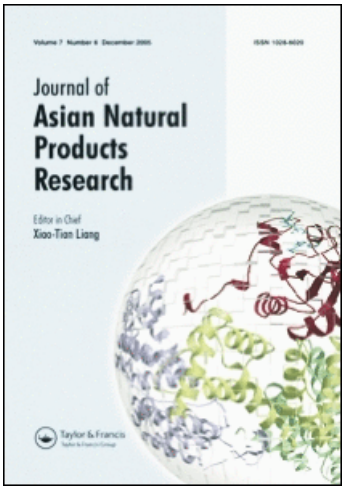

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Note: A new acetylenic ketone from the bark of Litsea rotundifolia var. oblongifolia

Ya Zhao[a]; Guo-Qiang Song[a]; Yue-Wei Guo[a]
[a] State Key Laboratory of Drug Research, Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences, Shanghai, China

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Note

A new acetylenic ketone from the bark of *Litsea rotundifolia* var. *oblongifolia*

YA ZHAO, GUO-QIANG SONG and YUE-WEI GUO*

State Key Laboratory of Drug Research, Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences, Shanghai 201203, China

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A new acetylenic ketone isolated from the bark of *Litsea rotundifolia* var. *oblongifolia* has been characterized as 13-tetradecyn-2-one on the basis of detailed spectroscopic analysis and comparison with related model compounds. Four known related lipids have also been isolated from this plant.

Keywords: *Litsea rotundifolia* var. *oblongifolia*; Lauraceae; Acetylenic ketone; 13-Tetradecyn-2-one

1. Introduction

Litsea is a genus in the family Lauraceae with about 72 species distributed in South and Southwest China [1]. Most *Litsea* plants contain alkaloids [2–4], flavonoids [5,6], terpenes [7,8], lactones [9], and volatile oil [10], which have been reported to possess various biological activities ranging from antimicrobial, hypothermic, to antitumor [2,11,12]. In continuation of our work on the chemical constituents of Chinese medicinal plants, we have examined the secondary metabolites present in the bark of *L. rotundifolia* var. *oblongifolia* since no phytochemical investigation has been done on the species. A new naturally occurring acetylenic ketone, 13-tetradecyn-2-one (**1**), together with four known related homologues (**2**, **6**–**8**) have been isolated from the title plant. This paper describes the isolation and structure elucidation of the new compound.

2. Results and discussion

The bark of *L. rotundifolia* var. *oblongifolia* was extracted exhaustively with MeOH, and the methanolic extract was partitioned between various organic solvents and water. The EtOAc-soluble portion was subjected to a combination of Sephadex LH-20 and silica gel column

*Corresponding author. Tel.: +86-21-50806600. Ext. 3318. Fax: +86-21-50807088.
E-mail: ywguo@mail.shcnc.ac.cn

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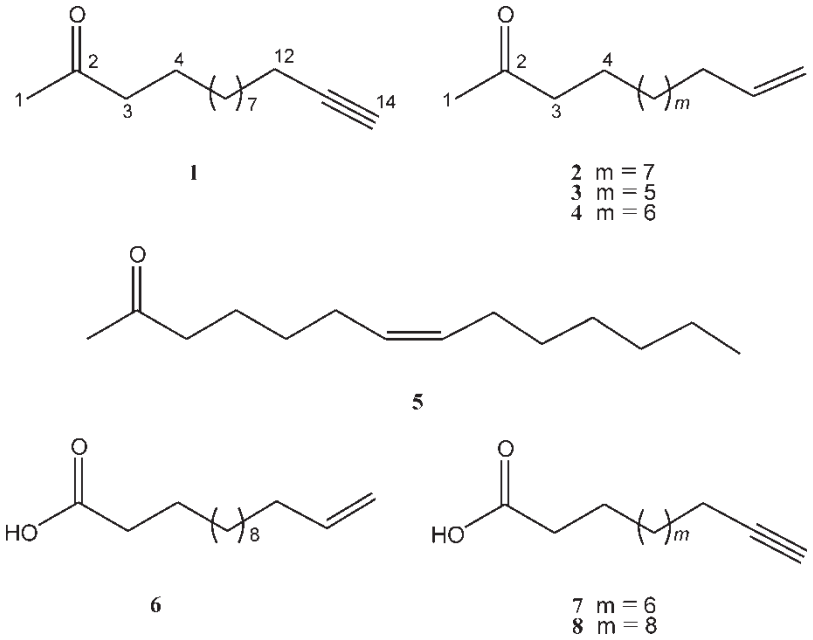

Figure 1. Structures of compounds **1**–**8**.

chromatography eluting with various solvent systems. This procedure resulted in the isolation of the new compound (**1**) and four known compounds (**2**, **6**–**8**), respectively (figure 1).

All the compounds showed similar and some common spectroscopic properties. The ^{1}H NMR spectra of **1**, **2**, and **6**–**8** displayed strong signals at δ 1.26, characteristic of long unbranched alkyl chains, whereas their IR spectra showed absorptions (1710–1720 cm^{-1}) indicative of ketone functions. In fact, the differences among them were only at the ends of the molecules.

Compound **1**, a colorless oil, responded positively to a 2,4-dinitrophenyl hydrazine test, showing the presence of a carbonyl function in the molecule. The positive ESIMS spectrum of **1** displayed a pseudo-molecular ion peak at *m/z* 231 $[M + Na]^+$ corresponding to a molecular formula of $C_{14}H_{24}O$, which was further confirmed by the HR-ESIMS spectrum. The ^{1}H NMR spectrum of **1** exhibited a two-proton triplet at δ 2.40 ($J = \mathbf{7.4\,Hz}$, H_2-3) and a methyl singlet at δ 2.12 (H_3-1), suggesting a terminal methyl ketone moiety, which was confirmed by the signals at δ 209.3 (s, C-2), 43.8 (t, C-3), and 29.8 (q, C-1) in the ^{13}C NMR spectrum, and a strong absorption at 1715 cm^{-1} in the IR spectrum. In addition, the ^{1}H NMR spectrum of **1** exhibited a one-proton triplet at δ 1.92 ($J = \mathbf{2.6\,Hz}$, H-14) and a two-proton triple-doublet at δ 2.15 ($J = \mathbf{7.0}$, 2.6 Hz, H_2-12) attributable to a terminal acetylene group which was further supported by comparison with model compounds [13]. These data led us to assign a linear structure, containing a terminal methyl ketone and a terminal acetylene group at the ends of the molecule, as formulated in **1**.

Compound **2** ($C_{14}H_{26}O$) exhibited spectral data that supported a structure identical to that already reported [14,15]. As **2** was, for the first time, isolated in pure form, its full ^{1}H and ^{13}C NMR (table 1) assignments are reported. Compound **2**, 13-tetradecen-2-one, is the 13,14-dihydro derivative of **1**.

Table 1. Selected ^{1}H and ^{13}C NMR data* of **1** and **2**.

	1		***2***	
Position	$\delta\ ^{1}H^{\dagger}$ (*mult., J in Hz*)	$\delta\ ^{13}C^{\ddagger}$ (*mult.*)	$\delta\ ^{1}H^{\dagger}$ (*mult., J in Hz*)	$\delta\ ^{13}C^{\ddagger}$ (*mult.*)
1	2.12 (s)	29.8 (q)	2.11 (s)	29.7 (q)
1b				
2	–	209.3 (s)	–	209.2 (s)
3	2.40 (t, 7.4)	43.8 (t)	2.39 (t, 7.4)	43.7 (t)
4	1.53 (m)	23.8 (t)	1.54 (m)	23.8 (t)
12	2.15 (td, 7.0, 2.7)	18.3 (t)	2.00 (m)	33.8 (t)
13	–	84.8 (s)	4.98 (dd, 2.2, 17.0) 4.92 (dd, 2.2, 10.1)	139.1 (d)
14	1.92 (t, 2.7)	68.0 (d)	5.78 (ddt, 6.6, 10.2, 17.0)	114.0 (t)

* Bruker AMX 400 MHz; measured in $CDCl_3$. Chemical shifts (δ in ppm) are expressed relative to TMS. Assignments were deduced by analysis of 1D and 2D spectra.
† Assignments for unreported methylene protons contributed to a large signal at δ 1.26.
‡ Methylenes not reported contributed to a large signal centered at δ 29.8.

Compounds **6**–**8** are all fatty acids. Their structures were identified as 13-tetradecenoic acid (**6**) [16], 11-dodecynoic acid (**7**) [17], 13-tetradecynoic acid (**8**) [18], respectively, by detailed spectroscopic analysis and comparison of their spectral data with reported values in the literature.

Compound **1** has not been previously reported from either synthetic or natural sources while the known compounds **2**, **6**–**8** were all isolated for the first time from the title plant. In addition, compounds **7** and **8** were also reported for the first time as natural products though they have been previously synthesized [17,18].

It is worthy to note that the inferior homologues of **2**, undec-10-en-2-one (**3**) and tridec-12-en-2-one (**4**), which possess attractive and toxic properties towards termites, have been isolated previously from the related Indonesian and Japanese species, *L. eliptica* and *L. odifera* [14], respectively. It is also of interest that compounds **1** and **2** show structural similarity with a type of sex pheromone (e.g. **5**) of scarab beetles [19]. Further study should be conducted to bioassay if these compounds possess also attraction activity to male beetles like compound **5**, as well as insect repellant activity.

3. Experimental

3.1 General experimental procedures

IR spectra were recorded on a Nicolet Magna FT-IR 750 spectrometer; ν_{max} (cm^{-1}). ^{1}H and ^{13}C NMR spectra were measured with a Bruker DRX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer with chemical shifts (δ ppm) relative to TMS as internal standard, and coupling constants (J) in Hz. The ESIMS and HR-ESIMS were obtained on a MAT-711 mass spectrometer. Commercial silica gel plates (Qing Dao Hai Yang Chemical Group Co.) were used for TLC. The chromatograms were sprayed with 0.1% $Ce(SO_4)_2$ in 2 N H_2SO_4 and heated at 80°C for 5 min to detect the spots.

3.2 Collection of plant material

The examined sample was collected from Guangdong province of China in August 2001 and identified by Professor F.-W. Xin of the South China Institute of Botany, Chinese Academy

of Sciences. A voucher specimen (no. PL02-5) has been deposited in the Herbarium of the Institute of Materia Medica, SIBS-CAS.

3.3 Extraction and isolation

The powdered bark of *L. rotundifolia* var. *oblongifolia* (1 kg) was repeatedly extracted with MeOH at room temperature. The extract was then concentrated under reduced pressure to give a brown syrup (132 g), which was partitioned with solvents into EtOAc-soluble (65 g) and *n*-BuOH-soluble (20 g) fractions. The EtOAc-soluble portion was subjected to Sephadex LH-20 column chromatography, eluting with $CHCl_3$–MeOH (1:1), by which five fractions (I–V) were obtained. Fraction V (3 g) was resubmitted to silica gel column chromatography (light petroleum–EtOAc in order of increasing polarity) to yield compounds **1** (8.9 mg), **2** (7.6 mg), **6** (12.0 mg), **7** (8.8 mg) and **8** (13.6 mg), respectively.

3.3.1 13-Tetradecyn-2-one (1). A colorless oil; IR (KBr) ν_{max} (cm^{-1}): 3363, 2919, 2848, 2114, 1641, 1465, 1070, 921, 723; ESIMS *m/z* 231 $[M + Na]^+$; HR-ESIMS *m/z* 231.1725 $[M + Na]^+$ (calcd. for $C_{14}H_{24}ONa$ 231.1727). ^1H and ^{13}C NMR: see table 1.

3.3.2 13-Tetradecen-2-one (2). A colorless oil; ESIMS *m/z* 211 $[M + H]^+$, 233 $[M + Na]^+$; ^1H and ^{13}C NMR: see table 1.

3.3.3 13-Tetradecenoic acid (6). A colorless oil; IR (KBr) ν_{max} (cm^{-1}): 3076, 2925, 1712, 1641, 1465, 1070, 908, 721; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.80 (1H, ddt, $J =$ **6.5**, 10.1, 17.0 Hz, H-13), 4.98 (1H, ddt, $J =$ **1.5**, 2.2, 17.0 Hz, H-14a), 4.92 (1H, ddt, $J =$ **0.8**, 2.2, 10.1 Hz, H-14b), 2.28 (2H, t, $J =$ **7.6 Hz**, H_2-2), 2.0 (2H, m, H_2-12), 1.60 (2H, m, H_2-3), 1.26 (16H, br s, H_2-4-H_2-11); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm): 180.2 (s, C-1), 138.2 (d, C-13), 114.0 (t, C-14), 34.1 (t, C-2), 33.8 (t, C-12), 29.5-28.9 (t, C-4–C-11), 24.6 (t, C-3); ESIMS *m/z* 225 $[M - H]^-$.

3.3.4 11-Dodecynoic acid (7). A colorless oil; IR (KBr) ν_{max} (cm^{-1}): 3284, 2919, 2852, 2114, 1708, 1410, 916, 636; ^1H NMR (C_5D_5N, 400 MHz) δ (ppm): 2.77 (1H, t, $J =$ **2.7 Hz**, H-12), 2.52 (2H, t, $J =$ **7.4 Hz**, H_2-2), 2.19 (2H, td, $J =$ **2.7**, 7.4 Hz, H_2-10), 1.79 (2H, m, H_2-3), 1.46 (2H, m, H_2-9), 1.35 (2H, m, H_2-4), 1.18 (6H, br s, H_2-5-H_2-7); ^{13}C NMR (C_5D_5N, 100 MHz): δ (ppm): 175.8 (s, C-1), 84.8 (s, C-11), 69.8 (d, C-12), 34.6 (t, C-2), 29.5–28.6 (t, C-4–C-9), 25.4 (t, C-3), 18.3 (t, C-10); ESIMS *m/z* 219 $[M + Na]^+$.

3.3.5 13-Tetradecynoic acid (8). A colorless oil; IR (KBr) ν_{max} (cm^{-1}): 3286, 2925, 2114, 1710, 1471, 916, 630; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm): 2.33 (2H, t, $J =$ **7.6 Hz**, H_2-2), 2.16 (2H, td, $J =$ **2.4**, 7.1 Hz, H_2-12), 1.92 (1H, t, $J =$ **2.4 Hz**, H-14), 1.61 (2H, m, H_2-3), 1.50 (2H, m, H_2-11), 1.26 (14H, br s, H_2-4–H_2-10); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm): 180.1 (s, C-1), 84.8 (s, C-13), 68.0 (d, C-14), 34.1 (t, C-2), 29.4-28.5 (t, C-4–C-11), 24.6 (t, C-3), 18.4 (t, C-12); ESIMS *m/z* 223 $[M - H]^-$.

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