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1-(2-HYDROXY-3,4,5,6-TETRAMETHOXYPHENYL)-3-PHENYLPROPENE FROM *LINDERA LUCIDA*

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Key Word Index—*Lindera lucida*; Lauraceae; twigs; 1-(2-hydroxy-3,4,5,6-tetramethoxyphenyl)-3-phenylpropene; structural elucidation.

Abstract—A new diarylpropene, 1-(2-hydroxy-3,4,5,6-tetramethoxyphenyl)-3-phenylpropene, has been isolated from twigs of *Lindera lucida*. Its structure was determined by spectral analysis and chemical correlation. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

We have recently reported [1] the presence of a novel dihydrochalcone derivative, 3′,5′-dihydroxy-2′,4′,6′-trimethoxydihydrochalcone, in a Malaysian sample of *Lindera lucida*. Analysis of a minor fraction remaining from the previous study has afforded a new diarylpropene, 1-(2-hydroxy-3,4,5,6-tetramethoxyphenyl)-3-phenylpropene (**1**).

RESULTS AND DISCUSSION

The minor compound (**1**) was isolated as a yellow oil, $C_{19}H_{22}O_5$, which gave a positive $FeCl_3$ test indicating its phenolic nature. The IR spectrum exhibited bands for hydroxyl (3519 cm^{-1}) and benzene ring (1601 and 1462 cm^{-1}) absorptions, whilst the presence of UV absorption bands at 262 and 308 nm supported its aromatic nature. The ^{1}H NMR spectrum showed signals for five aromatic protons [δ_H 7.27 (4H, *m*, H-2″, H-3″, H-5″ and H-6″) and 7.19 (1H, *tt*, $J = 1.7$ and 6.8 Hz, H-4″)], a *trans*-double bond [δ_H 6.79 (1H, *dt*, $J = 16.0$ and 7.0 Hz, H-2) and 6.59 (1H, *dt*, $J = 16.0$ and 1.3 Hz, H-1)], a phenolic hydroxyl proton [δ_H 5.92, *br s*, 2′-OH, exchangeable with D_2O)], four methoxyl groups [δ_H 3.94 (3H, *s*, 4′-OCH_3), 3.89 (3H, *s*, 3′-OCH_3), 3.84 (3H, *s*, 5′-OCH_3) and 3.78 (3H, *s*, 6′-OCH_3)], and a deshielded methylene group [δ_H 3.59 (2H, *dd*, $J = 1.3$ and 7.0 Hz, H_2-3)]. The appearance of the most shielded aromatic proton indicates that it has two *ortho*- and two *meta*-couplings, which is consistent with the presence of a phenyl group. This leaves the second benzene ring to be substituted with a hydroxyl and four methoxyl groups.

Homodecoupling experiments confirmed that the small couplings of the olefinic protons (H-1 and H-2) are to the deshielded methylene protons (H_2-3) and that this methylene group is therefore allylic. The C-3 methylene group is, in turn, directly attached to the monosubstituted benzene ring, since NOEs were observed at H-2″ and H-6″ upon saturation of the C-3 protons. Irradiation of the most shielded methoxyl protons (6′-OCH_3) resulted in NOE enhancements at H-1 and H-2 indicating that the olefinic group is conjugated with the fully-substituted benzene ring. Because this ring is not symmetrically substituted, C-4′ cannot be hydroxylated. The location of the hydroxyl group was determined to be C-2′ by NOE difference spectroscopy (Fig. 1). Hence, the compound is 1-(2-hydroxy-3,4,5,6-tetramethoxyphenyl)-3-phenylpropene (**1**).

The structure of **1** was confirmed by chemical correlation with dihydrokanakugiol (**2**). Dihydrokanakugiol was reduced to the alcohol (**3**) and subsequently dehydrated. The ^{1}H NMR spectrum of the product was identical to that of the natural compound (**1**).

Compound **1** is a novel compound and is the first diarylpropene to be reported from the Lauraceae. A number of diarylpropenes have been found in the

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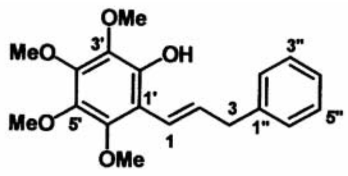
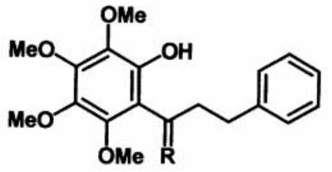
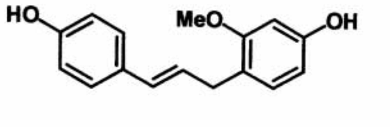


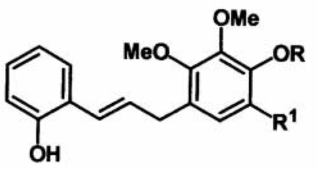
(1)



(2) R = O
(3) R = H, OH



(4)



(5) R = Me, R^1 = OH
(6) *Z* - isomer of (5)
(7) R = R^1 = H

Leguminosae, e.g. xenognosin A (**4**) was isolated from the exudate of *Astragalus* spp. [2] and as a stress metabolite of peas [3], whilst petrostyrene (**5**) [4], kuhlmannistyrene (**6**) [5] and mucronulastyrene (**7**) [6] have been reported from *Machaerium* spp.

EXPERIMENTAL

General

CC: silica gel (40 μm, Baker). UV: EtOH. IR: CCl_4. EI-MS: 70 eV. NMR: ^{1}H, 500 MHz; ^{13}C 125 MHz, in $CDCl_3$ relative to TMS at $\delta = 0.00$. Multiplicities were determined using the DEPT pulse sequence. Coupling constants (*J*) are measured in Hertz (Hz). Difference NOE spectra were run using the NOEMULT programme. The relaxation delay was 2.5 s and the total irradiation time was 3–4 s.

Plant material

Twigs of *L. lucida* (Bl.) Boerl. were collected and identified by the Forest Research Institute, Kuala Lumpur. A voucher specimen is retained in the Department of Chemistry, National University of Singapore. *1-(2-Hydroxy-3,4,5,6-tetramethoxyphenyl)-3-phenylpropene* (3.5 mg) was isolated from frs 7–8 of the earlier work [1], eluting between kanakugiol and dihydrokanakugiol on HPLC (silica gel, 6% Me_2Co in hexane).

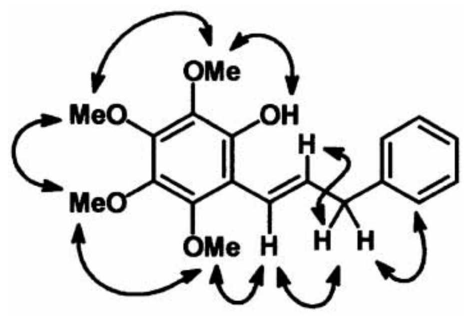


Fig. 1.

1-*(2-hydroxy*-3,4,5,6-*tetramethoxyphenyl)*-3-*phenylpropene (***1***)*

Orange oil. UV λ_{max} nm (log ε): 262 (3.04). 308 (2.39). IR ν_{max} cm^{-1}: 3519 (OH), 1601, 1462 (benzene ring), 1417, 1378, 1053. EI-MS *m*/*z* (rel. int.): 330 $[M]^+$ (100), 315 (11), 226 (39), 211 (36), 91 (93); HREI-MS: *m*/*z* 330.1476 ($C_{19}H_{22}O_5$ requires *m*/*z* 330.1467). ^{1}H NMR: see text. ^{13}C NMR: δ 147.9 (*s*), 145.0 (*s*), 143.4 (*s*), 140.8 (*s*), 139.9 (*s*), 136.1 (*s*), 133.6 (*d*), 128.7 (2 × *d*), 128.4 (2 × *d*), 126.0 (*d*), 121.3 (*d*), 113.4 (*s*), 61.5 (*q*), 61.4 (*q*), 61.2 (*q*), 61.0 (*q*), 40.9 (*t*).

Reduction of **2**

Excess $NaBH_4$ was added to the ketone (**2**) (22 mg) in EtOH and the soln was stirred for 2 h at room temp. H_2O was added to the mixt. and EtOH removed under red. pres. The crude product was obtained by extraction with $CHCl_3$. HPLC (CN, 10% EtOAc-hexane) afforded the diol (**3**) (6.5 mg) as a gum. UV λ_{max} nm (log ε): 284 (4.28), 228 (4.87). IR ν_{max} cm^{-1}: 3521, 3375 (OH), 1604, 1467 (benzene ring). EI-MS *m*/*z* (rel. int.): 348 $[M]^+$ (1), 330 $[M - H_2O]^+$ (100), 315 (20), 226 (72), 211 (70), 91 (97); HREI-MS: *m*/*z* 348.1553 ($C_{19}H_{24}O_6$ requires *m*/*z* 348.1573). ^{1}H NMR (300 MHz): δ 7.22 (5H, *m*, H-2″, H-3″, H-4″, H-5″ and H-6″), 6.61 (1H, *br s*, 2′-OH), 5.08 (1H, *dt*, *J* = 5.0 and 8.8 Hz, H-1), 3.92, 3.89, 3.812, 3.807 (each 3H, *s*, OCH_3), 3.25 (1H, *d*, *J* = 8.8 Hz, 1-OH), 2.90 (1H, *ddd*, *J* = 4.7, 10.1 and 14.0 Hz, H-3), 2.67 (1H, *ddd*, *J* = 6.6, 9.8 and 14.0 Hz, H-3), 2.25 (1H, *m*, H-2), 2.03 (1H, *m*, H-2).

Dehydration of **3**

Diol (**3**) (6.5 mg) was dissolved in pyridine (2 ml) and the soln cooled in an Me_2CO-ice bath. Freshly distilled $SOCl_2$ (12 drops) was added to the stirred soln. After 5 min, the soln was allowed to come to room temp. and poured into ice-cold 5% aq. $NaHCO_3$. The aq. soln was extracted with $CHCl_3$ and the crude product obtained chromatographed (silica gel, 6% Me_2CO-hexane) to give a compound (5 mg) identical (^1H NMR, TLC, MS) to the natural product (**1**).

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REFERENCES

1. Leong, Y.-W., Harrison, L. J., Bennett, G. J., Kadir, A. A. and Connolly, J. D., *Phytochemistry*, 1998, **47,** 891.
2. Lynn, D. G., Steffens, J. C., Kamut, V. S., Graden, D. W., Shabanowitz, J. and Riopel, J. L., *J. Am. Chem. Soc.*, 1981, **103,** 1868.
3. Carlson, R. E. and Dolphin, D. H., *Phytochemistry*, 1982, **21,** 1733.
4. Ollis, W. D., Redman, B. T., Sutherland, I. O. and Gottlieb, O. R., *Phytochemistry*, 1978, **17,** 1379.
5. Ollis, W. D., Redman, B. T., Roberts, R. J., Sutherland, I. O., Gottlieb, O. R. and Magalhães, M. T., *Phytochemistry*, 1978, **17,** 1383.
6. Kurosawa, K., Ollis, W. D., Sutherland, I. O., Gottlieb, O. R. and de Oliveira, A. B., *Phytochemistry*, 1978, **17,** 1389.