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3,4-DIHYDROXY-3′-METHOXYSTILBENE, THE FIRST MONOMERIC STILBENE DERIVATIVE FROM BRYOPHYTES*

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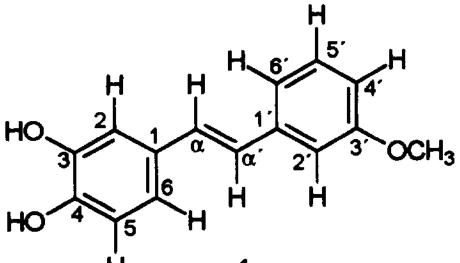
Key Word Index—*Marchesina bongardiana*; Lejeuneaceae; liverwort; isolation; synthesis; stilbene.

Abstract—3,4-Dihydroxy-3′-methoxystilbene, the first monomeric stilbene derivative to be discovered in bryophytes was isolated from the neotropic liverwort *Marchesina bongardiana*. Its structure has been elucidated on the basis of NMR spectral evidence and independent chemical synthesis of this hitherto unknown compound.

INTRODUCTION

Dihydrostilbenes, so called bibenzylic compounds, are a class of compounds typically found in bryophytes [1]. As a result of our systematic investigations [2] of the constituents of the neotropic liverwort *Marchesina bongardiana* (Lehm. & Lindenb.) Trev. [3], we now report on the isolation and total synthesis of the yet unknown compound **1** which to the best of our knowledge is the first genuine monomeric stilbene derivative to be isolated from this plant class.



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RESULTS AND DISCUSSION

Compound **1** was isolated from the chloroform extract of the liverwort *Marchesina bongardiana* by VLC on silica gel followed by MPLC on RP 18 and SC on Sephadex LH 20 (yield: 36 mg of a yellow oil from 190 g dry plant material). The structure and substitution pattern of **1** was elucidated from its EI-mass spectrum ($[M]^+$ m/z 242), which was in accordance with a molecular formula of $C_{15}H_{14}O_3$ and by NMR techniques (C-H-COSY, C-H-long-range-COSY, H-H-COSY).

The stilbene derivative **1** is a new natural product with an unusually unsymmetrical substitution pattern with regard to stilbenes from higher plants, e.g. *Myristicaceae* [4], *Orchideaceae* [5] and *Gymnosperms* [6]. Furthermore, and to our knowledge, compound **1** has not yet been described or synthesized.

We achieved the total synthesis of **1** on the basis of a carbonyl olefination reaction between bis(allyl) protected 3,4-dihydroxy benzaldehyde (**2**) [7] and the phosphonium salt **3** [8] derived from 3-(bromomethyl)anisole yielding the stilbene derivatives **4** and **5**. After separation of the *E*- and *Z*-isomers the allyl protective groups were selectively removed in each case by a method described recently for the cleavage of allyl aryl ethers [7], yielding **1** and the corresponding *Z*-stilbene **6**, respectively (Fig. 1). The *E*-stilbene (**1**) was identical in all spectroscopic data with the isolated natural compound.

EXPERIMENTAL

Plant material. The sample of *Marchesina bongardiana* (Lehm. & Lindenb.) Trev. originated from Columbia, Department Cundinamarca, San Antonio de Tena, Parque Montanes de Chicaque, alt. 2200 m; leg.: E. Linares, S.R. Gradstein 28.5.91; det.: S. R. Gradstein, P. Geissler. Voucher specimens are

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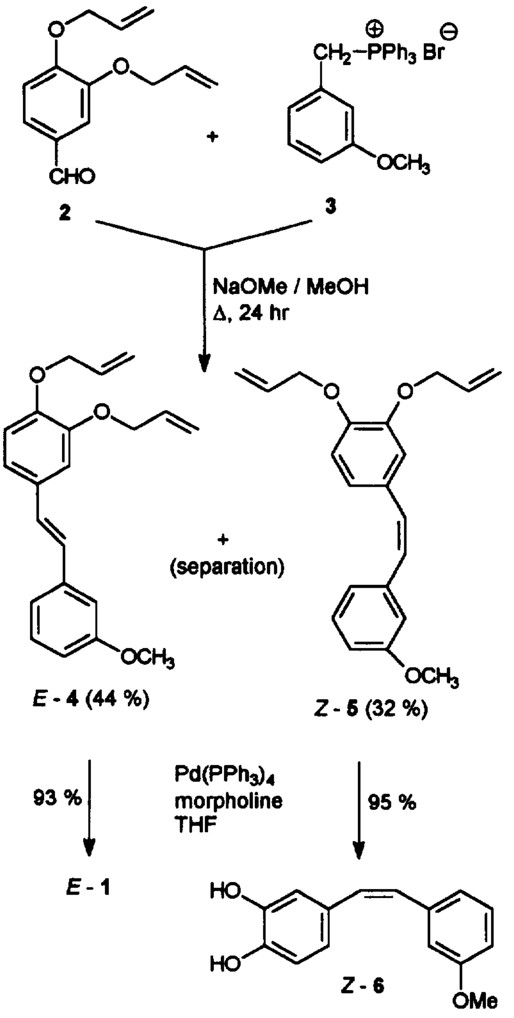

Fig. 1. Syntheses of compounds **1** and **6**.

deposited in the herbarium SAAR, no. 5041, Sarbrücken.

Extraction and isolation. Air-dried, powdered gametophytes of *M. bongardiana* (190 g) were extracted with $CHCl_3$ to give a lipid extract which was chromatographed on silica gel (15 μm) via VLC with 0–100% hexane–EtOAc. The fr. of medium polarity was further purified via MPLC on RP-18 (40–63 μm) with 50% MeOH–H_2O and finally purified via SC on Sephadex LH-20 with 100% MeOH to afford **1** (36 mg, yellow oil).

Synthesis of E- *and* Z-3,4-*bis*(*allyloxy*)-3′-*methoxystilbene* (**4** *and* **5**). To Na-methanolate (45.0 mmol) in dry MeOH (60 ml) was added the phosphonium salt **3** (9.20 g, 20.0 mmol) and the aldehyde **2** (3.27 g, 15.0 mmol) in MeOH (15 ml). The mixture was heated to reflux for 24 hr, concd and treated with Et_2O (25 ml) and H_2O (25 ml). The organic layer was dried ($MgSO_4$) and concd. The residue was purified by flash chromatography on silica gel (40–60 μm) with Et_2O–*n*-hexane (1:5) yielding **4** (2.10 g, 44%, mp 67°) and **5** (1.55 g, 32%, mp 56°). NMR data not documented.

Table 1. ^{1}H and ^{13}C NMR spectral data for the natural and synthetic stilbene derivative **1** (MeOH-d_4)

C-,H-	^{1}H (400 MHz) δ(ppm)	^{13}C (100 MHz)
1		131.1
2	7.00 (*d*, J = 2.0 Hz)	114.1
3		146.6*
4		146.5*
5	6.73 (*d*, J = 8.0 Hz)	116.5
6	6.86 (*dd*, J = 8.0, 2.0 Hz)	120.3
α	6.87 (*d*, 16.0 Hz)	126.8
α′	6.99 (*d*, J = 16.0 Hz)	130.2
1′		140.8
2′	7.02 (*d*, J = 2.0 Hz)	112.5
3′		161.5
4′	6.76 (*dd*, J = 8.0, 2.0 Hz)	113.7
5′	7.21 (*t*, J = 8.0 Hz)	130.5
6′	7.05 (*d*, J = 8.0 Hz)	119.9
-OMe	3.80 (*s*, 3H)	55.7

* Interchangeable.

The 2D-spectra (not documented) were measured at 500 and 125 MHz, respectively.

Synthesis of **1** *and* **6**. The allyl protected stilbene derivative **4**/**5** (485 mg, 1.50 mmol) and $Pd(PPh_3)_4$ (17.6 mg, 0.015 mmol, freshly prepd) were dissolved in degassed dry THF (75 ml) and morpholine (2.60 g, 30.0 mmol) was added dropwise. The green mixt. was stirred for 24 hr at room temp. (monitored by TLC; eluent: cyclohexane–Et_2O 5:1) and concd *in vacuo* (40°). The residue was taken up in Et_2O–1 M HCl (1:1) and the organic layer washed with small amounts of 1 M HCl (×4), dried ($MgSO_4$) and concd.

E-3,4-*dihydroxy*-3′-*methoxystilbene* (**1**). Yield 338 mg (93%) from **4**; mp 102° ($CHCl_3$–cyclohexane); solid. Found: C, 74.1; H, 5.9. $C_{15}H_{14}O_3$ requires: C, 74.3; H, 5.8%. ^{1}H and ^{13}C NMR: Table 1; EIMS (70 eV): *m/z* (rel. int.): 242.2 $[M]^+$ (100), 225 $[M-OH]^+$ (9), 210 $[M-OMe]^+$ (12).

Z-3,4-*Dihydroxy*-3′-*methoxystilbene* (**6**). Yield 350 mg (95%) from **5**; nearly colourless oil. Found: C, 74.1; H, 5.8. $C_{15}H_{14}O_3$ requires: C, 74.3; H, 5.82%. ^{1}H NMR (400 MHz, MeOH-d_4): δ 7.11 (*t*, J = 8.0 Hz), 6.82 (*d*, J = 1.2 Hz), 6.81 (*d*, J = 8.0 Hz), 6.72 (*d*, J = 1.2 Hz), 6.71 (*dd*, J = 8.0, 1.2 Hz), 6.64 (*d*, J = 8.0 Hz), 6.59 (*d*, J = 8.0 Hz), 6.46 (*d*, J = 12.2 Hz), 6.39 (*d*, J = 12.2 Hz) each 1H, 3.64 (*s*, 3H); ^{13}C NMR (100 MHz, MeOH-d_4): δ 160.9, 146.0, 145.9, 140.5, 131.6, 130.2, 129.2, 126.9, 122.6, 122.2, 117.1, 116.2, 114.9, 114.1, 55.5.

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