	3.85	C-3'/OMe	55.81	3.87
1″	132.99		C-1''/H-7, H-5″	133.20	
2″	110.95	6.66	C-2''/H-7, H-6″	110.85	6.67
3″	146.44		C-3''/H-2″, H-5″	146.33	
4″	143.99		C-4''/H-2″, H-5″, H-6″	143.72	
5″	114.34	6.82	C-5''/H-6″	114.20	6.81
6″	120.84	6.65	C-6''/H-7, H-2″	120.79	6.62
3″-OMe	55.91	3.88	C-3''/OMe	55.81	3.87

a. Determined in $CDCl_3$ with TMS as the internal standard.

Compound **1** was obtained as colorless oil, $[\alpha]_D^{25}$ +3.0 (c 0.60, $CHCl_3$). HR-ESI-MS gave a molecular ion peak at *m/z* 434.2164, corresponding to the molecular formula of $C_{23}H_{28}O_7$ (cald. for M+NH_4 434.2173). Its IR spectrum showed characteristic absorptions for hydroxyl (3434 cm^{-1}), carbonyl (1720 cm^{-1}) and aromatic (3015, 1606 and 1516 cm^{-1}) functionalities. The ^{1}H NMR signals at δ 6.81 (dd, 2H, *J* = 2.0, 8.0 Hz), 6.66 (d, 2H, *J* = 2.0 Hz) and 6.63 (d, 2H, *J* = 8.0 Hz), as well as those at δ 3.85 (s, 3H) and 3.87 (s, 3H), suggested the presence of two 1,3,4-trisubstituted phenyl groups bearing a methoxyl group that was supported by the characteristic base peak at *m/z* 137 ($[CH_2C_6H_3(OH)(OMe)]^+$) for the 4-hydroxy-3-methoxyphenyl moiety in curcumin derivatives[2a]. The ^{1}H NMR signal at δ 2.00 (3H, s) and the ^{13}C NMR signals at δ 21.04 and 170.41 revealed the presence of an acetyl group that was supported by the fragment ion peak at *m/z* 356 from the deacetoxylation of the molecule. Comparison of its ^{1}H and ^{13}C NMR data with those of hexahydrocurcumin[2a-c] suggested that **1** is the acetylated hexahydrocurcumin with the acetoxyl group at C-5 that was confirmed by its gHMBC spectrum which shows clear correlation of the acetyl carbonyl carbon (δ 170.41) with H-5 (δ 5.26). Total ^{1}H and ^{13}C assignments together with the HMBC correlations are listed in **Table 1**. In order to determine the stereochemistry of C-5, **1** was acetylated with acetic anhydride in pyridine to produce 5,4′,4″-triacetoxylhexahydrocurcumin **3** as the unique product, which is identical

to the acetylation product of hexahydrocurcumin obtained under the same experimental conditions. Since the configuration of hexahydrocurcumin was known to be *5S* [2a-c], compound **1** is assigned as (*5S*)-5-acetoxy-1,7-bis(4-hydroxy-3-methoxy-phenyl)-3-heptanone (5-acetyl-hexahydrocurcumin) which has not been reported previously.

Compound **2** was obtained as colorless oil, $[\alpha]_D^{26}$ + 7.0 (c 0.68, $CHCl_3$). HR-ESI-MS gave a molecular ion peak at *m/z* 478.2431, corresponding to the molecular formula of $C_{25}H_{32}O_8$ (cald. for M+NH_4 478.2435). The IR, UV and HR-ESI-MS spectra of **2** are completely identical with those of the known compound (*3R,5S*)-3,5-diacetoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)heptane **4**[2b] which was also obtained from the ethanol extract of the rhizomes of *Zingiber officinale*. However, different from **4**, **2** was found to be optical active. These facts suggested that **2** is a stereoisomer of **4**. Comparison of the ^{13}C NMR spectrum of **2** with that of **4** indicated that two signals of the two compounds are apparently distinguishable although most signals of **2** and **4** are indistinguishable. They are signals of C-3 and C-5 (δ 69.72 and 70.64 for **2** and **3,** respectively) and those of C-2 and C-6 (δ 36.66 and 35.91 for **2** and **3,** respectively. Deacetylation of **2** and **4** with KOH/MeOH gave the corresponding 3,5-dihydroxyl derivatives **2a** and **4a** which were identified as (*3S,5S*)- and (*3R,5S*)-3,5-dihydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl) heptanes, respectively, by comparing their ^1H and ^{13}C NMR spectral data and optical rotations with those reported in the liturature[2c]. Therefore, compound **2** was assigned as (*3S,5S*)-3,5-diacetoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)heptane which is a new compound. Total ^1H and ^{13}C NMR assignments are listed in **Table 1**. Investigation of antioxidation and anticancer activities of compounds **1**, **2** and other diarylheptanoids obtained from the rhizomes of *Zingiber officinale* is in progress in this laboratory.

Acknowledgments

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