Chemistry of Natural Compounds, Vol. 48, No. 4, September, 2012 [Russian original No. 4, July–August, 2012]

BRIEF COMMUNICATIONS

GINGERDIONE FROM THE RHIZOMES OF *Curcuma longa*

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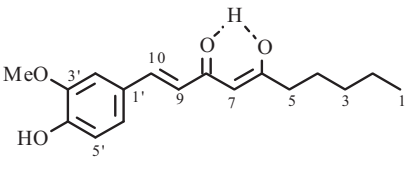
UDC 547.631.6+547.913

Turmeric (*Curcuma longa* L.) belongs to the Zingiberaceae family along with the other noteworthy members like ginger, cardamom, and galangal. It belongs to the genus *Curcuma*, which consists of hundreds of species of plants that possess rhizomes. It is widely grown in warm, rainy regions of the world such as India, Indonesia, Malaysia, and South China [1]. Turmeric is of special importance to humans with the discovery that its rhizome powder, when added to various food preparations, preserves their freshness and imparts a characteristic flavor. Traditional Indian medicine claims the use of its powder against biliary disorders, anorexia, coryza, cough, diabetic wounds, hepatic disorder, rheumatism, and sinusitis [2]. The diarylheptanoids are the principal active constituents contained in *Curcuma longa*. About 11 diarylheptanoids have been isolated [3], and 19 diarylheptanoids were detected by the method of LC-MS [4] from the rhizome of *Curcuma longa*.

The chromatographic separation of the *Curcuma longa* rhizomes extract gave four compounds **1–4**. The literature survey of *Curcuma longa* L. indicated the presence of diarylheptanoids that represent the major secondary metabolites that are responsible for the yellow color of its powder. On the other hand, the literature survey of ginger (*Zingiber officinale*) indicated the presence of gingerols and shogaols that are responsible for the taste of ginger. The ^{1}H NMR spectrum of compound **1** was consistent with the expected signal pattern of gingerols.

The ^{1}H NMR spectrum of compound **1** (Table 1) showed only one 1,3,4-trisubstituted benzene ring (a broad singlet at δ 7.3 ppm corresponding to H-2′, a doublet of doublet at δ 7.14 ppm with coupling constants J = 8.05, 1.5 Hz corresponding to H-6′, and a doublet at δ 6.84 ppm with coupling constant J = 8.00 Hz corresponding to H-5′) (Table 1). The presence of a downfield doublet at δ 7.55 ppm, with coupling constant, J = 15.45 Hz complementing an upfield doublet at δ 6.66 ppm with the same coupling constant, suggested the presence of an AB system for two *trans* protons coupled with the benzene ring. The singlet at 5.95 ppm was assigned to the H-7 because the methylene protons at C-7 are enolyzed to an α, β-unsaturated carbonyl and appeared as a singlet, in agreement with the presence of a 1,3-diketone moiety. A methoxyl group singlet at δ 3.89 ppm was assigned to the C-3′-methoxyl of 1-dehydrogingerdione (**1**), which has been isolated previously from ginger (*Zingiber officinale*) by [5]. This is the first report on isolation of **1** from *Curcuma longa* L. However, it may be present in the commercial processed sample as a result of either adulteration or contamination by ginger (*Zingiber officinale*), but [6] reported the isolation of 1-dehydrogingerdione (**1**) with 6-gingerol and 6-shogaol from *Zingiber officinale* in quantities 0.032, 0.078, and 0.042 g. Thus **1** is the minor constituent in *Zingiber officinale*. Since the other two constituents are present in greater quantity than **1** and are not isolated with it from the sample under investigation, so we conclude that **1** is a constituent of *Curcuma longa* and did not originate from adulteration or contamination.



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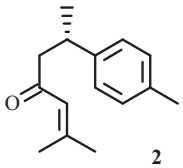

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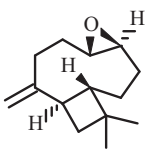

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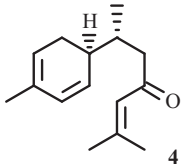

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 0009-3130/12/4804-0646

TABLE 1. ^{1}H NMR Spectral Data for 1-Dehydrogingerdione (**1**) (δ, ppm, J/Hz)

C atom	δ_H	C atom	δ_H
2′	7.3 (1H, br.s)	9	6.66 (1H, d, J = 15.45)
5′	6.84 (1H, d, J = 8.00)	7	5.95 (1H, s)
6′	7.14 (1H, dd, J = 8.05, 1.5)	3′-OMe	3.89 (3H, s)
10	7.55 (1H, d, J = 15.45)		

TABLE 2. Identified Compounds from *Curcuma longa* Oil by GC/MS

Compound*	R_f, min	Mol. Wt.	Area, %
ar-Tumerone (**2**)	28.68	216	0.41
(–)-Caryophyllene oxide (**3**)	28.95	220	0.40
α-Tumerone (**4**)	32.52	218	23.42

*The identification was based on a high percentage of matching with an authentic spectrum using the NIST library.

A sample of turmeric oil was analyzed using GC/MS to give *ar*-turmerone (**2**), (–)-caryophyllene oxide (**3**), and α-turmerone (**4**). The identification was based on good matching with authentic spectra using the NIST library [7].

A sample of *Curcuma longa* oil was analyzed using GC/MS to give the compounds indicated in Table 2.

The three major curcuminoids are curcumin, demethoxycurcumin, and bisdemethoxycurcumin, and their structures were proved by their ^{1}H NMR spectral data [3]. In this article we report the isolation of 1-dehydrogingerdione for the first time from *Curcuma longa*.

^{1}H NMR spectra were recorded on a 500 MHz JEOL spectrometer. Chemical shifts are given in δ (ppm) relative to TMS as internal standard at the Faculty of Science, Alexandria University. GC/MS analyses were performed on a Varian GC interfaced to a Finnigan SSQ 7000 mass selective detector (SMD) with ICIS V2.0 data system for MS identification of the GC components. The column used was a DB-5 (J & W Scientific, Folsom, CA) cross-linked fused silica capillary column (30 m long, 0.25 mm internal diameter) coated with polydimethylsiloxane of 0.5 μm film thickness (National Research Center, Dokki, Cairo, Egypt). Thin-layer chromatography and preparative TLC were performed on silica gel (Kieselgel 60, GF 254) of 0.25 thickness.

Plant Material. A commercial powder sample of *Curcuma longa* L. (Zingiberaceae) was purchased from a local market in Mansoura, Egypt in December 2007.

Processing of Plant Material. The sample of *Curcuma longa* (375 g) was extracted by soaking at room temperature in ethanol. The ethanol extract was evaporated under reduced pressure to a suitable volume, then successively extracted by petroleum ether (40–60°C) to afford about 7 g oily materials. Extraction by chloroform afforded 1.34 g. The petroleum ether fraction (oil, 2 g) was introduced to a silica gel column and eluting with 100% benzene to afford an oily fraction (*ar*-turmerone, α-turmerone, and caryophyllene oxide). Then the polarity was increased using EtOAc to give compound **1** at 90% benzene:10% EtOAc. The isolated compounds were further purified using precoated TLC. Compound **1** was purified by elution with 100% benzene followed by chloroform to afford yellow crystals (0.25g, R_f 0.5 from benzene).

The $CHCl_3$ fraction (1.34 g) was separated over a silica gel column and eluted by benzene–ethyl acetate solvent system with increasing polarity to afford the curcuminoids at 80% benzene:20% ethyl acetate as a yellowish brown solid. These curcuminoids were further purified using precoated TLC by 85% benzene:15% ethyl acetate followed by elution with $CHCl_3$ to afford the three major curcuminoids. Curcumin I (0.5 g, R_f 0.24) from hexane–ethyl acetate (2:1), curcumin II (0.24 g, R_f 0.27), and curcumin III (0.1 g, R_f 0.25) were isolated.

The phytochemical investigation of *Curcuma longa* L. has led to the isolation and identification of several known natural products, including 1-dehydrogingerdione, which is reported for the first time from *Curcuma longa*.

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