Synthesis of (5*E*,9*E*)-5,9-Hexacosadienoic Acid via Copper- and Palladium-Mediated Reactions Using 1-Acetoxy-4-chloro-2-butene as a Synthon

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Bäckvall, J.-E., Sellén, M. and Nyström, J.-E., 1988. Synthesis of (5*E*,9*E*)-5,9-Hexacosadienoic Acid via Copper- and Palladium-Mediated Reactions Using 1-Acetoxy-4-chloro-2-butene as a Synthon. – Acta Chem. Scand., Ser. B 42: 397–402.

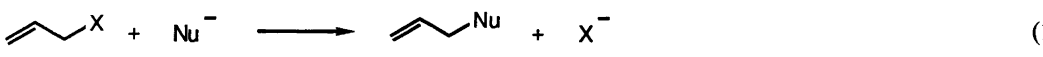
A synthesis of (5*E*,9*E*)-5,9-hexacosadienoic acid (**1**), a double-bond isomer of a marine natural product, was performed using 1-acetoxy-4-chloro-2-butene (**2**) as a building block.

Metal-mediated nucleophilic substitutions of allylic substrates [eqn. (1)] have become important reactions in organic synthesis.[1–5] Several different metals are known to promote such reactions and among those frequently studied one finds palladium[1,2] and copper.[3,4] As a consequence, the importance of allylic substrates as starting materials and synthons has increased. We recently developed a reaction for the oxidation of conjugated dienes to 1-acetoxy-4-chloro-2-alkenes.[6] These chloroacetates are versatile synthons since they contain two allylic leaving groups of differing reactivity. The synthetic utility of these 1,4-allylic compounds has been demonstrated by the use of palladium-catalyzed reactions,[6,7] and more recently by their use in regio-controlled copper-catalyzed Grignard couplings.[8] In this paper we describe the use of 1-acetoxy-4-chloro-2-butene as building block and the application of palladium- and copper-mediated reactions for the synthesis of (5*E*,9*E*)-5,9-hexacosadienoic acid (**1**),[9] a double-bond isomer of a marine natural product.

A retrosynthetic analysis of **1** is shown in Scheme 1. By making the disconnections indicated, a possible starting material would be 1-acetoxy-4-chloro-2-butene (**2**), which is readily available from 1,3-butadiene in one step.[6,10] Stepwise nucleophilic addition of the n-$C_{15}H_{31}$ and $PhSO_2$ fragments to **2**, followed by coupling with another molecule of **2** and a subsequent three-carbon elongation would give **1**.

We first studied the reactions of chloroacetate **2** with lithium dialkylcuprates and with Grignard reagents using copper catalysis. In both cases the product was a mixture of regioisomers where the pentadecyl anion had attacked α or γ with displacement of the chloride. The latter attack predominated, leading mainly to branched product. We therefore prepared the sulfonylacetate **3**[6] and allowed it to react with lithium dialkylcuprates. This, however, led to elimination of acetic acid to give 1-phenylsulfonyl-1,3-butadiene[11] and to the formation of a number of secondary products from the diene [eqn. (2)]. The desired 2-nonadecenylsulfone was only a minor component of this mixture and it was presumably of the *cis* configuration.[12]

In order to circumvent the problem of elimin-



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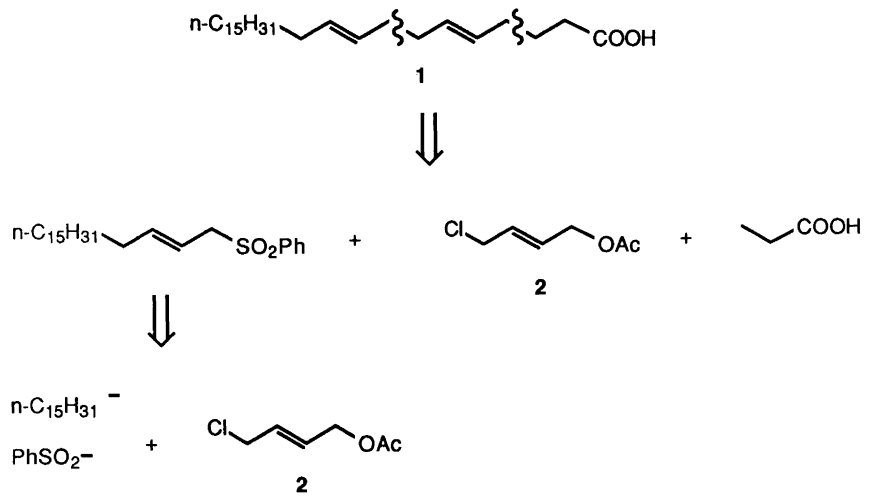
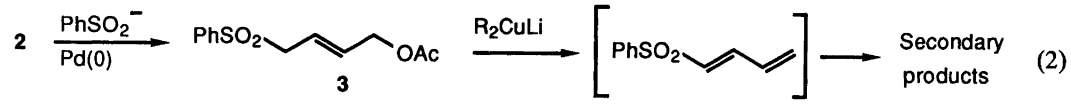


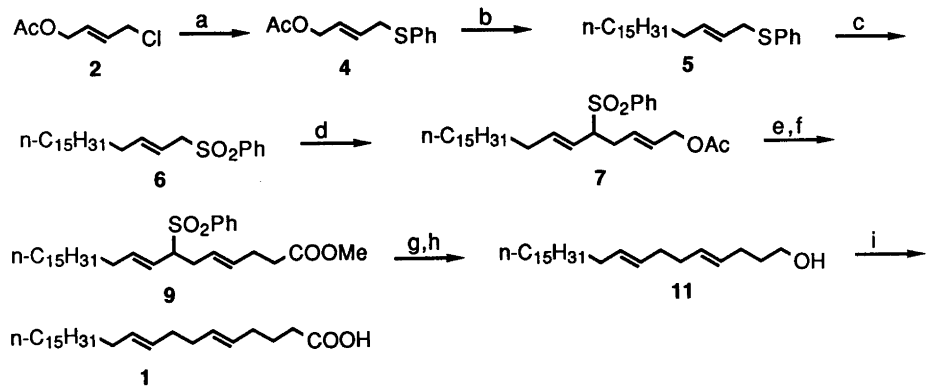
Scheme 1.

ation, the route to the sulfone via the sulfide was chosen (Scheme 2). Reaction of the chloroacetate **2** with thiophenol in the presence of potassium carbonate afforded the sulfide **4** in 86 % yield. This sulfide showed interesting reactivity in copper-catalyzed Grignard reactions. By a slight change in reaction conditions (amount of catalyst, addition time of Grignard reagent) it was possible to control the regiochemistry of the reaction to give either α or γ attack by the carbanion.[8] In the case of the pentadecyl anion the reaction using the pre-formed magnesium cuprate gave a better result than the copper-catalyzed coupling with pentadecylmagnesium bromide. Analysis of the crude product revealed a 90:10 mixture of α and γ product, which on recrystallization afforded a 76 % isolated yield of pure **5** (>99.5 % α product). Oxidation of **5** to **6** by *m*-chloroperbenzoic acid and subsequent coupling of the product (via its anion) with chloroacetate **2** afforded **7**. The yield was improved by replacing **2** with the corresponding iodoacetate, (*E*)-4-acetoxy-1-iodo-2-butene. A palladium-catalyzed alkylation of **7** with sodium dimethyl malonate and subsequent decarboxylation afforded **9**. It is interesting to note that the malonate anion attacks only the α-position in this case. This is probably due to the directing effect of the phenylsulfonyl group, since primary allylic acetates give a mixture of regioisomers from α and γ attack upon similar reaction with sodium dimethyl malonate.[13] Reduction of the ester and subsequent removal of the phenylsulfonyl group by Li/EtNH$_2$[14] afforded **11**, which was transformed via the mesylate and nitrile to the acid **1**.

The purity of the acid **1** was determined on its methyl ester according to Djerassi,[9] using reversed phase HPLC with silver nitrate in the mobile phase. The analysis showed that **1** contained approximately 86 % of the *E,E*-isomer, the ratio (5*E*,9*E*): (5*E*,9*Z*): (5*Z*,9*E*): (5*Z*,9*Z*) being 86:8:4:2. The isomers were separated and they were characterized by their ^{13}C NMR spectra. The distribution of isomers observed is due to the fact that the *E*:*Z* ratio of the chloroacetate **2** (and the corresponding iodoacetate) is 91/9.[§] Pre-purification of **2** to the *E*-isomer would lead to a

[§]From an *E*/*Z* ratio of 91/9 in the chloroacetate **2**[7,11] the statistical distribution between the isomers (5*E*,9*E*); (5*E*,9*Z*); (5*Z*,9*E*); (5*Z*,9*Z*); would be 83:8:8:1. With the assumption that the 5*Z* double bond of the minor isomers is isomerizing to 5*E* by approximately 50 % during the palladium-catalyzed alkylation with sodium dimethyl malonate, the expected ratio would be 87:8:4:1, which is close to that observed.





a. PhSH, K_2CO_3, acetone, 86 %; b. $(n\text{-}C_{15}H_{31})_2CuMgBr$, THF, 76 %; c. m-chloroperbenzoic acid, CH_2CL_2, 94 %; d. BuLi, THF, (E)-1-acetoxy-4-iodo-butene, 78 %; e. $NaCH(CO_2Me)_2$, $Pd(OAc)_2$ (2 %), PPh_3, THF, 97 %; f. LiCl-H_2O, DMSO, 173 °C, 89 %; g. 2 DIBAH, benzene, 93 %; h. Li, $EtNH_2$, 88 %; i. according to ref. 10: 1. MsCl/Et_3N. 2. NaCN/DMSO. 3. KOH/EtOH.

Scheme 2.

considerably higher proportion of *E,E,* isomer in **1**.

In the previous synthesis of **1**, compound **11** was obtained in 10 steps from (*Z,Z*)-1,5-cyclooctadiene in an overall yield of 13 %.[9] In the present synthesis, **11** was obtained from **2** in 8 steps in an overall yield of 34 %.

Concluding remarks. In this paper we have demonstrated the use of 1-acetoxy-4-chloro-2-butene (**2**) as a building block for the synthesis of **1** using regioselective copper- and palladium-catalyzed reactions. This methodology should be useful for the synthesis of a number of naturally occurring 1,5-dienes. By using other 1-acetoxy-4-chloro-2-alkenes,[6] variously substituted 1,5-dienes would be accessible.

Experimental

General. IR spectra were recorded on a Perkin Elmer model 257 spectrometer and are reported in cm^{-1}. All ^1H NMR spectra were obtained on a Bruker WP 200 FT (200 MHz) and a Bruker AM 400 FT (400 MHz) instrument using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ containing TMS at 50.3 MHz (WP 200 FT) or at 100.6 MHz (AM 400 FT). Chemical shifts are reported in δ units, parts per million (ppm) downfield from TMS. High performance liquid chromatography (HPLC) was performed on a Waters Associates system (M 45 pump, R 401 differential refractometer) with a straight-phase μ-Porasil column (silica, 10-μm packing, 0.39×30 cm), using different mixtures of hexane/ethyl acetate as the mobile phase, and with a reversed-phase Altex Ultrasphere 5-μm ODS column (0.46×25 cm), using 5 % aqueous methanol containing 50 mM silver nitrate as the mobile phase. Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. Bulb-to-bulb distillations were performed with a Büchi Kugelrohr apparatus. Microanalyses were performed by *Analytische Laboratorien,* Engelskirchen, West Germany.

Tetrahydrofuran (THF) was distilled from a deep blue solution of potassium/benzophenone in THF. Dichloromethane was distilled from CaH_2 and stored over 4 Å molecular sieves. Dimethyl malonate was distilled and stored over 4 Å molecular sieves. Thiophenol was distilled prior to use. Dimethyl sulfoxide (DMSO) was distilled from CaH_2 and stored over 4 Å molecular sieves. Pentadecyl bromide, purchased from Aldrich, was distilled prior to use. All chromatography and extraction solvents were distilled before use.

Copper(I) iodide was dried under low pressure (0.5 mmHg) at 100 °C. Palladium acetate was purchased from Engelhard Industries. Ethylamine was purchased from Fluka AG and was distilled from lithium prior to use. (*E*)-1-Ace-

toxy-4-chloro-2-butene (**2**) was prepared according to a literature procedure.[6,10] Butylllithium was purchased from Aldrich and was titrated before use. Sodium iodide, potassium carbonate, lithium chloride and triphenylphosphine were 99 % grade and were used without further purification. Lithium was purchased from Aldrich and was washed with 2–3 portions of distilled hexane prior to use. Silica gel for flash chromatography (silica gel 60 230–400 mesh) and thin-layer chromatography plates (TLC) (dc-alufolien kieselgel 60 F 254) were purchased from Merck. Glassware for experiments requiring anhydrous conditions was flame-dried and allowed to cool under an atmosphere of dry nitrogen.

(E)-1-Acetoxy-4-phenylthio-2-butene (**4**). (*E*)-1-Acetoxy-4-chloro-2-butene (**2**) (4.46 g, 30 mmol), thiophenol (6.6 g, 60 mmol), sodium iodide (1.12 g, 7.5 mmol) and potassium carbonate (8.29 g, 60 mmol) were mixed in acetone (150 ml) and the mixture heated under reflux overnight. Diethyl ether (ca. 100 ml) was added and the organic phase was washed with 2 M NaOH (3×60 ml), water (60 ml), and finally with brine (60 ml). The organic phase was dried ($MgSO_4$) and evaporated. The residual oil was purified by flash chromatography (hexane/ethyl acetate, 95/5), followed by kugelrohr distillation. This afforded 5.69 g (86 %) of **4** as a light yellow oil; IR (neat): 1740, 1235 cm^{-1}; ^1H NMR: δ 7.35–7.22 (m, 5H, Ar), 5.83 (dtt, J = 15.3, J = 6.7, J = 0.9, 1H, C*H*–CH_2–S), 5.64 (dtt, J = 15.3, J = 5.9, J = 0.9, 1H, C*H*–CH_2–OAc), 4.49 (dd, J = 5.9, J = 0.9, 2H, CH_2–OAc), 3.54 (dd, J = 6.7, J = 0.9, 2H, CH_2–S), 2.04 (s, 3H, OAc); ^{13}C NMR: δ 170.4, 135.6, 130.3, 130.2, 128.8, 127.2, 124.4, 64.1, 36.0, 20.8. Anal. $C_{12}H_{14}O_2S$: C, H.

(E)-1-Phenylthio-2-nonadecene (**5**). A flask fitted with a septum and a large magnetic stirring bar was charged with copper (I) iodide (2.73 g, 14.3 mmol). After flushing the flask with dry nitrogen, dry THF (70 ml) was added and the flask was cooled to −40 °C. To the resulting stirred suspension was added a Grignard solution (79 ml, 0.4 M, 31.6 mmol), prepared from pentadecyl bromide and magnesium turnings in THF. The gray mixture was stirred at −30 °C for 20 min and then warmed to 0 °C. The resulting dark-red mixture was stirred for an additional 30 min after which a pre-cooled (0 °C) solution of **4** (2.91 g, 13 mmol) in dry THF (35 ml) was added. After stirring the mixture for 30 min the reaction was quenched with saturated NH_4Cl (60 ml). Diethyl ether (100 ml) was added and the water phase was extracted with diethyl ether (3×40 ml). The combined organic phases were washed with water (60 ml) and brine (60 ml), and then dried ($MgSO_4$). The solvent was evaporated and the residue purified by flash chromatography (hexane) to give 4.2 g of white crystals which consisted of two regio isomers, α and γ product, in a 90:10 ratio.

Recrystallisation from ethanol (99.5 %) gave 3.7 g (76 %) of **5** as white crystals (>99.5 % α-product); m.p. 47 °C; IR (KBr): 2920, 2860, 1470, 965, 735, 695 cm^{-1}; ^1H NMR: δ 7.35–7.16 (m, 5H, Ar), 5.52–5.49 (m, 2H, C*H*=C*H*), 3.51 (d, J = 5.5, 2H, CH_2–S), 2.03–1.91 (m, 2H, CH_2–CH=CH), 1.26 [bs, 28H, $(CH_2)_{14}$], 0.88 (t, 3H, –CH_3); ^{13}C NMR: δ 135.6, 133.8, 129.9, 127.9, 125.3, 124.2, 36.4, 32.1, 31.8, 29.6, 29.3, 29.2, 29.1, 28.9, 22.6, 14.0. Anal. $C_{25}H_{42}S$: C, H.

(E)-1-(Phenylsulfonyl)-2-nonadecene (**6**). To a stirred, cooled (0 °C) solution of 85 % 3-chloroperbenzoic acid (3.39 g, 16.70 mmol) in CH_2Cl_2 (80 ml) was added **5** (3.00 g, 8.02 mmol) in CH_2Cl_2 (20 ml). The resulting solution was stirred for 2 h, and the white suspension was then diluted with CH_2Cl_2 (200 m), washed with aqueous $Na_2S_2O_3$ (50 ml), saturated $NaHCO_3$ (50 ml), water (50 ml), brine (50 ml), and dried ($MgSO_4$). The solvent was evaporated to give 3.06 g (94 %) of **6** as white crystals; m.p. 63 °C; IR (KBr): 2920, 2850, 1470, 1320, 1305, 1150 cm^{-1}; ^1H NMR: δ 7.87–7.83 and 7.60–7.53 (two m, 5H, Ar), 5.59–5.30 (m, 2H, C*H*=C*H*), 3.74 (d, J = 6.4, 2H, CH_2–SO_2), 2.05–1.90 (m, 2H, CH=CH–CH_2), 1.26 [bs, 28H, $(CH_2)_{14}$], 0.88 (t, 3H, –CH_3): ^{13}C NMR: δ 141.0, 138.2, 132.7, 128.2, 127.8, 115.2, 59.9, 32.4, 31.8, 29.6, 29.2, 28.9, 28.6, 22.6, 14.0. Anal. $C_{25}H_{42}O_2S$: C, H.

(2E,6E)-5-(Phenylsulfonyl)-2,6-tricosadienyl acetat (**7**). To a cooled (−40 °C) solution of **6** (2.98 g, 7.34 mmol) in dry THF (150 ml) was added butyllithium in hexane (5.055 ml, 8.09 mmol). The resulting yellow slurry was stirred for 5 min at −40 °C and then warmed to 20 °C, after which it

was added over 2 h using a syringe-pump to neat (*E*)-acetoxy-4-iodo-2-butene* (2.98 g, 12.0 mmol). The resulting yellow solution was stirred for 30 min and then partitioned between diethyl ether (100 ml) and saturated NH_4Cl (50 ml). The two layers were separated and the aqueous layer was extracted with diethyl ether (3×30 ml). The combined organic layers were washed with brine (30 ml) and then dried ($MgSO_4$). The solvent and excess (*E*)-acetoxy-4-iodo-2-butene were removed *in vacuo*. The crude product was purified by flash chromatography using gradient elution (hexane and ethyl acetate), yielding 2.98 g (78%) of **7** as a light yellow oil; IR (neat): 2930, 2860, 1740, 1310, 1230, 1150 cm^{-1}; ^1H NMR: δ 7.83–7.79 and 7.55–7.48 (two m, 5H, Ar), 5.65–5.60 (m, 2H, CH=CH–CH_2–OAc), 5.36 (dt, J = 15.4, J = 6.3, 1H, $C_{15}H_{31}$–CH_2–CH=CH), 5.22 (dd, J = 15.5, J = 8.8, 1H, $C_{15}H_{31}$–CH_2–CH=CH), 4.47 (d, J = 3.7, 2H, CH_2–OAc), 3.49 (ddd, J = 10.7, J = 8.7, J = 3.8, 1H, SO_2–CH–CH_2), 2.86 (m, 1H, one of SO_2–CH–CH_2), 2.44 (m, 1H, one of SO_2–CH–CH_2), 2.04 (s, 3H, OCa), 2.02–1.88 (m, 2H, $C_{15}H_{31}$–CH_2), 1.26 [bs, 28H, $(CH_2)_{14}$], 0.88 (t, 3H, –CH_3); ^{13}C NMR: δ 169.5, 140.2, 136.2, 132.7, 129.3, 128.4, 128.0, 126.9, 120.5, 77.3, 76.6, 76.0, 68.1, 64.1, 32.3, 31.8, 30.2, 29.5, 29.2, 28.9, 28.6, 22.6, 20.8, 14.0. Anal. $C_{31}H_{50}O_4S$: C, H.

*Dimethyl [(2*E*,6*E*)-5-(phenylsulfonyl)-2,6-tricosadienyl]-malonate* (**8**). A solution of sodium dimethyl malonate in dry THF [30.5 ml of a 0.20 M solution (6.1 mmol), prepared from equimolar amounts of dimethyl malonate and sodium hydride (80 % in oil)], was added to a mixture of palladium acetate (24.0 mg, 0.11 mmol), triphenylphosphine (115 mg, 0.43 mmol) and **7** (2.769 g, 5.35 mmol) under nitrogen at 20 °C. After stirring for 1.5 h, saturated $NaHCO_3$ (30 ml), water (15 ml) and diethyl ether (40 ml) were added. The two layers were separated and the aqueous layer was extracted with diethyl ether (4×25 ml). The combined organic layers were washed with brine (25 ml), dried ($MgSO_4$), concentrated to approximately 10 ml, and finally filtered through a silica gel column. Elution with diethyl ether followed by evaporation of the solvent and removal of excess dimethyl malonate by bulb-to-bulb distillation (100 °C/1 mmHg) afforded 3.07 g (97%) of **8** as a light yellow oil; IR (neat): 2930, 2860, 1740, 1310, 1150 cm^{-1}; ^1H NMR: δ 7.82–7.77 and 7.62–7.51 (two m, 5H, Ar), 5.47–5.38 (m, 2H, SO_2–CH–CH_2–CH=CH), 5.34 (dt, J = 15.5, J = 6.4, 1H, $C_{15}H_{31}$–CH_2–CH=CH), 5.18 (dd, J = 15, J = 8.7, 1H, $C_{15}H_{31}$–CH_2–CH=CH), 3.71 (s, 6H, 2×OMe), 3.43 (m, 1H, SO_2–CH), 3.37 (t, J = 5.5, 1H, $CH(COOMe)_2$), 2.79 (m, 1H, one of SO_2–CH CH_2), 2.56 (t, J = 6.5, 2H, CH_2–$CH(COOMe)_2$), 2.35 (m, 1H, one of SO_2–CH–CH_2), 2.00–1.86 (m, 2H, $C_{15}H_{31}$–CH_2), 1.26 [bs, 28H, $(CH_2)_{14}$], 0.88 0t, 3H, –CH_3); ^{13}C NMR: δ 169.1, 140.8, 137.6, 133.5, 129.2, 128.7, 121.3, 77.7, 77.1, 76.5, 68.8, 52.4, 51.7, 32.5, 31.9, 31.7, 30.6, 29.7, 29.4, 29.1, 28.7, 22.7, 14.1. Anal. $C_{34}H_{54}O_6S$: C, H.

*Methyl (4*E*,8*E*)-7-(phenylsulfonyl)-4,8-pentacosadienoate* (**9**). A solution of **8** (2.436 g, 4.13 mmol), LiCl (357 mg, 8.42 mmol) and H_2O (74 mg, 4.13 mmol) in DMSO (10 ml) was heated at 173 °C. After 1 h, the reaction mixture was poured onto ice (10 g) and the resulting mixture extracted with diethyl ether (5×10 ml). The combined organic layers were washed with water (5 ml) and brine (5 ml), and then dried ($MgSO_4$). The solvent was evaporated and the DMSO was removed by bulb-to-bulb distillation (80 °C/1 mmHg) yielding 1.946 g (89 %) of **9** as a light yellow oil; IR (neat): 2930, 2860, 1740, 1310, 1150 cm^{-1}; ^1H NMR: δ 7.82–7.79 and 7.64–7.45 (m, 5H, Ar), 5.58–5.10 (m, 4H, CH=CH–CH–CH_2–CH=CH), 3.65 (s, 3H, OMe), 3.46 (ddd, J = 10.5, J = 8.6, J = 3.6, 1H, SDO_2–CH), 2.79 (m, 1H, one of SO_2–CH–CH_2), 2.45–2.23 (bm, 5H, one of SO_2–CH–CH_2 and CH_2–CH_2–COOMe), 2.00–1.86 (m, 2H, $C_{15}H_{31}$–CH_2), 1.26 (bs, 28H, $(CH_2)_{14}$), 0.88 (t, 3H, –CH_3); ^{13}C NMR: δ 172.2, 139.9, 136.9, 132.6, 131.3, 128.4, 127.9, 125.3, 120.8, 77.2, 76.6, 76.0, 68.6, 51.2, 33.6, 32.3, 31.8, 30.4, 29.5, 29., 29.2, 28.9, 28.6, 27.6, 22.6, 14.0. Anal. $C_{32}H_{52}O_4S$: C, H.

*(4*E*,8*E*)-7-(Phenylsulfonyl)-4,8-pentacosadienol* (**10**). To a cooled (0 °C) solution of **9** (1.634 g, 3.07 mmol) in benzene (15 ml) was added DIBAH (Diisobutylaluminium hydride; 6.4 ml, 7.68 mmol) 1.2 M in toluene) and the resulting

*Prepared from (*E*)-1-acetoxy-4-chloro-2-butene, NaI and acetone (reflux, 1 h).

mixture was stirred at 0 °C for 1.5 h. The reaction was quenched with a large excess of methanol (300 ml), and precipitated Al salts were removed by filtration and washed several times with hot methanol. The solvents were evaporated to give 1.44 g (93 %) of **10** as a light yellow oil; IR (neat): 3480, 2930, 2860, 1310, 1150 cm^{-1}; ^1H NMR: δ 7.83–7.79 and 7.65–7.48 (two m, 5H, Ar), 5.60–5.25 (m, 3H, CH=CH−CH−CH_2−CH=CH), 5.20 (dd, J_{trans} = 15, J = 8.5, 1H, $C_{15}H_{31}$−CH_2−CH=CH), 3.61 (t, J = 6.4, CH_2−OH), 3.47 (ddd, J = 10.4, J = 8.5, J = 3.7, 1H, SO_2−CH), 2.81 (m, 1H, one of the SO_2−CH−CH_2), 2.37 (m, 1H, one of SO_2−CH−CH_2), 2.11–1.98 [m (partly obscured), 2H, CH_2−CH_2−CH_2−OH], 1.98–1.86 [m (partly obscured), 2H, $C_{15}H_{31}$−CH_2], 1.59 (quint., J = 7, 2H, CH_2−CH_2−CH_2−OH), 1.26 (bs, 28H, $(CH_2)_{14}$), 0.88 (t, 3H, −CH_3); ^{13}C NMR: δ 139.9, 136.9, 132.8, 132.6, 128.6, 128.4, 128.0, 124.5, 120.8, 77.3, 76.6, 76.0, 68.7, 61.8, 32.2, 31.9, 31.7, 30.5, 29.5, 29.3, 29.2, 28.9, 28.7, 28.6, 22.6, 14.0. Anal. $C_{31}H_{52}O_3S$: C, H.

(4E,8E)-4,8-Pentacosadienol (**11**). To a solution of **10** (321 mg, 0.64 mmol) in dry ethylamine (48 ml, freshly distilled from lithium) at −78 °C was added lithium wire (415 mg, 59 mmol) cut into small pieces. After stirring for 1.5 h at −78 °C, saturated NH_4Cl was added slowly and the blue colour disappeared. The amine was allowed to evaporate and the residue was partitioned between water and diethyl ether. The ether layer was dried $MgSO_4$) and concentrated to approximately 5 ml, and was finally filtered through a short silica gel column. Elution with diethyl ether followed by evaporation of the solvent afforded 205 mg (88%) of **11**[9] as white crystals; m.p. 45 °C; IR (KBr): 3300, 2920, 2850, 1530, 1120, 965 cm^{-1}; ^1H NMR: δ 5.47–5.35 (m, 4H, CH=CH−CH_2−CH_2−CH=CH), 3.64 (t, J = 6.4, 2H, CH_2−OH), 2.15–1.87 (bm, 8H, CH_2−CH=CH−CH_2−CH_2−CH=CH−CH_2), 1.63 (quint., J ≈ 7, 2H, CH_2−CH_2−OH), 1.26 [bs, 28H, $(CH_2)_{14}$], 0.88 (t, 3H, −CH_3); ^{13}C NMR: δ 1.301, 129.9, 129.0, 128.8, 77.2, 76.6, 76.0, 62.9, 32.5, 32.4, 31.8, 29.6, 29.1, 28.8, 22.6, 14.0. Anal. $C_{25}H_{48}O$: C, H.

Acknowledgements. Financial support from the Swedish Natural Science Research Council and the Swedish Board of Technical Development is gratefully acknowledged.

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Received January 27, 1988.