A New Method of Synthesizing 7-(2-Hydroxy-5-oxo-1-cyclopentenyl)heptanoic Acid and Related Compounds

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A useful prostanoid synthon, 7-(2-hydroxy-5-oxo-1-cyclopentenyl)heptanoic acid (**3**), was prepared from commercially available cyclooctanone in two steps. Nine other related cyclopentanoids which are also valuable synthons for prostaglandins were obtained from **3** in reasonable yields via several steps. The procedure is capable of generating these useful synthons on a laboratory scale.

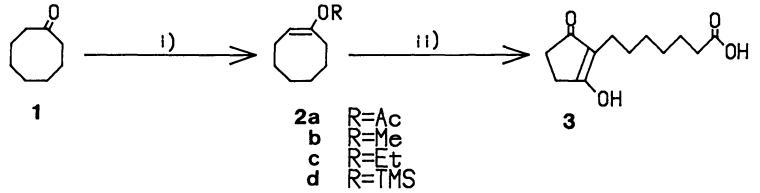
New methods of constructing of cyclopentane derivatives **3**—**7** are highly desirable, since these compounds have served as useful precursors in the synthesis of the naturally occurring prostaglandins and their congeners. In a preliminary report,[1] we described a synthesis of the 15-dehydroPGB$_1$ methyl ester from 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate (**4a**) and 1-octen-3-one. Furthermore, some prostaglandin derivatives have been prepared from methyl 7-(2-bromo-3-hydroxy-5-oxo-1-cyclopentenyl)-heptanoate (**5b**) in our laboratory.[2] PGB$_1$ was obtained[3] from 7-(2-hydroxy-5-oxo-1-cyclopentenyl)-heptanoic acid (**3**) and ω-chain moieties via a Grignard reaction as a key step. PGE$_1$, PGF$_1$ and their analogues were prepared from methyl 7-(3-hydroxy-5-oxo-1-cyclopentenyl)heptanoate (**6b**)[4] by means of a Michael-type reaction with several ω-chain moieties, and 11-deoxyPGE$_1$, 11-deoxyPGF$_1$, and their derivatives were derived from methyl 7-(5-oxo-1-cyclopentenyl)heptanoate (**7**).[5]

Recently, we reported[6] the use of the Cleisen condensation of dimethyl 4-oxo-1,12-undecanedioate in preparing methyl 7-(2-hydroxy-5-oxo-1-cyclopentenyl)heptanoate (**3'**). Novák et al.[7] converted **3'** to **4c** by phosphorus trichloride in a 70% yield, and dechlorinated **4c** with a silver–zinc couple to give **7** in a 62% yield. Compound **6b** was prepared via several steps from methyl 7-(2-oxocyclopentyl)heptanoate by Alvarez et al.[8] In this report, we will describe in detail an entirely novel method for the preparation of **3** and the derivation of other prostanoid synthons **4**—**7**.

The precursors **2** were prepared[9] from commercially available starting substances. The yields and conditions are shown in Scheme 1. 1-Cyclooctenyl acetate (**2a**) was allowed to react with succinic anhydride to afford 7-(2-hydroxy-5-oxo-1-cyclopentenyl)heptanoic acid (**3**). The reaction was achieved in 1,2-dichloroethane mediated by aluminium trichloride. The yield, via two steps from cyclooctanone (**1**), was 23%. Compound **3** was obtained from **2b**—**2d** under almost the same conditions (Table 1). The reaction may include Friedel–Crafts-type C–C bond-formations and acid-catalyzed hydrolysis with a C–C bond-cleavage.[10]

Succinyl dichloride instead of succinic anhydride could be available, but the yield of the product was lower. Aluminium tribromide could also mediate the reaction. As for the reaction solvents, the reaction occurred in 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, nitromethane, and nitrobenzene. When chlorotrimethylsilane was added to the reaction system, an improvement in its yield was observed.

Compound **3** was converted to **4a** in one pot by bromination with dibromotriphenylphosphorane and subsequent esterification with absolute methanol. 7-(2-Bromo-5-oxo-1-cyclopentenyl)heptanoic acid (**4b**) was obtained by a similar method without methanol. After the removal of the triphenylphosphine oxide by silica-gel chromatography, pure **4a** or **4b** was obtained in a 68 or 67% yield respectively. Methyl 7-(2-chloro-5-oxo-1-cyclopentenyl)heptanoate (**4c**) was obtained from **3** in a 55% yield by chlorination with phosphorus trichloride and by subsequent esterification. Methyl 7-(2-iodo-5-oxo-1-cyclopentenyl)-



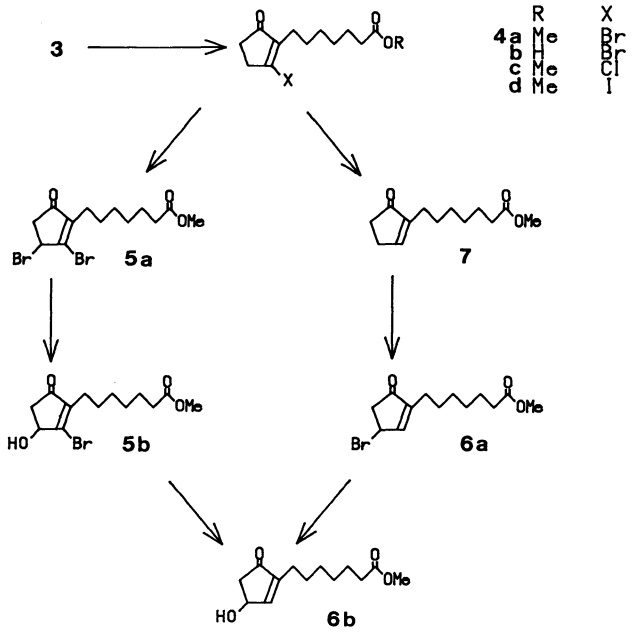
i) a) Isopropenyl acetate, p-TsOH, 115 °C, 95%; b) $HC(OMe)_3$, p-TsOH, r.t., 75%;
c) $HC(OEt)_3$, p-TsOH, r.t., 45%; d) TMSCl, Et_3N, DMF, reflux, 80%.
ii) Succinic anhydride, $AlCl_3$, 1,2-dichloroethane, 80 °C.

Scheme 1.

Table 1. Synthesis of **3** from **2**

	Starting material	Condition[a]				Yield/%	
		Catalyst	Solvent	Time/h	Temp/°C	Crude	Recrystal.
1	**2a** (R=Ac)	$AlCl_3$	A	28	80	20	18
2	**2a** (R=Ac)	$AlCl_3$	A	92	80	42	22
3[b]	**2a** (R=Ac)	$AlCl_3$	A	28	80	47	24
4	**2a** (R=Ac)	$AlCl_3$	B	24	110	31	16
5	**2a** (R=Ac)	$AlCl_3$	C	24	110	27	12
6	**2a** (R=Ac)	$AlCl_3$	D	3	100	16	10
7	**2a** (R=Ac)	$AlCl_3$	E	3	100	19	13
8	**2a** (R=Ac)	$AlBr_3$	A	28	80	20	18
9	**2b** (R=Me)	$AlCl_3$	A	63	80	27	17
10	**2c** (R=Et)	$AlCl_3$	A	92	80	16	10
11	**2d** (R=TMS)	$AlCl_3$	A	28	80	29	13

a) Catalyst: 1.95 equiv to **2**. Solvent: A: 1,2-dichloroethane; B: 1,1,2-trichloroethane; C: 1,1,2,2-tetrachloroethane; D: nitromethane; E: nitrobenzene. b) TMSCl was added (2.3 equiv to **2a**).



Scheme 2.

heptanoate (**4d**) was derived from methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate (**4a**) with sodium iodide quantitatively.

Methyl 7-(2,3-dibromo-5-oxo-1-cyclopentenyl)-heptanoate (**5a**) was obtained in a 51% yield from **4a** by allyl bromination with *N*-bromosuccinimide in tetrachloromethane. The substitution of the 3-bromo group of **5a** to the 3-hydroxyl group was achieved by the treatment of silver perchlorate, giving methyl 7-(2-bromo-3-hydroxy-5-oxo-1-cyclopentenyl)heptanoate (**5b**) in an 86% yield. Compound **5b** could be converted to methyl 7-(3-hydroxy-5-oxo-1-cyclopentenyl)heptanoate (**6b**) in a 90% yield by debromination with a silver–zinc couple.

Methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate (**4a**) was debrominated by a method similar to that described above to give a known prostaglandin intermediate **7** in a 96% yield. Methyl 7-(3-bromo-5-oxo-1-cyclopentenyl)heptanoate (**6a**) was obtained from **7** with *N*-bromosuccinimide in a 43% yield and converted to **6b** in a 92% yield with silver perchlorate.

The outlined synthesis represents a short and facile route to prostaglandin synthons **3**—**7**, because the starting materials are easily accessible and the operations of the reactions and purifications are suitable for the preparation of a sample.

Experimental

The ^1H NMR spectra were measured with a Varian EM-390 (90 MHz) spectrometer. The chemical shifts are expressed in parts per million (ppm) (δ) downfield from tetramethylsilane. The infrared spectra were obtained using a JASCO IR-810 Spectrometer. The low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were determined on a JEOL G-300 Mass Spectrometer. The melting points and boiling points are uncorrected.

7-(2-Hydroxy-5-oxo-1-cyclopentenyl)heptanoic Acid (3).[3] Succinic anhydride (1.00 g: 10.0 mmol) was added to a suspension of 2.60 g (19.5 mmol) of aluminium trichloride in 1,2-dichloroethane, and the mixture was stirred for 1.5 h at room temperature. At 0 °C, to the resultant mixture were added dropwise 1.70 g (10.0 mmol) of 1-cyclooctenyl acetate (**2a**) and 2.50 g of chlorotrimethylsilane successively. The reaction mixture was then stirred at room temperature for 24 h, heated at 80 °C for 28 h, and then poured into 1.5 M (1 M=1 mol dm^{-3}) HCl with ice, and extracted with 40 ml of ethyl acetate five times. The combined organic layer was washed with 20 ml of water and extracted with 80 ml of aq. sat. $NaHCO_3$ and 20 ml of water. The resultant inorganic layer was adjusted to pH 1.5 and extracted with 40 ml of ethyl acetate four times. After washing with 30 ml of brine, the solvents were removed to give 1.06 g of a solid (47%). Recrystallization from water gave 0.54 g (24%) of **3**; mp 154.5—156 °C (lit,[3] mp 156—157 °C). ^1H NMR (acetone-d_6) δ=4.2—2.5 (br, 2H), 2.37 (s, 4H), 2.36—2.00 (m, 4H), and 1.8—1.2 (m, 8H); (methanol-d_4) δ=2.43 (s, 4H), 2.4—1.9 (m, 4H), and 1.8—1.2 (m, 8H); IR (KBr) 3400, 2900, 2830, 1690, 1550, and 1360 cm^{-1}.

Methyl 7-(2-Bromo-5-oxo-1-cyclopentenyl)heptanoate (4a). At 0 °C, to a stirred solution of 28.8 g (0.11 mol) of triphenylphosphine in 700 ml of benzene was added 110 ml of a 1 M bromine–benzene solution drop by drop, over a

15-min period. To the resultant mixture were then added 10 ml of triethylamine and 11.3 g of **3**. The reaction mixture was stirred at room temperature for 17 h, and then 10 ml of absolute methanol was added. After stirring for 15 min, the reaction mixture was poured into 300 ml of water. After ethereal extraction, the removal of the solvents gave crude **4a**. Silica-gel column chromatography (Merck Kieselgel 60 No. 7734: 300 g; hexane:ethyl acetate=2:1) gave 10.3 g (68%) of pure **4a**; bp 122 °C/0.15 mmHg (1 mmHg=133.322 Pa). ^{1}H NMR (chloroform-d_1) δ=3.56 (s, 3H), 2.95—2.7 (m, 2H), 2.65—2.4 (m, 2H), 2.4—2.15 (m, 4H), and 1.8—1.2 (m, 8H); IR (film) 2930, 2850, 1735, 1705, and 1630 cm^{-1}; Found: C, 51.41; H, 6.35; Br, 26.48%. Calcd for $C_{13}H_{19}O_3Br$ (Mw=303.2): C, 51.50; H, 6,32; Br, 26.35%. MS *m/z* 304, 302 (M^+), 273, 271 (M−MeO), and 223 (M−Br).

7-(2-Bromo-5-oxo-1-cyclopentenyl)heptanoic Acid (4b). To a solution of 288 mg of triphenylphosphine in 10 ml of benzene was added 1.1 ml of a 1 M bromine-benzene solution, drop by drop, at 0 °C. After the mixture had then been stirred for 15 min at room temperature, 0.15 ml of triethylamine and 113 mg of **3** were added at 0 °C. The reaction mixture was then stirred for 24 h at room temperature and poured into 20 ml of ice water. The mixture was extracted with 20 ml of ether three times. The organic layer was washed with equal volumes of water and brine, and then dried. After the evaporation of the solvent, the residue was purified on silica-gel chromatography (benzene:acetone=1:1) to give 97 mg (67%) of **4b**; ^{1}H NMR (chloroform-d_1) δ=3.0—2.8 (m, 2H), 2.60—2.43 (m, 2H), 2.30 (t, J=7 Hz, 2H), 2.20 (t, J=6 Hz, 2H), and 1.9—1.25 (m, 8H); IR (film) 3100 (br), 2920, 2840, 1730, 1700, and 1620 cm^{-1}.

To a solution of 50 mg of **4b** in 5 ml of methanol was added an excess of an ethereal diazomethane solution. An ordinary work-up and purification by means of silica-gel column chromatography (LiChroprep Si 60) gave 39 mg (78%) of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate (**4a**); The ^{1}H NMR and IR spectra of this agreed with those of an authentic sample.

Methyl 7-(2-Chloro-5-oxo-1-cyclopentenyl)heptanoate (4c).[7] At 0 °C, to a stirred suspension of 2.24 g of 7-(2-hydroxy-5-oxo-1-cyclopentenyl)heptanoic acid (**3**) in 10 ml of benzene (dried with zeolite A-4) were added 2 ml of phosphorus trichloride and 2.02 g of triethylamine successively. The reaction mixture was then stirred for 30 min at room temperature and heated under reflux for 2 h. Methanol (1 ml) and then 10 ml of water were stirred in, drop by drop, at 0 °C. The reaction mixture was extracted with 10 ml of ether three times. A combined organic layer was washed with equal volumes of water, 0.1 M $NaHCO_3$ (twice), water, and brine successively, and then dried. Silica-gel column chromatography (LiChroprep Si 60, hexane:ethyl acetate=2:1) gave 1.42 g (55%) of **4c**; ^{1}H NMR (chloroform-d_1) δ=3.60 (s, 3H), 2.85—2.67 (m, 2H), 2.60—2.40 (m, 2H), 2,35 (t, J=6.6 Hz, 2H), 2.22 (t, J=6.6 Hz, 2H), and 1.8—1.1 (m, 8H); IR (film) 2920, 2850, 1735, 1705, and 1630 cm^{-1}; MS *m/z* 260, 258 (M^+), 229, 227 (M−MeO), 223 (M−Cl), and 191 (M−Cl−MeOH).

Methyl 7-(2-Iodo-5-oxo-1-cyclopentenyl)heptanoate (4d). Sodium iodide (0.5 g) which had been dried at 100 °C under 1 mmHg for 3 h and 0.05 g of *p*-toluenesulfonic acid were added to a solution of 100 mg of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate (**4a**) in acetone dried by zeolite A-4. The reaction mixture was then stirred at room temperature for 21 h. The resultant mixture was filtered, and the precipitate was washed with 20 ml of ether. The combined solution was concentrated under reduced pressure. Ether and water (10 ml and 5 ml respectively) were added to the residue. After vigorous shaking, the separated inorganic layer was extracted with 5 ml of ether twice. The combined ethereal layer was washed with equal volumes of water four times and with brine twice, and then dried. The removal of the solvents gave 116 mg (100%) of **4d**; bp 143 °C/0.3 mmHg; ^{1}H NMR (chloroform-d_1) δ=3.60 (s, 3H), 2.95 (m, 2H), 2.43 (m, 2H), 2.27 (t, J=6 Hz, 2H), 2.23 (t, J=6 Hz, 2H), and 1.8—1.2 (m, 8H); IR (film) 2920, 2840, 1730, 1700, and 1605 cm^{-1}; Found: C, 44.61; H, 5.48; I, 35.24%. Calcd for $C_{13}H_{19}O_3I$ (Mw=350.2): C, 44.59; H, 5.47; I, 35.60%.

Methyl 7-(2,3-Dibromo-5-oxo-1-cyclopentenyl)heptanoate (5a). *N*-Bromosuccinimide (0.8 g) and 0.03 g of benzoyl peroxide were added to a solution of 1.21 g of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate (**4a**) in 20 ml of tetrachloromethane (distilled from P_2O_5), and the resultant mixture was heated under reflux for 3 h. Furthermore, 0.4 g of *N*-bromosuccinimide and 0.01 g of benzoyl peroxide were added at room temperature, and the mixture was heated under reflux for 1.5 h. The reaction mixture was then filtered, and the precipitates were washed with 10 ml of tetrachloromethane. After the subsequent removal of the solvents, silica-gel column chromatography (LiChroporep Si 60; hexane:ethyl acetate=2:1) gave 0.78 g (51%) of the oily title compound **5a**; bp 85 °C/0.18 mmHg. ^{1}H NMR (chloroform-d_1) δ=4.98 (dd, J=6, 3 Hz, 1H), 3.60 (s, 3H), 3.13 (dd, J=6, 18 Hz, 1H), 2.93 (dd, J=18, 3 Hz, 1H), 2.27 (t-like, J=7.5 Hz, 4H), and 1.8—1.2 (m, 8H); IR (film) 2940, 2860, 1740, 1720, and 1620 cm^{-1}; MS *m/z* 353, 351, 349 (M−MeO), 303, 301 (M−Br), and 271, 269 (M−Br−MeOH); (HRMS) Found: *m/z* 352.9392, 350.9452, 348.9471. Calcd for $C_{12}H_{15}O_2Br_2$: (M−MeO): 352.9398, 350.9441, 348.9940; Found: C, 40.73; H, 4.87; Br, 42.22%. Calcd for $C_{13}H_{18}O_3Br_2$ (Mw=382.1):C, 40.87; H, 4.75; Br, 41.82%.

Methyl 7-(2-Bromo-3-hydroxy-5-oxo-1-cyclopentenyl)-heptanoate (5b). To a solution of 0.76 g of methyl 7-(2,3-dibromo-5-oxo-1-cyclopentenyl)heptanoate (**5a**) in 21 ml of aq. acetone (acetone:water=20:1) was added 1 g of silver perchlorate at room temperature under argon. The reaction mixture was stirred at room temperature for the first 50 min and at 50 °C for the next hour. To the mixture was then added 0.5 g of $NaHCO_3$ at room temperature, after which the mixture was stirred for 3 min. The reaction mixture was filtered, and the filtrate, with 70 ml of ether added, was washed with an equal volume of aq.sat.$NaHCO_3$, water and brine, and dried. The subsequent removal of the solvents gave 0.55 g (86%) of the oily title compound **5d**; ^{1}H NMR (chloroform-d_1) δ=4.77 (m, 1H), 3.58 (s, 3H), 2.87 (dd, J=18, 6 Hz, 1H), 2.6—2.1 (m, 5H), and 1.9—1.2 (m, 8H); IR (film) 3450 (br), 2940, 2860, 1740, 1720, and 1630 cm^{-1}; MS *m/z* 240 (M+H−Br), 222 (M+H−Br−H_2O), 208 (M+H−Br−MeOH), and 190 (M+H−Br−MeOH−H_2O); (HRMS) Found: *m/z* 240.1373. Calcd for $C_{13}H_{20}O_4$: (M+H−Br), 240.1362.

Methyl 7-(3-Hydroxy-5-oxo-1-cyclopentenyl)heptanoate (6b).[5] To a solution of 48 mg of silver acetate in 1 ml of glacial acetic acid at 100 °C was added 107 mg of zinc powder which had been activated by 10% HCl. The reaction

mixture was then stirred at 100 °C for 30 min. The supernatant liquid was removed by decantation at room temperature, after which the precipitate was washed with 1 ml of acetic acid twice and with 2 ml of ether five times. To the resultant precipitate was added a solution of 100 mg of methyl 7-(2-bromo-3-hydroxy-5-oxo-1-cyclopentenyl)-heptanoate (**5b**) in 2 ml of methanol, and the mixture was heated under reflux while being vigorously stirred for 2 h. The reaction mixture was filtered through a sintered-glass filter (G-4). The precipitate was then washed with methanol, and the washing was combined with the mother liquid. The resultant solution was concentrated under reduced pressure to dryness, and 5 ml of ether was added. The precipitate was separated, dissolved in 5 ml of 1 M HCl, and extracted three times by the use of 5 ml of ether. The ethereal layers thus obtained were washed with water and brine, and dried. The removal of the solvents from the combined ethereal layer gave 61 mg (90%) of **6b**. The ^{1}H NMR and IR spectra of this substance agreed with those in the literature.[5]

Methyl 7-(5-Oxo-1-cyclopentenyl)heptanoate (7).[7] To a solution of 49 mg of silver acetate in 5 ml of glacial acetic acid at 100 °C was added 1 g of zinc powder which had been activated by 10% HCl. The reaction mixture was then stirred at 100 °C for 7 min. The supernatant liquid was removed by decantation at room temperature. The precipitate was washed with 5 ml of acetic acid once and with 5 ml of ether five times. To the resultant precipitate was added a solution of 700 mg of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)-heptanoate (**4a**) in 5 ml of methanol. The reaction mixture was then stirred at 60 °C for 24 h and filtered through a sintered-glass filter (G-4). The precipitate was washed with methanol, and the washing was combined with the mother liquid. The resultant solution was concentrated under reduced pressure to dryness, and 10 ml of ether was added. The precipitate was dissolved in 10 ml of 1 M HCl and extracted with 10 ml of ether three times. The extracts thus obtained were washed with water and brine, and then dried. The subsequent removal of the solvents gave 496 mg (96%) of **7**. The ^{1}H NMR and IR spectra of this substance agreed with those in the literature.[7]

Methyl 7-(3-Bromo-5-oxo-1-cyclopentenyl)heptanoate (6a).[11] A solution of 780 mg of methyl 7-(5-oxo-1-cyclopentenyl)heptanoate (**7**), 682 mg of *N*-bromosuccinimide, and 24 mg of benzoyl peroxide in 35 ml of anhydrous tetrachloromethane was heated under reflux for 2.5 h under argon. The reaction mixture was then filtered, and the precipitate was washed with 50 ml of tetrachloromethane. After the removal of the solvents from the combined mother liquid and washing, purification by silica-gel column chromatography (LiChroprep Si 60; hexane:ethyl acetate=2:1) gave 450 mg (43%) of the oily title compound. The ^{1}H NMR and IR spectra of this substance agreed with those in the literature.[11]

Conversion to 6b from 6a. To a solution of 450 mg of methyl 7-(3-bromo-5-oxo-1-cyclopentenyl)heptanoate (**6a**) in 18 ml of aq. acetone (acetone:water=15:3) at 0 °C was added 306 mg of silver perchlorate under argon, after which the reaction mixture was stirred for 1 h. To the reaction mixture was then added 175 mg of $NaHCO_3$, and the mixture was stirred for 5 min. After the filtration of the AgBr, the filtrate was extracted with 20 ml of ether. The ethereal extracts were washed with equal volumes of aq. sat.$NaHCO_3$, water, and brine successively, and then dried. After the subsequent removal of the solvents, 326 mg (92%) of the title compound was obtained. The ^{1}H NMR and IR spectra of this substance agreed with those in the literature.[5]

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