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EXCELSAOCTAPHENOL, A STILBENE DIMER FROM *CHLOROPHORA EXCELSA*

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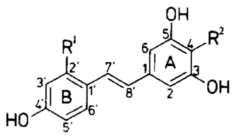
Key Word Index—*Chlorophora excelsa*; Moraceae; stilbenes; phenylbenzofuran derivative; 1,10-bis-(3,5,2′,4′-tetrahydroxy-*trans*-stilbenyl)-3,8-dimethyl-deca-2,8-diene; excelsaoctaphenol.

Abstract—Three stilbenes and one phenylbenzofuran derivative of known structures, together with a new stilbene dimer, have been isolated from the acetone extract of the wood of *Chlorophora excelsa*. The structures of these compounds were determined by UV, IR, NMR and mass spectrometry.



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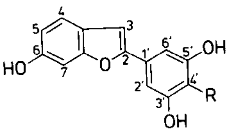
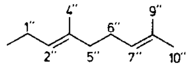
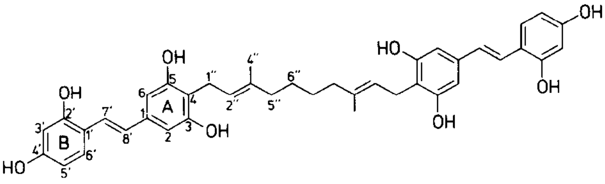
2 R¹ = H, R² = geranyl
4 R¹ = OH, R² = H



3 R = geranyl

geranyl =




5

Scheme 1. The above numeration of compound 5 is used to assign its NMR signals.

INTRODUCTION

We have previously reported the isolation of 4-geranyl-3,5,2′,4′-tetrahydroxy-*trans*-stilbene (chlorophorin, **1**) and the new stilbene, 4-geranyl-3,5,4′-trihydroxy-*trans*-stilbene (**2**), from the diethyl ether extract of the wood of *Chlorophora excelsa* (B. & H.) [1]. In our continuing work with this plant, we undertook a chemical investigation of the acetone extract, which yielded **1** and **2** together with 4′-geranyl-3′,5′,6-trihydroxy-2-phenylbenzofuran (albafuran B, **3**) [2]. Furthermore, 3,5,2′,4′-tetrahydroxy-*trans*-stilbene (hydroxyresveratrol, **4**) [3–6] and a new stilbene dimer were isolated. This paper describes the isolation and characterization of this new dimer **5**, which we give the trivial name 'excelsaoctaphenol'.

RESULTS AND DISCUSSION

Flash chromatography of the crude acetone extract on silica gel afforded the four known compounds (**1**–**4**) together with the highly polar excelsaoctaphenol (**5**). On the basis of mass spectrometry and NMR spectroscopy the molecular formula of **5** was assigned as $C_{40}H_{42}O_8$ (see Experimental).

The IR spectrum of **5** displayed the presence of hydroxy groups (3380 cm^{-1}), C=C and an aromatic structure (1610, 1585 and 1520 cm^{-1}), *trans* C=C (975 cm^{-1}) and the UV spectrum showed λ_{max} at 222, 303 and 329 nm (log ε, respectively, 4.47, 4.31 and 4.46), which is characteristic for 3,5,2′,4′-tetrahydroxy-*trans*-stilbenes. The presence of such a system was also confirmed by the ^{1}H NMR of **5**, which showed signals from a *trans*-stilbene at δ6.83, 7.27 (2 × 2H†, AB-system, $J = 16.4$ Hz) and a symmetrically substituted ring A [δ6.58 (2 × 2H, *s*)], with two phenol groups placed at positions 3 and 5 [δ8.06 (2 × 2H, *s*)], respectively, and an ABX pattern for ring B at δ6.37 (2 × 1H, *dd*, $J = 8.4$, 2.3 Hz), 6.43 (2 × 1H, *d*, $J = 2.3$ Hz), 7.39 (2 × 1H, *d*, $J = 8.4$ Hz), with two phenol groups placed at position 2′ and 4′ [δ8.37 (2 × 1H, *br s*), 8.55 (2 × 1H, *br s*)], respectively.

The ^{1}H and ^{13}C NMR of **5** revealed in addition the presence of an aliphatic chain with the following sequence Ph–CH$_2$–CH=C(Me)–(CH$_2$)$_2$–, showing signals at (^{1}H NMR) δ1.77 (2 × 3H, *d*, $J = 1.3$ Hz), 1.94 (2 × 2H, *t*, $J = 7.0$ Hz), 2.04–2.09 (2 × 2H, *m*, overlapping with the solvent), 3.37 (2 × 2H, *d*, $J = 7.1$ Hz), 5.32 (2 × 1H, *tq*, $J = 7.1$, 1.3 Hz) and (^{13}C NMR) δ15.53 (*q*), 22.34 (*t*), 22.82 (*t*), 40.49 (*t*), 123.48 (*d*), 134.03 (*s*). Compound **5** therefore has a 3,5,2′,4′-tetrahydroxy-*trans*-stilbene structure, with this aliphatic chain in position 4. The fact that all the NMR values are duplicates, which corresponds well with the empirical formula $C_{40}H_{42}O_8$, showed that **5** is a symmetrical compound with two equal moieties containing a *trans*-stilbene part linked to a methyl substituted

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†Because of symmetry in the molecule (**5**), twice the number of protons are given in the parenthesis here and in the following.

penten chain. Therefore we propose the structure 1,10-bis-(3,5,2′,4′-tetrahydroxy-*trans*-stilbenyl)-3,8-dimethyldeca-2,8-diene for **5**. The configuration about the double bonds at the carbon atoms 2,3 and 8,9 in the decadiene has not been sufficiently well elucidated.

The spectroscopic properties of **3** and **4** are also given (Experimental) because the values, to some extent, are in disagreement with literature values [2, 4–6].

EXPERIMENTAL

General. NMR spectra and 2D carbon-proton shift correlations were recorded on a Varian XL-300 (300 MHz) spectrometer. ^{13}C NMR spectra were obtained in CD_3CN, unless otherwise specified, using the septet at $\delta = -0.22$ ppm as reference. ^{1}H NMR spectra were obtained in Me_2CO-d_6, using TMS as int. standard. MS: (100 μA, 70 eV, 250°). Prep. TLC: silica gel 60 (ART No. 7748). Flash CC: silica gel 60, 230–400 mesh (ART No. 9385).

Plant material. See ref. [1].

Extraction and isolation. Chips of iroko wood (560 g) were first extracted twice with Et_2O (7 l) and then twice with Me_2CO (6 l) under reflux for 30 min, and the combined extracts dried (Na_2SO_4). Evapn of the Me_2CO extract gave an amorphous light brown solid, yield 1.9% (10.6 g). Flash chromatography of the crude Me_2CO extract on silica gel, using a petrol–Et_2O gradient (1:4, 1:9 and 100% Et_2O) as eluent, yielded the compounds **1** (5.9 g), **4** (0.74 g), **5** (0.08 g) with **2** and **3** in a mixture (0.39 g). The mixture was carefully purified by repeated prep. TLC on silica gel, using petrol–Et_2O (1:4) as eluent.

For the investigation of the Et_2O extract see ref. [1].

4-*Geranyl*-3,5,2′,4′-*tetrahydroxy*-trans-*stilbene* (**1**). Mp, ^{1}H and ^{13}C NMR, IR, UV and MS see ref. [1].

4-*Geranyl*-3,5,4′-*tetrahydroxy*-trans-*stilbene* (**2**). Mp, ^{1}H and ^{13}C NMR, IR, UV and MS see ref. [1].

4′-*Geranyl*-3′,5′,6-*trihydroxy*-2-*phenylbenzofuran* (**3**). Colourless amorphous solid, mp 157–159° (ref [2] mp 158–158.5°). UV $\lambda_{max}^{Et_2O}$ nm (log ε): 222 (4.43), 319 (4.53), 333 (4.46). IR $\nu_{max}^{Me_2CO}$ cm^{-1}: 3360 (OH), 2920 (CH), 1620, 1585, 1520 (C=C and aromatic). EIMS *m*/*z* (rel. int.): 378 $[M]^+$ (87), 310 (10), 309 (36), 294 (10), 293 (40), 256 (26), 255 (100), 123 (15), 83 (16), 81 (22), 71 (17), 69 (39). HRMS *m*/*z*: 378.183 $[M]^+$ ($C_{24}H_{26}O_4$ requires: 378.183). ^{1}H NMR: δ1.57 (3H, *d*, $J = 1.4$ Hz, Me-9″), 1.62 (3H, *d*, $J = 1.4$ Hz, Me-10″), 1.80 (3H, *d*, $J = 1.3$ Hz, Me-4″), 1.93–2.10 (4H, *m*, H_2-5″ and H_2-6″, overlapping with the solvent), 3.40 (2H, *d*, $J = 7.1$ Hz, H_2-1″), 5.10 (1H, *t* of septets, $J = 7.0$, 1.4 Hz, H-7″), 5.35 (1H, *tq*, $J = 7.1$, 1.3 Hz, H-2″), 6.80 (1H, *dd*, $J_{4,5} = 8.4$ Hz and $J_{5,7} = 2.1$ Hz, H-5), 6.91 (1H, *d*, $J_{3,7} = 1.0$ Hz, H-3), 6.92 (2H, *s*, H-2′ and H-6′), 6.96 (1H, *dq*, $J_{5,7} = 2.1$ Hz, $J_{3,7} = 1.0$ Hz and $J_{4,7} = 0.5$ Hz, H-7), 7.38 (1H, *dd*, $J_{4,5} = 8.4$ Hz and $J_{4,7} = 0.5$ Hz, H-4), 8.46 (2H, *s*, C3′–OH and C5′–OH), 8.63 (1H, *br s*, C6-OH). ^{13}C NMR δ14.73 (*q*, C-4″), 16.19 (*q*, C-9″), 21.35 (*t*, C-1″), 24.25 (*q*, C-10″), 25.82 (*t*, C-6″), 38.84 (*t*, C-5″), 97.03 (*d*, C-7), 100.43 (*d*, C-3), 102.49 (*d*, C-2′, C-6′), 111.64 (*d*, C-5), 114.77 (*s*, C-4′), 120.59 (*d*, C-4), 121.41 (*s*, C-3a), 121.79 (*d*, C-2″), 123.64 (*d*, C-7″), 128.46 (*s*, C-1′), 130.65 (*s*, C-8″), 134.54 (*s*, C-3″), 154.04 (*s*, C-7a), 154.58 (*s*, C-6), 155.04 (*s*, C-2), 155.37 (*s*, C-3′, C-5′).

3,5,2′,4′-*Tetrahydroxy*-trans-*stilbene* (**4**). Colourless amorphous solid, mp 199–201° (lit. [4] mp 199–200°). UV $\lambda_{max}^{Et_2O}$ nm (log ε): 222 (4.40), 301 (4.30), 327 (4.43). IR $\nu_{max}^{Me_2CO}$ cm^{-1}: 3320 (OH), 2920 (CH), 1610, 1600, 1520 (C=C and aromatic), 975 (trans C=C). EIMS *m*/*z* (rel. int.): 244 $[M]^+$ (100), 227 (22), 226 (27), 215 (6), 199 (7), 198 (32), 197 (12), 110 (75). HRMS *m*/*z*: 244.038 $[M]^+$ ($C_{14}H_{12}O_4$ requires: 244.038). ^{1}H NMR*: δ6.26 (1H, *t*, $J_{2,4} = 2.1$ Hz and $J_{4,6} = 2.1$ Hz, H-4), 6.40 (1H, *dd*, $J_{5',6'} = 8.5$ Hz and $J_{3',5'} = 2.3$ Hz, H-5′), 6.45 (1H, *d*, $J_{3',5'} = 2.3$ Hz, H-3′), 6.54 (2H, *d*, $J_{2,4} = J_{4,6} = 2.1$ Hz, H-2 and H-6), 6.91 (1H, *d*, $J_{7',8'} = 16.5$ Hz, H-8′), 7.35 (1H, *d*, $J_{7',8'} = 16.5$ Hz, H-7′), 7.43 (1H, *d*, $J_{5',6'} = 8.5$ Hz, H-6′), 8.15–8.55 (4H, very *br s* C2-, C6-, C2′-, C4′–OH). ^{13}C NMR*: δ100.71 (*d*, C-4), 102.00 (*d*, C-3′), 104.16 (*d*, C-2, C-6), 107.21 (*d*, C-5′), 115.92 (*s*, C-1′), 122.82 (*d*, C-7′), 125.23 (*d*, C-8′), 127.17 (*d*, C-6′), 140.15 (*s*, C-1), 154.94 (*s*, C-2′), 157.17 (*s*, C-4′), 157.63 (*s*, C-3, C-5).

1,10-*Bis*-(3,5,2′,4′-*tetrahydroxy*-trans-*stilbenyl*)-3,8-*dimethyldeca*-2,8-*diene* (**5**). Light brown amorphous solid, mp 210–216°. UV $\lambda_{max}^{Et_2O}$ nm (log ε): 222 (4.47), 303 (4.31), 329 (4.46). IR $\nu_{max}^{Me_2CO}$ cm^{-1}: 3380 (OH), 2920 (CH), 1610, 1585, 1520 (C=C and aromatic), 975 (trans C=C). EIMS *m*/*z* (rel. int.): 650 $[M]^+$ (9), 541 (8), 540 (99), 455 (7), 417 (20), 416 (9), 404 (11), 381 (11), 380 (33), 378 (7), 332 (10), 319 (10), 295 (16), 293 (54), 281 (26), 258 (16), 257 (43), 255 (7), 244 (13), 226 (6), 197 (7), 124 (10), 123 (52), 121 (12), 111 (15), 110 (100), 109 (38), 83 (18), 82 (22), 81 (53), 71 (22), 69 (70). HRMS *m*/*z*: 650.288 $[M]^+$ ($C_{40}H_{42}O_8$ requires: 650.288). ^{1}H NMR*: δ1.77 (6H, *d*, $J = 1.3$ Hz, 2 × Me-4″), 1.94 (4H, *t*, $J = 7.0$ Hz, 2 × H_2-6″), 2.04–2.09 (4H, *m*, 2 × H_2-5″, overlapping with the solvent), 3.37 (4H, *d*, $J = 7.1$ Hz, 2 × H_2-1″), 5.32 (2H, *tq*, $J = 7.1$, 1.3 Hz, 2 × H-2″), 6.37 (2H, *dd*, $J_{5',6'} = 8.4$ Hz and $J_{3',5'} = 2.3$ Hz, 2 × H-5′), 6.43 (2H, *d*, $J_{3',5'} = 2.3$ Hz, 2 × H-3′), 6.58 (4H, *s*, 2 × H-2 and 2 × H-6), 6.83 (2H, *d*, $J_{7',8'} = 16.4$ Hz, 2 × H-8′), 7.27 (2H, *d*, $J_{7',8'} = 16.4$ Hz, 2 × H-7′), 7.39 (2H, *d*, $J_{5',6'} = 8.4$ Hz, 2 × H-6′), 8.06 (4H, *s*, 2 × C3–OH and 2 × C5–OH), 8.37 (2H, *br s*, 2 × C2′–OH), 8.55 (2H, *br s*, 2 × C4′-OH). ^{13}C NMR* (Me_2CO-d_6; TMS int. standard): δ15.53 (*q*, 2 × C-4″), 22.34 (*t*, 2 × C-1″), 22.82 (*t*, 2 × C-6″), 40.49 (*t*, 2 × C-5″), 102.85 (*d*, 2 × C-3′), 104.85 (*d*, 2 × C-2 and 2 × C-6), 107.69 (*d*, 2 × C-5′), 114.15 (*s*, 2 × C-4), 116.73 (*s*, 2 × C-1′), 122.73 (*d*, 2 × C-7′), 123.48 (*d*, 2 × C-2″), 125.57 (*d*, 2 × C-8′), 127.34 (*d*, 2 × C-6′), 134.03 (*s*, 2 × C-3″), 137.40 (*s*, 2 × C-1), 156.10 (*s*, 2 × C-2′), 156.34 (*s*, 2 × C-3 and 2 × C-5), 158.27 (*s*, 2 × C-4′).

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*Assignments based on 2D carbon-proton shift correlations.