

## The Synthesis of the First Natural Host Germination Stimulant for *Striga asiatica* (Witchweed)<sup>1</sup>

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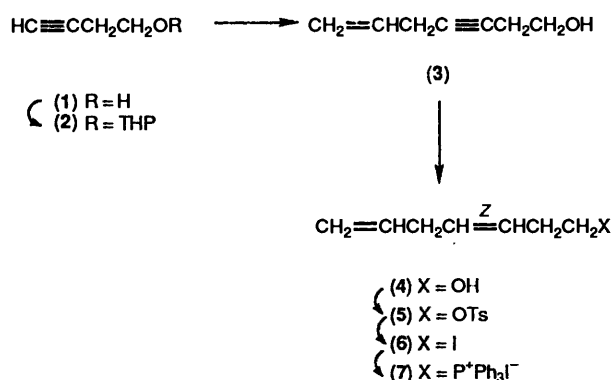
The synthesis of 5-methoxy-3-(8'*Z*,11'*Z*)-pentadeca-8',11',14'-trienylbenzene-1,2,4-triol (**18**), a germination stimulant for *Striga asiatica* (witchweed), isolated from *Sorghum bicolor*, is reported. The key step was a (*Z*)-stereoselective Wittig reaction between the ylide derived from 3-(*Z*)-hepta-3,6-dien-1-yltriphenylphosphonium iodide (**7**) and 8-(2,3,6-triacetoxy-5-methoxyphenyl)octanal (**16**). The synthesis of the structurally related catechol, 3-(8'*Z*,11'*Z*)-pentadeca-8',11',14'-trienylbenzene-1,2-diol (**22**), which occurs in the Anacardaceous species, *Toxicodendron radicans* (poison ivy), is also reported.

Witchweed (*Striga asiatica*) is a widely distributed parasitic plant which damages many economically important gramineous crops including sorghum, maize, millet, rice, and sugar cane. The host-parasite relationship is complex and the control of the weed is not simple since the wind-borne seeds may lie dormant in the soil for many years until their germination is stimulated by a substance exuded from the host plant. Great effort has been expended over many years on the isolation and characterization of the stimulant<sup>2</sup> with the ultimate objective of the chemical control of witchweed. In 1966 a potent germination stimulant for *Striga*, which is active at concentrations of less than 10<sup>-5</sup> ppm, was isolated from cotton.<sup>3</sup> This substance proved to be the sesquiterpene strigol.<sup>4</sup> Cotton, however, is not a natural host plant for witchweed.

In 1986 the isolation, in minute amount, and structural determination was announced of the first witchweed germination stimulant from the natural host plant *Sorghum bicolor*.<sup>5</sup> The spectroscopic properties of this compound and its ready oxidation to the quinone (**19**) (Scheme 2) allowed the structural proposal 5-methoxy-3-(8'*Z*,11'*Z*)-pentadeca-8',11',14'-trienylbenzene-1,2,4-triol (**18**) to be advanced. This labile hydroquinone, which is biologically active at concentrations of 10<sup>-7</sup> M, is able to define the distance from the host plant at which the *Striga* seed germinates, since as it diffuses from the host it undergoes oxidation to the inactive quinone (**19**). We now report a synthesis of the germination stimulant (**18**) which can be adapted to the synthesis of analogues and we report one such example.

A convergent synthetic route was adopted for the germination stimulant and we planned to construct the double bond in the 8'-position of the side chain by a (*Z*)-stereoselective Wittig reaction<sup>6</sup> at a late stage in the synthetic sequence. Consequently we required the phosphonium iodide (**7**) (Scheme 1) and the aldehyde (**16**), in which the hydroxy groups are protected as acetates, as the key synthons.

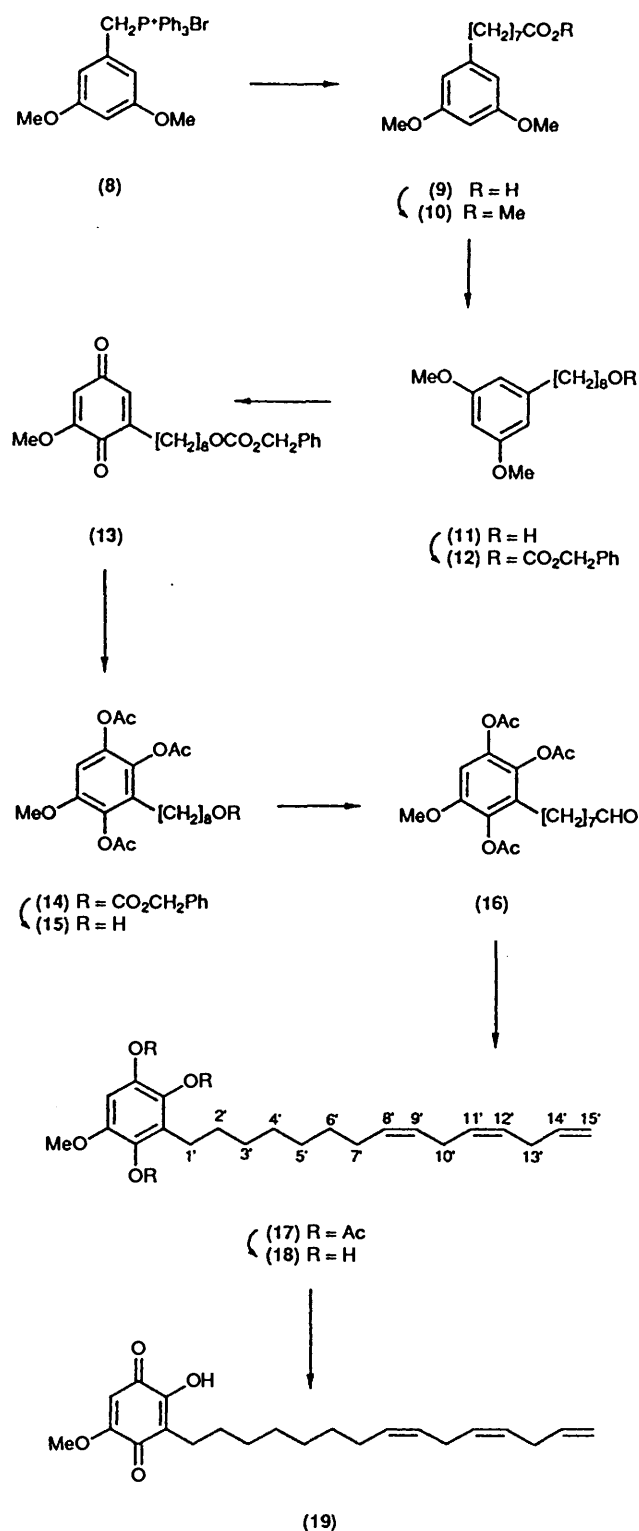
For the synthesis of the phosphonium iodide the starting material was but-3-yn-1-ol (**1**) which was converted into the known tetrahydropyranyl ether (**2**).<sup>7</sup> The derived Grignard reagent was allowed to react with allyl bromide in the presence of copper(I) chloride and deprotection of the crude product gave the heptenynol (**3**). Partial reduction of a solution of this intermediate in pyridine with hydrogen at atmospheric pressure over a 5% palladized barium sulphate catalyst smoothly gave the pure (*Z*)-dienol (**4**). The stereochemical homogeneity of this compound followed from GLC, from the <sup>13</sup>C NMR spectrum which exhibited the olefinic carbons at δ 114.73 (C-7), 126.37 (C-4), 129.77 (C-3), and 136.65 (C-6), and from the 300 MHz <sup>1</sup>H



Scheme 1.

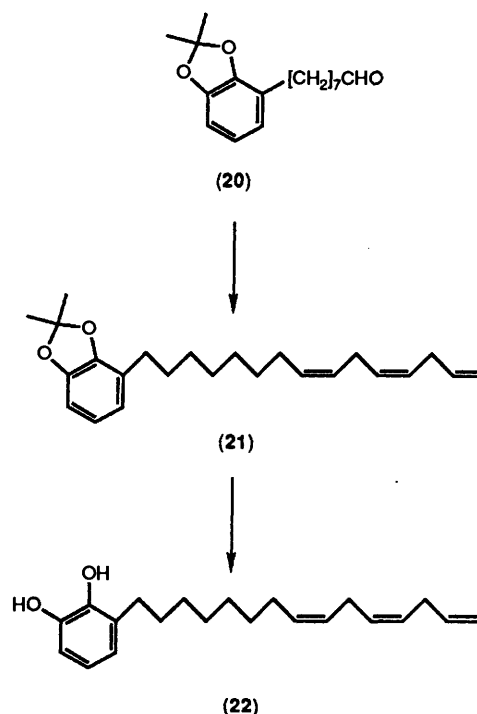
NMR spectrum. The alcohol (**4**) was converted sequentially, by standard methods, into the tosylate (**5**), the iodide (**6**), and finally the phosphonium salt (**7**). The 75.5 MHz <sup>13</sup>C and 300 MHz <sup>1</sup>H NMR spectra of these intermediates confirmed that no isomerization had occurred during these transformations.

The starting material for the synthesis of the aldehyde (**16**) was the known phosphonium salt (**8**)<sup>8</sup> which was converted into its ylide and then allowed to react with ethyl 7-oxoheptanoate (Scheme 2).<sup>9</sup> The isomeric mixture of esters thereby obtained was hydrolysed and the resultant isomeric acids were reduced by catalytic hydrogenation thus supplying the octanoic acid (**9**). The derived methyl ester (**10**) was reduced with lithium aluminium hydride to the octanol (**11**). The primary alcohol function in compound (**11**) was protected as its benzyloxycarbonyl derivative (**12**). This protective group proved to be stable to treatment of compound (**12**) with chromium trioxide in aqueous acetic acid at room temperature since these conditions oxidized only the benzenoid ring and thus provided the quinone (**13**). Thiele acetylation of the quinone (**13**) with acetic anhydride and concentrated sulphuric acid at room temperature furnished the triacetoxy compound (**14**). Again the protective group survived these somewhat harsh conditions. The regiochemistry of the Thiele acetylation followed from a NOESY experiment on compound (**14**) which showed a strong off-diagonal interaction between the <sup>1</sup>H NMR signal of the aromatic proton and that of the methoxy group. This regiochemistry is in accord with literature precedent.<sup>10</sup> Deprotection of compound (**14**) by hydrogenolysis gave the octanol (**15**) which on oxidation with pyridinium chlorochromate in the presence of anhydrous sodium acetate furnished the required aldehyde (**16**).



Scheme 2.

A Wittig reaction between an excess of the ylide derived from the phosphonium iodide (7) and the aldehyde (16) gave the triacetoxyltriene (17) in 56% yield. None of the (*E*)-isomer could be detected in this product by either  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectroscopy. Deprotection was smoothly achieved by reduction with lithium aluminium hydride and this reaction gave the germination stimulant (18) as an oil which was readily oxidized



Scheme 3.

to the crystalline quinone (19) by briefly shaking its solution in benzene with aqueous iron(III) chloride. The spectroscopic properties of these compounds were identical with those reported in the literature and their stereochemical purity follows from their high-resolution  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra.

The trienylcatechol (22) is a vesicant constituent of the Anacardaceous species *Toxicodendron radicans* (poison ivy).<sup>11</sup> The isolation and characterization of this and similar compounds from the same source is difficult owing to their propensity to undergo aerial oxidation and polymerization. Little synthetic work had been recorded on this and similar compounds until our own work on the alkadienylcatechols of Burmese lac.<sup>12</sup> We now report the synthesis of the trienylcatechol (22) (Scheme 3). The known aldehyde (20),<sup>12</sup> on Wittig reaction with the ylide derived from the phosphonium salt (7), gave the triene (21) (75%) which was deprotected by boiling its solution in aqueous acetic acid in an inert atmosphere. The resultant trienylcatechol (22) had spectroscopic properties identical with those recorded in the literature.<sup>11</sup>

This method of synthesis should allow the ready preparation of analogues of the *Striga* germination stimulant.

### Experimental

General directions have been given previously.<sup>12</sup> The assignment of  $^{13}\text{C}$  NMR spectra was assisted by the DEPT technique and that of  $^1\text{H}$  NMR spectra by double irradiation.

**2-(But-3-yn-1-yloxy)tetrahydropyran (2).**—A solution of but-3-yn-1-ol (1) (5.0 g), pyridinium toluene-*p*-sulphonate (1.87 g), and dihydropyran (9.48 g) in anhydrous dichloromethane (150 ml) was stirred at room temperature under an argon atmosphere for 16 h. The solution was then diluted with ether and worked up in the usual manner. The pyran (2) was obtained as an oil (11.0 g, 100%), b.p. 160–170 °C at 30 mmHg (lit.,<sup>7</sup> b.p. 100–102 °C at 20 mmHg).

**Hept-6-en-3-yn-1-ol (3).**—Ethylmagnesium bromide was

prepared under argon from magnesium (2.68 g), bromoethane (8.48 g), and anhydrous tetrahydrofuran (56 ml). The foregoing acetylene (2) (10.0 g) was added and the solution was stirred and heated at 60 °C (bath) for 45 min and then cooled to 20 °C. The solution was transferred under argon to another flask containing anhydrous copper(I) chloride (0.44 g) and the mixture was stirred for 15 min and then allyl bromide (7.84 g) was added dropwise and the mixture was stirred and heated for 45 min at 60 °C (bath). The cooled solution was poured into a solution of ammonium chloride (8.64 g) and sodium cyanide (1.08 g) in water (45 ml). The mixture was shaken vigorously and extracted with ether. The ethereal extract was washed with water and with saturated brine and the crude product was heated under argon at 55 °C (bath) in anhydrous methanol (320 ml) containing pyridinium toluene-*p*-sulphonate (1.56 g) for 18 h. The methanol was removed under reduced pressure and the residue was dissolved in ethyl acetate and washed with water and with saturated brine. The alcohol (3) (4.8 g, 67%) was obtained as an oil, b.p. 45 °C at 0.01 mmHg (Found: C, 76.15; H, 9.35. C<sub>7</sub>H<sub>10</sub>O requires C, 76.35; H, 9.15%; δ<sub>H</sub>(300 MHz) 2.48 (2 H, t, J<sub>2,1</sub> 6, J<sub>2,5</sub> 2 Hz, 2-CH<sub>2</sub>), 2.82 (1 H, s, D<sub>2</sub>O exchangeable, OH), 2.95 (2 H, m, 5-CH<sub>2</sub>), 3.69 (2 H, t, J<sub>1,2</sub> 6 Hz, 1-CH<sub>2</sub>), 5.10 (1 H, ddt, J<sub>7,6</sub> 10, J<sub>7,5</sub> 2, J<sub>7,7</sub> 2 Hz, 7-H), 5.30 (1 H, ddt, J<sub>7,6</sub> 17, J<sub>7,5</sub> 2, J<sub>7,7</sub> 2 Hz, 7-H), and 5.82 (1 H, ddt, J<sub>6,7</sub> 17, J<sub>6,7</sub> 10, J<sub>6,5</sub> 5 Hz, 6-H); δ<sub>C</sub>(75.5 MHz) 22.88 (C-2 and -5), 61.07 (C-1), 78.48 and 78.97 (C-3 and -4), 115.64 (C-7), and 132.80 (C-6); *m/z* 110 (M<sup>+</sup>, 6%), 109 (8), 95 (16), 91 (18), 80 (26), 79 (100), 78 (14), 77 (74), and 69 (23).

(*Z*)-Hepta-3,6-dien-1-ol (4).—The foregoing acetylene (3) (1.1 g) was stirred with palladized barium sulphate (5%; 55 mg) in anhydrous pyridine (30 ml) under an atmosphere of hydrogen for 2 h during which it absorbed the theoretical amount of hydrogen. The catalyst was separated by filtration through Celite and the filtrate was diluted with ethyl acetate. The solution was washed in turn with dilute hydrochloric acid, water, and finally saturated brine. The alcohol (4) was distilled under diminished pressure and was obtained as an oil (1.0 g, 89%), b.p. 60 °C at 0.5 mmHg (Found: C, 74.85; H, 10.75. C<sub>7</sub>H<sub>12</sub>O requires C, 74.95; H, 10.8%; δ<sub>H</sub>(300 MHz) 2.34 (2 H, dtd, J<sub>2,3</sub> 7, J<sub>2,1</sub> 6.5, J<sub>2,4</sub> 1 Hz, 2-CH<sub>2</sub>), 2.48–2.59 (1 H, br, D<sub>2</sub>O exchangeable, OH), 2.79–2.87 (2 H, m, 5-CH<sub>2</sub>), 3.64 (2 H, t, J<sub>1,2</sub> 6.6 Hz, 1-CH<sub>2</sub>), 4.99 (1 H, ddt, J<sub>7,6</sub> 10, J<sub>7,7</sub> 2, J<sub>7,5</sub> 1.5 Hz, 7-H), 5.05 (1 H, ddt, J<sub>7,6</sub> 17, J<sub>7,7</sub> 2, J<sub>7,5</sub> 1.5 Hz, 7-H), 5.48 (1 H, dtd, J<sub>3,4</sub> 10.5, J<sub>3,2</sub> 7, J<sub>3,5</sub> 1.5 Hz, 3-H), 5.59 (1 H, dtd, J<sub>4,3</sub> 10.5, J<sub>4,5</sub> 7, J<sub>4,2</sub> 1.5 Hz, 4-H), and 5.82 (1 H, ddt, J<sub>6,7</sub> 17, J<sub>6,7</sub> 10, J<sub>6,5</sub> 6 Hz, 6-H); δ<sub>C</sub>(75.5 MHz) 30.56 (C-2), 31.47 (C-5), 62.02 (C-1), 114.73 (C-7), 126.37 (C-4), 129.77 (C-3), and 136.65 (C-6); ν<sub>max</sub>(film) 3 350, 3 080, 3 020, 2 940, 1 638, 1 425, 1 047, 990, 910, and 720 cm<sup>-1</sup>.

(*Z*)-Hepta-3,6-dien-1-yl Toluene-*p*-sulphonate (5).—A solution of the foregoing alcohol (4) (1.1 g) in ethanol-free chloroform (25 ml) was stirred and cooled to 0 °C and anhydrous pyridine (1.6 ml) was added followed by toluene-*p*-sulphonyl chloride (2.8 g) in portions. The solution was stirred at 0 °C for 6 h and then diluted with ether (30 ml) and water (10 ml). The ethereal phase was separated and was washed successively with dilute hydrochloric acid, water, saturated aqueous sodium hydrogen carbonate, water, and finally saturated brine. The crude product was purified by radial chromatography with 2.5% ethyl acetate–light petroleum as eluant. The tosylate (5) (2.14 g, 82%) was obtained as a viscous oil (Found: C, 63.3; H, 6.75; S, 12.0. C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>S requires C, 63.15; H, 6.8; S, 12.05%; δ<sub>H</sub>(300 MHz) 2.40 (2 H, dt, J<sub>2,3</sub> 7, J<sub>2,1</sub> 7 Hz, 2-CH<sub>2</sub>), 2.44 (3 H, s, ArMe), 2.73 (2 H, m, 5-CH<sub>2</sub>), 4.01 (2 H, t, J<sub>1,2</sub> 7 Hz, 1-CH<sub>2</sub>), 4.95 (1 H, ddt, J<sub>7,6</sub> 10, J<sub>7,7</sub> 2, J<sub>7,5</sub> 1.5 Hz, 7-H), 4.99 (1 H, ddt, J<sub>7,6</sub> 17, J<sub>7,7</sub> 2, J<sub>7,5</sub> 1.5 Hz, 7-H), 5.32 (1 H, dtd, J<sub>3,4</sub> 10, J<sub>3,2</sub> 7, J<sub>3,5</sub> 1.5 Hz, 3-H), 5.52 (1 H, dtd, J<sub>4,3</sub> 10, J<sub>4,5</sub> 7, J<sub>4,2</sub> 1 Hz, 4-H), 5.75 (1 H, ddt, J<sub>6,7</sub> 10, J<sub>6,7</sub> 17, J<sub>6,5</sub> 7 Hz, 6-H),

and 7.35 and 7.79 (4 H, AA'BB', ArH); δ<sub>C</sub>(75.5 MHz) 21.63 (Me), 27.01 (C-2), 31.48 (C-5), 69.64 (C-1), 115.04 (C-7), 124.12 and 129.84 (each 2 × ArCH), 127.89 (C-4), 130.58 (C-3), 133.12 (ArC), 136.17 (C-6), and 144.78 (ArC).

(*Z*)-1-Iodohepta-3,6-diene (6).—The foregoing tosylate (5) (690 mg) and powdered sodium iodide (780 mg) were stirred together in anhydrous acetone (20 ml) at room temperature in the dark. After 24 h a further quantity of sodium iodide (390 mg) was added and the mixture was stirred for a further 24 h when it was poured into water and extracted with ether. The extract was washed with aqueous sodium pyrosulphite and with saturated brine. The iodo-compound (6) (575 mg, 100%) was obtained as an oil; *m/z* 222 (M<sup>+</sup>, 3%), 95 (100), and 67 (39).

(*Z*)-Hepta-3,6-dien-1-yltriphenylphosphonium Iodide (7).—This experiment was conducted in the dark and the work-up was conducted in subdued light. A solution of the iodo-compound (6) (540 mg) and triphenylphosphine (640 mg) in anhydrous acetonitrile (20 ml) was stirred and heated at 80 °C (bath) under nitrogen for 48 h. The solvent was removed under reduced pressure and the residue was washed by trituration and decantation with light petroleum and next crystallized from dichloromethane–tetrahydrofuran when the salt (7) was obtained as unstable hygroscopic plates (1.096 g, 93%, m.p. 145–147 °C; δ<sub>H</sub>(300 MHz) 2.46 (2 H, m, 2-CH<sub>2</sub>), 2.60 (2 H, m, 5-CH<sub>2</sub>), 3.68 (2 H, dt, J<sub>1,P</sub> 12, J<sub>1,2</sub> 7.5 Hz, 1-CH<sub>2</sub>), 4.89 (1 H, dtd, J<sub>7,6</sub> 17, J<sub>7,5</sub> 2, J<sub>7,7</sub> 1.7 Hz, 7-H), 4.92 (1 H, dtd, J<sub>7,6</sub> 10.5, J<sub>7,5</sub> 2, J<sub>7,7</sub> 1.7 Hz, 7-H), 5.46 (1 H, dt, J<sub>4,3</sub> 10, J<sub>4,5</sub> 7.5 Hz, 4-H), 5.70 (1 H, m, J<sub>6,7</sub> 17, J<sub>6,7</sub> 10.5 Hz, 6-H), 5.73 (1 H, m, J<sub>3,4</sub> 10.5, J<sub>3,2</sub> 6 Hz, 3-H), and 7.81 (15 H, m, Ph); δ<sub>C</sub>(75.5 MHz) 20.22 (C-2, J<sub>P,2</sub> 3.2 Hz), 23.21 (C-1, J<sub>P,1</sub> 48.8 Hz), 31.30 (C-5), 115.06 (C-7), 117.73 (Ph-1-C, J<sub>C,P</sub> 85.6 Hz), 127.45 (C-4), 129.17 (C-3), 130.67 (*m*-C, J<sub>m,P</sub> 12.2 Hz), 133.63 (*o*-C, J<sub>o,P</sub> 10.5 Hz), 135.34 (*p*-C, J<sub>p,P</sub> 2.6 Hz), and 135.86 (C-6).

Methyl 8-(3,5-Dimethoxyphenyl)octanoate (10).—A solution of butyl-lithium in hexane (1.55M; 19.35 ml) was added slowly to a stirred solution of the phosphonium salt (8)<sup>8</sup> (14.79 g) in anhydrous tetrahydrofuran (180 ml) under an argon atmosphere at room temperature. The solution was then stirred for 15 min and a solution of ethyl 7-oxoheptanoate<sup>9</sup> (3.40 g) in anhydrous tetrahydrofuran (30 ml) was added and the solution was stirred under argon for 18 h. The solution was poured into ice-water and the crude product was isolated by extraction with ethyl acetate and then boiled under reflux in methanol (100 ml) and water (100 ml) with sodium hydroxide (20.0 g) for 5 h. The cooled solution was extracted with ether (2 ×) and these extracts were discarded. The aqueous phase was acidified and the crude acids were isolated by extraction with ethyl acetate. The crude acids in ethyl acetate (150 ml) were stirred under a hydrogen atmosphere with palladized charcoal (10%; 300 mg) until absorption ceased. The usual work up gave the acid (9) (5.46 g, 99%) which crystallized from dichloromethane–light petroleum as plates, m.p. 60–62 °C (Found: C, 68.3; H, 8.9%; M<sup>+</sup>, 280. C<sub>16</sub>H<sub>24</sub>O<sub>4</sub> requires C, 68.55; H, 8.65%; M, 280). This acid (9) (4.3 g) and anhydrous methanol (160 ml) were boiled under reflux with concentrated sulphuric acid (3.5 ml) for 16 h. The usual work up gave the ester (10) (4.15 g, 92%) as an oil, b.p. 200 °C at 0.01 mmHg (Found: C, 69.4; H, 8.95%; M<sup>+</sup>, 294. C<sub>17</sub>H<sub>26</sub>O<sub>4</sub> requires C, 69.35; H, 8.9%; M, 294); δ<sub>H</sub>(80 MHz) 1.16–1.81 (10 H, br, 5 × CH<sub>2</sub>), 2.30 (2 H, t, CH<sub>2</sub>CO), 2.54 (2 H, t, CH<sub>2</sub>Ar), 3.66 (3 H, s, CO<sub>2</sub>Me), 3.78 (6 H, s, 2 × OMe), and 6.33 (3 H, br, ArH).

8-(3,5-Dimethoxyphenyl)octan-1-ol (11).—A solution of the methyl ester (10) (1.60 g) in anhydrous ether (20 ml) was added dropwise to a stirred solution of lithium aluminium hydride

(207 mg) in ether (30 ml). The solution was stirred at room temperature for 3 h and then cooled to 0 °C and treated with an excess of saturated aqueous sodium sulphate. The usual work up gave the alcohol (11) (1.45 g, 100%) as a viscous oil, b.p. 230 °C at 0.01 mmHg (Found: C, 72.2; H, 9.7%;  $M^+$ , 266.  $C_{16}H_{26}O_3$  requires C, 72.15; H, 9.85%;  $M$ , 266);  $\delta_H$ (80 MHz) 1.20–1.84 (12 H, br, 6  $\times$   $CH_2$ ), 1.50 (1 H, s,  $D_2O$  exchangeable, OH), 2.55 (2 H, t,  $CH_2Ar$ ), 3.64 (2 H, t,  $CH_2OH$ ), 3.78 (6 H, s, 2  $\times$  OMe), and 6.33 (3 H, br, ArH).

**Benzyl 8-(3,5-Dimethoxyphenyl)octyl Carbonate (12).**—A solution of the alcohol (11) (600 mg) in anhydrous pyridine (10 ml) was stirred at 0 °C and treated dropwise with a solution of benzyl chloroformate (1.75 g) in toluene (37.5 ml). The solution was then stirred and heated at 60 °C (bath) for 3 h and then allowed to cool and diluted with ether. The solution was washed in turn with dilute hydrochloric acid, water, saturated aqueous sodium hydrogen carbonate, water, and finally saturated brine. The crude product was purified by radial chromatography with 5% ethyl acetate–light petroleum as eluant. The carbonate (12) (902 mg, 100%) was obtained as a pale yellow oil (Found: C, 71.65; H, 8.1%;  $M^+$ , 400.  $C_{24}H_{32}O_5$  requires C, 71.95; H, 8.05%;  $M$ , 400);  $\delta_H$ (80 MHz) 1.13–1.88 (12 H, br, 6  $\times$   $CH_2$ ), 2.54 (2 H, t,  $CH_2Ar$ ), 3.77 (6 H, s, 2  $\times$  OMe), 4.14 (2 H, t,  $CH_2OCO$ ), 5.15 (2 H, s,  $CH_2Ph$ ), 6.32 (3 H, br, ArH), and 7.36 (5 H, s, Ph).

**Benzyl 8-(5-Methoxy-3,6-dioxocyclohexa-1,4-dienyl)octyl Carbonate (13).**—A solution of chromium trioxide (400 mg) in water (1.0 ml) and acetic acid (5.0 ml) was added dropwise at 0 °C to a stirred solution of the carbonate (12) (400 mg) in acetic acid (6.0 ml). The solution was stirred at 0 °C for 0.5 h and then at room temperature for 1 h and poured into ice and water. The crude product was isolated by extraction with ethyl acetate in the usual way and was purified by radial chromatography with 10–20% ethyl acetate–light petroleum as eluant. The quinone (13) (360 mg, 90%) crystallized from dichloromethane–light petroleum as yellow needles, m.p. 40–41 °C (Found: C, 69.15; H, 7.35.  $C_{23}H_{28}O_6$  requires C, 69.0; H, 7.05%);  $\delta_H$ (300 MHz) 1.20–1.71 (12 H, m, 6  $\times$   $CH_2$ ), 2.42 (2 H, dt,  $J_{8,3}$  1.45 Hz, 8- $CH_2$ ), 3.81 (3 H, s, OMe), 4.14 (2 H, t,  $CH_2OCO$ ), 5.15 (2 H, s,  $CH_2Ph$ ), 5.87 (1 H, d,  $J_{5,3}$  2.32 Hz, 5-H), 6.48 (1 H, dt,  $J_{3,5}$  2.32,  $J_{3,8}$  1.45 Hz, 3-H), and 7.33–7.40 (5 H, m, Ph);  $\delta_C$ (75.5 Hz) 25.64, 27.68, 28.61, 28.69, 29.02, and 29.12 (each  $CH_2$ ), 56.27 (OMe), 68.25 and 69.47 ( $CH_2OCO$  and  $CH_2Ph$ ), 107.10 (quinone C-4), 128.33, 128.50, and 128.57 (each phenyl CH), 132.90 (quinone C-2), 135.32 (phenyl C-1), 147.48 (quinone C-1 or C-5), 155.24 and 158.84 (OCOO and quinone C-5 or C-1), and 182.11 and 187.67 (each CO);  $m/z$  (CI;  $CH_4$ ) 403 (28%,  $M^+$  + 3), 402 (34), and 401 (43).

**Benzyl 8-(2,3,6-Triacetoxo-5-methoxyphenyl)octyl Carbonate (14).**—A solution of the quinone (13) (110 mg) in acetic anhydride (2.0 ml) was stirred at room temperature for 12 h in the presence of concentrated sulphuric acid (2 drops). The solution was poured on ice and the crude product was isolated by extraction with ether. The usual work-up gave a crude product which was purified by radial chromatography with 30% ethyl acetate–light petroleum as eluant. The starting quinone (13) (29 mg) was isolated from a band of higher  $R_F$  and this was followed by the triacetate (14) (100.5 mg, 91%) which was obtained as an oil (Found: C, 63.7; H, 6.8.  $C_{29}H_{36}O_{10}$  requires C, 63.95; H, 6.65%);  $\delta_H$ (300 MHz) 1.26–1.71 (12 H, m, 6  $\times$   $CH_2$ ), 2.27, 2.30, and 2.32 (each 3 H, s, OAc), 2.42 (2 H, t,  $CH_2Ar$ ), 3.79 (3 H, s, OMe), 4.15 (2 H, t,  $CH_2OCO$ ), 5.16 (2 H, s,  $CH_2Ph$ ), 6.71 (1 H, s, ArH), and 7.32–7.41 (5 H, m, Ph);  $m/z$  544 ( $M^+$ , 0.5%), 502 (4), 460 (7), 418 (12), 368 (20), and 326 (100).

**8-(2,3,6-Triacetoxo-5-methoxyphenyl)octan-1-ol (15).**—A

solution of the carbonate (14) (84 mg) in ethyl acetate (50 ml) was stirred under an atmosphere of hydrogen with palladized charcoal (10%; 40 mg) until absorption ceased. The usual work up gave the octanol (15) (49 mg, 77%) as an oil (Found: C, 61.45; H, 7.45.  $C_{21}H_{30}O_8$  requires C, 61.45; H, 7.35%);  $\delta_H$ (300 MHz) 1.20–1.60 (12 H, m, 6  $\times$   $CH_2$ ), 2.05 (1 H, br,  $D_2O$  exchangeable, OH), 2.26, 2.29, and 2.31 (each 3 H, s, OAc), 2.41 (2 H, t,  $CH_2Ar$ ), 3.60 (2 H, t,  $CH_2OH$ ), 3.78 (3 H, s, OMe), and 6.70 (1 H, s, ArH);  $\delta_C$ (75.5 MHz) 20.18, 20.33, and 20.63 (each  $MeCO$ ), 25.20, 25.52, 28.80, 29.05, 29.35, and 32.58 (each  $CH_2$ ), 56.13 (OMe), 62.76 ( $CH_2OH$ ), 104.74 (ArCH), 130.00, 133.73, 135.82, 140.10, and 149.06 (each ArC), and 168.11, 168.28, and 168.37 (each  $MeCO$ );  $m/z$  410 ( $M^+$ , 2%), 368 (9), 327 (18), 326 (98), 285 (18), and 284 (100).

**8-(2,3,6-Triacetoxo-5-methoxyphenyl)octanal (16).**—A solution of the octanol (15) (170 mg) in dichloromethane (6.0 ml) was added to a stirred suspension of pyridinium chlorochromate (134 mg) and anhydrous sodium acetate (51 mg) in dichloromethane (8.0 ml) at 0 °C. The mixture was then stirred at room temperature for 3 h, diluted with ether (50 ml), and passed through a column of silica gel (10 g) with ether as eluant. The eluate was washed in turn with saturated aqueous sodium hydrogen carbonate, water, and finally saturated brine. Removal of the solvent left the aldehyde (16) (169 mg, 100%) which was used immediately;  $\delta_H$ (80 MHz) 1.09–1.88 (10 H, m, 5  $\times$   $CH_2$ ), 2.26, 2.29, and 2.31 (each 3 H, s, OAc), 2.42 (4 H, m,  $CH_2Ar$  and  $CH_2CHO$ ), 3.78 (3 H, s, OMe), 6.71 (1 H, s, ArH), and 9.76 (1 H, t,  $J$  1.8 Hz, CHO);  $m/z$  408 ( $M^+$ , 0.7%), 366 (5), 324 (15), 283 (15), and 282 (100).

**1,2,4-Triacetoxo-5-methoxy-3(8'Z,11'Z)-pentadeca-8',11',14'-triethylbenzene (17).**—Butyl-lithium (0.85M) in hexane (1.145 ml) was added at –78 °C under argon to a stirred solution of the phosphonium salt (7) (475 mg) in anhydrous tetrahydrofuran (12.5 ml). After 0.5 h at –78 °C hexamethylphosphoric triamide (3.0 ml) was added followed by a solution of the aldehyde (16) (100 mg) in anhydrous tetrahydrofuran (3 ml). The solution was stirred at –78 °C for 2 h and then poured into water. The crude product was isolated by extraction with ethyl acetate and purified by radial chromatography with 30% ethyl acetate–light petroleum as eluant. The triene (17) (42 mg, 56%) was isolated as an oil (Found: C, 69.15; H, 7.25.  $C_{28}H_{38}O_7$  requires C, 69.1; H, 7.85%);  $\delta_H$ (300 MHz) 1.20–1.49 (10 H, m, 5  $\times$   $CH_2$ ), 2.04 (2 H, dt,  $J_{7,8}$  6.5,  $J_{7,6}$  6.9 Hz, 7'- $CH_2$ ), 2.26, 2.29, and 2.31 (each 3 H, s,  $CH_3CO$ ), 2.41 (2 H, t,  $J_{1',2'}$  7.5 Hz, 1'- $CH_2$ ), 2.78 (2 H, m, 10'- $CH_2$ ), 2.83 (2 H, m, 13'- $CH_2$ ), 3.78 (3 H, s, OMe), 4.98 (1 H, ddt,  $J_{15',14'}$  10,  $J_{15',15'}$  2,  $J_{15',13'}$  1.5 Hz, 15'-H), 5.05 (1 H, ddt,  $J_{15',14'}$  17,  $J_{15',15'}$  2,  $J_{15',13'}$  1.5 Hz, 15'-H), 5.28–5.49 (4 H, m, 8', 9', 11', and 12'-H), 5.82 (1 H, ddt,  $J_{14',15'}$  17,  $J_{14',15'}$  10,  $J_{14',13'}$  6 Hz, 14'-H), and 6.70 (1 H, s, 6-H); irradiation at the frequency of the 10'- and 13'- $CH_2$  showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9',8'}$  10.5,  $J_{9',7'}$  1 Hz, the 8'-H ( $\delta$  5.39) as a dt with  $J_{8',9'}$  10.5,  $J_{8',7'}$  6.5 Hz, and the 11'- and 12'-H as an AB system ( $\delta$  5.42 and 5.43) with  $J_{11',12'}$  10.5 Hz; irradiation at the frequency of the 7'- $CH_2$  showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9',8'}$  10.5,  $J_{9',10'}$  6.5 Hz and the 8'-H ( $\delta$  5.39) as a dt with  $J_{8',9'}$  10.5,  $J_{8',10'}$  1 Hz;  $\delta_C$ (75.5 Hz) 20.25, 20.40, and 20.72 (each  $MeCO$ ), 25.32 (C-1'), 25.52 (C-10'), 27.20 (C-7'), 28.94, 29.13, and 29.61 (each  $CH_2$ ), 31.47 (C-13'), 56.20 (OMe), 104.79 (C-6), 114.67 (C-15'), 126.60, 127.59, and 129.23 (C-9', -11', and -12'), 130.12 (C-8'), 133.92 and 135.90 (each ArC), 136.79 (C-14'), 140.19, and 149.15 (each ArC), and 168.11, 168.27, and 168.35 (each CO);  $\nu_{max}$ (film) 3 010m, 2 930s, 2 858m, 1 770s, 1 621m, 1 600m, 1 485s, 1 449m, 1 370s, 1 351m, 1 190s, 1 118m, 1 058m, 1 018m, 932w, 882m, 850w, 788w, and 722w  $cm^{-1}$ . From a band of lower  $R_F$  the aldehyde (16) (37 mg) was isolated.

**5-Methoxy-3-(8'Z,11'Z)-pentadeca-8',11',14'-trienylbenzene-1,2,4-triol (18).**—The solvents used for this experiment were boiled and allowed to cool under argon before use. A solution of the triacetate (17) (30 mg) in anhydrous tetrahydrofuran (3 ml) was added to a stirred solution of lithium aluminium hydride (10 mg) in tetrahydrofuran (3 ml) and the solution was stirred under argon for 15 min. Dilute hydrochloric acid (10%; 2 ml) was then added and the product (18) was isolated by extraction with ether when it was obtained as an oil (22.2 mg, 100%);  $\delta_{\text{H}}$ (300 MHz) 1.20–1.43 (8 H, br, 4 × CH<sub>2</sub>), 1.50–1.62 (2 H, m, 2'-CH<sub>2</sub>), 2.04 (2 H, dt,  $J_{7,8}$ , 6.5,  $J_{7,6}$ , 6 Hz, 7'-CH<sub>2</sub>), 2.65 (2 H, t,  $J_{1,2}$ , 7.5 Hz, 1'-CH<sub>2</sub>), 2.78 (2 H, m, 10'-CH<sub>2</sub>), 2.83 (2 H, m, 13'-CH<sub>2</sub>), 3.78 (3 H, s, OMe), 4.70–4.90 (1 H, br, D<sub>2</sub>O exchangeable, OH), 4.98 (1 H, ddt,  $J_{15,14}$ , 10,  $J_{15,15}$ , 2,  $J_{15,13}$ , 1.5 Hz, 15'-H), 5.05 (1 H, ddt,  $J_{15,14}$ , 17,  $J_{15,15}$ , 2,  $J_{15,13}$ , 1.5 Hz, 15'-H), 5.27–5.49 (6 H, m, 8', 9', 11', 12'-H, and 2 × OH, D<sub>2</sub>O exchangeable), 5.80 (1 H, ddt,  $J_{14,15}$ , 10,  $J_{14,15}$ , 17,  $J_{14,13}$ , 6 Hz, 14'-H), and 6.39 (1 H, s, 6-H); irradiation at the frequency of the 10'- and 13'-CH<sub>2</sub> showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9,8}$ , 10.5,  $J_{9,7}$ , 1 Hz, the 8'-H ( $\delta$  5.39) as a dt with  $J_{8,9}$ , 10,  $J_{8,7}$ , 6.5 Hz, and the 11'- and 12'-H as an AB system ( $\delta$  5.41 and 5.44) with  $J_{11,12}$ , 10.5 Hz; irradiation at the frequency of the 7'-CH<sub>2</sub> showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9,8}$ , 10.5,  $J_{9,10}$ , 6.5 Hz, and the 8'-H ( $\delta$  5.39) as a dt with  $J_{8,9}$ , 10.5,  $J_{8,10}$ , 1 Hz;  $\delta_{\text{C}}$ (75.5 MHz) 23.83 (C-1'), 25.56 (C-10'), 27.22 (C-7'), 29.06, 29.25, 29.44, 29.63, and 29.66 (each CH<sub>2</sub>), 31.51 (C-13'), 56.56 (OMe), 97.95 (C-6), 114.67 (C-15'), 116.69 (ArC), 126.78, 127.51, and 129.31 (C-9', -11', and -12'), 130.46 (C-8'), 135.82 and 135.99 (each ArC), 136.83 (C-14'), and 137.70 and 139.88 (each ArC);  $m/z$  360 (1.5%, M<sup>+</sup>).

**2-Hydroxy-5-methoxy-3-(8'Z,11'Z)-pentadeca-8',11',14'-trienyl-1,4-benzoquinone (19).**—A solution of the triol (18) (22.2 mg) in benzene (15 ml) was shaken with aqueous iron(III) chloride (1%; 30 ml) for 15 min and ether (20 ml) was then added. The usual work-up gave the quinone (19) (22 mg, 100%) which was crystallized from pentane and formed yellow needles, m.p. 37–39 °C (Found: C, 73.55; H, 8.6. C<sub>22</sub>H<sub>30</sub>O<sub>4</sub> requires C, 73.7; H, 8.45%);  $\delta_{\text{H}}$ (300 MHz) 1.20–1.50 (10 H, m, 5 × CH<sub>2</sub>), 2.04 (2 H, dt,  $J_{7,8}$  =  $J_{7,6}$  = 6.5 Hz, 7'-CH<sub>2</sub>), 2.44 (2 H, t,  $J_{1,2}$ , 7.5 Hz, 1'-CH<sub>2</sub>), 2.78 (2 H, m, 10'-CH<sub>2</sub>), 2.83 (2 H, m, 13'-CH<sub>2</sub>), 3.86 (3 H, s, OMe), 4.97 (1 H, ddt,  $J_{15,14}$ , 10,  $J_{15,15}$ , 2,  $J_{15,13}$ , 1.5 Hz, 15'-H), 5.05 (1 H, ddt,  $J_{15,14}$ , 17,  $J_{15,15}$ , 2,  $J_{15,13}$ , 1.5 Hz, 15'-H), 5.38–5.49 (4 H, m, 8', 9', 11', and 12'-H), 5.82 (1 H, ddt,  $J_{14,15}$ , 17,  $J_{14,15}$ , 10,  $J_{14,13}$ , 6 Hz, 14'-H), 5.84 (1 H, s, 6-H), and 7.25 (1 H, s, D<sub>2</sub>O exchangeable OH); irradiation at the frequency of the 10'- and 13'-CH<sub>2</sub> showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9,8}$ , 10.5,  $J_{9,7}$ , 1 Hz, the 8'-H ( $\delta$  5.39) as a dt with  $J_{8,9}$ , 10.5,  $J_{8,7}$ , 6.5 Hz, and the 11'- and 12'-H as an AB system ( $\delta$  5.42 and 5.44) with  $J_{11,12}$ , 10.5 Hz; irradiation at the frequency of the 7'-CH<sub>2</sub> showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9,8}$ , 10.5,  $J_{9,10}$ , 6.5 Hz, and the 8'-H ( $\delta$  5.39) as a dt with  $J_{8,9}$ , 10.5,  $J_{8,10}$ , 1 Hz;  $\delta_{\text{C}}$ (75.5 MHz) 22.59 (C-1'), 25.54 (C-10'), 27.20 (C-7'), 27.99, 29.17, 29.26, 29.49, and 29.59 (each CH<sub>2</sub>), 31.50 (C-13'), 56.74 (OMe), 102.15 (C-6), 114.67 (C-15'), 119.20 (C-3), 126.78, 127.53, and 129.30 (C-9', -11', and -12'), 130.40 (C-8'), 136.83 (C-14'), 151.51 and 161.10 (C-2 and -5), and 181.68 and 182.79 (each CO);  $m/z$  360 (1%), 358 (M<sup>+</sup>, 2), 193 (13), 189 (19), 182 (10), 170 (14), 169 (100), 168 (89), 167 (21), 153 (25), 149 (15), 147 (15), 139 (23), 133 (22), 121 (13), 119 (14), 107 (19), and 105 (16);  $\nu_{\text{max}}$ (KBr) 3 350s, 3 015w, 2 920s, 2 855m, 1 725w, 1 640s, 1 607s, 1 458m, 1 438m, 1 382m, 1 355m, 1 315m, 1 205s, 1 110w, 1 040m, 990m, 838m, 792w, and 718w cm<sup>-1</sup>;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>) 282, 288, and 410 nm (log  $\epsilon$  4.10, 4.10, and 2.49 respectively).

**2,2-Dimethyl-4-(8'Z,11'Z)-pentadeca-8',11',14'-trienyl-1,3-benzodioxole (21).**—A stirred solution of the phosphonium salt (7) (625 mg) in anhydrous tetrahydrofuran (10 ml) was cooled

to -78 °C under argon, butyl-lithium (1.95M) in hexane (0.38 ml) was added, and the solution was stirred at -78 °C for 0.5 h. Hexamethylphosphoric triamide (3.2 ml) was added followed by a solution of the aldehyde (20)<sup>12</sup> (140 mg) in anhydrous tetrahydrofuran (2 ml). The solution was then stirred at -78 °C for 2 h and allowed to warm to 0 °C during 1 h. The solution was poured into water and the crude product was isolated by extraction with ethyl acetate and purified by radial chromatography with 0–5% ethyl acetate–light petroleum as eluant. The triene (21) (98 mg, 75%) was obtained as an oil (Found: C, 81.05; H, 9.3. C<sub>24</sub>H<sub>34</sub>O<sub>2</sub> requires C, 81.3; H, 9.65%);  $\delta_{\text{H}}$ (300 MHz) 1.20–1.43 (8 H, br, 4 × CH<sub>2</sub>), 1.54–1.65 (2 H, br, 2'-CH<sub>2</sub>), 1.66 (6 H, s, Me<sub>2</sub>), 2.04 (2 H, dt,  $J_{7,6}$ , 6.9,  $J_{7,8}$ , 6.5 Hz, 7'-CH<sub>2</sub>), 2.53 (2 H, t,  $J_{1,2}$ , 7.5 Hz, 1'-CH<sub>2</sub>), 2.79 (2 H, m, 10'-CH<sub>2</sub>), 2.83 (2 H, m, 13'-CH<sub>2</sub>), 4.98 (1 H, ddt,  $J_{15,14}$ , 10,  $J_{15,15}$ , 2,  $J_{15,13}$ , 1.5 Hz, 15'-H), 5.05 (1 H, ddt,  $J_{15,14}$ , 17,  $J_{15,15}$ , 2,  $J_{15,13}$ , 1.5 Hz, 15'-H), 5.28–5.49 (4 H, m, 8', 9', 11', and 12'-H), 5.82 (1 H, ddt,  $J_{14,15}$ , 17,  $J_{14,15}$ , 10,  $J_{14,13}$ , 6 Hz, 14'-H), 6.59 (1 H, dd,  $J_{5,6}$ , 7.5,  $J_{5,7}$ , 1.5 Hz, 5-H), 6.62 (1 H, dd,  $J_{7,6}$ , 7.5,  $J_{7,5}$ , 1.5 Hz, 7-H), and 6.71 (1 H, dd,  $J_{6,5}$ ,  $J_{6,7}$ , 7.5 Hz, 6-H); irradiation at the frequency of the 10'- and 13'-CH<sub>2</sub> showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9,8}$ , 10.5,  $J_{9,7}$ , 1 Hz, the 8'-H ( $\delta$  5.39) as a dt with  $J_{8,9}$ , 10.5,  $J_{8,7}$ , 6.5 Hz, and the 11'- and 12'-H as an AB system ( $\delta$  5.42 and 5.44) with  $J_{11,12}$ , 10.5 Hz; irradiation at the frequency of the 7'-CH<sub>2</sub> showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9,8}$ , 10.5,  $J_{9,10}$ , 6.5 Hz, and the 8'-H ( $\delta$  5.39) as a dt with  $J_{8,9}$ , 10.5,  $J_{8,10}$ , 1.5 Hz;  $\delta_{\text{C}}$ (75.5 MHz) 25.52 (C-10'), 25.66 (Me<sub>2</sub>), 27.20 (C-7'), 29.22, 29.30, 29.36, and 29.61 (each CH<sub>2</sub>), 31.49 (C-13'), 105.97 (C-7), 114.67 (C-15'), 116.69 (C-2), 120.57 (C-5), 121.81 (C-6), 123.98 (C-4), 126.78, 127.53, and 129.27 (C-9', -11', and -12'), 130.40 (C-8'), 136.79 (C-14'), 145.30 (C-8), and 146.70 (C-9);  $m/z$  355 (17%), 354 (M<sup>+</sup>, 57), 339 (13), 203 (15), 164 (37), 163 (100), 161 (28), 149 (34), 148 (15), 147 (35), 145 (15), 135 (15), 133 (26), 124 (12), 123 (87), 121 (24), 119 (17), 108 (12), 107 (54), 106 (16), and 105 (28);  $\nu_{\text{max}}$ (film) 3 060w, 3 020m, 2 930s, 2 860m, 1 640m, 1 600w, 1 482m, 1 462s, 1 385m, 1 378m, 1 225s, 1 220m, 1 662w, 1 112m, 1 040w, 990m, 910m, 854w, 838m, 792m, 762w, and 721m cm<sup>-1</sup>.

**3-(8'Z,11'Z)-Pentadeca-8',11',14'-trienylbenzene-1,2-diol (22).**—Acetic acid (8 ml) and water (2 ml) were boiled under argon for 30 min; to the cooled solution was added the triene (21) (70 mg) and the solution was heated under argon at 100 °C (bath) for 18 h. The cooled solution was poured into a mixture of ice and saturated aqueous sodium hydrogen carbonate and the crude product was isolated by extraction with ethyl acetate and purified by radial chromatography with 10% ethyl acetate–light petroleum as eluant. The first band contained the starting material (24 mg) and this was followed by the trienylcatechol (22) (40.8 mg, 100%) which was obtained as an oil (Found: C, 79.85; H, 9.0. C<sub>21</sub>H<sub>30</sub>O<sub>2</sub> requires C, 80.2; H, 9.6%);  $\delta_{\text{H}}$ (300 MHz) 1.22–1.44 (8 H, br, 4 × CH<sub>2</sub>), 1.53–1.67 (2 H, m, 2'-CH<sub>2</sub>), 2.04 (2 H, dt,  $J_{7,6}$ , 6.9,  $J_{7,8}$ , 6.5 Hz, 7'-CH<sub>2</sub>), 2.60 (2 H, t,  $J_{1,2}$ , 7.5 Hz, 1'-CH<sub>2</sub>), 2.79 (2 H, m, 10'-CH<sub>2</sub>), 2.83 (2 H, m, 13'-CH<sub>2</sub>), 4.99 (1 H, ddt,  $J_{15,14}$ , 10,  $J_{15,15}$ , 2,  $J_{15,13}$ , 1.5 Hz, 15'-H), 5.05 (1 H, ddt,  $J_{15,14}$ , 17,  $J_{15,15}$ , 2,  $J_{15,13}$ , 1.5 Hz, 15'-H), 5.17–5.28 (2 H, br, D<sub>2</sub>O exchangeable, OH), 5.28–5.49 (4 H, m, 8', 9', 11', and 12'-H), 5.82 (1 H, ddt,  $J_{14,15}$ , 17,  $J_{14,15}$ , 10,  $J_{14,13}$ , 6 Hz, 14'-H), and 6.71 (3 H, m, ArH); irradiation at the frequency of the 10'- and 13'-CH<sub>2</sub> showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9,8}$ , 10.5,  $J_{9,7}$ , 1 Hz, the 8'-H ( $\delta$  5.39) as a dt with  $J_{8,9}$ , 10.5,  $J_{8,7}$ , 6.5 Hz, and the 11'- and 12'-H as an AB system ( $\delta$  5.42 and 5.44) with  $J_{11,12}$ , 10.5 Hz; irradiation at the frequency of the 7'-CH<sub>2</sub> showed the 9'-H ( $\delta$  5.33) as a dt with  $J_{9,8}$ , 10.5,  $J_{9,10}$ , 6.5 Hz, and the 8'-H ( $\delta$  5.39) as a dt with  $J_{8,9}$ , 10.5,  $J_{8,10}$ , 1 Hz;  $\delta_{\text{C}}$ (75.5 MHz) 25.58 (C-10'), 27.23 (C-7'), 29.24, 29.41, 29.50, and 29.62 (each CH<sub>2</sub>), 29.76; (2 × CH<sub>2</sub>), 31.52 (C-13'), 112.66 (C-6), 114.72 (C-15'), 120.10 (C-5), 122.10 (C-4), 126.63, 127.58, and

129.32 (C-9', -11', and -12'), 129.36 (C-3), 130.43 (C-8'), 136.66 (C-14'), 141.70 (C-1), and 143.01 (C-2);  $m/z$  314 ( $M^+$ , 1.4%), 163 (10), 149 (10), 136 (19), 124 (22), 123 (100), and 107 (12);  $\nu_{\max}$ (film) 3 480s, 3 080w, 3 060w, 3 020m, 2 930s, 2 860s, 1 640m, 1 622m, 1 598m, 1 476s, 1 350m, 1 279s, 1 236m, 1 185m, 1 158m, 1 095w, 1 060w, 990m, 965w, 910m, 830w, 775m, and 730s  $\text{cm}^{-1}$ .

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