

ACID-CATALYZED SOLVOLYSIS OF POLYENOL ETHERS. II. EFFECT OF THE DEGREE OF UNSATURATION⁽¹⁾.

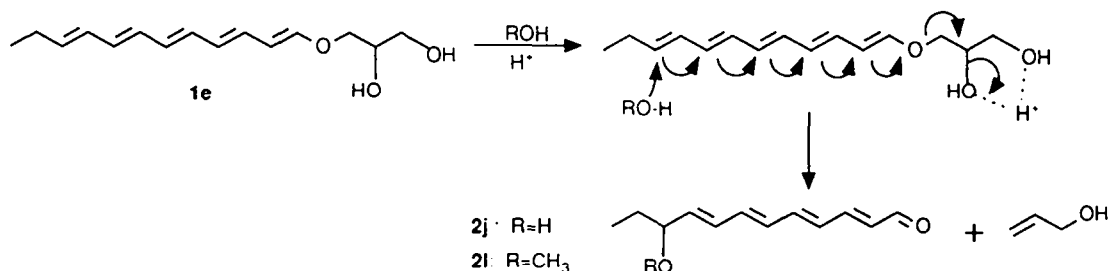
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ABSTRACT. The acid-catalyzed solvolysis of polyenol ethers of glycerol gradually changes with increasing unsaturation from the regular pattern into an anomalous one, in which hydroxy- and methoxy-substituted aldehydes are formed.

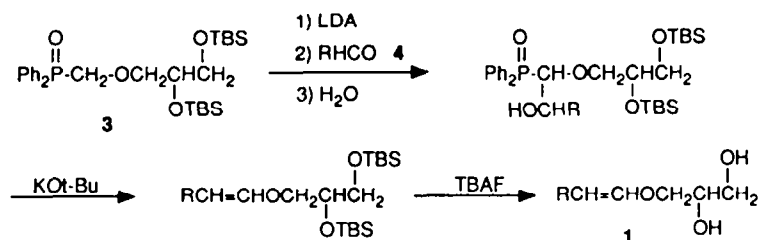
INTRODUCTION. Polyunsaturated enol ethers of glycerol, of which fecapentaene-12 **1g** is probably the best known example⁽²⁻⁹⁾, display unusual chemical reactivity. Under basic conditions an unprecedented ring closure has been observed, caused by base catalyzed nucleophilic addition of the 2'-hydroxyl group to the enol ether double bond⁽¹⁰⁾. Also external nucleophiles could be added to the polyene under basic conditions^(10,11). Recently, we reported the unusual chemical reactivity of fecapentaene-12 under acidic conditions, causing the formation of unsaturated aldehydes, substituted by the nucleophilic solvent at the original ω -carbon atom of the polyene⁽¹⁾. In the proposed mechanism⁽¹⁾, protonation at the glyceryl side chain is followed by loss of water, disruption of the carbon-oxygen bond (loss of allyl alcohol), a flow of π -electrons towards the enol ether oxygen atom (formation of a carbonyl group) and addition of the nucleophilic solvent to the ω -carbon atom of the polyene⁽¹²⁾. Using a THF/water mixture as the solvent, 10-hydroxy-2,4,6,8-dodecatetraenal **2j** was formed exclusively, while in a methanol/water mixture 10-methoxy-2,4,6,8-dodecatetraenal **2i** was formed as the sole product. (Scheme 1).



Scheme 1.

According to this mechanism, both the polyunsaturated side chain of fecapentaene-12 and the dihydroxypropyl structure of the glyceryl moiety play a crucial role in the anomalous outcome of the acid-catalyzed solvolysis.

In this paper the relation is described between the degree of unsaturation of polyenol ethers of glycerol and the outcome of acid-catalyzed solvolysis in methanol/water or THF/water mixtures. The enol ethers **1a-h** were prepared according to the reaction sequence depicted in scheme 2, which was developed earlier in our laboratories^(11,13). The lithiated anion of phosphine oxide **3**, which contains the glyceryl moiety in a properly protected form as a substituent at the α -carbon atom, is allowed to react with aldehyde **4**, containing the number of conjugated double bonds corresponding to the desired unsaturation in the final enol ether. The mixture of diastereomeric adducts, obtained after protonation of the reaction mixture at -70°C , is treated with a potassium base, to form the enol ether double bond. Upon removal of the *t*-butyldimethylsilyl (TBS) group with fluoride ion, the polyenol ethers of glycerol **1a-h** were obtained in good yields.



1a,4a; R = C₇H₅(CH₂-CH₂)₄

1b,4b; R = C₇H₅(CH₂-CH₂)₃CH=CH

1c,4c; R = C₇H₅(CH₂-CH₂)₂(CH=CH)₂

1d,4d; R = C₇H₅CH₂-CH₂(CH=CH)₃

1e,4e; R = C₇H₅(CH=CH)₄

1f,4f; R = C₇H₅(CH=CH)₅

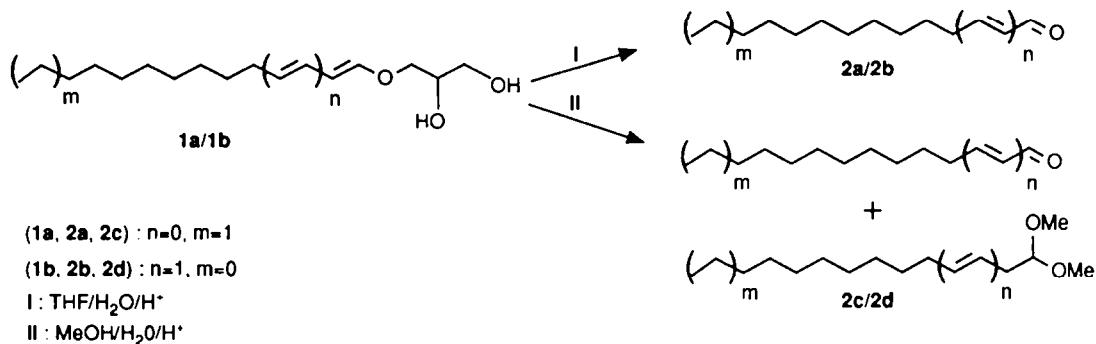
1g,4g; R = C₇H₅(CH=CH)₂

1h,4h; R = C₇H₅(CH=CH)₃

Scheme 2.

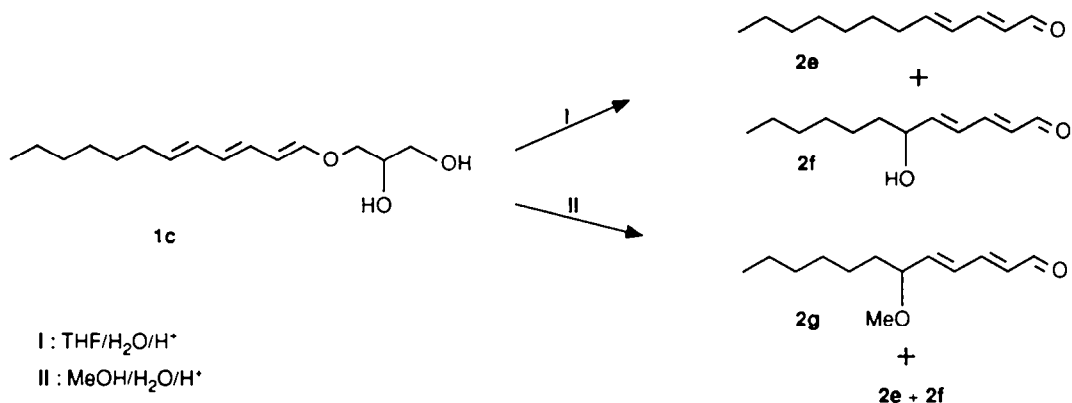
RESULTS.

In the acid-catalyzed solvolysis, the simple enol ether **1a** and the dienol ether **1b** reacted similarly. When using a THF/water mixture (reaction conditions I) they form the expected aldehydes, dodecanal (**2a**) and 2-dodecanal (**2b**), respectively. Using methanol/water (reaction conditions II), next to these aldehydes, acetals are formed: **1a** forms 1,1-dimethoxydodecane (**2c**) and **1b** forms 1,1-dimethoxydodec-3-ene (**2d**), (Scheme 3).



Scheme 3.

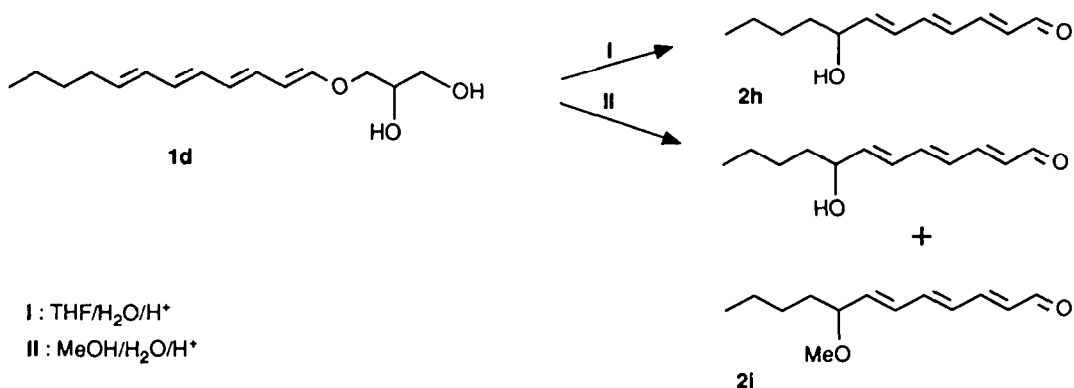
With enol ether **1c**, carrying two double bonds in conjugation with the enol ether, a change in mechanism becomes apparent. Under reaction conditions I, next to the expected aldehyde, 2,4-dodecadienal (**2e**), a hydroxy-substituted aldehyde, 6-hydroxy-2,4-dodecadienal (**2f**) is formed. Using reaction conditions II, in addition to these products, 6-methoxy-2,4-dodecadienal (**2g**) is formed, (Scheme 4).



Scheme 4.

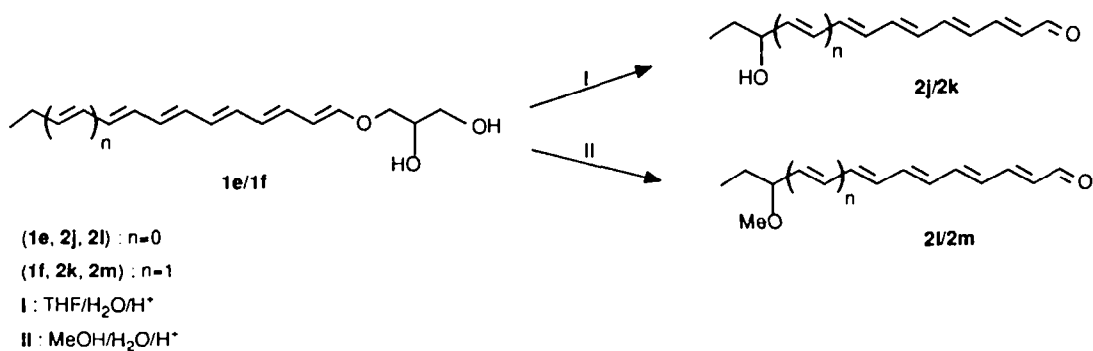
Originally, the solvolysis of the unsaturated enol ethers with a shorter aliphatic chain **1g** and **1h** was studied. Although the reaction pattern was quite similar, difficulties were encountered during the extraction of the reaction products from the aqueous layer. This led to appreciable loss of material. This disadvantage could be avoided by using enol ethers **1c** and **1d** with an aliphatic chain of twelve carbon atoms.

Using reaction conditions I, the enol ether **1d** only forms a single product: 8-hydroxy-2,4,6-dodecatrienal (**2h**). Using reaction conditions II, besides the hydroxy-substituted aldehyde, the corresponding methoxy substituted compound is formed i.e.: 8-methoxy-2,4,6-dodecatrienal (**2i**), (Scheme 5).



Scheme 5.

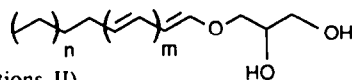
Applying reaction conditions I, enol ethers **1e** and **1f**, containing 4 and 5 double bonds in conjugation with the enol ether, also form a single product i.e.: 10-hydroxy-2,4,6,8-dodecatetraenal (**2j**) and 12-hydroxy-2,4,6,8,10-tetradecapentaenal (**2k**). Using reaction conditions II the corresponding methoxy substituted aldehydes: 10-methoxy-2,4,6,8-dodecatetraenal (**2l**) and 12-methoxy-2,4,6,8,10-tetradecapentaenal (**2m**) are now formed exclusively, (Scheme 6).



Scheme 6.

The solvolysis data are summarised in table 1.

TABLE 1. Acid-catalyzed solvolysis of polyenol ethers of glycerol in THF/water (reaction conditions I) or methanol/water (reaction conditions II).



Enol ether	Reaction conditions	Reaction time(h)	Reaction product	Yield*
1a: n=4, m=0	I	2	dodecanal (2a)	70%
1a: n=4, m=0	II	1	dodecanal (2a) 1,1-dimethoxydodecane (2c)	19% 43%
1b: n=3, m=1	I	141	2-dodecenal (2b)	32%
1b: n=3, m=1	II	21	2-dodecenal (2b) 1,1-dimethoxydodec-3-ene (2d)	35% 23%
1c: n=2, m=2	I	48	6-hydroxydodecadienal (2f) 2,4-dodecadienal (2e)	16% 17%
1c: n=2, m=2	II	2.25	6-hydroxydodecadienal (2f) 6-methoxydodecadienal (2g) 2,4-dodecadienal (2e)	24% 10% 8 %
1d: n=1, m=3	I	8	8-hydroxydodecatrienal (2h)	24%
1d: n=1, m=3	II	5.5	8-hydroxydodecatrienal (2h) 8-methoxydodecatrienal (2i)	11% 30%
1e: n=0, m=4	I	4	10-hydroxydodecatetraenal (2j)	49%
1e: n=0, m=4	II	4	10-methoxydodecatetraenal (2l)	40%
1f: n=0, m=5	I	4	12-hydroxytetradecapentaenal (2k)	30%
1f: n=0, m=5	II	4	12-methoxytetradecapentaenal (2m)	50%

a) Isolated yield after flash column chromatography.

DISCUSSION

It is well documented that in the acid-catalyzed hydrolysis of simple enol ethers, protonation at the β -carbon atom is the rate-determining step⁽¹⁴⁾. It is also known that the electron density at the β -carbon atom of conjugated polyenol ethers rapidly decreases with increasing length of the polyene⁽¹⁵⁾. The dramatic increase in reaction time needed for complete conversion of **1b** compared to **1a** is in agreement with these facts.

It is worthy of note, that acetal formation in the presence of methanol, a process also starting with protonation of the β -carbon atom, has only been observed in the solvolysis of **1a** and **1b**. In the case of **1b**, formation of 1,1-dimethoxydodec-3-ene clearly originates directly from the enol ether and not from the aldehyde. Reaction via the aldehyde would have resulted in formation of the isomeric 1,1-dimethoxydodec-2-ene. In the case of **1a** acetal formation via the aldehyde cannot be excluded.

Apparently, for the anomalous solvolysis mechanism to become operative, at least two additional double bonds need to be present in conjugation with the enol ether double bond. Extension of the conjugation beyond this point serves to further decrease the normal hydrolysis via protonation at the β -carbon atom and to increase the rate of the anomalous solvolysis reaction, starting with protonation and loss of water from the glyceryl moiety. In systems containing three or more double bonds in conjugation with the glyceryl enol ether, the normal hydrolysis is completely suppressed and only products resulting from attack of solvent at the ω -carbon atom of the polyene are formed. Although, with the exception of the simple enol ether **1a**, polymerisation is a serious side reaction in all cases studied, fair yields of hydroxy- and methoxy substituted polyenals can still be obtained, even in systems with a conjugation extended beyond four conjugated double bonds.

Work is in progress to determine the influence of variation in the hydroxylated side chain and in polarity of the solvent, on the outcome of the acid-catalyzed solvolysis reactions.

EXPERIMENTAL.

GENERAL.

¹H and ¹³C nmr spectra were recorded on a Jeol JNM FX-200 or on a Bruker 300-MHz spectrometer. The chemical shifts are given in ppm (δ) relative to tetramethylsilane as internal reference. Coupling constants (*J*) are given in Hz. **1h** and **1g** were measured in DMSO-D₆ as solvent and the other compounds in deuteriochloroform. Mass spectral data were obtained with an AEI MS 902 and a Kratos MS 9/50 apparatus. Uv absorptions were recorded on a Varian DMS 200 spectrometer, using 96% ethanol as the solvent. Flash column chromatography was performed with silica gel (230-400 mesh, Merck). Solvents and reagents were used as high grade commercial products. All syntheses were carried out under protection from light, in an inert atmosphere. *E/Z*-ratio's of the enol ethers were measured using ¹³C nmr and glc data; oventemp. 150-250°C, rise 7°C/min.

General procedure for the synthesis of polyunsaturated aldehydes 4e-h. The method developed by Wollenberg⁽¹⁶⁾ was used. Changing the reaction temperature as indicated led to higher yields.

41.3 Ml of a *n*-Butyllithium solution (1.6 M solution in hexane, 66 mmol) was slowly added at -60°C (lit

16, -80°C) to the stannane obtained by radical addition of tributyltin hydride to distilled methoxybutenyne (Fluka AG, Switzerland) (22.5 g, 60 mmol), dissolved in dry THF (80 ml). After stirring for 90 min at -60°C (lit 16, -80°C), the aldehyde (55 mmol) was added and stirring was continued for an additional 90 min at -60°C (lit 16, -80°C). The reaction mixture was quenched with saturated, aqueous, sodium hydrogen carbonate (100 ml). The THF layer was separated and the water layer was extracted with ether (3 x 50 ml). The combined organic layers were washed with saturated brine (2 x 25 ml), dried with anhydrous potassium carbonate and evaporated *in vacuo*. The crude adduct was purified by flash column chromatography [ether/petroleum ether 40-60°C/triethylamine (5:5:1, v/v/v)]. The purified adduct was dissolved in 5% aqueous THF (50 ml) and a catalytic amount of *p*-toluenesulfonic acid monohydrate (*p*-TsOH.H₂O) was added. After stirring for 90 min, the reaction mixture was filtered through a column with magnesium oxide and florisil (1/4). Evaporation of the solvent yielded the pure all-*E* aldehydes 4.

***E,E,E*-2,4,6-UNDECATRIENAL 4d.**

Starting aldehyde: heptanal⁽¹⁷⁾. Yield 7.8 g, 47.9 mmol, (87%); yellow solid.

uv: λ_{\max} (EtOH) 318 nm. $\epsilon = 41000 \text{ l mol}^{-1} \text{ cm}^{-1}$

ms: *m/z* 165(1), 164(M⁺, 16), 122(13), 108(70), 94(46), 80(79), 70(45), 56(36), 42(100).

¹H nmr: δ 0.90 (3H, t, J=6.9, CH₃), 1.2-1.5 (4H, m, CH₂CH₂, C9-H), 2.13 (2H, dt, J=6.9(2x), CH₂CH), 5.9-6.2 (3H, m, CHCHO, CHCH₂, C6-H), 6.32 (1H, dd, J=11.0 and 15.0, C4-H), 6.65 (1H, dd, J=15.0 and 10.0, C5-H), 7.12 (1H, dd, J=15.1 and 11.0, C3-H), 9.53 (1H, d, J=7.6, CHO) ppm.

¹³C nmr: δ 13.55 (C11), 21.90, 30.63, 32.41 (C8-C10), 127.43, 129.44, 130.23, 142.23, 142.96 (C2, C4-C7), 152.07 (C3), 193.01 (C1) ppm.

***E,E,E,E*-2,4,6,8-UNDECATETRAENAL 4e.**

Starting aldehyde: *E,E*-2,4-heptadienal, which is commercially available. Yield 7.1 g, 43.8 mmol, (80%); yellow solid.⁽¹⁸⁾

***E,E,E,E,E*-2,4,6,8,10-TRIDECAPENTAENAL 4f.**

Starting aldehyde: *E,E,E*-2,4,6-nonatrienal. Yield: 8.0 g, 42.6 mmol, (77%); yellow solid.

uv: λ_{\max} (EtOH) 380 nm. $\epsilon = 60000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

ms: *m/z* 189(17), 188(M⁺, 100), 117(40), 91(73), 79(43), 41(39), 39(32). Exact mass: 188.1198 (C₁₃H₁₆O requires 188.1201).

¹H nmr: δ 1.03 (3H, t, J=7.3, CH₃), 2.16 (2H, dq, J=7.3 and 7.0, CH₂CH₂), 5.87 (1H, dd, J=7.0 and 15.0, CHCH₂), 6.13 (1H, dd, J=7.8 and 15.1, CHCHO), 6.14 (1H, dd, J=15.0 and 10.9, C10-H), 6.21 (1H, dd, J=15.0 and 10.7, C8-H), 6.30 (1H, dd, J=14.9 and 11.3, C6-H), 6.37 (1H, dd, J=15.0 and 10.9, C9-H), 6.42 (1H, dd, J=11.3 and 14.9, C4-H), 6.50 (1H, dd, J=14.9 and 10.7, C7-H), 6.70 (1H, dd, J=14.9 and 11.3, C5-H), 7.12 (1H, dd, J=15.1 and 11.3, C3-H), 9.55 (1H, d, J=7.8, CHO) ppm.

¹³C nmr: δ 13.26 (C13), 25.93 (C12), 129.18, 129.30, 129.94, 130.52, 130.61, 137.07, 139.20, 139.90 (C2, C4, C6-C11), 142.91 (C5), 151.93 (C3), 193.36 (C1) ppm.

***E,E,E*-2,4,6-NONATRIENAL 4h.**

Starting aldehyde: *E*-2-pentenal, which is commercially available. Yield: 5.4 g, 39.7 mmol, (72%)⁽¹⁹⁾.

General procedure for the synthesis of 3'-(polyenyloxy)-1,2-propanediols 1a-h.

In an atmosphere of dry nitrogen, phosphine oxide 3^(11,13) (11.6 g, 21.6 mmol) dissolved in dry THF (100 ml) reacted smoothly with lithium diisopropylamine (23.8 mmol) at -50°C to give a solution of the deeply red colored anion. After stirring for 15 min, the solution was cooled to -80°C and the aldehyde (21.6 mmol) dissolved in dry THF (20 ml) was added dropwise. After stirring for 1 h at -80°C, the reaction mixture was quenched with saturated aqueous ammonium chloride (150 ml). The THF layer was separated and the water layer extracted with ether (3 x 150 ml). The combined organic layers were washed with saturated brine (50 ml), dried with anhydrous magnesium sulfate and evaporated *in vacuo* to yield the silyl protected adduct. The crude adduct was subsequently treated with potassium *t*-butoxide (KO^{*t*}-Bu) (2.7 g, 24.0 mmol) in dry THF (100 ml) at -50°C. The reaction mixture was stirred overnight at 4°C (in the case of aldehydes with three or more conjugated double bonds, stirring was performed at -17°C). After addition of saturated brine (200 ml), the THF layer was separated and the water layer extracted with ether (3 x 50 ml), dried with sodium carbonate, and evaporated *in vacuo* to afford the crude silyl protected enol ether, which was purified

by flash column chromatography (10% triethylamine in petroleum ether 40-60°C). The purified silyl protected enol ether was dissolved in THF (80 ml) and 2.2 equiv of tetrabutylammonium fluoride trihydrate in THF (80 ml) was added at 0°C. After stirring for 1 h at 0°C, the reaction mixture was concentrated *in vacuo* at temperatures not exceeding 10°C and the resulting syrup was subjected to flash column chromatography (5% methanol and 10% triethylamine in ether). The enol ethers were obtained as mixtures of geometric isomers around the enol ether double bond.

3'-(1E/Z-DODECAENYLOXY)-1,2-PROPANEDIOL (1a)⁽¹⁸⁾.

Starting aldehyde: undecanal, which is commercially available. Yield: 3.41 g, 13.2 mmol, (66%); white semi-solid. *E/Z*-ratio 1:1.

3'-(1E/Z,3E-DODECADIENYLOXY)-1,2-PROPANEDIOL (1b).

Starting aldehyde: *E*-2-undecenal.⁽¹⁷⁾ Yield: 2.70 g, 10.5 mmol, (53%); white solid. *E/Z*-ratio 1:1.

uv: λ_{\max} (EtOH) 240 nm. $\epsilon = 24000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

ms: m/z 257(5), 256(M⁺, 28), 182(7), 157(21), 83(100), 70(48), 57(49), 41(34), 31(15). Exact mass: 256.2040 (C₁₃H₂₂O₃, requires 256.2038).

¹H nmr: δ 0.86 (6H, t(2x), J=6.8(2x), CH₃, *E+Z*), 1.2-1.4 (12H, m, CH₂CH₂, *E+Z*, C6-H-C10-H, *E+Z*), 2.03 (4H, dt(2x), [J=6.6 and 6.9](2x), CH₂CH, *E+Z*), 3.6-3.8 (10H, m, CH₂O, *E+Z*, CHOH, *E+Z*, CH₂OH, *E+Z*), 5.04 (1H, dd, J=6.3 and 10.9, CHCHO, *Z*), 5.45 (1H, dt, J=14.8 and 7.2, CHCH₂, *E*), 5.53 (1H, dd, J=12.4 and 10.9, CHCHO, *E*), 5.56 (1H, dd, J=15.0 and 7.2, CHCH₂, *Z*), 5.84 (1H, dd, J=10.9 and 14.8, C3-H, *E*), 5.87 (1H, d, J=6.3, CHO, *Z*), 6.30 (1H, dd, J=10.9 and 15.0, C3-H, *Z*), 6.44 (1H, d, J=12.4, CHO, *E*) ppm.

¹³C nmr: δ 14.08(2x) (C12, *E+Z*), [22.63, 29.26, 29.46, 29.58, 31.86, 32.79, 32.94](2x) (C5-C11, *E+Z*), 63.45 (C1', *Z*), 63.54 (C1', *E*), 70.43 (C2', *E*), 70.55 (C3', *E*), 70.78 (C2', *Z*), 73.50 (C3', *Z*), 107.60 (C2, *Z*), 107.81 (C2, *E*), 122.32 (C3, *Z*), 125.33 (C3, *E*), 130.26 (C4, *E*), 132.28 (C4, *Z*), 144.01 (C1, *Z*), 147.93 (C1, *E*) ppm.

3'-(1E/Z,3E,5E-DODECATRIENYLOXY)-1,2-PROPANEDIOL (1c).

Starting aldehyde: *E,E*-2,4-undecadienal, which is commercially available. Yield: 2.40 g, 9.4 mmol, (47%); pale yellow solid. *E/Z*-ratio 1:1.

uv: λ_{\max} (EtOH) 279 nm. $\epsilon = 40000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

ms: m/z 255(6), 254(M⁺, 53), 180(39), 162(48), 120(81), 106(60), 96(89), 82(100), 66(50), 56(93), 42(27).

¹H nmr: δ 0.87 (6H, t(2x), J=6.8(2x), CH₃, *E+Z*), 1.2-1.4 (16H, m, CH₂CH₂, *E+Z*, C8-H-C10H, *E+Z*), 2.07 (4H, dt(2x), [J=7.0 and 6.5](2x), CH₂CH, *E+Z*), 3.6-4.0 (10H, m, CH₂O, *E+Z*, CHOH, *E+Z*, CH₂OH, *E+Z*), 5.12 (1H, dd, J=6.1 and 11.1, CHCHO, *Z*), 5.59 (1H, dt, J=13.4 and 6.5, CHCH₂, *E*), 5.60 (1H, dd, J=12.6 and 9.9, CHCHO, *E*), 5.63 (1H, dt J=13.8 and 6.5, CHCH₂, *Z*), 5.9-6.1 (5H, m, C3-H, *E*, C4-H, *E+Z*, C5-H, *E+Z*), 5.96 (1H, d, J=6.1, CHO, *Z*), 6.39 (1H, dd, J=11.1 and 14.9, C3-H, *Z*), 6.54 (1H, d, J=12.6, CHO, *E*) ppm.

¹³C nmr: δ 14.08(2x) (C12, *E+Z*), [22.60, 28.85, 31.71, 32.76](2x) (C8-C11, *E+Z*), 29.32, 29.41 (C7, *E+Z*), 63.39 (C1', *Z*), 63.48 (C1', *E*), 70.37 (C2', *E*), 70.75 (C2', *Z*), 70.84 (C3', *E*), 73.67 (C3', *Z*), 107.93(2x) (C2, *E+Z*), 122.87 (C3, *Z*), 126.26 (C3, *E*), 128.98, 130.44(2x), 130.61, 133.06, 134.50 (C4-C6, *E+Z*), 145.47 (C1, *Z*), 149.39 (C1, *E*) ppm.

3'-(1E/Z,3E,5E,7E-DODECATETRAENYLOXY)-1,2-PROPANEDIOL (1d).

Starting aldehyde: *E,E,E*-2,4,6-undecatrienal (4d). Yield: 1.30 g, 5.2 mmol, (28%); pale yellow solid. *E/Z*-ratio 1:1.

uv: λ_{\max} (EtOH) 297, 309, 322 nm. $\epsilon = 39000, 50000, 45000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

ms: m/z 253(1), 252(M⁺, 10), 178(9), 160(20), 134(36), 118(47), 104(52), 94(87), 80(50), 66(25), 56(100), 28(8).

¹H nmr: δ 0.86 (6H, t(2x), J=6.5(2x), CH₃, *E+Z*), 1.2-1.4 (12H, m, CH₂CH₂, *E+Z*, C10-H, *E+Z*), 2.05 (4H, dt(2x), J=6.9(4x), CH₂CH, *E+Z*), 3.2-3.4 (4H, dd(2x), CH₂OH, *E+Z*), 3.66 (2H, m, CHOH, *E+Z*), 3.73-3.91 (4H, d(2x), CH₂O, *E+Z*), 4.66 (2H, d(2x), CH₂OH, *E+Z*), 4.89 (2H, d(2x), CHOH, *E+Z*), 5.07 (1H, dd, J=6.2 and J=11.0, CHCHO, *Z*), 5.55-5.73 (3H, m, CHCHO, *E*, CHCH₂, *E+Z*), 5.9-6.2 (9H, m, C3-H, *E*, C4-H-C7-H, *E+Z*), 5.94 (1H, d, J=6.2, CHO, *Z*), 6.45 (1H, dd, J=11.0 and 14.4, C3-H, *Z*), 6.74 (1H, d, J=12.4, CHO, *E*) ppm.

¹³C nmr: δ 13.77(2x) (C12, *E+Z*), [21.72, 31.06, 31.94](2x) (C9-C11, *E+Z*), 62.45 (C1', *Z*), 62.51 (C1', *E*),

70.01 (C2', E), 70.51 (C2', Z), 71.91 (C1', E), 74.28 (C1', Z), 105.78 (C2, Z), 106.95 (C2, E), 125.79, 127.28, 128.59, 129.61, 129.93, 130.78(2x), 131.28, 131.48(2x), 133.32, 134.02 (C3-C8, E+Z), 147.93 (C1, Z), 151.92 (C1, E) ppm.

3'-(1E/Z,3E,5E,7E,9E-DODECAPENTAENYLOXY)-1,2-PROPANEDIOL (FECAPENTAENE-12) (1e)⁽¹⁸⁾

Starting aldehyde: *E,E,E,E*-2,4,6,8-undecatetraenal 4e. Yield: 2.30, 9.2 mmol, (46%); pale yellow solid *E/Z* ratio 1:1.⁽¹⁸⁾

3'-(1E/Z,3E,5E,7E,9E,11E-TETRADECAHEXAENYLOXY)-1,2-PROPANEDIOL (1f)

Starting aldehyde: *E,E,E,E,E*-2,4,6,8,10-tridecapentaenal (4f). Yield: 1.55 g, 5.6 mmol, (26%); yellow solid. *E/Z*-ratio 1:2.

uv: λ_{max} (EtOH) 348, 365, 385 nm. $\epsilon = 51000, 71000, 67000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

ms: *m/z* 277(7), 276(M⁺, 100), 224(5), 175(15), 167(22), 113(100), 103(52), 91(86), 61(46), 57(80), 43(64), 41(56), 29(49). Exact mass: 276.1725 (C₁₇H₃₂O₆, requires 276.1725).

¹H nmr: δ 0.95 (6H, t(2x), J=7.3(2x), CH₃, E+Z), 2.08 (4H, dq(2x), J=7.3(4x), CH₂CH₃, E+Z), 3.21-3.43 (4H, dd(2x), CH₂OH, E+Z), 3.61 (2H, m, CHOH, E+Z), 3.75-3.91 (4H, d(2x), OCH₂, E+Z), 4.60 (2H, d(2x), CH₂OH, E+Z), 4.90 (2H, d(2x), CHOH, E+Z), 5.07 (1H, dd, J=11.3 and 6.2, CHCHO, Z), 5.6-5.8 (3H, m, CHCHO, E, CH₂CH, E+Z), 5.9-6.3 (18H, m, CHO, Z, C3-H, E, C4-H-C11-H, E+Z), 6.50 (1H, dd, J=11.3 and 15.4, C3-H, Z), 6.76 (1H, d, J=12.4, CHO, E) ppm.

¹³C nmr: δ 13.42(2x) (C14, E+Z), 25.37(2x) (C13, E+Z), 62.45 (C1', Z), 62.60 (C1', E), 70.01 (C2', E), 70.51 (C2', Z), 72.06 (C3', E), 74.25 (C3', Z), 105.93 (C2, Z), 107.22 (C2, E), 126.69, 127.45, 128.76, 129.79(2x), 130.05, 130.69, 131.10(2x), 131.36, 131.57, 131.71, 132.33, 132.53, 132.79, 132.88(2x), 133.70 (C3-C11, E+Z), 136.44 (C12, E), 136.68 (C12, Z), 148.50 (C1, Z), 152.53 (C1, E) ppm.

3'-(1E/Z,3E,5E-OCTATRIENYLOXY)-1,2-PROPANEDIOL (1g)⁽¹⁸⁾

Starting aldehyde: *E,E*-2,4-heptadienal, which is commercially available. Yield: 2.26 g, 11.4 mmol, (57%); pale yellow solid.

3'-(1E/Z,3E,5E,7E-DECATETRAENYLOXY)-1,2-PROPANEDIOL (1h)⁽¹⁸⁾

Starting aldehyde: *E,E,E*-2,4,6-nonatrienal. Yield: 1.70 g, 7.6 mmol, (38%); pale yellow solid.

General procedure for solvolysis in THF/water (reaction conditions I)

In an atmosphere of dry argon, the enol ether (200 mg) was dissolved in 125 ml of THF. Subsequently, 125 ml of water and 7 ml of 36% aqueous HCl were added. After stirring for the period indicated in table 1, the reaction was quenched with water (200 ml). The mixture was extracted with ether (3 x 100 ml). The combined organic layers were washed with saturated brine (3 x 100 ml), dried with anhydrous potassium carbonate and evaporated *in vacuo*. The crude product was purified by flash column chromatography.

General procedure for solvolysis in methanol/water (reaction conditions II)

In an atmosphere of dry argon, the enol ether (200 mg) was dissolved in 125 ml of methanol. Subsequently, 125 ml of water and 7 ml of 36% aqueous HCl were added. After stirring for the period indicated in table 1, the reaction was quenched with water (200 ml). The mixture was extracted with ether (3 x 100 ml). The combined organic layers were washed with saturated brine (3 x 100) ml, dried with anhydrous potassium carbonate and evaporated *in vacuo*. The crude product was purified by flash column chromatography.

DODECANAL (2a)⁽¹⁹⁾

Yield: 99.8 mg, 0.54 mmol, (70%); colourless oil; eluent: (petroleum ether).

ms: *m/z* 185(9), 184(M⁺, 45), 128(100), 58(98).

¹H nmr: δ 0.88 (3H, t, J=6.6, CH₃), 1.2-1.4 (16H, m, CH₂CH₂, C4-H-C10-H), 1.60 (2H, m, J=6.2 and 7.6, C3-H), 2.39 (2H, dt, J=6.2 and 1.7, CH₂CHO), 9.74 (1H, t, J=1.7, CHO) ppm.

¹³C nmr: δ 14.05 (C12), 22.05, 22.63, 29.11, 29.29, 29.38, 29.46, 29.55, 31.86 (C3-C11), 43.86 (C2), 202.74 (C1) ppm.

2E-DODECENAL (2b)⁽¹⁹⁾

Yield: 49.8 mg, 0.27 mmol, (35%); colourless oil; eluent: (90% petroleum ether/10% ether).

uv: λ_{\max} (EtOH) 222 nm. $\epsilon=16000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

ms: m/z 183(2), 182(M⁺, 3), 83(60), 70(100), 55(81), 41(85). Exact mass: 182.1672 (C₁₂H₂₂O requires 182.1670).

¹H nmr: δ 0.86 (3H, t, J=6.9, CH₃), 1.2-1.6 (14H, m, CH₂CH₂, C5-H-C10-H), 2.31 (2H, dt, J=6.9(2x), CH₂CH), 6.10 (1H, dd, J=15.6 and 7.8, CHCHO), 6.84 (1H, dt, J=15.6 and 6.9, C3-H), 9.49 (1H, d, J=7.8, CHO) ppm.

¹³C nmr: δ 14.02 (C12), 22.60, 27.80, 29.08, 29.23, 29.29, 29.41, 31.80, 32.71 (C4-C11), 132.89 (C2), 159.02 (C3), 194.09 (C1) ppm.

1,1-DIMETHOXYDODECANE (2c)⁽¹⁹⁾

Yield: 77.3 mg, 0.34 mmol, (43%); colourless oil; eluent: (petroleum ether).

ms: m/z 230(M⁺, 3), 229(35), 199(44), 97(17), 83(24), 75(100), 71(35), 55(35), 41(37), 31(15). Exact mass: 230.2226 (C₁₄H₃₀O₂ requires 230.2228).

¹H nmr: δ 0.88 (3H, t, J=6.5, CH₃), 1.2-1.4 (18H, m, CH₂CH₂, C3-H-C10-H), 1.5-1.7 (2H, dt, CH₂CH), 3.31 (6H, s, OCH₃), 4.35 (1H, t, J=5.5, CH(OCH₃)₂) ppm.

¹³C nmr: δ 14.05 (C12), 22.08, 22.66, 24.59, 29.32, 29.46, 29.55, 29.61, 31.89, 32.47, 43.89 (C2-C11), 52.47 (C13, C13'), 104.56 (C1) ppm.

1,1-DIMETHOXYDODEC-3E-ENE (2d)⁽¹⁹⁾

Yield: 35.6 mg, 0.16 mmol, (23%); colourless oil; eluent: (90% petroleum ether/10% ether).

ms: m/z 228(M⁺, 1), 196(100), 164(94), 122(45), 108(88), 94(69), 80(26), 70(21), 46(26), 32(20).

¹H nmr: δ 0.87 (3H, t, J=6.5, CH₃), 1.2-1.4 (12H, m, CH₂CH₂, C6-H-C10-H), 2.00 (2H, dt, J=6.3 and 6.9, C5-H), 2.31 (2H, dd, J=6.2 and 6.4, CH₂CHOCH₃), 3.31 (6H, s, OCH₃), 4.34 (1H, t, J=6.2, CH(OCH₃)₂), 5.36 (1H, dt, J=14.2 and 6.4, CHCH₂CH), 5.51 (1H, dt, J=6.3 and 14.2, CHCH₂CH₂) ppm.

¹³C nmr: δ 14.08 (C12), 22.66, 29.14, 29.29, 29.38, 29.46, 31.89, 32.65, 36.18 (C2, C5-C11), 52.76 (C13, C13'), 124.07 (C4), 133.74 (C3), 104.39 (C1) ppm.

2E,4E-DODECADIENAL (2e)⁽¹⁹⁾

Yield: 24.4 mg, 0.14 mmol, (17%); yellow oil; eluent: (45% petroleum ether/45% ether/10% triethylamine).

uv: λ_{\max} (EtOH) 274 nm. $\epsilon=25000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

ms: m/z 181(1), 180(M⁺, 7), 166(100), 148(22), 106(17), 92(46), 82(98), 78(45), 54(72), 40(36).

¹H nmr: δ 0.88 (3H, t, J=6.9, CH₃), 1.2-1.4 (8H, m, CH₂CH₂, C8-H-C10-H), 1.44 (2H, m, J=6.7 and 7.4, C7-H), 2.22 (2H, dt, J=7.4 and 6.7, CH₂CH), 6.07 (1H, dd, J=15.3 and 8.0, CHCHO), 6.27-6.32 (2H, m, CHCH₂, CHCHCH₂), 7.08 (1H, dd, J=15.3 and 10.0, C3-H), 9.53 (1H, d, J=8.0, CHO) ppm.

¹³C nmr: δ 14.04 (C12), 22.54, 28.51, 28.85, 31.60, 33.20(2x) (C6-C11), 128.63, 130.01, 147.44 (C2, C4, C5), 152.89 (C3), 193.96 (C1) ppm.

6-HYDROXY-2E,4E-DODECADIENAL (2f)

Yield: 37.0 mg, 0.19 mmol, (24%); yellow oil; eluent: (45% petroleum ether/45% ether/10% triethylamine).

uv: λ_{\max} (EtOH) 272 nm. $\epsilon=20000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

ms: m/z 197(4), 196(M⁺, 100), 178(32), 150(29), 94(80), 66(99), 42(94).

¹H nmr: δ 0.88 (3H, t, J=6.2, CH₃), 1.2-1.5 (8H, m, CH₂CH₂, C8-H-C10-H), 1.57 (2H, dt, J=6.2(2x), CH₂CHOH), 4.29 (1H, dt, J=6.2(2x), CHOH), 6.15 (1H, dd, J=7.6 and 15.3, CHCHO), 6.29 (1H, dd, J=15.3 and 6.2, CHCHOH), 6.51 (1H, dd, J=10.6 and 15.3, C4-H), 7.11 (1H, dd, J=15.3 and 10.6, C3-H), 9.55 (1H, d, J=7.6, CHO) ppm.

¹³C nmr: δ 14.05 (C12), 22.54, 25.20, 29.11, 31.71, 37.00 (C7-C11), 71.83 (C6), 127.22, 131.69, 147.46 (C2, C4, C5), 151.52 (C3), 193.80 (C1) ppm.

6-METHOXY-2E,4E-DODECADIENAL (2g)

Yield: 13.8 mg, 0.07 mmol, (10%); yellow oil; eluent (90% petroleum ether/10% triethylamine).

uv: λ_{\max} (EtOH) 271 nm. $\epsilon=25000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

ms: m/z 211(3), 210(M⁺, 38), 194(67), 184(77), 178(83), 158(89), 150(94), 128(100), 96(73), 84(25), 56(4).

¹H nmr: δ 0.87 (3H, t, J=6.9, CH₃), 1.2-1.4 (8H, m, CH₂CH₂, C8-H-C10-H), 1.5-1.7 (2H, dt, CH₂CHOCH₃),

3.30 (3H, s, OCH₃), 3.69 (1H, dt, J=6.5(2x), CHOCH₃), 6.11 (1H, dd, J=15.1 and 6.5, CHCHOCH₃), 6.16 (1H, dd, J=8.1 and 15.3, CHCHO), 6.45 (1H, dd, J=11.0 and 15.1, C4-H), 7.12 (1H, dd, J=11.0 and 15.3, C3-H), 9.58 (1H, d, J=8.1, CHO) ppm.

¹³C nmr: δ 14.05 (C12), 22.60, 25.11, 29.26, 31.74, 35.13 (C7-C11), 56.88 (C13), 81.44 (C6), 129.18, 131.81, 145.77 (C2, C4, C5), 151.20 (C3), 193.71 (C1) ppm.

8-HYDROXY-2E,4E,6E-DODECATRIENAL (2h).

Yield: 37.0 mg, 0.19 mmol, (24%); yellow oil; eluent: (90% ether/10% triethylamine).

uv: λ_{max} (EtOH) 314 nm. ε=34000 l mol⁻¹ cm⁻¹.

ms: m/z 195(11), 194(M⁺, 77), 176(63), 148(17), 120(17), 94(44), 64(100), 31(23).

¹H nmr: δ 0.91 (3H, t, J=6.2, CH₃), 1.3-1.4 (4H, m, CH₂CH₂, C10-H), 1.56 (2H, dt, J=6.2(2x), CH₂CHOH), 4.23 (1H, dt, J=6.2(2x), CHOH), 6.00 (1H, dd, J=15.5 and 6.2, CHCHOH), 6.14 (1H, dd, J=8.1 and 15.3, CHCHO), 6.37 (1H, dd, J=15.5 and 10.8, C6-H), 6.43 (1H, dd, J=11.4 and 15.0, C4-H), 6.66 (1H, dd, J=15.0 and 10.8, C5-H), 7.12 (1H, dd, J=11.4 and 15.3, C3-H), 9.56 (1H, d, J=8.1, CHO) ppm.

¹³C nmr: δ 13.99 (C12), 22.57, 27.45, 36.88 (C9-C11), 72.09 (C8), 128.80, 129.79, 131.37 (C2, C4, C6), 141.91, 142.88 (C5, C7), 151.72 (C3), 193.54 (C1) ppm.

8-METHOXY-2E,4E,6E-DODECATRIENAL (2i).

Yield: 49.3 mg, 0.24 mmol, (30%); yellow oil; eluent: (90% petroleum ether/10% triethylamine).

uv: λ_{max} (EtOH) 313 nm. ε=29000 l mol⁻¹ cm⁻¹.

ms: m/z 209(6), 208(M⁺, 53), 176(100), 152(88), 130(87), 116(85), 106(59), 92(49), 56(50).

¹H nmr: δ 0.87 (3H, t, J=6.9, CH₃), 1.2-1.6 (6H, m, CH₂CH₂, C10-H, CH₂CHOCH₃), 3.26 (3H, s, OCH₃), 3.62 (1H, dt, J=6.9(2x), CHOCH₃), 5.83 (1H, dd, J=6.9 and 15.1, CHCHOCH₃), 6.14 (1H, dd, J=7.8 and 15.3, CHCHO), 6.30 (1H, dd, J=10.8 and 15.1, C6-H), 6.42 (1H, dd, J=10.3 and 14.3, C4-H), 6.67 (1H, dd, J=10.8 and 14.3, C5-H), 7.12 (1H, dd, J=10.3 and 15.3, C3-H), 9.55 (1H, d, J=7.8, CHO) ppm.

¹³C nmr: 13.96 (C12), 22.60, 27.33, 34.98 (C9-C11), 56.53 (C13), 81.67 (C8), 129.76, 130.76, 131.43 (C2, C4, C6), 141.01, 141.65 (C5, C7), 151.58 (C3), 193.39 (C1) ppm.

10-HYDROXY-2E,4E,6E,8E-DODECATETRAENAL (2j).

Yield: 75.3 mg, 0.39 mmol, (49%); yellow solid; eluent: (90% ether/10% triethylamine).

uv: λ_{max} (EtOH) 351 nm. ε=37000 l mol⁻¹ cm⁻¹.

ms: m/z 193(15), 192(M⁺, 100), 177(3), 174(45), 163(7), 138(3), 110(44). Exact mass: 192.1156 (C₁₂H₁₈O₂ requires 192.1150).

¹H nmr: δ 0.94 (3H, t, J=7.4, CH₃), 1.59 (2H, dq, J=7.4 and 6.4, CH₂CH₃), 4.15 (1H, dt, J=6.4(2x), CHOH), 5.89 (1H, dd, J=6.4 and 15.0, CHCHOH), 6.16 (1H, dd, J=15.2 and 8.0, CHCHO), 6.33 (1H, dd, J=15.0 and 10.7, C8-H), 6.34 (1H, dd, J=14.7 and 10.8, C6-H), 6.46 (1H, dd, J=11.2 and 14.9, C4-H), 6.49 (1H, dd, J=10.7 and 14.7, C7-H), 6.70 (1H, dd, J=10.8 and 14.9, C5-H), 7.14 (1H, dd, J=11.2 and 15.2, C3-H), 9.56 (1H, d, J=8.0, CHO) ppm.

¹³C nmr: δ 9.61 (C12), 30.14 (C11), 73.64 (C10), 129.79, 131.11 (C2, C4), 130.03, 131.55 (C6, C8), 137.91, 139.90 (C7, C9), 142.38 (C5), 151.66 (C3), 193.45 (C1) ppm.

12-HYDROXY-2E,4E,6E,8E,10E-TETRADECAPENTAENAL (2k).

Yield: 47.4 mg, 0.22 mmol, (30%); reddish solid; eluent: (90% ether/10% triethylamine).

uv: λ_{max} (EtOH) 376 nm. ε=44000 l mol⁻¹ cm⁻¹.

ms: m/z 219(6), 218(M⁺, 69), 161(40), 91(68), 57(100), 41(22). Exact mass: 218.1284 (C₁₄H₁₈O₂ requires 218.1307).

¹H nmr: δ 0.94 (3H, t, J=7.6, CH₃), 1.60 (2H, dq, J=7.6 and 6.5, CH₂CH₃), 4.14 (1H, dt, J=6.5(2x), CHOH), 5.83 (1H, dd, J=6.5 and 15.1, CHCHOH), 6.1-6.6 (7H, m, CHCHO, C4-H, C6-H-C10-H), 6.72 (1H, dd, J=14.4 and 10.6, C5-H), 7.14 (1H, dd, J=11.0 and 15.1, C3-H), 9.56 (1H, d, J=8.2, CHO) ppm.

¹³C nmr: δ 9.61 (C14), 30.19 (C13), 73.76 (C12), 129.91, 130.17, 130.99, 131.72, 132.28, 135.66, 138.55 (2x) (C2, C4, C6-C11), 142.50 (C5), 151.58 (C3), 193.33 (C1) ppm.

10-METHOXY-2E,4E,6E,8E-DODECATETRAENAL (2l).

Yield: 65.9 mg, 0.32 mmol, (40%); yellow solid; eluent: (90% petroleum ether/10% triethylamine).

uv: λ_{max} (EtOH) 351 nm. ε=35000 l mol⁻¹ cm⁻¹.

ms: m/z 207(14), 206(M⁺, 100), 177(26), 149(14), 117(59), 91(44), 75(45), 51(47), 41(32). Exact mass: 206.1301 (C₁₁H₁₈O₂ requires 206.1307).

¹H nmr: δ 0.90 (3H, t, J=7.4, CH₃), 1.59 (2H, dq, J=7.4 and 6.2, CH₂CH₃), 3.28 (3H, s, OCH₃), 3.56 (1H, dt, J=6.2(2x), CHOCH₃), 5.73 (1H, dd, J=6.2 and 15.5, CHCHOCH₃), 6.16 (1H, dd, J=8.0 and 15.2, CHCHO), 6.29 (1H, dd, J=10.4 and 15.5, C8-H), 6.33 (1H, dd, J=10.9 and 14.9, C6-H), 6.47 (1H, dd, J=11.1 and 14.8, C4-H), 6.50 (1H, dd, J=14.9 and 10.4, C7-H), 6.71 (1H, dd, J=14.8 and 10.9, C5-H), 7.15 (1H, dd, J=15.2 and 11.1, C3-H), 9.57 (1H, d, J=8.0, CHO) ppm.

¹³C nmr: δ 9.51 (C12), 27.67 (C11), 55.74 (C13), 82.13 (C10), 130.43, 130.87 (C2, C4), 131.60, 131.74 (C6, C8), 137.79, 137.96 (C7, C9), 142.66 (C5), 152.50 (C3), 193.94 (C1) ppm.

12-METHOXY-2E,4E,6E,8E,10E-TETRADECAPENTAENAL (2m).

Yield: 83.6 mg, 0.36 mmol, (50%); reddish solid; eluent: (70% petroleum ether/20% ether/10% triethylamine).

uv: λ_{max} (EtOH) 376 nm. ε=53000 l mol⁻¹ cm⁻¹.

ms: m/z 233(3), 232(16), 203(4), 167(30), 149(100), 91(11), 57(39), 43(32), 41(29). Exact mass: 232.1466 (C₁₅H₂₆O₂ requires 232.1463).

¹H nmr: δ 0.89 (3H, t, J=7.6, CH₃), 1.58 (2H, dq, J=7.6 and 6.5, CH₂CH₃), 3.28 (3H, s, OCH₃), 3.54 (1H, dt, J=6.5(2x), CHOCH₃), 5.66 (1H, dd, J=15.1 and 6.5, CHCHOCH₃), 6.1-6.6 (7H, m, CHCHO, C4-H, C6-H, C10-H), 6.73 (1H, dd, J=10.8 and 14.6, C5-H), 7.14 (1H, dd, J=11.0 and 15.1, C3-H), 9.57 (1H, d, J=7.9, CHO) ppm.

¹³C nmr: δ 9.64 (C14), 28.33 (C13), 56.39 (C15), 83.31 (C12), 129.91, 131.02, 131.75, 132.07, 135.60, 136.83(2x), 138.50, (C2, C4, C6-C11), 142.47 (C5), 151.52 (C3), 193.27 (C1) ppm.

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