Stereoselective Synthesis of Plant-Growth-Regulating Steroids: Brassinolide, Castasterone, and Their 24,25-Substituted Analogues[1]

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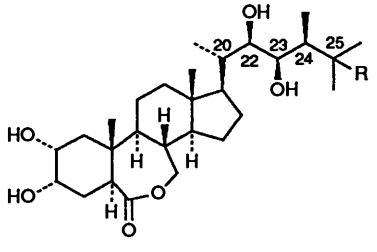
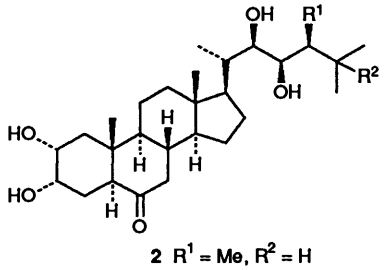
Brassinosteroids and their congeners, brassinolide **1**, castasterone **2**, 25-methylbrassinolide **3**, 25-methylcastasterone **4** and (24*R*)-24-phenylbrassinone **5**, have been stereoselectively synthesized by employing the pyranone derivative **19** as a versatile intermediate for the construction of the side chain.

Since the discovery of brassinolide **1** as a plant-growth-regulating substance in 1979,[2] a number of brassinosteroids, such as castasterone **2**,[3] have been isolated from plant sources.[4] Much effort has been devoted to the synthesis of brassinolide and related brassinosteroids because of their novel structural features and their remarkable biological activities.[5] Recently, Mori and Takeuchi synthesized a new brassinosteroid, 25-methyldolichosterone, with a *tert*-butyl group at the C-24 position, and its derivative, 25-methylbrassinolide **3**, was found to be a plant-growth promotor more potent than brassinolide itself.[6] This finding prompted us to establish a novel method for the construction of the brassinolide side chains, in which modification at the C-24 and -25 positions could be easily achieved. Here we describe the synthesis of brassinolide **1**, castasterone **2**, 25-methylbrassinolide **3**, 25-methylcastasterone **4** and (24*R*)-24-phenylbrassinone **5**.



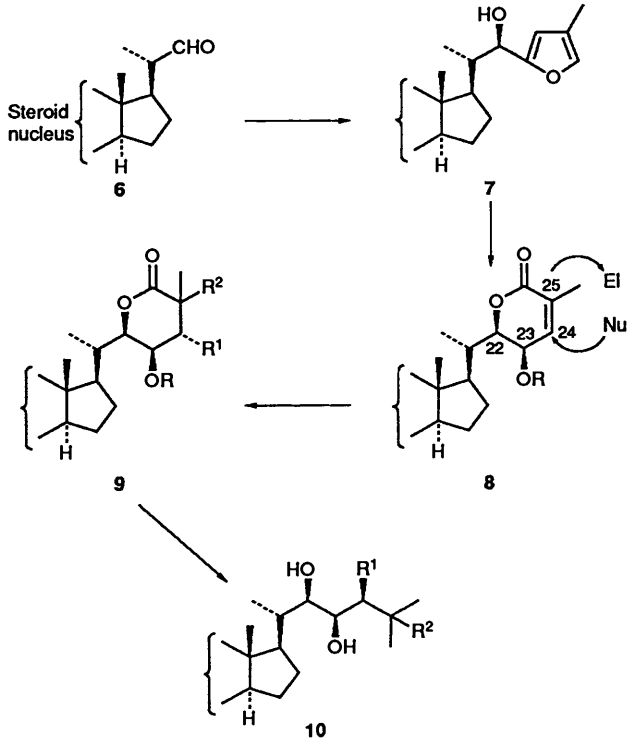
1 R = H
3 R = Me



2 R^1 = Me, R^2 = H
4 R^1 = R^2 = Me
5 R^1 = Ph, R^2 = H

Results and Discussion

The key feature of our synthesis of brassinosteroid side chains is based on stereoselective conversion of the furfuryl alcohol **7**, easily derived from the aldehyde **6**, into the unsaturated lactone **8** followed by functionalisation of **8** with appropriate



Scheme 1

nucleophiles and electrophiles to provide the saturated lactone **9**. Lactone **9** could be easily transformed into the required side chains **10** (Scheme 1).

The requisite α,β-unsaturated lactone **19** was prepared as follows (Scheme 2). Reaction of the known aldehyde **11**[5d] with 2-lithio-4-methylfuran **12**[7] in tetrahydrofuran (THF) at −78 °C afforded the Cram product **13** as the major isomer in 58% yield together with the anti-Cram product **14** (20%). Treatment of the furfuryl alcohol **13** with *N*-bromosuccinimide (NBS)[8] in aq. THF gave the lactol **15**, which was further oxidised with pyridinium chlorochromate (PCC) in CH_2Cl_2 to produce the lactone **16** in 81% overall yield from the alcohol **13**. Sodium borohydride reduction of keto lactone **16** in the presence of cerium(III) chloride[9] in methanol–CH_2Cl_2 furnished the allyl alcohol **17** as the sole product in 97% yield. The stereochemistry at the C-23 position was deduced by the ^1H NMR spectrum of the derived acetate **18**, which showed the 23-H signal as a double doublet ($J_{22,23}$ 3.1, $J_{23,24}$ 6.1 Hz), indicating the presence of pseudoequatorial and pseudoaxial substituents at the C-22 and -23 positions, respectively. The observed selectivity would be explained by assuming that the reduction occurred preferentially from the less hindered side

(the same side as the hydrogen at the C-22). Protection of the alcohol **17** with ethyl vinyl ether in the presence of pyridinium toluene-*p*-sulfonate (PPTS) gave the ether **19** quantitatively.*

With the key intermediate **19** having the desired *syn*-diol system in hand, we began to explore a concise synthesis of brassinolide **1** and castasterone **2**. Introduction of a methyl group into the α,β-unsaturated lactone **19** with lithium dimethylcuprate in THF afforded the adduct **20**, as a 1:1 diastereoisomeric mixture at the acetal carbon with a single stereochemistry at the C-24 and -25 positions, in 85% yield. Since the 1,4-conjugate addition is considered to proceed in the *anti* sense with respect to the adjacent ether group at the C-23 position,[10] the product should have the 24*S* configuration. The structure of compound **20** was supported by the ^{1}H NMR spectrum of its acetate **21**, derived by deprotection of the ethoxyethyl group on treatment with toluene-*p*-sulfonic acid (PTSA) followed by acetylation of the corresponding alcohol. Acetate **21** showed an axial–equatorial coupling between the 23- and 24-H (*J* 1.8 Hz) and a nuclear Overhauser effect between 22-H and the 24-methyl group, indicating the structure to have the 22*R*,23*R*,24*S* configuration. Moreover, the stereochemistry at the C-25 position in the ether **20** was tentatively assigned to be *S* because the all-*trans* conformation for the δ-lactone seemed to be thermodynamically stable. The lactone moiety in structure **20**, possessing four contiguous asymmetric centres, was further converted into the brassinolide side chain as follows. Reduction of compound **20** with lithium aluminium hydride (LAH) in diethyl ether gave the diol **22**, whose hydroxymethyl group was converted into a methyl group by successive methanesulfonylation and reduction of ester **23** with LAH to afford compound **24** in 79% yield from compound **22**. Finally, cleavage of the ethoxyethyl ether and deketalisation of compound **24** was carried out in one step on treatment with 10% hydrochloric acid at reflux to provide castasterone **2** in 94% yield. The physicochemical properties of the synthetic castasterone was identical with those reported.[2,5b,5d,5h] Since the conversion of castasterone **2** into brassinolide **1** has already been achieved by several groups,[5a–d] this constitutes its formal synthesis.

Having developed a novel method for the stereoselective construction of the brassinolide side chain, we focused our attention on the synthesis of more potent brassinosteroids, 25-methylbrassinolide **3** and 25-methylcastasterone **4** from the above intermediate **20**. Treatment of compound **20** with lithium diisopropylamide (LDA) and methyl iodide in THF afforded the lactone **25** with a geminal dimethyl group (93%), which was reduced with LAH to give the diol **26** in 84% yield. Attempted reduction of its methanesulfonate **27** with LAH gave products other than the expected compound **28**. We therefore examined deoxygenation of diol **26** by Barton's method.[11] Protection of the hydroxy group at the C-22 position of diol **26** was carried out by acid treatment to provide the ethylidene acetal **29** in 80% yield. Alcohol **29** was deoxygenated by reduction of the derived dithiocarbonate **30** with tributyltin hydride in refluxing toluene to afford the desired compound **31** in 66% overall yield. Deprotection of the acetonide, ketal and acetal groups in compound **31** was achieved in stepwise fashion by treatment with 10% hydrochloric acid followed by hydrolysis of the acetal **32** to furnish 25-methylcastasterone **4** in 68% yield from compound **31**. The physicochemical properties, including spectroscopic data, were identical with those reported.[6] Conversion of 25-methylcastasterone **4** into 25-methylbrassinolide **3** has been accomplished by Mori and Takeuchi,[6] and this synthesis therefore constitutes its formal synthesis.

* The mixture of diastereoisomeric ethers, which was epimeric at the acetal carbon of the ethoxyethyl group, was used without separation in the following reactions since the ethoxyethyl group was removed at a later stage in the synthesis.

We next applied this method to the synthesis of a new brassinosteroid derivative with a phenyl group at the C-24 position in order to gain further insight into the C-24 substituent effect on biological activity. Reaction of the α,β-unsaturated lactone **19** with lithium diphenylcuprate in diethyl ether proceeded smoothly to afford the desired compound **33** as the sole product in 79% yield. Conversion of the lactone moiety in compound **33** into the side chain was carried out by the same procedure as above. Thus, reduction of compound **33** with LAH, followed by acid treatment of the derived diol **34**, gave the acetal **35** (64% yield in 2 steps), which was further converted into compound **37** by successive methanesulfonylation and LAH reduction of mesate **36** in 72% yield. Finally, all the protecting groups in compound **37** were removed by acid hydrolysis to furnish (24*R*)-24-phenylbrassinone **5** in 70% yield, *via* the intermediate **38**.

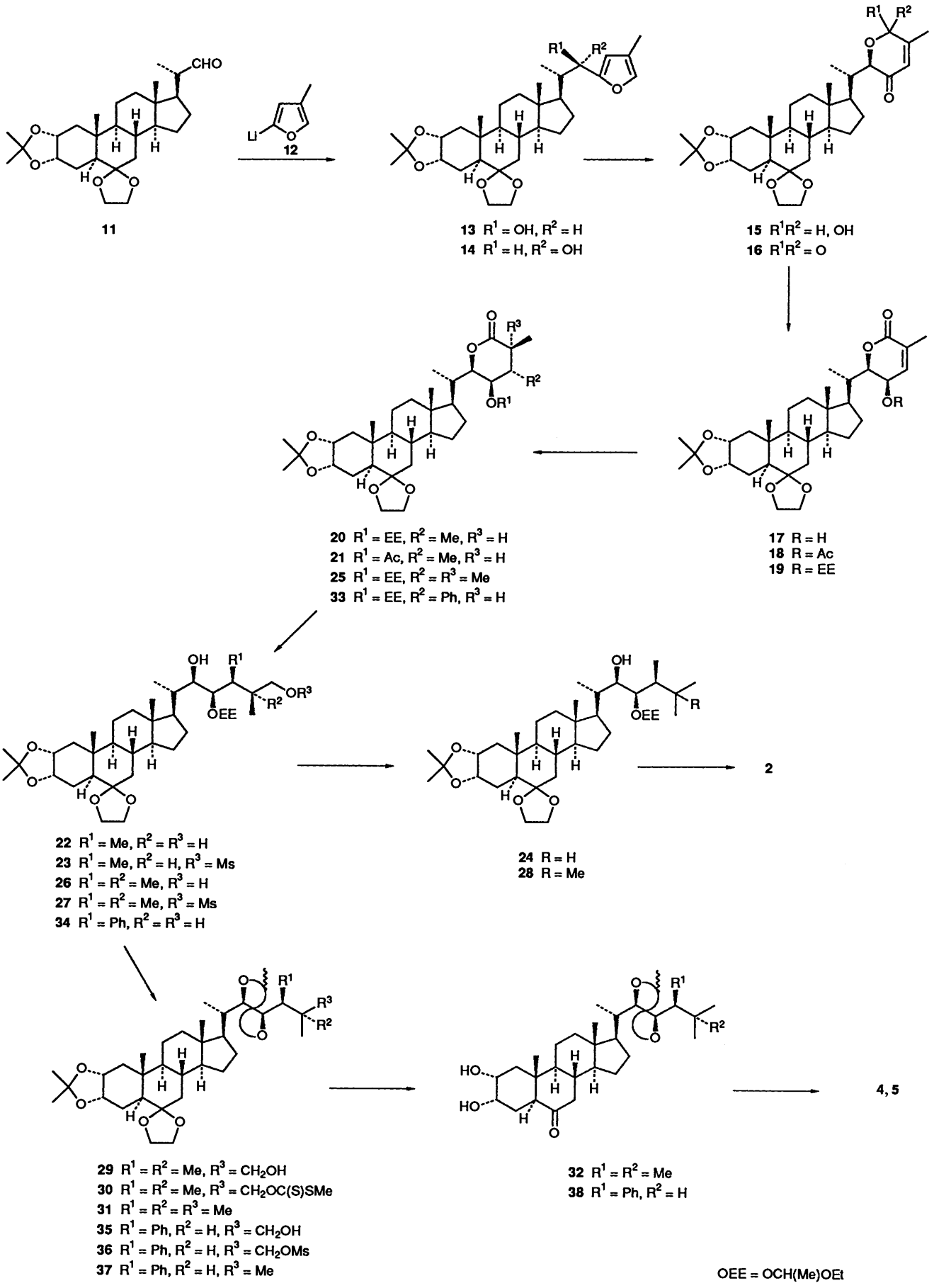
Thus, we have developed a new and useful method for the stereoselective construction of the brassinosteroid side chains; the biological activities of the synthesized compounds are under investigation.

Experimental

General Methods.—M.p.s were measured with a Yanagimoto MP apparatus and are uncorrected. IR spectra were recorded on a Hitachi 260-10 spectrophotometer. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ on a JEOL PMX GSX 270 instrument, and chemical shifts are reported in ppm on the δ-scale from internal Me_4Si. *J*-Values are given in Hz. Mass spectra were measured with a JEOL JMS D-300 spectrometer. Optical rotations were measured on a JASCO DIP 360 spectrometer; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}.

Reaction of 2-Lithio-4-methylfuran with Aldehyde **11**.—To a stirred solution of 2-lithio-4-methylfuran **12**[7] [prepared from 2-bromo-4-methylfuran (1.3 g, 8.07 mmol) and BuLi (1.6 mol dm^{-3}; 3.9 cm^3, 6.24 mmol) in hexane] in THF (4 cm^3) at −78 °C was added dropwise a solution of the aldehyde **11**[6] (1 g, 2.24 mmol) in THF (1 cm^3). The reaction mixture was stirred for 0.5 h at the same temperature and was then allowed to warm gradually to room temperature. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (7:1, v/v) as eluent to afford (20S,22S,23Z,25Z)-23,26-*epoxy*-6-*ethylenedioxy*-22-*hydroxy*-2α,3α-*isopropylidenedioxy*-5α-*cholesta*-23,25-*diene* **14** (242 mg, 20%) as an oil; $\nu_{max}(CHCl_3)$/cm^{-1} 3400; δ_H 0.71 (3 H, s, 18-H$_3$), 0.82 (3 H, s, 19-H$_3$), 1.01 (3 H, d, *J* 6.7, 21-H$_3$), 1.32 and 1.45 (each 3 H, each s, CMe_2), 2.01 (3 H, d, *J* 1.2, 27-H$_3$), 3.73–3.95 (4 H, m, OCH_2CH_2O), 4.07–4.13 (1 H, m, 2-H), 4.26–4.72 (1 H, m, 3-H), 4.72 (1 H, br s, 22-H), 6.08 (1 H, br s, 24-H) and 7.11 (1 H, t, *J* 1.2, 26-H); *m*/*z* 528 (M^+) (Found: M^+, 528.3450. $C_{32}H_{48}O_6$ requires *M*, 528.3451). The second fraction afforded (20S,22R,23Z,25Z)-23,26-*epoxy*-6-*ethylenedioxy*-22-*hydroxy*-2α,3α-*isopropylidenedioxy*-5α-*cholesta*-23,25-*diene* **13** (686 mg, 58%) as an oil; $\nu_{max}(CHCl_3)$/cm^{-1} 3400; δ_H 0.71 (3 H, s, 18-H$_3$), 0.84 (3 H, s, 19-H$_3$), 0.88 (3 H, d, *J* 6.7, 21-H$_3$), 1.32 and 1.48 (each 3 H, each s, CMe_2), 2.0 (3 H, d, *J* 1.2, 27-H$_3$), 3.73–3.97 (4 H, m, OCH_2CH_2O), 4.08–4.13 (1 H, m, 2-H), 4.27 (1 H, br d, *J* 4.3, 3-H), 4.78 (1 H, d, *J* 3.7, 22-H), 6.07 (1 H, br s, 24-H) and 7.1 (1 H, d, *J* 1.2, 26-H); *m*/*z* 528 (M^+) (Found: M^+, 528.3457).

(20S,22R,24Z)-22,26-*Epoxy*-6-*ethylenedioxy*-26-*hydroxy*-2α,3α-*isopropylidenedioxy*-5α-*cholest*-24-*en*-23-*one* **15**.—To a stirred solution of the furfuryl alcohol **13** (4 g, 7.58 mmol) in THF (80 cm^3)–water (20 cm^3) at 0 °C was added portionwise NBS[8] (1.6 h, 8.99 mmol). The reaction mixture was stirred for


CHO
Li
12
11
13 R1 = OH, R2 = H
14 R1 = H, R2 = OH
15 R1R2 = H, OH
16 R1R2 = O
17 R = H
18 R = Ac
19 R = EE
20 R1 = EE, R2 = Me, R3 = H
21 R1 = Ac, R2 = Me, R3 = H
25 R1 = EE, R2 = R3 = Me
33 R1 = EE, R2 = Ph, R3 = H
22 R1 = Me, R2 = R3 = H
23 R1 = Me, R2 = H, R3 = Ms
26 R1 = R2 = Me, R3 = H
27 R1 = R2 = Me, R3 = Ms
34 R1 = Ph, R2 = R3 = H
24 R = H
28 R = Me
2
29 R1 = R2 = Me, R3 = CH2OH
30 R1 = R2 = Me, R3 = CH2OC(S)SMe
31 R1 = R2 = R3 = Me
35 R1 = Ph, R2 = H, R3 = CH2OH
36 R1 = Ph, R2 = H, R3 = CH2OMs
37 R1 = Ph, R2 = H, R3 = Me
32 R1 = R2 = Me
38 R1 = Ph, R2 = H
4, 5
OEE = OCH(Me)OEt

Scheme 2

0.5 h at the same temperature before being washed successively with 10% aq. potassium iodide, saturated aq. sodium thiosulfate and saturated aq. sodium hydrogen carbonate, and extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (5:1) as eluent to afford the *lactol* **15** (3.8 g, 92%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 3260 and 1660; δ_H 0.72 (3 H, s, 18-H_3), 0.83 (3 H, d, *J* 6.1, 21-H_3), 0.84 (3 H, s, 19-H_3), 1.33 and 1.47 (each 3 H, each s, CMe_2), 2.02 (3 H, d, *J* 1.2, 27-H_3), 3.73–3.96 (4 H, m, OCH_2CH_2O), 3.81 (1 H, d, *J* 4.9, OH), 4.08–4.16 (1 H, m, 2-H), 4.28 (1 H, br s, 3-H), 4.45 (1 H, d, *J* 1.8, 22-H), 5.46 (1 H, d, *J* 4.9, 26-H) and 5.91 (1 H, d, *J* 1.2, 24-H); *m/z* 544 (M^+) (Found: M^+, 544.3397. $C_{32}H_{48}O_7$ requires *M*, 544.3398).

(20S,22R,24Z)-6-*Ethylenedioxy*-2α,3α-*isopropylidenedioxy*-23-*oxo*-5α-*cholest*-24-*eno*-26,22-*lactone* **16**.—To a stirred suspension of the lactol **15** (1 g, 1.84 mmol) and sodium acetate (150 mg, 1.84 mmol) in CH_2Cl_2 (10 cm^3) was added PCC (1.6 g, 7.35 mmol) at room temperature and the reaction mixture was stirred for 1 h at the same temperature. After dilution with diethyl ether, the organic layer was decanted and passed through a short column chromatography on silica gel. The organic solvent was evaporated off to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (5:1) as eluent to afford the *lactone* **16** (884 mg, 89%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1680; δ_H 0.71 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 0.89 (3 H, d, *J* 6.7, 21-H_3), 1.33 and 1.49 (each 3 H, each s, CMe_2), 2.2 (3 H, d, *J* 1.8, 27-H_3), 3.74–3.97 (4 H, m, OCH_2CH_2O), 4.08–4.13 (1 H, m, 2-H), 4.27 (1 H, br d, *J* 4.9, 3-H), 4.95 (1 H, d, *J* 1.8, 22-H) and 6.65 (1 H, d, *J* 1.8, 24-H); *m/z* 542 (M^+) (Found: M^+, 542.3232. $C_{32}H_{46}O_7$ requires *M*, 542.3233).

(20S,22R,23R,24Z)-6-*Ethylenedioxy*-23-*hydroxy*-2α,3α-*isopropylidenedioxy*-5α-*cholest*-24-*eno*-26,22-*lactone* **17**.—To a stirred solution of the lactone **16** (883 mg, 1.63 mmol) and cerium(III) chloride[9] (668 mg, 1.79 mmol) in MeOH (9 cm^3)–CH_2Cl_2 (1 cm^3) at 0 °C was added sodium borohydride (62 mg, 1.63 mmol) and the reaction mixture was stirred for 10 min at the same temperature. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (5:1) as eluent to afford the *alcohol* **17** (861 mg, 97%) as an amorphous solid after crystallisation from hexane–AcOEt, m.p. 278–280 °C (Found: C, 70.85; H, 9.15. $C_{32}H_{48}O_7$ requires C, 70.55; H, 8.9%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3350 and 1700; δ_H 0.72 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 1.25 (3 H, d, *J* 6.7, 21-H_3), 1.32 and 1.48 (each 3 H, each s, CMe_2), 1.95 (3 H, d, *J* 1.8, 27-H_3), 3.72–3.95 (4 H, m, OCH_2CH_2O), 4.08–4.13 (2 H, m, 2- and 23-H), 4.26 (1 H, br d, *J* 4.3, 3-H), 4.29 (1 H, d, *J* 1.8, 22-H) and 6.67 (1 H, dd, *J* 1.2 and 6.1, 24-H); *m/z* 544 (M^+) (Found: M^+, 544.3404. $C_{32}H_{48}O_7$ requires *M*, 544.3399).

(20S,22R,23R,24Z)-23-*Acetoxy*-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-5α-*cholest*-24-*eno*-26,22-*lactone* **18**.—A mixture of the alcohol **17** (20 mg, 0.03 mmol), acetic anhydride (0.5 cm^3) and pyridine (1 cm^3) was stirred for 8 h at room temperature. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (4:1) as eluent to afford the acetate **18** (17 mg, 94%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 3350 and 1700; δ_H 0.69 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 1.18 (3 H, d, *J* 6.7, 21-H_3), 1.33 and 1.48 (each 3 H, each s, CMe_2), 1.97 (3 H, d, *J* 1.8, 27-H_3), 2.09 (3 H, s, Ac), 3.74–3.97 (4 H, m, OCH_2CH_2O), 4.08–4.13 (1 H, m, 2-H), 4.27 (1 H, br d, *J* 4.3, 3-H), 4.48 (1 H, dd, *J* 1.2 and 3.1, 22-H), 5.19 (1 H, dd, *J* 3.1 and 6.1, 23-H) and 6.62 (1 H, dd, *J* 1.2 and 6.1, 24-H).

(20S,22R,23R,24Z)-23-(1-*Ethoxyethoxy*)-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-5α-*cholest*-24-*eno*-26,22-*lactone* **19**.—A solution of the alcohol **17** (102 mg, 0.19 mmol), a catalytic amount of PPTS and ethyl vinyl ether (0.18 cm^3, 1.88 mmol) in CH_2Cl_2 (1 cm^3) was stirred for 2 h at room temperature. After addition of brine, the product was extracted with CH_2Cl_2. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (3:1) as eluent to afford the *ether* **19** (106 mg, 94%) as an oily, inseparable diastereoisomeric mixture* (1:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1700; δ_H 0.7 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 1.19 and 1.2 (each 1.5 H, each t, *J* 6.7, OCH_2Me), 1.2 and 1.21 (each 1.5 H, each d, *J* 6.7, 21-H_3), 1.31 and 1.32 (each 1.5 H, each d, *J* 5.5, OCH*Me*O), 1.31 and 1.48 (each 3 H, each s, CMe_2), 1.95 (3 H, d, *J* 1.2, 27-H_3), 3.44-3.61 (2 H, m, OCH_2Me), 3.72–3.95 (4 H, m, OCH_2CH_2O), 4.02–4.18 (2 H, m, 2- and 23-H), 4.26 (1 H, br d, *J* 4.3, 3-H), 4.37 and 4.4 (each 0.5 H, each d, *J* 3.7, 22-H), 4.81 (1 H, q, *J* 5.5, OC*H*MeO) and 6.61 and 6.66 (each 0.5 H, each dd, *J* 1.8 and 5.5, 24-H); *m/z* 616 (M^+) (Found: M^+, 616.3976. $C_{36}H_{56}O_8$ requires *M*, 616.3975).

(20S,22R,23R,24S,25S)-23-(1-*Ethoxyethoxy*)-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-5α-*ergostano*-26,22-*lactone* **20**.—To a stirred solution of lithium dimethylcuprate [prepared from copper(I) iodide (167 mg, 0.88 mmol) and MeLi (1.5 mol dm^{-3}; 1.1 cm^3, 1.65 mmol) in diethyl ether] in diethyl ether (3 cm^3) at −10 °C was added dropwise a solution of the unsaturated lactone **19** (200 mg, 0.33 mmol) in diethyl ether (1 cm^3). The reaction mixture was stirred for 1 h at the same temperature. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (3:1) as eluent to afford the *lactone* **20** (174 mg, 85%) as an oily, inseparable diastereoisomeric mixture (1:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1700; δ_H 0.7 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 1.15–1.27 (12 H, m, 21-, 27- and 28-H_3 and OCH_2Me), 1.29 and 1.3 (each 1.5 H, each d, *J* 5.5, OCH*Me*O), 1.33 and 1.48 (each 3 H, each s, CMe_2), 3.44–3.57 (2 H, m, OCH_2Me), 3.47 and 3.7 (each 0.5 H, each s, 23-H), 3.72–3.95 (4 H, m, OCH_2CH_2O), 4.05–4.15 (1 H, m, 2-H), 4.15 and 4.21 (each 0.5 H, each s, 22-H), 4.26 (1 H, br d, *J* 4.3, 3-H) and 4.72 and 4.76 (each 0.5 H, each q, *J* 5.5, OC*H*MeO); *m/z* 632 (M^+) (Found: M^+, 632.4295. $C_{37}H_{60}O_8$ requires *M*, 632.4282).

(20S,22R,23R,24S,25S)-23-*Acetoxy*-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-5α-*ergostano*-26,22-*lactone* **21**.—A mixture of the ether **20** (30 mg, 0.047 mmol) and PTSA (9 mg, 0.047 mmol) in acetone (3 cm^3) was stirred for 1 h at 0 °C. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was used for the next reaction without purification.

A mixture of the crude alcohol, acetic anhydride (0.008 cm^3), triethylamine (0.007 cm^3) and CH_2Cl_2 (2 cm^3) was stirred for 0.5 h at 0 °C. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (3:1) as eluent to afford the *acetate* **21** (19 mg, 68%) as an oil;

* See note on p. 2644.

$\nu_{max}(CHCl_3)/cm^{-1}$ 1730; δ_H 0.67 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 1.11 (3 H, d, *J* 6.7, 21-H_3), 1.2 (3 H, d, *J* 6.7, 28-H_3), 1.24 (3 H, d, *J* 6.7, 27-H_3), 1.33 and 1.48 (each 3 H, each s, CMe_2), 2.07 (3 H, s, Ac), 3.7–4 (4 H, m, OCH_2CH_2O), 4–4.2 (1 H, m, 2-H), 4.27 (2 H, br s, 3- and 22-H) and 4.81 (1 H, t, *J* 1.8, 23-H); *m/z* 602 (M^+) (Found: M^+, 602.3817. $C_{35}H_{54}O_8$ requires *M*, 602.3817).

(20S,22R,23R,24S,25S)-23-(1-*Ethoxyethoxy*)-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-5α-*ergostane*-22,26-*diol* **22**.—To a stirred suspension of LAH (144 mg, 3.8 mmol) in diethyl ether (12 cm^3) at 0 °C was added a solution of the lactone **20** (1.2 g, 1.9 mmol) in diethyl ether (10 cm^3) and the reaction mixture was stirred for 3 h at room temperature. After addition of 20% aq. sodium hydroxide, the mixture was stirred for 0.5 h and the white precipitate was filtered off. The filtrate was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (3:1) as eluent to afford the *diol* **22** (1.2 g, 97%) as an oily, inseparable diastereoisomeric mixture (1:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400; δ_H 0.67 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 0.86 and 0.88 (each 1.5 H, each d, *J* 6.7, 2 × Me), 0.89 and 0.91 (each 1.5 H, each d, *J* 6.7, Me), 0.97 (3 H, d, *J* 6.7, Me), 1.24 and 1.26 (each 1.5 H, each t, *J* 6.7, OCH_2Me), 1.33 and 1.48 (each 3 H, each s, CMe_2), 1.34 and 1.36 (each 1.5 H, each d, *J* 5.5, OCH*Me*O), 3.4–4.0 (10 H, m, 22- and 23-H, 26-H_2, OCH_2Me and OCH_2CH_2O), 4.03–4.2 (1 H, m, 2-H), 4.27 (1 H, br d, *J* 4.3, 3-H) and 4.58 and 4.88 (each 0.5 H, each q, *J* 5.5, OC*H*MeO); *m/z* 621 (M^+ − 15) (Found: M^+ − 15, 621.4365. $C_{36}H_{61}O_8$ requires *m/z* 621.4365).

(20S,22R,23R,24S)-23-(1-*Ethoxyethoxy*)-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-5α-*ergostan*-22-*ol* **24**.—To a stirred solution of the alcohol **22** (60 mg, 0.09 mmol) and triethylamine (10.5 mg, 0.1 mmol) in CH_2Cl_2 (0.6 cm^3) at 0 °C was added dropwise methanesulfonyl chloride (11.9 mg, 0.1 mmol) and the reaction mixture was stirred for 10 min at the same temperature. After addition of brine, the product was extracted with CH_2Cl_2. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give the crude mesyl ester **23**, which was relatively unstable. A small sample was purified for analytical data by column chromatography on silica gel with hexane–AcOEt (4:1) as eluent to afford the mesate **23** as an oil; δ_H 0.66 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 0.94 (3 H, d, *J* 6.7, Me), 1.01 (6 H, d, *J* 6.7, 2 × Me), 1.26 (3 H, t, *J* 6.7, OCH_2Me), 1.3 (3 H, d, *J* 4.9, OCH*Me*O), 1.33 and 1.48 (each 3 H, each s, CMe_2), 3.01 (3 H, s, SO_2Me), 3.7–4.03 (8 H, m, 22- and 23-H, OCH_2Me and OCH_2CH_2O), 4.05–4.25 (1 H, m, 2-H), 4.27 (1 H, br d, *J* 4.3, 3-H) and 5.05 and 5.13 (each 0.5 H, each q, *J* 4.9, OC*H*MeO). The mesyl ester **23** was used for the next reaction without purification.

To a stirred suspension of LAH (6.2 mg, 0.16 mmol) in diethyl ether (10 cm^3) was added a solution of the mesate **23** in diethyl ether (2 cm^3) at 0 °C and the reaction mixture was stirred for 3 h at room temperature. After addition of 20% aq. sodium hydroxide, the mixture was stirred for 0.5 h and the white precipitate was filtered off. The filtrate was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (4:1) as eluent to afford the *title compound* **24** (46 mg, 79%) as an oily, inseparable diastereoisomeric mixture (1:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400; δ_H 0.66 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 0.9 (3 H, t, *J* 6.7, Me), 0.95 (3 H, d, *J* 6.7, Me), 1.1 (3 H, d, *J* 6.7, Me), 1.26 (3 H, t, *J* 6.7, OCH_2Me), 1.31 (3 H, d, *J* 5.5, OCH*MeO*), 1.33 and 1.48 (each 3 H, each s, CMe_2), 3.7–4.03 (8 H, m, 22- and 23-H, OCH_2Me and OCH_2CH_2O), 4.05–4.17 (1 H, m, 2-H), 4.27 (1 H, br d, *J* 4.3, 3-H) and 5.03 and 5.12 (each 0.5 H, each q, *J* 5.5, OC*H*MeO); *m/z* 560 (M^+ − 60) (Found: M^+ − 60, 560.4432. $C_{35}H_{60}O_5$ requires *m/z* 560.4438).

(20S,22R,23R,24S)-2α,3α,22,23-*Tetrahydroxy*-5α-*ergostan*-6-*one* (*Castasterone*) **2**.—A mixture of the ether **24** (124 mg, 0.2 mmol) and 10% hydrochloric acid (1 cm^3) in THF (2 cm^3) was refluxed for 3 h. After cooling, the product was extracted with $CHCl_3$. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with AcOEt as eluent to afford the title compound **2** (86.8 mg, 94%) as needles, m.p. 259–260 °C (from $CHCl_3$–MeOH) (lit., 259–261,[3] 252–255,[5b] and 258–260 °C [5d]), $[\alpha]_D^{25}$ +0.92 [*c* 1.46, $CHCl_3$–MeOH (9:1)] {lit.,[5d] $[\alpha]_D^{24.5}$ +0.03 (*c* 1.17, $CHCl_3$–MeOH (9:1)}. The spectroscopic data were identical with those reported.[5h]

(20S,22R,23R,24S)-23-(1-*Ethoxyethoxy*)-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-25-*methyl*-5α-*ergostano*-26,22-*lactone* **25**.—To a stirred solution of LDA [prepared from diisopropylamine (0.21 cm^3, 1.46 mmol) and BuLi (1.62 mol dm^{-3}; 0.75 cm^3, 1.22 mmol) in hexane] in THF (1 cm^3) at −78 °C was added dropwise a solution of the lactone **20** (308 mg, 0.49 mmol) in THF (1 cm^3). The reaction mixture was allowed to warm gradually to −20 °C and was then recooled to −78 °C. Methyl iodide (0.05 cm^3, 0.73 mmol) was added dropwise to the mixture at −78 °C and the reaction mixture was allowed to warm to 0 °C. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (3:1) as eluent to afford the *lactone* **25** (292 mg, 93%) as an oily, inseparable diastereoisomeric mixture (1:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1710; δ_H 0.69 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 1.03 (3 H, d, *J* 6.7, Me), 1.12 (3 H, d, *J* 6.7, Me), 1.16 and 1.32 (each 3 H, each s, $COCMe_2$), 1.2 (3 H, t, *J* 6.7, OCH_2Me), 1.31 (3 H, d, *J* 5.5, OCH*Me*O), 1.32 and 1.48 (each 3 H, each s, CMe_2), 3.4–4 (7 H, m, 23-H, OCH_2Me and OCH_2CH_2O), 4–4.2 (1 H, m, 2-H), 4.26 (1 H, br d, *J* 4.3, 3-H), 4.5 and 4.56 (each 0.5 H, each d, *J* 4.3, 22-H) and 4.71 and 4.73 (each 3 H, each q, *J* 5.5, OC*H*MeO); *m/z* 646 (M^+) (Found: M^+, 646.4447. $C_{38}H_{62}O_8$ requires *M*, 646.4445).

(20S,22R,23R,24S)-23-(1-*Ethoxyethoxy*)-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-25-*methyl*-5α-*ergostane*-22,26-*diol* **26**.—The same procedure as for the lactone **20** was applied to lactone **25** (67 mg, 0.1 mmol) to afford the *diol* **26** (56.7 mg, 84%) as an oily, inseparable diastereoisomeric mixture (1:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400; δ_H 0.67 and 0.68 (each 1.5 H, each s, 18-H_3), 0.84 (3 H, s, 19-H_3), 0.85–1.3 (15 H, m, 4 × Me and OCH_2Me), 1.33 and 1.48 (each 3 H, each s, CMe_2), 1.36 and 1.43 (each 1.5 H, each d, *J* 5.5, OCH*MeO*), 3.2–4 (10 H, m, 22- and 23-H, 26-H_2, OCH_2Me and OCH_2CH_2O), 4.04–4.2 (1 H, m, 2-H), 4.27 (1 H, br d, *J* 3.7, 3-H) and 4.71 and 5.02 (each 0.5 H, each q, *J* 5.5, OC*H*MeO); *m/z* 635 (M^+ − 15) (Found: M^+ − 15, 635.4520. $C_{37}H_{63}O_8$ requires *m/z*, 635.4521).

(20S,22R,23R,24S)-6-*Ethylenedioxy*-22,23-*ethylidenedioxy*-2α,3α-*isopropylidenedioxy*-25-*methyl*-5α-*ergostan*-26-*ol* **29**.—A solution of the ether **26** (32 mg, 0.049 mmol) and PTSA (3 mg, 0.016 mmol) in acetone (2 cm^3) was stirred for 1 h at room temperature. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (4:1) as eluent to afford the *acetal* **29** (23 mg, 80%) as an oily, inseparable diastereoisomeric mixture (4:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450; δ_H 0.67 (3 H, s, 18-H_3), 0.78 and 0.89 (0.6 H and 2.4 H, each s, Me), 0.83 and 0.93 (0.6 H and 2.4 H, each d, *J* 6.7, Me),

0.84 (3 H, s, 19-H_3), 0.89 and 1.01 (0.6 H and 2.4 H, each d, *J* 6.7, Me), 1.03 and 1.08 (2.4 H and 0.6 H, each s, Me), 1.28 and 1.32 (0.6 H and 2.4 H, each d, *J* 4.9, OCH*Me*O), 1.33 and 1.48 (each 3 H, each s, CMe_2), 3–4.2 (9 H, m, 2-, 22- and 23-H, 26-H_2 and OCH_2CH_2O), 4.27 (1 H, br d, *J* 3.7, 3-H) and 4.99 and 5.17 (0.2 H and 0.8 H, each q, *J* 4.9, OC*H*MeO); *m/z* 604 (M^+) (Found: M^+, 604.4339. $C_{36}H_{60}O_7$ requires *M*, 604.4339).

O-(20S,22R,23R,24S)-6-*Ethylenedioxy*-22,23-*ethylidenedioxy*-2α,3α-*isopropylidenedioxy*-25-*methyl*-5α-*ergostan*-26-*yl* S-*Methyl Dithiocarbonate* **30**.—A solution of the alcohol **29** (150 mg, 0.25 mmol), carbon disulfide (2 cm^3, 33 mmol) and 1,5-diazabicyclo[4.3.0]non-5-ene (0.12 cm^3, 0.99 mmol) in dimethylformamide (DMF) (1 cm^3) was stirred for 1 h at room temperature and methyl iodide (2 cm^3, 32 mmol) was added to the mixture. The reaction mixture was stirred at the same temperature for 1 h and then poured into water. The product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (4:1) as eluent to afford the *dithiocarbonate* **30** [99 mg, 89% based on the consumed starting material (54 mg)] as an oil; δ_H 0.66 (3 H, s, 18-H_3), 0.83 (3 H, s, 19-H_3), 0.93 and 0.96 (each 3 H, each d, *J* 6.7, 2 × Me), 1.02 and 1.06 (each 3 H, each s, 2 × Me), 1.3 (3 H, d, *J* 4.9, OCH*Me*O), 1.33 and 1.48 (each 3 H, each s, CMe_2), 3.6–4 (6 H, m, 22- and 23-H and OCH_2CH_2O), 4–4.2 (1 H, m, 2-H), 4.27 (1 H, br s, 3-H), 4.29 and 4.56 [each 1 H, each d, *J* 11, $CH_2OC(S)$] and 5.11 (1 H, q, *J* 4.9, OC*H*MeO); *m/z* 694 (M^+) (Found: M^+, 694.3944. $C_{38}H_{62}O_7S_2$ requires *M*, 694.3937).

(20S,22R,23R,24S)-6-*Ethylenedioxy*-22,23-*ethylidenedioxy*-2α,3α-*isopropylidenedioxy*-25-*methyl*-5α-*ergostane* **31**.—A solution of the ester **30** (200 mg, 0.29 mmol), a catalytic amount of azoisobutyronitrile (AIBN) and tributyltin hydride (0.16 cm^3, 0.58 mmol) in toluene (16 cm^3) was heated for 0.5 h. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (5:1) as eluent to afford the *title compound* **31** (126 mg, 74%) as an oily, inseparable diastereoisomeric mixture (1:1); δ_H 0.67 and 0.74 (each 1.5 H, each s, 18-H_3), 0.84 (3 H, s, 19-H_3), 0.84 and 0.88 (each 1.5 H, each d, *J* 6.7, Me), 0.91 and 0.93 (each 4.5 H, each s, CMe_3), 0.92 (3 H, d, *J* 6.1, Me), 1.3 and 1.34 (each 1.5 H, each d, *J* 4.9, OCH*Me*O), 1.32 and 1.48 (each 3 H, each s, CMe_2), 3.6–4.2 (7 H, m, 2-, 22- and 23-H and OCH_2CH_2O), 4.27 (1 H, br d, *J* 3.7, 3-H) and 4.72 and 5.12 (each 0.5 H, each q, *J* 4.9, OC*H*MeO); *m/z* 588 (M^+) (Found: M^+, 588.4385. $C_{36}H_{60}O_6$ requires *M*, 588.4387).

(20S,22R,23R,24S)-22,23-*Ethylidenedioxy*-2α,3α-*dihydroxy*-25-*methyl*-5α-*ergostan*-6-*one* **32**.—A solution of the acetal **31** (90 mg, 0.15 mmol) and 10% hydrochloric acid (1 cm^3) in THF (5 cm^3) was stirred at room temperature for 10 min. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (1:1) as eluent to afford the title compound **32** (62 mg, 80%) as an oily, inseparable diastereoisomeric mixture (1:1); δ_H 0.67 (3 H, s, 18-H_3), 0.74 and 0.76 (each 1.5 H, each s, 19-H_3), 0.85 and 0.89 (each 1.5 H, each d, *J* 6.7, Me), 0.91 and 0.93 (each 4.5 H, each s, CMe_3), 0.93 and 1.02 (each 1.5 H, each d, *J* 6.1, Me), 1.31 and 1.35 (each 1.5 H, each d, *J* 4.9, OCH*Me*O), 3.68 and 4.02 (each 1 H, each d, *J* 8.5, 22- and 23-H), 3.7–3.9 (1 H, m, 2-H) and 4.06 (1 H, br s, 3-H); FAB *m/z* 505 ($M^+ + 1$).

(20S,22R,23R,24S)-2α,3α,22,23-*Tetrahydroxy*-25-*methyl*-5α-*ergostan*-6-*one* (25-*Methylcastasterone*) **4**.—A solution of the acetal **32** (20 mg, 0.04 mmol) in AcOEt (4 cm^3)–water (1 cm^3) was refluxed for 1 h. After cooling, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with AcOEt as eluent to afford the tetraol **4** (16 mg, 84%) as needles, m.p. 249–250 °C (from MeOH) (lit.,[6] 251–253 °C); $[\alpha]_D^{29}$ +13.4 (*c* 0.24, MeOH) {lit.,[6] $[\alpha]_D^{22}$ +14.3 (*c* 0.11, MeOH)}. The spectroscopic data were identical with those reported.[6]

(20S,22R,23R,24R,25S)-23-(1-*Ethoxyethoxy*)-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-24-*phenyl*-5α-*cholestano*-26,22-*lactone* **33**.—To a stirred solution of lithium diphenylcuprate [prepared from copper(I) iodide (417 mg, 2.2 mmol) and PhLi (1.76 mol dm^{-3}; 2.3 cm^3, 4.06 mmol) in diethyl ether] in diethyl ether (5 cm^3) was added dropwise a solution of the unsaturated lactone **19** (500 mg, 0.81 mmol) in diethyl ether (5 cm^3) at −10 °C. The reaction mixture was stirred for 1 h at the same temperature. After addition of brine, the product was extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel with hexane–AcOEt (5:1) as eluent to afford the *lactone* **33** (442 mg, 79%) as an oily, inseparable diastereoisomeric mixture (1:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1700; δ_H 0.57 (3 H, s, 18-H_3), 0.8 (3 H, s, 19-H_3), 1.2 and 1.22 (each 3 H, each d, *J* 6.7, 21- and 27-H_3), 1.3 and 1.32 (each 1.5 H, each t, *J* 6.7, OCH_2Me), 1.32 and 1.48 (each 3 H, each s, CMe_2), 1.41 and 1.42 (each 1.5 H, each d, *J* 4.9, OCH*Me*O), 3.2–4.0 (8 H, m, 23- and 24-H, OCH_2Me and OCH_2CH_2O), 4.0–4.2 (1 H, m, 2-H), 4.25 (1 H, br d, *J* 4.3, 3-H), 4.35 and 4.39 (each 0.5 H, each d, *J* 2.4, 22-H), 4.85 and 5.02 (each 0.5 H, each q, *J* 4.9, OC*H*MeO) and 7.1–7.4 (5 H, m, Ph); *m/z* 694 (M^+) (Found: M^+, 694.4435. $C_{42}H_{62}O_8$ requires *M*, 694.4442).

(20S,22R,23R,24R,25S)-23-(1-*Ethoxyethoxy*)-6-*ethylenedioxy*-2α,3α-*isopropylidenedioxy*-24-*phenyl*-5α-*cholestane*-22,26-*diol* **34**.—The same procedure as for the lactone **20** was applied to lactone **33** (282 mg, 0.41 mmol) to afford the *diol* **34** (256 mg, 90%) as an oily, inseparable diastereoisomeric mixture (1:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400; δ_H 0.61 and 0.66 (each 1.5 H, each s, 18-H_3), 0.82 and 0.83 (each 1.5 H, each s, 19-H_3), 0.92 and 0.94 (each 1.5 H, each d, *J* 6.7, Me), 1.18 and 1.19 (each 1.5 H, each d, *J* 6.7, Me), 1.25 and 1.26 (each 1.5 H, each t, *J* 6.7, OCH_2Me), 1.32 and 1.47 (each 3 H, each s, CMe_2), 1.43 and 1.49 (each 1.5 H, each d, *J* 5.5, OCH*Me*O), 3–4 (10 H, m, 22- and 23-H, 26-H_2, OCH_2Me and OCH_2CH_2O), 4–4.2 (1 H, m, 2-H), 4.26 (1 H, br s, 3-H), 4.75 and 5.01 (each 0.5 H, each q, *J* 5.5, OC*H*MeO) and 7.1–7.4 (5 H, m, Ph); *m/z* 683 ($M^+ - 15$) (Found: $M^+ - 15$, 683.4519. $C_{41}H_{63}O_8$ requires *m/z* 683.4521).

(20S,22R,23R,24R,25S)-6-*Ethylenedioxy*-22,23-*ethylidenedioxy*-2α,3α-*isopropylidenedioxy*-24-*phenyl*-5α-*cholestan*-26-*ol* **35**.—The same procedure as for the ethoxyethyl ether **26** was applied to compound **34** (190 mg, 0.27 mmol) to afford the *acetal* **35** (126 mg, 71%) as a single oily isomer; $\nu_{max}(CHCl_3)/cm^{-1}$ 3420; δ_H 0.66 (3 H, s, 18-H_3), 0.82 (3 H, s, 19-H_3), 0.99 (3 H, d, *J* 5.5, Me), 1.15 (3 H, d, *J* 7.3, Me), 1.24 (3 H, d, *J* 4.9, OCH*Me*O), 1.31 and 1.46 (each 3 H, each s, CMe_2), 3.2 and 3.44 (each 1 H, each dd, *J* 4.3 and 11, CH_2OH), 3.36 (1 H, d, *J* 7.9, 22-H), 3.6–4 (4 H, m, OCH_2CH_2O), 4–4.2 (1 H, m, 2-H), 4.2 (1 H, dd, *J* 2.4 and 7.9, 23-H), 4.26 (1 H, br s, 3-H), 5.14 (1 H, q, *J* 4.9, OC*H*MeO) and 7.25–7.3 (5 H, m, Ph); *m/z* 637 ($M^+ - 15$) (Found: $M^+ - 15$, 637.4096. $C_{39}H_{57}O_7$ requires *m/z* 637.4102).

(20S,22R,23R,24R)-6-*Ethylenedioxy*-22,23-*ethylidenedioxy*-2α,3α-*isopropylidenedioxy*-24-*phenyl*-5α-*cholestane* **37**.—The same procedure as for the alcohol **22** was applied to compound

35 (112 mg, 0.17 mmol) to afford the *title compound* **37** (78.7 mg, 72%), *via* the mesate **36**, as an oil; δ_H 0.67 (3 H, s, 18-H_3), 0.71 (3 H, d, *J* 6.1, Me), 0.83 (3 H, s, 19-H_3), 1.0 and 1.11 (each 3 H, each d, *J* 6.7, 2 × Me), 1.22 (3 H, d, *J* 4.9, OCH*Me*O), 1.32 and 1.47 (each 3 H, each s, CMe_2), 3.38 (1 H, d, *J* 7.9, 22-H), 3.6–4.0 (4 H, m, OCH_2CH_2O), 4.0–4.2 (1 H, m, 2-H), 4.2–4.3 (2 H, m, 3- and 23-H), 5.12 (1 H, q, *J* 4.9, OC*H*MeO) and 7.1–7.3 (5 H, m, Ph); *m/z* 636 (M^+) (Found: M^+, 636.4393. $C_{40}H_{60}O_6$ requires *M*, 636.4390).

(20S,22R,23R,24R)-22,23-*Ethylidenedioxy*-2α,3α-*dihydroxy*-24-*phenyl*-5α-*cholestan*-6-*one* **38**.—The same procedure as for the acetal **31** was applied to compound **37** (75 mg, 0.12 mmol) to afford the *title compound* **38** (58 mg, 89%) as an oil; δ_H 0.67 (3 H, s, 18-H_3), 0.71 (3 H, d, *J* 6.1, Me), 0.71 (3 H, s, 19-H_3), 1.02 and 1.11 (each 3 H, each d, *J* 6.7, 2 × Me), 1.23 (3 H, d, *J* 4.9, OCH*Me*O), 2.66 (1 H, dd, *J* 3.1 and 9.8, 5-H), 3.38 (1 H, d, *J* 7.9, 22-H), 3.6–3.8 (1 H, m, 2-H), 4.03 (1 H, br d, *J* 2.5, 3-H), 4.22 (1 H, dd, *J* 2.5 and 7.9, 23-H), 5.13 (1 H, q, *J* 4.9, OC*H*MeO) and 7.2–7.3 (5 H, m, Ph); *m/z* 552 (M^+) (Found: M^+, 552.3814. $C_{35}H_{52}O_5$ requires *M*, 552.3814).

(20S,22R,23R,24R)-2α,3α,22,23-*Tetrahydroxy*-24-*phenyl*-5α-*cholestan*-6-*one* (24-*Phenylbrassinone*) **5**.—The same procedure as for the acetal **32** was applied to compound **38** (39 mg, 0.07 mmol) to afford the *title compound* **5** (29 mg, 78%) as plates, m.p. 134–135 °C (from Et_2O) (Found: C, 71.5; H, 9.65. $C_{33}H_{50}O_5 \cdot 1.5H_2O$ requires C, 71.6; H, 9.35%); $[\alpha]_D^{28}$ +4.32 (*c* 0.53, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3580 and 1705; δ_H 0.67 (3 H, s, 18-H_3), 0.68 (3 H, d, *J* 6.1, Me), 0.75 (3 H, s, 19-H_3), 0.94 and 1.13 (each 3 H, each d, *J* 6.7, 2 × Me), 2.65 (1 H, dd, *J* 2.4 and 12.2, 5-H), 3.09 (1 H, d, *J* 7.9, 22-H), 3.6–3.8 (1 H, m, 2-H), 4.02 (1 H, dd, *J* 2.4 and 7.9, 23-H), 4.04 (1 H, d, *J* 2.4, 3-H) and 7.2–7.3 (5 H, m, Ph); FAB *m/z* 527 ($M^+ + 1$).

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