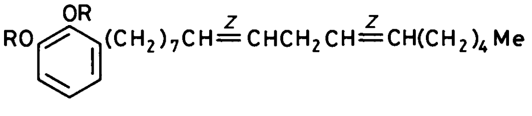
The Synthesis and Identification of Alkenyl and Alkadienyl Catechols of Burmese Lac

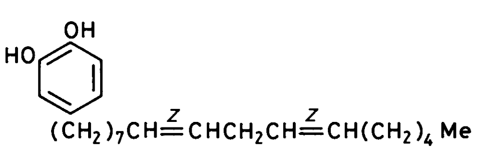
Melvyn V. Sargent* and Sirichai Wangchareontrakul
Department of Organic Chemistry, The University of Western Australia, Nedlands, Western Australia, 6009
and (in part) Alan Jefferson
School of Applied Chemistry, Curtin University of Technology, Bentley, Western Australia 6012

The presence of (*Z*)-(**4**), (*E*)-3-(heptadec-8′-enyl)-(**5**), (*Z*)-4-(heptadec-8′-enyl)-benzene-1,2-diol (**47**), (*Z,Z*)-3-(heptadeca-8′,11′-dienyl)-(**1**), and (*Z,Z*)-4-(heptadeca-8′,11′-dienyl)-benzene-1,2-diol (**3**) in Burmese lac, the sap of *Melanorrhoea usitata*, has been confirmed by the synthesis of these compounds, and of their methyl ethers, and a comparison of the gas chromatographic retention times of their bis-*o*-(trimethylsilyl) ethers with the derivatives of the natural products.

In previous papers we have shown that Burmese lac, the sap of the tree *Melanorrhoea usitata*, contains the dienes (*Z,Z*)-3- (**1**) (48%) and (*Z,Z*)-4-(heptadeca-8′,11′-dienyl)benzene-1,2-diol (**3**) (26%), the alkenes 3-pentadecenylbenzene-1,2-diol (0.4%), and 3-heptadecenylbenzene-1,2-diol (9%), as well as a series of ω-phenylalkylcatechols.[1,2] The positions of the double bonds in the alkenylcatechols were not determined and we now report details of the position and stereochemistry of the double bonds of the major alkenylcatechols of Burmese lac, the synthesis of these compounds and of the alkadienylcatechols (**1**) and (**3**).

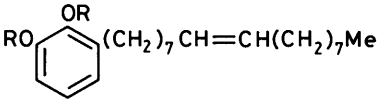


(**1**) R = H
(**2**) R = Me

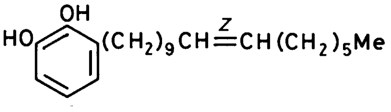


(**3**)

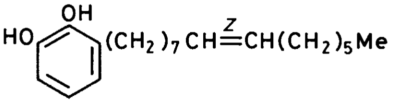
Our findings on the proportions of the constituents of Burmese lac differ from those of Du *et al.*,[3] and we have discussed this previously.[2] These authors also isolated the dienes (**1**) (12.0%) and (**3**) (12.4%) from Burmese lac, and have claimed that the alkenylcatechols present are a 3- and a 4-pentadecenylbenzene-1,2-diol, (*Z*)-3-(heptadec-8′-enyl)-(**4**) and (*Z*)-3-(heptadec-10′-enyl)-benzene-1,2-diols (**8**), and an (*E*)-3-(heptadec-10′-enyl)benzene-1,2-diol. Other species of the family Anacardiaceae are known to contain similar compounds, in particular the Japanese lac tree, *Rhus verniciflua*.[4] ElSohly *et al.*,[5] have isolated from North American poison oak (*Toxicodendron diversilobum*), (*Z*)-3-(heptadec-8′-enyl)-benzene-1,2-diol (**4**) and the diene (**1**) whilst the lower homologues (*Z*)-3-(pentadec-8′-enyl)benzene-1,2-diol (**9**) and (*Z,Z*)-3-(pentadeca-8′,11′-dienyl)benzene-1,2-diol were isolated from poison ivy (*Toxicodendron radicans*). Recently the diene (**1**) has been identified as the major vesicant principle of the African Anacardaceous species, *Smodingium argutum*.[6]



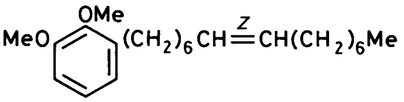
Z - (**4**) R = H
E - (**5**) R = H
Z - (**6**) R = Me
E - (**7**) R = Me



(**8**)



(**9**)

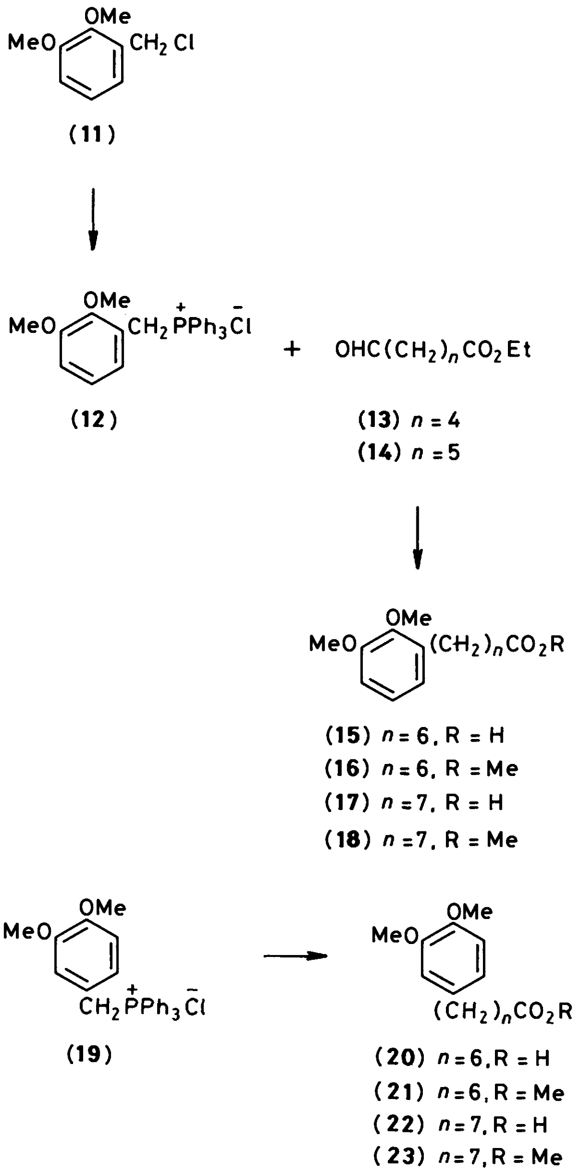


(**10**)

Synthetic work in the area of alkenyl- and alkadienylcatechols has been meagre probably on account of the propensity of these compounds to rapid aerial oxidation and polymerization. Tyman and Khor[7] have reported the synthesis of (*Z*)-3-(pentadec-8′-enyl)benzene-1,2-diol but full experimental details are still awaited. Locksley and his co-workers[8] have also reported a synthesis of this compound but these authors do not comment on its stereochemical homogeneity.

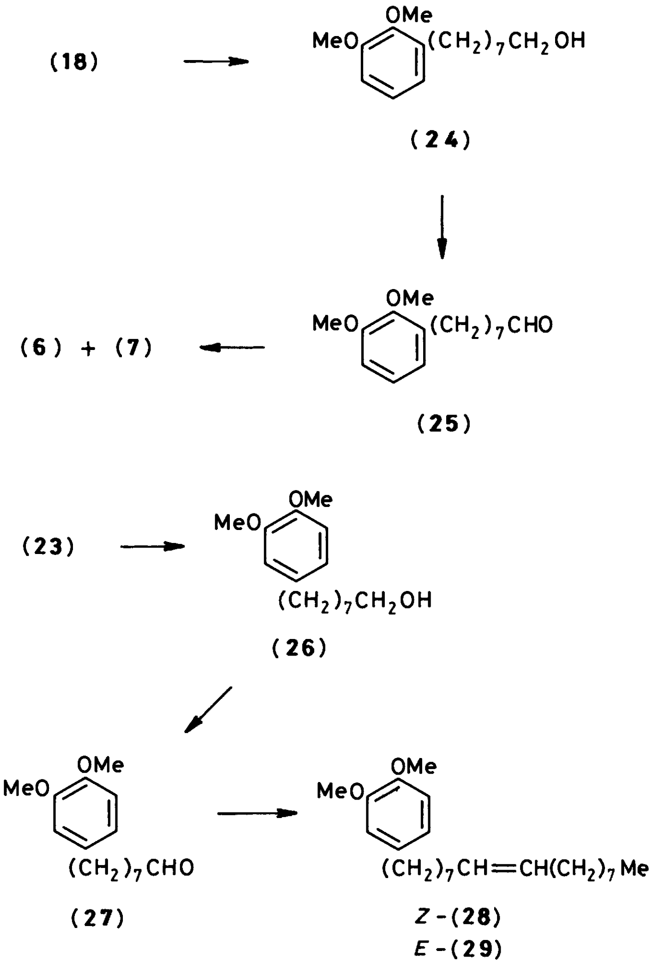
A sample of Burmese lac was subjected to *O*-methylation and repeated chromatography allowed the isolation of pure (*Z,Z*)-3-(heptadeca-8′-11′-dienyl)-1,2-dimethoxybenzene (**2**) which was identified by its spectroscopic properties.[6] In particular the ^{13}C n.m.r spectrum demonstrated its stereochemical homogeneity exhibiting the 8′- and 12′-olefinic carbon atoms at δ_C 130.18, and 9′- and 11′-olefinic carbon atoms at δ_C 127.96, and the 10′-carbon atom at δ_C 25.66, values typical for such a long-chain skipped diene.[9] The substitution pattern of the benzene ring followed from the ^1H n.m.r. spectrum. This structural assignment was subsequently confirmed by synthesis.

The aforementioned chromatographic separation also yielded an alkene fraction and, in order to identify the constituents, this was subjected to hydroxylation with osmium tetraoxide and the resultant diols were cleaved with Jones reagent; the carboxylic acids so produced were converted into their methyl esters. To assist with the identification of these esters by gas-liquid chromatography (g.l.c.) the dimethoxy heptanoates (**16**) and (**21**), and the dimethoxyoctanoates (**18**) and (**23**) were synthesized. Thus, the known benzyl chloride (11)[10] (Scheme 1) was converted into the phosphonium salt (12), and the derived ylide was caused to undergo a Wittig reaction with ethyl 5-formylpentanoate (**13**).[11] The resultant stereoisomeric mixture of unsaturated esters was subjected to basic hydrolysis thus allowing the ready separation of the unsaturated acids. Catalytic hydrogenation of this mixture then gave the heptanoic acid (**15**) which on esterification furnished the methyl ester (**16**). A similar series of reactions using ethyl 6-formylhexanoate (**14**)[12] gave the octanoic acid (**17**) and thence its methyl ester (**18**). By starting with the phosphonium salt (**19**)[13] the isomeric heptanoic (**20**) and octanoic acids (**22**) and their respective methyl esters (**21**) and (**23**) were also prepared.



Scheme 1.

G.l.c. analysis of the mixture of esters obtained by the aforementioned oxidative cleavage allowed the identification of the major components as methyl nonanoate, methyl 8-(2,3-dimethoxyphenyl)octanoate (**18**), and methyl 8-(3,4-dimethoxyphenyl)octanoate (**23**) so that the major components of this alkene fraction were probably (*Z*)-3- (**6**) and (*Z*)-4-(heptadec-8′-enyl)-1,2-dimethoxybenzene (**28**) (Scheme 2). Minor components of the ester mixture were identified as methyl octanoate and methyl 7-(2,3-dimethoxyphenyl)heptanoate (**16**) so that a minor component of the alkene fraction was probably (*Z*)-3-(pentadec-7′-enyl)-1,2-dimethoxybenzene (**10**). These assignments were confirmed by g.l.c.-m.s. of the components of the ester mixture.

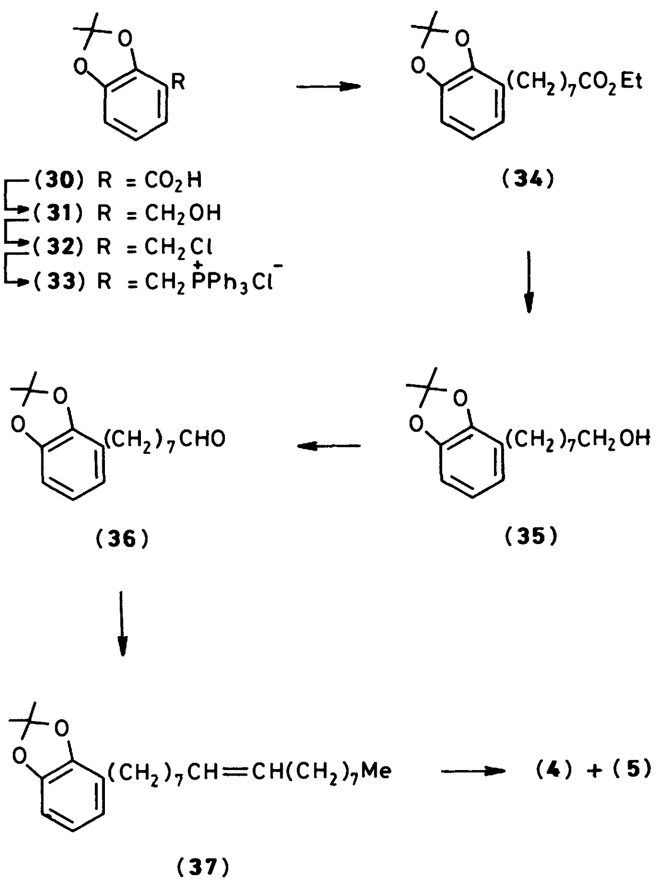


Scheme 2.

In order to confirm the identity of the major alkenes we undertook their synthesis. Thus the octanoate (**18**) (Scheme 2) was reduced with lithium aluminium hydride to the octanol (**24**) which on oxidation with pyridinium chlorochromate furnished the unstable octanal (**25**). Nonyltriphenylphosphonium iodide[14] was treated with sodium methylsulphinylmethanide in dimethyl sulphoxide (DMSO) and thereby converted into its ylide which was allowed to react with the octanal (**25**). These conditions are known to result in *Z*-stereoselective Wittig olefination.[15] The resultant alkene, as demonstrated by g.l.c., contained 91.1% *Z*-isomer (**6**) and 8.9% *E*-isomer (**7**). The olefinic carbon atoms of the *Z*-isomer occurred at δ_C 129.82 and 129.87 and those of the *E*-isomer occurred at δ_C 130.28 and 130.34 in the ^{13}C n.m.r. spectrum. Again these values are typical for such long-chain alkenes.[9]

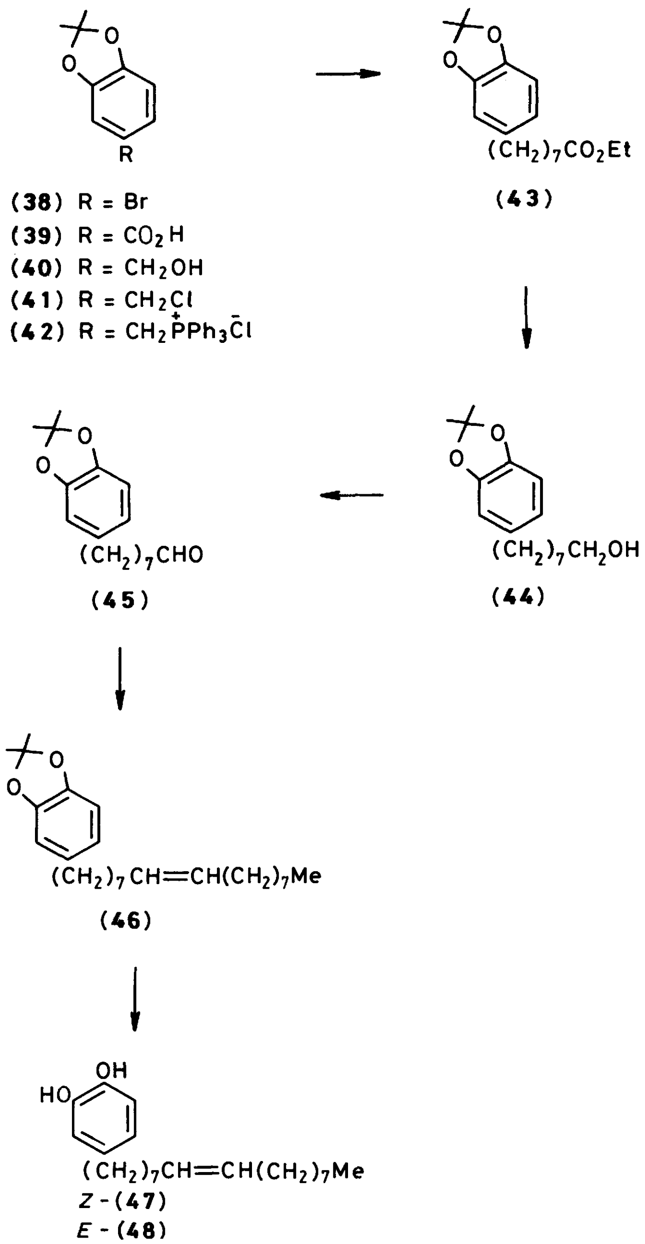
In a similar fashion the octanoate (**23**) was converted *via* the octanol (**26**) and the octanal (**27**) into the alkene which contained 90.9% Z-isomer (**28**) and 9.1% E-isomer (**29**). In this case the stereoisomers could not be resolved by g.l.c. so that the proportion of isomers was estimated from integration of the olefinic resonances in the decoupled ^{1}H n.m.r. spectrum. The presence of compounds (**6**), (**7**), and (**28**) in *O*-methylated Burmese lac was confirmed by separate co-injection of the synthetic alkenes.

For the synthesis of the natural products we adopted the acetonide as a protective group for the hydroxy groups of the catechols. Thus the known protected catechol (**30**)^{16} (Scheme 3) was reduced with lithium aluminium hydride to the benzyl alcohol (31). The derived chloride (32) on reaction with triphenylphosphine supplied the phosphonium salt (33). Wittig reaction of this salt with ethyl 6-formylhexanoate (14) and catalytic reduction of the stereoisomeric mixture of olefins thus obtained gave the octanoate (**34**). This last-mentioned compound on reduction yielded the octanol (**35**) and this on oxidation with pyridinium chlorochromate in the presence of anhydrous sodium acetate furnished the octanal (**36**). Wittig reaction of the octanal (**36**) with the ylide derived from nonyltriphenylphosphonium iodide gave the protected alkene (**37**). Deprotection of this alkene was achieved with hot aqueous acetic acid and this supplied the alkenylcatechol which contained 90.1% Z-isomer (**4**) and 9.9% E-isomer (**5**) as revealed by g.l.c. analysis of its bis(*O*-trimethylsilyl) ether.



Scheme 3.

In order to synthesize the isomeric alkenylcatechol the known bromo compound (**38**)^{17} (Scheme 4) was subjected to bromine-lithium exchange and the resultant lithio compound, on carboxylation with solid carbon dioxide, gave the protected catechol carboxylic acid (**39**). By a similar sequence of reactions to that employed previously and involving the intermediates (**40**)—(**46**) the required alkenylcatechol was obtained. This proved to contain 90.1% Z-isomer (**47**) and 9.9% E-isomer (**48**).

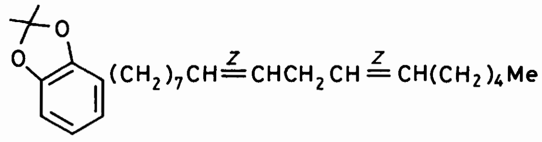


Scheme 4.

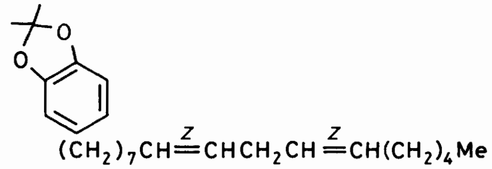
The presence of compounds (**4**), (**5**), and (**47**) in Burmese lac was confirmed using g.l.c. by separate co-injection of their bis(*O*-trimethyl)silyl ethers with the derivatized lac. Thus the lac contained 8.7% (**4**), 1.4% (**5**), and 2.6% (**47**). The E-isomer (**48**) could not be detected.

We now devoted our attention to the synthesis of the dimethoxy diene (**2**). This was achieved by a Wittig reaction between the ylide derived from (Z)-(non-3-enyl)triphenylphosphonium iodide^{18} and the octanal (**25**). In this reaction the ylide was generated in tetrahydrofuran (THF) solution at -78 °C using butyl-lithium as base and then hexamethylphosphoric triamide was added followed by the aldehyde; again these conditions give rise to Z-stereoselective olefination. In the event the resultant diene (**2**) proved to be identical with that obtained from Burmese lac and it was stereochemically homogeneous as indicated by its ^{13}C n.m.r. spectrum and by g.l.c.

The parent dienes (**1**) and (**3**) were synthesized in an analogous manner from the octanals (**36**) and (**45**) which yielded the protected dienes (**49**) and (**50**). After deprotection the stereochemically homogeneous dienes (**1**) and (**3**) were obtained.



(49)



(50)

The presence of the dienes (**1**) and (**3**) in Burmese lac was confirmed by g.l.c. by separate co-injection of the bis(*O*-trimethylsilyl) ethers of the dienes with the derivatized lac.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus. Distillations under diminished pressure were carried out using a Büchi GKR-50 Kugelrohr apparatus and the quoted b.p.s refer to the oven temperature. Light petroleum was a fraction b.p. *ca.* 55—65 °C. All organic extracts were washed with saturated brine and dried with anhydrous magnesium sulphate prior to evaporation under reduced pressure. Silica gel was B.D.H. 60—120 mesh. Radial chromatography was performed under nitrogen using a Harrison Research Chromatotron with plates coated with Merck Kieselgel 60 PF_{254}. ^1H N.m.r. spectra were recorded for solutions in deuteriochloroform at 80 MHz on a Bruker WP-80 instrument or at 300 MHz on a Bruker AM-300 instrument which was also used for ^{13}C n.m.r. spectra (75.5 MHz) and the DEPT technique was used to assist assignment. I.r. spectra were recorded on a Perkin-Elmer 680 spectrophotometer. Mass spectra (35 eV) were recorded using a Hewlett-Parkard 5986 instrument. G.l.c.-m.s. were recorded using a Hewlett-Packard 5985B computer data system.

Methylation and Fractionation of Crude Burmese Lac.—A sample of Burmese lac (51.9 g), supplied by the National Museum Division, Bangkok, was dissolved in acetone (300 ml) and filtered. The solvent was removed under reduced pressure and the residual oil (45.7 g) was dissolved in light petroleum (300 ml) and extracted with acetonitrile (300 ml). Evaporation of the acetonitrile phase gave a dark oil (19.4 g), a solution of which (19.0 g) in anhydrous acetone (1.0 l) was stirred with dimethyl sulphate (258.7 g) and potassium carbonate (280 g) for 2 h at room temperature and then boiled and stirred under reflux for 5.5 h. Work-up gave a crude product, a portion (7.65 g) of which was chromatographed over a column of silica gel (100 g) with 2% ethyl acetate–light petroleum as eluant. Examination of this material by t.l.c. (5% ethyl acetate–light petroleum) revealed spots with R_F 0.00, 0.05, 0.10, 0.17, and 0.25. Fractions rich in the higher R_F spots were combined and a portion of this material (1.09 g) was subjected to repeated radial chromatography first with a 4 mm plate and then with a 1 mm plate using 1—5% ethyl acetate–light petroleum as eluants; fractions were monitored by g.l.c. Fractions of higher R_F contained a mixture of alkenes (41 mg) and a fraction of slightly lower R_F yielded (*Z,Z*)-3-(heptadeca-8′-11′-dienyl)-1,2-dimethoxybenzene (**2**) (24.8 mg) as a thick oil; δ_H(300 MHz) 0.89 (3 H, t, 17′-Me), 1.21—1.43 (14 H, br, CH_2), 1.58 (2 H, quintet, 2′-CH_2), 1.98—2.10 (4 H, m, 7′- and 13′-H), 2.61 (2 H, t, 1′-CH_2), 2.77 (2 H, t, $J_{10',9'}$ = $J_{10',11'}$ = 5.86 Hz, 10′-CH_2), 3.81 and 3.85 (each 3 H, s, OMe), 5.27—5.43 (4 H, m, 8′-, 9′-, 11′-, and 12′-H), 6.75 (1 H, dd, $J_{4,5}$ 7.98 Hz, $J_{4,6}$ 1.5 Hz, 4-H), 6.77 (1 H, dd, $J_{6,5}$ 7.84, $J_{6,4}$ 1.5 Hz, 6-H), and 6.97 (1 H, apparent t, 5-H); δ_C 14.09 (C-17′), 22.60 (C-16′), 25.66 (C-10′), 27.22 and 27.25 (C-7′ and C-13′), 29.27, 29.38, 29.46, 29.60, 29.70, 29.82, 30.83, and 31.54 (each CH_2), 55.64 and 60.60 (each OMe), 109.01 (C-6), 121.90 (C-5), 123.67 (C-4), 127.96 (C-9′ and C-11′), 130.18 (C-8′ and C-12′), 136.78 (C-3), 147.07 (C-1), and 152.71 (C-2), *m/z* (372 (M^+, 10%), 341 (2), 290 (1), 262 (2), 245 (3), 218 (3), 191 (11), 189 (7), 177 (19), 165 (8), 164 (33), 152 (51), 151 (100), 137 (36), 136 (80), 121 (12), and 91 (15); $\nu_{max.}$(film) 3 000m, 2 920s, 2 845s, 1 590w, 1 580m, 1 474s, 1 424m, 1 264s, 1 215s, 1 168m, 1 080s, 1 003m, and 773m cm^{-1}.

Oxidative Degradation of the Alkene Mixture.—A solution of osmium tetraoxide (50.0 mg) in anhydrous ether (10 ml) was added to a solution of the foregoing alkene mixture (18.5 mg) in anhydrous ether (20 ml) and pyridine (26.7 mg) and the solution was stirred at room temperature for 24 h. Potassium hydroxide (10%; 20 ml) and mannitol (50 mg) were added and the whole was stirred for 15 min. The crude product (35.6 mg) was isolated by extraction with ethyl acetate in the usual way. This material (22.0 mg) was dissolved in acetone (15 ml) and the stirred solution was treated with Jones reagent (0.11 ml). After 2 min the solution was diluted with water (10 ml) and an excess of sodium metabisulphite was added. The crude acids were extracted with ether and purified by extraction with dilute aqueous sodium hydroxide in the usual way. The mixture of acids (7.0 mg) so obtained was dissolved in benzene (1.0 ml) and a solution of boron trifluoride in methanol (1.0 ml) was added; the mixture was then heated on a steam-bath for 30 min. Work-up gave the methyl esters, g.l.c. of which was carried out using a Hewlett-Packard 5890A chromatograph equipped with a flame ionization detector and recorded on a Shimadzu C-R3A Chromatopac integrator. A 50 m × 0.2 mm i.d. fused silica cross-linked methyl silicone column was used at a temperature of 35 °C (3 min) and then programmed from 35 to 280 °C at 8 °C per min, with hydrogen as carrier gas at a linear velocity of 60 cm s^{-1}. Major peaks were identified by co-injection of the authentic samples; methyl nonanoate (R_t 19.79 min), methyl 8-(2,3-dimethoxyphenyl)octanoate (**18**) (R_t 34.90 min), and methyl 8-(3,4-dimethoxyphenyl)octanoate (**23**) (R_t 36.15 min). Minor peaks were similarly identified as methyl octanoate (R_t 17.67 min) and methyl 7-(2,3-dimethoxyphenyl)heptanoate (**16**) (R_t 33.43 min). These assignments were confirmed by g.l.c.s-m.s.

2,3-*Dimethoxybenzyltriphenylphosphonium Chloride* (**12**).—A solution of 2,3-dimethoxybenzyl chloride (**11**) (10.0 g)[10] and triphenylphosphine (15.45 g) in anhydrous benzene (80 ml) was stirred and heated under reflux for 24 h. The mixture was allowed to cool and the hygroscopic *phosphonium salt* (**12**) (20.6 g, 86%) was filtered off and washed with warm light petroleum. A sample crystallized from dichloromethane–light petroleum as plates, m.p. 218—219.5 °C (Found: C, 69.0; H, 6.25; Cl, 7.55. $C_{27}H_{26}ClO_2P{\cdot}H_2O$ requires C, 69.45; H, 6.05; Cl, 7.6%); δ_H(80 MHz) 3.58 and 3.76 (each 3 H, s, OMe), 5.29 (2 H, d, $J_{CH_2,P}$ 14.4 Hz, CH_2), 6.70—6.92 (3 H, m, ArH), and 7.50—7.94 (15 H, m, Ph).

Methyl 7-(2,3-*Dimethoxyphenyl*)*heptanoate* (**16**).—A solution of butyl-lithium in hexane (5.94 ml; 1.61M) was added dropwise under an atmosphere of anhydrous argon to a stirred solution of the phosphonium salt (**12**) (4.26 g) in anhydrous tetrahydrofuran (15 ml). After 15 min a solution of ethyl 5-formylpentanoate (**13**) (1.0 g)[11] in anhydrous tetrahydrofuran (10 ml) was added dropwise and the solution was stirred for 18 h and then poured into ice–water. The crude product was isolated by extraction with ethyl acetate in the usual way and then boiled under reflux with sodium hydroxide (10.0 g) in water (50 ml) and methanol (50 ml) during 2 h. The cooled solution was twice extracted with ether and these extracts were discarded. The aqueous phase was acidified with hydrochloric acid and the crude unsaturated acid was isolated by extraction with ethyl acetate. This material in ethyl acetate (100 ml) was stirred under an atmosphere of hydrogen with palladized charcoal (10%; 200 mg) until absorption ceased. Work-up gave 7-(2,3-*dimethoxyphenyl)heptanoic acid* (**15**) (1.42 g, 85%) as an oil, b.p. 195 °C at 0.02 mmHg (Found: C, 67.65; H, 8.7%; M^+, 266. $C_{15}H_{22}O_4$ requires C, 67.65; H, 8.35%; *M*, 266). The acid (**15**) (850 mg), methanol (25 ml), and concentrated sulphuric acid (1.2 ml) were heated under reflux for 3.5 h. Work-up gave the *ester* (**16**) (890 mg, 100%) as an oil, b.p. 150 °C at 0.05 mmHg (Found: C, 68.5; H, 8.6. $C_{16}H_{24}O_4$ requires C, 68.55; H, 8.6%); δ_H(80 Mz) 1.19—1.84 (8 H, br, CH_2), 2.30 (2 H, t, CH_2CO), 2.62 (2 H, t, CH_2Ar), 3.66 (3 H, s, CO_2Me), 3.81 and 3.85 (each 3 H, s, OMe), and 6.68—7.11 (3 H, m ArH); *m/z* 280 (M^+, 54%), 249 (4), 206 (2), 177 (4), 165 (10), 152 (56), 151 (68), 137 (46) 136 (100), 121 (29), and 91 (57).

Methyl 8-(2,3-*Dimethoxyphenyl)octanoate* (**18**).—The *octanoic acid* (**17**) (79%), prepared from the phosphonium salt (**12**) and ethyl 6-formylhexanoate (**14**)[12] in a similar manner to the heptanoic acid (**15**) was obtained as an oil, b.p. 205 °C at 0.02 mmHg (Found: C, 68.35; H, 8.75%; M^+, 280. $C_{16}H_{24}O_4$ requires C, 68.55; H, 8.65%; *M*, 280). The *ester* (**18**) was also an oil, b.p. 170 °C at 0.05 mmHg (Found: C, 69.15; H, 9.0. $C_{17}H_{26}O_4$ requires C, 69.35; H, 8.9%); δ_H(300 MHz) 1.33 (6 H, br, CH_2), 1.58—1.65 (4 H, m, 2 × CH_2), 2.30 (2 H, t, CH_2CO), 2.61 (2 H, t, CH_2Ar), 3.66 (3 H, s, CO_2Me), 3.81 and 3.85 (each 3 H, s, OMe), 6.76 (2 H, d, $J_{4,5} = J_{4,6} =$ 8.0 Hz, 4- and 6-H), and 6.98 (1 H, t, $J_{5,4} = J_{5,6} =$ 8.0 Hz, 5-H); *m/z* 294 (M^+, 59%), 263 (4), 245 (3), 229 (1), 191 (1), 177 (3), 165 (10), 157 (1), 152 (62), 151 (75), 137 (45), 136 (100), 121 (26), 105 (6), 101 (6), and 91 (44).

Methyl 7-(3,4-*Dimethoxyphenyl)heptanoate* (**21**).—The *heptanoic acid* (**20**) (85%), prepared in a similar manner to the heptanoic acid (**15**) using 3,4-dimethoxybenzyltriphenylphosphonium chloride (**19**),[13] formed plates (from light petroleum), m.p. 63.5—64 °C (Found; C, 67.65; H, 8.6%; M^+, 266. $C_{15}H_{22}O_4$ requires C, 67.65; H, 8.35%; *M*, 266). The *ester* (**21**) was obtained as an oil, b.p. 170 °C at 0.05 mmHg (Found: C, 68.3; H, 8.65. $C_{16}H_{24}O_4$ requires C, 68.55; H, 8.65%); δ_H(300 MHz) 1.32—1.37 (4 H, br, CH_2), 1.60—1.66 (4 H, m, CH_2), 2.30 (2 H, t, CH_2CO), 2.55 (2 H, t, CH_2Ar), 3.66 (3 H, s, CO_2Me), 3.86 and 3.88 (each 3 H, s, OMe), 6.71 (1 H, d, $J_{3,5}$ 1.6 Hz, 3-H), 6.71 (1 H, dd, $J_{5,3}$ 1.6 Hz, $J_{5,6}$ 8.0 Hz, 5-H), and 6.79 (1 H, d, $J_{6,5}$ 8.0 Hz, 6-H); *m/z* 280 (M^+, 19%), 249 (1), 165 (2), 152 (15), 151 (100), 137 (6), 136 (1), 107 (5), and 91 (3).

Methyl 8-(3,4-*Dimethoxyphenyl)octanoate* (**23**).—The *octanoic acid* (**22**) (91%), prepared in a similar manner to the heptanoic acid (**15**), formed needles (from light petroleum), m.p. 55.5—57 °C (Found: C, 68.85; H, 8.85%; M^+, 280. $C_{16}H_{24}O_4$ requires C, 68.55; H, 8.65%, *M*, 280). The *ester* (**23**) was an oil, b.p. 180—185 °C at 0.05 mmHg (Found: C, 69.15; H, 8.95. $C_{17}H_{26}O_4$ requires C, 69.35; H, 8.90%); δ_H(80 MHz) 1.13—1.85 (10 H, br, CH_2), 2.30 (2 H, t, CH_2CO), 2.55 (2 H, t, CH_2Ar), 3.66 (3 H, s, CO_2Me), 3.85 and 3.87 (each 3 H, s, OMe), and 6.63—6.90 (3 H, m, ArH); *m/z* 294 (M^+, 19%), 263 (2), 177 (1), 165 (1), 152 (15), 151 (100), 137 (6), 121 (3), 107 (4), and 91 (3).

8-(2,3-*Dimethoxyphenyl)octanal* (**25**).—A solution of methyl 8-(2,3-dimethoxyphenyl)octanoate (**18**) (500 mg) in anhydrous ether (3.0 ml) was added to a stirred solution of lithium aluminium hydride (50 mg) in anhydrous ether (5.0 ml). After 3 h an excess of saturated aqueous sodium sulphate was added followed by sulphuric acid (10%; 5 ml) and ice (2.5 g). The crude product, isolated by extraction with ethyl acetate, on distillation gave 8-(2,3-*dimethyoxyphenyl)octan*-1-*ol* (**24**) as an oil (450 mg, 100%), b.p. 190 °C at 0.01 mmHg (Found: C, 72.2; H, 9.95%; M^+, 266. $C_{16}H_{26}O_3$ requires C, 72.15; H, 9.85%; *M*, 266); δ_H(80 MHz) 1.19—1.79 (13 H, br, CH_2 and D_2O exchangeable OH), 2.63 (2 H, t, CH_2Ar), 3.63 (2 H, t, CH_2O), 3.81 and 3.85 (each 3 H, s, OMe), and 6.68—7.13 (3 H, m, ArH). A solution of the octanol (**24**) (380 mg) in dichloromethane (4.0 ml) was added to a stirred suspension of pyridinium chlorochromate (375 mg) in dichloromethane (4.0 ml). After 2.5 h the suspension was diluted with ether (50 ml) and the ether was decanted from the black residue which was washed twice with a little ether. The combined ethereal solutions were passed through a short column of silica gel (10.0 g) which was eluted with more ether. The crude product was distilled under diminished pressure to give the aldehyde (**25**) (310 mg, 84%)[19] as an oil, b.p. 175 °C at 0.02 mmHg, which was used immediately; δ_H(80 MHz) 1.22—1.85 (10 H, br, CH_2), 2.41 (2 H, td, *J* 7.0 and 1.8 Hz, CH_2CHO), 2.62 (2 H, t, CH_2Ar), 3.81 and 3.85 (each 3 H, s, OMe), 6.68—7.13 (3 H, m, ArH), and 9.76 (1 H, t, *J* 1.8 Hz, CHO); *m/z* 264 (M^+).

3-(*Heptadec*-8′-*enyl*)-1,2-*dimethoxybenzene* (**6**) *and* (**7**).—Sodium hydride in oil (80%; 95 mg) was washed free from the oil with light petroleum under argon and then anhydrous dimethyl sulphoxide (5.0 ml) was added. The mixture was stirred and slowly heated to 75 °C (bath) and then held at that temperature for 10 min. The resulting solution was allowed to cool to room temperature when a solution of nonyltriphenylphosphonium iodide (1.64 g)[14] in anhydrous dimethyl sulphoxide (5.0 ml) was slowly added. After 30 min, a solution of the octanal (**25**) (280 mg) in dimethyl sulphoxide (7.0 ml) was added and stirring was continued for 18 h. The solution was poured into ice–water and the crude product was isolated by extraction with ethyl acetate. The crude product was chromatographed over a column of silica gel (10 g) with 0—5% ethyl acetate–light petroleum as eluant. The fractions rich in the alkene were further purified by radial chromatography with 0—1% ethyl acetate–light petroleum as eluant. The *alkene* was obtained as an oil (230 mg, 58%), b.p. 200 °C at 0.05 mmHg (Found: C, 79.9; H, 11.35. $C_{25}H_{42}O_2$ requires C, 80.15; H, 11.3%); δ_H(300 MHz) 0.88 (3 H, t, Me), 1.20—1.42 (20 H, br, CH_2), 1.58 (2 H, quintet, CH_2CH_2Ar), 1.94—2.08 (4 H, m, CH_2C=), 2.61 (2 H, t, CH_2Ar), 3.81 and 3.85 (3 H, s, OMe), 5.30—5.41 (2 H, m, HC=), 6.75 (1 H, dd, $J_{4,5}$ 8.0 Hz, $J_{4,6}$ 1.4 Hz, 4-H), 6.97 (1 H, dd, $J_{5,4} = J_{5,6} =$ 8.0 Hz, 5-H), and 6.77 (1 H, dd, $J_{6,5}$ 8.0, $J_{6,4}$ 1.4 Hz, 6-H); irradiation at the frequency of the 7′- and 10′-H gave singlets at δ5.34 (*Z*-olefinic H) and δ 5.38 (*E*-olefinic H); δ_C 14.08 (C-17′), 22.65 (C-16′), 27.18 [C-7′ and -10′ (*Z*-isomer)], 29.07, 29.21, 29.41, 29.50, 29.57, 29.63, 29.75, and 30.58 (each CH_2), 31.88 (C-15′), 32.58 [C-7′ and -10′ (*E*-isomer)], 55.59 and 60.54 (each OMe), 109.83 (C-6), 121.84 (C-5), 123.62 (C-4), 129.82 and 129.87 [C-8′ and -9′ (*Z*-isomer)], 130.28 and 130.34 [C-8′ and -9′ (*E*-isomer)], 136.73 (C-3), 147.04 (C-1), and 152.66 (C-2), *m/z* 374 (M^+, 58%), 261 (1), 235 (1), 177 (12), 164 (10), 152 (60), 151 (92), 137 (57), 136 (100), 121 (28), 107 (10), and 91 (45); $\nu_{max.}$(film) 3 000m, 2 922s, 2 855s, 1 599w, 1 583m, 1 475s, 1 429m, 1 270s, 1 220m, 1 167w, 1 081m, 1 010m, 800w, 775w, 740m, and 715w cm^{-1}. Analysis of the alkenes by g.l.c. under the conditions described previously at a temperature of 50 °C (1 min) and then programmed from 50 to 280 °C at 4 °C per min, revealed the mixture contained 91.1% *Z*-isomer (**6**) (R_t 66.13 min) and 8.9% *E*-isomer (**7**) (R_t 66.24 min).

8-(3,4-*Dimethoxyphenyl*)*octanal* (**27**).—Reduction of methyl 8-(3,4-dimethoxyphenyl)octanoate (**23**) with lithium aluminium hydride in a similar manner to that described for the preparation of the octanol (**24**) gave 8-(3,4-*dimethoxyphenyl*)*octan*-1-ol (**26**) (98%) as plates (from light petroleum), m.p. 31—32 °C (Found: C, 72.0; H, 9.75%; M^+, 266. $C_{16}H_{26}O_3$ requires C, 72.15; H, 9.85%; *M*, 266); δ_H(80 MHz) 1.19—1.88 (13 H, br, CH_2 and D_2O exchangeable OH), 2.56 (2 H, t, CH_2Ar), 3.64 (2 H, t, CH_2O), 3.85 and 3.87 (each 3 H, s, OMe), and 6.63—6.91 (3 H, m, ArH). On oxidation with pyridinium chlorochromate this compound afforded the octanal (**27**) (89%) as an oil, b.p. 190—200 °C at 0.05 mmHg; δ_H(80 MHz) 1.16—1.88 (10 H, br, CH_2), 2.41 (2 H, td, *J* 7.0 and 1.8 Hz, CH_2O), 2.55 (2 H, t, CH_2Ar), 3.85 and 3.87 (each 3 H, s, OMe), 6.66—6.93 (3 H, m, ArH), and 9.76 (1 H, t, *J* 1.8 Hz, CHO); *m*/*z* 264 (M^+).

4-(*Heptadec*-8′-*enyl*)-1,2-*dimethoxybenzene* (**28**) *and* (**29**).—This compound was prepared in an analogous manner to its isomers (**6**) and (**7**) from the octanal (**27**). The *alkene* (69%) was obtained as an oil, b.p. 225—230 °C at 0.02 mmHg (Found: C, 80.3; H, 11.0. $C_{25}H_{42}O_2$ requires C, 80.15; H, 11.3%); δ_H(300 MHz) 0.88 (3 H, t, Me), 1.23—1.43 (20 H, br, CH_2), 1.59 (2 H, quintet, CH_2CH_2Ar), 1.93—2.13 (4 H, m, CH_2C=), 2.55 (2 H, t, CH_2Ar), 3.85 and 3.87 (3 H, s, OMe), 5.30—5.40 (2 H, m, HC=), and 6.61—6.81 (3 H, m, ArH); irradiation at the frequency of the 7′- and 10′-H gave singlets at δ 5.35 (*Z*-olefinic H) and δ 5.38 (*E*-olefinic H); integration indicated 90.9% (*Z*)-isomer; δ_C 14.13 (C-17′), 22.71 (C-16′), 27.23 [C-7′ and -10′ (*Z*-isomer)], 29.13 29.27, 29.33, 29.44, 29.54, 29.67, 29.78, 31.74, and 31.93 (each CH_2), 32.62 [C-7′ and -10′ (*E*-isomer)], 35.59 (C-1′), 55.76 and 55.89 (each OMe), 111.2 and 111.73 (C-3 and C-6), 120.10 (C-5), 129.82 and 129.95 [C-8′ and -9′ (*Z*-isomer)], 130.29 and 130.41 [C-8′ and -9′ (*E*-isomer)], 135.59 (C-4), and 146.99 and 148.73 (C-1 and C-2); *m*/*z* 374 (M^+, 38%), 262 (1), 235 (1), 177 (5), 164 (5), 152 (13), 151 (100), 137 (8), and 107 (5); $\nu_{max.}$(film) 3 000m, 2 930s, 2 855s, 1 590m, 1 514s, 1 464s, 1 417m, 1 260m, 1 237m, 1 188w, 1 155s, 1 140s, 840w, 799w, 778w, and 760w cm^{-1}. G.l.c. did not resolve the mixture of alkenes which had R_t 68.01 min under the conditions used for the isomers (**6**) and (**7**).

2,2-*Dimethyl*-1,3-*benzodioxol*-4-*ylmethanol* (**31**).—A solution of 2,2-dimethyl-1,3-benzodioxole-4-carboxylic acid (**30**) (4.45 g)[16] in anhydrous ether (60 ml) was added dropwise to a stirred solution of lithium aluminium hydride (2.61 g) in anhydrous ether (150 ml). After 6 h, work-up gave the *alcohol* (**31**) (3.46 g, 84%) as an oil, b.p. 100 °C at 0.05 mmHg (Found: C, 66.75; H, 7.05%; M^+, 180. $C_{10}H_{12}O_3$ requires C, 66.65; H, 6.7%; *M*, 180); δ_H(80 MHz) 1.68 (6 H, s, 2 × Me), 1.68—1.85 (1 H, D_2O exchangeable OH), 4.66 (2 H, s, CH_2), and 6.66—6.89 (3 H, m, ArH).

4-*Chloromethyl*-2,2-*dimethyl*-1,3-*benzodioxole* (**32**).—A solution of the alcohol (**31**) (2.0 g) in anhydrous benzene (65 ml) and anhydrous pyridine (790 mg) was stirred and treated dropwise with thionyl chloride (1.78 g). After 3 h the solution was diluted with ethyl acetate and washed in turn with water, saturated aqueous sodium hydrogen carbonate, water, and finally with saturated brine. The *chloride* (**32**) (2.10 g, 95%) was obtained as an oil, b.p. 75 °C at 0.05 mmHg (Found: C, 60.75; H, 5.65; Cl, 17.75%; M^+, 198, 200. $C_{10}H_{11}ClO_2$ requires C, 60.45; H, 5.6; Cl, 17.85%; *M*, 198, 200); δ_H(80 MHz) 1.69 (6 H, s, 2 × Me), 4.56 (2 H, s, CH_2), and 6.63—6.90 (3 H, m, ArH).

2,2-*Dimethyl*-1,3-*benzodioxol*-4-*ylmethyltriphenylphosphonium Chloride* (**33**).—A solution of the chloride (**32**) (2.0 g) and triphenylphosphine (2.92 g) in anhydrous toluene (100 ml) was heated under reflux for 96 h. The *salt* (**33**) (3.95 g, 85%) was filtered off, washed with warm light petroleum, and recrystallised from dichloromethane–light petroleum to give needles, m.p. 290—292 °C (decomp.) (Found: C, 72.8; H, 5.8; Cl, 7.95. $C_{28}H_{26}ClO_2P$ requires C, 72.95; H, 5.7; Cl, 7.7%); δ_H(80 MHz) 1.33 (6 H, s, 2 × Me), 5.34 (2 H, d, $J_{CH_2,P}$ 14.0 Hz, CH_2), 6.55—6.70 (3 H, m, ArH), and 7.50—7.95 (15 H, m, Ph).

Ethyl 8-(2,2-*Dimethyl*-1,3-*benzodioxol*-4-*yl*)*octanoate* (**34**).—A solution of butyl-lithium (2.48 ml; 1.6M) in hexane was added to a stirred solution of the foregoing phosphonium salt (1.82 g) in anhydrous THF (30 ml) under an atmosphere of anhydrous argon. After 15 min a solution of ethyl 6-formylhexanoate (**14**) (500 mg) in anhydrous THF (5 ml) was added and the solution was stirred for 18 h. Ice and water were then added and the crude product, isolated by extraction with ethyl acetate, was chromatographed over a column of silica gel (40 g) with 10% ethyl acetate–light petroleum as eluant. The stereoisomeric mixture of olefins so obtained, in ethyl acetate (100 ml), was stirred under a hydrogen atmosphere with palladized charcoal (10%, 250 mg) until absorption ceased. Work-up gave the *ester* (**34**) (890 mg, 96%) as an oil, b.p. 160 °C at 0.01 mmHg (Found: C, 71.2; H, 8.65%; M^+, 320. $C_{19}H_{28}O_4$ requires C, 71.2; H, 8.8%; *M*, 320); δ_H(80 MHz) 1.25 (3 H, t, Me), 1.28—1.74 (10 H, br, CH_2), 1.66 (6 H, s, 2 × Me), 2.28 (2 H, t, CH_2CO), 2.54 (2 H, t, CH_2Ar), 4.12 (2 H, q, OCH_2), and 6.50—6.79 (3 H, m, ArH); $\nu_{max.}$(film) 1 740 cm^{-1}.

8-(2,2-*Dimethyl*-1,3-*benzodioxol*-4-*yl*)*octan*-1-*ol* (**35**).—The foregoing ester (**34**) was reduced with lithium aluminium hydride in ether in a manner similar to that described for the preparation of compound (**24**). The *octanol* (**35**) (100%) was obtained as an oil, b.p. 165—170 °C at 0.03 mmHg (Found: C, 73.35; H, 9.55%; M^+, 278. $C_{17}H_{26}O_3$ requires C, 73.35; H, 9.4%; *M*, 278); δ_H(80 MHz) 1.20—1.60 (13 H, br, CH_2 and D_2O exchangeable OH), 1.66 (6 H, s, 2 × Me), 2.54 (2 H, t, CH_2Ar), 3.65 (2 H, t, CH_2O), and 6.48—6.83 (3 H, m, ArH).

8-(2,2-*Dimethyl*-1,3-*benzodioxol*-4-*yl*)*octanol* (**36**).—A solution of the foregoing octanol (**35**) (280 mg) in dichloromethane (4.0 ml) was added to a stirred suspension of pyridinium chlorochromate (330 mg) and anhydrous sodium acetate (130 mg) in dichloromethane (5.0 ml). After 2.5 h the reaction was worked up in a similar manner to that described for the preparation of compound (**25**). The aldehyde (**36**) (234 mg, 84%) was obtained as an oil, b.p. 160 °C at 0.05 mmHg; δ_H(80 MHz) 1.20—1.63 (10 H, br, CH_2), 1.66 (6 H, s, 2 × Me), 2.41 (2 H, td, *J* 7.0 and 1.8 Hz, CH_2CHO), 2.54 (2 H, t, CH_2Ar), 6.49—6.79 (3 H, m, ArH), and 9.76 (1 H, t, *J* 1.8 Hz, CHO); *m*/*z* 276 (M^+).

4-(*Heptadec*-8′-*enyl*)-2,2-*dimethyl*-1,3-*benzodioxole* (**37**).—This compound was prepared in a manner similar to that described for the preparation of compounds (**6**) and (**7**). The *alkene* (56%) was obtained as an oil, b.p. 235 °C at 0.02 mmHg (Found: C, 81.05; H, 11.2. $C_{26}H_{42}O_2$ requires C, 80.75; H, 10.95%); δ_H(300 MHz) 0.88 (3 H, t, Me), 1.20—1.39 (20 H, br, CH_2), 1.53—1.63 (2 H, m, CH_2CH_2Ar), 1.66 (6 H, s, 2 × Me), 1.92—2.05 (4 H, m, CH_2C=), 2.53 (2 H, t, CH_2Ar), 5.30—5.40 (2 H, m, HC=), 6.58 (1 H, dd, $J_{5,6}$ 8.0, $J_{5,7}$ 1.4 Hz, 5-H), 6.61 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,5}$ 1.4 Hz, 7-H), and 6.70 (1 H, dd, $J_{5,6} = J_{6,7} =$ 8.0 Hz, 6-H); irradiation at the frequency of 7′- and 10′-H gave singlets at δ 5.34 (*Z*-olefinic H) and δ 5.38 (*E*-olefinic H); δ_C 14.13 (C-17′), 22.70 (C-16′), 25.88 (Me_2), 27.22 [C-7′ and -10′ (*Z*-isomer)], 29.13, 29.20, 29.28, 29.34, 29.40, 29.54, 29.65, and 29.78 (each CH_2), 31.92 (C-15′), 32.62 [C-7′ and -10′ (*E*-isomer)], 106.00 (C-7), 116.90 (C-2), 120.59 (C-6), 121.84 (C-5), 124.04, (C-4), 129.84 and 129.94 [C-8′ and -9′ (*Z*-isomer)], 130.31 and 130.41 [C-8′ and -9′ (*E*-isomer)], 145.35 (C-8), and

146.73 (C-9); *m/z* 286 (M^+, 98%), 371 (81), 273 (2), 191 (3), 177 (10), 164 (55), 163 (100), 149 (41), 147 (36), 123 (99), and 107 (50).

3-(*Heptadec-8′-enyl*)*benzene*-1,2-*diol* (**4**) *and* (**5**).—A solution of the alkene (**37**) (120 mg) in acetic acid (8.0 ml) and water (2.0 ml) was heated at 110 °C (bath) under nitrogen for 18 h. The solution was poured into ice and saturated aqueous sodium hydrogen carbonate and the crude product was isolated by extraction with ethyl acetate. Radial chromatography with 10% ethyl acetate–light petroleum as eluant gave first the starting alkene (**37**) (26.5 mg) and next the *catechol* (72.5 mg, 87%) as a gum which solidified to a waxy solid at −10 °C; it rapidly darkened in light and air (Found: C, 79.5; H, 11.15%. $C_{23}H_{38}O_2$ requires C, 79.7; H, 11.05%); δ_H(300 MHz) 0.88 (3 H, t, Me), 1.16—1.42 (20 H, br, CH_2), 1.52—1.67 (2 H, m, CH_2CH_2Ar), 1.93—2.08 (4 H, m, CH_2C=), 2.60 (2 H, t, CH_2Ar), 5.20 (1 H, s, D_2O exchangeable OH), 5.28—5.42 (3 H, m, HC= and D_2O exchangeable OH), and 6.71 (3 H, s, ArH); irradiation at the frequency of the 7′- and 10′-H gave singlets at δ_H 5.34 (*Z*-olefinic H) and δ_H 5.38 (*E*-olefinic H); δ_C 14.13 (C-17′), 22.70 (C-16′), 27.22 [C-7′ and -10′ (*Z*-isomer)], 29.20, 29.26, 29.34, 29.44, 29.53, and 29.78 (each CH_2), 31.95 (C-15′), 32.63 [C-7′ and -10′ (*E*-isomer)], 112.88 (C-6), 120.12 (C-5), 122.10 (C-4), 129.38 (C-3), 129.86 and 129.98 [C-8′ and -9′ (*Z*-olefinic H], 130.31 and 130.43 [C-8′ and -9′ (*E*-isomer)], 141.87 (C-1), and 143.01 (C-2); *m/z* 346 (M^+, 7%), 163 (5), 149 (6), 137 (6), 136 (27), 124 (38), 123 (100), 110 (3), 109 (1), 97 (4), and 95 (4); $\nu_{max.}$(film) 3 440s, 3 005m, 2 930s, 2 860s, 1 620m, 1 598m, 1 480s, 1 279m, 1 237w, 1 180m, 1 155m, 960w, 825w, 770w, and 728m cm^{-1}. G.l.c. analysis of the bis(*O*-trimethyl)silyl derivatives under the conditions used for the alkene mixture (**6**) and (**7**) (except that a 25 m column was used) revealed the presence of 90.1% *Z*-isomer (**4**) (R_t 50.82 min) and 9.9% *E*-isomer (**5**) (R_t 50.97 min). The presence of these isomers in derivatized Burmese lac was confired by co-injection.

2,2-*Dimethyl*-1,3-*benzodioxole*-5-*carboxylic Acid* (**39**).—A solution of butyl-lithium (28.6 ml; 1.6M) in hexane was added at −78 °C under an atmosphere of anhydrous argon to a stirred solution of 5-bromo-2,2-dimethyl-1,3-benzodioxole (**38**) (9.50 g)[17] in anhydrous tetrahydrofuran (120 ml). After being stirred for 30 min at −78 °C the solution was poured over an excess of solid carbon dioxide. After the carbon dioxide had evaporated the solution was diluted with water and ice and extracted with ether; these extracts were discarded. The aqueous layer was acidified and the crude product was isolated by extraction with ethyl acetate. The *acid* (**39**) (6.95 g, 86%) crystallized from dichloromethane–light petroleum as plates, m.p. 149—150 °C (Found: C, 61.6; H, 5.3%; M^+, 194. $C_{10}H_{10}O_4$ requires C, 61.85; H, 5.2%; *M*, 194) δ_H(80 MHz) 1.71 (6 H, s, 2 × Me), 6.77 (1 H, d, $J_{7,6}$ 8.2 Hz, 7-H), 7.44 (1 H, d, $J_{4,6}$ 1.7 Hz, 4-H), 7.71 (1 H, dd, $J_{6,4}$ 1.7 Hz, $J_{6,7}$ 8.2 Hz, 6-H), and 8.79—10.35 (1 H, D_2O exchangeable OH).

2,2-*Dimethyl*-1,3-*benzodioxol*-5-*ylmethanol* (**40**).—Reduction of the foregoing acid (**39**) with lithium aluminium hydride in ether by a manner similar to that described for the preparation of compound (**31**) gave the *alcohol* (**40**) (82%) as an oil, b.p. 110—115 °C at 0.01 mmHg (Found: C, 66.4; H, 6.64%; M^+, 180. $C_{10}H_{12}O_3$ requires C, 66.65; H, 6.7%; *M*, 180); δ_H(80 MHz) 1.57—1.66 (1 H, D_2O exchangeable OH), 1.67 (6 H, s, 2 × Me), 4.56 (2 H, s, CH_2OH), and 6.60—6.86 (3 H, m, ArH).

2,2-*Dimethyl*-1,3-*benzodioxol*-5-*ylmethyltriphenylphosphonium Chloride* (**42**).—The alcohol (**40**) was converted into the chloride (**41**) (100%) by a method similar to that used for the preparation of compound (**32**). The chloride (**41**) was obtained as an oil, b.p. 80—85 °C at 0.01 mmHg which quickly became dark on exposure to light and air; δ_H(80 MHz) 1.67 (6 H, s, 2 × Me), 4.51 (2 H, s, CH_2), and 6.58—6.89 (3 H, m, ArH); *m/z* 200, 198 (M^+). The chloride was converted into the hygroscopic *salt* (**42**) (90%) in a manner similar to that used in the preparation of compound (**33**). It crystallized from dichloromethane–light petroleum as prisms, m.p. 254—256 °C (Found: C, 67.65; H, 5.85; Cl, 7.15. $C_{28}H_{26}ClO_2P{\cdot}2H_2O$ requires C, 67.65; H, 6.1; Cl, 7.15%); δ_H(80 MHz) 1.59 (6 H, s, 2 × Me), 5.38 (2 H, d, $J_{CH_2,P}$ 14.0 Hz, CH_2) 6.33—6.58 (3 H, m, ArH), and 7.46—7.94 (15 H, m, Ph).

Ethyl 8-(2,2-*Dimethyl*-1,3-*benzodioxol*-5-*yl*)*octanoate* (**43**).—This compound was prepared from the foregoing phosphonium salt (**42**) in a manner analogous to that described for the preparation of its isomer (**34**). The *ester* (**43**) (98%) was obtained as an oil, b.p. 180—185 °C at 0.01 mmHg (Found: C, 71.3; H, 8.95%; M^+, 320. $C_{19}H_{28}O_4$ requires C, 71.2; H, 8.8%; *M*, 320); δ_H(80 MHz) 1.25 (3 H, t, Me), 1.27—1.63 (10 H, br, CH_2), 1.65 (6 H, s, 2 × Me), 2.29 (2 H, t, CH_2CO), 2.50 (2 H, t, CH_2Ar), 4.12 (2 H, q, CH_2O), and 6.48—6.70 (3 H, m, Ph); $\nu_{max.}$(film) 1 735 cm^{-1}.

8-(2,2-*Dimethyl*-1,3-*benzodioxol*-5-*yl*)*octan*-1-*ol* (**44**).—The foregoing ester (**43**) was reduced in a manner similar to that described for the preparation of compound (**24**). The *alcohol* (**44**) (100%) was obtained as an oil, b.p. 190—195 °C at 0.01 mmHg (Found: C, 73.1; H, 9.35%; M^+, 278. $C_{17}H_{26}O_3$ requires C, 73.35; H, 9.4%; *M*, 278); δ_H(80 MHz) 1.21—1.60 (13 H, br, CH_2 and D_2O exchangeable OH), 1.66 (6 H, s, 2 × Me), 2.50 (2 H, t, CH_2Ar), 3.63 (2 H, t, CH_2OH), and 6.49—6.73 (3 H, m, ArH).

8-(2,2-*Dimethyl*-1,3-*benzodioxol*-5-*yl*)*octanal* (**45**).—The foregoing octanol (**44**) was oxidized in a manner similar to that described for its isomer (**35**). The octanal (**45**) (92%) was obtained as an oil, b.p. 170—175 °C at 0.05 mmHg; δ_H(80 MHz) 1.20—1.60 (10 H, br, CH_2), 1.66 (6 H, s, 2 × Me), 2.42 (2 H, td, *J* 7.0 and 1.8 Hz, CH_2CHO), 2.50 (2 H, t, CH_2Ar), 6.46—6.72 (3 H, m, ArH), and 9.76 (1 H, t, *J* 1.8 Hz, CHO); *m/z* 276 (M^+).

5-(*Heptadec*-8′-*enyl*)-2,2-*dimethyl*-1,3-*benzodioxole* (**46**).—This compound, prepared from the octanal (**45**) in a similar manner to that described for the preparation of compounds (**6**) and (**7**), was an oil (68%), b.p. 230 °C (block) at 0.01 mmHg (Found: C, 80.65; H, 11.1. $C_{26}H_{42}O_2$ requires C, 80.75; H, 10.95%); δ_H(300 MHz) 0.88 (3 H, t, Me), 1.18—1.39 (20 H, br, CH_2), 1.55 (2 H, quintet, CH_2CH_2Ar), 1.66 (6 H, s, Me_2), 1.93—2.06 (4 H, m, CH_2C=), 2.49 (2 H, t, CH_2Ar), 5.29—5.40 (2 H, m, HC=), and 6.54—6.64 (3 H, m, ArH); irradiation at the frequency of 7′- and 10′-H gave singlets at δ 5.35 (*Z*-olefinic H) and δ 5.38 (*E*-olefinic H); δ_C 14.14 (C-17′), 22.71 (C-16′), 25.84 (Me_2), 27.22 [C-7′ and -10′ (*Z*-isomer)], 29.12, 29.26, 29.35, 29.44, 29.56, 29.68, 29.79, 31.84, and 31.93 (each CH_2), 32.63 [C-7′ and -10′ (*E*-isomer)], 35.75 (C-1′), 107.79 and 108.65 (C-4 and -7), 117.37 (C-2), 120.34 (C-6), 129.84 and 129.95 [C-8′ and -9′ (*Z*-isomer)], 130.31 and 130.42 [C-8′ and -9′ (*E*-isomer)], 136.14 (C-5), and 145.27 and 147.29 (C-8 and -9); *m/z* 386 (M^+, 42%), 371 (14), 177 (2), 176 (5), 164 (19), 163 (100), 149 (9), 123 (39), 121 (10), and 107 (5).

4-(*Heptadec*-8′-*enyl*)*benzene*-1,2-*diol* (**47**) *and* (**48**).—This compound, prepared from the alkene (**46**) by a method similar to that used for the isomeric catechols (**4**) and (**5**), was a gum (99%) which solidified to a waxy solid at −10 °C; it rapidly darkened on exposure to light and air (Found: C, 79.45; H, 10.9. $C_{23}H_{38}O_2$ requires C, 79.7; H, 11.05%); δ_H(300 MHz) 0.88 (3 H, t, Me), 1.20—1.38 (20 H, br, CH_2), 1.55 (2 H, m, CH_2CH_2Ar), 1.90—2.08 (4 H, m, CH_2C=), 2.48 (2 H, t, CH_2Ar), 5.25 (1 H, s,

D_2O exchangeable OH), 5.29—5.41 (3 H, m, HC= and D_2O exchangeable OH), 6.60 (1 H, dd, $J_{5,3}$, 1.9 $J_{5,6}$ 8.0 Hz, 5-H), 6.69 (1 H, d, $J_{3,5}$ 1.9 Hz, 3-H), and 6.76 (1 H, d, $J_{6,5}$ 8.0 Hz, 6-H); irradiation, after D_2O exchange, at the frequency of the 7′- and 10′H gave singlets at δ5.34 (*Z*-olefinic H) and at δ 5.38 (*E*-olefinic H); δ_C 14.13 (C-17′), 22.69 (C-16′), 27.21 [C-7′ and C-10′ (*Z*-isomer)], 29.11, 29.22, 29.25, 29.33, 29.42, 29.54, 29.66, 29.77, 31.60, and 31.91 (each CH_2), 35.24 (C-1′), 115.20 and 115.49 (C-3 and C-4), 120.75 (C-5), 129.85 and 129.97 [C-8′ and -9′ (*Z*-isomer)], 130.31 and 130.43 [C-8′ and -9′ (*E*-isomer)], 136.23 (C-4), and 141.21 and 143.35 (C-1 and C-2); *m*/*z* 346 (M^+, 9%), 177 (1), 136 (14), 124 (18), 123 (100), and 91 (2); $\nu_{max.}$(film) 3 370s, 3 000w, 2 930s, 2 855s, 1 604m, 1 520m, 1 465m, 1 455m, 1 445m, 1 352w, 1 280m, 1 190w, 1 108m, 950w, 860w, 805w, 780w, and 718w cm^{-1}. G.l.c. analysis of the bis(*O*-trimethylsilyl) derivatives under the conditions used for the alkene mixture (**4**) and (**5**) revealed the presence of 90.1% *Z*-isomer (**47**) (R_t 51.22 min) and 9.9% *E*-isomer (**48**) (R_t 51.45 min). The presence of compound (**47**) in derivatized Burmese lac was confirmed by co-injection.

(Z,Z)-3-(*Heptadeca*-8′,11′-*dienyl*)-1,2-dimethoxybenzene (**2**).—A solution of butyl-lithium (0.5 ml; 1.6M) in hexane was added to a stirred solution of (*Z*)-non-3-enyltriphenylphosphonium iodide (410 mg)[18] in anhydrous tetrahydrofuran (10.25 ml) under an argon atmosphere at −78 °C. The solution was stirred at −78 °C for 20 min and then anhydrous hexamethylphosphoric triamide (1.66 ml) was added followed by the dropwise addition of the octanal (**25**) (140 mg) in anhydrous tetrahydrofuran (3.0 ml). The solution was stirred at −78 °C for 0.5 h and the cooling bath was then removed. When the solution had attained 0 °C it was poured into water and the crude product was isolated by extraction with ethyl acetate. Purification by radial chromatography with light petroleum as eluant gave first the diene (**2**) (66 mg, 93%). Later fractions yielded the octanal (**25**) (90.0 mg). The *diene* (**2**) was obtained as a viscous oil (Found: C, 80.6; H, 10.6%; M^+, 372. $C_{25}H_{40}O_2$ requires C, 80.6; H, 10.8%; *M*, 372); it was identical with the natural derivative (^1H and ^{13}C n.m.r., mass and i.r. spectra).

(Z,Z)-4-(*Heptadeca*-8′,11′-*dienyl*)-2,2-*dimethyl*-1,3-*benzodioxole* (**49**).—This compound, prepared in 79% yield from the octanal (**39**) by a method similar to that described for the synthesis of compound (**2**), was obtained as a thick oil (Found: C, 81.1; H, 10.6%; M^+, 384. $C_{26}H_{40}O_2$ requires C, 81.2; H, 10.5%; *M*, 384); δ_H(300 MHz) 0.89 (3 H, t, 17′-Me), 1.21—1.42 (14 H, m, CH_2), 1.53—1.64 (2 H, m, 2′-CH_2), 1.66 (6 H, s, 2-Me_2), 2.00—2.10 (4 H, m, 7′-and 13′-CH_2), 2.53 (2 H, t, 1′-CH_2),2.77(2H,t,$J_{10',9'}$ = $J_{10',11'}$ = 5.81Hz,10′-CH_2)5.27—5.43 (4 H, m, 8′-, 9′-, 11′-, and 12′-H), 6.58 (1 H, dd, $J_{5,6}$ 7.49 Hz, $J_{5,7}$ 1.42 Hz, 5-H), 6.61 (1 H, dd, $J_{7,6}$ 8.69 Hz, $J_{7,5}$ 1.42 Hz, 7-H), and 6.70 (1 H, apparent t, 6-H); δ_C 14.06 (C-17′), 22.57 (C-16′), 25.62 (C-10′), 25.88 (Me_2), 27.22 (C-7′ and -13′), 29.25, 29.34, 29.38, and 29.63 (each CH_2), 105.99 (C-7), 116.87 (C-2), 120.59 and 121.82 (C-5 and -6), 123.98 (C-4), 127.91 and 127.96 (C-9′ and -11′), 130.11 and 130.17 (C-8′ and -12′), and 145.33 and 146.71 (C-8 and -9).

(Z,Z)-3-(*Heptadeca*-8′,11′-*dienyl*)*benzene*-1,2-*diol* (**1**).—Acetic acid (8 ml) and water (2 ml) were boiled under reflux under argon for 0.5 h. The solution was allowed to cool under argon and the foregoing benzodioxole (**49**) (120 mg) was added; the solution was then stirred at 110 °C (bath), under argon, for 18 h. The crude product was isolated with ethyl acetate and purified by radial chromatography with 10% ethyl acetate–light petroleum as eluant. The starting material (17.0 mg) was isolated from a band of high R_F and this was followed by the *diene* (**1**) (87 mg, 94%) which was obtained as a thick oil which rapidly darkened on exposure to light and air (Found: C, 80.0; H, 10.45. $C_{23}H_{36}O_2$ requires C, 80.2; H, 10.55%); δ_H(300 MHz) 0.89 (3 H, t, 17′-Me), 1.21—1.42 (14 H, br, CH_2), 1.60 (2 H, quintet, 2′-CH_2) 2.00—2.08 (4 H, m, 7′-and 13′-CH_2), 2.59 (2 H, t, 1′-CH_2), 2.77 (2 H, t, $J_{10',9'}$ = $J_{10',11'}$ = 6.0 Hz, 10′-CH_2), 5.26—5.44 (6 H, m, 8′-, 9′-, 11′- and 12′-H, and 2 × D_2O exchangeable OH), and 6.67—6.75 (3 H, m, ArH); δ_C 14.07 (C-17′), 22.58 (C-16′), 27.21 (C-7′ and -13′), 29.25, 29.35, 29.42, 29.50, 29.66, 29.74, and 31.52 (each CH_2), 112.88 (C-6), 120.11 (C-5), 122.10 (C-4), 127.94 and 127.98 (C-9′ and -11′), 129.39 (C-3), 130.15 and 130.22 (C-8′ and C-12′), 141.67 (C-1), and 142.99 (C-2); *m*/*z* 344 (M^+, 5%), 189 (4), 163 (9), 151 (3), 149 (7), 137 (8), 136 (26), 124 (25), 123 (100), 111 (2), 109 (11), 97 (4), and 95 (18); $\nu_{max.}$(film) 3 445s, 3 015m, 2 925s, 2 855s, 1 620w, 1 596m, 1 477s, 1 355m, 1 278s, 1 238w, 1 182w, 1 153w, 1 100w, 1 060w, 960w, 828w, 772m, and 729m cm^{-1}. The bis(*O*-trimethylsilyl) derivative was subjected to g.l.c. under the conditions described for the alkene mixture (**4**) and (**5**) which demonstrated the homogeneity of the synthetic material which had R_t 50.70 min. The presence of compound (**1**) in Burmese lac was demonstrated by co-injection with the derivatized lac.

(Z,Z)-6-(*Heptadeca*-8′,11′-*dienyl*)-2,2-*dimethyl*-1,2-*benzodioxole* (**50**).—This compound, prepared in 85% yield from the octanal (**45**) by a method similar to that described for the synthesis of compound (**2**), was obtained as a thick oil (Found: C, 81.15; H, 10.55; M^+, 384. $C_{26}H_{40}O_2$ requires C, 81.2; H, 10.5%; *M*, 384); δ_H(300 MHz) 0.89 (3 H, t, 17′-Me), 1.23—1.41 (14 H br, CH_2), 1.50—1.61 (2 H, m, 2′-CH_2), 1.65 (6 H, s, 2-Me_2), 2.00—2.10 (4 H, m, 7′-and 13′-CH_2), 2.50 (2 H, t, 1′-CH_2), 2.77 (2 H, t, $J_{10',9'}$ = $J_{10',11'}$ = 5.80 Hz, 10′-CH_2), 5.28—5.43 (4 H, m, 8′-, 9′-, 11′-, and 12′-H), and 6.54—6.64 (3 H, m, ArH); δ_C 14.07 (C-17′), 22.58 (C-16′), 25.66 (C-10′), 25.84 (Me_2), 27.23 (C-7′ and -13′), 29.25, 29.36, 29.42, 29.68, 31.54, and 31.80 (each CH_2), 35.75 (C-1′), 107.78 and 108.83 (C-4 and -7), 117.35 (C-2), 120.34 (C-6), 127.94 and 128.00 (C-9′ and -11′) 130.12 and 130.16 (C-8′ and -12′), 136.11 (C-5), and 145.29 and 147.31 (C-8 and -9).

(Z,Z)-4-(*Heptadeca*-8′,11′-*dienyl*)*benzene*-1,2-*diol* (**3**).—Deprotection of the benzodioxole (**50**) in a manner similar to that described for the preparation of compound (**1**) gave the *catechol* (**3**) (87%) as a viscous oil which rapidly darkened on exposure to light and air (Found: C, 80.0; H, 10.6. $C_{23}H_{36}O_2$ requires C, 80.2; H, 10.55%); δ_H(300 MHz) 0.89 (3 H, t, 17′-Me), 1.21—1.41 (14 H, br, CH_2), 1.55 (2 H, quintet, 2′-CH_2), 1.98—2.10 (4 H, m, 7′- and 13′-CH_2), 2.47 (2 H, t, 1′-CH_2), 2.77 (2 H, t, $J_{10',9'}$ = ${}_{10',11'}$ = 5.87 Hz, 10′-CH_2), 5.28—5.44 (6 H, m, 8′-, 9′-, 11′-, and 12′-H, and 2 × D_2O exchangeable OH), 6.60 (1 H, dd, $J_{5,6}$ 8.0 Hz, $J_{5,3}$ 1.9 Hz, 5-H), 6.69 (1 H, d, $J_{3,5}$ 1.9 Hz, 3-H), and 6.76 (1 H, d, $J_{6,5}$ 8.0 Hz, 6-H); δ_C 14.00 (C-17′), 22.58 (C-16′), 25.65 (C-10′) 27.23 (C-7′ and -13′), 29.22, 29.26, 29.36, 29.42, 29.68, 31.54, and 31.60 (each CH_2), 115.25 and 115.53 (C-3 and -6), 120.76 (C-5), 127.96 and 128.00 (C-9′ and -11′), 130.17 and 130.25 (C-8′ and -12′), 136.23 (C-4), 141.23 (C-1), and 143.36 (C-2), *m*/*z* 344 (M^+, 5%), 163 (8), 149 (12), 137 (7), 136 (19), 124 (18), 123 (100), 111 (1), 109 (7), 97 (2), and 95 (13); $\nu_{max.}$(film) 3 370s, 3 010m, 2 925s, 2 855s, 1 605m, 1 518s, 1 442m, 1 355m, 1 280s, 1 190m, 1 150w, 1 110m, 950w, 865w, 810w, 785w, and 715m cm^{-1}. The bis(*O*-trimethylsilyl)ether was homogeneous by g.l.c. under the previously described conditions when it had R_t 51.11 min. The presence of compound (**3**) in Burmese lac was demonstrated by co-injection with the derivatized lac.

References

1 A. Jefferson and S. Wangchareontrakul, *J. Chromatog.*, 1986, **367**, 145.

2 A. Jefferson, M. V. Sargent, and S. Wangchareontrakul, *Aust. J. Chem.*, 1988, **41**, 19.

3 Y. Du, R. Oshima, Y. Yamauchi, J. Kumanotani, and T. Miyakoshi, *Phytochemistry*, 1986, **25**, 2211.

4 J. H. P. Tyman and A. J. Mathews, *J. Chromatog.*, 1982, **235**, 149; Y. Yamauchi, R. Oshima, and J. Kumanotani, *ibid.*, 1982, **243**, 71; Y. Du and R. Oshima, *ibid.*, 1984, **284**, 463; Y. Du, R. Oshima, H. Iwatsuki, and J. Kumanotani, *ibid.*, 1984, **295**, 179.

5 M. A. ElSohly, P. D. Adawadkar, C.-Y. Ma, and C. E. Turner, *J. Nat. Prod.*, 1982, **45**, 532.

6 C. P. Gorst-Allman, P. S. Steyn, T. Heyl, M. J. Wells, and D. M. C. Fourie, *S. Afr. J. Chem.*, 1987, **40**, 82.

7 J. H. P. Tyman and C. H. Khor. *Chem. Ind.*, 1974, **41**, 526.

8 H. Halim, H. D. Locksley, and J. J. Memon, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2331.

9 J. Bus, I. Sies, and M. S. F. L. K. Jie, *Chem. Phys. Lipids*, 1976, **17**, 501.

10 H. S. Mason, *J. Am. Chem. Soc.*, 1945, **67**, 1538.

11 G. B. Brown, M. D. Armstrong, A. W. Mozer, W. P. Anslow, Jr., B. R. Baker, M. V. Querry, S. Bernstein, and S. R. Safir, *J. Org. Chem.*, 1947, **12**, 160.

12 R. K. Clark, Jr., and J. R. Schenck, *Arch. Biochem. Biophys.*, 1952, **40**, 270.

13 R. Brezny and A. Pufflerova, *Collect. Czech. Chem. Commun.*, 1978, **43**, 3263.

14 W. J. Dejarlais and E. A. Emken, *Lipids*, 1976, **11**, 594.

15 I. Gosney and A. G. Rowley in 'Organophosphorus Reagents in Organic Synthesis' ed. J. I. G. Cadogan, Academic Press, London, 1979, Ch. 2.

16 E. J. Corey and S. D. Hurt, *Tetrahedron Lett.*, 1977, 3923.

17 G. Slooff, *Rec. Trav. Chim.*, 1935, **54**, 995.

18 N. Cohen, B. L. Banner, R. J. Lopresti, F. Wong, M. Rosenberger, Y. Y. Liu, E. Thorn, and A. A. Liebman, *J. Am. Chem. Soc.*, 1983, **105**, 3661.

19 *Cf.* M. Sato, *Yukagaku*, 1973, **22**, 349 (*Chem. Abstr.*, 1973, **79**, 136684q).

Received 24*th May* 1988; *Paper* 8/02067A