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ARTICLE *in* FETT/LIPID · JANUARY 1998

DOI: 10.1002/lipi.200690051

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Lewis acid induced additions to unsaturated fatty compounds[1] IV: Synthesis of cyclopentenones from *Friedel-Crafts* acylation products of unsaturated fatty compounds with α,β-unsaturated acyl chlorides*

* Dedicated to Professor Carl Heinz Hamann on the occasion of his 60th birthday

Jürgen O. Metzger and Ursula Biermann[2]

The ethylaluminium dichloride induced *Friedel-Crafts* acylation of unsaturated fatty compounds such as oleic acid (**1a**), methyl oleate (**1b**) and 10-undecenoic acid (**9b**) and furthermore of 1-octene (**9a**) with α,β-unsaturated acyl chlorides e.g. crotonic acid chloride (**2a**) and acrylic acid chloride (**2b**) gave the corresponding allyl vinyl ketones. *Nazarov* cyclizations of the acylation products **3a/4a, 3b/4b, 10a** and **10b** afforded the alkyl substituted 2-cyclopentenones **5a/6a, 5b/6b, 11a/12a** and **11b/12b.** Catalytic hydrogenation of **5b/6b** and **11b/12b** gave the respective saturated cyclic products **7b/8b** and **13b/14b** as diastereomeric mixtures.

Lewis-Säure induzierte Additionen an ungesättigte Fettstoffe IV: Synthese von Cyclopentenonen aus *Friedel-Crafts*-Acylierungsprodukten ungesättigter Fettstoffe mit α,β-ungesättigten Acylchloriden. Ethylaluminiumdichlorid induzierte *Friedel-Crafts*-Acylierungen ungesättigter Fettstoffe, wie Ölsäure (**1a**), Ölsäuremethylester (**1b**) und 10-Undecensäure (**9b**) mit α,β-ungesättigten Acylchloriden, wie z.B. Crotonsäurechlorid (**2a**) und Acrylsäurechlorid (**2b**), ergaben die entsprechenden Allylvinylketone. Des weiteren wurden die Acylierungen auch mit 1-Octen (**9a**) durchgeführt. Mittels *Nazarov*-Cyclisierungen wurden die Acylierungsprodukte **3a/4a, 3b/4b, 10a** und **10b** in die alkylsubstituierten 2-Cyclopentenone **5a/6a, 5b/6b, 11a/12a** und **11b/12b** übergeführt. Katalytische Hydrierung von **5b/6b** und **11b/12b** ergab die gesättigten Produkte **7b/8b** und **13b/14b** als Diastereomerengemische.

1 Introduction

Friedel-Crafts acylations of alkenes induced by *Lewis* acids as $AlCl_3$, $SnCl_4$ or $ZnCl_2$ are well known [1–4]. β,γ-Unsaturated ketones are obtained as main products especially in acylations of cyclic and aliphatic alkenes in the presence of ethylaluminium dichloride ($EtAlCl_2$) [5]. We described recently acylations of unsaturated carboxylic acids and alcohols such as oleic acid, 10-undecenoic acid and oleyl alcohol [6] which are of interest as renewable raw materials [7]. The reactions, carried out with saturated acyl chlorides and cyclic anhydrides induced by $EtAlCl_2$, gave the corresponding β,γ-unsaturated ketones with ω-carboxy and ω-hydroxy functionality, respectively. We now report on the acylations of unsaturated fatty compounds with unsaturated acyl chlorides e.g. acrylic acid chloride or crotonic acid chloride to give the corresponding allyl vinyl ketones and their cyclizations in a *Nazarov* reaction to give 2-cyclopentenone derivatives which are useful intermediates in the synthesis of prostaglandins [8, 9] and jasmonic acid derivatives such as methyl dihydrojasmonate, an important fragrant compound [10]. Jasmonic acid itself is a widespread intracellular signal substance in plants that stimulates the synthesis of special proteins and induces defensive reactions of plants [11]. 2-(6-Methoxycarbonylhexyl)-2-cyclopentenone, synthesized in four steps starting from methyl 10-undecenoate in an isolated yield of 35%, is known as a useful prostanoid synthon [9].

The *Nazarov* reaction is the acid induced cyclization of a wide variety of allyl vinyl and divinyl ketones and is known as an efficient route to 2-cyclopentenones [12–14]. The synthesis of cyclopentenones via acylation of alkenes with α,β-unsaturated acids in the presence of polyphosphoric acid or with unsaturated acid halides is described as a one-pot procedure [15, 16]. However, these reactions are restricted to bicyclic products. Simple cyclopentenones are obtained in $AlCl_3$-induced acylations of *in situ* generated branched alkenes with α,β-unsaturated acyl chlorides followed by cyclizations of the intermediate divinyl ketones [17].

2 Results and Discussion

Acylations of oleic acid (**1a**) with crotonic acid chloride (**2a**) and of methyl oleate (**1b**) with acrylic acid chloride (**2b**) induced by $EtAlCl_2$ gave the corresponding allyl vinyl ketones **3a/4a** and **3b/4b,** respectively (Fig. 1). The 9- and 10-regioisomers were obtained in approximately equal amounts as pure (*E*)-adducts. The stereochemistry of the double bond in the molecule chain of the fatty acid was identified as the (*E*)-configuration by comparison of their ^{13}C NMR data with those reported in the literature [6] and their coupling constants of the olefinic protons in the ^1H NMR spectra. (*Z*)-isomers were detected neither in the ^1H NMR nor in the ^{13}C NMR spectra. The regioisomers **3a/4a** and **3b/4b,** respectively, could not be separated. They were distinguishable by their ^1H NMR and ^{13}C NMR spectra but they could not be assigned unambiguously to the respective products. The isolated yields were 59% for **3a/4a** after a reaction time of 2 h and 25% for

[1] III. Communication: Fat Sci. Technol. **94** (1992), 329.
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  0931-5985/98/0101-0002$17.50+.50/0

3b/4b after a reaction time of 15 min. Acylations with acrylic-acid chloride (**2b**) carried out with longer reaction times than 15 min gave polymerization products.

The cyclizations of the acylation products were carried out by the typical procedure used for many *Nazarov* reactions. The allyl vinyl ketones were heated for 3 h in a mixture of phosphoric acid and formic acid (3:1) at 90°C [18]. The crude acylation products **3a/4a** and **3b/4b** gave the respective 2-cyclopentenones **5a/6a** and **5b/6b** in isolated yields of 58% and 24%, respectively, based on charged oleic acid and methyl oleate, respectively. That means, that the yields of the *Nazarov* cyclizations were almost quantitative.

Furthermore, the cyclizations of **3a/4a** and **3b/4b** were carried out in a modified procedure. The crude acylation products were heated in chloroform for 24 h at 60°C in the presence of montmorillonite K10 to give the expected cyclic products in yields comparable to those obtained by the normally used method with phosphoric acid and formic acid.

Preliminary results have been obtained with cyclizations carried out under thermal conditions (190°C, 24 h) without using any solvent to give the expected *Nazarov* products.

Catalytic hydrogenation of **5b/6b** with Pd/C in CH_2Cl_2 at 2 bar gave the saturated cyclopentanone derivatives **7b/8b** in quantitative yield as a mixture of diastereomers in a ratio of [*cis*-**7b/8b**] : [*trans*-**7b/8b**] = 2.5 : 1 (Fig. 1).

The $EtAlCl_2$-induced acylations of 1-octene (**9a**) and 10-undecenoic acid (**9b**) with crotonic acid chloride (**2a**) gave after a reaction time of 2 h the corresponding allyl vinyl ketones **10a** and **10b** (Fig. 2). The products were obtained after column chromatography as (*E*)/(*Z*) mixtures (2 : 1 for **10a** and 3 : 1 for **10b**, ^{13}C NMR) in isolated yields of 28% and 60%. The alkylaluminium chloride induced acylation took place regioselectively at the terminal carbon atom.

Cyclization of **10a** and **10b** was carried out by heating the allyl vinyl ketone for 3 h at 90°C in a mixture of phosphoric acid and formic acid (3 : 1). The reaction did not afford the expected *Nazarov* cyclization products, the corresponding 3,4-dialkyl substituted 2-cyclopentenones, but gave the regioisomeric 2,3-dialkyl substituted 2-cyclopentenone derivatives **11a/12a** and **11b/12b**, respectively. Obviously, these are products of an abnormal *Nazarov* reaction as described in literature [18].

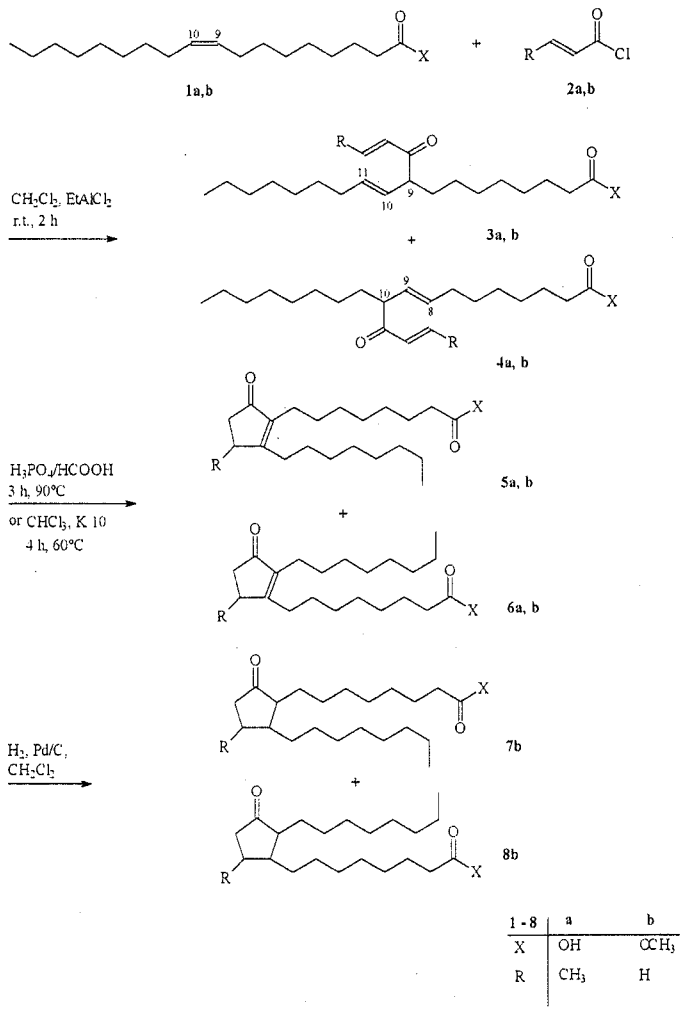
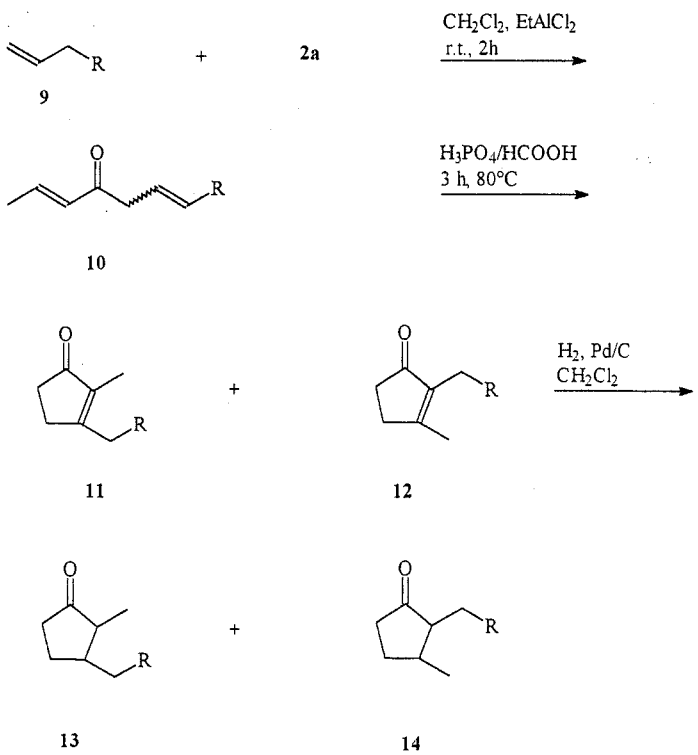


Fig. 1. $EtAlCl_2$-induced *Friedel-Crafts* acylation of oleic acid (**1a**) and methyl oleate (**1b**) with α,β-unsaturated acyl chlorides **2a** and **2b** followed by *Nazarov* cyclization of the obtained allyl vinyl ketones **3a/4a** and **3b/4b** to give alkyl substituted cyclopentenones **5a/6a** and **5b/6b.** Catalytic hydrogenation of **5b/6b** affords the saturated cyclopentanone derivatives **7b/8b.**



9 - 14	a	b
R	$(CH_2)_4CH_3$	$(CH_2)_7COOH$

Fig. 2. $EtAlCl_2$-induced *Friedel-Crafts* acylation of 1-octene (**9a**) and 10-undecenoic acid (**9b**) with crotonic acid chloride **2a** followed by *Nazarov* cyclization of the obtained allyl vinyl ketones **10a** and **10b** to give 2,3-dialkyl substituted cyclopentenones **11a/12a** and **11b/12b.** Catalytic hydrogenation of **11b/12b** affords the saturated cyclopentanone derivatives **13b/14b.**

Regioisomers **11a** and **12a** could be separated by preparative HPLC. So ^1H NMR and ^{13}C NMR data could be obtained of each regioisomer. In contrast, **11b** and **12b** could not be separated completely by HPLC.

Catalytic hydrogenation of **11b/12b** gave quantitatively the saturated product **13b/14b** as a diastereomeric mixture. The isomers were not separated but they could be assigned by their ^{13}C NMR data. The ratio of [*cis*] : [*trans*] was 5 : 1 for **13b** and 2 : 1 for **14b** (Fig. 2).

Allyl vinyl ketones obtained by $EtAlCl_2$-induced acylations of alkenes with α,β-unsaturated acyl chlorides are suitable substrates for the *Nazarov* reaction to give 2-cyclopentenones. In this paper for the first time we describe the *Nazarov* cyclization carried out in the presence of montmorillonite K10. The alkyl substituted 2-cyclopentanones obtained from acylation products of unsaturated fatty compounds and α,β-unsaturated acyl chlorides in two steps should be of interest because of their structural similarity to prostaglandins [8, 9] and jasmonic acid derivatives [10, 11].

3 Experimental

Refractive indices n_D: Zeiss-Abbé-Refraktometer. Elemental analysis: Fa. *Beller,* Göttingen. ^1H and ^{13}C NMR: *Bruker* AMX R 500 (**3b/4b, 5a/6a, 7b/8b, 10a, 11a/12a**) and *Bruker* AM 300 (**3a/4a, 10b, 11b/12b, 13b/14b**), 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 **3a/4a, 3b/4b** and **5a/6a** 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, 20 m). Mass spectra: *Finnigan* MAT 212 mass spectrometer. HPLC analysis: *Merck Hitachi* L 6250, LiChrosorb RP 18 (7 μm). 10-Undecenoic acid (*Atochem*). Oleic acid (new sunflower, 82% oleic acid, 3.5% palmitic acid, 0.6% stearic acid, 12% $C_{18:2}$), and methyl oleate (new sunflower, 82.8% methyl oleate, 3.6% methyl stearate, 3.5% methyl palmitate, 8.4% $C_{18:2}$) were obtained from *Henkel* KGaA. The amounts of the starting olefins used in the reactions were calculated based on 100% purity. Montmorillonite K10 was obtained from *Südchemie.* 1-Octene (*Merck*), acryloyl chloride (*Aldrich*) and crotonoyl chloride (*Aldrich*) were used after distillation. $EtAlCl_2$ (*Witco* GmbH) was used without further purification. All acylation reactions were run under N_2.

Acylation of alkenes with α,β-unsaturated acid chlorides – General procedure: A mixture of the alkene (1 equiv.) and the acylating agent (1 equiv.) in CH_2Cl_2 (10 ml) was stirred magnetically under nitrogen (1 bar) for 5 min at –15°C. After dropwise addition of $EtAlCl_2$ (1 M in hexane, 2 equiv.) the sample was stirred for additional 15 min or 2 h, depending on the used acylating agent, at room temp. The reaction was quenched by the 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 obtained crude product was used as substrate for the cyclization reaction. For characterization the product was purified by column chromatography [28 cm × 2 cm, silica gel 60 (*Merck*), 70–230 mesh] with the eluent petro-

leum ether/diethyl ether. Fractions containing the acylation product were collected, the solvent was evaporated and the residue dried at 20°C/0.01 mbar.

Cyclization of allyl vinyl ketones obtained by acylation of alkenes with α,β-unsaturated acid chlorides – General procedure:

- Method A (cyclization with phosphoric acid/formic acid): The acylation product (4 mmol crude product obtained by acylation reactions described above) was added to a mixture of 20 g of phosphoric acid (85%) and 7 g of formic acid and heated to 90°C. After being stirred for 3 h the reaction mixture was diluted with water and then extracted with diethyl ether. The organic extracts were washed with sodium bicarbonate solution, dried over Na_2SO_4, filtrated and then concentrated. The cyclization products were purified by HPLC with the eluent methanol/water (93 : 7) or by column chromatography [28 cm × 2 cm, silica gel 60 (*Merck*), 70–230 mesh] with the eluent petroleum ether /EtOAc. Fractions containing the cyclization product were collected, the solvent was evaporated and the residue dried at 20°C/0.01 mbar.
- Method B (cyclization with montmorillonite K10): The acylation product (4 mmol crude product obtained by acylation reactions described above) was refluxed for 24 h in $CHCl_3$ (5 ml) containing montmorillonite K 10 (3 g). After cooling diethyl ether (20 ml) was added and the sample was stirred for 1 h. The mixture was filtered and K 10 was washed with diethyl ether. The solvent was evaporated. The cyclization product was purified by column chromatography as described for method A.

*Rac-9-(1-oxobut-(E)-2-enyl)octadec-(E)-10-enoic acid (**3a**) and rac-10-(1-oxobut-(E)-2-enyl)octadec-(E)-8-enoic acid (**4a**) (1 : 1 mixture):* Acylation of oleic acid (**1b**, 4.2 mmol) with crotonoyl chloride (**2a**, 5 mmol) in CH_2Cl_2 (10 ml) in the presence of $EtAlCl_2$ (10 ml, 10 mmol) was carried out by stirring the mixture for 2 h at room temp. Column chromatography [petroleum ether : diethyl ether = 9 : 1 (200 ml) and 6 : 4 (250 ml)] gave 0.87 g (59%) of **3a/4a**, colourless liquid, n_D^{17} = 1.4791. – ^{1}H NMR ($CDCl_3$) : δ = 6.90 (dq, J = 15.5, 6.8 Hz, 1H, (CH_3**CH** = C), 6.20 and 6.19 (2 × d, J = 15.5 Hz, 1H, (CO**CH** = **C**), 5.51 (m, 1H, CH_2-**CH** = CH), 5.31 and 5.30 (2 × dd, J = 15.3, 8.6 Hz, 1H, CH-CH = CH), 3.18 (dt, J = 7.5, 7.5 Hz, 1H, COCH), 1.90 (2 × d, J = 6.8 Hz, 3H, **C**H_3CH = CH). – ^{13}C NMR ($CDCl_3$): δ = 200.6 (C = O), 179.7 (COOH), 142.5 (CH_3**C**H = CH), 134.2, 133.8, 128.4, 128.4 (C = C), 130.4 (CH_3CH = **C**H), 54.3 (CO**C**H), 18.2 (**C**H_3CH = CH), 14.1 (**C**H_3CH_2). – MS (70 eV): m/z (%) = 350(0.7)[M^+], 264(0.8), 263(0.7), 221(2.0), 207(2.1), 69(100). – $C_{22}H_{38}O_3$: calcd. 350.2821, found 350.2827 (MS/EI).

*2-(7-Carboxyheptyl)-4-methyl-3-octyl-2-cyclopentenone (**5a**) and 3-(7-carboxy-heptyl)-4-methyl-2-octyl-2-cyclopentenone (**6a**) (1 : 1 mixture):* Cyclization of the crude mixture of **3a** and **4a** by method A and method B, respectively, gave similar results. Column chromatography [petroleum ether : EtOAc = 9 : 1 (150 ml) and 6 : 4 (250 ml)] yielded 0.86 g (58% based on charged **1a**) of **5a/6a**, colourless liquid, n_D^{14} = 1.4890. – ^{1}H NMR ($CDCl_3$) : δ = 2.56 (dd, J = 18.4, 6.4 Hz, 1H, 5-H), 2.45 (m, 1H, 4-H), 2.27 (m, 4H, **C**H_2COOH and $COCCH_2$), 2.09 (2 × t, J = 7.0, 7.0 Hz, 2H, C = C CH_2), 1.91 (dd, J = 18.4, 1.9 Hz, 1H, 5-H'), 1.12 (d, J = 7.0 Hz, 3H, CH**C**H_3). – ^{13}C NMR ($CDCl_3$): δ = 209.1 (C = O), 179.8 (COOH), 177.8 and 177.5 (C-3), 140.1 and 140.0 (C-2), 43.1 (C-5), 34.5 (C-4), 34.0 (**C**H_2-COOH), 19.2 (**C**H_3CH), 14.0 (**C**H_3CH_2). – MS (70 eV): m/z (%) = 350(5.0) [M^+], 332(4.8), 250(15.5), 219(40.0), 44(100). – $C_{22}H_{38}O_3$ (350.54): calcd. C 75.37, H 10.93; found C 75.39, H 10.84.

*Methyl rac-9-(1-oxopropenyl)octadec-(E)-10-enoate (**3b**) and methyl rac-10-(1-oxopropenyl)octadec-(E)-8-enoate (**4b**) (1 : 1 mixture):* Acylation of methyl oleate (**1b**, 4.2 mmol) with acryloyl chloride (**2b**, 5 mmol) in CH_2Cl_2 (10 ml) in the presence of $EtAlCl_2$ (10 ml, 10 mmol) was carried out by stirring the mixture for 15 min at room temp. Column chromatography [petroleum ether : diethyl ether = 9 : 1 (200 ml) and 8 : 2 (250 ml)] gave 0.37 g (25%) of **3b/4b**, colourless liquid, n_D^{19} = 1.4709. – ^{1}H NMR ($CDCl_3$): δ = 6.43 (dd, J = 17.8, 10.8 Hz, 1H, CH_2 = **CH**), 6.25 (dd, J = 17.8, 1.3 Hz, 1H, **H**CH = C), 5.70 (dd, J = 10.8, 1.3 Hz, 1H, HC**H** = C), 5.53 and 5.51 (dt, J = 15.3, 6.4 Hz, 1H, CH_2-**CH** = CH), 5.29 and 5.28 (dd, J = 15.3, 7.6 Hz, 1H, HC-**CH** = CH), 3.23 (m, 1H, COCH). – ^{13}C NMR ($CDCl_3$): δ = 200.9 (C = O), 174.2 (**C**$OOCH_3$), 135.1 (**C**H_2 = C), 134.7, 134.3 (C = C), 127.9 (CH_2 = **C**), 127.8, 127.6 (C = C), 54.1 (CO**C**H), 51.4 (OCH_3). – MS (70 eV): m/z (%) = 350(3)[M^+], 319(6), 263(16), 207(10), 193(18), 55(100). – $C_{22}H_{38}O_3$: calcd. 350.2821, found 350.2817 (MS/EI).

*2-(7-Methoxycarbonylheptyl)-3-octyl-2-cyclopentenone (**5b**) and 3-(7-methoxycarbonylheptyl)-2-octyl-2-cyclopentenone (**6b**) (1 : 1 mixture):* Cyclization of the crude mixture of **3b** and **4b** by method A and method B, respectively, gave similar results. Column chromatography [petroleum ether : EtOAc = 9 : 1 (150 ml) and 8 : 2 (250 ml)] yielded 0.35 g (24% based on charged **1b**) of **5b/6b**, colourless liquid, n_D^{19} = 1.4909. – ^{1}H NMR ($CDCl_3$): δ = 3.64 (s, 3H, OCH_3), 2.46 (m, 2H, H-5), 2.38 (t, J = 7.6 Hz, 2H, 4-H), 2.33 (m, 2H, $COCCH_2$), 2.28 (t, J = 7.4 Hz, 2H, **C**H_2COOCH_3), 2.13 (t, J = 7.6 Hz, 2H, COC = CCH_2). – ^{13}C NMR ($CDCl_3$): δ = 210.0 (C = O), 174.3 and 174.0 (**C**$OOCH_3$), 164.9 (C-3), 140.3 (C-2), 51.3 (OCH_3), 34.1 (C-5), 31.7 (C-4). – MS (70 eV): m/z (%) = 350(32)[M^+], 319(8), 221(93), 193(100), 123(26), 110(31). – $C_{22}H_{38}O_3$: calcd. 350.2821, found 350.2804 (MS/EI).

*2-(7-Methoxycarbonylheptyl)-3-octylcyclopentanone (**7b**) and 3-(7-Methoxycarbonylheptyl)-2-octylcyclopentanone (**8b**) (1 : 1 mixture):* Catalytic hydrogenation of **5b/6b** (1 : 1 mixture, 0.5 g) gave 0.5 g (98%) of **7b/8b**, colourless liquid, n_D^{19} = 1.4809. – ^{1}H NMR ($CDCl_3$): δ = 3.62 (s, 3H, OCH_3), 2.26 – 1.49 (m, 14H, 2-H, 3-H, 4-H, 5-H, COCH**C**H_2, COCHCH**C**H_2, **C**H_2COOCH_3, **C**$H_2CH_2COOCH_3$). – ^{13}C NMR ($CDCl_3$): δ = 221.4, 220.8 (C = O), 174.2 (**C**$OOCH_3$), 55.0 (C-2, *cis*-**7b, 8b**), 53.3 (C-2, *trans*-**7b, 8b**), 51.3 (OCH_3), 41.5 (C-3, *cis*-**7b, 8b**), 38.7 (C-3, *trans*-**7b, 8b**), 37.7 (C-5, cis-**7b, 8b**), 35.2 (C-5, *trans*-**7b, 8b**). – MS 70 eV): m/z (%) = 352(0.1)[M^+], 321(0.2), 240(2.0), 195(6.2), 83(100). – $C_{22}H_{40}O_3$: calcd. 352.2977, found 352.2953 (MS/EI).

*4-Oxo-2,6-dodecadien (**10a**) [(E) : (Z) = 2 : 1, ^{13}C NMR]:* Acylation of 1-octene (**9a**, 5 mmol) with crotonoyl chloride (**2a**, 5 mmol) in CH_2Cl_2 (10 ml) in the presence of $EtAlCl_2$ (5 ml, 5 mmol) was carried out by stirring the mixture for 2 h at room temp. Column chromatography [petroleum ether : diethyl ether = 9 : 1 (400 ml)] gave 0.25 g (27.7%) of **10a**, colourless liquid, n_n^{19} = 1.4732. – ^{1}H NMR ($CDCl_3$): δ = 6.84 and 6.81 (dq, J = 15.4, 6.6 Hz, 1H, 2-H), 6.09 (dq, J = 15.4, 1.7 Hz, 1H, 3-H), 5.51 (m, 2H, 6-H and 7-H), 3.17 (d, J = 4.4 Hz, 2H, 5-H), 1.98 (m, 2H, 8-H), 1.84 (dd, J = 7.2, 1.7 Hz, 3H, 1-H), 0.83 (t, J = 6.8 Hz, 3H, 12-H). – ^{13}C NMR ($CDCl_3$): δ = 198.3 (C = O), 142.7 [C-2, (*E*)], 142.0 [C-2, (*Z*)], 134.8 [C-7 (*E*)], 133.4 [C-7, (*Z*)], 131.9 [C-3, (*Z*)], 133.2 [C-3 (*E*)], 122.0 [C-6, (*E*)], 121.7 [C-6 (*Z*)], 44.1 (C-5), 32.4–28.5 (C-8, C-9, C-10), 22.4 (C-11), 18.0 (C-1),

13.9 (C-12). – MS (70 eV): m/z (%) = 180(4) [M^+], 165(3), 123(8), 110(18), 69(100). – $C_{12}H_{20}O$: calcd. 180.1514, found 180.1500 (MS/EI).

*3-Hexyl-2-methyl-2-cyclopentenone (**11a**) and 2-hexyl-3-methyl-2-cyclopentenone (**12a**) (1 : 1.5 mixture, GC):* Cyclization of the crude product **10a** by method A. HPLC gave 0.20 g (22% based on charged **9a**) of **11a/12a**, colourless liquid, n_D^{19} = 1.4742. **11a** and **12a** could be separated by HPLC (methanol-water = 93 : 7). ^{1}H NMR ($CDCl_3$) of **11a:** δ = 2.47 (m, 2H, 5-H), 2.39 (t, J = 7.9 Hz, 2H, $COC=CCH_2$), 2.35 (m, 2H, 4-H), 1.67 (s, 3H, $COCCH_3$). – ^{13}C NMR ($CDCl_3$): δ = 210.2 (C = O), 173.9 (C-3), 136.1 (C-2), 34.1 (C-5), 31.7 (C-4), 14.0 ($CH_2\mathbf{C}H_3$), 8.0 ($COC\mathbf{C}H_3$). MS (70 eV) of **11a/12a**: m/z (%) = 180(26) [M^+], 165(11), 123(36), 110(100), 95(26). – $C_{12}H_{20}O$: calcd. 180.1514, found 180.1471 (MS/EI).
^{1}H NMR ($CDCl_3$) of **12a:** δ = 2.45 (m, 2H, 5-H), 2.33 (m, 2H, 4-H), 2.13 (t, J = 7.6 Hz, 2H, $COCCH_2$), 2.02 (s, 3H, $COC=CCH_3$). – ^{13}C NMR ($CDCl_3$): δ = 209.6 (C = O), 169.8 (C-3), 140.8 (C-2), 34.3 (C-5), 31.9 (C-4), 14.0 ($CH_2\mathbf{C}H_3$), 8.0 ($COC=\mathbf{C}CH_3$).

*12-Oxo-(E/Z)-9,13-pentadienoic acid (**10b**) [(E) : (Z) = 3 : 1, ^{13}C NMR]:* Acylation of 10-undecenoic acid (**9b**, 5 mmol) with crotonoyl chloride (**2a**, 5 mmol) in CH_2Cl_2 (10 ml) in the presence of $EtAlCl_2$ (10 ml, 10 mmol) was carried out by stirring the mixture for 2 h at room temp. Column chromatography [petroleum ether : diethyl ether = 9 : 1 (200 ml) and 6 : 4 (250 ml)] gave 0.75 g (60%) of **10b**, colourless liquid, n_D^{14} = 1.4800. – ^{1}H NMR ($CDCl_3$): δ = 6.86 (dq, J = 15.4, 7.0 Hz, 1H, 14-H) 6.12 (2 × d, J = 15.4 Hz, 1H, 13-H), 5.53 (m, 2H, 9-H and 10-H), 3.20 (d, J = 4.4 Hz, 2H, 11-H), 2.30 (t, J = 7.7 Hz, 2H, 2-H), 2.0 (m, 2H, 8-H), 1.87 (dd, J = 6.6, 1.1 Hz, 3H, 15-H). – ^{13}C NMR ($CDCl_3$): δ = 198.7 (C = O), 179.7 (C-1), 143.1 [C-14, (*E*)], 142.5 [C-14, (*Z*)], 134.8 [C-9, (*E*)], 133.3 [C-9 (*Z*)], 131.8 [C-13, (*Z*)], 131.1 [C-13, (*E*)], 122.0 [C-10, (*E*)], 121.1 [C-10, (*Z*)], 44.0 (C-11), 18.1 (C-15). – $C_{15}H_{24}O_3$: calcd. 252.1725, found 252.1727 (MS/EI).

*3-(8-Carboxyoctyl)-2-methyl-2-cyclopentenone (**11b**) and 2-(8-carboxyoctyl)-3-methyl-2-cyclopentenone (**12b**) (1 : 1.5 mixture, GC):* Cyclization of the crude product **10b** by method A. HPLC gave 0.59 g (47% based on charged **9b**) of **11b/12b**, colourless liquid, n_D^{14} = 1.5020. – ^{1}H NMR ($CDCl_3$): δ = 2.49 (m, 5-H, **11b** and **12b**), 2.37 [m, 10H, $\mathbf{C}H_2COOH$ (**11b** and **12b**), 4-H (**11b** and **12b**), $COCCH_2$ (**12b**)], 2.16 [t, J = 7.4 Hz, 2-H, $COC=CCH_2$ (**11b**)], 2.04 [s, 3H, CH_3 (**12b**)], 1.68 [s, 3H, CH_3 (**11b**)]. – ^{13}C NMR ($CDCl_3$): δ = 210.6 and 210.0 (C = O, **11b** and **12b**), 179.3 (COOH), 174.2 (C-3, **11b**), 170.4 (C-3, **12b**), 140.7 (C-2, **12b**), 136.1 (C-2, **11b**), 34.3 and 34.1 (C-5, **11b** and **12b**), 34.0 ($\mathbf{C}H_2COOH$), 17.2 (CH_3, **12b**), 8.0 (CH_3, **11b**). – $C_{15}H_{24}O_3$ (252.35): calcd. C 71.38, H 9.59; found C 71.26, H 9.56.

*3-(8-Carboxyoctyl)-2-methylcyclopentanone (**13b**) ([cis] : [trans]) = 5 : 1, and 2-(8-carboxyoctyl)-3-methylcyclopentanone (**14b**) ([cis] : [trans] = 1.7 : 1.* Catalytic hydrogenation of **11b/12b** (1 : 1.5 mixture, 0.50 g) gave 0.48 g (96%) of **13b/14b** (1 : 1.5 mixture), colourless liquid, n_D^{19} = 1.4900. – ^{1}H NMR ($CDCl_3$): δ = 2.36 [t, J = 7.2 Hz, 3H, 5-H (**13b** and **14b**)], 2.34 [t, J = 7.7 Hz, 4H, $\mathbf{C}H_2COOH$ (**13b** and **14b**)], 2.11 [m, 6H, 4-H and 2-H (**13b** and **14b**)], 1.14, 1.07, 0.97 and 0.66 [4 × d, J = 6.0, 6.6, 7.2, 7.1 Hz, 12H, CH_3 (*cis*-**13b**, *trans*-**13b**, *cis*-**14b**, *trans*-**14b**)]. – ^{13}C NMR ($CDCl_3$): δ = 221.7 (C = O), 179.8 (COOH), 56.5 (C-2, *cis*-**14b**), 54.1 (C-2, *trans*-**14b**), 50.5 (C-2, *cis*-**13b**), 46.9 (C-2, *trans*-**13b**), 44.7 (C-3, *cis*-**13b**), 40.0 (C-3, *trans*-**13b**), 38.1 and 37.4 (C-5), 36.8 (C-3, *cis*-**14b**), 32.8 (C-3, *trans*-**14b**), 19.7 (CH_3, *cis*-**14b**), 14.5 (CH_3, *trans*-**14b**), 12.6 (CH_3, *cis*-**13b**), 9.6 (CH_3, *trans*-**13b**). – $C_{15}H_{26}O_3$ (254.37): calcd. C 70.81, H 10.31; found C 69.18, H 9.90.

Acknowledgement

The authors would like to thank the *Bundesministerium für Ernährung, Landwirtschaft und Forsten* for financial support of this work (Förderkennzeichen 93NR066-F). Furthermore, we thank *Henkel* KGaA, *Witco* GmbH, *Südchemie* and *Atochem* for providing chemicals.

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[Received: October 20, 1997; accepted: December 10, 1997].