1-Phenylheptane-1,5-dione from Phellinus tremulus

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1-PHENYLHEPTANE-1,5-DIONE FROM *PHELLINUS TREMULUS*

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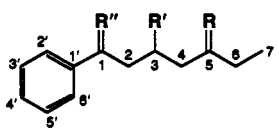
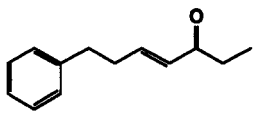
ABSTRACT.—1-Phenylheptane-1,5-dione [**1**], which has not been previously reported as a natural product, has been isolated from *Phellinus tremulus*. This compound is the first naturally occurring phenylheptane oxidized in the 1 position and the first dione of this class of natural products.

Phellinus tremulus Bondarzew et Borissov (Polyporaceae) is a fungus responsible for heart rot in aspen (*Populus tremuloides*) (1). The fungus, which is rich in melanin pigments (2), gradually renders the infected wood unsuitable for pulping due to low levels of essential carbohydrates (3). The phenylheptanes **2–5** have been isolated from the decayed heartwood of aspens infected with the organism (4). We report herein the isolation of the dione **1** directly from the fungus. This is the first report of this compound as a natural product, the first report of the isolation of any phenylheptane natural product directly from the fungus rather than the infected wood, the first report of a phenylheptanedione, and the first report of a phenylheptane oxidized at the 1 position isolated from this fungus.

Compound **1** was isolated from the hexane-soluble fractions of the MeOH extract of *Ph. tremulus* by chromatography on Si gel using EtOAc in hexane. Elution first afforded the known esters **6–13** and the phenylheptanone **3**, after which the new phenylheptanedione **1** eluted as a pale yellow oil which crystallized on standing. Long-chain fatty acids similar to those isolated from *Ph. tremulus* occur in several species of fungus and plants, including *Fomes igniarius* (5), *Agaricus bisporus* (6), and pecans (*Carya illinoensis*) (7).

The mass spectrum of the new natural product exhibited a molecular ion at *m/z* 204 and a base peak at *m/z* 105, consistent with the molecular formula as $C_{13}H_{16}O_2$ and the presence of a C_6H_5CO- moiety. The ^1H (Table 1) and ^{13}C nmr (Experimental) revealed the presence of two ketonic carbonyl groups (one of which is conjugated), a monosubstituted aromatic ring, an isolated ethyl group, and a trimethylene group. The ir spectrum showed carbonyl absorptions at 1684 and 1717 cm^{-1}. These data clearly estab-





1 R=O, R′=H, R″=O
2 R=O, R′=OH, R″=H_2
3 R=O, R′=H, R″=H_2
4 R=H, OH; R′=H, R″=H_2

5

$CH_3(CH_2)_nCO_2CH_3$

6 n=14
7 n=16
8 n=18
9 n=19
10 n=20
11 n=21
12 n=22

$(CH_3)_2CH(CH_2)_{12}CO_2CH_3$

13

TABLE 1. ^{1}H-nmr Spectral Data (200 MHz) for **1**.

Proton	Chemical Shift	Multiplicity	Coupling Constants
H-7	1.02	t	$J_{6,7}$=7.35
H-6	2.40	q	$J_{6,7}$=7.35
H-4	2.51	t	$J_{3,4}$=7.14
H-3	1.98	t of t	$J_{3,4}$=7.14, $J_{2,3}$=6.96
H-2	2.98	t	$J_{2,3}$=6.96
H-2′, H-6′	7.93	d	$J_{2',3'}$=$J_{5',6'}$=7.40
H-3′, H-4′, H-5′	7.6–7.36	m	—

lished the constitution of the natural product as **1**. Comparison of the observed ^{1}H-nmr spectral data with those published (8) for **1** confirmed the assignments.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Nmr spectra were obtained using a Varian Gemini 200 spectrometer at 200 MHz (^{1}H) and 50 MHz (^{13}C) using $CDCl_3$ solutions with TMS as standard. Ms were obtained using a Hewlett-Packard 5970 MSD gc-ms system containing a 30 m capillary column with a 5% phenylsilicone/95% methylsilicone liquid phase with oven temperatures being programmed at 100° for 3 min, then ramped at 10°/min for 18 min; ionization was carried out at 70 eV. Ir spectra were recorded by diffuse reflectance from KBr using a BioRad FTS 60-A ir spectrophotometer.

FUNGAL MATERIAL.—*Ph. tremulus* was collected in the Snake River State Forest in central Minnesota in April and May 1992. A voucher specimen is preserved in the Department of Chemistry, South Dakota State University, Brookings.

ISOLATION OF COMPOUND **1**.—Dried fungus (11.3 kg) was extracted three times with MeOH (30 liters) for a week, and the combined extracts were evaporated under reduced pressure to yield 163 g of oil. The crude extract (67 g) was partitioned between H_2O-CH_2Cl_2 (1:1) to yield 27 g of a CH_2Cl_2-soluble fraction; further partitioning of this fraction between 10% H_2O/MeOH and hexane yielded 11.0 g of a hexane-soluble fraction. This fraction (5.0 g) was subjected to cc on Si gel (125 g adsorbent; EtOAc in hexane eluent). The material eluted from the column with 20% EtOAc in hexane was subjected to preparative tlc (Si gel, 20% EtOAc/hexane); the fractions of R_f 0.6–0.7 were subjected to preparative hplc (Si gel, 10% EtOAc/hexane) and afforded **1** as a pale yellow oil (18 mg) which crystallized on standing. Recrystallization from C_6H_6/hexane afforded **1** as a white crystalline solid: mp 62–64°; ν max cm^{-1} (KBr) 3068, 2970, 2942, 1717, 1684, 1456, 1387, 1279, 1218, 1122, 755, 706 cm^{-1}; λ max nm (log ϵ) (EtOH) 238 (4.04); ^{13}C nmr δ 211.8 (C-3), 200.2 (C-1), 137.5 (C-1′), 133.5 (C-4′), 129.0, 128.5 (C-2′, C-3′), 41.7, 37.8 (C-2, C-4), 36.0 (C-6), 18.5 (C-3), 8.0 (C-7) ppm; ^{1}H nmr see Table 1; eims *m/z* (%) $[M]^+$ 204 (9), 175 (8), 148 (4), 147 (21), 120 (29), 105 (100), 77 (46).

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