Stereoselective Synthesis of Solanesol and all-*trans*-Decaprenol

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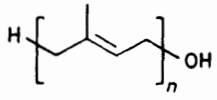
Allylic *p*-tolyl sulphones (5), (14), and (16) couple with allylic bromide (7) and geranyl bromide to produce regio- and stereo-chemically pure 1,5-diene systems. The coupling of all-*trans*-ω-bromogeranyl acetate (7) with geranyl *p*-tolyl sulphone (5) and higher isoprenologues (21), (24), and (27), followed by reductive elimination of *p*-tolylsulphonyl group, furnishes a stereoselective synthesis of all-*trans*-polyprenols (3), (23),(26), and decaprenol (1b). Solanesol (1a) was synthesised using *trans*-4-chloroprenyl acetate (29) instead of (7).

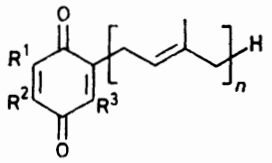
SOLANESOL (1a) has been isolated from tobacco leaves,[1] mulberry leaves,[2] and from unsaponifiable matter of silkworm faeces.[2] Analogous alcohols such as decaprenyl alcohol (1b), undecaprenyl alcohol (1c), and dodecaprenyl alcohol (1d) have also been found in mulberry leaves.[2,3]



(1)

a; $n = 9$
b; $n = 10$
c; $n = 11$
d; $n = 12$

Solanesol and its analogues are important materials for the synthesis of biologically active isoprenoid quinones.[4] For example, ubiquinone (coenzyme Q) (2a) has been prepared by the condensation of 2,3-dimethoxy-5-methylhydroquinone with the isoprenoid alcohol (1),[5] and menaquinones (vitamin K_2) (2b) have been prepared from 2-methyl-1,4-naphthohydroquinone and



(2)

a; $R^1 = R^2 = MeO$, $R^3 = Me$
b; $R^1—R^2 = —CH=CH—CH=CH—$, $R^3 = Me$
c; $R^1 = R^2 = Me$, $R^3 = H$
d; $R^1 = R^3 = Me$, $R^2 = NH_2$

(1).[6,†] Plastoquinones (2c) and rhodoquinones (2d) are also among the same kind of compounds.

Because of their importance for the synthesis of isoprenoid quinones of biological importance and their minute occurrence in quantity in natural products, it would clearly be desirable to have synthetic access to all-*trans*-polyprenyl alcohols. In this paper we report stereoselective syntheses of all-*trans*-polyprenyl alcohols up to C_{50} including solanesol (C_{45}). Solanesol (1a) [9] and all-*trans*-decaprenyl alcohol (1b) [10] have previously been synthesized by Isler *et al.* in a nonstereoselective fashion by means of the sequential C_2 and C_3 extension of the requisite carbon skeleton.

The recent need for stereochemically pure 1,5-dienes in the field of natural insect hormones and in the study of biogenetic-like cyclizations of polyolefinic compounds has greatly stimulated research on the stereoselective synthesis of trisubstituted olefins,[11] resulting in the invention of many excellent methods. However, most of these consist of extension of a carbon skeleton by one C_5 or smaller unit at a time. Because of the unstable nature of polyenes to heat and acids, stepwise construction of the polyene systems by at least C_{10} extension would be favourable for the current synthetic purposes.

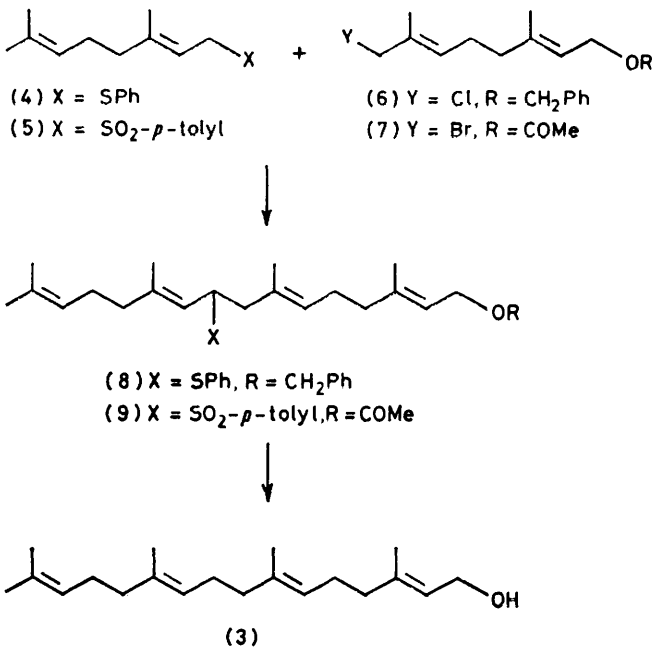
Altman *et al.*[12] have reported the synthesis of all-*trans*-geranylgeraniol (3) originating from geraniol, which utilized ω-chlorogeranyl benzyl ether (6) to alkylate the carbanion derived from geranyl phenyl sulphide (4), followed by reductive cleavage of the phenylthio and benzyl groups in the coupling product (8). In order to synthesize all-*trans*-geranylgeraniol and polyprenyl alcohols, the reaction sequence was modified so as to facilitate operations on a larger scale (Scheme 1).

Thus, (2*E*,6*E*)-8-bromo-3,7-dimethylocta-2,6-dienyl acetate (7) was used as the key intermediate in our synthesis to alkylate the sulphone-stabilized allylic carbanion derived from *trans*-geranyl *p*-tolyl sulphone (5). Stereoselective oxidation [13] of geranyl acetate with 1.2 equiv. of selenium dioxide as described [14] gave rise to the aldehyde (10) in 44% yield (Scheme 2). The alcohol (11) was obtained by borohydride reduction of (10) at low temperature in anhydrous methanol, whereas similar treatment of (10) with sodium borohydride in 95% ethanol at 0 °C [14] resulted in competitive formation of the diacetate (11-acetate). The corresponding bromide (7) was prepared by the usual procedure and utilized to alkylate 1-*p*-tolylsulphonylgeranyl-lithium. An arylsulphonyl group rather than an arylthio group was chosen because of its easy preparation, powerful activating effect, and ease of removal by reduction or elimin-

† Compounds (2a) and (2b) have also been prepared by coupling reactions using protected quinones and/or polyisoprenoid compounds (refs. 7 and 8).

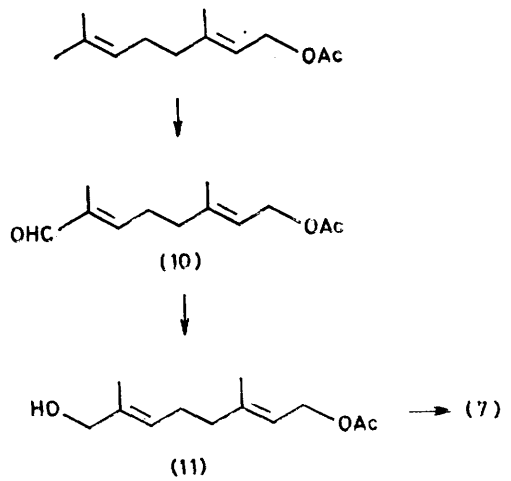
ation.[15] The sulphone (5) was obtained from *trans*-geraniol *via trans*-geranyl bromide in a high overall yield, as described.[16]

Allylic cross-coupling was performed by metallation of



SCHEME 1

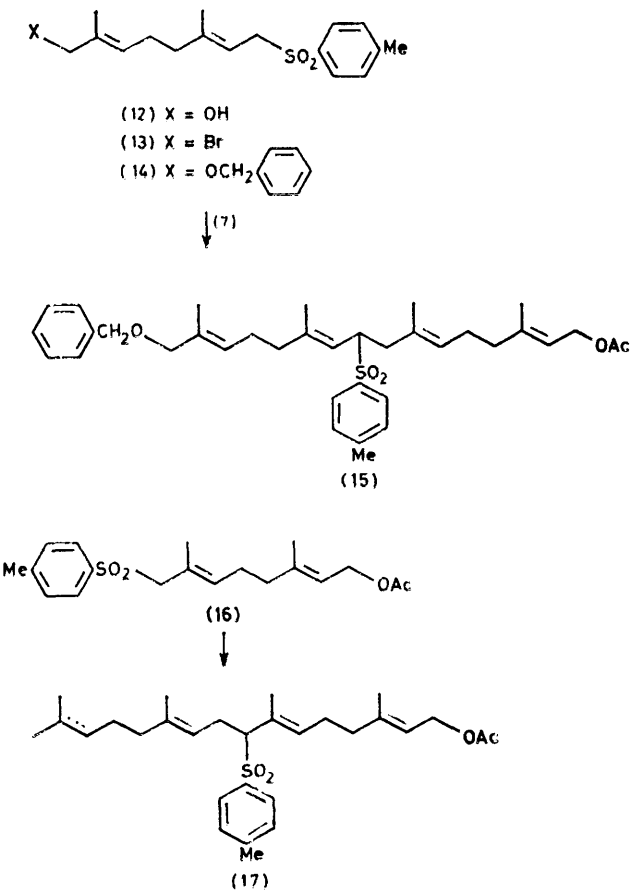
the sulphone (5) with n-butyl-lithium in tetrahydrofuran–hexamethylphosphoramide (4 : 1) followed by addition of the bromide (7) at −78 °C, resulting in formation of the pure sulphone (9) in 79% yield. Coupling at the γ position or geometrical isomerization during the reaction was rigorously ruled out by ^{1}H n.m.r. spectroscopy and by g.l.c. analysis of the product derived from



SCHEME 2

reductive cleavage of the sulphone moiety (see later). In the ^{1}H n.m.r. spectrum of the sulphone (9) the methyl group at C-11 (γ to the allylic sulphonyl group) appeared at a high field (δ 1.21) and no signals were observed near δ 1.70 (assignable to the *cis* olefinic methyl group) or near δ 6.60 (assignable to the β-sulphonyl-vinyl proton), indicating complete retention of geometry and stereochemistry of the allyl sulphone moiety.[17]

The allylic cross-coupling reaction was also employed for the synthesis of $\alpha\omega$-disubstituted geranylgeraniol (15), which was thought to serve as a synthon in the preparation of polyprenyl alcohols. Thus, the sulphone (5) was oxidized with selenium dioxide, the product then being treated with sodium borohydride, yielding *trans*-ω-hydroxygeranyl *p*-tolyl sulphone (12) in 55% overall yield (Scheme 3). The alcohol (12) was converted *via* the bromide (13) into the benzyl ether (14). Metallation of the sulphone (14) with n-butyl-lithium in tetrahydrofuran–hexamethylphosphoramide followed by addition



SCHEME 3

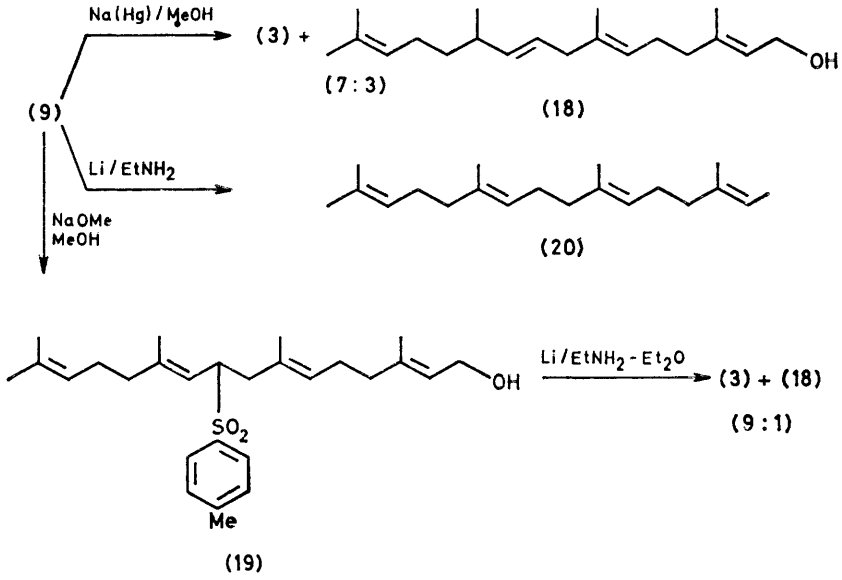
of the bromide (7) resulted in formation of a new sulphone (15) in 60% yield. Exclusive coupling at the α-position and retention of configuration were again confirmed by the ^{1}H n.m.r. spectrum.

As an alternative route to geranylgeraniol, we examined the coupling between ω-toluene-*p*-sulphonyl-geranyl acetate (16) and geranyl bromide. Thus, metallation of the sulphone (16), obtained from the bromide (7), with n-butyl-lithium was performed in tetrahydrofuran–hexamethylphosphoramide (4 : 1) at

—78 °C; geranyl bromide was then treated with the anion. Isolation by chromatography on silica gel gave the coupled sulphone (17) in 49% yield (based on the consumed bromide) along with a 42% recovery of geranyl bromide. There seemed to be some trouble in generating the carbanion from (16); however, the reaction was not investigated further, and was abandoned for further application to the synthesis of higher isoprenologues of (3).

Reductive cleavage of the carbon–sulphur bond of the sulphone (9) was first carried out by exposure to sodium amalgam in anhydrous methanol at 0 °C for 1.5 h,[18]

The allylic cross-coupling reaction and lithium–ethylamine reduction were also employed for the synthesis of farnesylfarnesol (23), octaprenol (26), and decaprenol (16). Thus, the all-*trans*-polyprenols (3), (23), and (26) were converted *via* their bromides into the corresponding sulphones (21), (24), and (27) in high yields (Scheme 5). The carbanions derived from the above sulphones were coupled with (7) to afford the coupled compounds (22a), (25a), and (28a), respectively, in good yields; these were then hydrolysed to the corresponding hydroxy-sulphones (22b), (25b), and (28b) respectively. More conveniently, the allylic cross-



SCHEME 4

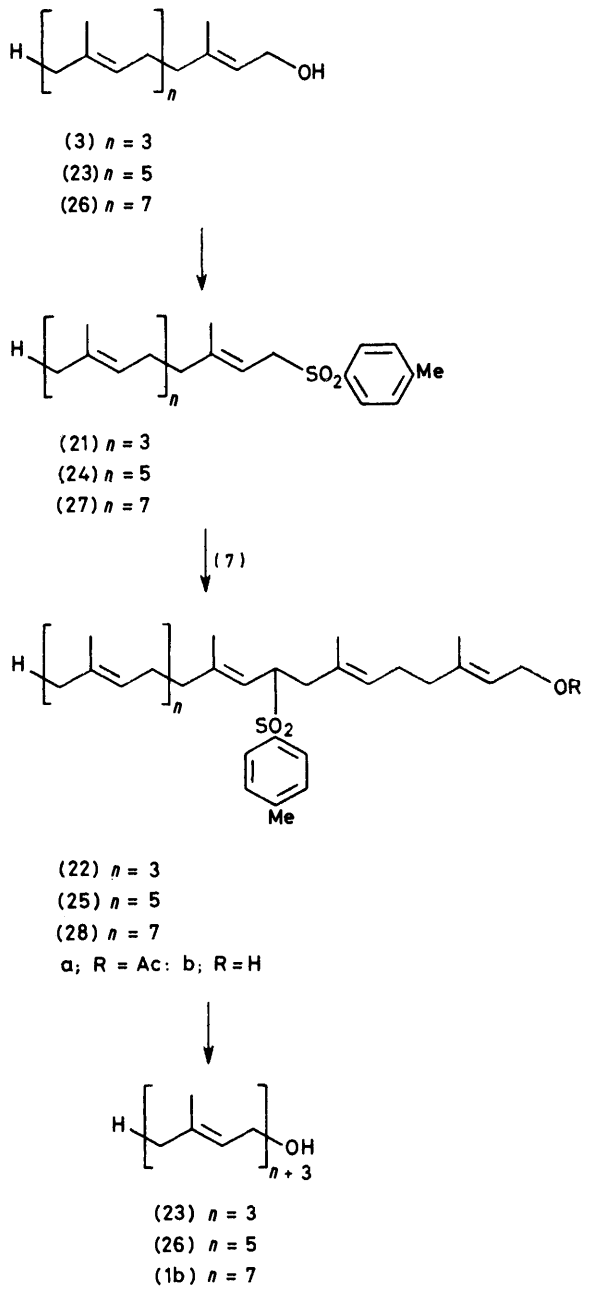
affording a mixture of the expected all-*trans*-geranylgeraniol (3) and the rearranged all-*trans*-tetraenol (18) in a ratio of 7 : 3; these products were separated by conventional chromatography on silica gel only with difficulty. Similar treatment of the hydroxy-sulphone (19) with sodium amalgam gave the same result (Scheme 4). Our results of the reductive cleavage are consistent with the earlier observations by Grieco [16] on the synthesis of bisgeranyl.

When the sulphone (9) was exposed to lithium in ethylamine at —78 °C for a short period, simultaneous reductive cleavage of the toluene-*p*-sulphonyl and acetoxy groups took place to afford the tetraene (20) in 70% yield. The best result was obtained when the hydroxy-sulphone (19) was treated with lithium in ethylamine with ether as co-solvent at —78 °C. The product consisted of (3) and (18) in the ratio 9 : 1, from which pure (3) was isolated by chromatography on silver nitrate-impregnated silica gel. The structure was confirmed by the ^{1}H n.m.r. spectrum and comparison (g.l.c.) of the acetate with an authentic sample under conditions which enabled us to distinguish between (2*E*,6*E*,10*E*)-, (2*E*,6*E*,10*Z*)-, (2*E*,6*Z*,10*E*)- and (2*E*,6*Z*,10*Z*)-isomers.

coupling reaction and the subsequent hydrolysis were performed in one pot to give the hydroxy-sulphones directly. Reductive elimination of the sulphonyl group of the coupled alcohols was carried out at —78 °C with lithium in ethylamine to afford the expected polyprenyl alcohols (23), (26), and (1b), together with the conjugate-reduction products in the ratio 9 : 1 (^{1}H n.m.r.). Although the alcohols were purified by careful chromatography on silver nitrate-impregnated silica gel, purification was more conveniently performed in the case of (23) and (26) after conversion into the corresponding sulphones. The structure of the final product, decaprenol (1b), was confirmed by ^{1}H n.m.r. and i.r. spectroscopy and by mixed melting point with an authentic sample prepared from natural solanesol.

We next examined the allylic cross-coupling reaction between the sulphone (5) and (*E*)-1-chloro-4-acetoxy-2-methylbut-2-ene (29) [19] as a model reaction for the synthesis of solanesol (1b), one of the polyprenyl alcohols having an odd number of isoprene units (Scheme 6). Coupling of *trans*-geranyl sulphone (5) with the chloride (29) followed by methanolysis gave the hydroxy-sulphone (30) in 85% yield. Reductive cleavage of the sulphone provided farnesol (31) in 55% yield, but g.l.c.

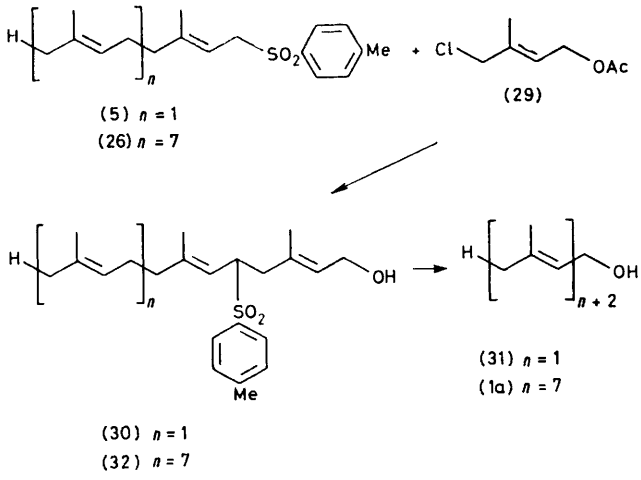
analysis of the product showed the presence of three by-products totalling 40% of the mixture. The farnesol was isolated after column chromatography in 28% yield, and the by-products were also isolated and identified as *cis,trans*-farnesol, (2*Z*,5*E*,10*E*)-3,7,11-trimethyldodeca-2,5,10-trienol, and (2*Z*,5*E*,10*E*)-3,7,11,trimethyldodeca-2,5,10-trienol based on their i.r. and ^{1}H n.m.r. spectra.



SCHEME 5

Considerable isomerization and conjugate reduction seem to be caused by the presence of a hydroxy-function close to the sulphonyl group. The all-*trans*-octaprenyl sulphone (26) was carried through the same three-step reaction sequence to produce solanesol (1a) in 50% yield [based on the coupled sulphone (32)].

As shown here, the coupling reaction of a reactive carbanion of a polyprenyl compound with ω-*trans*-halogenogeraniol or ω-*trans*-halogenoprenol derivatives



SCHEME 6

followed by reductive desulphonylation could well provide a general stereoselective synthesis of all-*trans*-polyprenyl alcohols.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded for CCl_4 solutions with a JEOL C-60 spectrometer using tetramethylsilane as an internal standard. I.r. spectra were taken for neat films on a Hitachi Model 215 spectrophotometer; mass spectra were determined on a Hitachi RMU-6E spectrometer. G.l.c. analyses were performed with Shimazu GC-4A or GC-3B instruments using the following columns: 3 m × 3 mm, 10% Carbowax 20M on 60—80 mesh Neopak 1A; 3 m × 3 mm, 20% Silicone DC 200 on 60—80 mesh Celite 545; 3 m × 3 mm, 5% Silicone OV-210 on 60—80 mesh Chromosorb W. Liquid column chromatography was carried out on Wakogel C-200. Silver nitrate-impregnated silica gel was prepared for column chromatography by addition of a solution of silver nitrate in acetonitrile to the silica gel and then removal of the solvent on a rotary evaporator. Tetrahydrofuran (THF) was dried by distillation from lithium aluminium hydride; hexamethylphosphoramide (HMPA) was dried by distillation from calcium hydride.

(2E,6E)-8-*Acetoxy*-2,6-*dimethylocta*-2,6-*dienal* (10).—Selenium dioxide (46.6 g, 0.42 mol) in 95% ethanol (500 ml) was added to a solution of geranyl acetate (68.6 g, 0.35 mol) in 95% ethanol (200 ml) under reflux over 2 h. The mixture was stirred under reflux for a further 7 h, filtered, and concentrated. The residue was dissolved in ether (300 ml), washed (aq. $NaHCO_3$, H_2O, and aq. NaCl), and dried ($MgSO_4$). Distillation gave the aldehyde (10) (32.3 g, 44%); $\nu_{max.}$ 1 740 (C=O), 1 690 (CH=O), and 1 235 cm^{-1}, δ 1.74 (6 H, s, CH_3), 1.96 (3 H, s, CH_3CO), 2.35 (4 H, m, CH_2CH_2), 4.55 (2 H, d, *J* 6.5 Hz, CH_2O), 5.38 (1 H, t, *J* 6.5 Hz, CH=), 6.40 (1 H, t, *J* 6.5 Hz, CH=), and 9.35 (1 H, s, CHO).

(2E,6E)-8-*Acetoxy*-2,6-*dimethylocta*-2,6-*dien*-1-*ol* (11).—To a solution of (10) (23.3 g, 0.11 mol) in anhydrous methanol

(250 ml) was added a solution of sodium borohydride (1.97 g, 0.055 mol) in anhydrous methanol (30 ml) at −10 °C over 1 h. After the mixture had been stirred for further 4 h, the excess of borohydride was decomposed by addition of saturated aqueous ammonium chloride. The mixture was poured into aqueous sodium chloride (300 ml) and extracted with ether. The extract was washed (aq. $NaHCO_3$ and aq. NaCl), dried ($MgSO_4$), and distilled to give the alcohol (11) (16.8 g, 72%), b.p. 114—122 °C at 0.3 mmHg; $\nu_{max.}$ 3 400 (OH), 1 740 (C=O), and 1 240 cm^{-1}; δ 1.65 (3 H, s, CH_3), 1.74 (3 H, s, CH_3), 2.00 (3 H, s, CH_3CO), 2.12br (4 H, s, CH_2CH_2), 3.37 (1 H, s, OH), 3.92 (2 H, s, CH_2OH), 4.56 (2 H, d, *J* 7 Hz, CH_2OAc), and 5.35 (2 H, t, *J* 7 Hz, CH=).

When the reaction was carried out in 95% ethanol at 0 °C, the product was obtained with a contaminant (*ca.* 10%) of (2*E*,6*E*)-2,6-dimethylocta-2,6-diene-1,8-diyl diacetate, $\nu_{max.}$ 2 930, 1 735, 1 240, and 1 030 cm^{-1}; δ 1.68 (3 H, s, CH_3), 1.75 (3 H, s, CH_3), 1.99 (3 H, s, CH_3CO), 2.01 (3 H, s, CH_3CO), 2.11br (4 H, s, CH_2CH_2), 4.41 (2 H, s, CH_2O), 4.52 (2 H, d, *J* 7 Hz, CH_2O), and 5.33br (2 H, m, CH=); *m/e* 134 (20%, M^+ −2AcOH), 118 (22, $C_{10}H_{14}^+$ −CH_4), and 43 (100, CH_3CO^+).

(2E,6E)-8-*Bromo*-3,7-*dimethylocta*-2,6-*dienyl Acetate* (7).—To a stirred mixture of (11) (4.2 g, 20 mmol) and pyridine (0.1 ml) in dry ether (50 ml) was added phosphorus tribromide (2.3 g, 8.7 mmol) in dry ether (20 ml) at 0 °C over 1 h. After the mixture had been stirred at 0 °C for 5 h, it was poured into ice–water (100 ml) and then extracted with ether. The extract was washed (H_2O, aq. $NaHCO_3$, H_2O, and aq. NaCl), dried ($MgSO_4$), and concentrated *in vacuo* to give the acetate (7) (5.1 g, 94%), which was homogeneous on t.l.c., and was used without further purification. An analytical sample was obtained by distillation, b.p. 95—100 °C at 0.09 mmHg, n_D^{20} 1.5158; $\nu_{max.}$ 1 740 (C=O), 1 235, and 1 210 cm^{-1}; δ 1.74 (6 H, s, CH_3), 1.98 (3 H, s, CH_3CO), 2.14br (4 H, s, CH_2CH_2), 3.94 (2 H, s, CH_2Br), 4.55 (2 H, d, *J* 6.5 Hz, CH_2OAc), 5.37 (1 H, m, CH=), and 5.58 (1 H, m, CH=).

(2E,6E,10E)-3,7,11,15-*Tetramethyl*-1-p-*tolylsulphonyl*-*hexadeca*-2,6,10,14-*tetraenyl Acetate* (9).—To a stirred solution of the sulphone (5) (3.0 g, 10 mmol) in anhydrous THF–HMPA (4 : 1 v/v; 40 ml) was added a solution of n-butyl-lithium (1.6M in hexane; 6.4 ml, 10 mmol) under nitrogen at −78 °C. After 1.5 h, a solution of (7) (2.4 g, 8.7 mmol) in THF–HMPA (4 : 1, 10 ml) was added over 1 h, and the mixture was stirred for 5 h. The mixture was allowed to warm to 0 °C, poured into ice–water, and extracted with n-hexane–ether (1 : 1 v/v). The extract was washed (H_2O, aq. NaCl), dried ($MgSO_4$), concentrated, and chromatographed on silica gel. Elution with 10% diisopropyl ether–hexane gave unchanged (5) (0.9 g, 3.0 mmol), and elution with 10% ethyl acetate–hexane gave the *coupled sulphone* (9) (3.3 g, 79%); $\nu_{max.}$ 1 740, 1 600, 1 500, 1 310, 1 300, 1 290, and 1 240 cm^{-1}; δ (CCl_4) 1.21 (3 H, *J* 1.2 Hz, 11-CH_3), 1.51 (3 H, s, CH_3), 1.57 (3 H, s, CH_3), 1.65 (6 H, s, CH_3), 1.95br (13 H, s, CH_3CO and CH_2CH_2), 2.41 (3 H, s, CH_3Ar), 3.65 (1 H, dt, *J* 10 and 3 Hz, $CHSO_2$), 4.42 (2 H, d, *J* 7 Hz, CH_2OAc), 4.80—5.32 (4 H, m, CH=), and 7.18 and 7.61 (4 H, AB q, aromatic).

(2E,6E)-2,6-*Dimethyl*-8-p-*tolylsulphonylocta*-2,6-*dien*-1-*ol* (12).—A solution of selenium dioxide (20.0 g, 0.18 mol) in 95% ethanol (400 ml) was added dropwise over 3 h to a solution of (5) (52.6 g, 0.18 mol) in 95% ethanol (200 ml) under reflux, and the mixture was stirred under reflux for 8 h. After the precipitated selenium had been filtered off, a solution of sodium borohydride (4.26 g, 0.11 mol) in anhydrous methanol (60 ml) was added to the filtrate at 0 °C over 1 h, and the solution was stirred for 6 h. Treatment of the resulting mixture as described previously and chromatography of the crude product on silica gel with 5—10% ethyl acetate–hexane as eluant provided the purified sulphone (12) (30.5 g, 55%); $\nu_{max.}$ 3 500, 1 660, 1 600, 1 310, 1 300, 1 290, and 740 cm^{-1}; δ 1.38 (3 H, s, CH_3), 1.59 (3 H, s, CH_3), 2.01 and 2.07 (4 H, CH_2CH_2), 2.40 (3 H, s, $ArCH_3$), 2.65br (1 H, s, OH), 3.63 (2 H, s, *J* 8 Hz, CH_2SO_2), 3.85 (2 H, s, CH_2O), 4.94—5.25 (2 H, m, CH=), and 7.23 and 7.65 (4 H, AB q, aromatic).

(2E,6E)-1-*Benzyloxy*-2,6-*dimethyl*-8-p-*tolylsulphonylocta*-2,6-*diene* (14).—The alcohol (12) was converted into the corresponding bromide (13) with phosphorus tribromide by the usual procedure in 80% yield. Benzyl alcohol (1.17 g, 11 mmol) was treated with sodium hydride (50% in mineral oil, 0.52 g, 11 mmol) in anhydrous ether (45 ml) under reflux for 3 h. To this mixture was added a solution of the bromide (13) (4.0 g, 11 mmol) in ether (30 ml) at −10 to −5 °C. After the mixture had been stirred for 24 h, it was poured into ice–water and extracted with ether. Column chromatography of the crude product on silica gel afforded the sulphone (14) (2.20 g, 50%); $\nu_{max.}$ 1 600, 1 500, 1 320, 1 310, 1 290, 745, and 700 cm^{-1}; δ 1.34 (3 H, s, CH_3), 1.62 (3 H, s, CH_3), 2.01br (4 H, s, CH_2CH_2), 2.38 (3 H, s, CH_3Ar), 3.60 (2 H, d, *J* 7.5 Hz, CH_2SO_2), 3.80 (2 H, s, CH_2O), 4.34 (2 H, s, CH_2Ph), 4.9—5.3 (2 H, m, CH=), 7.23 (5 H, s, C_6H_5), and 7.19 and 7.64 (4 H, AB q, aromatic).

(2E,6E,10E,14E)-16-*Benzyloxy*-3,7,11,15-*tetramethyl*-9-p-*tolylsulphonylhexadeca*-2,6,10,14-*tetraenyl Acetate* (15).—To a stirred solution of (14) (1.62 g, 4.2 mmol) in anhydrous THF–HMPA (4 : 1 v/v; 40 ml) was added a solution of n-butyl-lithium (1.2M in hexane; 3.52 ml, 4.2 mmol) at −78 °C under nitrogen. After 1.5 h, a solution of (7) (0.77 g, 2.8 mmol) in anhydrous THF–HMPA (4 : 1 v/v; 10 ml) was added at −78 °C over 30 min. After stirring for 4 h, the mixture was worked up as described previously. The crude product was chromatographed on silica gel using 5—10% ethyl acetate–hexane as eluant to give the acetate (15) (0.99 g, 60%); $\nu_{max.}$ 1 740, 1 600, 1 500, 1 320, 1 310, 1 290, 740, and 700 cm^{-1}; δ 1.23 (3 H, s, CH_3 at C-11), 1.61 (9 H, s, CH_3), 1.91 and 2.01 (4 H, CH_2CH_2), 2.36 (3 H, s, CH_3Ar), 3.61 (1 H, m, $CHSO_2$), 3.76 (2 H, s, CH_2O), 4.33 (2 H, s, CH_2Ph), 4.40 (2 H, d, *J* 7 Hz, CH_2OAc), 4.78—5.39 (3 H, m, CH=), 7.16 (5 H, s, C_6H_5), 7.12 and 7.57 (4 H, AB q, aromatic).

(2E,6E)-3,7-*Dimethyl*-8-p-*tolylsulphonylocta*-2,6-*dienyl Acetate* (16).—A stirred solution of (7) (7.2 g, 26 mmol) in DMF (110 ml) was treated with anhydrous sodium toluene-*p*-sulphinate (5.1 g, 29 mmol) at room temperature for 24 h. The usual work-up followed by chromatography on silica gel gave the pure sulphone (16) (5.6 g, 62%); $\nu_{max.}$ 1 730, 1 600, 1 315, 1 305, and 1 290 cm^{-1}; δ 1.63 (3 H, s, CH_3), 1.73 (3 H, s, CH_3), 1.96 (3 H, s, CH_3CO), 1.96 and 2.01 (4 H, m, CH_2CH_2), 2.42 (3 H, s, CH_3Ar), 3.56 (2 H, s, CH_2SO_2), 4.44 (2 H, d, *J* 7 Hz, CH_2OAc), 4.98 (1 H, t, *J* 6 Hz, CH=), 5.16 (1 H, t, *J* 7 Hz, CH=), and 7.23 and 7.63 (4 H, AB q, aromatic).

(2E,6E,10E)-3,7,11,15-*Tetramethyl*-8-p-*tolylhexadeca*-2,6,10,14-*tetraenyl Acetate* (17).—The sulphone (16) (1.89 g, 5.4 mmol) in anhydrous THF–HMPA (4 : 1 v/v; 30 ml) was treated with a solution of n-butyl-lithium (2.43M; 2.22 ml, 5.4 mmol) at −78 °C for 1.5 h. Geranyl bromide

(0.98 g, 4.5 mmol) in anhydrous THF–HMPA (4 : 1 v/v; 10 ml) was added to the carbanion solution at −78 °C over 25 min. After stirring for 5 h, the mixture was worked up as described previously to give geranyl bromide (0.41 g, 42%) and the coupled sulphone (17) (0.62 g, 49% based on consumed geranyl bromide) after chromatography on silica gel; $\nu_{max.}$ 1 735, 1 600, 1 320, 1 305, 1 290, and 1 240 cm^{-1}; δ 1.61br (15 H, s, CH_3), 1.94br (13 H, s, CH_2CH_2 and CH_3CO), 2.41 (3 H, s, CH_3Ar), 3.53 (1 H, m, $CHSO_2$), 4.42 (2 H, d, *J* 7 Hz, CH_2OAc), 4.97 (4 H, m, CH=), and 7.20 and 7.57 (4 H, AB q, aromatic).

(2E,6E,10E)-3,7,11,15-*Tetramethyl*-9-p-*tolylsulphonyl*-*hexadeca*-2,6,10,14-*tetraen*-1-*ol* (19).—(*a*) The acetate (9) was stirred in methanol in the presence of a catalytic amount of sodium methoxide at room temperature for 2 h to yield the *hydroxy-sulphone* (19) in quantitative yield; n_D^{20} 1.5355; $\nu_{max.}$ 3 500, 1 600, 1 310, 1 300, 1 290, and 1 140 cm^{-1}; δ 1.21 (3 H, s, CH_3), 1.52 (3 H, s, CH_3), 1.55 (6 H, s, CH_3), 1.65 (3 H, s, CH_3), 1.94br (10 H, s, CH_2CH_2), 2.23 (1 H, s, OH), 2.41 (3 H, s, CH_3Ar), 3.75 (1 H, dt, *J* 10 and 3 Hz, $CHSO_2$), 3.97 (2 H, d, *J* 7 Hz, CH_2O), 4.90 (1 H, d, *J* 10 Hz, CH=), 5.05—5.20 (2 H, m, CH=), 5.37 (1 H, t, *J* 7 Hz, CH=), and 7.18 and 7.61 (4 H, AB q, aromatic).

(*b*) The lithium carbanion generated from (5) (1.75 g, 6.0 mmol) in THF–HMPA (4 : 1 v/v; 15 ml) with n-butyl-lithium (2.62M; 2.2 ml, 5.8 mmol) was coupled with (9) (1.10 g, 4.0 mmol) at −78 °C for 2 h. Methanol (5.0 ml) was added, and the mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was worked-up as usual. Chromatography of the crude product on silica gel using 20% ethyl acetate–hexane as eluant yielded (19) (1.41 g, 79%).

(2E,6E,10E)-3,7,11,15-*Tetramethylhexadeca*-2,6,10,14-*tetraen*-1-*ol* (*all*-trans-*Geranylgeraniol*) (3) and (2E,6E,9E)-3,7,11,15-*Tetramethylhexadeca*-2,6,9,14-*tetraen*-1-*ol* (18).—To a stirred solution of (19) (783 mg, 1.76 mmol) in anhydrous ethylamine–ether (1 : 1 v/v; 20 ml) was added lithium (246 mg, 35.2 mmol) at −78 °C. The reaction mixture turned blue after *ca.* 1 h, and it was stirred at −78 °C for a further 15 min. The excess of lithium was quenched with butadiene, then methanol (1 ml) was added to the mixture and the ethylamine was evaporated off. The residue was poured into saturated aqueous ammonium chloride and the mixture was extracted with ether. The extract was washed (H_2O, aq. NaCl), dried ($MgSO_4$), concentrated, and chromatographed on silica gel, using 10% ethyl acetate–hexane for elution, to afford geranylgeraniol (255 mg, 48%). G.l.c (OV-210, 180 °C) indicated the presence of (3) and (18) in the ratio 9 : 1.

Column chromatography of this mixture (302 mg, 9 : 1) on 5% silver nitrate-impregnated silica gel (12 g) using 15% ethyl acetate–hexane as eluant afforded the tetraenol (18) (20 mg); n_D^{20} 1.4968; $\nu_{max.}$ 3 300, 2 920, 1 450, 1 380, and 980 cm^{-1}; δ (CCl_4) 0.97 (3 H, d, *J* 6.5 Hz, CH_3CH), 1.25 (2 H, m, 12-CH_2), 1.56 (6 H, s, CH_3), 1.64 (6 H, s, CH_3), 2.01br (7 H, s, CH_2CH_2 and CH), 2.61 (2 H, m, 8-CH_2), 3.99 (2 H, d, *J* 6 Hz, CH_2O), and 4.81—5.46 (5 H, m, CH=).

Further elution using the same solvent afforded *all*-trans-*geranylgeraniol* (3) (264 mg); n_D^{20} 1.4964; $\nu_{max.}$ 3 300, 2 900, 1 660, 1 440, 1 380, and 1 000 cm^{-1}; δ 1.56 (9 H, s, CH_3), 1.64 (6 H, s, CH_3), 1.96 and 2.01 (12 H, s, CH_2CH_2), 3.70br (1 H, s, OH), 4.01 (2 H, d, *J* 6.5 Hz, CH_2O), 5.06 (3 H, m, CH=), 5.33br (1 H, t, *J* 6.5 Hz, CH=). G.l.c. of the acetate (Carbowax 20M, 200 °C) showed a single peak with a retention time of 38 min which coincided with an authentic sample of all-*trans*-geranylgeranyl acetate prepared by the known procedure [20] from *trans,trans*-farnesylacetone *via* ethyl all-*trans*-geranylgeranate, whereas isomeric acetates of *trans,cis,cis*- (25 min), *trans,cis,trans*- (29 min), and *trans,trans,cis*-geranylgeraniols (33 min), obtained from geranyl bromide and (7) by the π-allylic nickel complex-mediated coupling reaction,[21] showed individual peaks at shorter retention times.

Li-*Ethylamine Reduction of* (9).—To a solution of lithium (0.25 g, 36 mmol) in ethylamine (45 ml) was added a solution of (9) (1.18 g, 2.4 mmol) in ether (10 ml) during 5 min at −78 °C. After 25 min, the excess of lithium was destroyed with butadiene and methanol. The ethylamine was allowed to evaporate and the product was isolated by extraction and chromatography on silica gel using 5% ethyl acetate–hexane as eluant to give (2*E*,6*E*,10*E*)-2,6,10,14-tetramethylhexadeca-2,6,10,14-tetraene (0.46 g, 70%); $\nu_{max.}$ 1 450, 1 380, 1 270, 1 100, and 810 cm^{-1}; δ 1.59br (13 H, s, CH_3), 1.96br (12 H, s, CH_2CH_2), and 5.02br (4 H, m, CH=); *m/e* 274 (M^+).

Na(Hg)-*Methanol Reduction of* (9).—To a stirred mixture of (9) (1.21 g, 2.49 mmol) and disodium hydrogen phosphate (1.4 g, 10 mmol) in anhydrous methanol (30 ml) was added 5% sodium amalgam (4.5 g) at 0 °C. After the mixture had been stirred at 0 °C for 2 h, it was poured into cold water and extracted with ether. The crude product was chromatographed on silica gel with 10% ethyl acetate–hexane as eluant to give geranylgeraniol (0.36 g, 50%). G.l.c. (OV-210, 180 °C) showed the presence of (3) and (18) in the ratio 7 : 3.

Na(Hg)-*Methanol Reduction of* (19).—A mixture of (19) (3.20 g, 7.21 mmol) and disodium hydrogen phosphate (4.1 g, 28.8 mmol) and 5% sodium amalgam was stirred at 0 °C for 2 h. The resulting mixture was worked up as described above to give the purified product (1.14 g, 55%); (9) : (19) = 7 : 3.

(2E,6E,10E)-3,7,11,15-*Tetramethyl*-1-p-*tolylsulphonyl*-*hexadeca*-2,6,10,14-*tetraene* (*all*-trans-*Geranylgeranyl Toluene*-p-*sulphonyl Sulphone*) (21).—(*a*) To a stirred mixture of (3) (27.5 g, 94.8 mmol) and pyridine (2 ml) in anhydrous ether (200 ml) was added a solution of phosphorus tribromide (11.1 g, 41.1 mmol) in ether (90 ml) at −5 °C over 3 h, and the mixture was stirred for a further 3 h. The usual work-up gave (2*E*,6*E*,10*E*)-1-bromo-3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraene (all-*trans*-geranylgeranyl bromide) (30.3 g, 91%), which was used without purification for the next reaction; n_D^{20} 1.5101; $\nu_{max.}$ 2 930, 1 660, 1 450, 1 380, and 1 210 cm^{-1}. The crude geranylgeranyl bromide (23.3 g, 66 mmol) was treated with sodium toluene-*p*-sulphinate (15.3 g, 86 mmol) in DMF at ambient temperature for 24 h. The usual work-up and chromatography on silica gel using 7% ethyl acetate–hexane as eluant gave (21) (21.9 g, 78%), n_D^{20} 1.5270; $\nu_{max.}$ 1 600, 1 500, 1 320, 1 300, 1 290, and 1 150 cm^{-1}; δ 1.35 (3 H, d, *J* 1.2 Hz, 3-CH_3), 1.56 (9 H, s, CH_3), 1.66 (3 H, s, CH_3), 1.96 and 2.01 (12 H, s, CH_2CH_2), 2.41 (3 H, s, CH_3Ar), 3.60 (2 H, d, *J* 7.5 Hz, CH_2SO_2), 5.00 (4 H, m, CH=), and 7.17 and 7.61 (4 H, AB q, aromatic) (Found: C, 75.2; H, 9.8. $C_{27}H_{40}O_2S$ requires C, 75.65; H, 9.4%).

(*b*) Geranylgeraniol as prepared by sodium amalgam reduction of (19) [mixture of (3) and (18) in the ratio 7 : 3] (1.24 g, 4.28 mmol) was converted into the bromide (1.12 g), which was treated with sodium toluene-*p*-sulphinate (0.68 g, 3.8 mmol) as described above to afford the sulphone (1.12 g, 82%) after chromatography on silica gel. A portion of the

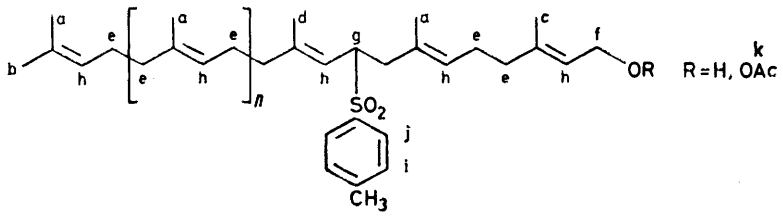
product (552 mg) was chromatographed on silica gel (20 g) impregnated with 5% silver nitrate, using 40% di-isopropyl ether in hexane for elution, affording pure (2*E*,6*E*,9*E*)-3,7,11,15-tetramethyl-1-*p*-tolylsulphonylhexadeca-2,6,9,14-tetraene (127 mg), n_D^{20} 1.5276; $\nu_{max.}$ 1 600, 1 500, 1 320, 1 300, 1 290, 1 150, and 980 cm^{-1}; δ 0.97 (3 H, d, *J* 6.3 Hz, 11-CH_3), 1.25 (2 H, m, 12-CH_2), 1.38 (3 H, d, *J* 1.2 Hz, 3-CH_3), 1.55 (6 H, s, CH_3), 1.66 (3 H, s, CH_3), 1.98 and 2.04br (7 H, s, CH_2CH_2 and CH), 2.42 (3 H, s, CH_3Ar), 2.60 (2 H, m, 8-CH_2), 3.62 (2 H, d, *J* 7.5 Hz, CH_2SO_2), 4.8—5.3 (5 H, m, CH=), and 7.17 and 7.60 (4 H, AB q, aromatic).

—78 °C. The reaction was quenched with butadiene and worked up as usual to give farnesylfarnesol (23) and the conjugate reduction product (7.34 g, 75%; 9 : 1 by 100 MHz ^1H n.m.r. spectroscopy) after chromatography on silica gel with 7% ethyl acetate–hexane as eluant.

A portion (2.19 g) of the product was chromatographed on 5% silver nitrate-impregnated silica gel to afford (2*E*,6*E*,-9*E*,14*E*,18*E*)-3,7,11,15,19,23-hexamethyltetracosa-2,6,9,-14,18,22-hexaen-1-ol [0.20 g, 7% based on (22b)], n_D^{20} 1.5025; $\nu_{max.}$ (neat) 3 300, 2 900, 1 440, 1 380, and 980 cm^{-1}; δ 0.98 (3 H, d, *J* 7 Hz, 11-CH_3), 1.25 (2 H, m, 12-CH_2),

TABLE 1

Physical characterisation of coupling products



Compound	*n*	R	Yield (%)	n_D^{20}	δ a	b	c	d	e	f	g	h	i	j	k	$\nu_{max.}$ (cm^{-1})	Analysis (%) Found (Calc.) C	H
(9)	0	Ac	79	*a*	1.51 1.57	1.65	1.65	1.21	1.95	4.42	3.65	4.8— 5.3	2.41	7.18 7.61	1.95	1 740 1 600 1 310 1 300 1 240 1 140	71.35 (71.60)	8.8 (8.64)
(19)	0	H	79	1.5355	1.52 1.55	1.65	1.55	1.21	1.94	3.97	3.75	4.8— 5.5	2.41	7.18 7.61		3 500 1 600 1 310 1 300 1 290 1 140	*a*	
(22a)	2	Ac	73	1.5218	1.58	1.66	1.66	1.23	1.95	4.44	3.67	4.7— 5.3	2.41	7.20 7.62	1.95	1 740 1 315 1 300 1 290 1 240	74.95 (75.24)	9.75 (9.32)
(22b)	2	H	73	1.5307	1.59	1.66	1.59	1.23	1.96	8.98	3.68	4.7— 5.4	2.42	7.21 7.63		3 500 1 600 1 500 1 320 1 300 1 290	*a*	
(25b)	4	H	66	1 5300	1.54	1.64	1.54	1.21	1.94	3.97	3.68	4.7— 5.4	2.41	7.19 7.61		3 500 1 600 1 500 1 320 1 300 1 290	78.4 (78.72)	10.5 (10.12)
(28b)	6	H	59	1.5249	1.57	1.63	1.57	1.23	1.96	3.97	3.67	4.6— 5.4	2.41	7.18 7.61		3 400 1 600 1 500 1 320 1 300 1 290	80.05 (80 .28)	10.55 (10.33)

[a] Not determined.

Further elution with the same solvent afforded (21) (324 mg).

(2E,6E,10E,14E,18E)-3,7,11,15,19,23-*Hexamethyl*-9-p-*tolylsulphonyltetracosa*-2,6,10,14,18,22-*hexaenyl Acetate* (22a).—Essentially the procedure for the preparation of (9) was applied to the synthesis of (22a). Spectral data are shown in Table 1.

(2E,6E,10E,14E,18E)-3,7,11,15,19,23-*Hexamethyl*-9-p-*tolylsulphonyltetracosa*-2,6,10,14,18,22-*hexaen*-1-*ol* (22b), (2E,6E,10E,14E,18E,22E,26E)-3,7,11,15,19,23,27,31-*Octamethyl*-9-p-*tolylsulphonyldotriaconta*-2,6,10,14,18,22,26,30-*octaen*-1-*ol* (25b), and (2E,6E,10E,14E,18E,22E,26E,30E,-34E)-3,7,11,15,19,23,27,31,35,39-*decamethyl*-9-p-*tolylsulphonyltetraconta*-2,6,10,14,18,22,26,30,34,38-*decaen*-1-*ol* (28b).—These compounds were prepared similarly to (19) [method (b)]. In some runs, both the alcohol and the acetate were obtained owing to incomplete alcoholysis. The acetate was hydrolysed to the alcohol in quantitative yield with potassium hydroxide in 80% methanol.

(2E,6E,10E,14E,18E)-3,7,11,15,19,23-*Hexamethyltetracosa*-2,6,10,14,18,22-*hexaen*-1-*ol* (*all*-trans-*Farnesylfarnesol*) (23).—To a solution of (22b) (13.3 g, 22.9 mmol) in anhydrous ethylamine–ether (2 : 1 v/v; 150 ml) was added lithium (3.21 g, 0.46 mol) at —78 °C. The mixture was stirred for *ca.* 1 h until it turned blue, and for a further 15 min at 1.57 (12 H, s, CH_3), 1.65 (6 H, s, CH_3), 1.97 and 2.02 (15 H, s, CH_2CH_2 and CH), 2.62 (2 H, m, 8-CH_2), 4.02 (2 H, d, *J* 7 Hz, CH_2), and 4.9—5.5 (7 H, m, CH=).

Further elution afforded pure (23) [1.85 g, 63% based on (22b)].

(2E,6E,10E,14E,18E)-3,7,11,15,19,23-*Hexamethyl*-1-p-*tolylsulphonyltetracosa*-2,6,10,14,18,22-*hexaene* (24) *and* (2E,6E,10E,14E,18E,22E,26E)-3,7,11,15,19,23,27,31-*Octamethyl*-1-p-*tolylsulphonyldotriaconta*-2,6,10,14,18,22,26,30-*octaene* (27).—These compounds were prepared by a similar procedure as for the synthesis of (21). Spectral properties are shown in Table 2.

(2E,6E,10E,14E,18E,22E,26E)-3,7,11,15,19,23,27,31-*Octamethyldotriaconta*-2,6,10,14,18,22,26,30-*octaen*-1-*ol* (*all*-trans-*Octaprenol*) (26) *and* (2E,6E,10E,14E,18E,22E,26E,30E,34E)-3,7,11,15,19,23,27,31,35,39-*Decamethyltetraconta*-2,6,10,14,18,22,26,30,34,38-*decaen*-1-*ol* (*all*-trans-*Decaprenol*) (1b).—These compounds were obtained from (25b) and (28b), respectively, by a similar procedure to that used for (23).

An authentic sample of (1b) was obtained as follows. Natural solanesol was converted into solanesylacetone,[10] which was condensed with the carbanion of triethyl phosphonoacetate to afford a 1 : 4 mixture of ethyl *cis*- and *trans*-γ-solanesylsenecioate. The pure *trans*-isomer was

isolated by careful chromatography on silica gel, and was reduced with lithium aluminium hydride to give decaprenol (1b), m.p. 42.5—43.5 °C.

(2E,6E,10E)-3,7,11-*Trimethyl*-5-p-*tolylsulphonyldodeca*-2,6,10-*trien*-1-*ol* (30).—To a solution of the carbanion of (5) (8.14 g, 27.9 mmol) in THF–HMPA (80 ml) was added a solution of (29) [19] (3.52 g, 21.7 mmol) in THF (20 ml) at −78 °C, and the mixture was stirred for 3 h. Usual work-up and chromatography on silica gel afforded the hydroxy-sulphone (30) (7.10 g, 85%), n_D^{20} 1.5251; $\nu_{max.}$ 3 300, 1 310, 1 290, 1 280, and 1 140 cm^{-1}; δ 1.24 (3 H, s, 7-CH_3), 1.57 (6 H, s, CH_3), 1.78 (3 H, s, CH_3), 1.92 and 1.97 (4 H, s, CH_2CH_2), 2.43 (3 H, s, CH_3Ar), 2.26 and 2.80 (2 H, d, *J* 13 Hz, 4-CH_2), 3.81 (1 H, dt, *J* 3 and 10 Hz, $CHSO_2$), 3.97 (2 H, d, *J* 6 Hz, CH_2O), 4.83 (1 H, d, *J* 10 Hz, 6-CH=), 4.92br (1 H, s, 10-CH=), 5.33 (1 H, t, *J* 6 Hz, 2-CH=), and 7.22 and 7.62 (4 H, AB q, aromatic).

(2E,6E,10E)-3,7,11-*Trimethyldodeca*-2,6,10-*trien*-1-*ol* (*all*-trans-*Farnesol*) (31).—A solution of (30) (3.71 g, 9.87 mmol) in ethylamine–ether (7 : 3 v/v; 100 ml) was treated with lithium (1.38 g, 197 mmol) at −78 °C for 2.5 h. The reaction was worked up as usual to give a crude product (1.21 g, 55%). G.l.c. (OV-210, 140 °C) showed four peaks in a relative area of 7 : 19 : 14 : 60. The major peak and the third peak coincided with *trans,trans*-farnesol (31) and *cis,trans*-farnesol, respectively. The crude oil was chromatographed on silica gel using 10% ethyl acetate–hexane as eluant to effect isolation of three isomers and (31). (3*Z*,6*E*)-3,7,11-Trimethyldodeca-3,6,11-trien-1-ol had $\nu_{max.}$ 3 300, 2 910, 1 380, and 980 cm^{-1}; δ 0.96 (3 H, d), 1.66 (6 H, s), 1.74 (3 H, s), 1.98br (7 H, s), 3.36 (1 H, s), 3.97 (2 H, d), and 5.0—5.3 (4 H, m); (3*Z*,7*E*)-3,7,11-trimethyldodeca-3,7,11-trien-1-ol had $\nu_{max.}$ 3 300, 2 910, and 1 380 cm^{-1}; δ 1.62br (9 H, s), 1.73br (3 H, s), 1.99br (8 H, s), 3.32 (1 H, s), 3.98 (2 H, d), and 5.02 (3 H, m); all-*trans*-farnesol (31) (0.59 g, 27%) had n_D^{20} 1.4915; $\nu_{max.}$ 3 300, 2 910, 1 650, 1 440, and 1 380 cm^{-1}; δ 1.62br (12 H, s), 1.98br (8 H, s), 3.20 (1 H, s), 3.97 (2 H, d), and 5.01 (3 H, m).

(2E,6E,10E,14E,18E,22E,26E,30E)-3,7,11,15,19,23,27,31,35-*Nonamethyl*-5-p-*tolylsulphonylhexatriaconta*-2,6,10,14,18,22,26,30,34-*nonaen*-1-*ol* (32).—To a solution of the lithium carbanion derived from (26) (0.60 g, 0.86 mmol) in THF–HMPA (4 : 1 v/v; 10 ml) was added a solution of (29) (0.11 g, 0.66 mmol) in THF (1 ml) at −78 °C. The reaction was worked up as usual to afford the sulphone (32) (0.14 g, 27%), n_D^{20} 1.5249; $\nu_{max.}$ 3 300, 1 320, 1 300, 1 290, and 1 140 cm^{-1}; δ 1.20 (3 H, s, 7-CH_3), 1.57 (27 H, s, CH_3), 1.95br (32 H, s, CH_2CH_2), 2.40 (3 H, s, CH_3Ar), 3.93 (2 H, d, *J* 6 Hz, CH_2O), 5.01 (9 H, m, CH=), and 7.15 and 7.56 (4 H, AB q, aromatic).

(2E,6E,10E,14E,18E,22E,26E,30E)-3,7,11,15,19,23,27,31,35-*Nonamethylhexatriaconta*-2,6,10,14,18,22,26,30,34-*nonaen*-1-*ol* (*Solanesol*) (1a).—A solution of (32) (0.137 g, 0.18 mmol) in ether (5 ml) and ethylamine (12 ml) was treated with lithium (0.1 g, 14 mmol) at −78 °C. The reaction was worked up as usual, and the crude product was chromatographed on silica gel using 15% ethyl acetate–hexane for elution to give (1a) (57 mg, 50%); m.p. 41.5—42.5 °C. The product was identical in all respects with an authentic sample obtained from natural sources.

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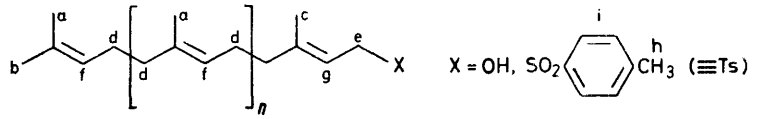
[0/1057 *Received*, 7*th July*, 1980]

TABLE 2

Physical characterisation of polyprenyl alcohols and sulphones



Compound	*n*	X	Yield (%)	n_D^{20}	δ a	b	c	d	e	f	g	h	i	$\nu_{max.}$ (cm^{-1})	Analysis (%) Found (Calc.) C	H
(3)	2	OH	48	1.4964	1.56	1.64	1.64	1.96, 2.01	4.01	5.06	5.33			3 300 2 900 1 660, 1 440 1 380 1 000	*e*	
(21)	2	Ts	78	1.5270	1.56	1.66	1.35	1.96, 2.01	3.60	5.00	5.00	2.41	7.17, 7.61	1 600 1 500 1 320, 1 300 1 290 1 150	75.2 (75.65)	9.8 (9.4)
(23)	4	OH	63	1.5056	1.58	1.66	1.66	1.98	3.98	5.03	5.30			3 300 2 920 1 660, 1 440 1 380 1 000	84.15 (84.45)	12.1 (11.8)
(24)	4	Ts	76	*a*	1.58	1.68	1.38	1.97	3.63	5.04	5.04	2.43	7.20, 7.63	1 600 1 440 1 320, 1 300 1 150 1 090	78.8 (78.65)	10.15 (10.0)
(26)	6	OH	70	*b*	1.57	1.65	1.65	1.97, 2.02	3.99	5.03	5.31			3 300 2 900 1 660, 1 440 1 380 1 000	85.15 (85.35)	11.95 (11.8)
(27)	6	Ts	67	1.5248	1.57	1.66	1.38	1.95	3.62	5.03	5.03	2.43	7.21, 7.64	1 600 1 440 1 320, 1 305 1 150 1 090	80.45 (80.5)	10.8 (10.35)
(1b)	8	OH	45	*c*	1.58	1.67	1.67	2.00, 2.05	4.12	5.08	5.40			3 350 2 920 1 660, 1 440 1 380 1 000	85.7 (85.9)	12.0 (11.8)
(1a)	7	OH	50	*d*	1.58	1.66	1.66	1.96, 2.01	4.00	5.03	5.30			3 300 2 920 1 660, 1 440 1 380 1 000	*e*	

[a] M.p. 30—32 °C. [b] M.p. 36—37 °C. [c] M.p. 42.5—3.5 °C. [d] M.p. 41.5—2.5 °C. [e] Not determined.

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