Synthesis of 2-Polyprenyl-Substituted Polyprenols and Their Conversion into Phosphates

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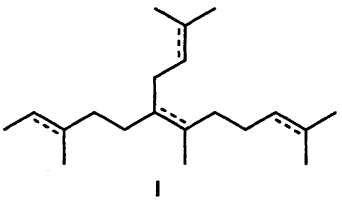
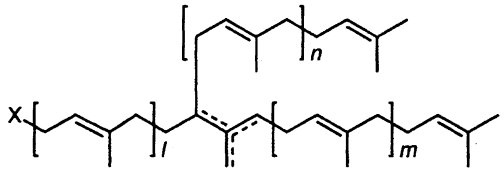
Highly Branched polyprenols, {(6*E*)-2-[(2*E*)-3,7-dimethyl-2,6-octadienyl]-7,11-dimethyl-3-methylene-6,10-dodecadien-1-ol and (6*E*,10*E*)-2-[(2*E*,6*E*)-3,7,11-trimethyl-2,6,10-dodecatrienyl]-7,11,15-trimethyl-3-methylene-6,10,14-hexadecatrien-1-ol}, were synthesized (1) from diethyl malate, geranyl bromide, and homogeranyl iodide, and (2) from ethyl acetoacetate and geranyl (or farnesyl) bromide. These alcohols were transformed into disodium phosphates, which have been postulated to be primitive lipids in the evolution of membranes.

Highly branched isoprenoid hydrocarbons, such as **I**, which are distributed widely and abundantly in sediments,[1] have been postulated by Ourisson and Nakatani to be derived from the corresponding polyprenylated polyprenyl amphiphiles **II** present in biomembranes in microorganisms.[2,3] The recent isolation of these branched isoprenoid hydrocarbons from diatomaceous algae indicates that such primitive branched membrane constituents may still exist on earth,[4,5] although these phosphates and alcohols **III** have been isolated neither from sediments nor from present-day microbial sources (Chart 1). The availability of synthetic samples of these highly branched polyprenoids would greatly facilitate the search for such primitive microorganisms and the testing of this interesting speculation by evaluating the physicochemical properties of phosphates **II** in water.[3] We have recently reported the synthesis of 2-geranyl- and 2-farnesyl-substituted geranylgeranyl phosphates (**1a**), (**1b**), (**2a**), and (**2b**) together with their isomers, **3a** and **3b**.[6,7] We now report on the synthesis of 2-polyprenyl-substituted polyprenols having a methylene $=CH_2$ at C-3, **4a** and **4b**, and their conversion into phosphates **5a** and **5b** (Chart 2).[8]



I



II X = OPO_3^{2-} $l + m = 2$
III X = OH $n = 0, 1, 2$

Chart 1. Chemical formulae **I**—**III**.

Results and Discussion

Retrosynthetic pathways for the synthesis of branched polyprenols **4a** and **4b** are shown in Scheme 1. Alcohols **4a** and **4b** consist of four parts: (1) a homogeranyl ($m = 1$) [or a homofarnesyl ($m = 2$)] chain, a geranyl ($n = 1$) [or a farnesyl ($n = 2$)] chain, a methylene group, and a central C_3 unit, or (2) two geranyl ($m = n = 1$) [or farnesyl ($m = n = 2$)] chains, a methylene group, and a C_4 unit (= acetoacetic acid ester).

Scheme 2 shows two synthetic pathways starting from diethyl malate (**6**),[9] which is equivalent to the central C_3 unit in retrosynthetic pathway (1). Following the procedure reported by Seebach,[10] the dianion of diethyl malate (**6**) was allylated with geranyl bromide (**7a**) to give hydroxy ester **8** stereoselectively. The reduction of ester **8** with lithium aluminium hydride and a subsequent acid-catalyzed acetalization of the resulting triol **9** with acetone gave an inseparable mixture of dioxolanyl alcohol **10** and a trace of dioxanyl alcohol.[11]

In the first synthetic route, from **10** to **4a** via **11**, shown in Scheme 2, alcohol **10** was converted to MOM ether **11**. The acid-catalyzed hydrolysis of acetonide **11** gave diol **12**, which was then oxidized with sodium periodate to give aldehyde **13**. The introduction of the second chain into aldehyde **13** using homogeranylmagnesium iodide **14**[12,13] gave alcohol **15**. The oxidation of the alcohol with CrO_3·2pyridine followed by methylenation with a large excess of Wittig reagent $Ph_3P{=}CH_2$ gave olefin **17**. The desired alcohol **4a** was unstable under acidic condition and the hydrolysis of MOM ether **17** with *p*-toluenesulfonic acid/methanol (60 °C), CF_3COOH/THF (0 °C), Me_3SiCl/CH_2Cl_2 (−50 °C), or 2.4% HCl (room temperature) gave a complex mixture. The

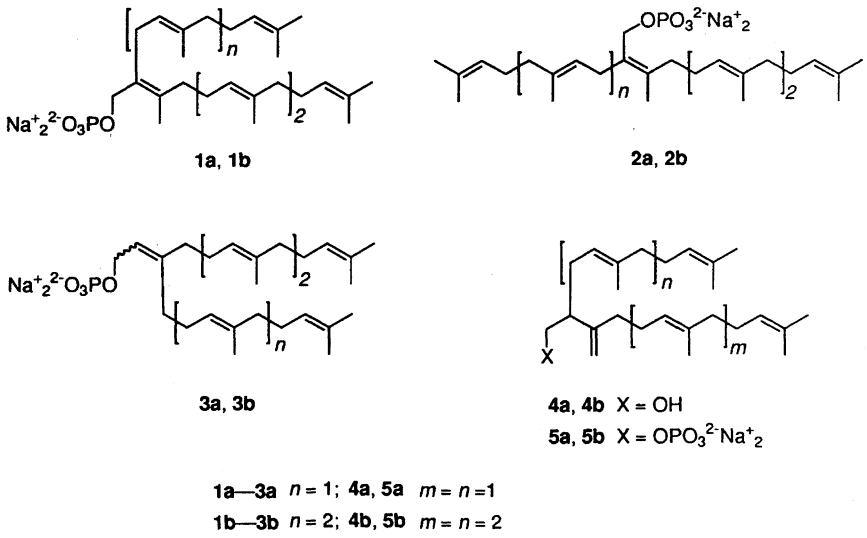
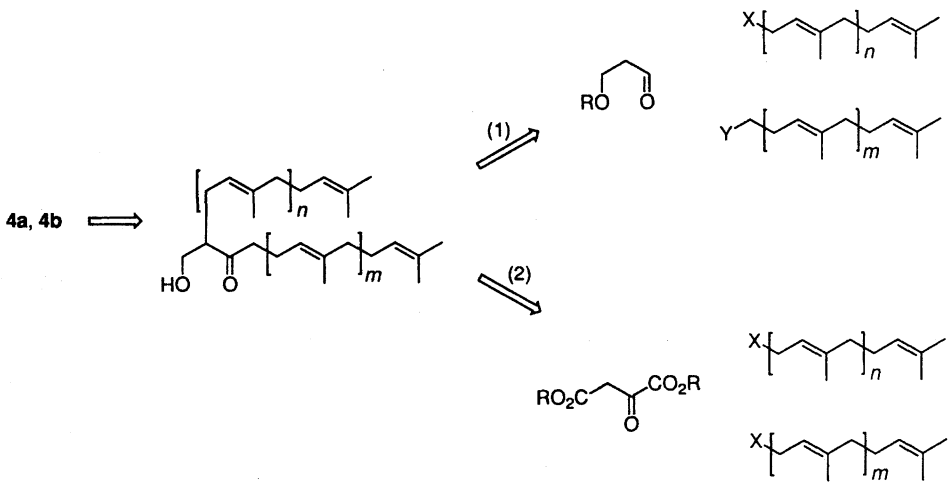


Chart 2. Chemical formulae **1a**—**5a** and **1b**—**5b**.



Scheme 1. Retrosynthetic pathways for the synthesis of **4a** and **4b**.

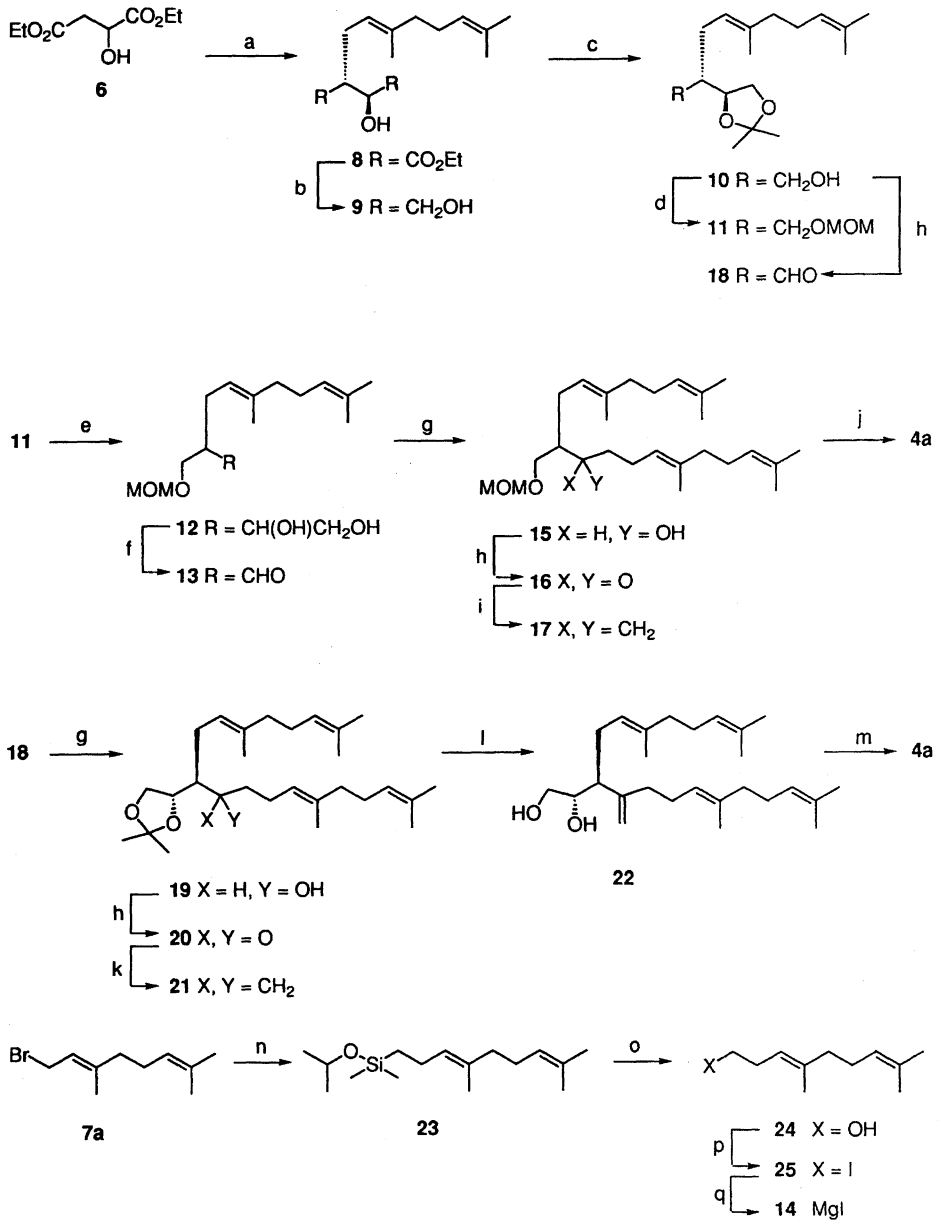
treatment of **17** with *p*-toluenesulfonic acid in methanol at 50 °C for a short time gave 2-geranyl-substituted farnesol **4a** [25% yield from ketone **16**; 7% overall yield from diethyl malate (**6**)].

The second synthetic route, from **10** to **4a** via **18**, is shown in Scheme 2. The oxidation of alcohol **10** with CrO_3·2pyridine gave aldehyde **18**. The treatment of the aldehyde with Grignard reagent **14**, followed by oxidation with pyridinium chlorochromate, gave ketone **20**. The methylenation of the ketone with $Ph_3P{=}CH_2$ or the $Zn{-}CH_2Br_2{-}TiCl_4$ system of Oshima and Nozaki[14] yielded compound **21** in poor yield. However, methylenation using the $Zn{-}CH_2Br_2{-}TiCl_4$ system modified by Lombardo[15] gave **21** in 70% yield. Acetal **21** was hydrolyzed under mild acidic condition to give diol **22**. Finally, the diol was oxidized with sodium periodate and then reduced with sodium borohydride to give 2-geranyl-substituted farnesol (**4a**) [12% overall yield from diethyl malate (**6**)].

Polyprenol **4a** would be a key intermediate in the synthesis of 6-geranyl-substituted geranylgeraniol. Therefore, the development of an alternative synthetic pathway with shorter steps and higher yields was required. Scheme 3 shows a synthetic pathway starting from ethyl acetoacetate (**26**) [retrosynthetic pathway (2)]. The introduction of two geranyl chains into **26** was achieved in two steps via α-geranyl-substituted β-keto ester **27a**[16] to give α,γ-bis(geranyl)-substituted β-keto ester **28a**. Allylation of the dianion of ethyl acetoacetate (**26**) with 2 mol. amt. of geranyl bromide (**7a**) was inferior in yield.[17] The reduction of keto ester **28a** with lithium aluminium hydride gave diol **29a**, whose primary hydroxy group was selectively protected with *t*-butyldimethylsilyl chloride (TBDMSCl) to give alcohol **30a**. The alcohol was then oxidized with pyridinium chlorochromate, and the resulting ketone **31a** was methylenated with the $Zn{-}CH_2Br_2{-}TiCl_4$ system of Lombardo[15] to give compound **32a**. The TBDMS ether of **32a** was easily cleaved with tetrabutylammonium fluoride to give 2-geranyl-substituted farnesol (**4a**) [26% overall yield from geranyl bromide (**7a**)].

Polyprenol **4a** was transformed into disodium phosphate **5a** via tetrabutylammonium hydrogenphosphate **33a** in 53% overall yield.[6]

2-Farnesyl-substituted geranylgeraniol (**4b**) was prepared



Scheme 2. (a) 2 equiv LiN(*i*-Pr)$_2$, HMPT, THF, then **7a**; (b) $LiAlH_4$; (c) acetone, *p*-TsOH; (d) MOMCl, N(Et)$_2$*i*-Pr; (e) 80% AcOH; (f) $NaIO_4$; (g) **14**; (h) CrO_3·2pyridine; (i) $Ph_3P{=}CH_2$; (j) *p*-TsOH, MeOH, 50 °C; (k) Zn-CH_2Br_2–$TiCl_4$; (l) 60% AcOH; (m) $NaIO_4$ then $NaBH_4$; (n) *i*-PrOSi(Me$_2$)CH_2MgCl, THF; (o) 30% H_2O_2; (p) i, *p*-TsCl, pyridine; ii, NaI; (q) Mg, Et_2O.

similarly using farnesyl bromide (**7b**) instead of geranyl bromide (**7a**) in 22% overall yield (Scheme 3). Polyprenol **4b** was transformed into disodium phosphate **5b** via tetrabutylammonium hydrogenphosphate **33b** in 50% overall yield.[6]

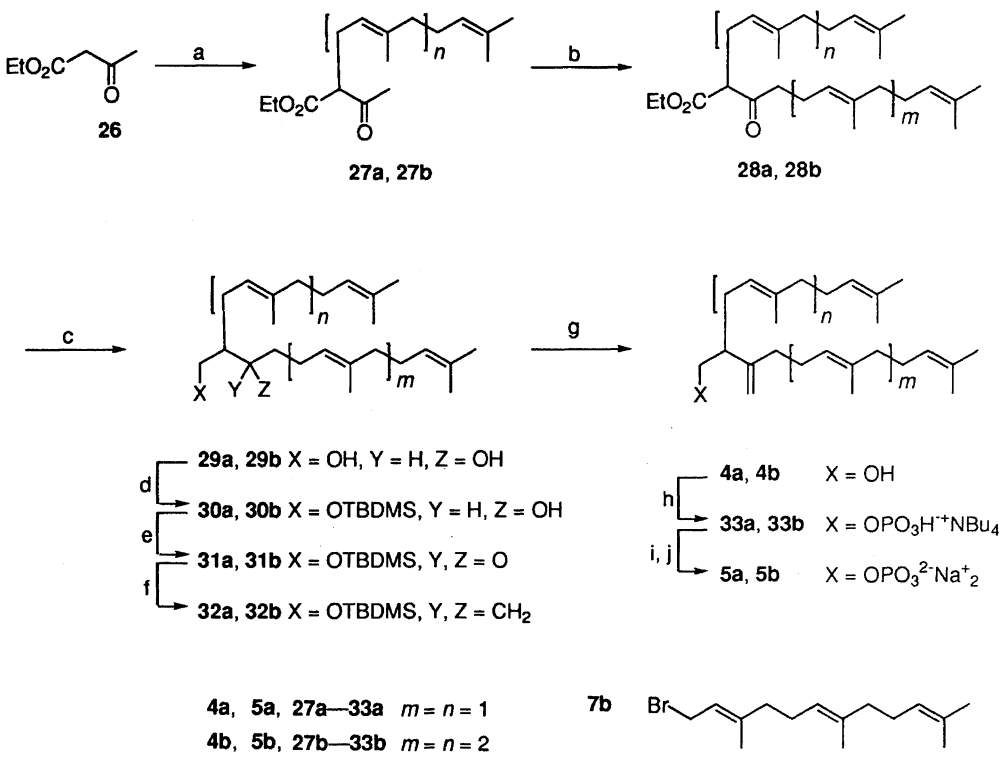
Experimental

For technical details, see Ref. 6.

Diethyl (2*S,3*R**)-3-[(2*E*)-3,7-Dimethyl-2,6-octadienyl]-2-hydroxybutanedioate (8).** Following the reported procedure (Ref. 10), the dianion of racemic diethyl malate (**6**) (204 mg, 1.1 mmol) was allylated with geranyl bromide (**7a**) (304 mg, 1.7 mmol). Flash chromatography (SiO_2, 17 g; hexane–EtOAc, 7 : 1) gave ester **8** (150 mg, 45% yield) and its diastereomer (8 mg, 2%). **8**: An oil; IR 3500, 1740, 1190, 1110, and 1030 cm^{-1}; ^{1}H NMR δ = 5.14 (1H, t, J = 6.5 Hz), 5.07 (1H, t, J = 6.5 Hz), 4.27 (3H, m), 4.15 (2H, q, J = 7.2 Hz), 3.18 (1H, d, J = 7.3 Hz, OH), 2.87 (1H, td, J = 7.6 and 3.0 Hz), 2.49 (2H, t, J = 7.6 Hz), 2.04 (4H, m), 1.67 (6H, s), 1.60 (3H, s), 1.30 (3H, t, J = 7.2 Hz), and 1.24 (3H, t, J = 7.2 Hz); ^{13}C NMR δ = 173.8, 172.6, 138.8, 131.6, 124.1, 120.4, 70.2, 61.8, 60.8, 48.6, 39.8, 26.52, 26.46, 25.6, 17.7, 16.0, 14.15, and 14.11.

(2*S,3*S**)-3-[(2*E*)-3,7-Dimethyl-2,6-octadienyl]-1,2,4-butanetriol (9).** Ester **8** (684 mg, 2.1 mmol) was reduced with $LiAlH_4$ (605 mg, 16 mmol) in anhydrous diethyl ether (17 cm^3) under reflux. The usual work-up and flash chromatography (SiO_2, 20 g; hexane–EtOAc, 1 : 3) gave **9** (429 mg, 86%) as an oil; IR 3350 cm^{-1}; ^{1}H NMR δ = 5.16—5.04 (2H, m), 3.85—3.60 (5H, m), 2.15—1.95 (7H, m). 1.68 (3H, s), 1.61 (3H, s), and 1.60 (3H, s); ^{13}C NMR δ = 137.3, 131.5, 124.0, 121.6, 74.8, 65.4, 63.8, 43.2, 39.8, 27.3, 26.6, 25.7, 17.8, and 16.2; MS *m*/*z* 242 (M^+; 0.4%), 224 (2), 95 (20), 81 (26), and 69 (100).

(2*S,4*E*)-2-[(4*S**)-2,2-Dimethyl-1,3-dioxolan-4-yl]-5,9-dimethyl-4,8-decadien-1-ol (10).** A solution of triol **9** (211 mg, 0.87



Scheme 3. (a) NaH then **7a** (or **7b**); (b) 2 equiv $LiN(i\text{-}Pr)_2$, THF, then **7a** (or **7b**); (c) $LiAlH_4$; (d) TBDMSCl, imidazole, DMF; (e) $C_5H_6N^+ClCrO_3^-$; (f) $Zn\text{-}CH_2Br_2\text{–}TiCl_4$; (g) $(n\text{-}Bu_4)NF$; (h) Cl_3CCN, $(n\text{-}Bu_4N)H_2PO_4$, $CHCl_3$; (i) Sephadex LH-20 (eluent: MeOH); (j) CM-Sepharose FF (Na^+) (eluent: MeOH–$CHCl_3$, 2 : 1).

mmol) and *p*-TsOH·H_2O (33 mg, 0.2 mmol) in anhydrous acetone (3 cm^3) was stirred at room temperature for 2.5 h. After neutralization with aqueous $NaHCO_3$ and evaporation of the organic solvent, the product was extracted with diethyl ether. An oily product **10** (223 mg, 91%) contained a trace of dioxane derivative. **10**: ^{1}H NMR δ = 5.12 (1H, t, J = 7.3 Hz), 5.09 (1H, t, J = 7.3 Hz), 4.12—4.00 (2H, m), 3.75—3.65 (3H, m), 2.83 (1H, brs, OH), 2.12—1.90 (7H, m), 1.68 (3H, s), 1.59 (6H, s), 1.42 (3H, s), and 1.36 (3H, s).

(2*S,4*E*)-2-[(4*S**)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-[(methoxymethoxy)methyl]-5,9-dimethyl-4,8-decadiene (11).** To a solution of alcohol **10** (201 mg, 0.70 mmol) were added chloromethyl methyl ether (0.3 cm^3) and *N*,*N*-diisopropylethylamine (0.75 cm^3); the solution was stirred at room temperature for 16 h. The usual work-up and flash chromatography (SiO_2, 10 g; hexane–EtOAc, 20 : 1) gave **11** (177 mg, 76% yield) as an oil; IR 1245, 1210, 1145, 1107, 1040, 918, and 860; ^{1}H NMR δ = 5.17—5.03 (2H, m), 4.60 (2H, s), 4.10 (1H, m), 4.00 (1H, dd, J = 7.8 and 6.0 Hz), 3.68 (1H, dd, J = 7.8 and 7.8 Hz), 3.59 (2H, d, J = 4.6 Hz), 3.36 (3H, s), 2.20—1.95 (6H, m), 1.80 (1H, m), 1.68 (3H, s), 1.60 (6H, s), 1.40 (3H, s), and 1.35 (3H, s); ^{13}C NMR δ = 136.9, 131.5, 124.2, 121.7, 108.3, 96.7, 76.4, 67.8, 66.9, 55.2, 42.7, 39.8, 26.7, 26.5, 25.9, 25.7, 25.6, 17.7, and 16.0; MS *m*/*z* 326 (M^+; 2%), 149 (19), 137 (10), 123 (11), 109 (14), 101 (23), 95 (20), 81 (22), and 69 (100).

(2*S,3*S**,5*E*)-3-[(Methoxymethoxy)methyl]-6,10-dimethyl-5,9-undecadiene-1,2-diol (12).** A solution of **11** (161 mg, 0.50 mmol) in 80% acetic acid (1.5 cm^3) was stirred at room temperature for 18 h. After neutralization with aqueous $NaHCO_3$ the hydrolyzed product was extracted with diethyl ether three times. Flash chromatography (SiO_2, 10 g; hexane–EtOAc, 2 : 1) gave **12** (126 mg, 88%) as an oil; IR 3420, 1150, 1110, and 1045 cm^{-1}; ^{1}H NMR δ = 5.15—5.03 (2H, m), 4.62 (2H, s), 3.80—3.70 (5H, m), 3.38 (3H, s), 3.16 (1H, brs, OH), 2.47 (1H, brs, OH), 2.20—1.95 (6H, m), 1.80 (1H, m), 1.68 (3H, s), 1.61 (3H, s), and 1.60 (3H, s); ^{13}C NMR δ = 137.7, 131.9, 124.6, 122.0, 97.2, 74.6, 69.2, 65.8, 56.1, 42.0, 40.3, 27.8, 27.1, 26.2, 18.2, and 16.7; MS *m*/*z* 286 (M^+; 0.02%), 254 (0.6), 137 (7), 123 (9), 109 (13), 107 (13), 95 (20), 93 (19), 81 (24), and 69 (100).

2-[(Methoxymethoxy)methyl]-5,9-dimethyl-4,8-decadienal (13). To a solution of diol **12** (112 mg, 0.39 mmol) in THF (3 cm^3) cooled to 0 °C was added a solution of $NaIO_4$ (282 mg, 1.32 mmol) in water (3 cm^3); the solution was stirred at 0 °C for 1 h. After evaporation of the solvent the residue was extracted with diethyl ether to give **13** (98 mg, 99%); IR 2720, 1145, 1110, 1040, and 920 cm^{-1}; ^{1}H NMR δ = 9.73 (1H, d, J = 1.7 Hz), 5.10 (1H, m), 4.60 (2H, s), 3.75 (2H, m), 3.35 (3H, s), 2.58 (1H, m), 2.41 (1H, m), 2.30 (1H, m), 2.20—1.95 (4H, m), 1.68 (3H, s), 1.62 (3H, s), and 1.60 (3H, s); ^{13}C NMR δ = 204.1, 138.6, 132.0, 124.5, 120.4, 97.1, 66.1, 55.8, 52.8, 40.1, 26.9, 26.1, 24.9, 18.1, and 16.5.

(6*E*,13*E*)-9-[(Methoxymethoxy)methyl]-2,6,14,18-tetramethyl-2,6,13,17-nonadecatetraen-10-one (16). To a solution of homogeranylmagnesium iodide (**14**), prepared from homogeranyl iodide (**25**) (277 mg, 1.0 mmol) and magnesium turnings (33 mg, 1.4 mmol) in anhydrous diethyl ether under nitrogen, was added a solution of aldehyde **13** (98 mg, 0.39 mmol) in anhydrous diethyl ether (3 cm^3) at 0 °C. The mixture was gradually warmed to room temperature and stirred for 2 h. After a treatment with aqueous HN_4Cl the crude product was chromatographed on silica gel (15 g; hexane–EtOAc, 30 : 1) to give alcohol **15** (135 mg, 84%) as an oil. The oxidation of the alcohol (120 mg, 0.30 mmol) with CrO_3·2pyridine complex, prepared from CrO_3 (565 mg) and pyridine (1.4 cm^3) in CH_2Cl_2 (6.5 cm^3), and subsequent purification of

the product by flash chromatography (SiO_2, 10 g; hexane–EtOAc, 40 : 1) gave **16** (113 mg, 95%) as an oil; IR 1718, 1145, 1110, and 1040 cm^{-1}; ^1H NMR δ = 5.15—5.00 (4H, m), 4.56 (2H, s), 3.70 (1H, dd, J = 9.3 and 8.6 Hz), 3.55 (1H, dd, J = 9.3 and 4.6 Hz), 3.32 (3H, s), 2.80 (1H, m), 2.55—2.45 (2H, m), 2.35—1.90 (12H, m), 1.68 (6H, s), and 1.59 (12H, s); ^{13}C NMR δ = 212.4, 137.7, 136.1, 131.5, 131.4, 124.2, 124.1, 122.8, 120.6, 96.6, 68.2, 55.2, 52.1, 43.5, 39.71, 39.68, 27.1, 26.7, 26.5, 25.7, 21.9, 17.7, 16.04, and 15.97; MS m/z 404 (M^+; 1%), 372 (1), 137 (10), 123 (15), 109 (19), 95 (20), 81 (33), and 69 (100).

(6*E*)-2-[(2*E*)-3,7-Dimethyl-2,6-octadienyl]-7,11-dimethyl-3-methylene-6,10-dodecadien-1-ol (4a). To a solution of $Ph_3P{=}CH_2$, prepared from methyltriphenylphosphonium bromide (544 mg, 1.5 mmol) and *n*-BuLi (1.6 mol dm^{-3} in hexane; 1.0 cm^3, 1.6 mmol) in anhydrous THF (4 cm^3), was added a solution of ketone **16** (56 mg, 0.14 mmol) in anhydrous THF (2 cm^3) at 0 °C under nitrogen. The mixture was stirred at room temperature for 2 h. The usual work-up and flash chromatography (SiO_2, 5 g; hexane–EtOAc, 150 : 1) gave crude **17** (49 mg) containing triphenylphosphine oxide. The crude product was treated with *p*-TsOH·H_2O (5 mg) in methanol (6 cm^3) at 50 °C for 40 h. After neutralization with aqueous $NaHCO_3$ the organic solvent was evaporated and the residue was extracted with CH_2Cl_2. The extract was submitted to flash chromatography (SiO_2, 2.5 g; hexane–EtOAc, 40 : 1) to give **4a** (14 mg, 25% from **16**) and **17** (14 mg). Alcohol **4a**, an oil; HPLC (hexane–EtOAc, 20 : 1; 2.0 cm^3 min^{-1}): R_t = 13.0 min (purity > 93%); IR 3350, 1037, and 890 cm^{-1}; ^1H NMR δ = 5.11 (4H, m), 4.96 (1H, d, J = 1.2 Hz), 4.87 (1H, s), 3.57 (2H, m), 2.28 (1H, m), 2.20—1.90 (14H, m), 1.68 (6H, s), and 1.60 (12H, s); ^{13}C NMR δ = 149.6, 136.4, 135.5, 131.41, 131.35, 124.3, 124.2, 123.8, 122.2, 111.0, 63.9, 48.7, 39.8, 39.7, 34.3, 29.0, 26.7, 26.6, 26.2, 25.7, 17.7, 16.12, and 16.06; MS m/z 358 (M^+; 3%), 340 (4), 277 (24), 137 (8), 123 (15), 109 (21), 95 (25), 93 (21), 81 (38), and 69 (100). Found: m/z 358.3267 (M^+). Calcd for $C_{25}H_{42}O$: M, 358.3235.

(2*R,4*E*)-2-[(4*S**)-2,2-Dimethyl-1,3-dioxolan-4-yl]-5,9-dimethyl-4,8-decadienal (18).** Alcohol **10** (291 mg, 1.0 mmol) was oxidized with CrO_3·2pyridine complex, prepared from CrO_3 (1.0 g) and pyridine (1.8 cm^3) in anhydrous CH_2Cl_2 (17 cm^3), to give **18** (241 mg, 84%) as an oil; ^1H NMR δ = 9.73 (1H, d, J = 2.7 Hz), 5.10 (2H, m), 4.30 (1H, m), 4.09 (1H, dd, J = 8.3 and 6.1 Hz), 3.73 (1H, dd, J = 8.3 and 6.9 Hz), 2.50—1.90 (7H, m), 1.68 (3H, s), 1.62 (3H, s), 1.60 (3H, s), 1.40 (3H, s), and 1.35 (3H, s).

(9*R,6*E*,13*E*)-9-[(4*S**)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2,6,14,18-tetramethyl-2,6,13,17-nonadecatetraen-10-one (20).** To a solution of homogeranylmagnesium iodide (**14**), prepared from **25** (689 mg, 2.5 mmol) and magnesium turnings (78 mg, 3.2 mmol) in anhydrous diethyl ether (4 cm^3), was added a solution of aldehyde **18** (238 mg, 0.9 mmol) in anhydrous diethyl ether (2 cm^3) at 0 °C under nitrogen. The mixture was stirred at room temperature for 1.3 h. A work-up as described for the preparation of **15** followed by flash chromatography gave alcohol **19** (287 mg, 78%) as an oil. The alcohol (272 mg, 0.63 mmol) was oxidized with CrO_3·2pyridine complex, prepared from CrO_3 (1.3 g) and pyridine (3 cm^3) in anhydrous CH_2Cl_2 (17 cm^3) as described above, to give **20** (250 mg, 93%) as an oil; IR 1710 and 1060 cm^{-1}; ^1H NMR δ = 5.15—4.97 (4H, m), 4.21 (1H, m), 4.05 (1H, dd, J = 8.1 and 6.1 Hz), 3.64 (1H, dd, J = 8.1 and 7.1 Hz), 2.67 (1H, m), 2.48 (2H, m), 2.30—2.20 (3H, m), 2.10—1.90 (9H, m), 1.68 (6H, s), 1.60 (12H, s), 1.40 (3H, s), and 1.32 (3H, s); ^{13}C NMR δ = 212.1, 137.8, 136.0, 131.6, 131.4, 124.2, 124.0, 122.9, 120.1, 108.9, 67.9, 65.8, 55.8, 44.9, 39.7, 27.2, 26.7, 26.5, 25.7, 25.4, 21.7, 17.7, 16.02, 15.97, and 15.3; MS m/z 430 (M^+; 1.5%), 101 (22), 95 (18), 81 (28), and 69 (100).

(9*S,6*E*,13*E*)-9-[(4*S**)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2,6,14,18-tetramethyl-10-methylene-2,6,13,17-nonadecatetraene (21).** To a solution of ketone **20** (22 mg, 0.05 mmol) in anhydrous CH_2Cl_2 (2 cm^3) was added a suspension of the Lombardo's reagent[15] at room temperature until the disappearance of **20** (monitored by TLC). To the mixture cooled to 0 °C was gradually added an aqueous $NaHCO_3$ ($NaHCO_3$–H_2O, 2 : 1; 30 cm^3). A work-up as described in Ref. 15 and flash chromatography (SiO_2, 1.5 g; hexane–EtOAc, 40 : 1) gave **21** (15 mg, 70% yield) as an oil; IR 1260 and 1060 cm^{-1}; ^1H NMR δ = 5.17—5.00 (4H, m), 4.92 (1H, s), 4.86 (1H,s), 4.11 (1H, m), 4.00 (1H, dd, J = 7.8 and 6.1 Hz), 3.65 (1H, dd, J = 7.8 and 7.8 Hz), 2.30—1.93 (15H, m), 1.68 (6H, s), 1.60 (12 H, s), 1.40 (3H, s), and 1.35 (3H, s); MS m/z 428 (M^+; 2%), 123 (12), 107 (11), 101 (30), 81 (36), and 69 (100).

(2*S,3*S**,7*E*)-3-[(2*E*)-3,7-Dimethyl-2,6-octadienyl]-4-methylene-8,12-dimethyl-7,11-tridecadiene-1,2-diol (22).** A solution of **21** (15 mg, 0.035 mmol) in 60% acetic acid (1.5 cm^3) was stirred at room temperature for 23 h. Flash chromatography (SiO_2, 1.3 g; hexane–EtOAc, 5 : 1) gave **22** (5.8 mg, 42%) together with **21** (8.3 mg). Diol **22**: An oil; ^1H NMR δ = 5.13—5.00 (4H, m), 5.02 (1H, s), 4.93 (1H, s), 3.80 (1H, dd, J = 11.0 and 2.7 Hz), 3.70 (1H, m), 3.55 (1H, dd, J = 11.0 and 6.3 Hz), 2.30—1.90 (15H, m), 1.68 (6H, s), and 1.60 (12H, s).

Compound 4a. To a solution of diol **22** (5.8 mg, 0.015 mmol) in THF (1 cm^3) cooled to 0 °C was added a solution of $NaIO_4$ (16 mg, 0.08 mmol) in water (0.5 cm^3); the solution was stirred at 0 °C for 1 h. After a solution of $NaBH_4$ (16 mg, 0.43 mmol) in water (0.5 cm^3) was added at room temperature, the mixture was stirred for 20 min. After evaporation of the organic solvent the residue was extracted with diethyl ether. Flash chromatography (SiO_2, 0.3 g; hexane–EtOAc, 10 : 1) gave **4a** (3.8 mg, 82%).

(3*E*)-1-Iodo-4,8-dimethyl-3,7-nonadiene (25). To a solution of the Grignard reagent prepared from (chloromethyl)isopropoxyldimethylsilane (4.3 g, 26 mmol) and magnesium turnings (621 mg, 26 mmol) in anhydrous THF (22 cm^3) under nitrogen, was added Cu(I)I (203 mg, 1.1 mmol) at 0 °C. Geranyl bromide (**7a**) (1.92 g, 8.8 mmol) was added to the mixture cooled to −50 °C; the mixture was then gradually warmed to room temperature and stirred for 19 h. It was then worked up as described in Ref. 12, giving silyl ether **23**. The silyl ether was then added to a solution of Na_2CO_3 (3.7 g, 35 mmol) in MeOH–THF (1 : 1; 40 cm^3) and warmed to 60 °C. 30% H_2O_2 (30 cm^3) was added over 1 h, and the mixture was heated at this temperature for 15 h. A work-up as described in Ref. 12 and flash chromatography (SiO_2, 50 g; hexane–EtOAc, 10 : 1) gave **24** (830 mg, 52%).[13]

Alcohol **24** was transformed into iodide **25** via tosylate, as usual (82% yield in two steps).[13]

Ethyl (4*E*)-2-Acetyl-5,9-dimethyl-4,8-decadienoate (27a). To a suspension of NaH (60% in mineral oil; 414 mg, 17.3 mmol) in anhydrous THF (12 cm^3) cooled to 0 °C was added a solution of ethyl acetoacetate **26** (2.2 g, 17.2 mmol) in anhydrous THF (7 cm^3) over a period of 20 min under nitrogen; the mixture was stirred at room temperature for 30 min. A solution of geranyl bromide **7a** (3.3 g, 15.4 mmol) in anhydrous THF (7 cm^3) was then added to the resulting solution over a period of 1 h, and the solution was heated under reflux for 1 h. After evaporation of the solvent under reduced pressure, the residue was extracted with diethyl ether. The usual work-up and flash chromatography (SiO_2, 120 g, hexane–EtOAc, 30 : 1) gave an oil containing **27a**. The crude oil was again submitted to flash chromatography to give **27a** (3.4 g, 83%) as an oil. IR 1745, 1720, 1245, 1200, 1150, 1025, and 860 cm^{-1}; ^1H NMR δ = 5.04

(2H, m), 4.18 (2H, q, $J=7.1$ Hz), 3.44 (1H, t, $J=7.5$ Hz), 2.55 (2H, t, $J=7.5$ Hz), 2.22 (3H, s), 2.10–1.95 (4H, m), 1.67 (3H, s), 1.63 (3H, s), 1.59 (3H, s), and 1.27 (3H, t, $J=7.1$ Hz), ^{13}C NMR $\delta=201.5$, 168.7, 137.2, 130.4, 123.5, 119.5, 60.3, 59.0, 39.0, 28.1, 26.2, 25.9, 24.9, 16.9, 15.2, and 13.4.

Ethyl (6*E*)-2-[(2*E*)-3,7-Dimethyl-2,6-octadienyl]-7,11-dimethyl-3-oxo-6,10-dodecadienoate (28a). To a solution of LDA, prepared from diisopropylamine (4.5 cm^3) and *n*-BuLi (1.6 mol dm^{-3}; 20 cm^3) in anhydrous THF (20 cm^3) under nitrogen was added a solution of keto ester **27a** (3.4 g, 12.7 mmol) in anhydrous THF (11 cm^3) at −75 °C; the mixture was stirred for 30 min. After the addition of HMPT (2.0 cm^3) and a solution of geranyl bromide **7a** (3.4 g, 15.5 mmol) in anhydrous THF (9 cm^3), the solution was stirred at this temperature for 1.5 h. The usual work-up and flash chromatography (SiO_2, 120 g; hexane–EtOAc, 60 : 1) gave a mixture containing **27a** and **28a**. Flash chromatography of the mixture (SiO_2, 120 g; hexane–EtOAc, 100 : 1) gave **27a** (1.0 g, 31%) and **28a** (2.4 g, 49%). **28a**: An oil; IR 1743, 1715, 1215, 1178, 1150, and 1098 cm^{-1}; ^{1}H NMR $\delta=5.10$—5.00 (4H, m), 4.17 (2H, q, $J=7.1$ Hz), 3.44 (1H, t, $J=7.6$ Hz), 2.65—2.45 (4H, m), 2.28 (2H, m), 2.10—1.90 (8H, m), 1.67 (6H, s), 1.62 (3H, s), 1.60 (3H, s), 1.59 (6H, s), and 1.26 (3H, t, $J=7.1$ Hz); ^{13}C NMR $\delta=204.5$, 169.3, 137.9, 136.2, 131.2, 131.1, 124.0, 123.9, 122.2, 119.7, 60.9, 58.9, 42.1, 39.5, 26.7, 26.5, 26.4, 25.5, 21.9, 17.4, 15.9, 15.8, and 13.9. MS *m/z* 402 (M$^+$; 10%), 358 (3), 329 (4), 279 (4), 221 (9), 197 (18), 136 (32), 135 (23), 81 (50), and 69 (100). Found: *m/z* 402.3147 (M$^+$). Calcd for $C_{26}H_{42}O_3$: M, 402.3134.

(6*E*)-2-[(2*E*)-3,7-Dimethyl-2,6-octadienyl]-7,11-dimethyl-6,10-dodecadiene-1,3-diol (29a). Keto ester **28a** (3.0 g, 7.5 mmol) was reduced with lithium aluminium hydride (1.4 g, 37.6 mmol) in anhydrous diethyl ether (57 cm^3) at room temperature. The usual work-up and chromatography (SiO_2, 120 g; hexane–EtOAc, 3 : 1 then 1 : 1) gave diol **29a** (2.5 g, 91%) as an oil; IR 3350, 1110, 1055, and 1025 cm^{-1}; ^{1}H NMR (major diastereomer) $\delta=5.17$ (2H, m), 5.08 (2H, m), 3.87 (1H, m), 3.78 (1H, m, after addition of D_2O dd, $J=10.7$and 6.7 Hz), 3.70 (1H, m; after addition of D_2O dd, $J=10.7$ and 3.8 Hz), 2.40 (1H, d, $J=4.3$ Hz, 3-OH), 2.33 (1H, t, $J=5.0$ Hz, 1-OH), 2.22—1.95 (13H, m), 1.74—1.47 (2H, m), 1.68 (6H, s), 1.63 (3H, s), 1.62 (3H, s), and 1.60 (6H, s); ^{13}C NMR (major diastereomer) $\delta=136.6$, 136.0, 131.5, 124.2, 123.9, 122.5, 74.8, 64.7, 45.1, 39.8, 39.7, 33.3, 26.61, 26.56, 25.7, 24.9, 24.1, 17.7, and 16.0.

(6*E*,13*E*)-9-[(*t*-Butyldimethylsiloxy)methyl]-2,6,14,18-tetramethyl-2,6,13,17-nonadecatetraen-10-ol (30a). The treatment of diol **29a** (438 mg, 1.2 mmol) with imidazole (348 mg, 5.1 mmol) and *t*-butylchlorodimethylsilane (257 mg, 1.7 mmol) in DMF (10 cm^3) at room temperature followed by the usual work-up and flash chromatography (SiO_2, 30 g; hexane–diethyl ether, 50 : 1) gave **30a** (565 mg, 98%) as an oil; IR 3521, 1255, 1093, 837, and 777 cm^{-1}; ^{1}H NMR (major diastereomer) $\delta=5.17$—5.05 (4H, m), 3.81 (1H, m), 3.76 (1H, dd, $J=9.8$ and 5.6 Hz), 3.70 (1H, dd, $J=9.8$ and 3.7 Hz), 3.28 (1H, d, $J=4.0$ Hz, OH), 2.20—1.95 (13H, m), 1.68 (6H, s), 1.60 (12H, s), 1.68—1.44 (2H, m), 0.90 (9H, s), 0.07 (3H, s), and 0.06 (3H, s); ^{13}C NMR (major diastereomer) $\delta=136.3$, 135.3, 131.3, 131.2, 124.3, 124.22, 124.18, 122.8, 74.5, 65.6, 44.9, 39.8, 39.7, 33.8, 26.7, 26.6, 25.8, 25.6, 24.7, 23.4, 18.0, 17.6, 16.1, 15.9, and −5.7.

(6*E*,13*E*)-9-[(*t*-Butyldimethylsiloxy)methyl]-2,6,14,18-tetramethyl-2,6,13,17-nonadecatetraen-10-one (31a). Alcohol **30a** (1.5 g, 3.2 mmol) was treated with pyridinium chlorochromate (2.4 g, 11.1 mmol) in anhydrous dichloromethane (15 cm^3) at room temperature. Filtration through a short column of florisil and flash chromatography (SiO_2, 120 g; hexane–EtOAc, 100 : 1) gave ketone **31a** (1.1 g, 73%) as an oil; IR 1710, 1250, 1097, 835, and 775 cm^{-1}; ^{1}H NMR $\delta=5.10$—5.00 (4H, m), 3.73 (1H, dd, $J=9.8$ and 8.2 Hz), 3.63 (1H, dd, $J=9.8$ and 5.2 Hz), 2.73 (1H, m), 2.54—2.43 (2H, m), 2.25—2.18 (3H, m), 2.13—2.02 (5H, m), 1.99—1.94 (4H, m), 1.68 (6H, s), 1.60 (3H, s), 1.59 (6H, s), 1.58 (3H, s), 0.86 (9H, s), 0.03 (3H, s), and 0.01 (3H, s); ^{13}C NMR $\delta=213.3$, 137.3, 135.9, 131.5, 131.3, 124.3, 124.1, 123.0, 120.9, 64.1, 54.6, 44.3, 39.71, 39.68, 26.71, 26.68, 26.61, 25.8, 25.7, 21.8, 18.2, 17.7, 16.0, 15.9, and −5.6.

(6*E*,13*E*)-9-[(*t*-Butyldimethylsiloxy)methyl]-2,6,14,18-tetramethyl-10-methylene-2,6,13,17-nonadecatetraene (32a). To the Lombardo's reagent, prepared from zinc dust (5.6 g, 86 mmol), CH_2Br_2 (2.0 cm^3, 29 mmol), and $TiCl_4$ (2.3 cm^3, 21 mmol) in anhydrous THF (50 cm^3) was added a solution of ketone **31a** (1.1 g, 2.3 mmol) in anhydrous CH_2Cl_2 (4 cm^3); the mixture was stirred at room temperature for 7.5 h. After a work-up, as described for the preparation of **21**, the crude product was chromatographed on silica gel (30 g; hexane–benzene, 10 : 1) to give **32a** (939 mg, 86%), as an oil; IR 1255, 1105, 837, and 772 cm^{-1}; ^{1}H NMR $\delta=5.15$—5.05 (4H, m), 4.82 (1H, d, $J=1.5$ Hz), 4.75 (1H, s), 3.58 (1H, dd, $J=9.8$ and 5.8 Hz), 3.49 (1H, dd, $J=9.8$ and 7.0 Hz), 2.30 (1H, m), 2.28—1.95 (14H, m), 1.68 (6H, s), 1.602 (6H, s). 1.596 (6H, s), 0.88 (9H, s), and 0.03 (6H, s); ^{13}C NMR $\delta=150.4$, 135.5, 135.0, 131.3, 131.2, 124.42, 124.39, 124.28, 122.8, 109.5, 66.0, 48.6, 39.8, 39.7, 35.6, 29.0, 26.7, 26.3, 25.9, 25.7, 18.3, 17.7, 16.1, 16.0, and −5.4.

Compound 4a. The treatment of **32a** (939 mg, 2.0 mmol) with tetrabutylammonium fluoride monohydrate (1.7 g, 6.6 mmol) in anhydrous THF (20 cm^3) at room temperature for 3 h followed by the usual work-up and flash chromatography (SiO_2, 30 g; benzene) gave **4a** (689 mg, 96%); HPLC, purity > 99%.

Tetrabutylammonium (6*E*)-2-[(2*E*)-3,7-Dimethyl-2,6-octadienyl]-7,11-dimethyl-3-methylene-6,10-dodecadienyl Hydrogenphosphate (33a): ^{1}H NMR $\delta=5.08$ (4H, m), 4.74 (2H, s), 3.86 (1H, m), 3.75 (1H, m), 3.35 (8H, m), 2.45—1.92 (15H, m), 1.67 (3H, s), 1.66 (3H, s), 1.59 (3H, s), 1.57 (6H, s), 1.55 (3H, s), 1.67—1.55 (8H, m), 1.45 (8H, m), and 0.97 (12H, t, $J=7.3$ Hz); ^{13}C NMR $\delta=150.0$, 134.49, 134.46, 131.0, 130.8, 124.5, 124.4, 124.3, 123.5, 109.3, 67.3, 58.7, 47.5, 39.8, 39.6, 34.7, 29.1, 26.7, 26.1, 25.5, 24.1, 19.6, 17.5, 16.1, 15.9, and 13.7; ^{31}P NMR $\delta=1.40$ (s).

Disodium (6*E*)-2-[(2*E*)-3,7-Dimethyl-2,6-octadienyl]-7,11-dimethyl-3-methylene-6,10-dodecadienyl Phosphate (5a): ^{1}H NMR $\delta=5.08$ (4H, m), 4.84 (2H, m), 3.75 (2H, m), 2.36—1.93 (15H, m), 1.66 (3H, s), 1.64 (3H, s), 1.57 (6H, s), and 1.56 (6H, s); ^{13}C NMR $\delta=150.2$, 135.5, 134.9, 131.0, 130.9, 124.5, 124.3, 122.4, 110.3, 67.1, 47.6, 39.91, 39.85, 33.3, 28.7, 26.9, 26.8, 25.9, 25.6, 17.6, 16.2, and 16.0; ^{31}P NMR $\delta=5.41$ (s); negative FAB-MS (*m*-NBA+Glycerol) *m/z* 897 {2×[M−(2×Na$^+$)+H$^+$]+23; 34%} and 437 [M−(2×Na$^+$)+H$^+$; 100]. Found: *m/z* 437.2809 [M−(2×Na$^+$)+H$^+$]. Calcd for $C_{25}H_{42}O_4P$: [M−(2×Na$^+$)+H$^+$], 437.2821.

Ethyl (4*E*,8*E*)-2-Acetyl-5,9,13-trimethyl-4,8,12-tetradecatrienoate (27b): An oil, IR 1744, 1718, 1244, 1204, and 1149 cm^{-1}; ^{1}H NMR $\delta=5.11$—5.02 (3H, m), 4.18 (2H, q, $J=7.1$ Hz), 3.43 (1H, t, $J=7.6$ Hz), 2.55 (2H, t, $J=7.6$ Hz), 2.22 (3H, s), 2.05 (4H, m), 1.98 (4H, m), 1.68 (6H, s), 1.63 (3H, s), 1.60 (3H, s), 1.58 (3H, s), and 1.26 (3H, t, $J=7.1$ Hz); ^{13}C NMR $\delta=203.1$, 169.6, 138.4, 135.2, 131.3, 124.3, 123.9, 119.6, 61.3, 59.8, 39.7, 29.1, 26.9, 26.7, 26.5, 25.7, 17.7, 16.1, 16.0, and 14.1.

Ethyl (6*E*,10*E*)-2-[(2*E*,6*E*)-3,7,11-Trimethyl-2,6,10-dodecatrienyl]-7,11,15-trimethyl-3-oxo-6,10,14-hexadecatrienoate (28b): An oil; IR 1746, 1717, 1237, 1193, and 1153 cm^{-1};

^{1}H NMR δ = 5.15—5.00 (6H, m), 4.17 (2H, q, J = 7.1 Hz), 3.44 (1H, t, J = 7.5 Hz), 2.60—2.47 (4H, m), 2.29—2.24 (2H, m), 2.10—1.95 (16H, m), 1.68 (6H, s), 1.63 (3H, s), 1.61 (3H, s), 1.60 (6H, s), 1.59 (3H, s), 1.58 (3H, s), and 1.25 (3H, t, J = 7.1 Hz); ^{13}C NMR δ = 204.9, 169.6, 138.3, 136.6, 135.2, 135.1, 131.3, 124.3, 124.1, 123.9, 122.3, 119.8, 61.2, 59.1, 42.3, 39.7, 26.9, 26.8, 26.61, 26.56, 25.7, 22.1, 17.7, 16.1, 16.0, and 14.1; MS m/z 538 (M^+; 19%), 469 (3), 465 (3), 197 (22), 136 (69), 81 (96), and 69 (100). Found: m/z 538.4387 (M^+). Calcd for $C_{36}H_{58}O_3$: M, 538.4386.

(6*E*,10*E*)-2-[(2*E*,6*E*)-3,7,11-Trimethyl-2,6,10-dodecatrienyl]-7,11,15-trimethyl-6,10,14-hexadecatriene-1,3-diol (29b): An oil; IR 3352, 1108, 1028, and 836 cm^{-1}; ^{1}H NMR (major diastereomer) δ = 5.17 (2H, m), 5.10 (4H, m), 3.87 (1H, m), 3.76 (1H, m, after addition of D_2O, dd, J = 10.7 and 6.7 Hz), 3.71 (1H, m, after addition of D_2O, dd, J = 10.7 and 3.7 Hz), 2.35 (1H, d, J = 3.7 Hz, 3-OH), 2.26 (1H, t, J = 5.1 Hz, 1-OH), 2.21—1.95 (21H, m), 1.72—1.56 (2H, m), 1.68 (6H, d, J = 0.9 Hz), 1.64 (3H, s), 1.62 (3H, s), and 1.60 (12H, s); ^{13}C NMR (major diastereomer) δ = 136.7, 136.1, 135.14, 135.11, 131.33, 131.30, 124.3, 124.1, 124.0, 123.9, 122.5, 74.9, 64.8, 45.1, 39.8, 39.7, 33.3, 26.7, 26.5, 25.7, 24.9, 24.1, 17.7, 16.1, and 16.0.

(6*E*,10*E*,17*E*,21*E*)-13-[(*t*-Butyldimethylsiloxy)methyl]-2,6,10,18,22,26-hexamethyl-2,6,10,17,21,25-heptacosahexaen-14-ol (30b): An oil; IR 3525, 1256, 1095, 837, and 777 cm^{-1}; ^{1}H NMR (major diastereomer) δ = 5.11 (6H, m), 3.81 (1H, m), 3.76 (1H, dd, J = 9.8 and 5.5 Hz), 3.70 (1H, dd, J = 9.8 and 3.7 Hz), 3.24 (1H, d, J = 4.0 Hz, OH), 2.19—1.95 (20H, m), 1.62—1.54 (2H, m), 1.68 (6H, s), 1.62 (3H, s), 1.61 (3H, s), 1.60 (12H, m), 0.90 (9H, s), 0.07 (3H, s), and 0.06 (3H, s); ^{13}C NMR (major diastereomer) δ = 136.3, 135.3, 134.9, 134.8, 131.0, 124.4, 124.3, 124.2, 124.1, 122.8, 74.3, 65.5, 45.0, 39.8, 39.7, 33.9, 26.7, 26.6, 25.8, 25.6, 24.7, 23.4, 18.0, 17.6, 16.1, 15.9, and −5.7.

(6*E*,10*E*,17*E*,21*E*)-13-[(*t*-Butyldimethylsiloxy)methyl]-2,6,10,18,22,26-hexamethyl-2,6,10,17,21,25-heptacosahexaen-14-one (31b): An oil; IR 1717, 1257, 1106, 838, and 777 cm^{-1}; ^{1}H NMR δ = 5.09 (6H, m), 3.73 (1H, dd, J = 9.7 and 8.1 Hz), 3.63 (1H, dd, J = 9.7 and 5.2 Hz), 2.73 (1H, m), 2.47 (2H, m), 2.22 (3H, m), 2.05 (9H, m), 1.99 (8H, m), 1.68 (6H, s), 1.60 (6H, s), 1.59 (12H, s), 0.86 (9H, s), 0.02 (3H, s), and 0.01 (3H, s); ^{13}C NMR δ = 212.9, 137.2, 135.7, 134.9, 134.8, 131.0, 124.32, 124.28, 124.1, 123.9, 123.0, 120.9, 64.1, 54.5, 44.3, 39.7, 26.68, 26.65, 26.5, 25.7, 25.6, 21.8, 18.1, 17.6, 16.0, 15.9, and −5.7.

(6*E*,10*E*,17*E*,21*E*)-13-[(*t*-Butyldimethylsiloxy)methyl]-2,6,10,18,22,26-hexamethyl-14-methylene-2,6,10,17,21,25-heptacosahexaene (32b): An oil; IR 1256, 1110, 837, and 775 cm^{-1}; ^{1}H NMR δ = 5.11 (6H, m), 4.82 (1H, d, J = 0.9 Hz), 4.75 (1H, s), 3.57 (1H, dd, J = 9.8 and 5.8 Hz), 3.48 (1H, dd, J = 9.8 and 7.0 Hz), 2.35—1.95 (23H, m), 1.68 (6H, s), 1.60 (18H, s), 0.88 (9H, s), and 0.03 (6H, s); ^{13}C NMR δ = 150.3, 135.6, 135.0, 134.85, 134.82, 131.1, 124.4, 124.28, 124.25, 122.8, 109.5, 66.0, 48.6, 39.8, 39.75, 39.72, 35.6, 29.0, 26.79, 26.71, 26.65, 26.4, 25.9, 25.7, 18.3, 17.7, 16.1, 16.0, 15.97, and −5.4.

(6*E*,10*E*)-2-[(2*E*,6*E*)-3,7,11-Trimethyl-2,6,10-dodecatrienyl]-7,11,15-trimethyl-3-methylene-6,10,14-hexadecatrien-1-ol (4b): An oil; HPLC R_t = 9.2 min (purity 94%); IR 3364, 1667, 1642, 1034, 891, and 836 cm^{-1}; ^{1}H NMR δ = 5.14—5.08 (6H, m), 4.96 (1H, d, J = 1.2 Hz), 4.87 (1H, s), 3.55 [2H, m; after addition of D_2O, δ = 3.56, (1H, dd, J = 11.1 and 5.6 Hz) and 3.53 (1H, dd, J = 11.1 and 6.7 Hz)], 2.27 (1H, quint, J = 6.6 Hz), 2.17—1.95 (22H, m), 1.68 (6H, s), 1.61 (6H, s), 1.60 (12H, s), and 1.43 (1H, dd, J = 6.7 and 5.6 Hz, OH); ^{13}C NMR δ = 149.5, 136.3, 135.4, 134.94, 134.88, 131.1, 124.3, 124.12, 124.06, 123.8, 122.2, 110.9, 64.0, 48.7, 39.72, 39.68, 39.63, 34.4, 29.0, 26.7, 26.5, 26.2, 25.6, 17.6, 16.1, 16.0, and 15.9; MS m/z 494 (M^+; 30%), 463 (10), 425 (11), 357 (9), 289 (12), 243 (43), 189 (16), 137 (40), 81 (99), and 69 (100). Found: m/z 494.4496 (M^+). Calcd for $C_{35}H_{58}O$: M, 449.4488.

Tetrabutylammonium (6*E*,10*E*)-2-[(2*E*,6*E*)-3,7,11-Trimethyl-2,6,10-dodecatrienyl]7,11,15-trimethyl-3-methylene-6,10,14-hexadecatrienyl Hydrogenphosphate (33b): ^{1}H NMR δ = 5.10 (6H, m), 4.77 (2H, s), 3.85 (1H, m), 3.76 (1H, m), 3.31 (8H, m), 2.37—1.96 (23H, m), 1.68 (6H, s), 1.60 (18H, s), 1.68—1.58 (8H, m), 1.45 (8H, m), and 0.99 (12H, t, J = 7.3 Hz); ^{13}C NMR δ = 150.0, 134.81, 134.78, 134.72, 134.6, 131.2, 124.44, 124.40, 124.3, 123.3, 109.4, 67.4, 58.4, 47.5, 39.9, 39.73, 39.69, 34.8, 29.2, 26.9, 26.8, 26.2, 25.7, 24.1, 19.7, 17.6, 16.3, 16.0, 15.94, 15.89, and 13.7; ^{31}P NMR δ = 1.36 (s).

Disodium (6*E*,10*E*)-2-[(2*E*,6*E*)-3,7,11-Trimethyl-2,6,10-dodecatrienyl]- 7, 11, 15- trimethyl- 3- methylene- 6, 10, 14- hexadecatrienyl Phosphate (5b): ^{1}H NMR δ = 5.08 (6H, m), 4.85 (2H, s), 3.74 (2H, s), 2.35—1.96 (23H, m), 1.66 (6H, s), and 1.58 (18H, s); ^{13}C NMR δ = 150.2, 135.7, 135.1, 134.7, 131.1, 124.4, 124.3, 124.1, 122.2, 110.3, 67.0, 47.6, 40.0, 39.9, 39.8, 33.4, 28.8, 27.0, 26.8, 25.9, 25.7, 17.6, 16.3, 16.1, and 15.9; ^{31}P NMR δ = 5.69 (s); negative FAB-MS (*m*-NBA+Glycerol) m/z 1169 {2×[M−(2×Na$^+$)+H$^+$]+23; 25%} and 573 [M−(2×Na$^+$)+H$^+$;100]. Found: m/z 573.4037 [M−(2×Na$^+$)+H$^+$]. Calcd for $C_{35}H_{58}O_4P$: [M−(2×Na$^+$)+H$^+$], 573.4073.

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