Pheromone Synthesis, CLXXXVII[◇]

Synthesis of the Analogues of Lurlenic Acid with Modification in the Side-Chain or in the Aromatic Nucleus: Summary of the Structure−Activity Relationships

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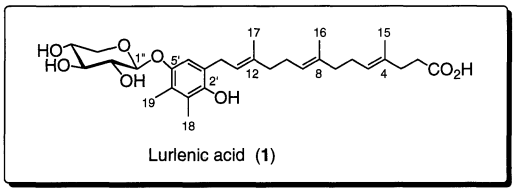
Received July 21, 1997

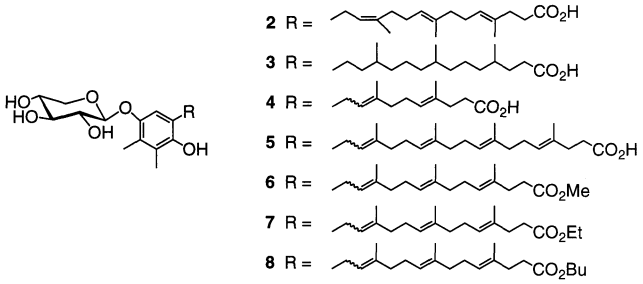
Keywords: *Chlamydomonas* / Glycosides / Lurlenic acid / Pheromones / Sex attractant / Structure-activity relationships

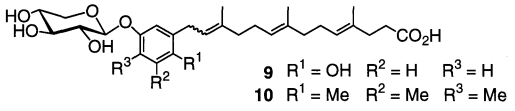
Nine analogues of lurlenic acid {(4*E*,8*E*,12*E*)-14-[2′-hydroxy-3′,4′-dimethyl-5′-(1″-β-D-xylopyranosyloxy)phenyl]-4,8,12-trimethyltetradeca-4,8,12-trienoic acid (**1**)}, a component of the mating pheromone of the green flagellate *Chlamydomonas allensworthii*, were synthesized. They are the (12*Z*) isomer **2**, the hexahydro derivative **3**, the norprenyl analogue **4**, the homoprenyl analogue **5**, methyl lurlenate (**6**), ethyl lurlenate (**7**), butyl lurlenate (**8**), the bisdemethyl analogue **9**, and the 2′-deoxy-2′-methyl analogue **10**. Structural requirements for the expression of the pheromonal activity is briefly discussed, indicating the importance of the sugar part, the phenolic hydroxy group, the appropriate length and the unsaturation of the side-chain part, and the presence of a polar group at the terminal position of the side-chain.

Lurlenic acid (**1**) (Scheme 1) is a component of the sex pheromone excreted by the female gametes of the green flagellate *Chlamydomonas allensworthii* to attract the male gametes for mating[1][2][3]. It is attractive to the male gametes at a concentration as low as 10^{-12} M[1]. The structure **1** proposed for lurlenic acid[2] was confirmed by our synthesis[4]. Compound **1** consists of three parts: the sugar, the aromatic nucleus, and the isoprenoidal side-chain. We therefore started our project to modify these three parts one by one so as to clarify the structure−activity relationships. The first phase of our endeavor to modify the sugar part revealed only the D-xyloside **1** to be extremely bioactive, indicating the importance of the sugar in pheromone perception by the male gametes[5]. This paper describes the modification of other two parts, and reports the synthesis of the seven analogues **2**−**8** with a modified side-chain, and the two analogues **9** and **10** with a modified aromatic nucleus. The present work confirms the importance of all of the three parts of **1** for the expression of its pheromone activity.

Scheme 1. Structures of lurlenic acid (**1**) and its analogues







(12*Z*) Isomer 2 of Lurlenic Acid

In our first synthesis of lurlenic acid[4][6], what we obtained as the final product was a 2:1 mixture of lurlenic acid (**1**) and its (12*Z*) isomer **2**. Its bioassay against the male gametes of *Chlamydomonas allensworthii* showed it to be almost as active as **1** itself. Then in the second synthesis[4][7], we secured pure lurlenic acid (**1**) with its bioactivity equal to the natural product. We therefore became interested in preparing the pure (12*Z*) isomer **2** of **1** so as to evaluate its bioactivity exactly.

Scheme 2 summarizes the synthesis of **2**. The (12*Z*) double bond of **2** was constructed by Still's (*Z*)-selective

[◇] Part CLXXXVI: H. Takikawa, S. Sano, K. Mori, *Liebigs Ann.* **1997**, 2495−2498.

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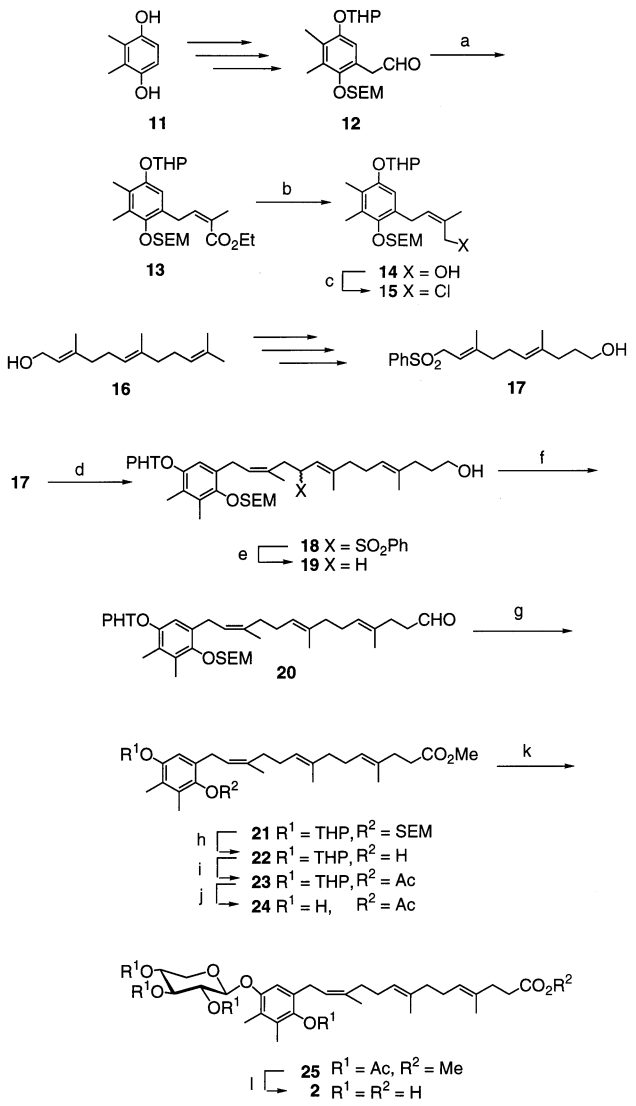
Scheme 2. Synthesis of the (12*Z*) isomer **2** of lurlenic acid

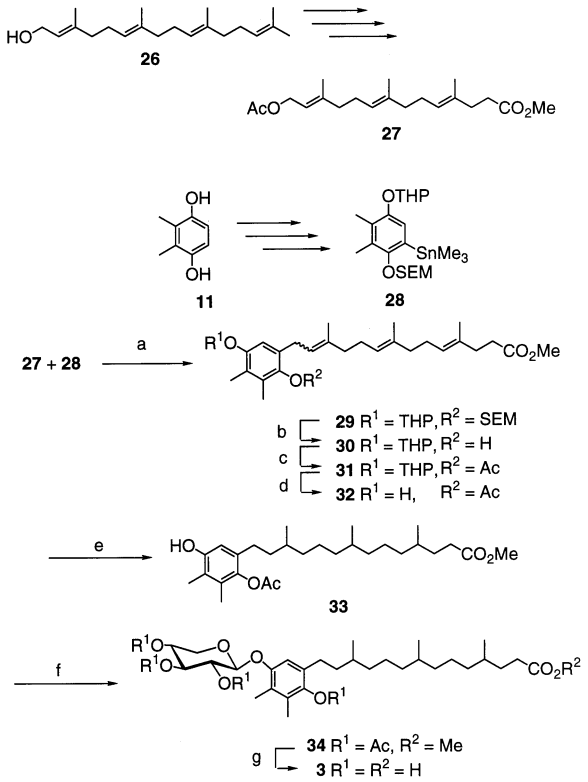


Reagents: (a) $(CF_3CH_2O)_2P(O)CH(Me)CO_2Et$, 18-crown-6 MeCN complex, $KN(TMS)_2$, THF (81%). – (b) $LiAlH_4$, Et_2O (85%). – (c) MsCl, LiCl, *sym*-collidine, DMF (94%). – (d) 2 equiv. BuLi, HMPA, THF, **15** (85%). – (e) 0.1 equiv. $(dppp)PdCl_2$, 3 equiv. $LiBEt_3H$, THF (89%). – (f) Dess–Martin periodinane, C_5H_5N, CH_2Cl_2. – (g) 1) $NaClO_2$, NaH_2PO_4, DMSO/H_2O/MeCN; 2) CH_2N_2, Et_2O (75% based on **19**). – (h) 9 equiv. CsF, HMPA . – (i) Ac_2O, C_5H_5N (80% based on **21**). – (j) TsOH, MeOH (92%). – (k) 3 equiv. 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl fluoride, 3 equiv. 1,1,3,3-tetramethylguanidine, 8 equiv. $BF_3 \cdot OEt_2$, MeCN. – (l) NaOH, MeOH, H_2O (54% based on **24**).

modification[8][9] of the Horner–Wadsworth–Emmons reaction. The starting aldehyde **12** was prepared from 2,3-dimethyl-*p*-hydroquinone (**11**) according to the published method[4]. Reaction of **12** with ethyl 2-[bis(2,2,2-trifluoroethyl)phosphono]propanoate in the presence of potassium hexamethyldisilazide [$KN(TMS)_2$] and 18-crown-6 in THF furnished the (*Z*)-unsaturated ester **13** as the single isomer as revealed by its ^{1}H-NMR analysis [δ = 1.90, d, *J* = 1 Hz, 3 H, CH=C(*Me*)CO_2Et]. Reduction of **13** with lithium tetrahydridoaluminate gave the alcohol **14**, which was converted to the corresponding chloride **15**. The dianion derived from the known C_{12} building block **17**, which was prepared from farnesol (**16**)[4], was alkylated with **15** to give the new phenylsulfone **18**. Reductive removal of the phenylsulfonyl group of **18** was achieved with lithium triethylhydroborate in the presence of palladium chloride 1,3-bis(diphenylphosphanyl)propane [$(dppp)PdCl_2$] complex in THF[10] to give **19**. This alcohol **19** was converted to the (12*Z*) isomer **2** of lurlenic acid via **20**–**25** by the sequence of reactions used in our previous synthesis of lurlenic acid (**1**)[4]. In the ^{1}H-NMR spectrum of **2**, the proton signals of the methyl group at C-12 (17-H_3) appeared at δ = 1.76 as a singlet confirming the (12*Z*) geometry of **2**. The overall yield of **2** was 4.0% based on 3,4-dimethyl-*p*-hydroquinone (**11**, 18 steps), or 5.3% based on farnesol (**16**, 16 steps).

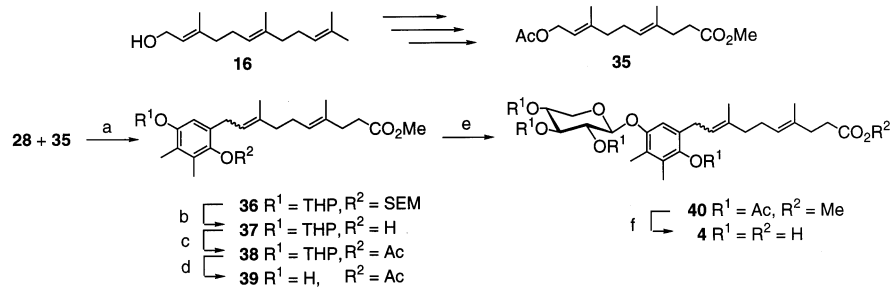
A bioassay revealed **2** to be approximately 0.1% as active as **1**. Since all the intermediates as well as **2** itself are noncrystalline and cannot be purified rigorously by recrystallization, a possibility cannot be excluded that **2** contains 0.1% of lurlenic acid (**1**) while **2** is totally inactive. The seemingly full activity of the previously synthesized 2:1 mixture of **1** and **2**[4] manifests the difficulty of discerning the full activity from 66% activity by the bioassay method employed.

Scheme 3. Synthesis of hexahydrolurlenic acid (**3**)



Reagents: (a) 0.05 equiv. $(dba)_2Pd$, 3 equiv. LiCl, DMF (98%). – (b) 9 equiv. CsF, HMPA . – (c) Ac_2O, C_5H_5N (82% based on **29**). – (d) TsOH, MeOH (95%). – (e) H_2, PtO_2, EtOH (quant.). – (f) 3 equiv. 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl fluoride, 3 equiv. 1,1,3,3-tetramethylguanidine, 8 equiv. $BF_3 \cdot OEt_2$, MeCN. – (g) NaOH, MeOH, H_2O (55% based on **33**).

Scheme 4. Synthesis of norprenyl analogue **4** of lurlenic acid



Reagents: (a) 0.025 equiv. $(dba)_3Pd_2$, 3 equiv. LiCl, DMF (83%). – (b) 9 equiv. CsF, HMPA . – (c) Ac_2O, C_5H_5N (74% based on **36**). – (d) TsOH, MeOH (97%). – (e) 3 equiv. 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl fluoride, 3 equiv. 1,1,3,3-tetramethylguanidine, 8 equiv. $BF_3 \cdot OEt_2$, MeCN. – (f) NaOH, MeOH, H_2O (42% based on **39**).

Additional Three Analogues 3, 4 and 5 with a Modified Side-Chain

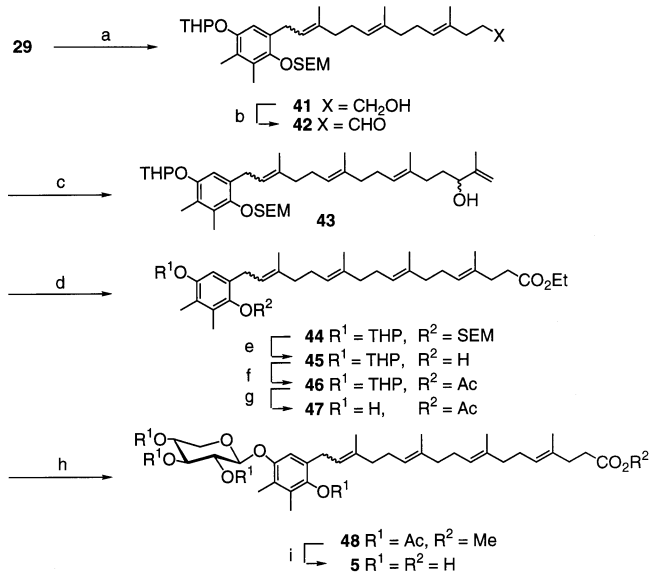
To further clarify the structural requirement at the side-chain part for the expression of bioactivity, three analogues **3**, **4** and **5** of lurlenic acid were synthesized.

Hexahydrolurlenic acid (**3**) was synthesized as shown in Scheme 3. By the methods previously reported[4], geranylgeraniol (**26**) and 2,3-dimethyl-*p*-hydroquinone (**11**) were converted to the acetoxy ester **27** and the stannane **28**, respectively. These two building blocks were coupled in the presence of bis(dibenzylideneacetone)palladium [$(dba)_2Pd$], and further transformation of the protective groups of the coupling product **29** yielded **32** via **30** and **31**[4]. Hydrogenation of **32** over Adams' platinum oxide afforded the hexahydroaglycone part **33** as a stereoisomeric mixture. Glycosidation of **33** with 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl fluoride by Yamaguchi's method[11] afforded **34**, whose deprotection provided hexahydrolurlenic acid (**3**). This derivative **3** was biologically inactive.

The next target was the lower prenylogue **4** (Scheme 4). The necessary and known intermediate **35**[12] was prepared from farnesol (**16**) by the method used for the preparation of its higher prenylogue **27**[4]. The coupling of the stannane **28** with **35** afforded **36**, which was converted to **39** via **37** and **38**. Glycosidation of **39** was followed by removal of the protective groups of **40** to give the lower prenylogue **4** (norprenyllurlenic acid). This acid **4** was a 1.3:1 mixture of (8*E*) and (8*Z*) isomer, and weakly bioactive (0.1% as active as lurlenic acid).

Scheme 5 summarizes the synthesis of the higher prenylogue **5**. The known protected aglycone **29** of lurlenic acid was reduced with lithium tetrahydridoaluminate to give the corresponding primary alcohol **41**. This was oxidized with Dess–Martin periodinane[13] to give the aldehyde **42**. Treatment of **42** with 2-lithiopropene yielded the allyic alcohol **43**, which was subjected to the Johnson orthoester Claisen rearrangement[14] to give **44** with clean stereoselectivity at C-4 to give (4*E*)-**44**. Conversion of **44** to **47** was carried out in the usual manner[4] via **45** and **46**, and **47** was glycosylated to give **48**. Removal of the protective groups of **48** furnished the higher prenylogue **5** (homoprenyllurlenic acid) as a 1.3:1 mixture of (16*E*) and (16*Z*) isomers. This higher prenylogue **5** was as active as lurlenic acid against the male gametes of *Chlamydomonas allensworthii.*

Scheme 5. Synthesis of homoprenyl analogue **5** of lurlenic acid



Reagents: (a) $LiAlH_4$, Et_2O (95%). – (b) Dess–Martin periodinane, C_5H_5N, CH_2Cl_2 (90%). – (c) 2-lithiopropene, THF (89%). – (d) $MeC(OEt)_3$, $EtCO_2H$ (83%). – (e) 9 equiv. CsF, HMPA . – (f) Ac_2O, C_5H_5N (90% based on **44**). – (g) TsOH, MeOH (quant.). – (h) 3 equiv. 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl fluoride, 3 equiv. 1,1,3,3-tetramethylguanidine, 8 equiv. $BF_3 \cdot OEt_2$, MeCN. – (i) NaOH, MeOH, H_2O (47% based on **47**).

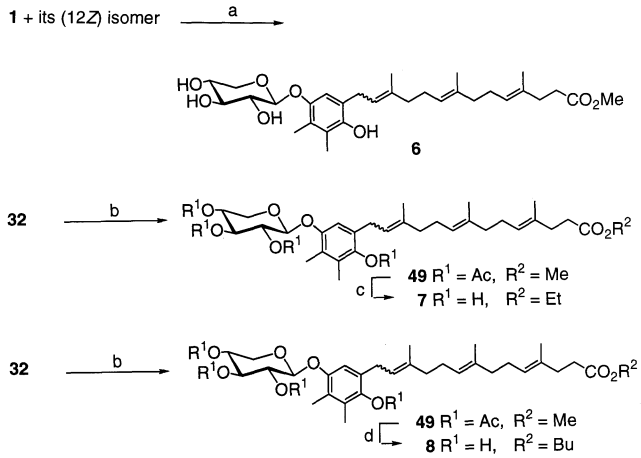
Ester Derivatives 6, 7 and 8 of Lurlenic Acid

It is known that lurlenol [the alcohol (CH_2OH instead of CO_2H of **1**) corresponding to lurlenic acid] is another naturally occurring pheromone component of *Chlamydomonas allensworthii*[3], and our synthetic lurlenol is also highly bioactive[4]. It is of interest to clarify whether the esters of lurlenic acid (**1**) are bioactive or not. To solve this problem, we synthesized three esters **6**, **7** and **8** of a mixture of **1** and its (12*Z*) isomer obtained by the palladium-catalyzed coupling route[4].

As shown in Scheme 6, lurlenic acid was methylated with diazomethane to give amorphous methyl lurlenate (**6**) as a

1.5:1 mixture of its (12*E*) and (12*Z*) isomers. It was as bioactive as lurlenic acid itself. Secondly, the known methyl lurlenate tetraacetate (**49**)[4] was prepared from **32** by glycosidation, and treated with sodium ethoxide in ethanol to effect transesterification, yielding amorphous ethyl lurlenate (**7**) as a 1.3:1 mixture of (12*E*) and (12*Z*) isomers. Ethyl lurlenate (**7**) was 0.1% as bioactive as lurlenic acid. Thirdly, treatment of **49** with sodium butoxide in 1-butanol afforded butyl lurlenate (**8**), which was obtained as an amorphous solid consisting of 1.3:1 ratio of (12*E*) and (12*Z*) isomers contaminated with about 10% of an unknown purity. This butyl ester (**8**) was weakly bioactive to show 0.1% bioactivity of **1**.

Scheme 6. Synthesis of ester **6**, **7** and **8** of lurlenic acid



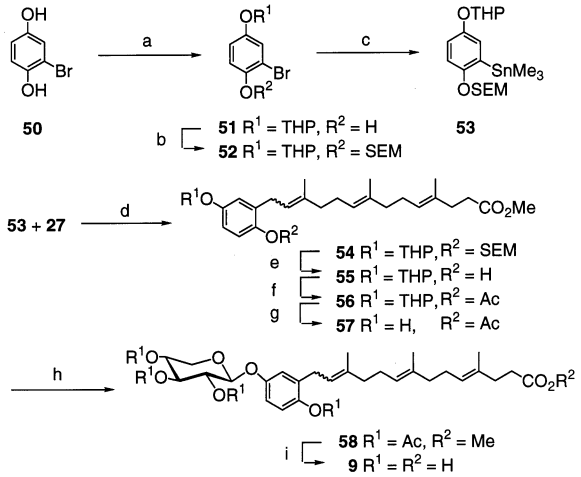
Reagents: (a) CH_2N_2, MeOH (99%). – (b) 3 equiv. 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl fluoride, 3 equiv. 1,1,3,3-tetramethylguanidine, 8 equiv. $BF_3 \cdot OEt_2$, MeCN. – (c) EtONa, EtOH (53% based on **32**). – (d) BuONa, BuOH (46% based on **32**).

Analogues 9 and 10 with a Modified Aromatic Nucleus

Scheme 7 summarizes the synthesis of 3′,4′-didemethyllurlenic acid (**9**), which is necessary to evaluate the role of the two methyl groups attached to the aromatic nucleus. Commercially available bromohydroquinone (**50**) was protected twice to give **52** via **51**. Lithiation of **52** was followed by stannylation with trimethylstannyl chloride to furnish **53**. Palladium-catalyzed coupling of **53** with **27** gave **54**. Transformation of protective groups of **54** via **55** and **56** yielded **57**. Glycosylation of **57** to **58** was followed by the removal of its protective groups to give 3′,4′-bisdemethyllurlenic acid (**9**) as a 1.3:1 mixture of (12*E*) and (12*Z*) isomers. This analogue **9** was weakly bioactive (0.1% activity of **1**).

Finally, the phenolic hydroxy group at C-2′ of lurlenic acid was replaced by a methyl group to give **10** (Scheme 8). For that purpose, the known intermediate **30** was converted to the triflate **59**. Treatment of **59** with tetramethylstannane and bis(triphenylphosphane)palladium chloride complex in DMF[15] afforded **60**. Removal of the tetrahydropyranyl (THP) protective group of **60** furnished **61**, which was glycosylated to give **62**. Further removal of the protective

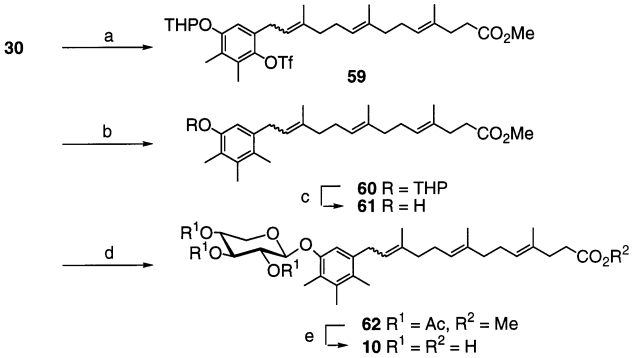
Scheme 7. Synthesis of 3′,4′-bisdemethyllurlenic acid (**9**)



Reagents: (a) 1.2 equiv. DHP, TsOH, THF. – (b) 1.5 equiv. SEMCl, $(i\text{Pr})_2\text{NEt}$, CH_2Cl_2 (44% based on **50**). – (c) 1.5 equiv. BuLi, 1.5 equiv. Me_3SnCl, THF (quant.). – (d) 0.025 equiv. $(dba)_3Pd_2$, 3 equiv. LiCl, DMF (92%). – (e) 9 equiv. CsF, HMPA. – (f) Ac_2O, C_5H_5N (77% based on **54**). – (g) TsOH, MeOH (88%). – (h) 3 equiv. 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl fluoride, 3 equiv. 1,1,3,3-tetramethylguanidine, 8 equiv. $BF_3 \cdot OEt_2$, MeCN. – (i) NaOH, MeOH, H_2O (44% based on **57**).

groups of **62** yielded 2′-deoxy-2′-methyllurlenic acid (**10**) as a 1.5:1 mixture of (12*E*) and (12*Z*) isomers. A bioassay of **10** proved it to be biologically inactive.

Scheme 8. Synthesis of 2′-deoxy-2′-methyllurlenic acid (**10**)



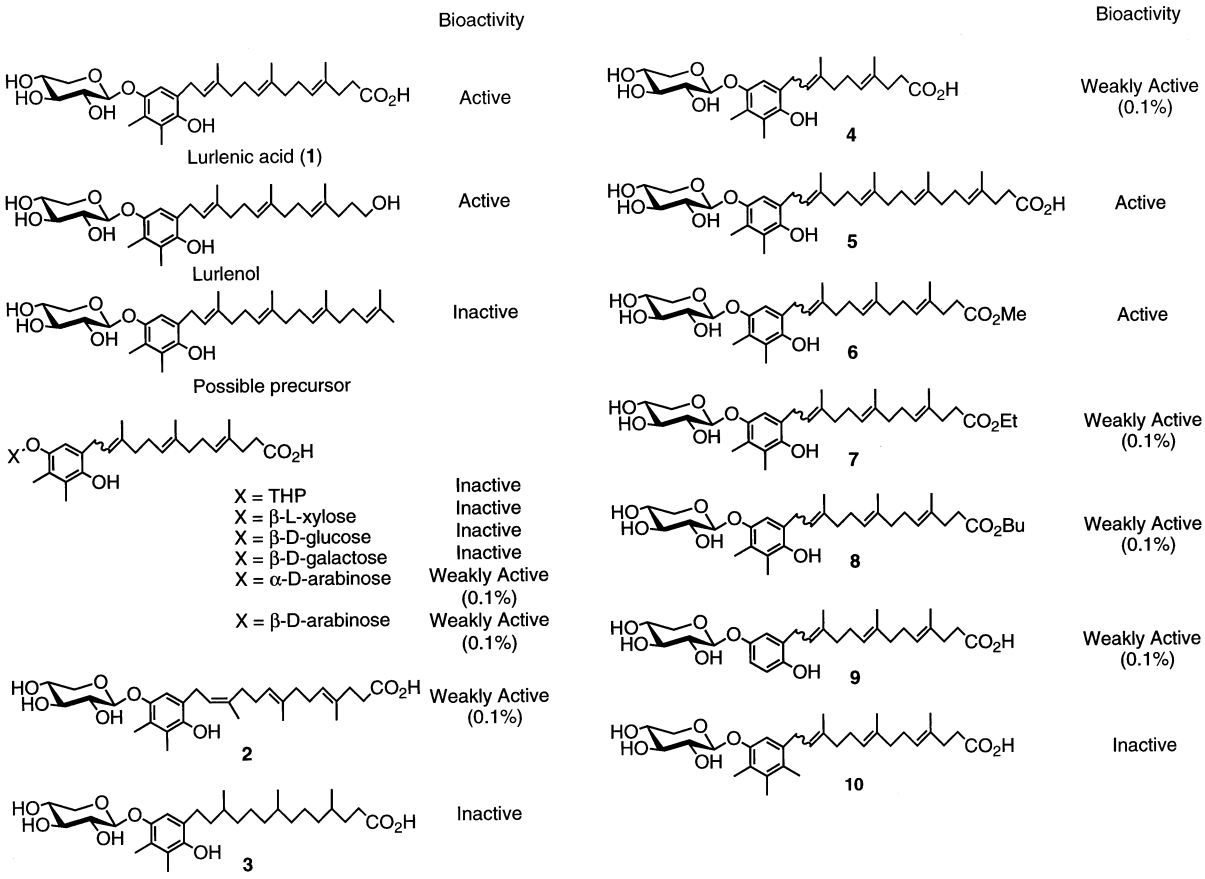
Reagents: (a) Tf_2O, C_5H_5N. – (b) Me_4Sn, LiCl, $(Ph_3P)_2PdCl_2$, DMF. – (c) TsOH, MeOH (63% based on **30**). – (d) 3 equiv. 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl fluoride, 3 equiv. 1,1,3,3-tetramethylguanidine, 8 equiv. $BF_3 \cdot OEt_2$, MeCN. – (e) NaOH, MeOH, H_2O (51% based on **61**).

Brief Summary of the Pheromone Structure–Activity Relationships

Although the full details of the pheromone structure-activity relationship will be discussed separately by Jaenicke et al. in due course, Scheme 9 summarizes the results of bioassay of lurlenic acid (**1**) and related compounds so far synthesized.

Fully bioactive compounds are lurlenic acid (**1**), lurlenol, homoprenyllurlenic acid (**5**) and methyl lurlenate (**6**), while the totally inactive compounds are the possible precursor of **1** derived from Plastoquinone 4, glycosides other than β-

Scheme 9. Pheromone structure-activity relationships



D-xylopyranoside and α- or β-D-arabinopyranoside, hexahydrolurlenic acid (**3**), and 2′-deoxy-2′-methyllurlenic acid (**10**). Those which show a bioactivity of 0.1% of that of active **1** are its (12*Z*) isomer **2**, norprenyllurlenic acid (**4**), ethyl and butyl lurlenate (**6** and **7**), and 3′,4′-bisdemethyllurlenic acid (**9**).

Accordingly, the important structural features for the expression of bioactivity are : (i) the sugar part, (ii) the phenolic hydroxy group, (iii) the appropriate length and the unsaturation of the side-chain part, and (iv) the presence of a polar group such as a carboxy, a hydroxymethyl or an ester group at the terminal position of the side-chain.

We thank Prof. *L. Jaenicke* (Universität Köln) for bioassays and stimulating discussions. Our thanks are also due to Prof. *R. C. Starr* (University of Texas) for discussions. Geranylgeraniol and farnesol were supplied by *Kuraray Co.*, to whom we express our thanks. Financial support of this work by a Grant-in-Aid for Scientific Research (No. 09680576), Japanese *Ministry of Education, Science, Sports and Culture* is gratefully acknowledged. This work was also supported by *Kyowa Hakko Kogyo Co.*, *Takasago International Corporation*, *T. Hasegawa Co.*, and *Mitsubishi Chemical Co.*

Experimental Section

General: Melting points: Uncorrected values. − IR: Perkin-Elmer 1640. − ^{1}H NMR: Jeol JNM-EX 90A (90 MHz) and Bruker DPX 300 (300 MHz), (TMS at δ_H = 0.00, $CHCl_3$ at δ_H = 7.26 or CHD_2OD at δ_H = 3.31 as an internal standard). − ^{13}C NMR: Bruker DPX 300 (75.5 MHz), ($CDCl_3$ at δ_C = 77.0 or CD_3OD at δ_C = 49.0 as an internal standard). − MS: Jeol JMS-SX 102A. − Optical rotation: Jasco DIP-1000. − Column chromatography: Merck Kieselgel 60 Art 1.07734 and Merck Kieselgel 60 Art 1.15111. − TLC: 0.25 mm Merck silica gel plates (60F-254).

Ethyl (Z)-2-Methyl-4-{3′,4′-dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-2-butenoate (**13**): To a stirred solution of ethyl 2-[bis(2,2,2-trifluoroethyl)phosphono]propanoate (4.52 g, 13.0 mmol) and 18-crown-6 acetonitrile complex (19.8 g, 64.9 mmol) in THF (100 ml), potassium bis(trimethylsilyl)-amide (0.6 M in toluene, 21.7 ml, 13.0 mmol) was added dropwise at −78°C under argon. Then the aldehyde **12** (3.42 g, 8.66 mmol) was added and the resulting mixture was stirred for 30 min at −78°C. After the addition of water (100 ml), the mixture was extracted three times with diethyl ether (200 ml). The combined ethereal extracts were successively washed with water and brine, dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by chromatography on silica gel (150 g, hexane/ethyl acetate, 30:1) to give 3.36 g (81%) of **13** as a colorless oil; n_D^{22} = 1.5064. − IR (film): $\tilde{\nu}_{max}$ = 1715 cm^{-1} (s, C=O), 1640 (w, C=C), 1585 (w, C=C), 1250 (m, Si−C), 1220 (s, C−O), 1200 (m, C−O), 1125 (s, C−O), 1080 (m, C−O), 1065 (m, C−O), 1040 (m, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.02 (s, 9 H, $SiMe_3$), 0.99 (br. t, *J* = 9 Hz, 2 H, CH_2Si), 1.32 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.50−2.10 (m, 6 H, THP), 1.90 [d, *J* = 1 Hz, 3 H, CH=C(*Me*)CO_2Et], 2.16 (s, 3 H, ArCH_3), 2.21 (s, 3 H, ArCH_3), 3.55−3.65 (m, 1 H, THP), 3.80−4.00 (m, 5 H, THP, ArCH_2, CH_2CH_2Si), 4.23 (q, *J* = 7 Hz, 2 H, CH_3CH_2), 4.91 (s, 2 H, OCH_2O), 5.30 (t, *J* = 3 Hz, 1 H, THP), 6.08 (dt, *J* = 1 Hz, *J′* = 7 Hz, 1 H, olefinic H), 6.80 (s, 1

H, aromatic H). − $C_{26}H_{42}O_6$ (428.7): calcd. C 65.24, H 8.84; found C 64.90, H 8.48.

(Z)-4-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-2-methyl-2-buten-1-ol (**14**): To a stirred suspension of lithium tetrahydroaluminate (238 mg, 6.26 mmol) in diethyl ether (20 ml) was added a solution of **13** (3.00 g, 6.26 mmol) in diethyl ether (40 ml) at 0°C. After stirring for 1 h at 0°C, water (0.25 ml), 15% NaOH (0.25 ml) and water (0.75 ml) were added to the reaction mixture with ice-cooling. The mixture was filtered through a Celite pad and washed with diethyl ether. The ethereal solution was dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (75 g, hexane/ethyl acetate, 10:1) to give 2.31 g (85%) of **14** as a colorless oil; n_D^{23} = 1.5093. − IR (film): $\tilde{\nu}_{max}$ = 3440 cm^{-1} (m, O−H), 1585 (w, C=C), 1250 (m, Si−C), 1220 (m, C−O), 1125 (s, C−O), 1080 (s, C−O), 1065 (s, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 1.01 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.52−1.75 (m, 3 H, THP), 1.81 [s, 3 H, CH=C(*Me*)CH_2], 1.82−2.27 (m, 4 H, THP, OH), 2.15 (s, 3 H, ArC*H*$_3$), 2.20 (s, 3 H, ArC*H*$_3$), 3.39 (br. d, *J* = 10 Hz, 2 H, ArC*H*$_2$), 3.53−3.63 (m, 1 H, THP), 3.80−3.95 (m, 1 H, THP), 3.87 (t, *J* = 9 Hz, 2 H, C*H*$_2$$CH_2Si$), 4.18 (d, *J* = 5 Hz, 2 H, C*H*$_2$OH), 4.91 (s, 2 H, OCH_2O), 5.33 (t, *J* = 3 Hz, 1 H, THP), 5.39 (t, *J* = 3 Hz, olefinic H), 6.79 (s, 1 H, aromatic H). − HRMS: $C_{24}H_{40}O_5Si$ [M^+]: calcd. 436.2640, found 436.2642. Due to the instability of **14**, the correct combustion analytical data could not be obtained.

(Z)-4-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-2-methyl-2-butenyl Chloride (**15**): To a solution of **14** (2.05 g, 4.69 mmol) in DMF (40 ml) were added lithium chloride (595 mg, 14.1 mmol) and *sym*-collidine (2.27 g, 18.8 mmol) at 0°C. The mixture was stirred for 30 min at 0°C to dissolve lithium chloride and then methanesulfonyl chloride (1.08 g, 9.40 mmol) was added. After stirring for 1 h at 0°C, the reaction mixture was diluted with water (100 ml) and extracted three times with diethyl ether (100 ml). The combined ethereal extracts were washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (70 g, hexane/ethyl acetate, 25:1) to give 2.01 g (94%) of **15** as a colorless oil; IR (film): $\tilde{\nu}_{max}$ = 1585 cm^{-1} (w, C=C), 1250 (m, Si−C), 1200 (m, C−O), 1125 (s, C−O), 1080 (s, C−O), 1065 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 1.01 (br. t, *J* = 9 Hz, 2 H, CH_2Si), 1.45−2.30 (m, 6 H, THP), 1.85 [d, *J* = 1 Hz, 3 H, CH=C(*Me*)CH_2], 2.15 (s, 3 H, ArC*H*$_3$), 2.20 (s, 3 H, ArC*H*$_3$), 3.42 (d, *J* = 8 Hz, 2 H, ArC*H*$_2$), 3.55−4.10 (m, 2 H, THP), 3.87 (br. t, *J* = 9 Hz, 2 H, C*H*$_2$$CH_2Si$), 4.18 (s, 2 H, CH_2Cl), 4.91 (s, 2 H, OCH_2O), 5.25 (t, *J* = 3 Hz, 1 H, THP), 5.54 (dt, *J* = 1 Hz, *J′* = 8 Hz, 1 H, olefinic H), 6.78 (s, 1 H, aromatic H). This compound was used for the next reaction without further purification.

(4E,8E,12Z)-14-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-4,8,12-trimethyl-10-(phenylsulfonyl)tetradeca-4,8,12-trien-1-ol (**18**): To a stirred solution of **17** (1.66 g, 5.16 mmol) in THF (20 ml) and HMPA (7 ml) was added dropwise butyllithium (1.58 M in hexane, 6.53 ml, 10.3 mmol) at −50°C under argon, and the mixture was stirred at −50°C for 30 min. Then a solution of **15** (1.95 g, 4.29 mmol) in THF (15 ml) was added dropwise, and the stirring was continued for 20 h at 4°C. After the addition of water (100 ml), the mixture was neutralized with acetic acid and extracted three times with diethyl ether (100 ml). The combined ethereal extracts were successively washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (100 g, hexane/ethyl acetate, 3:1) to give 2.71 g (85%) of **18** as a colorless oil; n_D^{22} = 1.5250. − IR (film): $\tilde{\nu}_{max}$ = 3445 cm^{-1} (m, O−H), 1650 (m, C=C), 1305 (s, SO_2), 1250 (m, Si−C), 1145 (s, SO_2), 1085 (s, C−O), 1065 (s, C−O), 1035 (m, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 1.00 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.10 (s, 3 H, 17-H_3), 1.50−1.75 (m, 5 H, THP, 2-H_2), 1.56 (s, 3 H, 15-H_3), 1.62 (s, 3 H, 16-H_3), 1.75−2.10 (m, 8 H, OH, THP, 6,7-H_2), 2.01 (t, J = 8 Hz, 2 H, 3-H_2), 2.14 (s, 3 H, ArC*H*$_3$), 2.19 (s, 3 H, ArC*H*$_3$), 2.62 (ddd, *J* = 3 Hz, *J′* = 14 Hz, *J″* = 14 Hz, 1 H, 11-H), 2.89 (dd, *J* = 3 Hz, *J′* = 14 Hz, 1 H, 11-H), 3.15−3.45 (m, 2 H , 14-H_2), 3.50−3.62 (m, 1 H, THP), 3.58 (t, *J* = 8 Hz, 2 H, 1-H_2), 3.80−3.95 (m, 2 H, THP, 10-H), 3.85 (br. t, *J* = 9 Hz, 2 H, C$H_2$$CH_2Si$), 4.91 (d, *J* = 1 Hz, 2 H, OCH_2O), 4.95−5.10 (m, 2 H, 5,9-H), 5.29 (br. d, *J* = 2 Hz, 1 H, THP), 5.40 (t, *J* = 6 Hz, 1 H, 13-H), 6.72 (s, 1 H, aromatic H), 7.50 (dt, *J* = 1 Hz, *J′* = 11 Hz, 2 H, aromatic H), 7.60 (dt, *J* = 1 Hz, *J′* = 11 Hz, 1 H, aromatic H), 7.86 (dd, *J* = 1 Hz, *J′* = 11 Hz, 2 H, aromatic H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = −1.5, 12.3, 13.6, 15.8, 16.1, 18.2, 19.1, 23.6, 23.7, 25.3, 25.9, 29.1, 29.6, 30.6, 30.7, 35.8, 39.5, 62.1, 62.5, 63.5, 67.3, 96.8, 96.9, 97.9, 113.6, 117.0, 123.7, 125.1, 127.3, 128.6, 129.2, 130.6, 130.7, 131.0, 131.3, 133.3, 135.1, 137.9, 145.1, 148.3, 151.2, 151.3. − HRMS: $C_{42}H_{64}O_7SSi$ [M^+]: calcd. 740.4142, found 740.4160. This compound so strongly retained the solvents that the correct combustion analytical data could not be obtained.

(4E,8E,12Z)-14-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-4,8,12-trimethyltetradeca-4,8,12-trien-1-ol (**19**): To a stirred solution of **18** (2.50 g, 3.37 mmol) and [1,3-bis(diphenylphosphanyl)propane]palladium chloride complex (199 mg, 0.337 mmol) in dry THF (45 ml) was added dropwise lithium triethylhydroborate (1.0 M in THF, 10.1 ml, 10.1 mmol) at 0°C under argon. The stirring was continued for 3 h at 4°C. Then the mixture was diluted with 10% NaCN aqueous solution (50 ml) and extracted three times with diethyl ether (100 ml). The combined ethereal extracts were successively washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (75 g, hexane/ethyl acetate, 10:1) to give 1.81 g (89%) of **19** as a colorless oil; n_D^{22} = 1.5079. − IR (film): $\tilde{\nu}_{max}$ = 3420 cm^{-1} (m, O−H), 1250 (m, Si−C), 1200 (m, C−O), 1125 (m, C−O), 1080 (m, C−O), 1065 (m, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.04 (s, 9 H, $SiMe_3$), 1.01 (br. t, *J* = 8 Hz, 2 H, CH_2Si), 1.50−1.80 (m, 5 H, THP, 2-H_2), 1.61 (s, 6 H, 15,16-H_3), 1.74 (d, *J* = 1 Hz, 3 H, 17-H_3), 1.80−1.92 (m, 2 H, THP), 1.92−2.25 (m, 12 H, OH, THP, 3,6,7,10,11-H_2), 2.16 (s, 3 H, ArC*H*$_3$), 2.21 (s, 3 H, ArC*H*$_3$), 3.28−3.45 (m, 2 H, 14-H_2), 3.53−3.65 (m, 1 H, THP), 3.60 (t, *J* = 7 Hz, 2 H, 1-H_2), 3.85−4.00 (m, 1 H, THP), 3.87 (br. t, *J* = 8 Hz, 2 H, C$H_2$$CH_2Si$), 4.91 (s, 2 H, OCH_2O), 5.12−5.22 (m, 2 H, 5,9-H), 5.25−5.37 (m, 2 H, THP, 13-H), 6.77 (s, 1 H, aromatic H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = −1.5, 12.3, 13.6, 15.8, 15.9, 18.2, 19.1, 23.4, 25.3, 26.4, 26.5, 28.7, 30.6, 30.7, 32.1, *35.8*, 35.9, 39.6, 62.1, 62.7, *62.9*, 67.3, 96.9, 97.8, 113.5, 123.7, 124.3, 124.6, 124.9, 125.8, 130.8, 132.1, 134.5, 134.9, 136.0, 148.2, 151.3. This product was contaminated with about 5% of an inseparable impurity and therefore was used for the next reaction without further purification. The impurity disappeared after further operation at the steps to convert **19** to **21**. The NMR signals (in italics) are due to the impurity.

Methyl (4E,8E,12Z)-14-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-4,8,12-trimethyltetradeca-4,8,12-trienoate (**21**): To a stirred solution of Dess-Martin periodinane (3.59 g, 8.49 mmol) in dichloromethane (60 ml) was added pyridine (3.36 g, 42.5 mmol) under argon. The stirring was continued at room temperature until a clear solution was obtained

and a solution of **19** (1.70 g, 2.83 mmol) in dichloromethane (10 ml) was added. The mixture was stirred at room temperature for 1 h, diluted with a saturated $NaHCO_3$ solution (25 ml) and a saturated $Na_2S_2O_3$ solution (25 ml), and extracted three times with dichloromethane (50 ml). The combined extracts were successively washed with water and brine, dried with Na_2SO_4, and filtered through silica gel. The filtrate was concentrated in vacuo to give 1.47 g of crude **20**. – IR (film): $\tilde{\nu}_{max}$ = 2715 cm^{-1} (m, CHO), 1725 (s, C=O), 1580 (w, C=C), 1250 (m, Si–C), 1200 (m, C–O), 1125 (s, C–O), 1080 (s, C–O), 1065 (s, C–O), 1035 (m, C–O). – ^1H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 1.01 (br. t, *J* = 9 Hz, 2 H, CH_2Si), 1.40–2.50 (m, 18 H, THP, 2,3,6,7,10,11-H_2), 1.60 (s, 6 H, 15,16-H_3), 1.73 (br. s, 3 H, 17-H_3), 2.16 (s, 3 H, ArCH_3), 2.21 (s, 3 H, ArCH_3), 3.33 (d, *J* = 6 Hz, 2 H, 14-H_2), 3.45–4.00 (m, 2 H, THP), 3.93 (br. t, *J* = 9 Hz, 2 H, CH_2CH_2Si), 4.92 (s, 2 H, OCH_2O), 5.00–5.40 (m, 4 H, 5,9,13-H, THP), 6.78 (s, 1 H, aromatic H), 9.75 (t, *J* = 2 Hz, 1 H, CHO). – To a solution of crude **20** (1.47 g) in dimethyl sulfoxide (20 ml) and acetonitrile (20 ml) was added a solution of potassium dihydrogen phosphate (1.32 g, 8.46 mmol) in water (24 ml). The mixture was stirred at room temperature for 10 min and sodium chlorite (512 mg, 5.66 mmol) was added. After stirring for 2 h at room temperature, the mixture was diluted with brine (70 ml) and extracted three times with diethyl ether (100 ml). The combined ethereal extracts were washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was dissolved in diethyl ether (10 ml) and treated with a solution of diazomethane (8.49 mmol) in diethyl ether (10 ml) at 0°C. The mixture was stirred at room temperature for 1 h and concentrated in vacuo. The residue was purified by chromatography on silica gel (50 g, hexane/ethyl acetate, 50:1) to give 1.33 g (75% based on **19**) of **21** as a yellowish oil; n_D^{23} = 1.5095. – IR (film): $\tilde{\nu}_{max}$ = 1740 cm^{-1} (s, C=O), 1585 (w, C=C), 1250 (s, Si–C), 1200 (s, C–O), 1150 (s, C–O), 1125 (s, C–O), 1080 (s, C–O), 1065 (s, C–O), 1035 (s, C–O). – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 1.00 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.52–1.80 (m, 3 H, THP), 1.60 (s, 6 H, 15,16-H_3), 1.73 (d, *J* = 1 Hz, 3 H, 17-H_3), 1.80–1.90 (m, 2 H, THP), 1.90–2.22 (m, 9 H, THP, 6,7,10,11-H_2), 2.15 (s, 3 H, ArCH_3), 2.20 (s, 3 H, ArCH_3), 2.28 (t, *J* = 9 Hz, 2 H, 3-H_2), 2.40 (br. t, *J* = 9 Hz, 2 H, 2-H_2), 3.25–3.45 (m, 2 H, 14-H_2), 3.50–3.65 (m, 1 H, THP), 3.65 (s, 3 H, CO_2CH_3), 3.80–4.00 (m, 1 H, THP), 3.86 (t, *J* = 9 Hz, 2 H, CH_2CH_2Si), 4.91 (s, 2 H, OCH_2O), 5.10–5.20 (m, 2 H, 5.9-H), 5.25–5.35 (m, 2 H, THP, 13-H), 6.78 (s, 1 H, aromatic H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –1.5, 12.3, 13.6, 15.86, 15.95, 18.2, 19.1, 23.5, 25.3, 26.5, 26.6, 28.7, 30.6, 32.1, 33.0, 34.6, 39.5, 51.4, 62.1, 67.2, 96.9, 97.8, 113.5, 123.7, 124.2, 124.9, 125.1, 130.8, 132.1, 133.2, 135.0, 136.0, 148.2, 151.3, 173.9. – $C_{37}H_{60}O_6Si$ (629.0): calcd. C 70.66, H 9.62; found C 70.28, H 9.38

Methyl (4E,8E,12Z)-14-(2′-Hydroxy-3′,4′-dimethyl-5′-tetrahydropyranyloxyphenyl)-4,8,12-trimethyltetradeca-4,8,12-trienoate (**22**): To a stirred solution of **21** (900 mg 1.43 mmol) in HMPA (9 ml) was added cesium fluoride (1.74 g, 11.4 mmol) under argon. The stirring was continued for 2 h at 120°C. Then the mixture was diluted with diethyl ether (200 ml), and the solution was washed with water and brine. The ethereal solution was dried with Na_2SO_4 and concentrated in vacuo to give 948 mg of crude **22** as a brown oil. – IR (film): $\tilde{\nu}_{max}$ = 3480 cm^{-1} (m, O–H), 1740 (s, C=O), 1200 (s, C–O), 1120 (s, C–O), 1080 (s, C–O), 1035 (s, C–O). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.40–2.45 (m, 18 H, 2,3,6,7,10,11-H_2, THP), 1.60 (s, 6 H, 15,16-H_3), 1.77 (s, 3 H, 17-H_3), 2.17 (s, 6 H, ArCH_3), 3.31 (d, *J* = 9 Hz, 2 H, 14-H_2), 3.50–4.10 (m, 2 H, THP), 3.65 (s, 3 H, CO_2CH_3), 4.90–5.40 (m, 5 H, OH, 5,9,13-H, THP), 6.75 (s, 1 H, aromatic H). This compound was used for the next reaction without further purification.

Methyl (4E,8E,12Z)-14-(2′-Acetoxy-3′,4′-dimethyl-5′-tetrahydropyranyloxyphenyl)-4,8,12-trimethyltetradeca-4,8,12-trienoate (**23**): To a stirred and ice-cooled solution of crude **22** (948 mg) in dry pyridine (5.0 ml) was added acetic anhydride (500 mg, 4.90 mmol). The stirring was continued for 20 h at room temperature and for another 1 h after the addition of water (50 ml). The mixture was extracted three times with diethyl ether (50 ml). The combined ethereal extracts were successively washed with water, a saturated $CuSO_4$ solution, a saturated $NaHCO_3$ solution and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (50 g, hexane/ethyl acetate, 10:1) to give 615 mg (80% based on **21**) of **23** as a colorless oil; n_D^{23} = 1.5161. – IR (film): $\tilde{\nu}_{max}$ = 1760 cm^{-1} (s, C=O), 1740 (s, C=O), 1585 (w, C=C), 1200 (s, C–O), 1195 (s, C–O), 1125 (s, C–O), 1080 (s, C–O), 1035 (s, C–O). – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.55–1.80 (m, 3 H, THP), 1.60 (s, 6 H, 15,16-H_3), 1.72 (d, *J* = 1 Hz, 3 H, 17-H_3), 1.80–1.90 (m, 2 H, THP), 1.90–2.20 (m, 9 H, THP, 6,7,10,11-H_2), 2.03 (s, 3 H, ArCH_3), 2.16 (s, 3 H, ArCH_3), 2.24–2.34 (m, 2 H, 3-H_2), 2.29 (s, 3 H, acetyl), 2.41 (br. t, *J* = 9 Hz, 2 H, 2-H_2), 3.15 (d, *J* = 7 Hz, 2 H, 14-H_2), 3.52–3.62 (m, 1 H, THP), 3.66 (s, 3 H, CO_2CH_3), 3.90 (ddd, *J* = 2 Hz, *J′* = 12 Hz, *J″* = 12 Hz, 1 H, THP), 5.14 (br. t, *J* = 6 Hz, 2 H, 5,9-H), 5.21 (dt, *J* = 1 Hz, *J′* = 7 Hz, 1 H, 13-H), 5.32 (t, *J* = 3 Hz, 1 H, THP), 6.83 (s, 1 H, aromatic H). – $C_{33}H_{48}O_6$ (540.7): calcd. C 73.30, H 8.95; found C 72.95, H 8.60.

Methyl (4E,8E,12Z)-14-(2′-Acetoxy-5′-hydroxy-3′,4′-dimethylphenyl)-4,8,12-trimethyltetradeca-4,8,12-trienoate (**24**): To a stirred solution of **23** (550 mg, 1.02 mmol) in methanol (5 ml) was added *p*-toluenesulfonic acid monohydrate (10 mg, 0.058 mmol). The stirring was continued for 4 h at room temperature. Then the mixture was quenched with a saturated $NaHCO_3$ solution (50 ml) and extracted three times with diethyl ether (50 ml). The combined ethereal extracts were washed with water and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by chromatography on silica gel (50 g, hexane/ethyl acetate, 10:1) to give 431 mg (92%) of **24** as a yellowish oil; n_D^{23} = 1.5170. – IR (film): $\tilde{\nu}_{max}$ = 3445 cm^{-1} (m, O–H), 1760 (s, C=O), 1740 (s, C=O), 1590 (w, C=C), 1190 (s, C–O), 1080 (s, C–O). – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (s, 6 H, 15,16-H_3), 1.72 (d, *J* = 1 Hz, 3 H, 17-H_3), 1.95–2.20 (m, 8 H, 6,7,10,11-H_2), 2.02 (s, 3 H, ArCH_3), 2.11 (s, 3 H, ArCH_3), 2.25–2.35 (m, 2 H, 3-H_2), 2.31 (s, 3 H, acetyl), 2.42 (br. t, *J* = 8 Hz, 2 H, 2-H_2), 3.11 (d, *J* = 8 Hz, 2 H, 14-H_2), 3.67 (s, 3 H, CO_2CH_3), 5.02–5.17 (m, 2 H, 5,9-H), 5.21 (dt, *J* = 1 Hz, *J′* = 6 Hz, 1 H, 13-H), 5.58 (s, 1 H, OH), 6.48 (s, 1 H, aromatic H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.9, 13.1, 15.8, 20.5, 23.4, 26.3, 26.4, 28.5, 31.9, 33.0, 34.6, 39.4, 51.6, 113.4, 121.6, 122.4, 124.1, 125.1, 125.8, 129.8, 130.9, 133.1, 135.0, 136.5, 140.8, 151.6, 169.8, 174.3. – $C_{28}H_{40}O_5$ (456.6): calcd. C 73.65, H 8.83; found C 73.32, H 8.97.

Methyl (4E,8E,12Z)-14-[2′-Acetoxy-3′,4′-dimethyl-5′-(2″,3″,4″-tri-O-acetyl-1″-β-D-xylopyranosyloxy)phenyl]-4,8,12-trimethyltetradeca-4,8,12-trienoate (**25**): To a stirred solution of **24** (350 mg, 0.743 mmol), 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl fluoride (620 mg, 2.23 mmol) and 1,1,3,3-tetramethylguanidine (513 mg, 4.46 mmol) in dry acetonitrile (8 ml) was added boron trifluoride–diethyl ether (844 mg, 5.94 mmol) at room temperature under argon. After stirring at room temperature for 20 h, The mixture was quenched with a saturated $NaHCO_3$ solution (20 ml) and extracted three times with diethyl ether (50 ml). The combined ethereal extracts were successively washed with water and brine, dried with

Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (50 g, hexane/ethyl acetate, 3:1) to give 413 mg of crude **25** as a colorless oil. – IR (film): $\tilde{\nu}_{max}$ = 1755 cm^{-1} (s, C=O), 1585 (w, C=C), 1245, (s, C–O), 1220 (s, C–O), 1195 (s, C–O), 1080 (s, C–O), 1060 (m, C–O), 1040 (s, C–O). This was employed in the next step without further purification.

(4E,8E,12Z)-14-[2′-Hydroxy-3′,4′-dimethyl-5′-(1″-β-D-xylopyranosyloxy)phenyl]-4,8,12-trimethyltetradeca-4,8,12-trienoic Acid (**2**): To a solution of crude **25** (413 mg) in methanol (3.0 ml) was added a 10% NaOH aqueous solution (3.0 ml). The stirring was continued for 2 h at room temperature. The mixture was neutralized with acetic acid, and extracted three times with chloroform (50 ml). The combined extracts were dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (25 g, chloroform/methanol, 10:1) to give 213 mg (54% based on **24**) of **2** as a colorless amorphous solid. – $[\alpha]_D^{24}$ = –15 (*c* = 0.15, MeOH). – R_f = 0.65 (*i*BuOH/MeOH/H_2O, 8:1:1) (ref[4]. R_f = 0.65). – IR (KBr): $\tilde{\nu}_{max}$ = 3395 cm^{-1} (s, O–H), 2965 (m), 2930 (m), 2900 (m), 2865 (m), 1715 (m, C=O), 1560 (w, C=C), 1480 (m), 1440 (m), 1385 (w), 1280 (m, C–O), 1215 (s, C–O), 1165 (s, C–O), 1100 (m, C–O), 1065 (s, C–O), 1055 (s, C–O), 1005 (m), 985 (m), 845 (m). – ^{1}H NMR (300 MHz, CD_3OD): δ = 1.60 (s, 6 H, 15,16-H_3), 1.76 (s, 3 H, 17-H_3), 1.90–2.00 (m, 2 H, 6-H_2), 2.00–2.25 (m, 6 H, 7,10,11-H_2), 2.14 (s, 3 H, 18 or 19-H_3), 2.16 (s, 3 H, 18 or 19-H_3), 2.25 (br. t, *J* = 7 Hz, 2 H, 3-H_2), 2.35 (br. t, *J* = 7 Hz, 2 H, 2-H_2), 3.19 (t, *J* = 10 Hz, 1 H, 5″a-H), 3.20–3.30 (m, 2 H, 14-H_2), 3.38 (t, *J* = 7 Hz, 1 H, 3″-H), 3.42 (t, *J* = 7 Hz, 1 H, 2″-H), 3.56 (ddd, *J* = 5 Hz, *J′* = 7 Hz, *J″* = 10 Hz, 1 H, 4″-H), 3.86 (dd, *J* = 5 Hz, *J′* = 10 Hz, 1 H, 5″e-H), 4.60 (d, *J* = 7 Hz, 1 H, 1″-H), 5.15 (br. s, 2 H, 5,9-H), 5.33 (t, *J* = 7 Hz, 1 H, 13-H), 6.72 (s, 1 H, 6′-H). – ^{13}C NMR (75.5 MHz, CD_3OD): δ = 12.7, 12.9, 16.07, 16.13, 23.8, 27.6, 29.5, 32.9, 34.6, 36.0, 40.7, 66.9, 71.1, 74.9, 77.9, 105.1, 116.5, 124.4, 125.4, 125.9, 126.1, 126.5, 127.3, 127.9, 134.8, 136.1, 137.4, 148.9, 150.6, 178.6. – MS (70 eV); *m/z* (%): 532 (1) [M^+], 514 (3), 496 (1), 472 (1), 400 (73), 189 (74), 151 (100), 81 (33). – HRMS: $C_{30}H_{42}O_7$ [$M^+ - H_2O$]: calcd. 514.2930, found 514.2933.

Methyl 14-(2′-Acetoxy-5′-hydroxy-3′,4′-dimethylphenyl)-4,8,12-trimethyltetradecanoate (**33**): To a stirred solution of **32** (300 mg, 0.656 mmol) in ethanol (6 ml) was added platinum oxide (60.0 mg, 0.264 mmol) under hydrogen. The stirring was continued for 24 h at room temperature. Then the mixture was filtered through a Celite pad and washed with diethyl ether. The ethereal solution was concentrated in vacuo. The residue was purified by chromatography on silica gel (30 g, hexane/ethyl acetate, 10:1) to give 310 mg (quantitative) of **33** as a colorless oil; n_D^{22} = 1.4928. – IR (film): $\tilde{\nu}_{max}$ = 3445 cm^{-1} (m, O–H), 1760 (s, C=O), 1730 (s, C=O), 1590 (w, C=C), 1195 (s, C–O), 1080 (s, C–O). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6 Hz, 3 H, 15 or 16-H_3), 0.87 (d, *J* = 6 Hz, 3 H, 15 or 16-H_3), 0.91 (d, *J* = 6 Hz, 3 H, 17-H_3), 1.00–1.75 (m, 19 H, 3,5,6,7,9,10,11,13-H_2, 4,8,12-H), 2.03 (s, 3 H, ArCH_3), 2.11 (s, 3 H, ArCH_3), 2.20–2.45 (m, 4 H, 2,14-H_2), 2.33 (s, 3 H, acetyl), 3.67 (s, 3 H, CO_2CH_3), 5.15–5.30 (m, 1 H, OH), 6.47 (s, 1 H, aromatic H). – $C_{28}H_{46}O_5$ (462.7): calcd. C 72.69, H 10.02; found C 72.48, H 10.03.

Methyl 14-[2′-Acetoxy-3′,4′-dimethyl-5′-(2″,3″,4″-tri-O-acetyl-1″-β-D-xylopyranosyloxy)phenyl]-4,8,12-trimethyltetradecanoate (**34**): This was prepared from **33** (250 mg, 0.540 mmol) in the same manner as described for **25** to give 345 mg of crude **34** as a colorless oil. – IR (film): $\tilde{\nu}_{max}$ = 1760 cm^{-1} (s, C=O), 1580 (w, C=C), 1245, (s, C–O), 1220 (s, C–O), 1195 (s, C–O), 1120 (m, C–O), 1080 (s, C–O), 1060 (s, C–O), 1040 (s, C–O). This was employed in the next step without further purification.

14-[2′-Hydroxy-3′,4′-dimethyl-5′-(1″-β-D-xylopyranosyloxy)-phenyl]-4,8,12-trimethyltetradecanoic Acid (**3**): This was prepared from crude **34** (345 mg) in the same manner as described for **2** to give 159 mg (55% based on **33**) of **3** as a colorless waxy solid. – $[\alpha]_D^{24}$ = –16 (*c* = 0.10, MeOH). – R_f = 0.65 (*i*BuOH/MeOH/H_2O, 8:1:1). – IR (film): $\tilde{\nu}_{max}$ = 3370 cm^{-1} (s, O–H), 2925 (s), 2860 (s), 1710 (m, C=O), 1550 (w), 1460 (m), 1455 (m), 1415 (m), 1380 (w), 1225 (m, C–O), 1075 (m, C–O), 1050 (s, C–O), 1030 (s, C–O). – ^{1}H NMR (300 MHz, CD_3OD): δ = 0.86 (d, *J* = 6 Hz, 3 H, 15 or 16-H_3), 0.88 (d, *J* = 6 Hz, 3 H, 15 or 16-H_3), 0.94 (d, *J* = 6 Hz, 3 H, 17-H_3), 1.00–1.75 (m, 19 H, 3,5,6,7,9,10,11,13-H_2, 4,8,12-H), 2.14 (s, 3 H, 18 or 19-H_3), 2.16 (s, 3 H, 18 or 19-H_3), 2.20–2.35 (m, 2 H, 2-H_2), 2.45–2.70 (m, 2 H, 14-H_2), 3.22 (t, *J* = 10 Hz, 1 H, 5″a-H), 3.41 (t, *J* = 8 Hz, 1 H, 3″-H), 3.46 (t, *J* = 8 Hz, 1 H, 2″-H), 3.57 (ddd, *J* = 5 Hz, *J′* = 8 Hz, *J″* = 10 Hz, 1 H, 4″-H), 3.89 (dd, *J* = 5 Hz, *J′* = 10 Hz, 1 H, 5″e-H), 4.64 (d, *J* = 8 Hz, 1 H, 1″-H), 6.71 (s, 1 H, 6′-H). – ^{13}C NMR (75.5 MHz, CD_3OD): δ = 12.8, 13.0, 19.7, 19.8, 20.12, 20.19, 20.24, 25.4, 29.1, 33.37, 33.46, 33.53, 33.61, 33.68, 33.74, 33.9, 38.2, 38.4, 38.5, 66.8, 71.0, 74.9, 77.8, 105.2, 105.3, 117.1, 126.1, 126.5, 126.6, 129.2, 129.3, 148.9, 150.4, 150.5, 179.6. – MS (70 eV); *m/z* (%): 538 (1) [M^+], 520 (1), 478 (1), 420 (28), 406 (43), 388 (42), 151 (100). – HRMS: $C_{30}H_{50}O_8$ [M^+]: calcd. 538.3506, found 538.3499.

Methyl (4E)-10-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-4,8-dimethyldeca-4,8-dienoate (**36**): To a stirred solution of **28** (3.58 g, 6.96 mmol) and **35** (1.50 g, 5.60 mmol) in DMF (30 ml) were added lithium chloride (885 mg, 20.9 mmol) and tris(benzylideneacetone)dipalladium(0) (159 mg, 0.174 mmol) under argon. The stirring was continued for 7 h at 100°C. Then the mixture was diluted with water (50 ml) and extracted three times with diethyl ether (50 ml). The combined ethereal extracts were successively washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (100 g, hexane/ethyl acetate, 20:1) to give 2.63 g (84%) of **36** as a yellowish oil; n_D^{23} = 1.5058. – IR (film): $\tilde{\nu}_{max}$ = 1740 cm^{-1} (s, C=O), 1580 (w, C=C), 1250 (m, Si–C), 1200 (m, C–O), 1155 (m, C–O), 1125 (m, C–O), 1080 (m, C–O), 1065 (m, C–O), 1035 (m, C–O). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 1.01 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.50–2.25 (m, 10 H, 6,7-H_2, THP), 1.60 (s, 3 H, 11-H_3), 1.70 (s, 3 H, 12-H_3), 2.16 (s, 3 H, ArCH_3), 2.21 (s, 3 H, ArCH_3), 2.25–2.45 (m, 4 H, 2,3-H_2), 3.35 (d, *J* = 7 Hz, 2 H, 10-H_2), 3.45–4.10 (m, 2 H, THP), 3.64 (s, 3 H, CO_2CH_3), 3.86 (t, *J* = 9 Hz, 2 H, C$H_2$$CH_2Si$), 4.92 (s, 2 H, OCH_2O), 5.00–5.40 (m, 3 H, 5,9-H, THP), 6.79 (s, 1 H, aromatic H). – $C_{32}H_{52}O_6Si$ (560.8): calcd. C 68.53, H 9.35; found C 68.69, H 9.38.

Methyl (4E)-10-(2′-Hydroxy-3′,4′-dimethyl-5′-tetrahydropyranyloxyphenyl)-4,8-dimethyldeca-4,8-dienoate (**37**): This was prepared from **36** (1.95 g, 3.48 mmol) in the same manner as described for **22** to give 2.30 g of crude **37** as a brown oil. – IR (film): $\tilde{\nu}_{max}$ = 3415 cm^{-1} (m, O–H), 1740 (s, C=O), 1200, (s, C–O), 1170 (s, C–O), 1125 (s, C–O), 1075 (s, C–O), 1035 (s, C–O). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.50–2.25 (m, 10 H, 6,7-H_2, THP), 1.60 (s, 3 H, 11-H_3), 1.77 (s, 3 H, 12-H_3), 2.17 (s, 6 H, ArCH_3), 2.15–2.45 (m, 4 H, 2,3-H_2), 3.29 (d, *J* = 7 Hz, 2 H, 10-H_2), 3.40–4.20 (m, 2 H, THP), 3.64 (s, 3 H, CO_2CH_3), 4.90–5.40 (m, 4 H, 5,9-H, THP, OH), 6.74 (s, 1 H, aromatic H). This was employed in the next step without further purification.

Methyl (4E)-10-(2′-Acetoxy-3′,4′-dimethyl-5′-tetrahydropyranyloxyphenyl)-4,8-dimethyldeca-4,8-dienoate (**38**): This was prepared from crude **37** (2.30 g) in the same manner as described for **23** to give 1.21 g (74% based on **36**) of **38** as a yellowish oil; n_D^{23} =

1.5148. – IR (film): $\tilde{\nu}_{max}$ = 1760 cm^{-1} (s, C=O), 1740 (s, C=O), 1585 (w, C=C), 1220 (s, C–O), 1195 (s, C–O), 1125 (s, C–O), 1080 (s, C–O), 1035 (s, C–O). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.50–2.25 (m, 10 H, 6,7-H_2, THP), 1.60 (s, 3 H, 11-H_3), 1.65 [s, 5/3 H, 12-H_3 (*E*)], 1.70 [br. s, 4/3 H, 12-H_3 (*Z*)], 2.03 (s, 3 H, ArCH_3), 2.17 (s, 3 H, ArCH_3), 2.25–2.45 (m, 4 H, 2,3-H_2), 2.30 (s, 3 H, acetyl), 3.17 (d, *J* = 7 Hz, 2 H, 10-H_2), 3.40–4.20 (m, 2 H, THP), 3.64 (s, 3 H, CO_2CH_3), 5.00–5.25 (m, 2 H, 5,9-H), 5.32 (br. s, 1 H, THP), 6.82 (s, 1 H, aromatic H). – $C_{28}H_{40}O_6$ (472.6): calcd. C 71.16, H 8.53; found C 70.78, H 8.62.

Methyl (4E)-10-(2′-Acetoxy-5′-hydroxy-3′,4′-dimethylphenyl)-4,8-dimethyldeca-4,8-dienoate (**39**): This was prepared from **38** (950 mg, 2.01 mmol) in the same manner as described for **24** to give 753 mg (97%) of **39** as a yellowish oil; n_D^{22} = 1.5171. – IR (film): $\tilde{\nu}_{max}$ = 3445 cm^{-1} (s, O–H), 1760 (s, C=O), 1735 (s, C=O), 1590 (m, C=C), 1245 (s, C–O), 1215 (s, C–O), 1200 (s, C–O), 1080 (s, C–O). – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 3 H, 11-H_3), 1.65 [s, 5/3 H, 12-H_3 (*E*)], 1.70 [s, 4/3 H, 12-H_3 (*Z*)], 2.00–2.20 (m, 4 H, 6,7-H_2), 2.04 (s, 3 H, ArCH_3), 2.11 (s, 3 H, ArCH_3), 2.25–2.40 (m, 2 H, 3-H_2), 2.32 (s, 3 H, acetyl), 2.44 (t, *J* = 7 Hz, 2 H, 2-H_2), 3.11 (d, *J* = 7 Hz, 2 H, 10-H_2), 3.67 [s, 5/3 H, CO_2CH_3 (*E*)], 3.68 [s, 4/3 H, CO_2CH_3 (*Z*)], 5.10–5.35 (m, 2 H, 5,9-H), 6.49 (s, 1 H, aromatic H), 6.55–6.63 (m, 1 H, OH). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.7, 12.9, 15.6, 15.7, 15.8, 20.4, 23.0, 25.6, 25.7, 28.2, 31.0, 32.7, 34.4, 34.5, 39.1, 51.6, 113.0, 113.1, 121.6, 121.9, 122.5, 124.6, 124.7, 129.45, 129.51, 130.5, 133.0, 133.2, 135.9, 136.2, 140.5, 151.78, 151.81, 169.9, 174.6, 174.7. – $C_{23}H_{32}O_5$ (388.5): calcd. C 71.11, H 8.30; found C 71.09, H 8.08.

Methyl (4E)-10-[2′-Acetoxy-3′,4′-dimethyl-5′-(2″,3″,4″-tri-O-acetyl-1″-β-D-xylopyranosyloxy)phenyl]-4,8-dimethyldeca-4,8-dienoate (**40**): This was prepared from **39** (400 mg, 1.03 mmol) in the same manner as described for **25** to give 423 mg of crude **40** as a colorless oil. – IR (film): $\tilde{\nu}_{max}$ = 1755 cm^{-1} (s, C=O), 1585, (w, C=C), 1225 (s, C–O), 1195 (s, C–O), 1060 (s, C–O), 1040 (s, C–O). This was employed in the next step without further purification.

(4E)-10-[2′-Hydroxy-3′,4′-dimethyl-5′-(1″-β-D-xylopyranosyloxy)phenyl]-4,8-dimethyldeca-4,8-dienoic Acid (**4**): This was prepared from crude **40** (423 mg) in the same manner as described for **2** to give 200 mg (42% based on **39**) of **4** as a colorless amorphous solid. – $[\alpha]_D^{25}$ = –17 (*c* = 0.18, MeOH). – R_f = 0.62 (*i*BuOH/MeOH/H_2O, 8:1:1). – IR (KBr): $\tilde{\nu}_{max}$ = 3440 cm^{-1} (s, O–H), 2915 (m), 1715 (m, C=O), 1645 (m), 1480 (m), 1455 (m), 1425 (m), 1385 (m), 1215 (m, C–O), 1160 (m, C–O), 1075 (m, C–O), 1055 (s, C–O), 985 (m), 845 (m). – ^1H NMR (300 MHz, CD_3OD): δ = 1.61 (s, 3 H, 11-H_3), 1.71 [s, 5/3 H, 12-H_3 (*E*)], 1.76 [s, 4/3 H, 12-H_3 (*Z*)], 2.00–2.20 (m, 4 H, 6,7-H_2), 2.14 (s, 3 H, 13 or 14-H_3), 2.16 (s, 3 H, 13 or 14-H_3), 2.24 (t, *J* = 7 Hz, 2 H, 3-H_2), 2.31 (br. t, *J* = 7 Hz, 2 H, 2-H_2), 3.19, 3.20 (each t, *J* = 10 Hz, total 1 H, 5″a-H), 3.27 (d, *J* = 7 Hz, 2 H, 10-H_2), 3.38 (t, *J* = 8 Hz, 1 H, 3″-H), 3.44 (t, *J* = 8 Hz, 1 H, 2″-H), 3.58 (ddd, *J* = 5 Hz, *J′* = 8 Hz, *J″* = 10 Hz, 1 H, 4″-H), 3.87 (dd, *J* = 5 Hz, *J′* = 10 Hz, 1 H, 5″e-H), 4.60 (d, *J* = 8 Hz, 1 H, 1″-H), 5.17, 5.19 (each t, *J* = 7 Hz, total 1 H, 5-H), 5.31, 5.33 (each t, *J* = 7 Hz, total 1 H, 9-H), 6.71 (s, 1 H, 6′-H). – ^{13}C NMR (75.5 MHz, CD_3OD): δ = 12.7, 12.9, 16.06, 16.11, 16.3, 23.8, 27.5, 27.6, 29.4, 29.6, 32.8, 34.1, 34.2, 35.8, 35.9, 40.7, 66.9, 71.1, 74.9, 77.9, 105.07, 105.10, 116.46, 116.53, 124.1, 124.5, 125.8, 126.1, 126.2, 126.56, 126.59, 127.7, 127.8, 134.9, 135.1, 136.9, 137.2, 148.8, 150.5, 150.6, 178.3. – MS (70 eV); *m/z* (%): 464 (1) [M^+], 446 (1), 332 (97), 205 (17), 189 (53), 151 (100). – HRMS: $C_{25}H_{36}O_8$ [M^+]: calcd. 464.2410, found 464.2418. This material is an inseparable mixture of (8*E*) and (8*Z*) isomers (1.3:1).

(4E,8E)-14-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-4,8,12-trimethyltetradeca-4,8,12-trien-1-ol (**41**): This was prepared from **29** (3.30 g, 5.25 mmol) in the same manner as described for **14** to give 3.00 g (95%) of **41** as a colorless oil; n_D^{24} = 1.5150. – IR (film): $\tilde{\nu}_{max}$ = 3435 cm^{-1} (m, O–H), 1250 (m, Si–C), 1200 (m, C–O), 1150 (m, C–O), 1125 (s, C–O), 1080 (s, C–O), 1065 (s, C–O), 1035 (s, C–O). – ^1H NMR (90 MHz, $CDCl_3$): δ = 0.05 (s, 9 H, $SiMe_3$), 1.01 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.40–2.20 (m, 19 H, THP, 2,3,6,7,10,11-H_2, OH), 1.60 (s, 6 H, 15,16-H_3), 1.70 (s, 3 H, 17-H_3), 2.15 (s, 3 H, ArCH_3), 2.21 (s, 3 H, ArCH_3), 3.35 (d, *J* = 7 Hz, 2 H, 14-H_2), 3.40–4.10 (m, 2 H, THP), 3.60 (t, *J* = 6 Hz, 2 H, 1-H_2), 3.85 (t, *J* = 9 Hz, 2 H, CH_2CH_2Si), 4.92 (s, 2 H, OCH_2O), 5.00–5.40 (m, 4 H, 5,9,13-H, THP), 6.78 (s, 1 H, aromatic H). These spectral data are identical to those reported in ref[4], and very similar to those of **19**.

(4E,8E)-14-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-4,8,12-trimethyltetradeca-4,8,12-trienal (**42**): This was prepared from **41** (2.25 g, 3.74 mmol) in the same manner as described for **20** to give 2.01 g of crude **42** as a colorless oil. – IR (film): $\tilde{\nu}_{max}$ = 2715 cm^{-1} (m, CHO), 1725 (s, C=O), 1585 (w, C=C), 1250 (m, Si–C), 1200 (m, C–O), 1150 (m, C–O), 1125 (s, C–O), 1080 (s, C–O), 1065 (s, C–O), 1035 (s, C–O). – ^1H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 1.01 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.40–2.25 (m, 14 H, THP, 6,7,10,11-H_2), 1.60 (s, 6 H, 15,16-H_3), 1.70 (s, 3 H, 17-H_3), 2.17 (s, 3 H, ArCH_3), 2.21 (s, 3 H, ArCH_3), 2.25–2.65 (m, 4 H, 2,3-H_2), 3.36 (d, *J* = 7 Hz, 2 H, 14-H_2), 3.40–4.20 (m, 2 H, THP), 3.86 (t, *J* = 9 Hz, 2 H, CH_2CH_2Si), 4.92 (s, 2 H, OCH_2O), 5.00–5.45 (m, 4 H, 5,9,13-H, THP), 6.79 (s, 1 H, aromatic H), 9.75 (t, *J* = 2 Hz, 1 H, CHO). This was employed in the next step without further purification.

(6E,10E)-16-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-2,6,10,14-tetramethylhexadeca-1,6,10,14-tetraen-3-ol (**43**): To a stirred solution of 2-bromopropene (1.53 g, 12.6 mmol) in THF (40 ml) was added dropwise *s*-butyllithium (1.03 M in cyclohexane, 9.23 ml, 9.51 mmol) at –78°C under argon, and the mixture was stirred at –78°C for 30 min. Then a solution of **42** (1.90 g, 3.17 mmol) in THF (20 ml) was added dropwise, and the stirring was continued for 2 h at room temperature. After the addition of water (50 ml), the mixture was extracted three times with diethyl ether (50 ml). The combined ethereal extracts were successively washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (50 g, hexane/ethyl acetate, 20:1) to give 0.40 g (21%) of the recovered **42** and 1.42 g (70%) of **43** as a colorless oil; n_D^{23} = 1.5152. – IR (film): $\tilde{\nu}_{max}$ = 3475 cm^{-1} (m, O–H), 1250 (m, Si–C), 1200 (m, C–O), 1150 (m, C–O), 1125 (s, C–O), 1080 (s, C–O), 1065 (s, C–O), 1035 (s, C–O). – ^1H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 1.01 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.55–2.30 (m, 19 H, THP, 4,5,8,9,12,13-H_2, OH), 1.61 (s, 6 H, 18,19-H_3), 1.72 (s, 6 H, 17,20-H_3), 2.15 (s, 3 H, ArCH_3), 2.21 (s, 3 H, ArCH_3), 3.32 (d, *J* = 7 Hz, 2 H, 16-H_2), 3.40–4.20 (m, 3 H, 3-H, THP), 3.87 (t, *J* = 9 Hz, 2 H, CH_2CH_2Si), 4.80–5.45 (m, 6 H, 1-H_2, 7,11,15-H, THP), 4.92 (s, 2 H, OCH_2O), 6.78 (s, 1 H, aromatic H). – $C_{39}H_{64}O_5Si$ (641.0): calcd. C 73.08, H 10.06; found C 73.03, H 10.06.

Ethyl (4E,8E,12E)-18-{3′,4′-Dimethyl-5′-tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-4,8,12,16-tetramethyloctadeca-4,8,12,16-tetraenoate (**44**): To a stirred solution of **43** (1.35 g, 2.11 mmol) in $MeCH(OEt)_3$ (10.0 g, 61.3 mmol) was added a catalytic amount of propionic acid (10 mg). The stirring

was continued for 1 h at 140°C under the condition for distillative removal of ethanol. Then the mixture was concentrated to remove $MeCH(OEt)_3$. After cooling, the mixture was diluted with diethyl ether (150 ml). The ethereal solution was successively washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (70 g, hexane/ethyl acetate, 20:1) to give 1.31 g (83%) of **44** as a colorless oil; n_D^{24} = 1.5080. − IR (film): $\tilde{\nu}_{max}$ = 1735 cm^{-1} (s, C=O), 1250 (s, Si−C), 1200 (s, C−O), 1150 (s, C−O), 1125 (s, C−O), 1080 (s, C−O), 1065 (s, C−O), 1035 (s, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.04 (s, 9 H, $SiMe_3$), 1.01 (br. t, *J* = 9 Hz, 2 H, CH_2Si), 1.25 (t, *J* = 8 Hz, 3 H, CH_3CH_2), 1.55−1.75 (m, 3 H, THP), 1.59, 1.61 (each s, total 9 H, 19,20,21-H_3), 1.71 [s, 5/3 H, 22-H_3 (*E*)], 1.73 [d, *J* = 1 Hz, 4/3 H, 22-H_3 (*Z*)], 1.80−1.90 (m , 2 H, THP), 1.90−2.15 (m, 13 H, 6,7,10,11,14,15-H_2, THP), 2.15 (s, 3 H, ArCH_3), 2.21 (s, 3 H, ArCH_3), 2.29 (t, *J* = 7 Hz, 2 H, 3-H_2), 2.39 (br. t, *J* = 7 Hz, 2 H, 2-H_2), 3.28−3.45 (m, 2 H, 18-H_2), 3.52−3.64 (m, 1 H, THP), 3.80−4.00 (m, 1 H, THP), 3.86 (br. t, *J* = 9 Hz, 2 H, CH_2CH_2Si), 4.12 (q, *J* = 8 Hz, 2 H, CH_3CH_2), 4.91 (s, 2 H, OCH_2O), 5.05−5.20 (m, 3 H, 5,9,13-H), 5.25−5.35 (m, 2 H, 17-H, THP), 6.78 [s, 5/9 H, aromatic H (*E*)], 6.79 [s, 4/9 H, aromatic H (*Z*)]. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = −1.5, 12.2, 13.5, 14.2, 15.8, 15.9, 16.2, 18.2, 19.1, 23.4, 25.3, 26.6, 26.8, 28.7, 30.6, 32.1, 33.2, 34.6, 39.5, 39.63, 39.66, 39.72, 60.1, 62.0, 67.2, 96.8, 97.7, 113.42, 113.48, 123.0, 123.7, 124.06, 124.14, 124.3, 124.75, 124.80, 125.0, 130.7, 132.0, 133.1, 134.60, 134.65, 134.9, 135.1, 135.9, 148.1, 148.2, 151.3, 173.4. − $C_{43}H_{70}O_6Si$ (711.1): calcd. C 72.63, H 9.92; found C 72.14, H 9.77.

Ethyl (4E,8E,12E)-18-(2′-Hydroxy-3′,4′-dimethyl-5′-tetrahydropyranyloxyphenyl)-4,8,12,16-tetramethyloctadeca-4,8,12,16-tetraenoate (**45**): This was prepared from **44** (1.10 g, 1.55 mmol) in the same manner as described for **22** to give 1.53 g of crude **45** as a brown oil. − IR (film): $\tilde{\nu}_{max}$ = 3420 cm^{-1} (s, O−H), 1735 (m, C=O), 1200, (s, C−O), 1170 (s, C−O), 1065 (m, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.55−2.40 (m, 25 H, 2,3,6,7,10,11,14,15-H_2, 22-H_3, THP), 1.60 (s, 9 H, 19,20,21-H_3), 2.16 (s, 6 H, ArCH_3), 3.31 (d, *J* = 7 Hz, 2 H, 18-H_2), 3.40−4.00 (m, 2 H, THP), 4.12 (q, *J* = 7 Hz, 2 H, CH_3CH_2), 4.90−5.40 (m, 6 H, 5,9,13,17-H, THP, OH), 6.72 (s, 1 H, aromatic H). This was employed in the next step without further purification.

Ethyl (4E,8E,12E)-18-(2′-Acetoxy-3′,4′-dimethyl-5′-tetrahydropyranyloxyphenyl)-4,8,12,16-tetramethyloctadeca-4,8,12,16-tetraenoate (**46**): This was prepared from crude **45** (1.53 g) in the same manner as described for **23** to give 873 mg (90% based on **44**) of **46** as a yellowish oil; n_D^{23} = 1.5069. − IR (film): $\tilde{\nu}_{max}$ = 1760 cm^{-1} (s, C=O), 1735 (s, C=O), 1585 (w, C=C), 1220 (m, C−O), 1190 (s, C−O), 1150 (w, C−O), 1125 (m, C−O), 1080 (m, C−O), 1040 (m, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.40−2.40 (m, 22 H, 2,3,6,7,10,11,14,15-H_2, THP), 1.60 (s, 9 H, 19,20,21-H_3), 1.68 [s, 5/3 H, 22-H_3 (*E*)], 1.71 [br. s, 4/3 H, 22-H_3 (*Z*)], 2.02 (s, 3 H, ArCH_3), 2.18 (s, 3 H, ArCH_3), 2.29 (s, 3 H, acetyl), 3.17 (d, *J* = 7 Hz, 2 H, 18-H_2), 3.40−4.00 (m, 2 H, THP), 4.12 (q, *J* = 7 Hz, 2 H, CH_3CH_2), 5.00−5.40 (m, 5 H, 5,9,13,17-H, THP), 6.82 (s, 1 H, aromatic H). − $C_{39}H_{58}O_6$ (622.9): calcd. C 75.20, H 9.39; found C 74.88, H 9.63.

Ethyl (4E,8E,12E)-18-(2′-Acetoxy-5′-hydroxy-3′,4′-dimethylphenyl)-4,8,12,16-tetramethyloctadeca-4,8,12,16-tetraenoate (**47**): This was prepared from **46** (700 mg, 1.12 mmol) in the same manner as described for **24** to give 601 mg (quantitative) of **47** as a yellowish oil; n_D^{23} = 1.5171. − IR (film): $\tilde{\nu}_{max}$ = 3435 cm^{-1} (m, O−H), 1760 (s, C=O), 1735 (s, C=O), 1710 (m, C=O), 1590 (w, C=C), 1240 (m, C−O), 1190 (s, C−O), 1080 (m, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.60 (s, 9 H, 19,20,21-H_3), 1.66 [s, 5/3 H, 22-H_3 (*E*)], 1.73 [d, *J* = 1 Hz, 4/3 H, 22-H_3 (*Z*)], 1.90−2.15 (m, 12 H, 6,7,10,11,14,15-H_2), 2.03 (s, 3 H, ArCH_3), 2.11 (s, 3 H, ArCH_3), 2.25-2.35 (m, 2 H, 3-H_2), 2.307 [s, 4/3 H, acetyl (*Z*)], 2.313 [s, 5/3 H, acetyl (*E*)], 2.39 (br. t, *J* = 7 Hz, 2 H, 2-H_2), 3.11 (d, *J* = 7 Hz, 2 H, 18-H_2), 4.13 (q, *J* = 7 Hz, 2 H, CH_3CH_2), 5.05−5.25 (m, 4 H, 5,9,13,17-H), 5.49 [s, 5/9 H, OH (*E*)], 5.51 [s, 4/9 H, OH (*Z*)], 6.47 (s, 1 H, aromatic H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.9, 13.1, 14.2, 15.8, 15.9, 16.1, 20.5, 23.4, 26.4, 26.5, 28.46, 28.54, 31.9, 33.2, 34.6, 39.5, 39.6, 39.7, 60.4, 113.28, 113.34, 121.48, 121.53, 122.4, 123.9, 124.1, 124.3, 125.1, 129.7, 129.8, 130.86, 130.92, 133.1, 134.7, 134.8, 135.0, 135.3, 136.60, 136.63, 140.8, 140.9, 151.5, 169.9, 173.9. − $C_{34}H_{50}O_5$ (538.8): calcd. C 75.80, H 9.36; found C 75.66, H 9.06.

Ethyl (4E,8E,12E)-18-[2′-Acetoxy-3′,4′-dimethyl-5′-(2″,3″,4″-tri-O-acetyl-1″-β-D-xylopyranosyloxy)phenyl]-4,8,12,16-tetramethyloctadeca-4,8,12,16-tetraenoate (**48**): This was prepared from **47** (400 mg, 0.742 mmol) in the same manner as described for **25** to give 378 mg of crude **48** as a colorless oil. − IR (film): $\tilde{\nu}_{max}$ = 1760 cm^{-1} (s, C=O), 1245 (s, C−O), 1220 (s, C−O), 1080 (s, C−O), 1060 (s, C−O), 1040 (s, C−O). This was employed in the next step without further purification.

(4E,8E,12E)-18-[2′-Hydroxy-3′,4′-dimethyl-5′-(1′′-β-D-xylopyranosyloxy)phenyl]-4,8,12,16-tetramethyloctadeca-4,8,12,16-tetraenoic Acid (**5**): This was prepared from crude **48** (378 mg) in the same manner as described for **2** to give 208 mg (47% based on **47**) of **5** as a colorless amorphous solid. − $[\alpha]_D^{25}$ = −15 (*c* = 0.079, MeOH). − R_f = 0.69 (*i*BuOH/MeOH/H_2O, 8:1:1). − IR (KBr): $\tilde{\nu}_{max}$ = 3430 cm^{-1} (s, O−H), 2925 (s), 2860 (m), 1715 (s, C=O), 1550 (w, C=C), 1480 (m), 1445 (m), 1380 (m), 1280 (m, C−O), 1255 (m, C−O), 1215 (m, C−O), 1165 (m, C−O), 1100 (m, C−O), 1050 (s, C−O), 985 (m), 845 (w). − ^{1}H NMR (300 MHz, CD_3OD): δ = 1.58, 1.60 (each s, total 9 H, 19,20,21-H_3), 1.71 [s, 5/3 H, 22-H_3 (*E*)], 1.76 [s, 4/3 H, 22-H_3 (*Z*)], 1.90−2.20 (m, 12 H, 6,7,10,11,14,15-H_2), 2.14 (s, 3 H, 23 or 24-H_3), 2.16 (s, 3 H, 23 or 24-H_3), 2.25 (t, *J* = 7 Hz, 2 H, 3-H_2), 2.35 (br. t, *J* = 7 Hz, 2 H, 2-H_2), 3.18, 3.20 (each t, *J* = 10 Hz, total 1 H, 5″a-H), 3.25−3.35 (m, 2 H, 18-H_2), 3.37 (t, *J* = 7 Hz, 1 H, 3″-H), 3.43 (t, *J* = 7 Hz, 1 H, 2″-H), 3.57 (ddd, *J* = 5 Hz, *J′* = 7 Hz, *J″* = 10 Hz, 1 H, 4″-H), 3.86, 3.87 (each dd, *J* = 5 Hz, *J′* = 10 Hz, total 1 H, 5″e-H), 4.59, 4.60 (each d, *J* = 8 Hz, total 1 H, 1″-H), 5.05−5,20 (m, 3 H, 5,9,13-H), 5.32 (t, *J* = 7 Hz, 1 H, 17-H), 6.72 (s, 1 H, 6′-H). − ^{13}C NMR (75.5 MHz, CD_3OD): δ = 12.7, 12.9, 16.06, 16.14, 16.18, 16.3, 23.8, 27.5, 27.62, 27.68, 27.74, 29.5, 29.6, 33.0, 34.5, 36.0, 40.7, 40.8, 41.0, 66.9, 71.1, 75.0, 78.0, 105.1, 116.5, 123.9, 124.4, 125.4, 125.60, 125.62, 126.0, 126.11, 126.13, 126.5, 126.6, 127.7, 127.9, 134.7, 135.68, 135.72, 136.0, 136.2, 137.1, 137.4, 148.9, 150.58, 150.60, 178.4. − MS (70 eV); *m/z* (%): 600 (2) [M^+], 582 (2), 564 (1), 482 (20), 468 (100), 255 (25), 189 (100), 151 (100), 81 (100). − HRMS: $C_{35}H_{52}O_8$ [M^+]: calcd. 600.3662, found 600.3672. This material is an inseparable mixture of (16*E*) and (16*Z*) isomers (1.3:1).

Methyl (4E,8E)-14-[2′-Hydroxy-3′,4′-dimethyl-5′-(1″-β-D-xylopyranosyloxy)phenyl]-4,8,12-trimethyltetradeca-4,8,12-trienoate (**6**): To a stirred and ice-cooled solution of mixture of lurlenic acid (**1**) and its (12*Z*) isomer (50 mg) in methanol (1.0 ml) was added a solution of diazomethane (20.2 mmol) in diethyl ether (2 ml). The stirring was continued for 2 h at room temperature. Then the mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel (2.5 g, chloroform/methanol, 30:1)

to give 51 mg (99%) of **6** as a colorless amorphous solid. – $[\alpha]_D^{24}$ = –17 (*c* = 0.040, MeOH). – R_f = 0.45 ($CHCl_3$/MeOH, 7:1). – IR (KBr): $\tilde{\nu}_{max}$ = 3460 cm^{-1} (s, O–H), 2920 (s), 2855 (m), 1740 (s, C=O), 1485 (m), 1445 (m), 1385 (m), 1320 (m), 1220 (m, C–O), 1190 (m, C–O), 1150 (m, C–O), 1100 (m, C–O), 1075 (m, C–O), 1040 (s, C–O), 970 (m), 895 (w), 855 (w). – ^{1}H NMR (300 MHz, CD_3OD): δ = 1.60 (s, 6 H, 15,16-H_3), 1.71 [s, 9/5 H, 17-H_3 (*E*)], 1.76 [s, 6/5 H, 17-H_3 (*Z*)], 1.90–2.20 (m, 8 H, 6,7,10,11-H_2), 2.14 (s, 3 H, 18 or 19-H_3), 2.16 (s, 3 H, 18 or 19-H_3), 2.24 (t, *J* = 7 Hz, 2 H, 3-H_2), 2.38 (t, *J* = 7 Hz, 2 H, 2-H_2), 3.19, 3.20 (each t, *J* = 10 Hz, total 1 H, 5″a-H), 3.25–3.35 (m, 2 H, 14-H_2), 3.38 (t, *J* = 7 Hz, 1 H, 3″-H), 3.44 (t, *J* = 7 Hz, 1 H, 2″-H), 3.50–3.65 (m, 1 H, 4″-H), 3.62 (s, 3 H, CO_2CH_3), 3.86, 3.88 (each dd, *J* = 5 Hz, *J′* = 10 Hz, total 1 H, 5″e-H), 4.60 (d, *J* = 7 Hz, 1 H, 1″-H), 5.08–5.20 (m, 2 H, 5,9-H), 5.33 (t, *J* = 7 Hz, 1 H, 13-H), 6.72 (s, 1 H, 6′-H). – ^{13}C NMR (75.5 MHz, CD_3OD): δ = 12.7, 12.9, 16.0, 16.1, 16.2, 16.3, 23.8, 27.5, 27.6, 27.7, 29.4, 29.6, 32.9, 33.9, 35.7, 40.6, 40.9, 52.0, 66.9, 71.1, 74.9, 77.9, 79.4, 105.1, 116.5, 123.9, 124.4, 125.5, 126.0, 126.1, 126.2, 126.51, 126.54, 127.2, 127.6, 127.8, 134.4, 135.8, 136.0, 137.1, 137.3, 148.9, 150.6, 175.6. – MS (70 eV); *m/z* (%): 546 (2) [M^+], 414 (100), 346 (8), 206 (10), 189 (38), 151 (58), 81 (34). – HRMS: $C_{31}H_{46}O_8$ [M^+]: calcd. 546.3193, found 546.3182. This material is an inseparable mixture of (12*E*) and (12*Z*) isomers (1.5:1).

Ethyl (4E,8E)-14-[2′-Hydroxy-3′,4′-dimethyl-5′-(1″-β-D-xylopyranosyloxy)phenyl]-4,8,12-trimethyltetradeca-4,8,12-trienoate (**7**): To a stirred solution of crude **49** (150 mg) in ethanol (2.0 ml) was added a solution of sodium ethoxide (50 mg) in ethanol (1.0 ml). The stirring was continued for 6 h at room temperature. After the addition of chloroform (100 ml), the mixture was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (25 g, chloroform/methanol, 100:1) to give 82 mg (53% based on **32**) of **7** as a colorless amorphous solid. – $[\alpha]_D^{24}$ = –15 (*c* = 0.18, MeOH). – R_f = 0.45 ($CHCl_3$/MeOH, 7:1). – IR (KBr): $\tilde{\nu}_{max}$ = 3380 cm^{-1} (s, O–H), 2975 (m), 2920 (s), 2860 (m), 1735 (s, C=O), 1485 (m), 1445 (m), 1425 (m), 1385 (m), 1320 (m), 1220 (m, C–O), 1190 (m, C–O), 1150 (s, C–O), 1100 (s, C–O), 1075 (s, C–O), 1040 (s, C–O), 970 (m), 890 (w), 860 (w). – ^{1}H NMR (300 MHz, CD_3OD): δ = 1.21 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.59 (s, 6 H, 15,16-H_3), 1.71 [s, 5/3 H, 17-H_3 (*E*)], 1.75 [s, 4/3 H, 17-H_3 (*Z*)], 1.90–2.20 (m, 8 H, 6,7,10,11-H_2), 2.14 (s, 3 H, 18 or 19-H_3), 2.16 (s, 3 H, 18 or 19-H_3), 2.24 (t, *J* = 7 Hz, 2 H, 3-H_2), 2.37 (br. t, *J* = 7 Hz, 2 H, 2-H_2), 3.19, 3.22 (each t, *J* = 10 Hz, total 1 H, 5″a-H), 3.23–3.33 (m, 2 H, 14-H_2), 3.39 (t, *J* = 8 Hz, 1 H, 3″-H), 3.45 (t, *J* = 8 Hz, 1 H, 2″-H), 3.58 (ddd, *J* = 5 Hz, *J′* = 8 Hz, *J″* = 10 Hz, 1 H, 4″-H), 3.86, 3.87 (each dd, *J* = 5 Hz, *J′* = 10 Hz, total 1 H, 5″e-H), 4.07 (q, *J* = 7 Hz, 2 H, CH_3CH_2), 4.595, 4.600 (each d, *J* = 8 Hz, total 1 H, 1″-H), 5.05–5.20 (m, 2 H, 5,9-H), 5.32 (t, *J* = 7 Hz, 1 H, 13-H), 6.72 (s, 1 H, 6′-H). – ^{13}C NMR (75.5 MHz, CD_3OD): δ = 12.7, 12.9, 14.6, 16.0, 16.2, 16.3, 23.8, 27.5, 27.6, 27.7, 29.5, 29.6, 32.9, 34.1, 35.8, 40.6, 40.9, 61.4, 66.9, 71.1, 74.9, 77.9, 105.1, 116.5, 123.9, 124.5, 125.5, 126.02, 126.05, 126.2, 126.51, 126.54, 127.6, 127.8, 134.39, 134.42, 135.8, 136.0, 137.1, 137.3, 148.9, 150.54, 150.56, 175.2. – MS (70 eV); *m/z* (%): 560 (1) [M^+], 514 (1), 428 (100), 189 (49), 151 (83), 81 (32). – HRMS: $C_{32}H_{48}O_8$ [M^+]: calcd. 560.3349, found 560.3344. This material is an inseparable mixture of (12*E*) and (12*Z*) isomers (1.3:1) and is contaminated with about 10% of an inseparable impurity.

Butyl (4E,8E)-14-[2′-Hydroxy-3′,4′-dimethyl-5′-(1″-β-D-xylopyranosyloxy)phenyl]-4,8,12-trimethyltetradeca-4,8,12-trienoate (**8**): To a stirred and ice-cooled solution of crude **49** (300 mg) in 1-butanol (3.0 ml) was added a solution of sodium butoxide (50 mg) in 1-butanol (1.5 ml). The stirring was continued for 6 h at room temperature. After the addition of chloroform (150 ml), the mixture was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (25 g, chloroform/methanol, 100:1) to give 152 mg (46% based on **32**) of **8** as a colorless amorphous solid. – $[\alpha]_D^{24}$ = –15 (*c* = 0.21, MeOH). – R_f = 0.45 ($CHCl_3$/MeOH, 7:1). – IR (KBr): $\tilde{\nu}_{max}$ = 3380 cm^{-1} (s, O–H), 2965 (s), 2920 (s), 2860 (m), 1735 (s, C=O), 1480 (m), 1455 (m), 1425 (m), 1385 (m), 1320 (m), 1220 (m, C–O), 1190 (m, C–O), 1150 (s, C–O), 1100 (s, C–O), 1075 (s, C–O), 1040 (s, C–O), 970 (m), 890 (w), 860 (w), 835 (w). – ^{1}H NMR (300 MHz, CD_3OD): δ = 0.93 (t, *J* = 7 Hz, 3 H, $CH_3CH_2CH_2CH_2$), 1.36 (sext, *J* = 7 Hz, 2 H, $CH_3CH_2CH_2CH_2$), 1.55–1.65 (m, 2 H, $CH_3CH_2CH_2CH_2$), 1.59 (s, 6 H, 15,16-H_3), 1.71 [s, 5/3 H, 17-H_3 (*E*)], 1.76 [s, 4/3 H, 17-H_3 (*Z*)], 1.90–2.20 (m, 8 H, 6,7,10,11-H_2), 2.14 (s, 3 H, 18 or 19-H_3), 2.16 (s, 3 H, 18 or 19-H_3), 2.25 (t, *J* = 7 Hz, 2 H, 3-H_2), 2.39 (br. t, *J* = 7 Hz, 2 H, 2-H_2), 3.19, 3.20 (each t, *J* = 10 Hz, total 1 H, 5″a-H), 3.25–3.35 (m, 2 H, 14-H_2), 3.38 (t, *J* = 8 Hz, 1 H, 3″-H), 3.44 (t, *J* = 8 Hz, 1 H, 2″-H), 3.58 (ddd, *J* = 5 Hz, *J′* = 8 Hz, *J″* = 10 Hz, 1 H, 4″-H), 3.86, 3.87 (each dd, *J* = 5 Hz, *J′* = 10 Hz, total 1 H, 5″e-H), 4.04 (t, *J* = 7 Hz, 2 H, $CH_3CH_2CH_2CH_2$), 4.60 (d, *J* = 8 Hz, 1 H, 1″-H), 5.08–5.20 (m, 2 H, 5,9-H), 5.32 (t, *J* = 7 Hz, 1 H, 13-H), 6.72 (s, 1 H, 6′-H). – ^{13}C NMR (75.5 MHz, CD_3OD): δ = 11.8, 12.0, 13.1, 15.08, 15.19, 15.24, 15.4, 19.2, 22.9, 26.56, 26.62, 26.74, 28.7, 30.9, 33.2, 34.8, 39.7. 39.9, 64.3, 66.0, 70.1, 74.0, 77.0, 104.2, 115.6, 123.0, 123.5, 124.5, 125.07, 125.11, 125.3, 125.6, 126.7, 126.8, 133.4, 133.5, 134.9, 135.1, 136.1, 136.3, 147.9, 149.60, 149.63, 174.3. – MS (70 eV); *m/z* (%): 588 (1) [M^+], 542 (1), 514 (6), 456 (75), 388 (12), 206 (17), 189 (52), 151 (100), 81 (25). – HRMS: $C_{34}H_{52}O_8$ [M^+]: calcd. 588.3662, found 588.3652. This material is an inseparable mixture of (12*E*) and (12*Z*) isomers (1.3:1) and is contaminated with about 10% of an inseparable impurity.

2-Bromo-4-tetrahydropyranyloxyphenol (**51**): To a stirred and ice-cooled solution of **50** (9.00 g, 47.6 mmol) in THF (230 ml) were added 3,4-dihydro-2*H*-pyran (4.80 g, 57.1 mmol) and *p*-toluenesulfonic acid monohydrate (100 mg, 0.582 mmol). The stirring was continued for 20 h at room temperature. Then the mixture was diluted with a saturated $NaHCO_3$ solution (200 ml) and extracted three times with diethyl ether (200 ml). The combined ethereal extracts were successively washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (400 g, hexane/ethyl acetate, 30:1) to give 3.77 g of the recovered **50** and 8.62 g of crude **51** as a colorless oil. – IR (film): $\tilde{\nu}_{max}$ = 3335 cm^{-1} (s, O–H), 1200 (s, C–O), 1120 (s, C–O), 1110 (s, C–O), 1075 (m, C–O), 1035 (s, C–O), 1020 (s, C–O). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.30–2.10 (m, 6 H, THP), 3.30–3.75 (m, 1 H, THP), 3.75–4.10 (m, 1 H, THP), 5.26 (br. s, 1 H, THP), 5.77 (s, 1 H, OH), 5.89 (br. s, 2 H, 5,6-H), 7.22 (t, *J* = 2 Hz, 1 H, 3-H). This was employed in the next step without further purification.

1-Bromo-5-tetrahydropyranyloxy-2-[2-(trimethylsilyl)-ethoxymethoxy]benzene (**52**): To a stirred solution of crude **51** (4.50 g) in dichloromethane (45 ml) were added dropwise *N*,*N*-diisopropylethylamine (6.14 g, 49.5 mmol) and 2-(trimethylsilyl)ethoxymethyl chloride (4.13 g, 24.7 mmol) under argon. The stirring was continued for 3 h at room temperature. Then the mixture was diluted with a saturated $NaHCO_3$ solution (50 ml) and extracted three times with dichloromethane (50 ml). The combined extracts were successively washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (250 g, hexane/ethyl acetate, 50:1) to give 4.37 g (44% based on **50**) of **52** as a colorless oil; n_D^{23} = 1.5151. –IR

(film): $\tilde{\nu}_{max}$ = 1600 (w, C=C), 1250 cm^{-1} (m, Si−C), 1200 (s, C−O), 1180 (m, C−O), 1105 (s, C−O), 1095 (s, C−O), 1035 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.10 (s, 9 H, $SiMe_3$), 1.07 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.60−2.15 (m, 3 H, THP), 3.50−4.20 (m, 2 H, THP), 3.92 (t, *J* = 9 Hz, 2 H, CH_2CH_2Si), 5.32 (s, 2 H, OCH_2O), 5.32−5.50 (m, 1 H, THP), 7.03 (dd, *J* = 3 Hz, *J′* = 11 Hz, 1 H, 4-H), 7.21 (d, *J* = 11 Hz, 1 H, 3-H), 7.39 (d, *J* = 3 Hz, 1 H, 6-H). − $C_{17}H_{27}O_4BrSi$ (403.4): calcd. C 50.62, H 6.75; found C 50.50, H 6.71.

1-Tetrahydropyranyloxy-4-[2-(trimethylsilyl)ethoxymethoxy]-3-(trimethylstannyl)benzene (**53**): To a stirred solution of **52** (2.50 g, 6.20 mmol) in THF (25 ml) was added dropwise butyllithium (1.59 M in hexane, 5.85 ml, 9.30 mmol) at −50°C under argon, and the mixture was stirred at −50°C for 30 min. Then trimethylstannyl chloride (1.85 g, 9.30 mmol) was added, and the stirring was continued for 3 h at room temperature. After the addition of water (50 ml), the mixture was extracted three times with diethyl ether (100 ml). The combined ethereal extracts were successively washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo to give 3.02 g (quantitative) of **53** as a colorless oil; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 0.27 (s, 9 H, $SnMe_3$), 0.97 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.50−2.10 (m, 6 H, THP), 3.40−4.10 (m, 2 H, THP), 3.71 (br. t, *J* = 9 Hz, 2 H, CH_2CH_2Si), 5.15 (s, 2 H, OCH_2O), 5.32 (br. s, 1 H, THP), 6.90−7.10 (m, 3 H, aromatic H). This compound was employed in the next step without further purification.

Methyl (4E,8E)-14-{5′-Tetrahydropyranyloxy-2′-[2-(trimethylsilyl)ethoxymethoxy]phenyl}-4,8,12-trimethyltetradeca-4,8,12-trienoate (**54**): This was prepared from **53** (3.00 g, 6.16 mmol) and **27** (1.50 g, 4.10 mmol) in the same manner as described for **36** to give 2.28 g (92%) of **54** as a yellowish oil; n_D^{23} = 1.5082. − IR (film): $\tilde{\nu}_{max}$ = 1740 cm^{-1} (s, C=O), 1590 (w, C=C), 1250 (m, Si−C), 1200 (s, C−O), 1155 (m, C−O), 1080 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 0.97 (t, *J* = 9 Hz, 2 H, CH_2Si), 1.50−2.22 (m, 14 H, THP, 6,7,10,11-H_2), 1.60 (s, 6 H, 15,16-H_3), 1.70 (br. s, 3 H, 17-H_3), 2.22−2.43 (m, 4 H, 2,3-H_2), 3.30 (d, *J* = 8 Hz, 2 H, 14-H_2), 3.40−4.10 (m, 2 H, THP), 3.66 (s, 3 H, CO_2CH_3), 3.75 (t, *J* = 9 Hz, 2 H, CH_2CH_2Si), 5.00−5.40 (m, 4 H, 5,9,13-H, THP), 5.17 (s, 2 H, OCH_2O), 6.70−7.10 (m, 3 H, aromatic H). − $C_{35}H_{56}O_6Si$ (600.9): calcd. C 69.96, H 9.39; found C 70.28, H 9.32.

Methyl (4E,8E)-14-(2′-Hydroxy-5′-tetrahydropyranyloxyphenyl)-4,8,12-trimethyltetradeca-4,8,12-trienoate (**55**): This was prepared from **54** (2.00 g, 3.33 mmol) in the same manner as described for **22** to give 1.86 g of crude **55** as a brown oil. − IR (film): $\tilde{\nu}_{max}$ = 3435 cm^{-1} (s, O−H), 1735 (s, C=O), 1190 (s, C−O), 1110 (s, C−O), 1035 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.40−2.25 (m, 14 H, 6,7,10,11-H_2, THP), 1.60 (s, 6 H, 15,16-H_3), 1.77 (br. s, 3 H, 17-H_3), 2.25−2.45 (m, 4 H, 2,3-H_2), 3.32 (d, *J* = 7 Hz, 2 H, 14-H_2), 3.40−4.10 (m, 2 H, THP), 3.64 (s, 3 H, CO_2CH_3), 4.80−5.40 (m, 5 H, OH, 5,9,13-H, THP), 6.72−6.90 (m, 3 H, aromatic H). This compound was used for the next reaction without further purification.

Methyl (4E,8E)-14-(2′-Acetoxy-5′-tetrahydropyranyloxyphenyl)-4,8,12-trimethyltetradeca-4,8,12-trienoate (**56**): This was prepared from crude **55** (1.86 g) in the same manner as described for **23** to give 1.32 g (77% based on **54**) of **56** as a yellowish oil; n_D^{23} = 1.5169. − IR (film): $\tilde{\nu}_{max}$ = 1760 cm^{-1} (s, C=O), 1740 (s, C=O), 1210 (s, C−O), 1190 (s, C−O), 1180 (s, C−O), 1125 (m, C−O), 1040 (m, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.40−2.15 (m, 14 H, 6,7,10,11-H_2, THP), 1.60 (s, 6 H, 15,16-H_3), 1.70 [s, 5/3 H, 17-H_3 (*E*)], 1.75 [d, *J* = 1 Hz, 4/3 H, 17-H_3 (*Z*)], 2.15−2.43 (m, 4 H, 2,3-H_2), 2.26 (s, 3 H, acetyl), 3.19 (d, *J* = 7 Hz, 2 H, 14-H_2), 3.40−4.05 (m, 2 H, THP), 3.64 (s, 3 H, CO_2CH_3), 5.00−5.30 (s, 3 H, 5,9,13-H), 5.35 (br. t, *J* = 3 Hz, 1 H, THP), 6.89 (s, 3 H, aromatic H). − $C_{31}H_{44}O_6$ (512.7): calcd. C 72.63, H 8.65; found C 72.72, H 8.76.

Methyl (4E,8E)-14-(2′-Acetoxy-5′-hydroxyphenyl)-4,8,12-trimethyltetradeca-4,8,12-trienoate (**57**): This was prepared from **56** (1.00 g, 1.95 mmol) in the same manner as described for **24** to give 735 mg (88%) of **57** as a yellowish oil; n_D^{23} = 1.5172. − IR (film): $\tilde{\nu}_{max}$ = 3430 cm^{-1} (m, O−H), 1760 (s, C=O), 1740 (s, C=O), 1590 (m, C=C), 1215 (s, C−O), 1185 (s, C−O), 1100 (w, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 6 H, 15,16-H_3), 1.66 [s, 5/3 H, 17-H_3 (*E*)], 1.72 [s, 4/3 H, 17-H_3 (*Z*)], 1.90−2.20 (m, 8 H, 6,7,10,11-H_2), 2.22−2.32 (m, 2 H, 3-H_2), 2.27 (s, 3 H, acetyl), 2.42 (t, *J* = 7 Hz, 2 H, 2-H_2), 3.15 (d, *J* = 7 Hz, 2 H, 14-H_2), 3.66 (s, 3 H, CO_2CH_3), 5.10 (t, *J* = 7 Hz, 1 H, 5 or 9-H), 5.12 (t, *J* = 7 Hz, 1 H, 5 or 9-H), 5.20 (t, *J* = 7 Hz, 1 H, 13-H), 6.35−6.50 (m, 1 H, OH), 6.59 (dd, *J* = 3 Hz, *J′* = 8 Hz, 1 H, 4′-H), 6.66 (d, *J* = 3 Hz, 1 H, 6′-H), 6.81 (d, *J* = 8 Hz, 1 H, 3′-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.77, 15.83, 15.9, 16.0, 20.8, 23.3, 26.3, 26.4, 28.4, 28.5, 31.8, 33.0, 34.5, 39.4, 39.6, 51.6, 113.50, 113.55, 116.4, 121.2, 121.9, 122.59, 122.63, 123.97, 124.02, 125.1, 125.2, 132.9, 133.0, 134.36, 134.39, 134.8, 135.0, 136.8, 136.9, 141.86, 141.90, 153.9, 170.3, 174.5. − $C_{26}H_{36}O_5$ (428.6): calcd. C 72.87, H 8.47; found C 73.06, H 8.58.

Methyl (4E,8E)-14-[2′-Acetoxy-5′-(2″,3″,4″-tri-O-acetyl-1″-β-D-xylopyranosyloxy)phenyl]-4,8,12-trimethyltetradeca-4,8,12-trienoate (**58**): This was prepared from **57** (400 mg, 0.932 mmol) in the same manner as described for **25** to give 444 mg of crude **58** as a colorless oil. − IR (film): $\tilde{\nu}_{max}$ = 1760 cm^{-1} (s, C=O), 1590 (w, C=C), 1220 (s, C−O), 1180 (s, C−O), 1070 (s, C−O), 1045 (s, C−O). This was employed in the next step without further purification.

(4E,8E)-14-[2′-Hydroxy-5′-(1″-β-D-xylopyranosyloxy)phenyl]-4,8,12-trimethyltetradeca-4,8,12-trienoic Acid (**9**): This was prepared from crude **58** (444 mg) in the same manner as described for **2** to give 206 mg (44% based on **57**) of **9** as a colorless amorphous solid. − $[\alpha]_D^{24}$ = −16 (*c* = 0.18, MeOH). − R_f = 0.65 (*i*BuOH/MeOH/H_2O, 8:1:1). − IR (KBr): $\tilde{\nu}_{max}$ = 3345 cm^{-1} (s, O−H), 2930 (m), 1700 (m, C=O), 1655 (m), 1505 (m), 1440 (m), 1375 (w), 1265 (w, C−O), 1200 (m, C−O), 1100 (m, C−O), 1075 (m, C−O), 1040 (m, C−O). − ^{1}H NMR (300 MHz, CD_3OD): δ = 1.60 (br. s, 6 H, 15,16-H_3), 1.70 [s, 5/3 H, 17-H_3 (*E*)], 1.74 [s, 4/3 H, 17-H_3 (*Z*)], 1.90-2.20 (m, 8 H, 6,7,10,11-H_2), 2.25 (t, *J* = 7 Hz, 2 H, 3-H_2), 2.35 (br. t, *J* = 7 Hz, 2 H, 2-H_2), 3.22−3.35 (m, 3 H, 14-H_2, 5″a-H), 3.39 (t, *J* = 6 Hz, 1 H, 3″-H,), 3.42 (t, *J* = 6 Hz, 1 H, 2″-H), 3.50−3.62 (m, 1 H, 4″-H), 3.89 (dd, *J* = 5 Hz, *J′* = 12 Hz, 1 H, 5″e-H), 4.62−4.72 (m, 1 H, 1″-H), 5.13 (t, *J* = 7 Hz, 1 H, 5 or 9-H), 5.15 (t, *J* = 7 Hz, 1 H, 5 or 9-H), 5.32 (t, *J* = 7 Hz, 1 H, 13-H), 6.65 (d, *J* = 9 Hz, 1 H, 3′-H), 6.74 (dd, *J* = 3 Hz, *J′* = 9 Hz, 1 H, 4′-H), 6.81 (br. s, 1 H, 6′-H). − ^{13}C NMR (75.5 MHz, CD_3OD): δ = 16.08, 16.12, 16.2, 16.3, 23.8, 27.53, 27.57, 27.62, 28.9, 29.1, 32.9, 34.5, 35.9, 40.6, 40.8, 66.8, 71.0, 74.7, 77.6, 104.20, 104.23, 115.9, 116.0, 116.3, 119.8, 123.6, 124.2, 125.4, 125.9, 130.0, 130.1, 134.65, 134.69, 135.8, 136.0, 137.0, 137.2, 151.5, 152.0, 178.5. − MS (70 eV); *m/z* (%): 504 (1) [M^+], 486 (2), 468 (1), 372 (78), 249 (20), 177 (48), 161 (100), 123 (99), 81 (89). − HRMS: $C_{28}H_{40}O_8$ [M^+]: calcd. 504.2723, found 504.2723. This material is an inseparable mixture of (12*E*) and (12*Z*) isomers (1.3:1).

Methyl (4E,8E)-4,8,12-Ttrimethyl-14-(2′,3′,4′-trimethyl-5′-tetrahydropyranyloxyphenyl)tetradeca-4,8,12-trienoate (**60**): To a stirred and ice-cooled solution of **30** (700 mg, 1.40 mmol) in dry

pyridine (25 ml) was added trifluoromethanesulfonic anhydride (592 mg, 2.10 mmol). The stirring was continued for 6 h at room temperature and for another 1 h after the addition of water (50 ml). The mixture was extracted three times with diethyl ether (50 ml). The combined ethereal extracts were successively washed with water, a saturated $CuSO_4$ solution, a saturated $NaHCO_3$ solution and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (50 g, hexane/ethyl acetate, 50:1) to give 829 mg of **59** as a yellowish oil. − IR (film): $\tilde{\nu}_{max}$ = 1740 cm^{-1} (s, C=O), 1575 (w, C=C), 1245 (m, Si−C), 1210 (s, C−O), 1175 (m, C−O), 1140 (s, C−O), 1125 (m, C−O), 1085 (m, C−O), 1040 (m, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.45−2.40 (m, 18 H, 2,3,6,7,10,11-H_2, THP), 1.60 (s, 6 H, 15,16-H_3), 1.70 [s, 9/5 H, 17-H_3 (*E*)], 1.74 [s, 6/5 H, 17-H_3 (*Z*)], 2.18 (s, 3 H, ArCH_3), 2.27 (s, 3 H, ArCH_3), 3.30−4.00 (m, 2 H, THP), 3.40 (d, *J* = 8 Hz, 2 H, 14-H_2), 3.64 (s, 3 H, CO_2CH_3), 5.00−5.10 (m, 3 H, 5,9,13-H), 5.15 (br. s, 1 H, THP), 6.88 (s, 1 H, aromatic H). − To a stirred solution of **59** (700 mg) and tetramethylstannane (1.18 g 6,59 mmol) in DMF (14 ml) were added lithium chloride (140 mg, 3.30 mmol) and bis(triphenylphosphane)palladium(II) dichloride (7.7 mg, 0.11 mmol). The stirring was continued for 12 h at 110°C. The mixture was filtered through a Celite pad and the Celite was washed with diethyl ether. The ethereal solution was washed with water and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (50 g, hexane/ethyl acetate, 100:1) to give 409 mg of crude **60** as a colorless oil. − IR (film): $\tilde{\nu}_{max}$ = 1740 cm^{-1} (s, C=O), 1585 (w, C=C), 1200 (m, C−O), 1160 (m, C−O), 1120 (s, C−O), 1080 (s, C−O), 1040 (s, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.55−1.75 (m, 3 H, THP), 1.56, 1.58, 1.59, 1.61 (each s, total 6 H, 15,16-H_3), 1.79, 1.80 (each s, total 1 H, 17-H_3), 1.82−1.90 (m, 2 H, THP), 1.90−2.23 (m, 9 H, 6,7,10,11-H_2, THP), 2.14, 2.15 (each s, total 3 H, ArCH_3), 2.19 (s, 3 H, ArCH_3), 2.28 (br. t, *J* = 7 Hz, 2 H, 3-H_2), 2.35−2.45 (m, 2 H, 2-H_2), 3.29 (d, *J* = 6 Hz, 2 H, 14-H_2), 3.53−3.64 (m, 1 H, THP), 3.66 (s, 3 H, CO_2CH_3), 3.92 (br. t, *J* = 9 Hz, 1 H, THP), 5.07−5.25 (m, 3 H, 5,9,13-H), 5.33, 5.34 (each t, *J* = 3 Hz, total 1 H, THP), 6.80 [s, 2/5 H, aromatic H (*Z*)], 6.81 [s, 3/5 H, aromatic H (*E*)]. This was employed in the next step without further purification.

Methyl (4E,8E)-14-(5′-Hydroxy-2′,3′,4′-trimethylphenyl)-4,8,12-trimethyltetradeca-4,8,12-trienoate (**61**): This was prepared from crude **60** (350 mg) in the same manner as described for **24** to give 263 mg (63% based on **30**) of **61** as a colorless oil; n_D^{23} = 1.5298. − IR (film): $\tilde{\nu}_{max}$ = 3445 cm^{-1} (s, O−H), 1740 (s, C=O), 1720 (s, C=O), 1595 (m, C=C), 1260 (s, C−O), 1205 (s, C−O), 1160 (s, C−O), 1080 (s, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58, 1,59, 1.61 (each s, total 6 H, 15,16-H_3), 1.70 [s, 9/5 H, 17-H_3 (*E*)], 1.72 [d, *J* = 1 Hz, 6/5 H, 17-H_3 (*Z*)], 1.92−2.23 (m, 8 H, 6,7,10,11-H_2), 2.13 [s, 9/5 H, 2′-CH_3 (*E*)], 2.14 [s, 6/5 H, 2′-CH_3 (*Z*)], 2.17 (s, 3 H, 3′-CH_3), 2.20 (s, 3 H, 4′-CH_3), 2.23−2.35 (m, 2 H, 3-H_2), 2.35−2.45 (m, 2 H, 2-H_2), 3.26 (d, *J* = 7 Hz, 2 H, 14-H_2), 3.67 (s, 3 H, CO_2CH_3), 4.77 [s, 3/5 H, OH (*E*)], 4.88 [s, 2/5 H, OH (*Z*)], 5.05−5.30 (m, 3 H, 5,9,13-H), 6.51 (s, 1 H, 6′-H). − $C_{27}H_{40}O_3$ (412.6): calcd. C 78.60, H 9.77; found C 78.36, H 9.69.

Methyl (4E,8E)-4,8,12-Trimethyl-14-[2′,3′,4′-trimethyl-5′-(2″,3″,4″-tri-O-acetyl-1″-β-D-xylopyranosyloxy)phenyl]tetradeca-4,8,12-trienoate (**62**): This was prepared from **61** (200 mg, 0.484 mmol) in the same manner as described for **25** to give 197 mg of crude **62** as a colorless oil. − IR (film): $\tilde{\nu}_{max}$ = 1755 cm^{-1} (s, C=O), 1585 (w, C=C), 1245 (s, C−O), 1220 (s, C−O), 1160 (m, C−O), 1120 (m, C−O), 1060 (s, C−O), 1040 (s, C−O). This was employed in the next step without further purification.

(4E,8E)-4,8,12-Trimethyl-14-[2′,3′,4′-trimethyl-5′-(1″-β-D-xylopyranosyloxy)phenyl]tetradeca-4,8,12-trienoic Acid (**10**): This was prepared from crude **62** (197 mg) in the same manner as described for **2** to give 131 mg (51% based on **61**) of **10** as a colorless amorphous solid. − $[\alpha]_D^{24}$ = −12 (*c* = 0.14, MeOH). − R_f = 0.64 (*i*BuOH/MeOH/H_2O, 8:1:1). − IR (KBr): $\tilde{\nu}_{max}$ = 3410 cm^{-1} (s, O−H), 2970 (s), 2935 (s), 2905 (s), 1710 (s, C=O), 1580 (w, C=C), 1545 (s, C=C), 1445 (s), 1385 (s), 1305 (m), 1270 (m, C−O), 1155 (m, C−O), 1075 (s, C−O), 1050 (s, C−O), 985 (m), 756 (s). − ^{1}H NMR (300 MHz, CD_3OD): δ = 1.56, 1.588, 1.593 (each s, total 6 H, 15,16-H_3), 1.70 [s, 9/5 H, 17-H_3 (*E*)], 1.73 [s, 6/5 H, 17-H_3 (*Z*)], 1.90−2.20 (m, 8 H, 6,7,10,11-H_2), 2.10 [s, 9/5 H, 18-H_3 (*E*)], 2.11 [s, 6/5 H, 18-H_3 (*Z*)], 2.15 (s, 3 H, 19-H_3), 2.18 (s, 3 H, 20-H_3), 2.20−2.28 (m, 2 H, 3-H_2), 2.28−2.40 (m, 2 H, 2-H_2), 3.20−3.29 (m, 1 H, 5″a-H), 3.26 (d, *J* = 7 Hz, 2 H, 14-H_2), 3.39 (t, *J* = 7 Hz, 1 H, 3″-H,), 3.46 (t, *J* = 7 Hz, 1 H, 2″-H), 3.52−3.64 (m, 1 H, 4″-H), 3.89 (dd, *J* = 5 Hz, *J′* = 11 Hz, 1 H, 5″e-H), 4.70 [d, *J* = 7 Hz, 2/5 H, 1″-H (*Z*)], 4.72 [d, *J* = 7 Hz, 3/5 H, 1″-H (*E*)], 5.02−5.25 (m, 3 H, 5,9,13-H), 6.75 (s, 1 H, 6′-H). − ^{13}C NMR (75.5 MHz, CD_3OD): δ = 12.8, 15.6, 16.11, 16.14, 16.2, 16.4, 16.5, 23.7, 27.4, 27.5, 27.6, 33.0, 33.7, 34.1, 35.3, 36.2, 40.65, 40.73, 66.8, 71.0, 74.8, 77.7, 104.1, 115.5, 115.7, 124.6, 125.0, 125.19, 125.25, 125.3, 125.7, 129.6, 129.7, 134.97, 135.01, 135.8, 136.1, 136.3, 136.9, 137.21, 137.24, 138.6, 154.5, 180.1. − MS (70 eV); *m/z* (%): 530 (1) [M^+], 512 (1), 503 (1), 476 (1), 398 (68), 203 (98), 149 (100), 81 (49). − HRMS: $C_{31}H_{46}O_7$ [M^+]: calcd. 530.3244, found 530.3257. This material is an inseparable mixture of (12*E*) and (12*Z*) isomers (1.5:1).

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