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Preparation of a Prostanoid Intermediate from Loganin

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Iridoids[1,2] have been used successfully as optically active synthons for prostaglandins and prostaglandin analogues.[3] Moreover, the wide variety of iridoid substitution patterns available in nature suggests new and physiologically interesting prostaglandin analogues, such as relatives of the 11-deoxy-11-methyl group represented by the antiulcer agent **2**.[4] Here, we report the conservative conversion of loganin (1) into prostaglandin analogue intermediate **8**.

Oxidation of an iridoid enol ether to a lactone has been accomplished in several ways, in particular by the method of D'Ascoli et al. (I_2/PDC, $Na_2S_2O_3$).[5,3h] Bromination with NBS and reduction of bromo lactone **4** with Zn/HOAc was also effective, giving lactone **5** in 83% yield, as shown in Scheme I. Ring opening, glucose cleavage, and decarboxylation were accomplished in one pot with 80% aqueous HOAc and gave the aldehyde ester **6** in 67% yield (after partial reesterification with diazomethane).

Wadsworth–Emmons reaction of aldehyde ester **6** with *gem*-dimethyl phosphonate reagent **7**[6] then gave the desired enone **8** as a 9/1 mixture of epimers in 81% yield. The epimers were cleanly separated by HPLC. The following evidence leads us to conclude that the major isomer has prostanoid-like trans side chains, and the minor isomer is cis substituted.

Table I. 15-Ketoprostanoids

$J_{12,13}$, Hz	H-13, ppm	H-14, ppm	ref
	trans-8,12		
8.0	6.69	6.20	3b
8.6	6.61	6.18	3h
8.9	6.77	6.19	3k
8	6.71	6.19	7a
8	6.80	6.22	7a
7.0	7.04	6.29	7b
7.5	6.84	6.29	7b
	cis-8,12		
11.0	7.03	6.19	3b
10.6	6.84	6.23	3k
10.3	6.74	6.16	3k
10.0	6.74	6.29	7b
	gem-Dimethyl Enone 8		
10.0 (minor isomer)	6.69	6.45	
8.8 (major isomer)	6.82	6.40	

The ^1H NMR (400 MHz) spectrum of the major product (8) of the Emmons–Horner reaction exhibited a doublet at 6.40 ppm with a coupling constant of J = 15.2 Hz, assigned to the vinyl proton at C-14, confirming the presence of a trans double bond, and a doublet of doublets at 6.82 ppm, assigned to the C-13 proton, with coupling constants of $J_{13,14}$ = 15.0 Hz and $J_{12,13}$ = 8.8 Hz. The minor component of the mixture showed peaks at 6.45 ppm ($J_{13,14}$ = 15.2 Hz) and 6.69 ($J_{13,14}$ = 15.0 Hz, $J_{12,13}$ = 10.0 Hz). A two-dimensional COSY ^1H NMR experiment allowed the estimation of $J_{8,12}$ = 8.3–9.8 Hz for the cis isomer, but no value was obtainable for the trans isomer.

Literature data as summarized in Table I[3k,q] indicate that $J_{12,13}$ values fall within the range of 7.0–8.9 Hz for the trans configuration of the side chains in 15-ketoprostaglandin analogues, while for the cis configuration the J values fall within the range of 10.0–11.0 Hz. By extension, the J value for the cis configuration is always higher than that of the corresponding trans epimer. Consequently, we assign the trans configuration to the major isomer isolated from the Wadsworth–Emmons reaction of **6** with **7**.

Experimental Section

Melting points are uncorrected. Routine proton spectra were obtained in the indicated solvent on a Varian EM 360 nuclear magnetic resonance (NMR) spectrometer, with use of tetramethylsilane as the internal standard. High-field proton and ^{13}C spectra were determined on an IBM Bruker WP-200-SY (200 MHz) or JEOL JMM-GX 400 (400 MHz) instrument. (We are indebted to M. Blumenstein of Hunter College for technical assistance). Infrared spectra (IR) were recorded on a Perkin-Elmer IR 598 instrument. High-performance liquid chromatography (HPLC) was conducted with a Waters Associates (Milford, MA) system consisting of two 4 mm × 30 cm μ-Porasil silica gel columns in series, a 6000 SDS pump, a U6K injector, and a Model 401 differential refractometer. Flash chromatography was carried out on E. Merck silica gel (230–400 mesh) according to the usual Still procedure. Preparative column chromatography was performed on E. Merck 7747 silica gel. Several separations were efficiently done with a Chromatotron (Harrison) apparatus with rotating plates coated with E. Merck 7749 silica gel. Thin-layer chromatography (TLC) was carried out on Machery-Nagel (MN)

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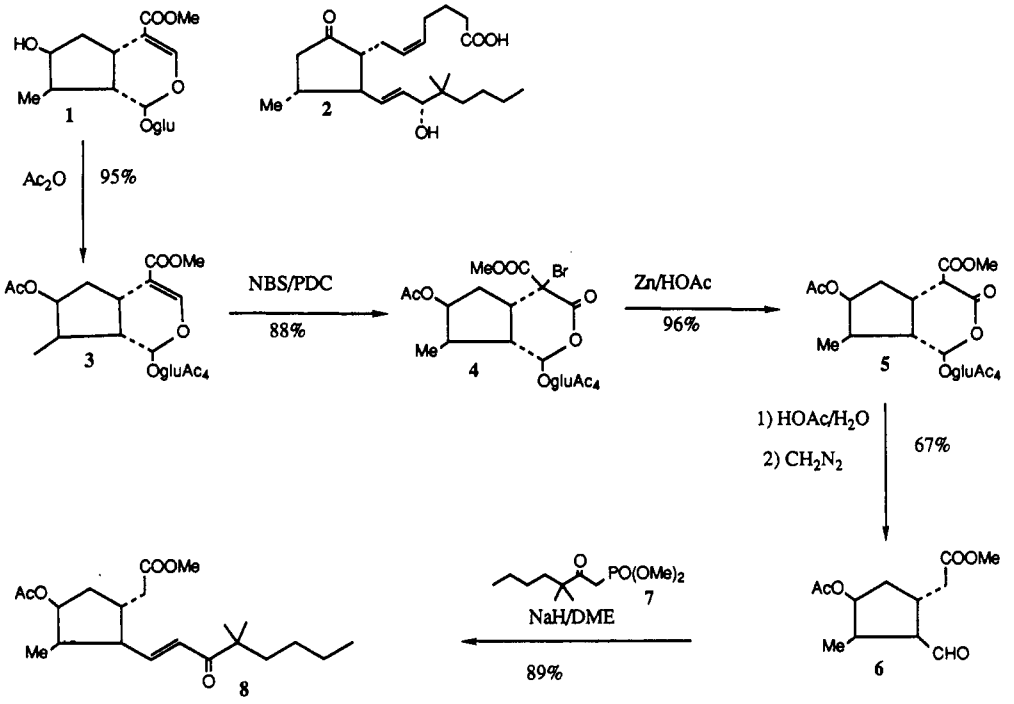
Scheme I



precoated Polygram Sil N/HR UV silica plates. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

5: Loganin Pentaacetate Lactone. To a solution of 150 mg (0.250 mmol) of loganin pentaacetate[8a-c] (**3**) in 5.0 mL of dry CH_2Cl_2 (CaH_2) under nitrogen was added 90 mg (0.506 mmol) of NBS, the mixture was stirred for 3 m, and then 100 mg (0.265 mmol) of PDC was added to the reaction mixture. The reaction was followed by TLC and was complete after 24 h. The reaction mixture was diluted with 50 mL of ether, filtered, and evaporated to give a residue of 168 mg. Upon flash chromatography, this gave 115 mg (88%) of a yellowish white solid bromo lactone **4**: mp 174–176 °C; TLC (hexane/EtOAc, 1/1) R_f 0.51–0.52; IR ($CHCl_3$) 1750, 1735 cm^{-1}; ^1H NMR (CCl_4) δ 5.90 (1 H, d), 4.95–5.30 (6 H, m), 3.80 (3 H, s), 2.15 (15 H, m), 1.10 (3 H, d); MS *m/e* 367, 369, 317, 319. Anal. Calcd for $C_{27}H_{35}O_{16}Br$: C, 46.65; H, 5.04; Br, 11.49. Found: C, 46.52; H, 5.15; Br, 11.67.

To a stirred solution of 80 mg (0.115 mmol) of bromo lactone **4** in 6.0 mL of dry CH_2Cl_2 at room temperature was added a premixed solution of 13 mg (0.198 mmol) of Zn powder and 0.3 mL of glacial acetic acid. After 60 min, the reaction mixture was diluted with 25 mL of CH_2Cl_2, filtered, and washed twice with 5% sodium bicarbonate and finally with water. The organic layer was dried over sodium sulfate and concentrated in vacuo to yield 76 mg of crude lactone. Upon purification by flash chromatography (hexane/EtOAc, 3/2), this gave 68 mg (96%) of a white solid lactone **5**: mp 167–168 °C; TLC (hexane/EtOAc, 1/1) R_f 0.40–0.41; IR ($CHCl_3$) 1750 (sh), 1725 (br) cm^{-1}; ^1H NMR (CCl_4) δ 3.75 (3 H, s), 2.10 (15 H, m), 1.15 (3 H, d); MS, *m/e* 331, 269, 209, 109. Anal. Calcd for $C_{27}H_{36}O_{16}$: C, 52.62; H, 5.90. Found: C, 52.56; H, 6.12.

6: Glucolysis and Decarboxylation of 5. Into a 200-mL flask fitted with a reflux condenser was added 1.00 g (1.62 mmol) of the lactone **5** to 100 mL of AcOH/H2O, 5/1. The reaction mixture was stirred and the temperature was raised from room temperature to 120–125 °C for 36 h. The reaction mixture was then cooled, concentrated, and dried under reduced pressure to give 880 mg of crude product. NMR and IR analyses showed it contained acidic and aldehydic protons. To this crude product was added 10.0 mL of water, and the mixture was acidified with 0.1 N HCl and then extracted with ethyl acetate (3 × 50 mL). The combined organic layers were separated, washed with water, and dried over anhydrous Na_2SO_4 to give 285 mg of crude product, which proved to be a mixture of acid and aldehyde. A Benedict's test on the aqueous layer indicated that glucose was present.

To the crude aldehyde/acid mixture, without further purification, was added 5.00 mL of ether, followed by an excess of a solution of diazomethane in ether, with stirring at room temperature. Stirring was continued for an additional 30 min, and then the mixture was concentrated in vacuo to give 280 mg of oil. Purification on the Chromatron (hexane/EtOAc, 3/1) gave 270 mg (69%) of aldehyde ester **6**: ^1H NMR ($CDCl_3$) δ 9.65 (1 H, d, J = 4 Hz), 5.20 (1 H, m), 3.65 (3 H, s), 2.10 (3 H, s); IR ($CHCl_3$) 1715, 1730 cm^{-1}; TLC (hexane/EtOAc, 1/1) R_f 0.65–0.67. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.52; H, 7.44. Found: C, 59.67; H, 7.53.

8: Preparation of the *gem*-Dimethyl Enone.[6] A suspension of 4.00 mg (0.167 mmol) of granular NaH in 2.00 mL of dry DME (CaH_2) was prepared under dry nitrogen. A solution of dimethyl (2-oxo-3,3-dimethylheptyl)phosphonate **7**[6] (45.0 mg, 0.180 mmol) in 1.00 mL of dry DME was added to this stirred suspension all at once. Stirring was continued for 30 min at room temperature. The mixture was then cooled to −78 °C, and a solution of 40.0 mg (0.165 mmol) of aldehyde **6** in 1.00 mL of dry DME was also added. Stirring was continued for 1 h at −78 °C followed by 4 h at room temperature. The reaction was complete in 5 h (TLC, hexane/EtOAc, 3/1). The reaction mixture was neutralized with acetic acid, diluted with 10 mL of water, and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and then concentrated in vacuo to obtain 61.0 mg of crude product **8**. TLC showed a UV-active spot at R_f 0.47, which proved to be the desired product. Purification of the crude product on the Chromatron (hexane/EtOAc, 5/1) gave 49.0 mg (81%) of a thick, clear liquid, R_f (hexane/EtOAc, 3/1) 0.47–0.48 (UV active), which 200-MHz NMR and HPLC (hexane/EtOAc, 4/1) showed to be a 90/10 mixture of epimers (see discussion above): IR ($CHCl_3$) 1615, 1685, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.90 (1 H, dd, J = 6, 15 Hz), 6.35 (1 H, d, J = 15 Hz), 5.25 (1 H, m), 3.65 (3 H, s), 2.15 (3 H, s), 1.15 (6 H, s), 0.80 (3 H, d). Anal. (mixture) Calcd for $C_{21}H_{34}O_5$: C, 68.86; H, 9.29. Found: C, 68.72; H, 9.52.

Cis isomer, *gem*-dimethyl enone: ^1H NMR (400 MH_2; prostaglandin numbering) δ 6.69 (d, 1 H, $J_{13,14}$ = 15.0 Hz, $J_{13,12}$ = 10.0 Hz, H-13), 6.45 (dd, 1 H, $J_{14,13}$ = 15.2 Hz, H-14), 5.22 (m, 1 H, H-10), 3.60 (s, 3 H, OMe), 2.83 (d, d, d, d, d, 1 H, J_{av} = 8.3 Hz, H-8), 2.62 (d, d, d, 1 H, J_{av} = 9.8 Hz, H-12), 2.34, 2.17 (d, AB q, 2H, $J_{7A,7B}$ = 15.7 Hz, $J_{7A,8}$ = 6.8 Hz, $J_{7B,8}$ = 9.0 Hz, H-7A,7B),

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2.03 (s, 3 H, CH_3CO), 1.96–2.08 (m, 2 H, H-9A,11), 1.69 (d, d, d, 1 H, $J_{9B,8}$ = 8.6 Hz, $J_{9B,9A}$ = 14.1 Hz, $J_{9B,10}$ = 5.1 Hz, H-9B), 1.49, 1.49 (t, 2 H, $J_{17A,18}$ = 9.5 Hz, t, 1 H, $J_{17B,18}$ = 7.3 Hz, H-17A,17B), 1,24 (t, q, 2 H, $J_{19,18}$ = 7.0 Hz, $J_{19,20}$ = 7.0 Hz, H-19), 1.089 (s, 3 H, H-21), 1.085 (s, 3 H, H-22), 1.17–1.03 (m, 2 H, H-18), 0.86 (d, 3 H, $J_{23,11}$ = 6.7 Hz, H-23), 0.84 (t, 3 H, $J_{20,19}$ = 7.0 Hz, H-20). Trans isomer: ^{1}H NMR (400 MH_2; prostaglandin numbering) δ 6.82 (d, d, 1 H, $J_{13,14}$ = 15.0 Hz, $J_{13,12}$ = 8.8 Hz, H-13), 6.40 (d, 1 H, $J_{14,13}$ = 15.2 Hz, H-14), 5.17 m, 1 H, C-10), 3.61 (s, 3 H, OMe), 2.43 (m, 3 H, H-8,11,12), 2.36, 2.24 (d, AB q, 2 H, $J_{7A,7B}$ = 15.0 Hz, $J_{7A,8}$ = 5.3 Hz, $J_{7B,8}$ = 8.2 Hz, H-7A,7B), 2.11–2.03 (m, 1 H, H-9A), 2.04 (s, 3 H, CH_3CO), 1.67 (d, d, d, 1 H, $J_{9B,8}$ = 8.2 Hz, $J_{9B,9A}$ = 14.5 Hz, $J_{9B,10}$ = 6.3 Hz, H-9B), 1.493 (t, 1 H, $J_{17A,18}$ = 7.4 Hz, H-17A), 1.493 (t, 1 H, $J_{17B,18}$ = 9.4 Hz, H-17B), 1.24 (t, q, 2 H, $J_{19,18}$ = 7.4 Hz, $J_{19,20}$ = 7.0 Hz, H-19), 1.15–1. 05 (m, 2 H, H-18), 1.092, s, 3 H, H-21), 1.085 (s, 3 H, H-22), 0.84 (t, 3 H, $J_{20,19}$ = 7.2 Hz, H-20), 0.81 (d, 3 H, $J_{23,11}$ = 6.3 Hz, H-23).

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Preparation of Hexacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}]tetradecane-10,14-dione and Derivatives

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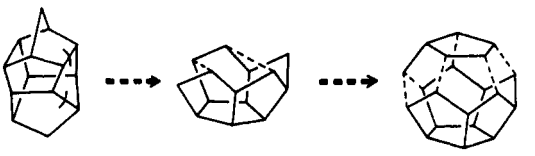
The highly symmetrical structure of heptacyclo-[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (1) has attracted wide interest since its discovery in 1961.[2,3] The synthesis of 1 can be completed in one step by coupling two units of norbornadiene through the mediation of certain transition metals. This reaction has provided an efficient method for the synthesis of a highly compact molecule which otherwise would be difficult to prepare.[4] The cage geometry of these molecules makes them attractive to both organic and theoretical chemists.[5] For a particular example, selective cleavage of two C–C bonds would produce a polyquinane with a folded geometry (*cisoid* fused) which might be used for a more efficient synthesis of dodecahedrane (Scheme I).[6] In this report we describe the preparation of hexaquinanedione 2 and its derivatives by cutting open the cage of 1.

Compound 1 was oxidized smoothly by lead tetraacetate in the presence of trifluoroacetic acid to form two major alcohols, 3 and 4, in 20% and 70% yields, respectively[7] (corrected for unreacted starting materials). The structure of 3 was confirmed by comparison with an authentic sample, while the structure of 4 was determined by analysis of its spectroscopic data. The presence of a hydroxy group in 4 is evident in both its ^{1}H NMR (signal disappears upon D_2O) and IR spectra (3605 cm^{-1}). The mass spectrum shows a strong parent peak at m/z 200 (base peak). The appearance of 14 separate signals in the ^{13}C NMR spectrum rules out the more symmetrical structure with the hydroxy group located on the bridgehead (i.e. C(6) of 1). A DEPT experiment indicates the presence of 2 secondary, 11 tertiary, and 1 quaternary carbons. Most of its ^{1}H NMR absorptions seriously overlapped each other, but they can be resolved clearly on a two-dimensional ^{1}H–^{13}C correlation spectrum.

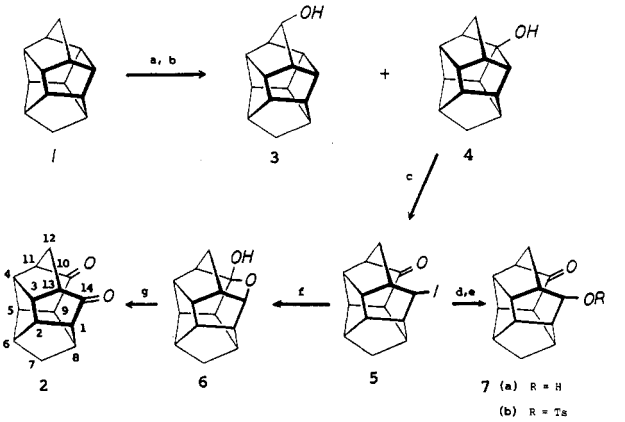
Selective ring-opening of 4 was carried out by a reagent combining I_2 and $Pb(OAc)_4$.[8] Bond cleavage happened mainly between C(1) and C(2) to produce 5 in 63% yield. The structure was proved indirectly by conversion to the more symmetrical diketone 2 (Scheme II). In the ^{13}C NMR spectrum of 5, the upfield signal at δ 31.8 indicates the presence of an iodo carbon. The iodide 5 can be hydrolyzed either in base or in acid. Basic hydrolysis produced the hemiketal 6, while acidic hydrolysis produced the hydroxide 7a. The iodide 5 was also converted to the *p*-toluensulfonate 7b by reaction with silver *p*-toluenesulfonate in acetonitrile.

Both the keto alcohol 7a and the hemiketal 6 were easily oxidized to the diketone 2 by Jones reagent. The ^{13} NMR spectrum of 2 contains only 9 peaks, demonstrating the presence of a plane of symmetry.

Scheme I



Scheme II[a]



[a] (a) $Pb(OAc)_4$, CF_3COOH, LiCl, CH_2Cl_2; (b) 5% NaOH; (c) $Pb(OAc)_4$, I_2; (d) CF_3COOH; (e) AgOTs, CH_3CN; (f) 10% NaOH; (g) Jones.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a Brucker MSL-200 FT spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane (δ scale). Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrophotometer. Melting points were determined on a Yamato Model MP-21

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