J Am Oil Chem Soc (2008) 85:561–565
DOI 10.1007/s11746-008-1226-x

ORIGINAL PAPER

Synthesis of Ethyl 5*Z*,9*Z*,12*Z*-octadecatrienoate (ethyl pinolenate) and Methyl 12*Z*,15*Z*-octadecadienoate

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Received: 9 November 2007 / Revised: 13 February 2008 / Accepted: 14 February 2008 / Published online: 11 March 2008

Abstract Pinolenic acid (5*Z*,9*Z*,12*Z*-octadecatrienoic acid, **1a**), one of the most abundant trienoic fatty acids in nature, is very difficult to obtain in quantity in a pure state from the highly complex mixture of unsaturated tall oil fatty acids. For this reason its chemistry has been little studied when compared to linolenic or linoleic acids. A simple synthesis of esters of **1a** and of 12*Z*,15*Z*-octadecadienoic acid **3** using the one pot double Wittig procedure is described here. The products of double Wittig reactions were purified by argentation chromatography, and their structural purity was established by ^{1}H-, ^{13}C-NMR and 2D-NMR spectroscopies.

Keywords Pinolenic acid (5*Z*,9*Z*,12*Z*-octadecatrienoic acid) · 12*Z*,15*Z*-octadecadienoic acid · Wittig reaction · Argentation chromatography

Introduction

Up to 10% of the fatty acids in northern European and Siberian spruce and pine consist of pinolenic acid (5*Z*,9*Z*,12*Z*-octadecatrienoic acid, **1a**), which is one of the most abundant[1] trienoic fatty acids in nature, second only to linolenic acid. Owing to the difficulties in obtaining pinolenic acid in quantity in a pure state, its chemistry has been little studied when compared to linolenic or linoleic acids. We reported [1] earlier the isolation of **1a** from tall oil by an iodo-lactonization method, its alkali isomerization and the synthesis of many of the isomers [2] and their intramolecular Diels-Alder cyclization reactions [3, 4].

There are no reported syntheses of **1a** in the literature, nor in fact of any all-*cis* (n, $n + 4$, $n + 7$)-alkatriene systems as far as we know. The sensitive methylene/ethylene interrupted triene functionality poses major problems for synthesis, particularly if the double bonds are introduced one at a time. This is because an initially created *cis* double bond with allylic functionality must survive subsequent operations required for the remaining C=C bond forming chemistry.

The use of bisphosphonium salts in the one pot Wittig syntheses of methylene skipped dienes was first reported [5] by Wittig himself in 1958 for the preparation of cycloalkapolyenes. Bestmann et al. [6] relied on this strategy in syntheses of a number of 1,4-alkadienoic pheromones and related compounds starting from C_3–C_8 bisphosphonium salts with simultaneous use of two different aldehydes. More recently Pohnert and Boland [7] used a double alkenylation of bis-ylides from propylene-1,3-bis(triphenylphosphonium) dibromide **2** or (*Z*)-hex-3-enyl-l,6-bis-(triphenylphosphonium) diiodide to prepare several methylene interrupted *cis*-trienoic hydrocarbons and fatty acid esters. In all of these procedures strong organic bases were used for bis-ylide generation, thus requiring strictly anhydrous conditions and operation at low temperatures.

We have for years successfully used the exceptionally simple and robust K_2CO_3 mediated aqueous Wittig procedure [8] for the synthesis of various alkali isomerization products of pinolenic [2] and linolenic [4] acid esters, as

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[1] In Finland alone, several tens of thousands of tons of tall oil fatty acids, containing ca. 10% of pinolenic acid, are annually distilled in the tall oil industry.

well as other straight chain compounds [9, 10] capable of producing hexahydroindenes via intramolecular Diels-Alder reactions. We now report the results of using **2** as the ylide generating precursor in the potassium carbonate mediated one-pot aqueous double Wittig synthesis of methylene skipped *cis* diene and triene structures, and show that the obstacles just mentioned may be overcome to an extent. Although moderate overall yields are obtained in our synthesis, it is clear that the route makes macroscopic amounts of pure pinolenic acid and related compounds available for the first time in a fairly expedient manner.

To widen the scope of our synthetic procedure also 12*Z*,15*Z*-octadecadienoic acid **3** as methyl ester was synthesized. This compound is one of the byproducts formed on hydrogenation of linolenic acid containing vegetable oils in the margarine industry.

Experimental Procedures

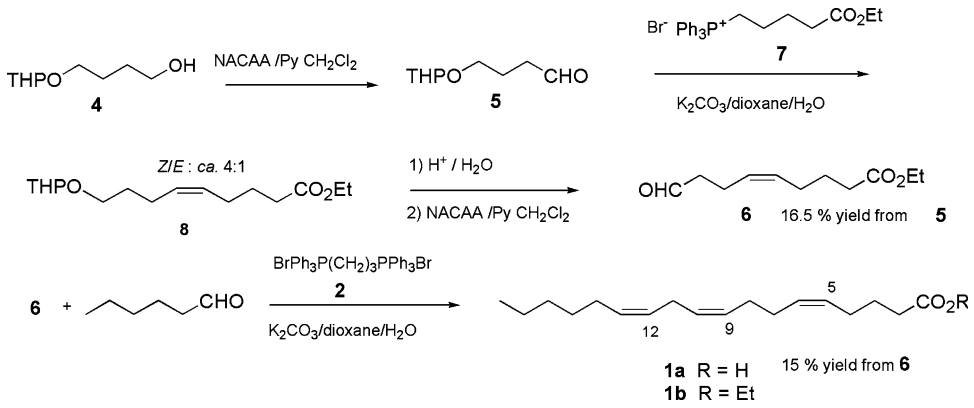
The structure and purity of the products were established by GC/MS and NMR (^{1}H, ^{13}C, 2D NMR) techniques. NMR spectra were acquired with Varian Inova or Varian Unity spectrometers running at 300 MHz and at 500 MHz, respectively. Solvent was $CDCl_3$ in all cases and running temperature 30 °C. Assignments are based on 2D-NMR spectra (COSY 135, NOESY, HMBC, HSQC-TOCSY). Especially the HSQC-TOCSY traces at appropriate ^{13}C-chemical shifts proved to be very effective in solving ambiguous cases.

Full spectral details are given for new compounds only. For argentation chromatography, silica gel (60 g; Kieselgel 60, E. Merck, Darmstadt, 230–400 mesh ASTM; kept overnight in an oven at 120 °C) was treated with 100 mL of a 10% solution of $AgNO_3$ in acetonitrile, the latter predried over 3-Å molecular sieves. After the removal of acetonitrile under vacuum in a rotary evaporator at 70 °C, the impregnated silica was ready for use. Details of argentation chromatography are given for ethyl pinolenate below. The drier the argentation chromatography system is, the better a separation can be obtained, and it is important that, when preparing a new batch, drying should be performed as described above. If one attempts to oven dry a new $AgNO_3$–silica batch containing moisture, a vigorous reaction usually ensues with evolution of NH_3 gas (presumably originating from CH_3CN), the surface of the material becoming covered with a black layer of Ag(0). This reaction does not occur when recovered material is dried in the oven for reuse.

For ordinary thin layer chromatography, aluminum sheets coated with silica gel 60 F, Merck, were used. For thin layer argentation chromatography, the sheets were immersed in a 10% solution of $AgNO_3$ in acetonitrile and dried at ambient temperature.

*4-(Tetrahydropyran-2-yloxy)butanol (**4**)*

3,4-Dihydropyran (45 g, 0.53 mol) (Scheme 1) was added slowly to a stirred mixture of 1,4-butanediol (60 g, 0.67 mol) and conc. H_2SO_4 (0.2 mL) in CH_2Cl_2 (70 mL) in ice bath (exothermic !). Over a period of 10 min, the temperature rose to *ca*. 35 °C. After stirring for 30 min at room temperature the reaction mixture was neutralized with 10% aq. $NaHCO_3$ and CH_2Cl_2 was evaporated under reduced pressure. One hundred and fifty milliliters of water was added, the mixture was extracted with 70 mL of diethyl ether and the organic phase was separated and extracted once with 100 mL of water. The combined water phases were extracted with 30 mL of diethyl ether (discarded), saturated with NaCl and extracted five times with diethyl ether (5 × 20 mL). The combined ether phases were dried on Na_2SO_4 and the solvent evaporated to give 4-(tetrahydropyran-2-yloxy)butanol **4** (23.5 g, 19%). ^{1}H NMR δ 1.38 −1.54 (m, 4H, H-3′b, H-4′b, H-2′b and H-4′a), 1.61–1.67 (m, 5H, H-2, H-3 and H-2′a), 1.77 (m, 1H, H-3′a), 2.78 (br s, 1H, OH), 3.38 (dt, J = 9.8 Hz, 5.6 Hz, 1H, H-4b), 3.47 (m, 1H, H-5′b), 3.60 (m, 2H, H-1), 3,74 (dt, J = 9.8 Hz, 5.8 Hz, 1H, H-4a), 3.82 (m, 1H, H-5′a), 4.56 (t, J = 3.5 Hz, 1H, H-1′). ^{13}C NMR δ 19.39 (C-3′),



Scheme 1 Synthesis of pinolenic acid ethyl ester

25.25 (C-4′), 26.31 (C-3), 29.79 (C-2), 30.48 (C-2′), 62.15 (C-5′), 62.33 (C-1), 67.35 (C-4), 98.70 (C-1′).

*4-(Tetrahydropyran-2-yloxy)butanal (**5**)*

4-(Tetrahydropyran-2-yloxy)butanol (**4**) (20 g, 0.12 mol) was added to a suspension of NACAA [11] (nicotinic acid chromic acid mixed anhydride betaine) (66 g, 280 mmol) in CH_2Cl_2 (200 mL) and pyridine (45 mL). After vigorous stirring at ambient temperature for 1 h, the reaction mixture was run through a column of silica gel (70–230 mesh). The eluate was monitored by TLC (CH_2Cl_2/EtOAc 5:1) and the fractions containing the product collected to give 10.2 g (50%) of **5** as an oil. ^{1}H NMR δ 1.45–1.58 (m, 4H, H-3′b, H-4′b, H-2′b and H-4′a), 1.65 (m, 1H, H-2′a), 1.75 (m, 1H, H-3′a), 1.96 (quintet, $J = 6.6$ Hz, 2H, H-3), 2.50 (m, 2H, H-2), 3.38 (dt, $J = 9.7$ Hz, 6.1 Hz, 1H, H-4b), 3.46 (m, 1H, H-5′b), 3.74 (dt, $J = 9.7$ Hz, 6.2 Hz,1H, H-4a), 3.78 (m, 1H, H-5′a), 4.52 (dd, $J = 4.4$ Hz, 2,7 Hz, 1H, H-1′), 9.75 (t, $J = 1.7$ Hz, 1H, H-1). ^{13}C NMR δ 19.36 (C-3′), 22.54 (C-3), 25.30 (C-4′), 30.46 (C-2′), 40.97 (C-2), 62.14 (C-5′), 66.27 (C-4), 98.72 (C-1′), 202.19 (C-1).

*9-Oxo-5Z-nonenoic Acid Ethyl Ester (**6**)*

The triphenylphosphonium salt from ethyl 5-bromopentanoate **7** (35.0 g, 74 mmol), K_2CO_3 (10.0 g, 72 mmol), the aldehyde **5** (10.0 g, 58.0 mmol), 1,4-dioxane (60 mL) and H_2O (1.5 mL) were refluxed with stirring under Ar for 20 h. The solvent was evaporated under reduced pressure, and the residue extracted with 5% ethyl acetate in CH_2Cl_2. Flash chromatography of the concentrate in a silica gel column (elution with 5% ethyl acetate in CH_2Cl_2) yielded 14.8 g of crude 9-(tetrahydropyran-2-yloxy)-5*Z*-nonenoic acid ethyl ester **8** containing *ca.* 15% of the 5*E*-isomer (by ^{1}H-integrals). This mixture was treated with 80 mL of acetone and 30 mL of 3% H_2SO_4 in H_2O at 50 °C for 3 h. After neutralization with 10% $NaHCO_3$ and evaporation of acetone, the residue was extracted with ethyl acetate (2 × 50 mL), dried on Na_2SO_4 and solvent evaporated to yield 12.8 g of crude 9-hydroxy-5-nonenoic acid ethyl ester. This was added to a suspension of NACAA (18 g) in CH_2Cl_2 (60 mL) and pyridine (13 mL) to yield 7.4 g of crude **6**. Flash chromatography (silica gel, elution with 5% ethyl acetate in CH_2Cl_2) yielded 1.88 g (overall 16.5% from **5**) of **6** containing *ca* 15% of the 5*E*-isomer. ^{1}H NMR δ 1.26 (t, $J = 7.1$ Hz, 3H, H-2′), 1.70 (quintet, $J = 7.4$ Hz, 2H, H-3), 2.10 (td, $J = 7.4$ Hz, 6.6 Hz, 2H, H-4), 2.36 (td, $J = 7.2$ Hz, 6.7 Hz, 2H, H-7), 2.30 (t, $J = 7.4$ Hz, 2H, H-2), 2.49 (td, $J = 7.2$ Hz, 1.6 Hz, 2H, H-8), 4.13 (q, $J = 7.1$ Hz, 2H, H-1′), 5.38 (dt, $J = 10.7$ Hz, 6.7 Hz, 1H, H-6), 5.41 (dt, $J = 10.7$ Hz, 6.6 Hz, 1H, H-5), 9.77 (t, $J = 1.6$ Hz, 1H, H-9). ^{13}C NMR δ 14.09 (C-2′), 19.92 (C-3), 24.62 (C-4), 26.41 (C-7), 33.56 (C-2), 43.61 (C-8), 60.09 (C-1′), 128.20 (C-6), 130.14 (C-5), 174.28 (C-1), 201.82 (C-9). Anal. calc. for $C_{11}H_{18}O_3$, C 66.6, H 9.2; found, C 66.9, H 9.1.

*Propylene-1,3-bis(triphenylphosphonium dibromide) (**2**)*

1,3-Dibromopropane (16.0 g, 0.080 mol), triphenylphosphine (40.5 g, 0.15 mol) and 1.0 g of K_2CO_3 were refluxed in acetonitrile (200 mL) for 2 days under Ar to give 31.5 g (54%) of white crystals of **2**.

*Pinolenic Acid Ethyl Ester (**1**)*

The bisphosphonium salt **2** (305 mg, 0.42 mmol), powdered K_2CO_3 (120 mg, 0.87 mmol), the aldehyde **6** (83 mg, 0.42 mmol), hexanal (110 mg, 1.10 mmol), 1,4-dioxane (1.5 mL) and H_2O (25 μL) were heated and stirred under Ar at 105 °C in an oil bath for 20 h. The solvent was evaporated under reduced pressure, and the residue extracted with hexane (15 mL) and filtered. Flash chromatography of the concentrate (silica gel, elution with hexane/CH_2Cl_2 1:2) yielded 19.4 mg (15%) of crude **1**, containing a small amount of hexanal aldol condensation product (R_f approximately the same as of ethyl pinolenate). This by-product is easily removed by argentation chromatography on $AgNO_3$ impregnated silica gel (CH_2Cl_2/ethyl acetate 2:1). Elution was monitored by ordinary TLC and, when all esters had eluted, a second analysis of fractions was carried out on $AgNO_3$ impregnated TLC plates. The later fractions giving only one spot on an $AgNO_3$ TLC plate (R_f ca. 0.18) were combined, the solvent evaporated under reduced pressure and the residue filtered through a pad of silica gel (elution with hexane/CH_2Cl_2 1:1) to remove silver residues from the preparate. The yield of pure **1b** (99% by GC and ^{1}H NMR) was 12.0 mg (9.3%). ^{1}H NMR δ 0.90 (t, $J = 6.9$ Hz, 3H, H-18), 1.26 (t, $J = 7.1$ Hz, 3H, H-2′), 1.30 (m, 2H, H-16), 1.31 (m, 2H, H-17), 1.36 (quintet, $J = 7.1$ Hz, 2H H-15), 1.70 (quintet, $J = 7.4$ Hz, 2H, H-3), 2.06 (q, $J = 7.1$ Hz, 2H, H-4), 2.09 (q, $J = 7.0$ Hz, 2H, H-14), 2.11 (m, 4H, H-7 and H-8), 2.31 (t, $J = 7.5$ Hz, 2H, H-2), 2.79 (br t, $J = 6.2$ Hz, 2H, H-11), 4.13 (t, $J = 7.1$ Hz, 2H H-2′), 5.33 (dtt, $J = 10.7$, 7.1, 1.5 Hz, 1H, H-12), 5.36 (m, 1H, H-5), 5.37 (m, 1H, H-10), 5.38 (m, 2H, H-9 and H-13), 5.42 (dtt, $J = 10.9$, 6.8, 1.4 Hz, 1H, H-6). ^{13}C NMR δ 14.05 (C-18), 14.24 (C-2′), 22.56 (C-17), 24.89 (C-3), 25.67 (C-11), 26.60 (C-14), 27.20 (C-4), 27.26 and 27.29 (C-7 and C-8), 29.32 (C-15), 31.51 (C-16), 33.75 (C-2), 60.19 (C-1′), 127.78 (C-12), 128.57 (C-10), 128.99 (C-5), 129.25 (C-9), 130.21 (C-6), 130.30 (C-13), 173.67 (C-1). HRMS calc. for $C_{20}H_{34}O_2$ 306.2559, found 306.2572.

*12-Oxododecanoic Acid Methyl Ester (**9**)*

12-Hydroxydodecanoic acid was prepared by reduction [12] of commercial (Fluka) dodecadienoic acid. 12-Hydroxydodecanoic acid was then oxidized with NACAA [(as above for 4-(tetrahydropyran-2-yloxy)butanal 5)] to give the aldehyde ester 9 in 38% yield. ^{1}H NMR δ 1.25 (m, 12 H, H-4, H-5, H-6, H-7, H-8 and H-9), 1.59 (sextet, $J = 7.1$ Hz, 4 H, H-3 and H-10), 2.27 (t, $J = 7.6$ Hz, 2H, H-2), 2.39 (td, $J = 7.4$ Hz, 1.8 Hz, 2H, H-11), 3.64 (s, 3H, H-1′), 9.74 (t, $J = 1.8$ Hz, 1H, H-12). ^{13}C NMR δ 21.98 (C-10), 24.85 (C-.3), 29.02, 29.05, 29.11, 29.22, 29.24 (2C) (C-4–C-9), 34.00 (C-2), 43.81 (C-11), 51.32 (C-1′), 174.19 (C-1), 202.75 (C-12).

*12Z,15Z-Octadecadienoic Acid Methyl Ester (**3**)*

The bisphosphonium salt **2** (7.0 g, 9.6 mmol), powdered K_2CO_3 (5 g, 36 mmol), the aldehyde **9** (2 g, 8.77 mmol), propanal (5 g, 8.6 mmol), 1,4-dioxane (60 mL) and H_2O (0.25 mL) were stirred in an autoclave under Ar at 100 °C. Flash and argentation chromatography gave 76 mg (10%) of **3**. ^{1}H NMR δ 0.97 (t, $J = 7.6$ Hz, 3H, H-18), 1.27 (m, 12H, H-4, H-5, H-6, H-7, H-8 and H-9), 1.33 (m, 2H, H-10), 1.52 (quintet, $J = 7.3$ Hz, 2H, H-3), 2.05 (q, $J = 7.2$ Hz, 2H, H-11), 2.07 (quintet, $J = 7.6$ Hz, 2H, H-17), 2.30 (t, $J = 7.6$ Hz, 2H, H-2), 2.77 (t, $J = 6.8$ Hz, 2H, H-14), 3.66 (s, 3H, H-1′), 5.33 (m, 1H, H-15), 5.36 (m, 1H, H-13), 5.38 (m, 1H, H-12), 5.39 (m, 1H, H-16). ^{13}C NMR δ 14.23 (C-18), 20.49 (C-17), 24.92 (C-3), 25.49 (C-14), 27.17 (C-11), 29.12, 29.22, 29.25, 29.40, 29.45, 29.51 (C-4, C-5, C-6, C-7, C-8 and C-9), 29.62 (C-10), 34.07 (C-2), 51.35 (C-1′), 127.39 (C-15), 127.92 (C-13), 130.13 (C-12), 131.69 (C-16), 174.25 (C-1). HRMS calc. for $C_{19}H_{34}O_2$ 294.2559, found 294.2570.

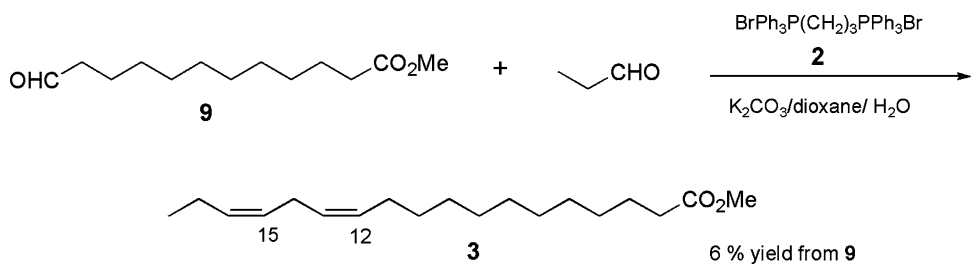
Results and Discussion

A symmetric bisphosphonium ylide, undergoing a double Wittig reaction between two different aldehydes (R^1CHO and R^2CHO), all used in equimolar quantities, may in principle form three different dienes R^1CH=CH- - -CH=CHR^1, R^1CH=CH- - -CH=CHR^2 and R^2CH=CH- - -CH=CHR^2 (ignoring geometric isomers) in a 1:2:1 ratio, respectively. Assuming equal reaction rates, the maximal yield for the mixed product is just 50%, and the entire concept may therefore appear somewhat wasteful. However, the aqueous potassium carbonate-based procedure is very simple and may readily be scaled up.

Furthermore, if the two aldehydes are chosen so that one is a simple alkanal, while the other carries an ester group at the remote end of the chain, the three products (a hydrocarbon, a monoester and a diester) possess widely differing polarities, which may be readily exploited in a chromatographic isolation of the individual products. Alternatively, one may try to improve the yield of a desired product by introducing one aldehyde first and then after a time the second. In our experience this approach [5] affords only rather modest improvements.

4-(Tetrahydropyran-2-yloxy)butanal **5**, Scheme 1, prepared from the corresponding diol by mono-THP ether formation, followed by oxidation using the NACAA reagent [11], was reacted with the phosphonium salt from ethyl 5-bromo-pentanoate under the K_2CO_3–aqueous dioxane conditions to give 9-oxo-5*Z*-nonenoic acid ethyl ester **6** with a *Z*:*E* selectivity ratio of 4:1 (16.5 % from **5**). This mixture was used as such for the subsequent step, the minor impurities of *E*-isomers being removed by argentation chromatography in the final purification. Better *Z*-selectivity was observed in the one pot double Wittig reaction with the bisphosphonium salt **2**, propanal and the aldehyde ester **5**, there being less than 10% of *E*-isomers (by ^{1}H-integrals) formed. Ethyl pinolenate **1b** was obtained from the aldo ester **6** in 15% yield (as explained above, the maximal theoretical yield of **1b** is 50%). Ethyl pinolenate was purified by argentation chromatography, and its structural purity was established by ^{1}H-, ^{13}C-NMR and 2D-NMR spectroscopy.

For comparison, an authentic reference sample of **1a** was also separated from tall oil fatty acids [13] using urea crystallization. Although the concentrate, 60% in pinolenic acid, contains about 5% of 5*Z*,11*Z*,14*Z*-eicosatrienoic acid (sciadonic acid), repeated argentation chromatography of esterified material gave pure (99.7% by GC) **1b**, with spectral data and other properties identical with synthetic ethyl pinolenate.



Scheme 2 Synthesis of methyl 12*Z*,15*Z*-octadecadienoate

The double Wittig technique was also applied to the synthesis of methyl 12*Z*,15*Z*-octadecadienoate **3** (Scheme 2). The aldehyde ester **9** was obtained from the corresponding ω-hydroxy ester by NACAA oxidation. The K_2CO_3–H_2O phase transfer double Wittig reaction furnished **3** in 10% yield, containing less than 10% of *E* isomers (by ^{1}H-integrals).

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