PREPARATION OF METHYL 8c,11c-OCTADECADIENOATE-17,17,18,18-d_4 AND METHYL 8c,11c,14c-OCTADECATRIENOATE-17,17,18,18-d_4

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SUMMARY

Multi-gram quantities of methyl 8c,11c-octadecadienoate-17,17,18,18-d_4 and methyl 8c,11c,14c-octadecatrienoate-17,17,18,18-d_4 were synthesized for use in human metabolism studies. The deuterium atoms were incorporated using tris(triphenylphosphine)chlororhodium (I) catalyst and deuterium gas. The double bonds in the Δ11 and Δ14 positions were incorporated by acetylenic coupling. The double bond in the Δ8 position was introduced by the Wittig coupling of the mono- or di-unsaturated triphenyl phosphonium halide to 7-formylheptanoate. The 15-25% trans isomers formed by the Wittig coupling reaction were removed by silver resin chromatography. Overall yields were 15% for the diene ester (an 8-step synthesis) and 12% for the triene (a 12-step synthesis). Both compounds were shown to have an isotopic purity of > 97% d_4.

Key Words: Deuterium, fatty acids, Wittig reaction, methyl 8c,11c-octadecadienoate, methyl 8c,11c,14c-octadecatrienoate

INTRODUCTION

Synthesis of methyl 8c,11c-octadecadienoate-17,17,18,18-d_4 (8c,11c-18:2-d_4) and methyl 8c,11c,14c-octadecatrienoate-17,17,18,18-d_4 (8c,11c,14c-18:3-d_4) was undertaken as part of a study to investigate the metabolism of isomeric fats in humans. The 8c,11c-18:2 fatty acid is an intermediate in the conversion of palmitoleic acid (9c-16:1) to 4c,7c,10c,13c-20:4 which is an isomer of arachidonic acid (1). The 8c,11c,14c-18:3 fatty acid has been examined for essential fatty acid activity (2), and its incorporation into liver mitochondria has been measured (3).

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Investigation of the interconversion of these fatty acids in human studies required the preparation of multi-gram quantities of these polyunsaturated fatty acids. Many reviews and papers report the syntheses of both labelled (4,5) and unlabelled (6-10) polyunsaturated fats. We utilized a variation of Bergelson's (11) procedure in which the double bond in the Δ8 position is incorporated by the Wittig reaction and the other double bonds are introduced by acetylenic coupling followed by reduction with Lindlar's catalyst. While our yields were not optimized, overall yields were better than previously reported syntheses (6,8). This higher yield was accomplished despite the extra synthetic steps required to incorporate the deuterium atoms. The deuterium atoms were located in the 17 and 18 positions to minimize potential isotope effects.

EXPERIMENTAL

Instruments. Isotopic purity and deuterium distribution (12) were determined with a Finnigan gas chromatograph (GC)/EI-CI mass spectrograph (MS) equipped with a 30 m x .319 mm DB-1 capillary column by utilizing helium (He) carrier gas. Percentages of cis and trans were determined with a Packard Model 428 gas chromatograph equipped with a 100 m x 0.22 mm SP2560 capillary column and either a 180 x 0.3 cm glass column packed with 10% Carbowax 20 M/TPA (for analysis of 1-iodopropane-d_4) or a 300 x 1.0 cm glass column packed with 3% EGSS-X (for analysis of other starting materials and intermediates). The instrument was equipped with flame ionization detectors and He was used as carrier gas. The preparation of silver resin columns (13,14) and the separation of fatty acid isomers by use of mixed solvents (15) have been described previously. ^{13}C-NMR spectra were obtained with a Bruker WM300WB pulsed Fourier transform spectrometer operating at 75.5 MHz. Except where indicated, solvents were removed on a rotary evaporator.

Reagents. The following reagents were used as received: 5-hexyn-1-ol and 3-butyn-1-ol (Farchan), dihydropyran, Lindlar catalyst, triphenylphosphine, cyclooctene, 2-propyn-1-ol, ethyl magnesium bromide (2 M in hexane) and n-butyl

lithium (2.6 M in hexane) [All Aldrich], tris (triphenylphosphine)chlororhodium (I) (Strem), and deuterium gas (98.9%) (Matheson). Other chemicals were "ACS Certified" and, unless specified, were used without further purification. The molarity of the n-butyl lithium and ethylmagnesium bromide solutions was determined by the method of Watson and Eastham (16).

methyl 7-formylheptanoate, 1. Compound 1 was prepared by ozonolysis of cyclooctene (68% yield) (17) and esterification of the resultant aldehydic acid via the acetal-ester intermediate (90% overall yield) (18). (aldehydic acid m.p. = 42-44°C, b.p. = 130-150°C/0.1 mmHg; aldehydic ester b.p. = 76-78°C/0.1 mmHg).

2-(5-hexynyloxy)tetrahydropyran, 2. Compound 2 was prepared as described previously (19) in 96% yield.

2-(hexyloxy-5,5,6,6-d_4)tetrahydropyran, 3. Compound 3 was prepared from 2 (48.0 g; 0.26 mol) in a manner analagous to the 5-carbon tetrahydropyranyl (THP) ether as described previously (20) in 93% yield (99% pure).

1-iodohexane-5,5,6,6-d_4, 4. Compound 4 was prepared from 3 (46.0 g; 0.24 mol) in 82% yield as described previously for the 5-carbon analogue (20) (b.p. = 56-58°C/3.7 mmHg).

3-decyn-1-ol-9,9,10,10-d_4, 5. Liquid ammonia (NH_3; 600 mL) was condensed into a 3-necked, 1 L round-bottomed flask equipped with N_2 inlet, thermometer, mechanical stirrer, NH_3 inlet, and an outlet with a dry-ice/isopropyl alcohol trap. A dry-ice/isopropyl alcohol bath was used to maintain the temperature at -35 to -40°C. Ferric nitrate (0.2 g) was added and the slurry was stirred for 45 minutes. Lithium metal (3.26 g:0.47 mol) was added in ca.0.5 g pieces over 20 minutes and then stirred for 1 hour. After ca. 0.5 hour lithium amide formation was complete (the color of the slurry changed from blue-black to gray). 3-butyne-1-ol (16.5 g:0.24 mol) was added dropwise over 0.5 hour, the reaction was stirred for 1 hour and compound 4 (34.0 g: 0.16 mol) was added dropwise over 0.5 hour. The slurry was allowed to warm to room temperature and stirred overnight. The thick slurry was heated to 35°C with a water bath

and flushed with N_2 to remove any remaining NH_3 (1.5 hrs), cooled to 15°C and then 250 mL of H_2O was added dropwise over a 20 minute period. The reaction mixture was transferred to a 1 L separatory funnel with 250 mL Et_2O, the layers were separated and the water layer was acidified with 5 N H_2SO_4 and extracted with Et_2O. The Et_2O layers were combined and washed with saturated NH_4Cl, 5% sulfuric acid and H_2O, respectively. The Et_2O layer was dried over Na_2SO_4, vacuum filtered through a Buchner funnel and the Et_2O was removed. The residue was distilled through a 15 cm Vigreux column. (65-69°C/0.06 mmHg) to yield compound 5 (19.99 g; 80% yield).

3-decen-1-ol-9,9,10,10-d_4, 6. Compound 5 (17.0 g:0.108 mol) was reduced in petroleum ether (PE) to 6 using Lindlar's catalyst (10.0 g total) and quinoline (0.9 mL total). Hydrogen gas uptake was very slow. The same batch of compound 5 was reduced three times (utilizing 3.3 g Lindlar and 0.3 g quinoline each time), the slurry being filtered through Celite and washed with 5% HCl and H_2O after each reduction. Final removal of the PE yielded 17.1 g of 6 (94% yield) consisting of 93.9% 6, 3.2% 5 and 2.5% of further reduced material.

1-bromo-3-decene-9,9,10,10-d_4, 7. Triphenylphosphine (27.9 g:0.106 mol) was added to a 250 ml, 3-necked round-bottomed flask equipped with N_2 inlet, thermometer, mechanical stirrer and addition funnel, and containing 100 mL methylene chloride (CH_2Cl_2). Bromine (17.0 g:0.106 mol) was added dropwise over 0.5 hour while the temperature was maintained at ca. 15°C by an ice bath. The slurry was stirred for 0.5 hour and compound 6 (17.0 g:0.106 mol) was added dropwise over 0.5 hour. Stirring was continued for two more hours. The homogeneous reaction mixture was diluted with 300 mL PE (to precipitate the triphenylphosphine oxide) and vacuum filtered through a Buchner funnel, and the solvents were removed. The residue was chromatographed with PE through a 2.5 x 60 cm column containing 70 g silica gel, and the solvent was again removed. The residue was distilled through a short-path column to yield 19.89 g of 7 (99% pure; 89% yield).

1-dec-3-enyl-9,9,10,10-d_4-triphenylphosphonium bromide, 8. Compound 7 (19.8 g; 0.080 mol), triphenylphosphine (29.7 g; 0.113 mol) and 200 mL acetonitrile (ACN) were combined in a 500 mL, 1-necked round-bottomed flask equipped with an N_2 inlet and a reflux condenser. The slurry was heated by an oil bath and stirred by a magnetic stirrer. The solution was refluxed at 80°C for 46 hours. The reaction mixture was cooled to room temperature and the ACN removed. The viscous residue was triturated with 4 x 250 mL portions of diethyl ether until crystallization occurred. The white, crystalline solid was removed by filtration and dried in a vacuum dessicator (39.9 g; 93% yield). The melting point of 8 was 58-62°C.

methyl 8c,11c-octadecadienoate-17,17,18,18-d_4, 9. The 8,11 isomer was prepared in a manner similar to the previously reported 9c,12c-18:2 compound (20). Compound 8 (30.0 g; 0.062 mol) was reacted with compound 1 (12.77 g; 0.074 mol) in 100 ml Et_2O utilizing sodium methoxide (3.34 g; 0.062 mol). After work-up, the residue was chromatographed with CH_3OH on a 91% silver resin column giving 6.3 g 9 (34% yield).

2-(2-propynyloxy)tetrahydropyran, 11. The THP ether was prepared as previously described for the 5-carbon THP analogue (20) in 85% yield (98% pure). Compound 11 had a boiling point of 43-44°C at 15 mmHg.

2-(propyloxy-2,2,3,3-d_4)tetrahydropyran, 12. Compound 12 was prepared as previously described for the 5-carbon THP analogue (20) in 69% yield. Some product was lost during the rotary evaporation step due to its high volatility. Compound 12 was distilled at 32-38°C/15 mmHg.

1-propanol-2,2,3,3-d_4, 13. The alcohol was prepared by transacetalization. Compound 12 (118 g; 0.80 mol), 1-octanol (280 g; 2.15 moles) and 1.0 g of p-toluenesulfonic acid were mixed in a 1 L, 3-necked round-bottomed flask equipped with an N_2 inlet, a reflux condenser and a magnetic stirrer. The reaction mixture was heated to 60°C by a heating mantle, and stirred for 1 hour. The reflux condenser was replaced with a 15 cm Vigreux column and compound 13 was removed by distillation to yield 63.2 g of product (76% pure; b.p. 94-96°C/760 mmHg) for a yield of 94%.

1-iodopropane-2,2,3,3-d_4, 14. Compound 14 was prepared from 13 (63.2 g (76% pure); 0.74 mol) as previously described for 2-(pentyloxy-3,3,4,4-d_4) tetrahydropyran (20) in 80% yield. However, the Et_2O was removed by distillation through a 30 cm Vigreux column. Compound 14 (103.0 g; 99 + % pure) was distilled at 94-100°C/760 mmHg.

2-hexyn-1-ol-5,5,6,6-d_4, 15. Compound 14 (45.46 g; 0.26 mol) was reacted with 2-propyn-1-ol (20.1 g; 0.35 mol) in a manner similar to the preparation of compound 5 to yield 24.00 g (93% pure; 87% yield) of 15 (b.p. = 75-78°C/ 17 mmHg).

1-bromo-2-hexyne-5,5,6,6-d_4, 16. See preparation of 7. The halide was synthesized by the reaction of compound 15 (24.0 g; 0.235 mol) with triphenylphosphine (62.88 g; 0.24 mol) and bromine (38.4 g; 0.24 mol). Work-up and distillation afforded 34.3 g (88% yield) of 16 (b.p. 75-83°C/35mmHg).

3,6 decadiyn-1-ol-9,9,10,10-d_4, 17. A 3-necked round-bottomed flask (1L) equipped with an N_2 inlet, thermometer, mechanical stirrer, septum and reflux condenser was utilized. Tetrahydrofuran (THF; 400 mL) and 3-butyn-1-ol (20.05 g; 0.286 mol) were added and cooled to 10°C in an ice bath. A solution of ethylmagnesium bromide in hexane (1.95 molar; 294 mL) was added dropwise via syringe over 1 hour while the temperature was maintained at 10-15°C. The slurry was warmed to room temperature and stirred for 2.5 hrs, 0.7 g of cuprous chloride was added, and stirring was continued for another hour. Compound 16 (31.5 g; 0.191 mol) in 40 mL THF was added dropwise over 30 minutes at 10°C. The mixture was refluxed at 67°C overnight, cooled by an ice bath and acidified with 2N sulfuric acid. The mixture was extracted three times with Et_2O and the Et_2O fractions were combined and washed with NH_4Cl and H_2O and dried over Na_2SO_4. The Na_2SO_4 was removed by filtration and the Et_2O by evaporation. The residue was chromatographed on a 5 X 40 cm glass column packed with 150 g silica gel. (100% PE ⟶ 75%PE/25% Et_2O). Solvent removal from the eluate yielded 32.3 g residue which was then distilled through a short-path column to yield 22.9 g (92% pure; 72% yield) of 17 (b.p. = 94-96°C/0.3 mmHg).

3,6 decadien-1-ol-9,9,10,10-d_4, 18. See compound 6. The Lindlar-catalyzed

reduction of 17 proceeded very slowly. Even when no poison such as quinoline was present, a 22.9 g (0.138 mol) sample of 17 still required the addition of 4 x 5 g batches of "catalyst" and 8 hours of stirring for reduction to be complete. The final product (26.05 g) contained 96% 18, 1% 17 and 2.5% of further reduced material.

1-bromo-3,6-decadiene-9,9,10,10-d_4, 19. See synthesis of 7. Compound 18 (26.05 g; 0.165 mol) was reacted with triphenylphosphine (44.92 g; 0.17 mol) and bromine (27.43 g; 0.171 mol). Work-up and distillation through a short path column resulted in 30.24 g (96% pure; 84% yield) of 19 (b.p. = 65-70/0.2 mmHg).

1-iodo-3,6-decadiene-9,9,10,10-d_4, 20. Sodium iodide (12.73 g; .085 mol), 100 mL acetone and 19 (15.0 g; .068 mol) were combined in a 250 mL round-bottomed flask equipped with an N_2 inlet, reflux condenser and magnetic stirrer and heated by an oil bath. The reaction mixture was refluxed for 1 hour, then cooled to room temperature. The sodium bromide precipitate was removed by filtration and the solvent by evaporation. The residue (91% pure; 18.44 g) 20 was used in the next reaction without further purification.

1-deca-3,6-dienyl-9,9,10,10-d_4-triphenylphosphonium iodide, 21. See compound 8. Compound 20 (18.44 g; 0.065 mol) was refluxed with triphenylphosphine (20.44 g; 0.078 mol) for 16 hours. Work-up yielded 33.20 g (98% yield) of 21 (m.p. = 100-102°C).

methyl 8c,11c,14c-octadecatrienoate-17,17,18,18-d_4, 22. Compound 21 (15.0 g; 0.028 mol) was dissolved in 150 mL THF in a 250 mL, 3-necked round-bottomed flask equipped with an N_2 inlet, thermometer, mechanical stirrer, and syringe septum. The solution was cooled to 10°C by an ice bath and n-BuLi (2.6 M in hexane; 0.031 mol) was added dropwise by syringe over 20 minutes at 11-14°C. The deep red-brown solution was stirred for 1 hour at room temperature, cooled to 6°C and compound 1 (6.41 g; 0.037 mol) was added dropwise by syringe over 20 minutes. The reaction mixture was stirred for 2 hours at room temperature, 100 mL saturated NaCl solution was added and the mixture was

extracted several times with Et_2O. The Et_2O layers were combined, dried over Na_2SO_4, vacuum filtered and the Et_2O was removed. The residue was chromatographed on a 2.5 x 30 cm glass colum packed with 25 g silica gel and was eluted with 100% PE. After removal of the solvent, trans isomers were removed by silver resin chromatography on a 47 x 450 mm Michel-Miller column packed with 100% Ag^+/Na^+ resin (100/200 mesh). Samples (3-4 g each) were eluted with 5% ACN in methanol. Work-up resulted in 4.6 g (49% yield) of 22 with a purity of >98%.

RESULTS AND DISCUSSION

The synthetic sequences for the 8c,11c and 8c,11c,14c isomers are given in Figure 1. The yields for each step are listed in brackets. The yields for compounds 18—>22 were not listed individually because the final purification was not made until the silver resin chromatography step.

Several points of interest were noted in these synthetic sequences. The direct conversion of $C_3H_3d_4OTHP$ to $C_3H_3d_4I$ (12—>14) with H_3PO_4/KI gave yields of only 25-35%, perhaps due, in part, to problems in isolation of the iodide from the THP polymerization by-products. Synthesis of the iodide via the alcohol intermediate (12—>13—>14) provided a higher over-all yield (75%). Ph_3PBr_2 was better for the preparation of acetylenic bromides from the corresponding alcohols than PBr_3; yields were usually 5-10% higher. Reduction of acetylenic alcohols 5 and 17 using Lindlar catalyst was very slow, perhaps due to the presence of poisons to palladium. Even when no quinoline was used, an almost 1 to 1 ratio (w/w) of "catalyst" to substrate was necessary to reduce diynol 17. Use of the iodide for preparation of the phosphonium salt and subsequent Wittig coupling provided several advantages over the bromide. Preparation of the triphenylalkenylphosphonium bromide 7 required 46 hours of reflux, while the corresponding iodide 21 required only 1/3 of that time. Upon isolation, the phosphonium iodide 21 remained an easily workable, white, crystalline solid while the corresponding bromide was sticky and became a glass at room temperature. When these phosphonium compounds were coupled by the Wittig reaction to the C_8 aldehydic ester, the bromide provided yields of

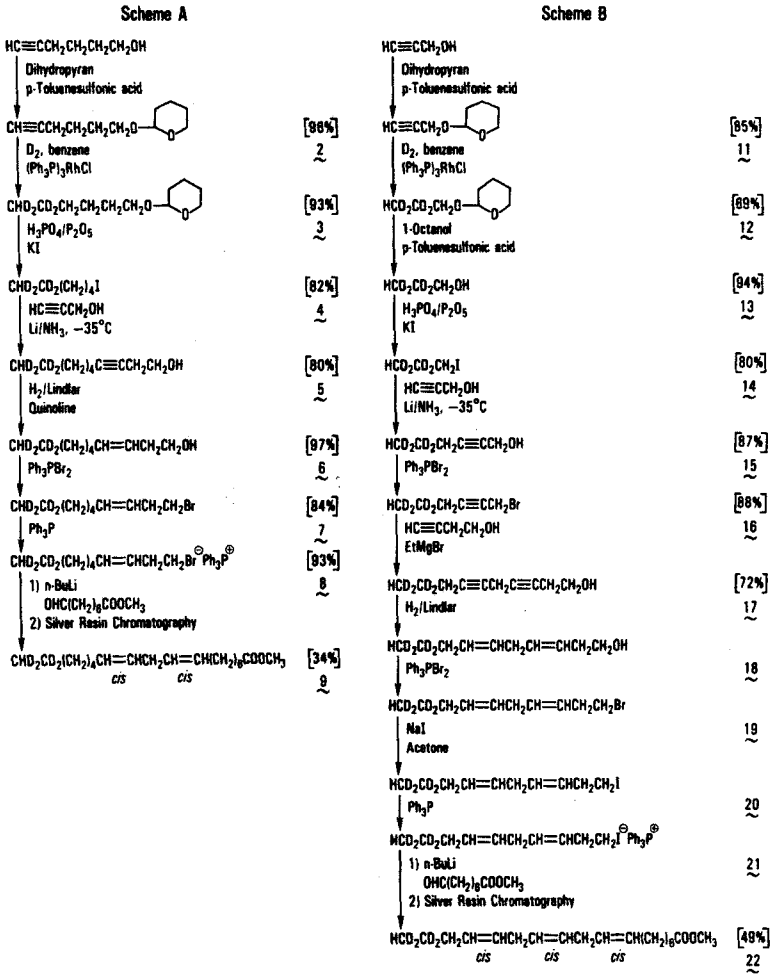

Figure 1. Synthetic schemes for Methyl 8c,11c-Octadecadienoate-17,17,18,18-d_4 (Scheme A) and Methyl 8c,11c,14c-Octadecatrienoate-17,17,18,18-d_4 (Scheme B).

10-15% of 22 while the iodide resulted in 49% 22. Our most consistent yields resulted when n-BuLi rather than $NaOCH_3$ was employed. Difficulties in obtaining pure sodium methoxide have always been a problem. The main advantage of $NaOCH_3$ is that only 5-8% trans isomer is produced during the Wittig coupling; n-BuLi generated 15-22% trans.

^{13}C-NMR Chemical Shifts for Methyl 8c,11c-Octadecadienoate- and 8c,11c,14c-Octadecatrienoate-17,17,18,18-d.[a]

Carbon	8c,11c	8c,11c,14c		Carbon	8c,11c	8c,11c,14c	
	Obs	Lit (21,22)	Obs		Obs	Lit (21,22)	Obs
1	174.12	174.30	174.30	10	25.71	25.75	25.80
2	34.14	34.20	34.22	11	128.19	128.35	128.40
3	24.98	25.00	25.06	12	129.93	128.45	128.54
4	28.96	29.15	29.18	13	27.31[b]	25.75	25.80
5	29.09	29.00	29.01	14	29.69[b]	128.05	128.05
6	29.49	29.55	29.56	15	29.09[b]	130.25	130.31
7	27.20	27.25	27.30	16	31.55[b]	29.45	29.56
8	130.24	130.25	130.31	17	----	22.90	----
9	127.93	128.05	128.05	18	----	13.85	----

[a] ppm downfield from $(CH_3)_4$ Si

[b] Tentative assignments

TABLE 1

Table I lists the ^{13}C-NMR chemical shifts recorded for the 8c,11c-18:2 and 8c,11c,14c-18:3 isomers. Our results for the 8c,11c,14c-18:3 isomer compare favorably with those reported in the literature (21, 22). The 8c,11c-18:2 isomer has not previously been examined by ^{13}C-NMR. The chemical shifts for C-7, C-10, and C-13 are indicative of carbons alpha to 1 or 2 double bonds. Since the deuterium atoms were located on carbons 17 and 18, no chemical shifts were noted for these carbons (23).

The deuterium distribution of the intermediates and final products are listed in Table II. Very little change was noted between the THP ethers and the final fatty ester products. Wilkinson's catalyst $[(Ph_3P)_3RhCl]$ promoted very little scattering during incorporation of the deuterium atoms and the synthetic sequences employed had no effect on the deuterium distribution.

Mass Analyses for Deuterium

Compound (No.)[a]	Number of deuterium atoms (%) 1	2	3	4	5	6	7	Average no. of deuterium atoms per molecule
2-(Hexyloxy-5,5,6,6-d_4)-tetrahydropyran (3)	0.1	0.1	1.9	97.8	0.1	0.0	0.0	3.98
Methyl 8c,11c-octadecadienoate-d_4 (9)	---	0.1	2.0	97.9	---	---	0.1	3.99
2-(Propyloxy-2,2,3,3-d_4)-tetrahydropyran (12)	---	0.1	1.7	97.0	1.1	---	0.1	4.00
methyl 8c,11c,14c-octadecatrienoate-d_4 (22)	---	0.1	1.6	97.2	1.0	---	0.1	4.00

[a] See Fig. 1.

TABLE 2

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