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## A POLYACETYLENE FROM HONDURAS MAHOGANY, *SWIETENIA MAHAGONI*

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**ABSTRACT.**—A new C<sub>17</sub> epoxydiol polyacetylene,  $\alpha$ -hexyl-3-(6-hydroxy-2,4-octadiynyl) oxiranemethanol [**1**] was isolated from Honduras mahogany, *Swietenia mahagoni*. Occurrence of a polyacetylene in the family Meliaceae is unusual.

During an investigation for insect feeding deterrents in the wood of Honduras mahogany, a new polyacetylene was isolated. Polyacetylenes are mainly found in plants of the families Compositae, Umbelliferae, Santalaceae, Araliaceae, Campanulaceae, Pittosporaceae, and Oleaceae (1,2). To our knowledge, this is the first report of their occurrence in the family Meliaceae. A number of insect feeding deterrent compounds are known to occur in the Meliaceae. Perhaps the best known among them is the limonoid azadirachtin (3,4), but other limonoid compounds (5-7) with biological activity have been discovered. Hence, the isolation of a polyacetylene was unexpected. Although this compound was not active in our bioassay, antifeedant activities of

substituted butadiynes have been reported (8).

The ir spectrum of the isolated compound had a very strong hydroxyl peak at 3386 cm<sup>-1</sup> and a sharp weak band at 2251 cm<sup>-1</sup>, indicative of an alcohol and an acetylene. <sup>1</sup>H-nmr data are in Table 1. Assignments were based on the findings that follow. The COSY nmr spectrum indicated a partial structure, Me-CH<sub>2</sub>-C(OR)H-, that was isolated from the remainder of the molecule. Another part of the molecule started with geminal hydrogens at  $\delta$  2.48 and  $\delta$  2.80 followed by a sequence, based on cross-peaks in the COSY, of one hydrogen at  $\delta$  3.26, one hydrogen at  $\delta$  2.96, one hydrogen at  $\delta$  3.52, two hydrogens at  $\delta$  1.61, eight hydrogens at ca.  $\delta$  1.31, and a skewed triplet at  $\delta$  0.86 that was

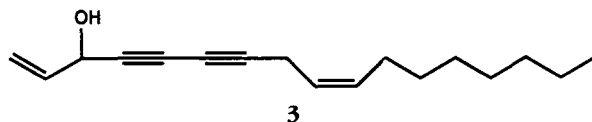
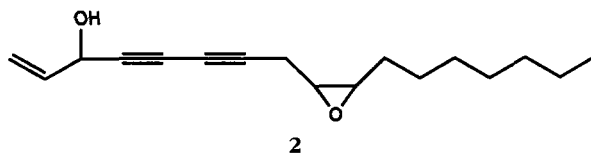
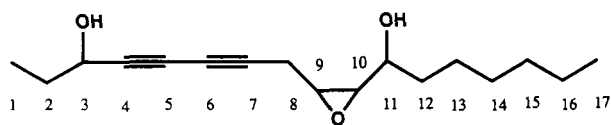


TABLE 1. <sup>1</sup>H-nmr Data of Compound **1** and Structurally Similar Compounds.

Proton	Compound			
	<b>1</b>	Bis(3,5-dinitrobenzoate) of <b>1</b>	<b>2</b> <sup>a</sup>	<b>3</b> <sup>b</sup>
H-1 . . . . .	1.02, t, <i>J</i> = 7.5 Hz	1.14	5.28 5.53	5.24 5.46
H-2 . . . . .	1.74, s, <i>J</i> = 7.5, 6.3	2.04	5.95	5.94
H-3 . . . . .	4.36, t, <i>J</i> = 6.3	5.67	4.91	4.90
H-8a . . . . .	2.48, dd, <i>J</i> = 17.7, 7.0	2.57	2.35	3.03
H-8b . . . . .	2.80, dd, <i>J</i> = 17.7, 5.7	2.95	2.71	3.03
H-9 . . . . .	3.26, m, <i>J</i> = 7.0, 5.7, 3.9	3.35	3.06	5.51
H-10 . . . . .	2.96, dd, <i>J</i> = 7.5, 3.9	3.26	2.96	5.37
H-11 . . . . .	3.52, m, <i>J</i> = 7.8, 7.5, 5.4	5.14	1.42	2.02
H-12 . . . . .	1.61, m	1.92	1.3	1.27
H-13 to H-16 . . . . .	1.31, s	1.30	1.3	1.27
H-17 . . . . .	0.86, t, <i>J</i> = 6.6	0.86	0.92	0.88
3,5-Dinitrobenzoate				
H-2', 6' . . . . .	m	9.17		
H-4' . . . . .	m	9.25		

<sup>a</sup>Data for this compound are from Silverstein *et al.* (9).

<sup>b</sup>Data for this compound are from Poplawski *et al.* (10).

typical of a methyl terminus of a long hydrocarbon chain. The COSY spectrum of its bis(3,5-dinitrobenzoate) showed the same coupling pattern as the parent compound, but the hydrogen at  $\delta$  4.36 had shifted to  $\delta$  5.67 and the one at  $\delta$  3.52 to  $\delta$  5.14. These two hydrogens were assigned to carbons bearing hydroxyl groups. Seventeen carbon atoms could be counted in the <sup>13</sup>C-nmr spectrum of the natural product, and a polyacetylene structure (**1**) was suggested by the evidence. The mol wt of the compound was 278 [determined from cims (NH<sub>3</sub>)], and a molecular formula of C<sub>17</sub>H<sub>26</sub>O<sub>3</sub> was indicated. An epoxide satisfies the molecular formula and the chemical shifts of the hydrogens at  $\delta$  3.26 and  $\delta$  2.96. The coupling constant, *J* = 3.9 Hz, allows us to assign *cis* substitution to the oxirane ring (9). The structure of the isolated compound is, therefore,  $\alpha$ -hexyl-3-(6-hydroxy-2,4-ocadiynyl)oxiranemethanol [**1**].

The presence of an epoxide was confirmed as follows. Refluxing in MeOH for 4 days in the presence of pyridinium tosylate yielded a material that showed

two closely eluting peaks on gc, both having a mol wt of 310, corresponding to the addition of a molecule of MeOH. The nmr spectrum displayed two methoxyls at  $\delta$  3.46 and 3.51. These findings can be accounted for by the non-regiospecific opening of the epoxide.

The most closely related compounds found in the literature were panaxydol [**2**] from *Panax ginseng* (Araliaceae) (10) and falcariol [**3**] from several plant species (11) (Table 1). 2-(6-Heptenyl)-3-(octa-6-ene-2,4-diynyl)oxirane was tentatively identified in *Solidago virgaurea* (Compositae) (12). <sup>1</sup>H-nmr data reported for **2** and **3** are in Table 1, along with the data for **1** and its bis(3,5-dinitrobenzoate).

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.<sup>1</sup>—<sup>1</sup>H (300 MHz) and <sup>13</sup>C nmr (75 MHz) were recorded on a GE QE-300 nmr spectrometer with TMS as internal standard and CDCl<sub>3</sub> as solvent.

<sup>1</sup>The mention of a trade name does not constitute an official endorsement or recommendation by the USDA.

Decoupling was employed to obtain coupling constants for some hydrogens. Ms was obtained on a Finnigan model 4500 gc-ms. The ir spectrum was obtained on a Perkin-Elmer 1320 infrared spectrophotometer and the uv spectrum on a Beckman DU-70 uv-vis spectrophotometer. Eims (70 eV) were collected at an indicated source temperature of 150°. NH<sub>3</sub> was employed for generation of cims for confirmation of molecular mass. Electron capture negative ion (ecni) spectra were produced using CH<sub>4</sub> as a buffer gas for the generation of thermal energy level electrons. Optical rotation was measured with a Perkin-Elmer Model 241 polarimeter. Whatman MK6F plates were used for tlc with 1,2-dichloroethane-methyl *t*-butyl ether (80:20) as solvent. Detection was either by uv absorption, for the bis(3,5-dinitrobenzoate), or by charring.

**EXTRACTION AND ISOLATION.**—Honduras mahogany wood was purchased from Craft Woods, Cockeysville, Maryland. (A voucher specimen has been deposited at the Botany Division, National Museum of Natural History, Washington, DC.) About 1 mm of the surface was removed by planing to guard against contamination during shipment. The wood was shredded in a Wiley mill, then extracted sequentially with Et<sub>2</sub>O and MeOH in a Soxhlet apparatus. A portion of the MeOH extract (50 g) was partitioned in the solvent system CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (13:7:4), and the CHCl<sub>3</sub>-soluble material (5.86 g) was chromatographed on a column of Florisil (120 g) using increasing amounts of Me<sub>2</sub>CO in a mixture of petroleum ether/Me<sub>2</sub>CO/CHCl<sub>3</sub>. The fraction (1.43 g) that was eluted with petroleum ether-Me<sub>2</sub>O-CHCl<sub>3</sub> (70:20:10) was subjected to flash chromatography with petroleum ether-Me<sub>2</sub>CO-CHCl<sub>3</sub> (60:30:10) as eluent, and the fractions with only one spot at R<sub>f</sub> 0.53 on tlc were collected and distilled (bath temperature 210°; 0.04 mm of Hg) through a short-path still to obtain ca. 100 mg of distillate.

**α-Hexyl-3-(6-hydroxy-2,4-octadiynyl)oxirane-methanol [1].**—The compound was obtained as a clear, colorless liquid: [α]<sub>D</sub> -63.8 (c = 1.95, MeOH); <sup>1</sup>H nmr see Table 1; <sup>13</sup>C nmr (75 MHz, CDCl<sub>3</sub>) δ 9.30, 14.03, 19.89, 22.61, 24.99, 29.26, 30.78, 31.71, 34.30, 41.08, 55.15, 60.32, 64.13, 66.97, 69.36, 75.24, 77.75; ir cm<sup>-1</sup> ν max (neat) 3386 (vs), 2924 (vs), 2854 (vs), 2251 (w), 1457 (m), 1377 (m), 1297 (m), 1266 (m), 1044 (m), 1011 (m), 917 (m), 836 (w); uv nm λ max (ε) 284 (182), 268 (190), 230–255 (190); Gc-eims (70 eV) *m/z* (rel. int.) [M]<sup>+</sup> 278 (0.025), 259 (0.15), 245 (3), 231 (3), 175 (20), 146 (23), 131 (100), 119 (19), 113 (19), 105

(26), 91 (41), 85 (22), 77 (40), 69 (20); Gc-cims (NH<sub>3</sub>) *m/z* (rel. int.) [M + H + 2NH<sub>3</sub>]<sup>+</sup> 313 (2), [M + H + NH<sub>3</sub>]<sup>+</sup> 296 (100).

**Bis(3,5-dinitrobenzoate) of 1.**—A mixture of **1** (200 mg), 3,5-dinitrobenzoyl chloride (900 mg) and 4-dimethylaminopyridine (150 mg) in CH<sub>2</sub>Cl<sub>2</sub> (25 ml) was treated with pyridine (1.2 g) and allowed to stand for 4 h. The crude product, after usual workup, on standing in petroleum ether-Me<sub>2</sub>CO-CHCl<sub>3</sub> (8:1:1), solidified to yield an off-white solid (208 mg): mp 120–130; <sup>1</sup>H nmr see Table 1; eims (probe, 70 eV) *m/z* (rel. int.) [M]<sup>+</sup> 666 (10), 369 (3), [C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>CO]<sup>+</sup> 195 (100), 149 (38), 131 (7), 105 (14); ecnims (probe) *m/z* (rel. int.) [M]<sup>-</sup> 666 (100), [C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>COO]<sup>-</sup> 211 (45).

**Addition of MeOH to 1.**—A mixture of **1** (40 mg), pyridinium *p*-toluenesulfonate (125 mg), and MeOH (2 ml) was refluxed for 4 days. The product was purified by flash chromatography with 1,2-dichloroethane-methyl *t*-butyl ether (75:25) as eluent to yield a white solid (35 mg): <sup>1</sup>H nmr (300 MHz, CDCl<sub>3</sub>) δ 3.46 (s, OMe), 3.51 (s, OMe); Gc-cims (NH<sub>3</sub>) *m/z* (M + H + NH<sub>3</sub>)<sup>+</sup> 328 for each of 2 closely eluting peaks.

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