and concd aq. hydrolysate from each showed the presence of D-glucuronic acid and D-xylose (co-PC and co-TLC with authentic sugars, solvents D.E).

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A NOVEL STILBENE FROM THE WOOD OF *CHLOROPHORA EXCELSA*

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Key Word Index—*Chlorophora excelsa*; *Moraceae*; chlorophorin; 4-geranyl-3,5,4′-trihydroxy-*trans*-stilbene.

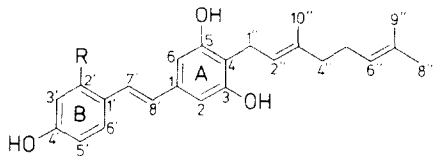
Abstract—A novel stilbene, has been isolated from the diethyl ether extract of the wood of *Chlorophora excelsa* and its structure established as 4-geranyl-3.5,4′-trihydroxy-*trans*-stilbene through spectral studies.

INTRODUCTION

The West African timber *Chlorophora excelsa* (Bentham and Hooker), is generally known under the trade names Iroko and Kambala. It is resistant to fungus and insect attack and is known to cause a cell mediated type of allergy (allergic contact dermatitis) [1]. The allergenic principle of this timber has been identified as chlorophorin [2, 3]. In the present paper we report the isolation and structure elucidation of a novel stilbene from *Chlorophora excelsa*. Its sensitizing potency is not known, but is under investigation.

RESULTS AND DISCUSSION

From the diethyl ether extract of the wood of *Chlorophora excelsa* two stilbenes were isolated by flash chromatography and prep. TLC. These included a new stilbene (**1**) and the known chlorophorin (**2**) [4–7]. Moreover a third compound, possibly a stilbene, is present in a mixture with **1** showing a molecular ion peak at *m/z* 378. This compound could not be separated from **1** in a pure state, which made the structure determination impossible. The main compound was **2** with the molecular formula $C_{24}H_{28}O_4$. The obtained spectroscopic data (see Experimental and Table 1) confirmed the already estab-



1 R = H
2 R = OH

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Table 1. ^{13}C NMR spectral data of compounds **1** and **2** (CD_3CN, δ in ppm)

	1		2	
C	Chemical shift	Multiplicity (DEPT)	Chemical shift	Multiplicity (DEPT)
1	134.34[b]	*s*	134.11[b]	*s*
2	104.40	*d*	104.13	*d*
3	155.15	*s*	154.83	*s*
4	113.63	*s*	113.15	*s*
5	155.15	*s*	154.83	*s*
6	104.40	*d*	104.13	*d*
1′	128.84	*s*	115.91	*s*
2′	127.21	*d*	154.51	*s*
3′	114.92	*d*	101.84	*d*
4′	156.10	*s*	156.70	*s*
5′	114.92	*d*	107.06	*d*
6′	127.21	*d*	121.62[a]	*d*
7′	125.27[a]	*d*	124.94[a]	*d*
8′	126.90[a]	*d*	126.74[a]	*d*
1″	21.34	*t*	21.32	*t*
2″	122.10[a]	*d*	121.93[a]	*d*
3″	136.01[b]	*s*	136.40[b]	*s*
4″	38.85	*t*	38.79	*t*
5″	25.84	*t*	25.80	*t*
6″	123.67[a]	*d*	123.49[a]	*d*
7″	130.64	*s*	130.41	*s*
8″	24.27	*q*	24.26	*q*
9″	16.20	*q*	16.21	*q*
10″	14.72	*q*	14.73	*q*

[a,b] Assignments may be interchanged.

lished structure of **2** [4–7] as a 4-geranyl-3,5,2′,4′-tetrahydroxy-*trans*-stilbene.

High resolution mass spectrometry (HRMS) of **1** gave a molecular ion which corresponded well with the empirical formula $C_{24}H_{28}O_3$ (364.203, calculated 364.204). Its mass spectral fragmentation pattern with ions at *m/z* 295 $[M-69]^+$, 281 $[M-83]^+$, and 241 $[M-123]^+$ (base peak), in the low resolution mass spectrum (EIMS), indicates that a geranyl side chain is present. Its ^1H NMR spectrum was very similar to that of **2** (Experimental), showing the presences of a *trans*-stilbene at δ6.82, 6.91 (2H,AB-system, $J = 16.4$ Hz, H-7′ and H-8′) and a symmetrically substituted ring A [δ6.59 (2H, *s*, H-2 and H-6)] with a geranyl part linked to position 4 and two phenol groups placed at position 3 and 5 [δ 8.19 (2H, *s*, C3-OH and C5-OH)], respectively. However the aromatic proton signals from ring B were different. Compound **1** showed an AA′BB′-system and **2** an ABX-system and together with the fact that **1** gave a signal from a third phenol group [δ 8.58 (1H, *br s*)], indicated that it had a phenol group at position 4′.

Comparing the ^{13}C NMR spectrum of **1** with that of **2** showed only significant differences in the chemical shifts of the B ring carbons, except for the quaternary carbon at position C-4′, (Table 1). In addition the ^{13}C NMR spectrum of **1** revealed that the pairs C-2′, C-6′ and C-3′, C-5′ are chemically equivalent, respectively, which is in agreement with the AA′BB′ pattern found for the B ring protons. All these facts show that the two compounds are related to each other and that the structure of **1** is 4-geranyl-3,5,4′-trihydroxy-*trans*-stilbene.

It may be noticed that the UV and IR spectral data of compound **1** are in agreement with its structure (Experimental).

EXPERIMENTAL

General. DEPT experiments were carried out with the polarization pulse $\Theta = 45°$, 90° and 135°. EIMS (low and high resolution) were obtained with a VG-analytical Micromass 7070F (100 μA, 70 eV, 250°) mass spectrometer. Prep. TLC was performed on silica gel 60 $PF_{254+360}$ (ART No. 7748) layers (0.15 × 20 × 20 cm) on glass plates. Silica gel 60, 230–400 mesh (ART No. 9385) was used for flash chromatography [8].

Plant material. The wood of *Chlorophora excelsa* was obtained from the Ivory Coast, via a Danish factory.

Extraction and isolation. Chips of iroko wood (1.29 kg) were extracted twice with Et_2O (17 l) under reflux for 30 min, and the combined extracts were dried (Na_2SO_4). Evapn of the soln gave an amorphous lightbrown solid, yield, 5.5% (71.0 g). Flash chromatography of the crude extract on silica gel, using a petrol–Et_2O gradient (11:9, 1:1, 9:11, 2:3, 1:9 and 100% Et_2O) as eluent, gave compound **2**, yield, 85% (60.4 g) of extract, as an almost colourless amorphous powder and compound **1** in a mixture with an unidentified stilbene, yield, 2.5% (1.8 g) of extract.

The mixture was purified by flash chromatography and prep. TLC on silica gel using a petrol–Et_2O gradient (3:2, 11:9, 1:1, 9:11, 2:3 and 100% Et_2O) and petrol–Et_2O (1:9) as eluents, respectively. This afforded **1** as a light-yellow amorphous pow-

der. However, it was not possible to isolate the unknown stilbene in a pure state even with the use of other methods such as GLC and HPLC.

4-*Geranyl*-3,5,4′-*trihydroxy*-*trans*-*stilbene* (**1**). Mp 145–150°. UV $\lambda_{max}^{Et_2O}$ nm (log ε): 222 (4.32), 312 (4.46), 326 (4.45). IR $\nu_{max}^{acetone}$ cm^{-1}: 3400 (OH), 2920 (CH), 1610, 1585, 1520 (C=C and aromatic), 1050, 975 (*trans* C=C). EIMS *m/z* (rel. int.): 364 $[M]^+$ (89), 295 (36), 281 (18), 279 (28), 242 (43), 241 (100), 205 (17), 167 (20), 123 (27), 83 (23), 69 (41). HRMS *m/z*: 364.203 $[M]^+$($C_{24}H_{28}O_3$ requires: 364.204). ^{1}H NMR (acetone-d_6; TMS int. standard): δ 1.57, 1.62, 1.78 (3H each, *s*, 3 × Me), 1.93–2.09 (4H, *m*, CH_2–CH_2), 3.36 (2H, *d*, J = 6.8 Hz, Ph-CH_2), 5.10 (1H, *m*, CH=CR_2), 5.33 (1H, *m*, CH=CR_2), 6.59 (2H, *s*, H-2 and H-6), 6.82, 6.91 (2H, AB-system, J = 16.4 Hz, H-7′ and H-8′), 6.81, 6.84, 7.36, 7.39 (4H, AA′BB′-system, H-2′, H-3′,-H-5′ and H-6′), 8.19 (2H, *s*, C3-OH and C5-OH), 8.58 (1H, *br s*, C4′-OH). ^{13}C NMR (see Table 1).

4-*Geranyl*-3,5,2′,4′-*tetrahydroxy*-trans-*stilbene* (**2**). Mp 159–160° UV $\lambda_{max}^{Et_2O}$ nm (log ε): 222 (4.31), 304 (4.31), 329 (4.46), 338 (4.45). IR identical with lit. values [7]. EIMS *m/z* (rel. int.): 380 $[M]^+$ (80), 312 (10), 311 (30), 297 (7), 296 (7), 295 (33), 258 (26), 257 (100), 187 (10), 123 (14), 110 (17), 81 (16), 69 (22). HRMS *m/z*: 380.198 $[M]^+$ ($C_{24}H_{28}O_4$ requires: 380.199). ^{1}H NMR (acetone-d_6; TMS int. standard): δ 1.57, 1.62, 1.79 (3H each, *s*, 3 × Me), 1.93–2.10 (4H, *m*, CH_2–CH_2), 3.37 (2H, *d*, J = 7.1 Hz, Ph–CH_2), 5.10 (1H, *m*, CH=CR_2), 5.34 (1H, *m*, CH=CR_2), 6.38 (1H, *dd*, $J_{3'5'}$ = 2.4 Hz and $J_{5'6'}$ = 8.5 Hz, H-5′), 6.44 (1H, *d*, $J_{3'5'}$ = 2.4 Hz, H-3′), 6.58 (2H, *s*, H-2 and H-6), 6.83, 7.27 (2H, AB-system, J = 16.4 Hz, H-7′ and H-8′), 7.39 (1H, *d*, $J_{5'6'}$ = 8.5 Hz, H-6′), 8.10 (2H, *s*, C3-OH and C5-OH), 8.42 (1H, *br s*, C2′-OH), 8.60 (1H, *br s*, C4′-OH). ^{13}C NMR (see Table 1).

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