A Short and Efficient Total Synthesis of (±) Prostaglandin D_2 Methyl Ester involving a New Method for the Cleavage of a Dimethyl-t-butylsilyl Ether

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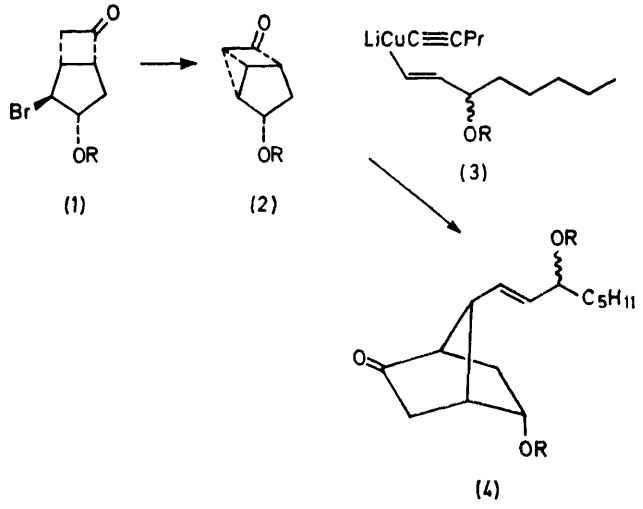
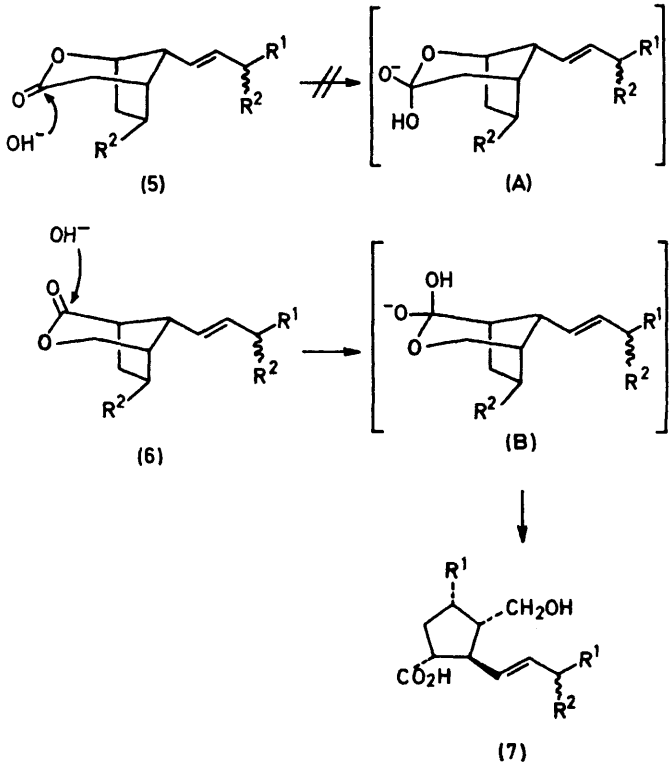
Baeyer-Villiger oxidation of the bicyclo[2.2.1]heptanone (4; R = $SiMe_2Bu^t$) afforded a mixture of isomeric lactones (5) and (6), the minor component (6) being conveniently removed by selective hydrolysis. Reduction of the lactone (5) by di-isobutylaluminium hydride gave the corresponding lactol (8). Conversion of (8) into the 9α-silyloxyprostanoid (10) was performed so as to minimise silyl group migration. Oxidation of (10) gave the ketone (12) but the hindered siloxy-group at C-9 was extremely resistant to cleavage by the usual reagents. Satisfactory deprotection of (12) was achieved by treatment with aqueous HF in acetonitrile to give (±)-prostaglandin D_2 methyl ester (14) and (±)-15-*epi*-prostaglandin D_2 methyl ester (15). The high 'silicophilicity' and low acidity of HF make it the reagent of choice for cleavage of silyl ethers under mildly acidic conditions.

Only four routes to prostaglandin D_2 (PG D_2) have been reported previously, one from prostaglandin $F_{2\alpha}$,[1] and three protracted *de novo* syntheses.[2-4] Three of the processes [1-3] suffer from the concurrent production of quantities of PG E_2 detracting from their efficiency and quality. The fourth [4] involves a lengthy protection and deprotection sequence and gives only moderate yields of the desired product.



Scheme

Earlier we described [5] a synthesis of prostaglandin $F_{\alpha 2}$ from a protected bromohydrin (1). Substitution of the bromine atom by an hydroxy-octenyl side-chain is a key step and was accomplished by a double S_N2 process. Initial intramolecular nucleophilic attack at C-2 by the carbanion derived by proton abstraction at C-7 afforded the tricyclo[3.2.0.$0^{2,7}$]heptanone (2) and homoconjugate addition of the mixed organocuprate (3) then gave the bicyclo[2.2.1]heptanone (4). Our preferred choice of hydroxy-protecting group, R, was the dimethyl-t-butylsilyl group.[6] This makes the reactants (2; R = $SiMe_2Bu^t$) and (3; R = $SiMe_2Bu^t$) highly ether soluble at the low temperatures required for successful homoconjugate addition and resulted in the highest yield of product. Elaboration of the resultant bicyclo[2.2.1]heptanone (4; R = $SiMe_2Bu^t$) readily afforded $PGF_{2\alpha}$.[5] We have now incorporated some refinements into the process and have



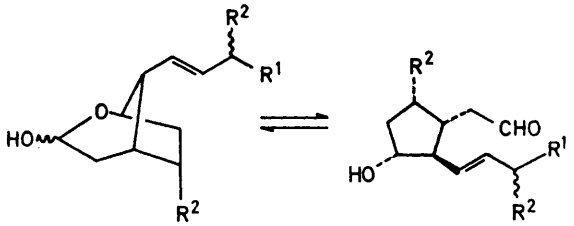
extended its scope to include the total synthesis of PG D_2 methyl ester.[7]

Baeyer-Villiger oxidation of the bicycloheptanone (4; R = $SiMe_2Bu^t$) using peracetic acid in dichloromethane at −20 °C, afforded in quantitive yield a mixture of isomeric lactones (5) and (6) [ratio 4 : 1 by g.l.c.].

Chromatographic separation [8] was difficult and it was found that the unwanted isomer (6) was more conveniently removed by selective hydrolysis.

As a consequence of stereoelectronic control [9] hydroxide-ion attack occurs from only one face of the conformationally rigid lactones to give the tetrahedral ortho-acid intermediates (A) and (B). The intermediate (A) has two 1,3-diaxial steric interactions between the axial OH group and the bridge carbon atoms and also with the associated substituents. Such steric interactions are absent from intermediate (B). Consequently the ortho-acid derived from the lactone (6) is formed at a much faster rate such that when the mixture of (5) and (6) was stirred with 0.2N-sodium hydroxide and acetonitrile at ambient temperature for 8 h, only the isomer (6) underwent hydrolysis to give the acid (7). This acid was readily separated from unchanged lactone (5). Using this procedure the overall yield for conversion of the bicycloheptanone (4; R = $SiMe_2Bu^t$) into the lactone (5) was 70%.

Reduction of the lactone (5) by di-isobutylaluminium hydride at −78 °C gave the corresponding lactol which

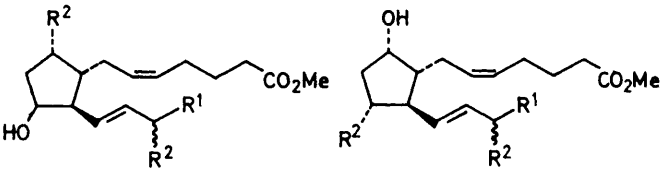


(8a) (8b)

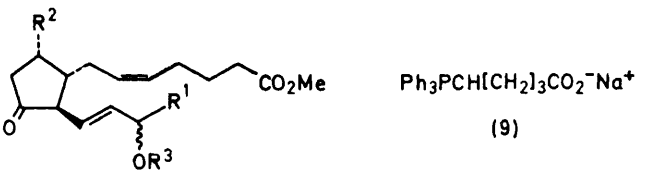
exists as an equilibrating mixture of the hydroxy-aldehyde (8b) and the lactol (8a). The open-chain aldehyde form (8b) predominated and the ratio in deuteriochloroform was estimated to be 2 : 1 by ^1H n.m.r. spectroscopy.

1,5-Migration of the $SiMe_2Bu^t$ group can occur during Wittig reactions involving prostaglandin intermediates,[10,11] and this migration had to be minimised in order to achieve the regioselective synthesis of PG D_2. This was accomplished by treatment of the aldehyde (8) with the ylide (9) in benzene at ambient temperature for just 5 min. After methylation with diazomethane and chromatography, the required 9α-silyl ether (10) was isolated in 79% yield. Only a trace (2%) of the more-polar product (11) resulting from silyl ether migration could be isolated. Under the same Wittig conditions, but with a reaction time of 24 h, the overall yield was unchanged but the ratio of 9α-silyl (10) to 11α-silyl (11) products was 2 : 1.

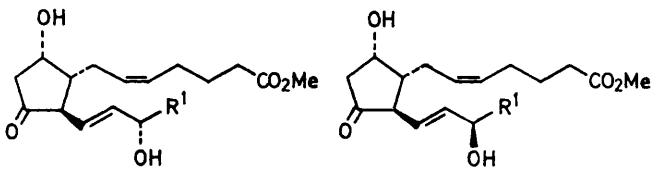
Oxidation of the 9α-silyl-11α-alcohol (10) with pyridinium chlorochromate gave the ketone (12) (91%). It proved impossible to convert (12) into PG D_2 using the reagents [$(NBu^n_4)F$ or AcOH–THF–H_2O] previously recommended for removal of silyl groups. The hindered silyloxy-group at C-9 in the compound (12) was extremely resistant to cleavage. HF was the only reagent with which we were able to achieve this cleavage without causing extensive decomposition of the sensitive β-ketol products (14) and (15). The best results were obtained with acetonitrile containing 30% (v/v) of a 40% (w/w) aqueous solution of hydrofluoric acid (*ca.* 6M in HF and 10M in H_2O). Treatment of (12) with this reagent at 25 °C for only 1 min afforded, in almost quantitative yield, the 9-monosilyloxy-ketone (13). A further 2.5 h were necessary for complete desilylation to give, after chromatography over silica gel, (±)-PG D_2 methyl ester (14) (38%) and (±)-15-*epi*-PG D_2 methyl ester (15) (32%). It is instructive to compare the results of HF-



(10) (11)



(12) $R^3 = SiMe_2Bu^t$
(13) $R^3 = H$



(14) (15)

$R^1 = C_5H_{11}$, $R^2 = OSiMe_2Bu^t$

and carboxylic acid-catalysed deprotections of (12). Formic acid (pK_a 3.75 in H_2O at 25 °C) [12] is only slightly less acidic than HF (pK_a 3.45 in H_2O at 25 °C),[12] but desilylation using HF (6M) and H_2O (10M) in acetonitrile was much faster than desilylation by HCO_2H (6M) and H_2O (10M) in the same solvent. Thus with the latter reagent conversion of the disilyloxy-ketone (12) into the monosilyloxy-ketone (13) required *ca.* 30 min at 25 °C. Further exposure resulted in very slow disappearance of the mono-silyl compound (13) which was still present in small amounts after 1 week. Several unidentified new products were detected by t.l.c., but (±)-PG D_2 methyl ester (14) and its epimer (15) were not observed at any time. It seems therefore that acid-catalysed decomposition of (14) and (15) is faster than cleavage of the C-9 silyloxy-group of (13) using aqueous HCO_2H in acetonitrile.

The position of the free hydroxy-group in (13) was established by ^{1}H n.m.r. spectroscopy. Decoupling experiments showed that the signal at τ 5.55 was due to C(9)-H and the signal at τ 5.90 to C(15)-H. Lanthanide shift reagents are known to co-ordinate strongly with hydroxy-groups but not with dimethyl-t-butylsilyl ethers.[13] Addition of Eu(fod)$_3$ to a sample of (13) in $CDCl_3$ induced a much larger shift of the signal for C(15)-H than C(9)-H and also caused a considerable shift of the signals from C(13)-H and C(14)-H. In another experiment the trifluoroacetyl derivative of (13) was prepared *in situ*. This shifted the C(15)-H signal from τ 5.9 to τ 4.6 but left the C(9)-H resonance unchanged.

The conversion of the bicyclo[2.2.1]heptanone (4; R = $SiMe_2Bu^t$) into (±)-PG D_2 methyl ester completes the shortest and most efficient total synthesis of this important natural product derivative yet devised. The yield for the full twelve-step sequence from cyclopentadiene is *ca.* 5%. The use of aqueous HF for the removal of the dimethyl-t-butylsilyl groups in the final stage was essential for the success of the synthesis. We believe that the high ' silicophilicity ' and low acidity of HF make it the method of choice for cleavage of silyl ethers under mildly acidic conditions. The generality of the method has been demonstrated [14] and it compliments the use of the basic reagent tetrabutylammonium fluoride in tetrahydrofuran.[6]

EXPERIMENTAL

Mass spectra were determined after chemical ionisation using ammonia (c.i.m.s.). T.l.c. was carried out with Camlab Polygram pre-coated silica-gel plates. Short-column chromatography used Merck Kieselgel H or G. Light petroleum refers to the fraction of b.p. 60—80 °C, and all solvents for chromatography were distilled before use.

Baeyer-Villiger Oxidation of endo-5-*Dimethyl-t-butylsilyloxy*)anti-7-(E)-[3-(*dimethyl-t-butylsilyoxy*)*oct*-1-*enyl*]*bicyclo*-[2.2.1]*heptan*-2-one.—The bicyclo[2.2.1]heptan-2-one (4; R = $SiMe_2Bu^t$) [5] (848 mg) in dichloromethane (5 ml) was added to a solution of commercial 40% peracetic acid in acetic acid (3.5 ml) and sodium acetate (2.0 g) in dichloromethane at −20 °C (freezer). After 4 days the reaction was quenched by addition to a mixture of aqueous sodium hydrogencarbonate and sodium sulphite. Extraction with dichloromethane followed by evaporation of the dried extracts, gave the product as an oil (908 mg, 100%) (Found: C, 65.0; H, 10.5. Calc. for $C_{27}H_{52}O_4Si_2$: C, 65.3; H, 10.55%). This was a mixture of the isomeric lactones (5) and (6) as shown by comparison (t.l.c., n.m.r., and g.l.c.) with authentic samples.[8] The isomer ratio (5) : (6) was 79 : 21 by g.l.c. (3% OV-275, 240 °C).

Hydrolysis of the Mixture of Lactones (5) *and* (6).—The mixture of lactones (5) and (6) (ratio 4 : 1) (940 mg) was stirred vigorously with a mixture of acetonitrile (5 ml) and 0.2N-sodium hydroxide (5 ml) for 8 h at room temperature. The mixture was then diluted with ether and washed with water. The dried ($MgSO_4$) organic layer was evaporated and the residue purified by short-column chromatography on silica gel (100 g) with 5% ethyl acetate–light petroleum as eluant. Two products were obtained: that with the highest R_f value was *endo*-6-(dimethyl-t-butylsilyoxy)-*anti*-8-(*E*)-[3-(dimethyl-t-butylsilyloxy)oct-1-enyl]-2-oxabicyclo[3.2.1]octan-3-one (5) (659 mg, 70%) an oil homogeneous by t.l.c. and g.l.c. and spectroscopically (n.m.r. and i.r.) identical with authentic material.[8]

The product with the lowest R_f value was 4-(*dimethyl-t-butylsilyoxy*)-2-[3-(*dimethyl-t-butylsilyoxy*)-(E)-*oct*-1-*enyl*]-3-*hydroxymethylcyclopentane*-1-*carboxylic acid* (7) (141 mg, 14%); $\nu_{max.}$ ($CHBr_3$) 3 500 (OH) and 1 740 and 1 705 cm^{-1} (CO_2H); τ ($CDCl_3$) 3.5—5.2 (4 H, complex, CH=CH and 2 × OH), 5.6 (1 H, q, H-4), 5.98 (1 H, q, CH=CH·*CH*·OSi), 6.31 (2 H, m, CH_2O), 7.0 (1 H, m, H-1), 7.5 (1 H, m, H-2), 7.2—9.0 (13 H, complex), 9.11 (18 H, s, 2 × CMe_3), 9.12 (3 H, tr, CH_2Me), 9.92 (6 H, s, $SiMe_2$), and 10.0 (6 H, s, $SiMe_2$) (Found: C, 63.2; H, 10.3. $C_{27}H_{54}O_5Si_2$ requires C, 63.0; H, 10.6%).

Reduction of the Lactone (5).—Di-isobutylaluminium hydride (2M in hexane) (4 ml, 8 mmol) was added to a solution of the lactone (5) (1.25 g, 2.5 mmol) in dry dichloromethane (15 ml) at −78 °C under nitrogen. After 2 h, water (15 ml) was added and the mixture warmed to room temperature. The layers were separated and the aqueous layer acidified with 2N-sulphuric acid (12 ml) and extracted with dichloromethane. The combined organic extracts were dried ($MgSO_4$) and evaporated to give a colourless oil (1.257 g, 100%); $\nu_{max.}$ ($CHBr_3$) 3 600 (OH), 2 720 (CHO), and 1 720 cm^{-1} (C=O) (Found: C, 64.7; H, 10.8. $C_{27}H_{54}O_4Si_2$ requires C, 65.0; H, 10.9%). The product was a mixture of hydroxy-aldehyde (8b) and lactol (8c) tautomers by ^{1}H n.m.r. in $CDCl_3$; τ 0.15 (<1 H, brs, CHO of aldehyde tautomer), 4.2—4.8 (>2 H, m, olefinic and OCHO of lactol tautomer), 5.3—6.4 (>3 H, m, 3 × CHO and OH), 7.0—8.9 (14 H, m), 9.1 (21 H, s and m, 2 × CMe_3 and CH_2Me), and 9.9—10.0 (6 H, several s, 2 × $SiMe_2$).

Wittig Reactions.—(i) *With* 5 *min reaction time.* Sodium 1,1-dimethylpropoxide (0.75M-solution in benzene) (26.6 ml, 20 mmol) was added to carboxybutyltriphenylphosphonium bromide (4.43 g, 10 mmol) and dimethyl sulphoxide (0.4 ml) in benzene (25 ml) at 70 °C under nitrogen. After 10 min at this temperature the mixture was cooled to ambient and a solution of the aldehyde (8) (1.25 g, 2.5 mmol) in benzene (25 ml) was added rapidly in one portion. After 5 min, saturated aqueous ammonium chloride was added and the layers separated. The aqueous layer was further extracted with ether. The combined organic extracts were dried ($MgSO_4$) and evaporated and the residue methylated by treatment with ethereal diazomethane. The products were separated by short-column chromatography on silica gel (200 g) with 5% ethyl acetate–light petroleum as eluant and collection of 15-ml fractions. Evaporation of fractions 100—170 gave *methyl* (5Z,13E)-9α,15-*bis*(*dimethyl-t-butylsilyloxy*)-11α-*hydroxyprosta*-5,13-*dienoate* (10) as a colourless oil (1.2 g, 79%); $\nu_{max.}$ ($CHBr_3$) 3 500 (OH) and 1 730 cm^{-1} (C=O); τ ($CDCl_3$) 4.3—5.0 (4 H, m, olefinic), 5.81 (1 H, m, H-1), 5.9—6.3 (2 H, m, H-9 and H-15), 6.39 (3 H, s, CO_2Me), 7.4—9.0 (21 H, complex), 9.12 (21 H, s and m, 2 × CMe_3 and CH_2Me), 9.9—10.0 (12 H, several s, 2 × $SiMe_2$) {Found: C, 65.9; H, 11.0; (c.i.m.s., NH_3) $[M + NH_4]^+$ 614.4658). $C_{33}H_{64}O_5Si_2$ requires C, 66.3; H, 10.7%; $M + NH_4$ 614.4636}.

Evaporation of fractions 210—270 afforded methyl (5Z,13E)-11α,15-bis(dimethyl-t-butylsilyoxy)-9α-hydroxyprosta-5,13-dienoate (11) (29 mg, 2%) as a colourless oil identical (t.l.c., i.r., and ^{1}H n.m.r.) with authentic material from an alternative route.[10]

(ii) *With* 24 *h reaction time.* A solution of the ylide (9) (20 mmol) in benzene was generated as described above and

treated with the aldehyde (8) (1.95 g, 3.9 mmol) in benzene at room temperature. After 24 h the reaction was quenched and worked up in the usual manner. Chromatography afforded the 9α-silyl product (10) (1.29 g, 55%) and the 11α-silyl product (11) (0.63 g, 27%).

Methyl (5Z,13E)-9α,15-*Bis*(*dimethyl-t-butylsilyloxy*)-11-*oxoprosta*-5,13-*dienoate* (12).—The 9α-silyl-11α-alcohol (10) (894 mg, 1.5 mmol) in dichloromethane (10 ml) was added to a mixture of pyridinium chlorochromate (647 mg, 3 mmol) and sodium acetate (350 mg) in dichloromethane at room temperature. After the mixture had been stirred for 2.75 h it was applied to a column of silica gel (50 g) and the product eluted with dichloromethane. Evaporation of the product containing fractions afforded *methyl* (5Z,13E)-9α,15-*bis*(*dimethyl-t-butylsilyloxy*)-11-*oxoprosta*-5,13-*dienoate* (12) (798 mg, 89%) as a colourless oil; $\nu_{max.}$ ($CHBr_3$) 1 740 cm^{-1} (C=O); τ ($CDCl_3$) 4.2—4.8 (4 H, m, olefinic), 5.6 1 H, m, H-9), 5.92 (1 H, m, H-15), 6.38 (3 H, s, CO_2Me), 7.28 (1 H, dd, H-12), 7.5—8.9 (19 H, complex), 9.12 (21 H, s and m, 2 × $SiMe_3$ and CH_2Me), 9.95 and 9.98 (12 H, 2 × s, 2 × $SiMe_2$) (Found: C, 67.0; H, 10.4. $C_{33}H_{62}O_5Si$ requires C, 66.6; H, 10.5%).

Deprotection of the Bis-silyloxy-ketone (12) *with Aqueous* HF.—(i) *Brief treatment*. A mixture of 40% (w/w) aqueous hydrofluoric acid (9 ml) and acetonitrile (21 ml) was added to methyl (5*Z*,9α,13*E*)-11,15-bis(dimethyl-t butylsilyloxy)-9-oxoprosta-5,13-dienoate (12) (281 mg) and stirred for 1 min at 25 °C in a Polythene bottle. The reaction was quenched by addition of 8% aqueous sodium hydrogencarbonate, and extracted with dichloromethane. Evaporation of the dried ($MgSO_4$) extracts gave *methyl* (5Z,13E)-11-(*dimethyl-t-butylsilyloxy*)-15-*hydroxy*-9α-*oxo*-*prosta*-5,13-*dienoate* (13) (225 mg, 99%) as a colourless oil; $\nu_{max.}$ ($CHBr_3$) 3 590 (OH), 1738 (C=O), and 968 cm^{-1} (CH=CH); τ ($CDCl_3$) 4 2—4.8 (4 H, m, olefinic), 5.55 (1 H, q, H-9), 15.90 (1 H, q, H-15), 6.35 (3 H, s, CO_2Me), 7.22 (1 H, dd, H-12), 7.5—8.9 (20 H, m), 9.15 (12 H, s and m, CMe_3 and CH_2Me), and 9.96 (6 H, s, $SiMe_2$) (Found: C, 67.4; H, 9.9. $C_{27}H_{48}O_5Si$ requires C, 67.45; H, 10.05%).

Irradiation of the olefinic protons decoupled the τ 5.90 signal but not the τ 5.55 signal, confirming their assignments as H-15 and H-9, respectively. Addition of $Eu(FOD)_3$ to the solution to give a molar ratio of 0.06 : 1 induced a small shift (0.2 p.p.m.) for the τ 5.55 signal but a much larger shift (1.2 p.p.m.) for the τ 5.90 signal. The olefinic signals (H-13 and H-14) were also shifted.

In a separate experiment, addition of a few drops of trifluoroacetic anhydride to a $CDCl_3$ solution of the sample at ambient temperature caused a downfield shift of 1.3 p.p.m. of the τ 5.9 signal whereas the position of the τ 5.55 signal was unchanged.

(ii) *Prolonged Treatment with Aqueous* HF.—Methyl (5*Z*,13*E*)-11,15-bis(dimethyl-t-butylsilyloxy)-9α-oxoprosta-5,13-dienoate (12) (350 mg) was treated with acetonitrile (24.5 ml) and 40% (w/w) aqueous hydrofluoric acid (10.5 ml). The mixture was stirred for 2.5 h at ambient temperature in a Polythene container after which dichloromethane was added and the solution washed with 8% aqueous sodium hydrogencarbonate. The dried ($MgSO_4$) organic solution was evaporated and the residue purified by short-column chromatography on silica gel (50 g) with 35% ethyl acetate–cyclohexane, as eluant and collection of 15-ml fractions. Evaporation of fractions 35—70 afforded (±)-15-epi-*prostaglandin* D_2 *methyl ester* (69 mg, 32%); $\nu_{max.}$ (film) 3 450 (OH), and 1 740 cm^{-1} (C=O); τ ($CDCl_3$) 4.2—4.8 (4 H, m, olefinic), 5.56 (1 H, q, H-9), 5.87 (1 H, q, H-15), 6.33 (3 H, s, CO_2Me), 7.15 (1 H, dd, H-12), 7.49—9.0 (21 H, m), and 9.11 (3 H, m, CH_2Me) {Found: (c.i.m.s. NH_3): $[M + NH_4]^+$ 384.2714; $[M + NH_4 - H_2O)^+$ 366.2634; $[M + H - H_2O]^+$ 349.2391; $[M + H - 2H_2O]^+$ 331.2279. $C_{21}H_{34}O_5$ requires $M + NH_4$ 384.2750; $M + NH_4 - H_2O$ 366.2645; $M + H - H_2O$ 349.2379; $M + H - 2H_2O$ 331.2273}.

Evaporation of fractions (71)—(150) afforded (±)-*prostaglandin* D_2 *methyl ester* (82 mg, 38%); $\nu_{max.}$ (CCl_4) 3 620 (free OH), 3 530 (H-bonded OH), 1 742 (C=O), 1 728 (C=O), and 963 (*trans*-CH=CH) {Found (c.i.m.s. NH_3): $[M + NH_4]^+$ 384.2772; $[M + NH_4 - H_2O]^+$ 366.2606; $[M + H - H_2O]$ 349.2421; $[M + H - 2H_2O]$ 331.2308. Calc. for $C_{21}H_{34}O_5$: $M + NH_4$ 384.2750; $M + NH_4 - H_2O$ 366.2644; $M + H - H_2O$ 349.2378; $M + H - 2H_2O$, 331.2273}. ^1H N.m.r. data were in agreement with the published spectrum.[3]

Authentic prostaglandin D_2 was prepared from commercially available prostaglandin F_{2a} (by Dr. R. J. Cave) using a published procedure.[1] Upon treatment with diazomethane this gave material identical (t.l.c. and c.i.m.s. comparison) with the methyl ester from the total synthesis.

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