Synthesis and Biological Evaluation of a “Natural” Insect Repellent

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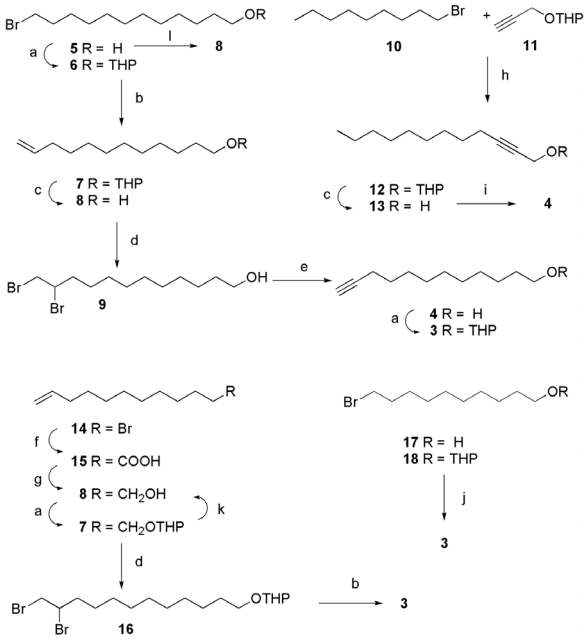
Z. Naturforsch. **59b,** 934 – 942 (2004); received April 30, 2004

(11Z)-11,19-Icosadienyl acetate (**1**) has been shown to be an efficient repellent against the ant *Myrmica rubra* whereas its corresponding (11*E*) stereoisomer **2** does not exhibit any repellent activity at all. Several synthetic strategies for these two compounds have been evaluated.

Key words: Insect Repellent, Long Chain Alkenes

Introduction

Several insects are very serious pests causing severe damage to crops, reforestation and human health. Addressing the latter problem the principal approach to prevention of vector-borne diseases is avoidance. Thus, the development of repellents [1] is still of high importance. “Natural” insect repellents have been in the focus of scientific interest [2, 3] for quite a long time due to the fact that repellents containing either *N*,*N*-diethyl-toluamide (DEET) or permethrin have been reported to cause toxic side effects. In addition, the use of permethrin containing repellents is limited [4, 5] to clothing, shoes and gear. Quite recently [6] we identified (11*Z*)-11,19-icosadienyl acetate (**1**) as a main constituent of the defensive secretion of the phlaeothripid *Suocerathrips linguis*. During the last decades there have been many reports dealing with the secretory components of thrips, small insects that live preferentially on *Sanseveria* plants. A preliminary bioassay [6] showed that **1** is an effective repellent against the ant *Myrmica rubra*. In order to develop “natural” repellents of enhanced activity we became interested in the synthesis and biological evaluation of **1** and of its (11*E*) isomer **2**.



Scheme 1. a) DHP, PPTS; b) *tert*-BuOK, 18-crown-6; c) PPTS; d) Br_2; e) KOH, 18-crown-6; f) Mg, CO_2; g) $LiAlH_4$; h) *n*-BuLi; i) $KNH(CH_2)_3NH_2$; j) Li-acetylide; k) PPTS in ethanol; l) *tert*-BuOK.

Results and Discussion

Retrosynthetic analysis revealed 11-dodecynyl tetrahydro-2*H*-2-pyranyl ether (**3**) as an ideal starting material for the straightforward synthesis of **1** and its analogues. Compound **3** and its unprotected precursor, 11-dodecynyl-1-ol (**4**), seem to be versatile starting materials for a variety of natural products. In this context, **4** has previously been used as a central intermediate in the synthesis of niphatesines, pyridine alkaloids from marine sponges [7], furthermore for the preparation of a variety of pheromones among them the sex pheromones of the processionary moth [8] and the female tea cluster caterpillar [9] and for the synthesis of fluorinated analogues of the Lepidoptera pheromones [10]. Quite recently, **4** has been used

0932–0776 / 04 / 0800–0934 $ 06.00

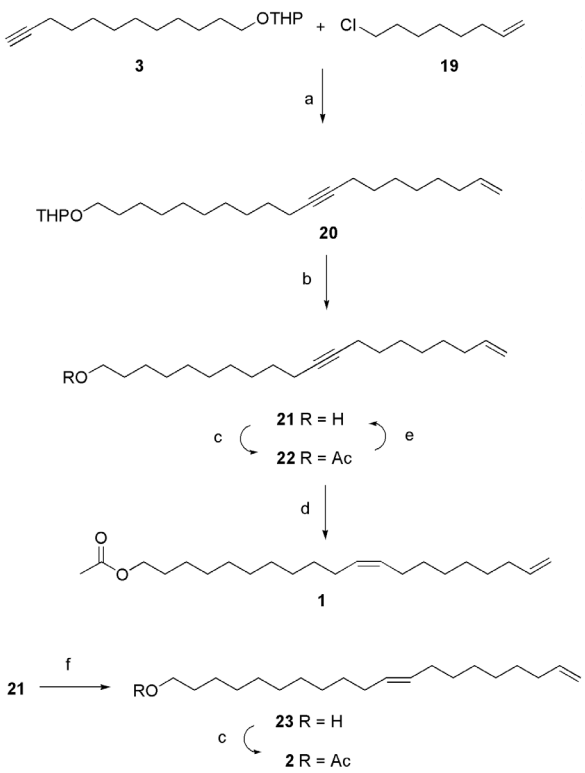
both as a starting material for enzymatic transformations [11], for Pd(0) mediated cross coupling reactions [12] and for the investigation of novel *Langmuir-Blodgett* films [13]. Unfortunately, neither **4** nor **3** are commercially available and a high yielding synthesis does not exist.

As a prerequisite for the synthesis and biological evaluation of repellents larger amounts of these compounds are mandatory and thus several synthetic routes were planned and carried out with a special focus for subsequent scaling up of the procedures.

Our first approach started from 12-bromo-dodecanol (**5**) that was protected as its tetrahydropyranyl acetal **6** [14 – 19] by reaction of **5** with 3,4-dihydro-2*H*-pyran (DHP) in the presence of catalytic amounts of pyridinium *p*-toluenesulfonate (PPTS) [15]. Treatment of **6** with potassium *tert*-butanolate and the crown ether 18-crown-6 resulted in the formation of 98% of the alkene **7** that was deprotected with PPTS in ethanol to yield 88% of 11-dodecen-1-ol (**8**) [20, 21] as a colourless liquid. Bromination of **8** with bromine in dichloromethane in the dark furnished 65% of the dibromo-dodecanol **9** [22] whose elimination reaction gave 55% of **4** [11, 23]. Hence, this route provides the target compound in an overall yield of 28%. This seemed to low for a large scale production of the repellents.

Thus, as an alternative, a route starting from 1-bromo-nonane (**10**) and 2-propynyl tetrahydro-2*H*-2-pyranyl (**11**) ether was investigated. The *n*-butyllithium mediated coupling [22, 24] of **10** and **11** in the presence of HMPT gave 41% of **12**; substitution of HMPT with DMSO as the solvent lowered the yield even under optimized conditions to 25% of isolated **12**. Deprotection of **12** gave 97% of **13** [25 – 28]. KAPA-mediated migration of the triple bond [29] finally resulted in the formation of 83% of **4**. Although this route is shorter than our first approach, an overall yield of 33% is not very attractive.

A third approach was planned starting from 11-bromo-1-undecene (**14**) whose *Grignard* reaction [30] furnished 96% of **15** [31 – 34]. Reduction of **15** gave **8** whose protextion with DHP/PPTS gave 78% of **7** that was subsequently subjected to a bromination to yield 54% of the dibromide **16**. Finally, treatment of **16** with *tert*-BuOK/18-crown-6 gave 87% of **3** [35 – 43]. Thus, an overall yield of 34% was achieved. Since the latter approach seems to offer no advantages over the routes starting either from **5** or from **10** / **11** it also has to be considered as non-optimal.



Scheme 2. a) *n*-BuLi; b) Amberlyst-H^+; c) Ac_2O, pyridine; d) H_2, *Lindlar* catalyst, quinoline; e) NaOH; f) $LiAlH_4$.

Hence, another effort was undertaken. This time our synthesis started from commercially available 10-bromodecanol (**17**) whose tetrahydropyranylation [44, 45] gave 80% of **18** [46] whose reaction with lithium acetylide/ethylenediamine furnished 79% of the target compound **3**. Hence, this route provides an overall yield of 63%. Since the scaling up of these reactions proceeded without any problems, this route represents a straightforward way for the synthesis of a variety of insect repellents and pheromones.

Thus, reaction of **3** with 8-chloro-1-octene (**19**) in the presence of *n*-BuLi furnished the 19-icosen-11-ynyl tetrahydropyranyl acetal **20** whose deprotection with an ion exchange resin in methanol proceeded very smoothly and gave the alcohol **21** in almost quantitative yield. Acetylation of **21** furnished **22** that was hydrogenated in the presence of *Lindlar* catalyst and quinoline to afford the (11*Z*) configurated alkene **1**. Reduction of **21** gave the (11*E*) olefin **23** whose acetylation yielded target (11*E*)-**2**.

Comparative bioassays were performed using the ant *Myrmica rubra*. As depicted in Fig. 1, (11*Z*)-**1** acts

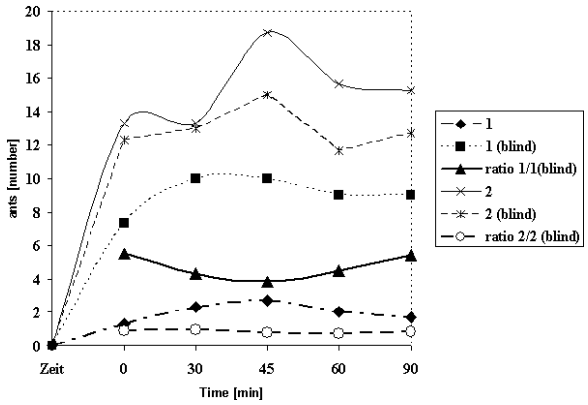


Fig. 1. Ants (*Myrmica rubra*) have to choose between two pieces of prey each surrounded by a circle. One circle is treated with **1** or **2** dissolved in methanol, and the second is treated with methanol [**1**(blind) and **2**(blind)]. The results of three independent experiments are summarized in the ratio of individual ants attacking the prey **1**/**1**(blind) and **2**/**2**(blind), respectively.

as a repellent whereas for (11*E*)-**2** no such activity can be observed. Evaluation of these data reveals, that a 10% solution of (11*Z*)-**1** retreats $> 85\%$ of the ants looking for prey. It seems reasonable to assume that **1** spreads fast on surfaces and in predators like ants and mites – using mainly olfactory sense – a coating of sensory organs will make these insects "blind". In consequence, the ants are not longer able to find their prey; additionally, it can be expected that they get serious problems to evaluate their own trail pheromones.

The synthesis of analogues and their biological screening against a variety of insects is presently under investigation in our laboratories.

Experimental Section

General: Melting points are uncorrected (*Leica* hot stage microscope), NMR spectra (internal Me_4Si) were recorded using the Varian spectrometers Gemini 200, Gemini 2000 or Unity 500 (δ given in ppm, J in Hz, internal Me_4Si for ^1H and ^{13}C NMR spectra), IR spectra (film or KBr pellet) were measured on a Perkin-Elmer FT-IR spectrometer Spectrum 1000, MS spectra were taken on a Intectra GmbH AMD 402 (electron impact, 70 eV) or on a Finnigan MAT LCQ 7000 (electrospray, voltage 4.5 kV, under nitrogen) instrument. For elemental analysis a Foss-Heraeus Vario EL instrument was used. TLC was performed on silica gel (Merck 5554, detection by treatment with a solution of 10% sulphuric acid, ammonium molybdate and cerium(IV) sulphate followed by gentle heating or by UV-vis absorption). Column chromatography was performed on silica gel 60 (FLUKA, 0.04 – 0.06 mm). The ants, *Myrmica rubra*, were obtained from the Antstore (Berlin).

Bio-assay

Three colonies of *Myrmica rubra* (about 25 – 40 individuals each) were reared separately in glass tanks. During the assay the ants were allowed to choose between two pieces of prey (*ca.* 75 mg turkey meat) that were placed on a sheet of paper at a distance of *ca.* 50 mm. Each piece was surrounded by a circle (20 mm radius) soaked (50 μl) either with pure methanol (for reference) or a solution of **1** or **2** (0.5 μl in 50 μl methanol). Statistical evaluation of the test results was made using the χ^2 test for pair-wise comparison of the number of ants ($p < 0.05$).

*(11Z)-11,19-Icosadienyl acetate (**1**)*

A solution of **22** (0.27 g, 0.81 mmol) in hexane (10 ml) containing quinoline (0.125 ml) and *Lindlar* catalyst (42 mg) was stirred under hydrogen (1 atm) for 1 h, then the catalyst was removed and the solvents were evaporated. Chromatographic purification (silica gel, hexane/ethyl acetate 95:5) gave **1** (0.25 g, 92%) as a colourless liquid. R_F (hexane/ethyl acetate 9:1) = 0.57. – IR (film): ν = 3467w, 3077m, 3004s, 2924s, 2853s, 1744s, 1641s, 1464s, 1387s, 1365s, 1237s, 1039s, 994s, 909s, 810w, 723s, 634m, 606m cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.40$ (m, 22 H, CH_2), 1.60 (m, 2 H, CH_2), 2.0 (m, 9 H, CH_2-C = C, CH_3), 4.05 (t, $^3J_{H,H} = 6.7$ Hz, 2 H, CH_2-O), 4.90 (m, 1 H, CH_2 = C), 4.95 (m, 1 H, CH_2 = C), 5.35 (ddd, $^3J_{H,H} = 9.6$ Hz, $^3J_{H,H} = 6.02$ Hz, $^3J_{H,H} = 5.81$ Hz, 2 H, C-CH = CH-C), 5.80 (m, 1 H, CH = C). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0 (CH_3), 26.0 (CH_2, 2 C), 27.2 (CH_2), 27.3 (CH_2), 28.7 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 ($2 \times CH_2$), 29.6 ($2 \times CH_2$), 29.7 (CH_2), 29.8 (CH_2), 33.8 (CH_2), 64.7 (CH_2-O), 114.1 (CH_2 = C), 129.8 (-CH = CH-), 129.9 (-CH = CH-), 139.1 (CH = C), 194.4 (C = O). – MS (GC-MS, EI, 70 eV): m/z(%) = 43 (100), 55 (83), 81 (53), 95 (40), 121 (12), 149 (4), 164 (2), 191 (1), 219 (1), 247 (1), 276 (1), 293 (1), 308 (1), 336 (2). – HRMS for $C_{22}H_{40}O_6$: calcd. 336.3028; found: 336.3028.

*(11E)-11,19-Icosadienyl acetate (**2**)*

To a solution of **23** (0.2 g, 0.68 mmol) in dry pyridine (2 ml) acetic anhydride (1 ml) was slowly added and stirring at room temperature was continued for 4 h. The solvents were removed under reduced pressure and the residue was dissolved in hexane (50 ml), washed with water (3×25 ml), and the solvent was stripped off. The residue was subjected to chromatography (silica gel, hexane/ethyl acetate 98:2) to afford **2** (64 mg, 28%) as a colourless liquid. R_F (hexane/ethyl acetate 9:1) 0.5. – IR (film): ν = 2924s, 2854s, 1744s, 1641w, 1464m, 1365m, 1237s, 1039m, 994w, 968m, 909m, 723w, 606w cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$):

$\delta = 1.20 - 1.40$ (m, 22 H, CH_2), 1.60 (m, 2 H, CH_2), 2.00 (m, 6 H, CH_2-C = C, 3 H, CH_3-CO), 4.05 (t, 2 H, CH_2-OH, $^3J_{H,H} = 6.7$ Hz), 4.90 (m, 1 H, CH_2 = C), 4.95 (m, 1 H, CH_2 = C), 5.35 (m, 2 H, CH = CH), 5.80 (m, 1 H, CH = C). – ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 18.8 (CH_2, 2 C), 26.0 (CH_2), 28.7 (CH_2, 2 C), 29.0 (CH_2, 2 C), 29.0 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 32.6 (CH_2), 32.6 (CH_2), 33.8 (CH_2), 64.7 (CH_2-O), 114.0 (CH_2 = C), 130.2 (CH = CH), 130.3 (CH = CH), 139.1 (CH = C), 232.3 (C = O). – MS (GC/MS, EI, 70 eV): m/z(%) = 43 (100), 55 (87), 81 (65), 96 (58), 121 (16), 149 (6), 177 (1), 191 (1), 233 (1), 247 (1), 276 (1), 293 (1), 308 (1), 336 (3). – HRMS for $C_{22}H_{40}O_6$: calcd. 336.3028; found: 336.3030.

*11-Dodecynyltetrahydro-2H-2-pyranyl ether (**3**)*

Method A: To a suspension of the lithium acetylide ethylenediamine complex (2.9 g, 32.0 mmol) in dry DMSO (17 ml) at 15 – 20 °C within 2 h a solution of **18** (4.9 g, 15.3 mmol) in dry DMSO) (17 ml) was slowly added and stirring was continued for 12 h. The reaction was quenched by the addition of water (15 ml), hexane (15 ml) and again water (15 ml). The aq. layer was extracted with hexane (3 × 100 ml), the combined organic phases were washed with brine (3 × 25 ml), dried (Na_2SO_4), the solvents were removed under diminished pressure and the residue was purified by chromatography (silica gel, hexane/ethyl acetate 98:2) to yield **3** (3.19 g, 79%) as a colourless liquid.

Method B: To a solution of **18** (1.0 g, 2.34 mmol) in hexane (20 ml) *tert*-BuOK (0.53 g, 4.77 mmol) and 18-crown-6 (35 mg, 0.13 mmol) were added and the reaction was stirred for 2 h at 60 – 65 °C and then for 12 h at room temperature. The reaction mixture was then poured into cold water (100 ml), the aq. layer was extracted with hexane (3 × 50 ml) and the combined organic phases were dried (Na_2SO_4). The solvents were removed *in vacuo* und the residue was subjected to chromatography (silica gel, hexane/ethyl acetate 95:5) to afford **3** (0.58 g, 94%) as a colourless liquid. R_F (hexane/ethyl acetate 9:1) = 0.5. – IR (film): ν = 3312m, 2929s, 2855s, 2118w, 1465s, 1455s, 1441m, 1384m, 1136s, 1121s, 1079s, 1034s, 990s, 906m, 869m, 844w, 815m, 722m, 628m cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.40$ (m, 13 H, CH_2), 1.55 (m, 8 H, CH_2), 1.75 (m, 1 H, CH_2), 1.90 (dd, $^4J_{H,H} = 2.69$ Hz, $^4J_{H,H} = 2.49$ Hz, 1 H, CH), 2.15 (m, 2 H, CH_2-C = C), 3.35 (m, 1 H, CH_2-O), 3.45 (m, 1 H, CH_2-O, THP), 3.70 (ddd, $^2J_{H,H} = 9.53$ Hz, $^3J_{H,H} = 6.84$ Hz, $^3J_{H,H} = 6.84$ Hz, 1 H, CH_2-O), 3.85 (m, 1 H, CH_2, THP), 4.55 (dd, $^3J_{H,H} = 4.57$ Hz, $^3J_{H,H} = 2.49$ Hz, 1 H, O-CH-O, THP). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.5$ (CH_2-C ≡ C), 19.8 (CH_2, THP), 25.6 (CH_2, THP), 26.3 (CH_2), 28.6 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 30.9 (CH_2, THP), 62.3 (CH_2-O, THP), 67.7 (CH_2-O), 68.0 (CH ≡ C), 84.7 (C ≡ C), 98.8 (O-CH-O, THP). – MS (GC-MS, EI, 70 eV): m/z(%) = 85 (100), 101 (28), 115 (4), 135 (1), 165 (1), 195 (1), 225 (1), 265 (1), 266 (1). – HRMS for $C_{17}H_{30}O_2$: calcd. 266.22458; found 266.22459. – Analysis for $C_{17}H_{30}O_2$ (266.42): calcd. C 76.64, H 11.35; found C 76.52, H 11.41.

*11-Dodecyn-1-ol (**4**)*

From **9**: To a solution of **9** (1.3 g, 3.78 mmol) in heptane (10 ml) 18-crown-6 (8 mg, 0.03 mmol) in heptane (1 ml) and then finely grounded potassium hydroxide (0.8 g, 14.26 mmol) were added. After stirring for 10 h at 90 – 100 °C and for 12 h at room temperature, water (5 ml) was added, the aq. layer was extracted with heptane (50 ml) and the combined organic layers were dried (Na_2SO_4). The solvents were removed under reduced pressure and the residue was subjected to chromatography (silica gel, hexane/ethyl acetate 9:1) to afford **4** (0.38 g, 55%) as a solid.

From **13**: To 1,3-diaminopropane (16 ml) under argon lithium (2.3 g, 33.1 mmol) was added and the blue reaction mixture was heated to 70 °C for 1 h. The colourless liquid was allowed to cool to room temperature and *tert*-BuOK (2.2 g, 19.3 mmol) was added in one portion. Stirring was continued for 45 min and **13** (1.0 g, 5.5 mmol) was added. After stirring for 1 day at 40 – 45 °C the reaction was quenched at 10 °C by the slow addition of hydrochloric acid (6 N, 100 ml). The aqueous phase was extracted with hexane (3 × 100 ml), dried (Na_2SO_4), and the solvents were removed. The residue was subjected to chromatography (silica gel, hexane/ethyl acetate 1. 9:1; 2. 7:3) to afford **4** (0.83 g, 83%) as a pale yellow solid. M.p. 25 – 27 °C (Lit.: 28 – 30 [12]). – R_F (hexane/ethyl acetate 9:1) = 0.13. – IR (film): ν = 3112s, 2926s, 2854s, 2118w, 1621w, 1465s, 1368m, 1058s cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.40$ (m, 12 H, CH_2), 1.55 (m, 4 H, CH_2), 1.90 (t, $^4J_{H,H} = 2.69$ Hz, 1 H, CH), 2.15 (m, 2 H, CH_2), 3.60 (t, $^3J_{H,H} = 6.63$ Hz, 2 H, CH_2-OH). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.4$ (CH_2-C = C), 25.8 (CH_2), 28.5 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 63.0 (CH_2-O), 68.0 (CH), 84.7 (C ≡ CH). – MS (GC-MS, EI 70 eV): m/z(%) = 41 (100), 55 (79), 57 (10), 67 (80), 81 (68), 95 (26), 97 (4), 107 (11), 121 (6), 135 (2), 149 (1). – Analysis for $C_{12}H_{22}O$ (182.30): calcd. C 79.06, H 12.16; found C 78.89, H 12.28.

*12-Bromododecyl tetrahydro-2H-2-pyranyl ether (**6**)*

A solution containing 12-bromo-dodecanol **5** (3.0 g, 11.32 mmol), DHP (1.43 g, 17.0 mmol) and PPTS (18.5 mg, 0.11 mmol) in dry dichloromethane (40 ml) was stirred at room temperature for 2 days, then an aq. solution of Na_2CO_3 (2 M, 11 ml) was added, the phases were separated and the organic layer was dried (K_2CO_3) and evaporated. The crude

product was purified by chromatography (silica gel, hexane/ethyl acetate 9:1) to afford **6** (3.65 g, 92%) as a colourless liquid. R_F (hexane/ethyl acetate 9:1) = 0.5. – IR (film): ν = 2926s, 2854s, 1466m, 1439m, 1352m, 1322m, 1260m, 1200m, 1184m, 1121m, 1078m, 1034s, 985m, 906m cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.35$ (m, 14 H, CH_2), 1.40 (m, 2 H, CH_2), 1.55 (m, 6 H, CH_2), 1.70 (m, 1 H, CH_2, THP), 1.80 (m, 3 H, CH_2-CH_2Br, CH_2, THP), 3.35 (m, 3 H, CH_2-Br, CH_2), 3.45 (m, 1 H, CH_2-O, THP), 3.70 (ddd, $^2J_{H,H}$ = 9.65 Hz, $^3J_{H,H}$ = 6.81 Hz, $^3J_{H,H}$ = 6.95 Hz, 1 H, CH_2-O), 3.85 (m, 1 H, CH_2-O, THP), 4.55 (dd, $^3J_{H,H}$ = 4.4 Hz, $^3J_{H,H}$ = 2.84 Hz, 1 H, O-CH-O). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7 (CH_2, THP), 25.5 (CH_2, THP), 26.2 (CH_2), 28.1 (CH_2), 28.7 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 30.8 (CH_2-CH), 32.8 (CH_2-CH_2Br), 34.0 (CH_2-Br), 62.3 (CH_2-O, THP), 67.7 (CH_2-O), 98.8 (O-CH-O). – MS (GC-MS, EI, 70 eV): m/z(%) = 85 (100), 101 (8), 137 (2), 150 (2), 177 (1), 205 (1), 218 (1), 247 (1), 275 (2), 292 (1), 320 (1), 349 (2). – Analysis for $C_{17}H_{33}BrO_2$ (349.35): calcd. C 58.45, H 9.52; found C 58.34, H 9.62.

*Dodecenyl tetrahydro-2H-2-pyranyl ether (**7**)*

From **6**: To a solution of *tert*-BuOK (2.92 g, 25.96 mmol) and 18-crown-6 (0.23 g, 0.86 mmol) in hexane (110 ml) a solution of **6** (3.0 g, 8.62 mmol) in hexane (80 ml) was added and stirring was continued for 1 day. The reaction was quenched by the addition of water (135 ml), the phases were separated, the aq. phase was extracted with ether (3 × 100 ml) and the combined organic layers were dried (Na_2SO_4). After evaporation of the solvents the crude product was purified by chromatography (silica gel, 1. hexane; 2. ethyl acetate) to afford **7** (2.2 g, 98%) as a colourless liquid.

From **8**: A solution of **8** (2.2 g, 11.96 mmol) in dichloromethane (35 ml) containing DHP (1.5 g, 18 mmol) and PPTA (33 mg, 0.13 mmol) was stirred at room temperature for 4 days. Work-up as described above followed by chromatography (silica gel, hexane/ethyl acetate 95:5) afforded **7** (2.5 g, 78%). R_F (hexane/ethyl acetate 9:1) = 0.54. – IR (film): ν = 3356w, 3076w, 2926s, 2854s, 1738w, 1641m, 1466m, 1441m, 1384m, 1352m, 1323w, 1260m, 1201m, 1184m, 1137m, 1121m, 1078m, 1034s, 992m, 907m, 869m, 815m, 722w, 638w cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.40$ (m, 14 H, CH_2), 1.55 (m, 6 H, CH_2), 1.70 (m, 1 H, CH_2, THP), 1.80 (m, 1 H, CH_2, THP), 2.0 (dd, $^3J_{H,H}$ = 6.64 Hz, $^3J_{H,H}$ = 6.84 Hz, 2 H, CH_2-C = C), 3.35 (m, 1 H, CH_2-O), 3.45 (m, 1 H, CH_2-O, THP), 3.70 (ddd, $^2J_{H,H}$ = 9.55 Hz, $^3J_{H,H}$ = 6.85 Hz, $^3J_{H,H}$ = 6.85 Hz, 1 H, CH_2-O), 3.85 (m, 1 H, CH_2-O, THP), 4.55 (dd, $^3J_{H,H}$ = 4.35 Hz, $^3J_{H,H}$ = 2.69 Hz, 1 H, O-CH-O THP), 4.90 (m, 1 H, CH_2 = C), 4.95 (m, 1 H, CH_2 = C), 5.80 (m, 1 H, C = CH-C). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7 (CH_2, THP), 25.6 (CH_2), 26.3 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 30.8 (CH_2, THP), 33.8 (CH_2-C = C), 62.3 (CH_2-O, THP), 67.7 (CH_2-O), 98.8 (O-CH-O, THP), 114.0 (CH_2 = C), 139.1 (CH = C). – MS (GC-MS, EI, 70 eV): m/z(%) = 85 (100), 101 (21), 111 (3), 123 (1), 139 (1), 166 (1), 182 (1), 195 (1), 211 (1), 267 (1). – HRMS for $C_{17}H_{32}O_2$: calcd. 268.24023; found 268.24025.

*11-Dodecen-1-ol (**8**)*

From **5**: To an ice-cold solution of **5** (3.0 g, 11.3 mmol) in abs. THF (100 ml), a solution of *tert*-BuOK (3.8 g, 33.9 mmol) in abs. THF (35 ml) was slowly added. Stirring at room temperature was continued overnight, and then aq. hydrochloric acid (1 M, 50 ml) and ether (20 ml) were added, the phases separated, and the aqueous layer was extracted with ether (2 × 50 ml). The combined organic phases were evaporated and the residue was subjected to chromatography (silica gel, hexane/ethyl acetate 9:1) to afford **8** (0.7 g, 35%) as a colourless liquid. R_F (hexane/ethyl 9:1) = 0.07. – IR (film): ν = 3333s, 3077m, 2924s, 2853s, 1821w, 1738w, 1641m, 1465s, 1416m, 1362m, 1198m, 1058s cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.40$ (m, 14 H, CH_2), 1.55 (m, 2 H, CH_2), 2.0 (dd, $^3J_{H,H}$ = 6.85 Hz, $^3J_{H,H}$ = 6.84 Hz, 2 H, C = C-CH_2), 3.60 (t, $^3J_{H,H}$ = 6.64 Hz, 2 H, CH_2-O), 4.90 (m, 1 H, CH_2 = C), 4.95 (m, 1 H, CH_2 = C), 5.80 (m, 1 H, C = CH-C). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.9 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 32.9 (CH_2=C), 33.9 (C = C-CH_2), 63.1 (CH_2-O), 114.0 (CH_2 = C), 139.1 (C = CH-C). – MS (EI, 70 eV): m/z(%) = 55 (100), 67 (78), 82 (79), 96 (63), 109 (28), 123 (11), 138 (9), 166 (3). – Analysis for $C_{12}H_{24}O$ (184.32): calcd. C 78.20, H 13.12; found C 78.11, H 13.29.

From **7**: A solution of **7** (1.0 g, 3.73 mmol) in ethanol (30 ml) containing PPTA (95 mg, 0.38 mmol) was stirred for 4.5 h at 55 °C; stirring at room temperature was continued for another 12 h, the solvents were evaporated under diminished pressure and the residue was subjected to chromatography (silica gel, hexane/ethyl acetate 9:1) to afford **8** (0.6 g, 88%) as a colourless liquid.

From **15**: To a suspension of $LiAlH_4$ (1.36 g, 9.5 mmol) in abs. ether (60 ml) a solution of **15** (4.7 g, 23.7 mmol) in abs. ether (15 ml) was slowly added at 0 °C. Stirring at room temperature was continued for 1 day, and then the reaction was quenched by the addition of ice water and aq. hydrochloric acid. The aqueous layer was extracted with ether (3 × 50 ml), and the combined organic phases were dried (Na_2SO_4). The solvent was evaporated and the residue purified by chromatography (silica gel, hexane/ethyl acetate 10:1) to afford **8** (4.2 g, 96%) as a colourless liquid.

*11,12-Dibromo-1-dodecanol (**9**)*

To a solution of **8** (0.5 g, 2.7 mmol) in abs. dichloromethane (5 ml) under argon a solution of bromine (0.5 g, 3.1 mmol) in abs. dichloromethane (3 ml) was added dropwise in the dark at −5 to −10 °C. After warming to room temperature the solvents were evaporated and the crude product was purified by chromatography (silica gel, hexane/ethyl acetate 7:3) to afford **9** (0.6 g, 65%) as a slightly yellow liquid. R_F (hexane/ethyl acetate 9:1) = 0.15. – IR (film): ν = 3355s, 2926s, 2854s, 1732w, 1632w, 1464m, 1434m, 1372m, 1228m, 1143m, 1057m cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 – 1.40 (m, 13 H, CH_2), 1.55 (m, 3 H, CH_2), 1.80 (m, 1 H, CH_2-CHBr), 2.05 (m, 1 H, CH_2-CHBr), 3.60 (m, 1 H, CH_2-Br, 2 H, CH_2-O), 3.80 (ddd, $^2J_{H,H}$ = 4.35 Hz, $^2J_{H,H}$ = 4.56 Hz, $^3J_{H,H}$ = 10.15 Hz, 1 H, CH_2-Br), 4.15 (m, 1 H, CH-Br). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.8 (CH_2), 28.8 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 32.8 (CH_2-CH_2OH), 36.1 (CH_2-CHBr), 36.3 (CH_2Br), 53.1 (CH-Br), 63.1 (CH_2-OH). – MS (GC/MS, EI, 70 eV): m/z(%) = 55 (100), 69 (55), 81 (45), 95 (53), 109 (32), 123 (13), 135 (5), 137 (13), 163 (6), 165 (11), 189 (8), 191 (6), 215 (2), 229 (2), 242 (7), 256 (2), 258 (3), 272 (1), 296 (1), 298 (2). – Analysis for $C_{12}H_{24}Br_2O_2$ (344.13): calcd. C 41.88, H 7.03; found C 41.68, H 7.24.

*2-(2-Dodecynyloxy)tetrahydro-2H-pyran (**12**)*

To a solution of 2-(2-propynyloxy)tetrahydro-2*H*-pyranyl ether (**11**) (8.3 ml, 58 mmol) in abs. THF (60 ml) a solution of BuLi (1.6 M in hexane, 58 mmol) was added at −15 to −18 °C. Stirring at this temperature was continued for another 30 min, then a solution of 1-bromo-nonane (**10**) (12.0 g, 58 mmol) in HMPT (35 ml) was added in the dark and stirring was continued for 12 h at room temperature. A satd. aq. solution of NH_4Cl (150 ml) was added, the aq. phase was extracted with hexane (4 × 100 ml) and the combined organic phases were dried (Na_2SO_4). The solvents were removed *in vacuo* und the crude product was purified by chromatography (silica gel, hexane/ethyl acetate 99:1) to afford **12** (6.3 g, 41%) as a pale yellow liquid. R_F (hexane/ethyl acetate 9:1) = 0.55. – IR film): ν = 3333w, 2926s, 2855s, 2238w, 1732w, 1456m, 1387m, 1345m, 1324w, 1264m, 1202m, 1183m, 1133m, 1118m, 1079m, 1054m, 1024s, 973m, 946m, 903m m^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (dd, $^2J_{H,H}$ = 13.69 Hz, $^3J_{H,H}$ = 6.43 Hz), 1.20 – 1.30 (m, 11 H, CH_2), 1.35 (m, 2 H, CH_2), 1.50 (m, 4 H, CH_2), 1.60 (m, 1 H, CH_2, THP), 1.70 (m, 1 H, CH_2, THP), 1.80 (m, 1 H, CH_2), 2,20 (m, 2 H, CH_2-C ≡ C), 3.50 (m, 1 H, CH_2-O, THP), 3.85 (m, 1 H, CH_2-O, THP), 4.20 (ddd, $^2J_{H,H}$ = 15.15 Hz, $^4J_{H,H}$ = 2.28 Hz, $^5J_{H,H}$ = 2.07 Hz, 2 H, O-CH_2-C ≡ C), 4.80 (dd, $^3J_{H,H}$ = 3.32 Hz, $^3J_{H,H}$ = 3.53 Hz, 1 H, O-CH-O, THP). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 18.9 (CH_2), 19.2 (CH_2), 22.7 (CH_2), 25.5 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 30.4 (CH_2), 31.9 (CH_2), 54.7 (CH_2-O), 62.0 (CH_2, THP), 75.7 (C ≡ C), 86.7 (C ≡ C) 96,6 (CH_2, THP). – MS (GC-MS, EI, 70 eV): m/z(%) = 85 (100), 95 (40), 123 (2), 139 (2), 153 (2), 167 (2), 195 (2), 211 (1), 223 (1), 251 (1), 265 (1). – HRMS for $C_{17}H_{30}O_2$: calcd. 266.22458; found 266.22456. – Analysis for $C_{17}H_{30}O_2$ (266.42): calcd. C 76.64, H 11.35; found C 76.51, H 11.52.

*2-Dodecyn-1-ol (**13**)*

A solution of **12** (1.5 g, 5.63 mmol) containing PPTA (0.14 g, 0.56 mmol) in ethanol (50 ml) was stirred for 5 h at 55 °C and then overnight at room temperature. The solvents were removed and the residue was purified by chromatography (silica gel, 1. hexane/ethyl acetate 9:1; 2. methanol) to afford **13** as a greasy solid. M. p. 29 – 31 °C. – R_F (hexane/ethyl acetate 9:1) = 0.2. – IR (KBr): ν = 3317s, 2955s, 2917s, 2850s, 2285w, 2219w, 1628w, 1471s, 1453m, 1432m, 1365m, 1341w, 1314w, 1278w, 1262w, 1028s, 892w cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (dd, $^2J_{H,H}$ = 13.68 Hz, $^3J_{H,H}$ = 6.63 Hz, 3 H, CH_3), 1.20 – 1.30 (m, 10 H, CH_2), 1.35 (m, 2 H, CH_2), 1.50 (m, 2 H, CH_2), 2.20 (m, 2 H, CH_2), 4.20 (dd, $^3J_{H,H}$ = 2.07 Hz, $^3J_{H,H}$ = 2.28 Hz, 2 H, CH_2-OH). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 51.4 (CH_2), 78.3 (C ≡ C), 86.6 (C ≡ C). – MS (EI, 70 eV): m/z(%) = 55 (100), 57 (38), 67 (85), 70 (83), 79 (74), 83 (61), 93 (61), 95 (50), 97 (19), 107 (21), 111 (36), 121 (22), 135 (13), 151 (8), 164 (1). – Analysis for $C_{12}H_{22}O$ (182.30): calcd. C 79.06, H 12.16; found C 78.91, H 12.27.

*11-Dodecenoic acid (**15**)*

To a suspension of finely grounded Mg (1.3 g, 53.5 mmol) in abs. ether (40 ml) 11-bromo-1-undecene (**14**) (9.3 g, 39.9 mmol) was slowly added. After heating under reflux for 6 h, stirring at room temperature was continued for another 5 h, then the reaction mixture was filtered. Abs. ether (100 ml) was cooled to −40 °C and solid carbon dioxide was added; simultaneously the *Grignard* reagent was added dropwise, stirring was continued for another 2 h and then the reaction was quenched by the addition of aq. hydrochloric acid (18%, 200 ml), the phases were separated, the aq. layer was extracted with ether (2 × 70 ml) and the solvents were evaporated. The crude product was dissolved in an aq. solution of sodium hydroxide (1 M, 50 ml). The solution was extracted with ether (100 ml), the aq. phase acidified by the addition of diluted hydrochloric acid and extracted with ether (2 × 200 ml). After drying and evaporation of the solvents the crude product was subjected to chromatography (silica gel, hexane/ethyl ac-

etate 10:1) to afford **15** (4.2 g, 96%) as a colourless liquid. IR (film): $\nu = 3077$m, 2926s, 2855s, 1712s, 1641m, 1548w, 1464m, 1413m, 1286m, 1118w cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.40$ (m, 12 H, CH_2), 1.60 (m, 2 H, CH_2), 2.0 (dd, $^3J_{H,H} = 6.87$ Hz, $^3J_{H,H} = 6.87$ Hz, 2 H, CH_2-C = C), 2.30 (t, $^3J_{H,H} = 7.4$ Hz, 2 H, 2 H, CH_2-COOH), 4.90 (m, 1 H, CH_2 = C), 4.95 (m, 1 H, CH_2 = C), 5.80 (m, 1 H, CH = C). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 24.7$ (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 33.8 (CH_2), 34.1 (CH_2), 114.1 (CH_2 = C), 139.2 (CH = C), 180.1 (C = O). – MS (EI, 70 eV): m/z(%) = 55 (100), 60 (21), 69 (70), 73 (30), 83 (39), 96 (39), 110 (21), 114 (13), 123 (12), 138 (17), 151 (4), 162 (4), 180 (10), 198 (1). – HRMS for $C_{12}H_{22}O_2$: calcd. 298.16198; found 198.16200.

*11, 12-Dibromododecyl-tetrahydro-2H-2-pyranyl ether (**16**)*

To a −15 °C cold solution of **7** (0.2 g, 0.75 mmol) in abs. dichloromethane (10 ml) a solution of bromine (0.1 g, 0.63 mmol) in abs. dichloromethane (3 ml) was slowly added, then the volatiles were removed *in vacuo* and the residue was subjected to chromatography (silica gel, hexane/ethyl acetate 9:1) to yield **16** (0.14 g, 54%) as a colourless liquid. R_F (hexane/ethyl acetate 9:1) = 0.54. – IR (film): $\nu = 2927$s, 2854s, 1742w, 1465m, 1440w, 1352w, 1322w, 1260w, 1200m, 1184w, 1136m, 1120m, 1078m, 1033s, 989w cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.40$ (m, 13 H, CH_2), 1.60 (m, 7 H, CH_2), 1.65 – 1.85 (m, 3 H, CH_2), 2.10 (m, 1 H, CH_2), 3.35 (ddd, $^2J_{H,H} = 9.55$ Hz, $^3J_{H,H} = 6.64$ Hz, $^3J_{H,H} = 6.64$ Hz, 1 H, CH_2-O), 3.45 (m, 1 H, CH_2, THP), 3.60 (t, $^3J_{H,H} = 10.17$ Hz, 1 H, CH_2-Br), 3.70 (ddd, $^2J_{H,H} = 9.55$ Hz, $^3J_{H,H} = 6.85$ Hz, $^3J_{H,H} = 6.85$ Hz, 1 H, CH_2-O), 3.85 (m, 2 H, CH_2, THP, CH_2-Br), 4.15 (m, 1 H, CH-Br), 4.55 (dd, $^3J_{H,H} = 4.56$ Hz, $^3J_{H,H} = 2.49$ Hz, 1 H, O-CH-O). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.7$ (CH_2), 25.6 (CH_2), 26.3 (CH_2), 26.8 (CH_2), 28.8 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.8 (CH_2), 30.8 (CH_2), 36.1 (CH_2-CHBr), 36.4 (CH_2-Br), 53.1 (CH-Br), 62.3 (CH_2-O, THP), 67.7 (CH_2-O), 98.8 (O-CH-O, THP). – MS (GC-MS, EI, 70 eV): m/z(%) = 85 (100), 101 (8), 123 (2), 163 (1), 189 (1), 211 (1), 245 (1), 267 (1), 324 (1), 353 (1), 355 (1), 427 (3). – HRMS for $C_{17}H_{32}Br_2O_2$: calcd. 426.0769; found 426.0770.

*10-Bromodecyl tetrahydro-2H-2-pyranyl ether (**18**)*

A solution of 10-bromo-1-decanol (**17**) (3.0 g, 11.39 mmol) containing DHP (1.43 g, 17,0 mmol) and PPTA (28 mg, 0.11 mmol) in dry dichloromethane (50 ml) was stirred for 2 days at room temperature, then an aq. solution of Na_2CO_3 (2 M, 11 ml) was added, the layers were separated and the organic phase was dried (K_2CO_3). The solvents were removed and the residue was purified by chromatography (silica gel, hexane/ethyl acetate 9:1) to afford **18** (2.92 g, 80%) as a colourless liquid. R_F (hexane/ethyl acetate 9:1) = 0.5. – IR (film): $\nu = 2927$s, 2854s, 1465m, 1455m, 1440m, 1383m, 1365m, 1352m, 1322m, 1260m, 1200s, 1184m, 1163m, 1136s, 1120s, 1078s, 1034s, 988m, 905m, 869m, 815m, 722m, 646m, 564w cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.25 - 1.35$ (m, 10 H, CH_2), 1.40 (m, 2 H, CH_2), 1.45 – 1.60 (m, 6 H, CH_2), 1.70 (m, 1 H, CH_2), 1.80 (m, 3 H, CH_2-CH_2Br, CH_2, THP), 3.35 (m, 3 H, CH_2Br, CH_2-O), 3.45 (m, 1 H, CH_2, THP), 3.70 (ddd, $^2J_{H,H} = 9.5$ Hz, $^3J_{H,H} = 6.84$ Hz, $^2J_{H,H} = 6.84$ Hz, 1 H, CH_2), 3.85 (m, 1 H, CH_2, THP), 4.55 (dd, $^3J_{H,H} = 4.35$ Hz, $^3J_{H,H} = 2.48$ Hz, 1 H, CH). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.8$ (CH_2, THP), 25.6 (CH_2, THP), 26.2 (CH_2), 28.2 (CH_2), 28.8 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.8 (CH_2), 30.9 (CH_2, THP), 32.9 (CH_2-CH_2Br), 34.0 (CH_2-Br), 62.3 (CH_2-O, THP), 67.7 (CH_2-O), 98.8 (CH). – MS (GC-MS, EI, 70 eV): m/z(%) = 85 (100), 101 (8), 115 (2), 137 (2), 163 (1), 190 (1), 219 (1), 241 (1), 247 (2), 267 (1), 292 (1), 319 (3). – Analysis for $C_{17}H_{33}BrO_2$ (349.35): calcd. C 58.45, H 9.52; found C 58.31, H 9.67.

*19-Icosen-11-ynyltetrahydro-2H-2-pyranyl ether (**20**)*

To a −10 °C cold solution of **3** (0.8 g, 3.0 mmol) in abs. THF (15 ml) a solution of *n*-BuLi (3.15 mmol, 1.6 M in hexane) was slowly added, stirring at that temperature was continued for 1 h and a solution of **19** (3.5 g, 3.15 mmol) in HMPT (8 ml) was slowly added at −18 °C. The mixture was allowed to warm to room temperature and stirring was continued for another 12 h, then the reaction was stopped by the addition of water (11 ml). The phases were separated, the aq. phase was extracted with hexane (3 × 100 ml), the combined organic layers were washed with water (2 × 20 ml) and brine (15 ml) and dried (Na_2SO_4). After evaporation of the solvents the residue was purified by chromatography (silica gel, hexane/ethyl acetate 98:2) to yield **20** (0.64 g, 57%) as a colourless liquid. R_F (hexane/ethyl acetate 9:1) = 0.6. – IR (film): $\nu = 3333$w, 3076w, 2926s, 2855s, 2360w, 1737w, 1676w, 1640m, 1465m, 1440m, 1352m, 1323m, 1284w, 1260m, 1200s, 1184m, 1137s, 1079s, 1034s, 992m, 908s, 869m, 815m cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.60$ (m, 28 H, CH_2), 1.70 (m, 1 H, CH_2), 1.80 (m, 1 H, CH_2), 2.00 (dd, $^3J_{H,H} = 6.84$ Hz, $^3J_{H,H} = 6.84$ Hz, 2 H, CH_2-C = C), 2.15 (m, 4 H, CH_2-C ≡ C), 3.35 (ddd, $^2J_{H,H} = 9.53$ Hz, $^3J_{H,H} = 6.63$ Hz, $^3J_{H,H} = 6.63$ Hz, 1 H, CH_2-O), 3.45 (m, 1 H, CH_2-O, THP), 3.70 (ddd, $^2J_{H,H} = 9.51$ Hz, $^3J_{H,H} = 6.83$ Hz, $^3J_{H,H} = 6.84$ Hz, 1 H, CH_2-O), 3.85 (m, 1 H, CH_2-O, THP), 4.55 (dd, THP, $^3J_{H,H} = 4.35$ Hz, $^3J_{H,H} = 2.69$ Hz, 1 H, O-CH-O), 4.90 (m, 1 H, CH_2 = C), 4.95 (m, 1 H, CH_2 = C) 5.80 (m, 1 H, CH = C). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.8$ (CH_2), 18.9 (CH_2),

19.8 (CH_2), 25.6 (CH_2), 26.3 (CH_2), 28.7 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 30.8 (CH_2), 33.8 (CH_2), 62.3 (CH_2-O, THP), 67.7 (CH_2-O), 80.1 (C ≡ C), 80.3 (C ≡ C), 98.8 (CH, THP), 114.1 (CH_2 = C), 139.0 (CH = C). – MS (GC-MS, EI, 70 eV): $m/z(\%) = 85$ (100), 101 (25), 109 (7), 135 (7), 149 (2), 163 (1), 177 (1), 189 (1), 219 (1), 221 (1%), 247 (1), 265 (2), 279 (1), 303 (2), 305 (1). – HRMS for $C_{25}H_{44}O_2$: calcd. 376.3341; found 376.3342.

*19-Icosen-11-yn-1-ol (**21**)*

From **20**: A solution of **20** (0.55 g, 1.46 mmol) in methanol (15 ml) was stirred with ion exchange resin (Amberlyst 15, H^+-form, 0.5 g) for 2 days. The resin was filtered off, the filtrate was evaporated and the residue purified by a chromatography (silica gel, hexane/ethyl acetate 9:1) to afford **21** (0.39 g, 91%) as a greasy solid.

From **22**: A solution of **22** (0.85 g, 2.55 mmol) in ethanol (20 ml) containing aq. NaOH (8 ml, 20%) was stirred at room temperature for 2.5 h. The hexane extract (3 × 70 ml) was washed with brine (3 × 70 ml) and dried (K_2CO_3), the solvents were evaporated and the residue subjected to chromatography (silica gel, hexane/ethyl acetate 9:1) to afford **21** (0.68 g, 92%) as a greasy solid. R_F (hexane/ethyl acetate 9:1) = 0.1. – IR (film): ν = 3331s, 3078m, 2927s, 2854s, 1829w, 1642m, 1461m, 1436m, 1335m, 1288m, 1262m, 1224w, 1190w, 1133m, 1060m, 1042m, 1024m, 994m, 969m, 910s cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.40$ (m, 19 H, CH_2), 1.45 (m, 4 H, CH_2), 1.55 (m, 2 H, CH_2), 2.0 (dd, $^3J_{H,H} = 6.84$ Hz, $^3J_{H,H} = 6.84$ Hz, 2 H, CH_2-C = C), 2.15 (m, 4 H, CH_2-C ≡ C), 3.60 (t, $^3J_{H,H} = 6.63$ Hz, 2 H, CH_2-OH), 4.90 (m, 1 H, CH_2 = C), 4.95 (m, 1 H, CH_2 = C), 5.8 (m, 1 H, CH = C). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8 (CH_2, 2 C), 25.8 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.2 (3 × CH_2), 29.5 (2 × CH_2), 29.6 (CH_2), 32.9 (CH_2), 33.8 (CH_2), 63.1 (CH_2-OH), 80.2 (C ≡ C), 80.3 (C ≡ C), 114.1 (CH_2 = C), 139.0 (CH = C). – MS (GC-MS, EI, 70 eV): $m/z(\%) =$ 67 (100), 95 (63), 121 (39), 135 (60), 150 (15), 163 (4), 191 (1), 210 (1), 235 (1), 249 (1), 263 (1), 292 (1). – HRMS for $C_{20}H_{36}O$: calcd. 292.2766; found 292.2766.

*19-Icosen-11-ynyl acetate (**22**)*

To a solution of **21** (1.3 g, 4.45 mmol) in dry pyridine (8.2 ml) acetic anhydride (4.3 ml) was added and the mixture was stirred for 3.5 h, then the volatiles were removed under diminished pressure. The residue was suspended in hexane (100 ml), washed with water (3 × 100 ml) and the solvents were evaporated to afford **22** (1.45 g, 98%) as a colourless liquid. R_F (hexane/ethyl acetate 9:1) = 0.65. – IR (film): ν = 3076w, 2929s, 2856s, 1743s, 1641w, 1465m, 1437m, 1387m, 1365m, 1332w, 1238s, 1039m, 995w, 910m cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.40$ (m, 19 H, CH_2), 1.45 (m, 4 H, CH_2), 1.60 (m, 2 H, CH_2), 2.0 (m, 5 H, CH_2-C = C, CH_3), 2.15 (m, 4 H, CH_2-C ≡ C), 4.05 (t, $^3J_{H,H} = 6.84$ Hz, 2 H, CH_2-O), 4.90 (m, 1 H, CH_2 = C), 4.95 (m, 1 H, CH_2 = C), 5.80 (m, 1 H, CH = C). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8 (2 × CH_2), 21.0 (CH_2), 26.0 (CH_2), 28.7 (2 × CH_2), 28,9 (2 × CH_2), 29.1 (CH_2), 29.2 (2 × CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 33.8 (CH_2), 64.6 (CH_2-O), 80.2 (2 × C ≡ C), 114.2 (CH_2 = C), 139.0 (CH_2=C), 171.1 (C = O). – MS (GC-MS, EI, 70 eV): $m/z(\%) =$ 63 (100), 178 (65), 192 (76), 203 (7), 217 (7), 231 (6), 238 (7), 252 (18), 263 (7), 277 (9), 291 (19), 305 (28), 319 (9), 320 (3), 334 (3). – HRMS for $C_{22}H_{38}O_2$: calcd. 334.2872; found 334.2872.

*(11E)-11,19-Icosadien-1-ol (**23**)*

A suspension of $LiAlH_4$ (1.0 g, 26 mmol) in abs. THF (200 ml) and diglyme (8 ml) was heated for 2 h at 120 °C. Then the mixture was cooled to 0 °C and a solution of **21** (0.6 g, 2.0 mmol) in diglyme (5 ml) and abs. THF (2 ml) was added dropwise. Stirring at 120 °C was continued for 57 h. The reaction mixture was then carefully hydrolyzed by the addition of crushed ice and the pH was adjusted to 7 by the addition of diluted aq. hydrochloric acid. The precipitate was filtered off and washed with hexane. The aq. layer was separated and washed with hexane (100 ml). The combined organic layers were washed with brine (2 × 50 ml) and dried (Na_2SO_4) and the solvents removed under reduced pressure. The residue was subjected to chromatography (silica gel, hexane/ethyl acetate 9:1) to afford **23** (0.3 g, 50%) as a colourless liquid. R_F (hexane/ethyl acetate 4:1) = 0.6. – IR (film): ν = 3331s, 3076m, 2926s, 2854s, 1722w, 1641m, 1465m, 1369m, 1057m, 993m, 968m, 910m, 758m, 722m, 638w cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20 - 1.60$ (m, 24 H, CH_2), 1.90 – 2.10 (m, 6 H, CH_2), 3.60 (t, 2 H, CH_2-OH, $^3J_{H,H} = 6.64$ Hz), 4.90 (m, 1 H, CH_2=C), 4.95 (m, 1 H, CH_2 = C), 5,35 (m, 2 H, CH = CH), 5.80 (m, 1 H, CH = C). – ^{13}C NMR (400 MHz, $CDCl_3$): δ = 18.9 (CH_2, 2 C), 25.9 (CH_2), 28.8 (CH_2, 2 C), 29.0 (CH_2, 2 C), 29.1 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 32.7 (CH_2), 32.9 (CH_2), 33.8 (CH_2), 63.1 (CH_2-O), 114.1 (CH_2 = C), 130.2 (CH = CH), 130.3 (CH = CH), 138.9 (CH = C). – MS (GC/MS, EI, 70 eV): $m/z(\%) =$ 67 (100), 81 (91), 95 (67), 107 (31), 121 (36), 135 (50), 136 (10), 150 (11), 163 (3), 177 (3), 191 (1). – Analysis for $C_{20}H_{38}O$ (294.52): calcd. C 81.56, H 13.01; found C 81.25, H 13.33.

Acknowledgments

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged. We like to thank Dr. R. Kluge for the MS spectra and Dr. D. Ströhl for his help with the NMR spectra.

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