Ethylaluminium Dichloride Induced Reactions of Acetals with Unsaturated Carboxylic Esters: Synthesis of Homoallyl Ethers

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The ethylaluminium dichloride induced reactions of methyl 10-undecenoate (**1**) with dimethyl acetals of formaldehyde **2a**, acetaldehyde **2b**, isobutyraldehyde **2c**, and pivaldehyde **2d** gave the corresponding homoallyl ethers **3a**, **3b**, **3c**, and **3d** in yields of 48–70%. The products were obtained as mixtures of the (*E*) and (*Z*) stereoisomers. With formaldehyde dimethyl acetal (**2a**), methyl oleate (**6**), and methyl petroselinate (**11**) gave the corresponding regioisomeric (*E*)-configured homoallyl ethers **7/8** and **12/13**.

Reactions of acetals with alkenes induced by Lewis acids, e.g. $TiCl_4$, $BF_3 \cdot OEt_2$ or $FeCl_3$, leading to the formation of a new carbon-carbon bond have been studied extensively[1]. Especially reactions of acetals with olefins with an activated double bond such as allylsilanes[2,3] and vinyl ethers[4,5], yielding homoallyl ethers and 1,1,3-trialkoxyalkanes, respectively, are well-known. The condensation of acetals with allylsilanes in liquid sulfur dioxide should also be an interesting method to synthesize homoallyl ethers[6]. Snider and Burbaum[7] reported on alkylaluminium halide-induced reactions of chiral acetals with alkenes to give chlorine-containing ethers and/or homoallyl ethers in yields of up to 60%. These reactions proceed, however, only with the most reactive acetals and alkenes. All attempts to extend the alkylaluminium halide-induced reaction to acetals of aliphatic aldehydes such as acetaldehyde and nonanal were unsuccessful leading to the recovery of the starting acetal. The condensation of peracetylated glycals with a wide spectrum of olefins was carried out in the presence of different Lewis acids, e.g. ethylaluminium dichloride ($EtAlCl_2$), to give C-glycosides in good to excellent yields[8]. However, there are only few examples of reactions of nonactivated alkenes with acetals in the presence of boron trifluoride[9,10]. Moreover, results on the Lewis acid-induced addition of acetals to 1-alkenes and 1,2-dialkyl-substituted ethenes are very limited[10].

Unsaturated fatty acids such as oleic acid, petroselenic acid and 10-undecenoic acid are of interest as renewable raw materials[11]. We could show that Lewis acid-induced additions to unsaturated fatty acids gave new products with interesting properties[12–14]. For example, the alkylaluminium chloride induced ene addition of formaldehyde to unsaturated fatty acids, esters and the respective alcohols gave the corresponding homoallyl alcohols in good yields[12]. We were interested now in the synthesis of homoallyl ethers by reactions of the methyl esters of the unsaturated fatty acids **1**, **6**, and **11** with acetals in the presence of alkylaluminium halides. We could show that dimethyl acetals of aliphatic aldehydes **2** can be added to 1-alkene **1** and to the 1,2-dialkyl substituted double bonds of **6** and **11** in good to moderate yields.

Results and Discussion

The reaction of methyl 10-undecenoate (**1**) with dimethyl acetals **2a–2d** in the presence of $EtAlCl_2$ in a molar ratio of 1:1:2 gave after a reaction time of 24 h the corresponding homoallyl ethers **3a**, **3b**, **3c**, and **3d**. A mixture of CH_2Cl_2 and hexane was used as solvent. The products were obtained as mixtures of the (*E*) and (*Z*) stereoisomers. **3a** and **3b** were isolated by "kugelrohr" distillation in yields of 69% and 51%. The ratio of the (*E*) and (*Z*) stereoisomers was 4:1 (**3a**) and 6:1 (**3b**). As minor products the corresponding diethers **4a** and **4b** (3–10%, GC) and β-chloro ethers **5a** and **5b** (10–14%, GC) were obtained (Table 1). In a modified procedure the addition of acetal **2a** to **1** could be carried out without CH_2Cl_2 as cosolvent. After a reaction time of 3 h **3a** was isolated in 74% yield.

The homoallyl ethers **3c** and **3d** were obtained in yields of 66% and 48%. The ratios of the stereoisomers were [(*E*)]:[(*Z*)] = 7:1 (**3c**) and [(*E*)]:[(*Z*)] = 7.5:1 (**3d**). Diethers **4c** and **4d** and β-chloro ethers **5c** and **5d** were detected only in small amounts of about 5%. In addition, the corresponding saturated ethers (5–7%, GC) were observed.

Reactions of dimethyl acetals were also carried out with 1,2-disubstituted double bonds of methyl oleate (**6**) and methyl petroselinate (**11**). The $EtAlCl_2$-induced reaction of **6** with acetal **2a** (**6**:**2a**:$EtAlCl_2$, 1:1:2) gave the correspoding regioisomeric homoallyl ethers **7** and **8**. The ratio of **7** to **8**, obtained as pure (*E*) adducts, was approximately 1:1. The stereochemistry was identified by comparison of the

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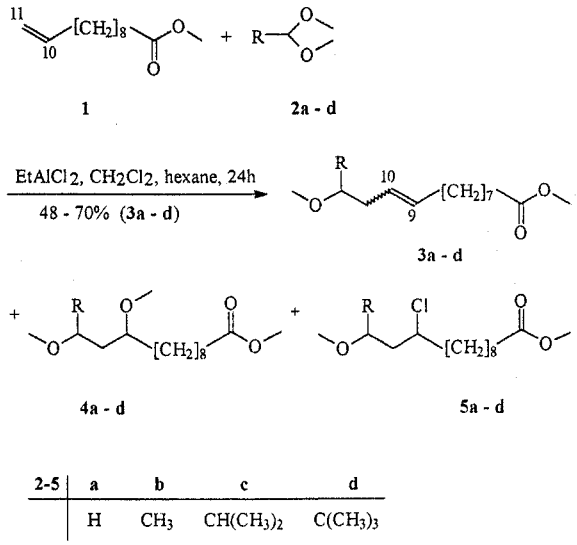
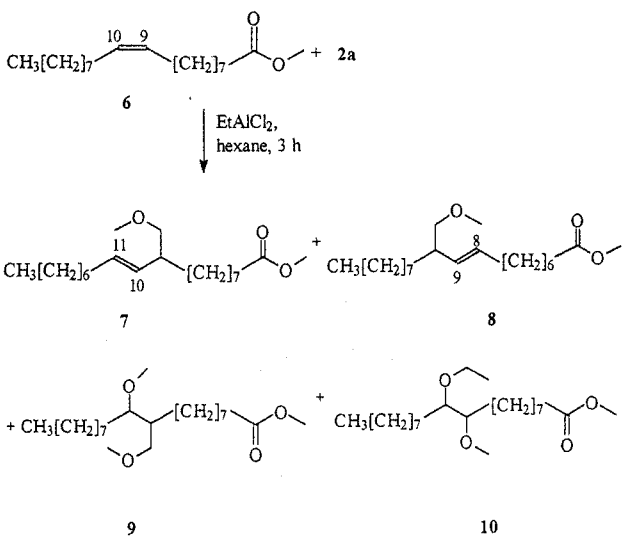


vicinal coupling constants of the olefinic protons in the ^{1}H-NMR spectrum with those reported recently for the homoallyl alcohols obtained by the $EtAlCl_2$-induced reaction of methyl oleate with formaldehyde[12]. (*Z*) Stereoisomers were detected neither in the ^{1}H-NMR nor in the ^{13}C-NMR spectra. The reaction of **11** with **2a** gave a regioisomeric mixture of the (*E*)-configured homoallyl ethers **12** and **13** in a ratio of 1:1.8. Separation of the regioisomers **7/8** and **12/13**, respectively, was not possible. They are distinguishable by their ^{1}H-NMR and ^{13}C-NMR spectra but they could not be assigned unambiguously. **7/8** and **12/13** were obtained after a reaction time of 3 h in yields of 53% (GC) and 57% (GC). As minor products only the corresponding diethers **9/10** and **14/15** were obtained. Chlorine-containing addition products were not formed (Table 1). "Kugelrohr" distillation gave the homoallyl ethers **7/8** and **12/13** in yields of 28% and 30% with 70% purity (GC).



The $EtAlCl_2$-induced reaction of **1** with isobutyraldehyde diethyl acetal (**16**) gave the expected homoallyl ether **17** in 36% (GC) yield only and the additional products **18** and **20**

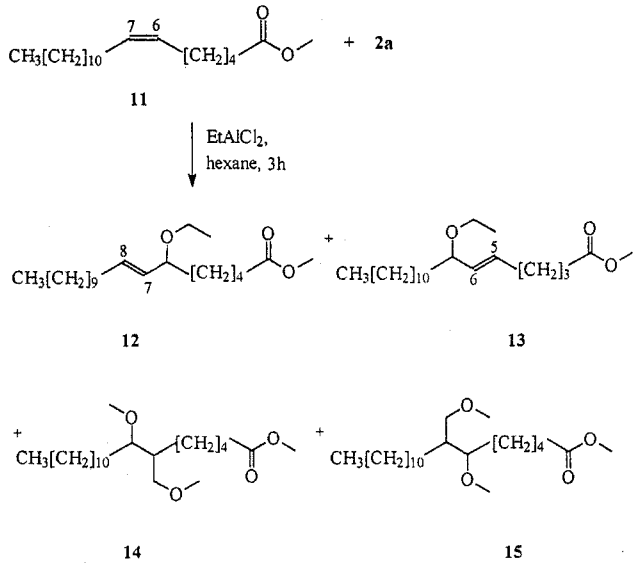


Table 1. $EtAlCl_2$-induced reactions of unsaturated fatty esters with acetals

Alkene	Acetal	Products (yield %, GC) Homoallyl ether	Diether	ß-Chloro ether
1	**2a**	**3a** (75)	**4a** (6)	**5a** (12)
1	**2b**	**3b** (69)	**4b** (13)	**5b** (4)
1	**2c**	**3c** (72)	**4c**[a]	**5c**[a]
1	**2d**	**3d** (54)	**4d**[a]	**5d**[a]
6	**2a**	**7/8** (53)	**9/10** (16)	-
11	**2a**	**12/13** (57)	**14/15** (22)	-

[a] **4c**, **5c**, **4d**, and **5d** were formed only in traces.

compared to the corresponding reaction of **1** with dimethyl acetal **2c**. The formation of product **18**, (38%, GC), can be explained by an intramolecular hydride shift in the intermediate **21** followed by ethylation of the new carbocation **22** to give the saturated ether **18**. The latter was isolated by column chromatography in a yield of 17% and obtained as a mixture of diastereomers (1:1.5, GC). The diastereomers are distinguishable by their ^{1}H- and ^{13}C-NMR spectra but they were not separated. Column chromatography gave the ketone **20** in 7% yield.

Our results show that homoallyl ethers can be synthesized in good to moderate yields by reactions of dimethyl acetals of aliphatic aldehydes with nonactivated alkenes such as methyl 10-undecenoate (**1**), methyl oleate (**6**), and methyl petroselinate (**11**). The selective formation of the homoallyl ethers can be explained by 1,5-proton shift to the ether oxygen atom in the intermediate carbeniumion[15]. The reactions have to be carried out in the presence of $EtAlCl_2$. Milder alkylaluminium halides such as Me_2AlCl do not induce reactions of nonactivated acetals with alkenes. These results are in agreement with the observations of Snider and Burbaum[7] who described Me_2AlCl-induced reactions only with the most reactive acetals and alkenes.

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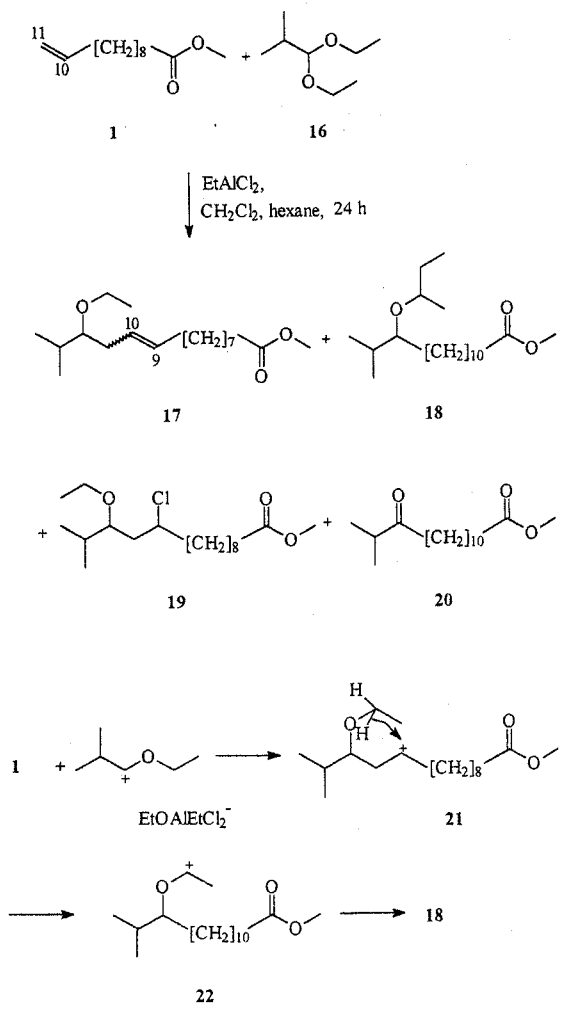

work (Förderkennzeichen 93NR066-F). Furthermore, we thank *Henkel KGaA, Witco GmbH* and *Atochem* for providing chemicals.

Experimental

Refractive indices n_D: Zeiss-Abbé-Refraktometer. – Elemental analysis: Fisons Instruments FA 1108 (**3a**), Fa. Beller, Göttingen (**3b**, **3c**, **3d**, **18**). – ^1H and ^{13}C NMR: Bruker AMX R 500 (**3a**, **3b**) and Bruker AM 300 (**3c**, **3d**, **7/8**, **12/13**, **18**, **20**), TMS as internal standard, selected data are given. Full ^1H- and ^{13}C-NMR data are available from the authors on request. The signals of the regioisomers of **7/8** and **12/13** and the diastereomers of **18** are distinguishable in the ^1H- and ^{13}C-NMR spectra but they could not be assigned unambiguously to the respective products. – Analytical GC: Carlo Erba GC Series 4160 with a FID (DB1-column, 29 m). – Mass spectra: Finnegan MAT 212 mass spectrometer. – Methyl 10-undecenoate, Atochem. Methyl oleate (new sun flower, 82.8% methyl oleate, 3.6% methyl stearate, 3.5% methyl palmitate, 8.4% $C_{18:2}$) and petroselinic acid (81.3% petroselinic acid, 3.3% palmitic acid, 0.4% stearic acid, 13.5% $C_{18:2}$) were obtained from Henkel KGaA. Methyl petroselinate was prepared in the usual manner. The amounts of the starting olefins used in the reactions were calculated based on 100% purity. Formaldehyde dimethyl acetal and acetaldehyde dimethyl acetal (Aldrich) were used without further purification. Isobutyraldehyde dimethyl acetal, pivaldehyde dimethyl acetal, and isobutyraldehyde diethyl acetal were prepared in the usual manner[16]. The acetals were purified by distillation. $EtAlCl_2$ and Me_2AlCl were obtained from Witco GmbH and used without further purification. – All reactions were run under N_2.

Reaction of Methyl Esters of Unsaturated Fatty Acids with Dialkyl Acetals. – General Procedure: A mixture of methyl 10-undecenoate (**1**, 5 mmol) and acetal **2a–d** (5 mmol) in CH_2Cl_2 (3 ml) was stirred magnetically under nitrogen (1 bar) for 5 min at −78 °C. After dropwise addition of $EtAlCl_2$ (1 M in hexane, 10 ml, 10 mmol) the mixture was stirred for additional 4 h at −78 °C and then for 20 h at room temp. The reaction was quenched by addition of Et_2O (100 ml) and H_2O (40 ml). 10% HCl was added until the precipitated aluminium salts had dissolved. The organic layer was separated and washed with H_2O (3 × 30 ml). The organic layer was dried (Na_2SO_4) and the solvent evaporated. The homoallylic ethers were purified by "kugelrohr" distillation (1.5×10^{-2} mbar, 90–100 °C for **3a** and **3b**, 125 °C for **3c** and **3d**). The minor products **4** and **5** were identified by GC MS.

Modified Reaction Conditions for Reactions of Methyl Esters of Unsaturated Fatty Acids **1**, **6**, *and* **11** *with Formaldehyde Dimethyl Acetal* (**2a**): A mixture of the appropriate methyl esters of the unsaturated fatty acids **1** (2.5 mmol), **6**, or **11** (2.1 mmol) and the acetal **2a** (2.5 mmol) was stirred magnetically under nitrogen (1 bar) for 5 min at −15 °C. Then $EtAlCl_2$ (1 M in hexane, 7.5 ml, 7.5 mmol) was added dropwise and the sample was stirred for additional 3 h at room temp. The reaction was stopped as described above. The products were purified by "kugelrohr" distillation (1.5×10^{-2} bar, 180 °C). The minor products **9/10** were identified by GC-MS analysis.

Reaction of Methyl 10-Undecenoate (**1**) *with Isobutyraldehyde Diethyl Acetal* (**16**): A mixture of **1** (2.5 mmol) and the acetal **16** (6 mmol) in CH_2Cl_2 (3 ml) was stirred magnetically under nitrogen (1 bar) for 5 min at −78 °C. After dropwise addition of $EtAlCl_2$ (1 M in hexane, 7.5 ml, 7.5 mmol) the mixture was stirred for additional 4 h at −78 °C and then for 20 h at room temp. The reaction was stopped as described above. GC-MS analysis showed a mixture of 36% of **17**, 38% of **18**, 12% of **19**, and 7% of **20**. The products **18** and **20** were isolated by column chromatography: 28 cm × 2 cm, silica gel 60 (Merck, 70–230 mesh), eluent petroleum ether/diethyl ether (9:1, 150 ml, and 8:2, 150 ml). Fractions containing **18** and **20**, respectively, were collected, the solvent was evaporated and the residue dried at 20 °C/1.5×10^{-2} mbar.

Methyl 12-Methoxydodec-9-enoate (**3a**) [(*E*):(*Z*) = 3.9:1, GC]: Yield 0.83 g (69%), colourless liquid, $n_D^{18} = 1.4503$. – ^1H NMR ($CDCl_3$): δ = 5.45 (dt, *J* = 15.3, 6.7 Hz, 1H, 10-H), 5.35 (dt, *J* = 15.3, 7.0 Hz, 1H, 9-H), 3.63 (s, 3H, $COOCH_3$), 3.35 [t, *J* = 7.0 Hz, 2H, 12-H, (*E*)], 3.34 [t, *J* = 7.0 Hz, 2H, 12-H, (*Z*)], 3.31 [s, 3H, OCH_3, (*Z*)], 3.30 [s, 3H, OCH_3, (*E*)], 2.26 (t, *J* = 7.6 Hz, 2H, 2-H), 2.23 (dt, *J* = 6.4, 6.4 Hz, 2H, 11-H), 2.0 [dt, *J* = 7.0, 6.8 Hz, 2H, 8-H, (*Z*)], 1.95 [dt, *J* = 7.0, 6.8 Hz, 2H, 8-H, (*E*)]. – ^{13}C NMR ($CDCl_3$): δ = 174.2 (C=O), 132.5 [(C-10, (*E*)], 131.9 [C-10, (*Z*)], 126.2 [C-9, (*E*)], 125.4 [C-9, (*Z*)], 72.6 [C-12, (*E*)], 72.4 (C-12, (*Z*)], 58.4 (OCH_3), 51.3 ($COOCH_3$), 38.5 (C-11). – MS/CI (isobutane); *m/z* (%): 243 (100) [MH^+], 211 (28) [MH^+ – MeOH]. – $C_{14}H_{26}O_3$ (242.2): calcd. C 69.4, H 10.7; found C 69.5, H 10.8.

Methyl (±)-12-Methoxytridec-9-enoate (**3b**) [(*E*):(*Z*) = 6:1, ^{13}C NMR]: Yield 0.65 g (51%), colourless liquid, $n_D^{18} = 1.4501$. – ^1H NMR ($CDCl_3$): δ = 5.41 (dt, *J* = 15.3, 6.7 Hz, 1H, 10-H), 5.33 (dt, *J* = 15.3, 6.7 Hz, 1H, 9-H), 3.61 (s, 3H, $COOCH_3$), 3.27 (s, 3H, OCH_3), 3.25 (m, 1H, 12-H), 2.25 (t, *J* = 7.3 Hz, 2H, 2-H), 2.20 (m, 1H, 11-H), 2.04 (ddd, *J* = 14.0, 13.4, 6.7 Hz, 1H, 11-H'), 1.94 (dt, *J* = 7.0, 6.8 Hz, 2H, 8-H), 1.06 (d, *J* = 5.7 Hz, 3H, 13-H). – ^{13}C NMR ($CDCl_3$): δ = 174.1 (C=O), 132.9 [C-10, (*E*)], 131.7 [C-10, (*Z*)], 125.9 [C-9, (*E*)], 125.3 [C-9, (*Z*)], 76.8 (C-12),

55.9 (OCH_3), 51.3 ($COOCH_3$), 39.1 (C-11), 18.9 [C-13, (*Z*)], 18.7 [C-13, (*E*)]. – MS/CI (isobutane); *m/z* (%): 257 (100) [MH^+], 225 (90) [MH^+ – MeOH]. – $C_{15}H_{28}O_3$ (256.2): calcd. C 70.3, H 10.9; found C 70.3, H 10.9.

Methyl (±)-12-Methoxy-13-methyltetradec-9-enoate (**3c**) [(*E*):(*Z*) = 7:1, ^{13}C NMR]: Yield 0.47 g (66%), n_D^{18} = 1.4517. – ^1H NMR ($CDCl_3$): δ = 5.42 (m, 2H, 9-H, 10-H), 3.64 (s, 3H, $COOCH_3$), 3.63 (m, 1H, 12-H), 3.34 [s, 3H, OCH_3, (*Z*)], 3.33 [s, 3H, OCH_3, (*E*)], 2.87 (ddd, *J* = 11.6, 10.5, 6.1 Hz, 1H, 11-H′), 2.28 (t, *J* = 7.7 Hz, 2H, 2-H), 2.15 (m, 1H, 11-H′), 1.97 (m, 2H, 8-H), 1.78 (m, 1H, 13-H), 0.88 and 0.86 (2 × d, *J* = 6.6 Hz, 6H, 14-H and $CHCH_3$). – ^{13}C NMR ($CDCl_3$): δ = 174.2 (C=O), 132.3 [C-10, (*E*)], 131.2 [C-10, (*Z*)], 126.6 [C-9, (*E*)], 126.0 [C-9, (*Z*)], 86.3 (C-12), 57.6 (OCH_3), 51.3 ($COOCH_3$), 33.5 (C-11), 18.4 and 17.8 [C-14, (*E*) and $CHCH_3$, (*E*)], 18.1 and 17.9 [C-14, (*Z*) and $CHCH_3$, (*Z*)]. – MS/CI (isobutane); *m/z* (%): 285 (10) [MH^+], 253 (100) [MH^+ – MeOH]. – $C_{17}H_{32}O_3$ (284.2): calcd. C 71.8, H 11.3; found C 71.6, H 11.1.

Methyl (±)-12-Methoxy-13,13-dimethyltetradec-9-enoate (**3d**) [(*E*):(*Z*) = 7.5:1, ^{13}C NMR]: Yield 0.36 g (48%), colourless liquid, n_D^{19} = 1.4531. – ^1H NMR ($CDCl_3$): δ = 5.48 (m, 2H, 9-H, 10-H), 3.66 (s, 3H, $COOCH_3$), 3.65 (m, 1H, 12-H), 3.41 [s, 3H, OCH_3, (*Z*)], 3.40 [s, 3H, OCH_3, (*E*)], 2.71 (ddd, *J* = 8.8, 8.8, 3.3 Hz, 1H, 11-H), 2.29 (t, *J* = 7.7 Hz, 2H, 2-H), 2.08 (m, 1H, 11-H′), 1.99 (m, 2H, 8-H), 0.88 [s, 9H, $C(CH_3)_3$, (*E*)], 0.87 [s, 9H, $C(CH_3)_3$, (*Z*)]. – ^{13}C NMR ($CDCl_3$): δ = 174.2 (C=O), 131.8 [C-10, (*E*)], 130.6 [C-10, (*Z*)], 128.5 [C-9, (*E*)], 127.9 [C-9, (*Z*)], 90.6 (C-12), 60.6 (OCH_3), 51.4 ($COOCH_3$), 35.8 (C-13), 34.3 (C-11), 26.2 [C-14, $C(CH_3)_2$]. – MS/CI (isobutane); *m/z* (%): 299 (50) [MH^+], 267 (100) [MH^+ – MeOH]. – $C_{18}H_{34}O_3$ (298.2): calcd. C 72.5, H 11.4; found C 72.4, H 11.4.

Methyl (E)-(±)-9-(Methoxymethyl)octadec-10-enoate (**7**) *and Methyl (E)-(±)-10-(methoxymethyl)octadec-8-enoate* (**8**, 1:1 mixture): Yield 0.24 g (28%), purity: 70% (GC). – ^1H NMR ($CDCl_3$): δ = 5.44 and 5.43 (dt, *J* = 15.4, 6.6 Hz, 1H, 8-H and 11-H), 5.18 [ddd, *J* = 15.4, 7.2, 1.1 Hz, 1H, 9(10)-H], 3.66 (s, 3H, $COOCH_3$), 3.30 (s, 3H, CH_2OCH_3), 3.25 (d, *J* = 6.6 Hz, 2H, CH_2OCH_3), 2.31 and 2.30 (t, *J* = 7.7 Hz, 2H, 2-H, **7** and **8**), 2.21 [m, 1H, 9(10)-H], 2.0 [dt, *J* = 6.6, 6.6 Hz, 2H, 12(7)-H]. – ^{13}C NMR ($CDCl_3$): 174.2 (C=O), 131.8, 131.7, 131.4 (C=C, **7** and **8**), 77.1 (CH_2OCH_3), 58.7 (OCH_3), 51.4 ($COOCH_3$), 42.9 [C-9 (10)]. – MS/CI (isobutane); *m/z* (%): 341 (62) [MH^+], 309 (100) [MH^+ – MeOH].

Methyl (E)-(±)-6-(Methoxymethyl)octadec-7-enoate (**12**) *and Methyl (E)-(±)-7-(Methoxymethyl)octadec-5-enoate* (**13**, 1:1.8 mixture): Yield 0.25 g (30%), purity: 73% (GC). – ^1H NMR ($CDCl_3$): δ = 5.44 [dt, *J* = 15.4, 6.6 Hz, 1H, 8(5)-H], 5.19 [dd, *J* = 15.4, 8.8 Hz, 1H, 7(6)-H], 3.65 and 3.64 (s, 3H, $COOCH_3$, **12** and **13**), 3.30 (s, 3H, OCH_3), 3.24 and 3.23 (d, *J* = 6.6 Hz, 2H, CH_2OCH_3, **12** and **13**), 2.29 and 2.28 (t, *J* = 7.7 Hz, 2H, 2-H, **12** and **13**), 2.21 [m, 1H, 8(7)-H], 2.05 and 1.97 [dt, *J* = 6.6, 6.9 Hz, 2H, 2(4)-H]. – ^{13}C NMR ($CDCl_3$): δ = 174.1 (C=O), 132.9, 132.0, 131.1, 130.1 (C=C, **12** and **13**), 77.0 (CH_2OCH_3), 58.7 (OCH_3), 51.3 ($COOCH_3$), 42.9, 42.7 [C-6(7)]. – GC MS/CI (isobutane); *m/z* (%): 341 (100) [MH^+], 309 (44).

Methyl (±)-12-(2-Butoxy)-13-methyltetradecanoate (**18**, 1:1.5 mixture of diastereomers, ^{13}C NMR): Yield 0.14 g (17%), colourless liquid, n_D^{23} = 1.4469. – ^1H NMR ($CDCl_3$): δ = 3.63 (s, 3H, $COOCH_3$), 3.30 (ddd, *J* = 6.1, 6.1, 3.3 Hz, 1H, 12-H), 3.02 [m, 1H, $OCH(CH_2CH_3)CH_3$], 2.30 (t, *J* = 7.7 Hz, 2H, 2-H), 1.78 (m, 1H, 13-H), 1.06 [d, *J* = 6.6 Hz, 3H, $CH(CH_2CH_3)CH_3$], 0.85 [m, 9H, 14-H, $CHCH_3$, $CH(CH_2CH_3)CH_3$]. – ^{13}C NMR ($CDCl_3$): δ = 174.1 (C=O), 81.8 and 81.7 (C-12), 75.0 and 74.5 [$OCH(CH_2CH_3)CH_3$], 51.3 (OCH_3), 30.6 (C-13), 20.0, 19.9, 18.6 and 18.4 [$CH(CH_3)_2$], 18.0 and 17.4 [$CH(CH_2CH_3)CH_3$], 10.3 and 10.0 [$CH(CH_2CH_3)CH_3$]. – MS/CI (isobutane); *m/z* (%): 329 (33) [MH^+], 225 (100) [MH^+ – $C_2H_5CH(OH)CH_3$]. – $C_{20}H_{40}O_3$ (328.2): calcd. C 73.2, H 12.2; found C 73.2, H 12.1.

Methyl (±)-13-Methyl-12-oxotetradecanoate (**20**): Yield 0.05 g (7%), colourless liquid, n_D^{19} = 1.4475. – **20** was identified by ^1H NMR, ^{13}C NMR, and MS.

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