A Stereoselective Total Synthesis of 17-*O*-Acetyl-14α-hydroxy-3-*O*-methyl-11-oxo-estradiol-17β

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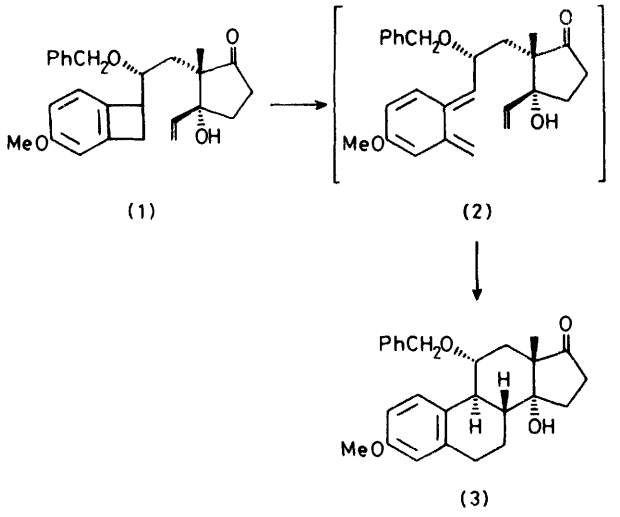
A stereoselective total synthesis of the title compound (13) was achieved with thermolysis of 3-hydroxy-2-[2-benzyloxy-2-(4-methoxy-1,2-dihydrobenzocyclobutenyl)ethyl]-2-methyl-3-vinylcyclopentan-1-one (1) as the key step. Compound (13) was converted into 14,15-didehydro-3-*O*-methylestradiol-17β which was identified by comparison with an authentic sample.

RECENTLY, extensive studies towards the synthesis of various types of 11-oxidised 14-hydroxyestrane derivatives have been reported.[1,2] These derivatives are of interest because of their biological importance [3] and in that they are synthetic precursors of the pharmaceutically important 19-nor-steroids [4], although a compound with the same stereochemistry as the natural estrane steroids has not yet been obtained. This prompted us to explore a stereoselective synthesis of 17-*O*-acetyl-14α-hydroxy-3-*O*-methyl-11-oxo-estradiol-17β (13). Synthesis of aromatic steroid nuclei based on novel BC

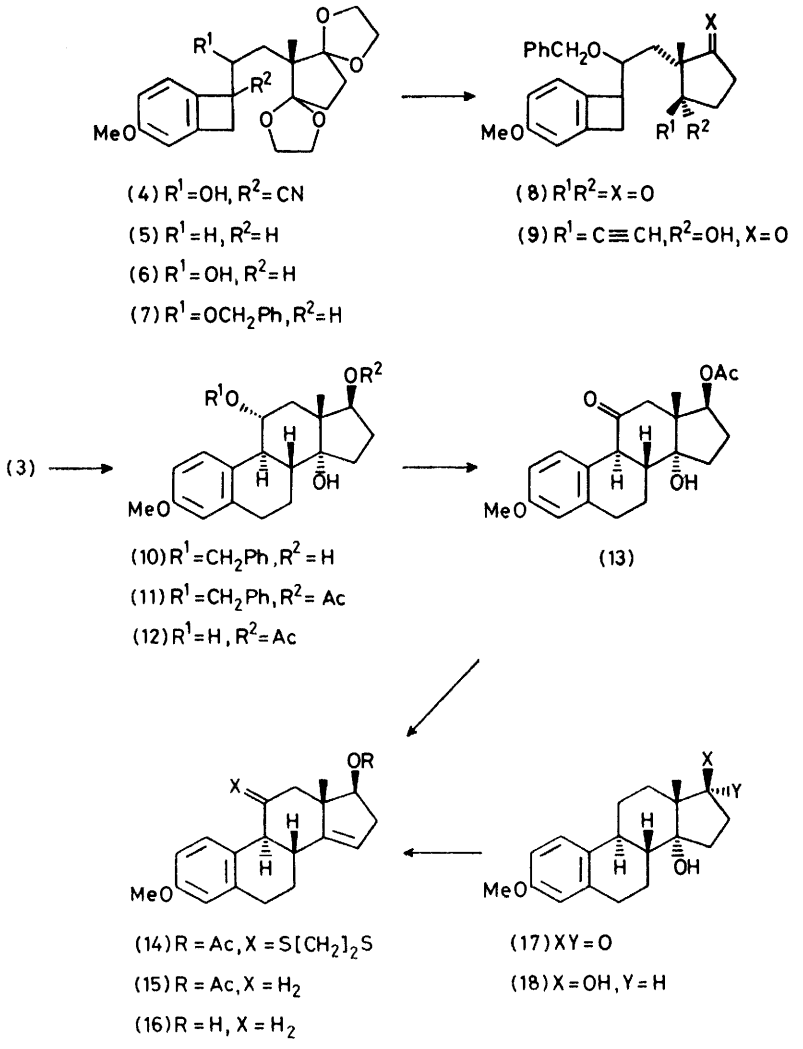


SCHEME 1

ring construction *via* intramolecular cycloaddition to *o*-quinodimethanes derived from benzocyclobutenes or other precursors is of current interest. The use of this type of reaction has already been established as an effective method for the synthesis of aromatic steroids.[5] We now report the stereoselective synthesis of 11β-benzyloxy-14α-hydroxyestrone methyl ether (3), by way of the *o*-quinodimethane (2) generated *in situ* by thermolysis of the benzocyclobutene (1).

Reduction of the sodium salt (generated using sodium hydride) of the hydroxy-cyanide (4) [5d,f] with sodium in liquid ammonia afforded the hydroxy-compound (6), in contrast to the direct reduction of (4) which yielded compound (5).[5d,f] The diketone (8), obtained in high yield by benzylation of (6) with benzyl bromide in the presence of sodium hydride in tetrahydrofuran followed by acid treatment of the resulting benzyloxy-compound (7), was treated with vinylmagnesium bromide in tetrahydrofuran to give the olefinic benzocyclobutene (1). This derivative exhibited an absorption at 1 735 cm^{-1} in its i.r. spectrum due to the five-membered ketone and signals due to the vinyl group at δ 4.86—6.20 in its n.m.r. spectrum. Alternatively, compound (1) was obtained in good yield using the following procedure. Thus, reaction of (8) with lithium acetylide, generated from acetylene and lithium, in liquid ammonia afforded compound (9) which showed absorptions at 3 320 and 1 740 cm^{-1} in its i.r. spectrum due to acetylenic hydrogen and five-membered ring ketone, respectively. Hydrogenation of (9), under an atmosphere of hydrogen in the presence of Lindlar catalyst in acetone, gave (1) in high yield. The product was identical (i.r. and n.m.r. spectra) to the compound obtained above. Heating the olefinic compound (1) in *o*-dichlorobenzene at 180 °C for 6 h under a current of nitrogen furnished, *via* the *o*-quinodimethane (2), the steroidal compound (3). Although the structure of compound (3) was deduced from the spectroscopic data and on the basis of previous work,[5] its stereochemistry could not be determined unambigously at this stage. Compound (3) thus obtained was reduced with sodium borohydride in methanol to give the diol (10) which was acetylated with acetic anhydride in pyridine, using 4-dimethylaminopyridine as catalyst, to afford the monoacetate (11). Finally, the title compound (13) was obtained by hydrogenolysis of (11) under a current of hydrogen in the presence of palladium–carbon in methanol, followed by Jones oxidation of the resulting compound (12). The stereochemistry of compound (13) was determined as follows.

Desulphurisation of the thioacetal (14), resulting from reduction of (13) with ethanedithiol in the presence of boron trifluoride, using Raney nickel in ethanol, furnished the acetate (15). Hydrolysis of (15) using potassium hydroxide in ethanol gave 14,15-didehydro-3-*O*-methylestradiol (16). An authentic sample of (15) was obtained by successive treatment of 14α-hydroxyestrone methyl ether (17) [5d,f] with sodium borohydride in ethanol and 5N-hydrochloric acid in acetone. Both samples thus obtained were shown to be identical [by spectroscopic



SCHEME 2

(i.r. and n.m.r.) comparison and by mixed m.p.].* Thus we have achieved an effective and stereoselective synthesis of 17-*O*-acetyl-14α-hydroxy-3-*O*-methyl-11-oxoestradiol-17β (3).

The stereoselective formation of (3), *i.e.* the stereoselective cycloaddition of *o*-quinodimethane (2) generated *in situ* by thermolysis of the benzocyclobutene (1), is readily understood in the light of preceding papers.[5] †

EXPERIMENTAL

1,1 : 3,3-*Bisethylenedioxy*-2-[2-*hydroxy*-2-(4-*methoxy*-1,2-*dihydrobenzocyclobuten*-1-*yl*)*ethyl*]-2-*methylcyclopentane* (6).—To a solution of the hydroxy-cyanide (4) (4.41 g) in anhydrous tetrahydrofuran (30 ml) at 0 °C was added sodium hydride (5.28 g; 50% dispersion in oil). The mixture was stirred for 30 min at room temperature, cooled to −78 °C, and then into it was distilled liquid ammonia (50 ml). Sodium metal (1.11 g) was added and the resulting mixture was stirred for 3 h at −78 °C and then quenched with an excess of solid ammonium chloride. After evaporation of the solvent, the residue was diluted with saturated aqueous ammonium chloride and extracted with ether. The extract was washed with saturated sodium chloride solution and dried (Na_2SO_4). Removal of the solvent afforded a reddish oil which was chromatographed on neutral alumina (grade III, 150 g) using benzene–hexane (9 : 1, v/v) as eluant to give the *hydroxy-compound* (6) (3.357 g, 81.2%) as a viscous syrup (Found: C, 65.85; H, 7.4. $C_{21}H_{28}O_6 \cdot 1/3H_2O$ requires C, 65.95; H, 7.8%), $\nu_{max.}$ ($CHCl_3$) 3 680 cm^{-1} (OH); δ(CCl_4), 1.07 (3 H, s, Me), 1.86 (4 H, s, CH_2CH_2), 3.70 (3 H, s, OMe), 3.80—4.23 [9 H, m, C*H*(OH) and 2 × OCH_2CH_2O], and 6.80—7.20 (3 H, m, ArH); *m/e* 376 (M^+).

* Since the stereochemistry at C-8, C-9, and C-13 was thus established the stereochemistry of the two hydroxy-groups at C-11 and C-14 of compound (12) could both readily be assigned as α from its n.m.r. spectrum. The aromatic proton on C-1 was observed at abnormally low field (δ 8.03) suggesting that the hydroxy-group was oriented as α and thus allowing the hydroxy-group and aromatic proton at C-1 to have a *peri*-interaction. The 18-methyl protons were observed at normal field (δ 0.93) suggesting the relative configuration of methyl and hydroxy-groups to be *trans*,[6] and therefore the C-14 hydroxy-group to be α. This was consistent with previous results.[5d,f]

† The exact mechanism for the stereoselective formation of compounds (1) and (9) remains unknown.

2-[2-*Benzyloxy*-2-(4-*methoxy*-1,2-*dihydrobenzocyclobuten*-1-*yl*)*ethyl*]-1,1 : 3,3-*bisethylenedioxy*-2-*methylcyclopentane* (7).—To a stirred solution of the hydroxy-compound (6) (4.082 g) in anhydrous tetrahydrofuran (25 ml) under nitrogen was added sodium hydride (5.211 g, 50% dispersion in oil) and benzyl bromide (2.228 g). Stirring was continued for 5 h at 60 °C, and then the reaction was quenched with an excess of ammonium chloride. After removal of the solvent, water was added and the resulting solution was extracted with ether. The extract was washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and evaporated. The residue was chromatographed on neutral alumina (grade III; 120 g) using benzene as eluant to give the *benzyloxy-compound* (7) (4.65 g, 92.1%) as an oil (Found: C, 72.35; H, 7.45. $C_{28}H_{34}O_6$ requires C, 72.1; H, 7.35%); δ(CCl_4), 1.16 (3 H, s, Me), 1.80 (4 H, s, CH_2CH_2), 2.80—3.40 (2 H, m, ArCH_2), 3.73 (3 H, s, OMe), 3.80—4.13 (8 H, m, 2 × OCH_2CH_2O), 4.45 and 4.51 (2 H, each d, *J* 10 Hz, OCH_2Ph), and 6.57—7.5 (8 H, m, ArH and OCH_2Ph); *m/e* 466 (M^+).

2-[2-*Benzyloxy*-2-(4-*methoxy*-1,2-*dihydrobenzocyclobuten*-1-*yl*)*ethyl*]-2-*methylcyclopentane*-1,3-*dione* (8).—A mixture of the benzyloxy-compound (7) (4.287 g), 10% hydrochloric acid (10 ml), and tetrahydrofuran (40 ml) was stirred for 5 h at room temperature. After addition of saturated aqueous sodium hydrogencarbonate (50 ml), the solution was extracted with ether. The extract was washed with saturated aqueous sodium chloride and dried (Na_2SO_4). Removal of the solvent left a yellow oil which was chromatographed on silica gel (80 g) using benzene as eluant to afford the *diketone* (8) (3.397 g, 97.7%) as a viscous syrup (Found: C, 74.7; H, 6.75. $C_{24}H_{26}O_4 \cdot 1/3H_2O$ requires C, 75.0; H, 7.0%), $\nu_{max.}$ ($CHCl_3$) 1 720 cm^{-1} (C=O); δ(CCl_4), 0.93 (3 H, s, Me), 1.50—2.60 [6 H, m, CH(OCH_2Ph)CH_2 and CH_2CH_2], 2.73—3.27 (2 H, m, ArCH_2), 3.67 (3 H, s, OMe), 4.29 and 4.48 (2 H, each d, *J* 11 Hz), and 6.50—7.20 (8 H, m, ArH and OCH_2Ph); *m/e* 378 (M^+).

2-[2-*Benzyloxy*-2-(4-*methoxy*-1,2-*dihydrobenzocyclobuten*-1-*yl*)*ethyl*]-3-*hydroxy*-2-*methyl*-3-*vinylcyclopentan*-1-*one* (1).—To a stirred solution of the diketone (8) (170 mg) in anhydrous tetrahydrofuran (5 ml) at 0 °C was added dropwise a 1.4M-solution of vinylmagnesium bromide in tetrahydrofuran (3 ml). After stirring for 4 h at room temperature, saturated aqueous ammonium chloride was added and the resulting solution was extracted with ether. The extract was washed with saturated aqueous sodium chloride and dried (Na_2SO_4). Evaporation afforded a brown oil which was chromatographed on silica gel (5 g) using benzene as eluant to give the *olefinic benzocyclobutene* (1) (85 mg, 46.6%) as an oil (Found: C, 76.3; H, 7.3. $C_{26}H_{30}O_4$ requires C, 76.8; H, 7.45%), $\nu_{max.}$ ($CHCl_3$) 3 680 (OH) and 1 735 cm^{-1} (C=O); δ(CCl_4) 0.90 (3 H, s, Me), 1.43—2.40 [6 H, m, CH_2CH_2 and CH(OCH_2Ph)CH_2], 2.90—3.33 (2 H, m, ArCH_2), 3.73 (3 H, s, OMe), 4.42 and 4.58 (2 H, each d, *J* 10 Hz, OCH_2Ph), 4.86—6.20 (3 H, m, CH=CH_2), and 6.50—7.50 (8 H, m, ArH and OCH_2Ph); *m/e* 406 (M^+).

2-[2-*Benzyloxy*-3-*ethynyl*-2-(4-*methoxy*-1,2-*dihydrobenzocyclobutenyl*)*ethyl*]-3-*hydroxy*-2-*methylcyclopentan*-1-*one* (9).—Lithium metal (92 mg) was added to liquid ammonia (50 ml), and acetylene gas was passed through the solution. After dissolution of the lithium, the mixture was cooled to −78 °C and the diketone (8) (468 mg) in anhydrous tetrahydrofuran (7 ml) was added during 10 min with vigorous stirring. The mixture was stirred for a further 1 h and quenched with an excess of solid ammonium chloride. The ammonia solution was evaporated and saturated aqueous ammonium chloride was added to the residue, which was then extracted with ether. The extract was washed with saturated aqueous sodium chloride and dried (Na_2SO_4). Evaporation left a reddish oil which was chromatographed on silica gel (15 g) using benzene as eluant to afford the *ethynyl compound* (9) (415 mg, 83.0%) as an oil (Found: M^+, 404.197 9. $C_{26}H_{28}O_4$ requires *M*, 404.198 6); $\nu_{max.}$ ($CHCl_3$) 3 675 (OH), 3 320 (C≡CH), and 1 740 cm^{-1} (C=O); δ(CCl_4) 1.03 (3 H, s, Me), 1.50—2.16 [2 H, m, CH(OCH_2Ph)CH_2], 2.20 (4 H, s, CH_2CH_2), 2.43 (1 H, s, C≡C*H*), 2.90—3.30 (2 H, m, ArCH_2), 3.73 (3 H, s, OMe), 4.35 and 4.50 (2 H, each d, *J* 11 Hz, OC$H_2C_6H_5$), and 6.50—7.50 (8 H, m, ArH and OCH_2Ph); *m/e* 404 (M^+).

Hydrogenation of Ethynyl Compound (9).—To a solution of the ethynyl compound (9) (325 mg) in acetone (70 ml) was added palladium carbonate (120 mg) and the mixture was stirred for 3 h under hydrogen. The solution was filtered and the solid was washed with acetone. The combined filtrate and washings were evaporated to yield a crude product which was chromatographed on silica gel (6 g) using benzene–ethyl acetate (97 : 3, v/v) as eluant to give the olefinic benzocyclobutene (1) (305 mg, 93.4%).

11-*Benzyloxy*-14α-*hydroxy*-3-*methoxyestra*-1,3,5(10)-*trien*-17-*one* (3).—A solution of compound (1) (81 mg) in *o*-dichlorobenzene (7 ml) was heated at 180 °C for 6 h under nitrogen. After evaporation of the solvent the residue was chromatographed on silica gel (3 g) using benzene–ethyl acetate (97 : 3, v/v) as eluant to give (3) (30 mg, 37%) as an *oil* (Found: M^+, 406.214 4. $C_{26}H_{30}O_4$ requires *M*, 406.214 4); $\nu_{max.}$ ($CHCl_3$) 1 740 cm^{-1} (C=O); δ($CDCl_3$) 1.02 (3 H, s, Me), 3.80 (3 H, s, OMe), 4.57 and 4.72 (2 H, each d, *J* 11 Hz, OCH_2Ph), 6.56—6.90 (2 H, m, ArH), 7.10—7.53 (5 H, m, OCH_2Ph), 7.67 (1 H, d, *J* 10 Hz, ArH); *m/e* 406 (M^+).

11α-*Benzyloxy*-14α-*hydroxy*-3-O-*methylestradiol*-17β (10).—To a stirred solution of (7) (824 mg) in methanol (180 ml) at 0 °C was added in small portions an excess of sodium borohydride. After reaction was complete the mixture was diluted with water and extracted with ether. The extract was washed with saturated aqueous sodium chloride and dried (Na_2SO_4). Evaporation of the solvent left a yellow crystalline solid which was recrystallised from ethanol to afford the *diol* (10) (620 mg, 74.9%) as needles, m.p. 177.0—178.5 °C (from ethanol) (Found: C, 73.9; H, 8.2. $C_{26}H_{32}O_4 \cdot 0.6H_2O$ requires C, 74.3; H, 8.0%); $\nu_{max.}$ ($CHCl_3$) 3 620 cm^{-1} (OH); δ($CDCl_3$) 0.90 (3 H, s, Me), 3.65 and 3.78 (2 H, each d *J* 12 Hz, OCH_2Ph), 3.83 (3 H, s, OMe), 6.70—6.96 (2 H, m, ArH), 7.36—7.57 (5 H, m, OCH_2Ph), and 7.76 (1 H, d, *J* 10 Hz, ArH); *m/e* 408 (M^+).

17-O-*Acetyl*-11α-*benzyloxy*-14α-*hydroxy*-3-O-*methylestradiol*-17β (11).—A solution of the diol (8) (470 mg) and 4-dimethylaminopyridine (146 mg) in pyridine (25 ml) and acetic anhydride (220 mg) was stirred overnight under nitrogen. The mixture was then diluted with water and extracted with ether. The extract was washed with saturated aqueous potassium hydrogensulphate and with saturated aqueous sodium chloride, and dried (Na_2SO_4). Evaporation left a yellow oil which was chromatographed on silica gel (15 g) using benzene–ethyl acetate (95 : 5, v/v) as eluant to give the *monoacetate* (11) (430 mg, 82.9%) as needles, m.p. 158—159 °C (from ethanol) (Found: C, 73.1; H, 7.5. $C_{28}H_{34}O_5 \cdot 0.5H_2O$ requires C, 73.15; H, 7.45%); $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1} (C=O); δ($CDCl_3$) 0.90 (3 H, s, Me), 3.10 (3 H, s, OCOMe), 3.80 (3 H, s, OMe), 4.80 and 4.76

(2 H, each d, *J* 12 Hz, OCH_2Ph), 5.20—5.60 (1 H, m, 17-H), 6.63—6.96 (2 H, m, ArH), 7.20—7.60 (5 H, m, OCH_2-*Ph*), and 7.75 (1 H, d, *J* 10 Hz, ArH); *m/e* 450 (M^+).

17-O-*Acetyl*-11α,14α-*dihydroxy*-3-O-*methylestradiol*-17β (12).—To a solution of compound (11) (410 mg) in methanol (65 ml) was added 10% palladium–carbon (100 mg) and the *mixture* stirred overnight under hydrogen. The mixture was filtered and the solid washed with methanol. The combined filtrates were evaporated to yield a crude crystalline solid which was recrystallised from ethyl acetate to give compound (12) (266 mg, 81.1%) as *needles*, m.p. 163—164 °C (from ethanol) (Found: M^+, 360.195 8. $C_{21}H_{28}O_5$ requires *M*, 360.193 7); $\nu_{max.}$ ($CHCl_3$) 3 625 (OH) and 1 730 cm^{-1} (C=O); δ($CDCl_3$) 0.93 (3 H, s, Me), 2.10 (3 H, s, OCOMe), 3.83 (3 H, s, OMe), 5.20—5.67 (1 H, m, 17-H), 6.70—7.10 (2 H, m, ArH), and 8.03 (1 H, d, *J* 9 Hz, ArH); *m/e* 360 (M^+).

17-O-*Acetyl*-14-*hydroxy*-3-O-*methyl*-11-*oxo-estradiol*-17β (13).—To a solution of the compound (12) (170 mg) in acetone (15 ml) at 0 °C was added Jones reagent (0.6 ml) and the mixture was stirred for 10 min at 0 °C. After dilution with water (15 ml), the solution was extracted with ethyl acetate. The extract was washed with saturated aqueous sodium chloride and dried (Na_2SO_4). Removal of the solvent afforded a pale yellow crystalline solid which was recrystallised from benzene to yield (13) (111 mg, 65.7%) as *needles*, m.p. 154—155 °C (Found: C, 70.15; H, 7.2. $C_{21}H_{26}O_5$ requires C, 70.35; H, 7.3%); $\nu_{max.}$ ($CHCl_3$) 3 610 (OH), 1 730 (C=O), and 1 710 cm^{-1} (11-C=O); δ($CDCl_3$) 0.90 (3 H, s, Me), 2.10 (3 H, s, OCOMe), 3.83 (3 H, s, OMe), 5.60—5.73 (1 H, m, 17-H), 6.63—7.03 (2 H, m, ArH), and 7.41 (1 H, d, *J* 10 Hz, ArH); *m/e* 358 (M^+).

17-O-*Acetyl*-14,15-*didehydro*-11,11-*ethylenedithio*-3-O-*methylestradiol*-17β (14).—A mixture of (13) (70 mg) in anhydrous dichloromethane (7 ml), ethanedithiol (40 mg), and boron trifluoride–ether (4 drops) was stirred for 5 h at 0 °C. After addition of water (10 ml), the reaction mixture was extracted with dichloromethane. This extract was washed with 5% aqueous sodium hydroxide and saturated aqueous sodium chloride and dried (Na_2SO_4). Evaporation left an oily product which was chromatographed on silica gel (5 g) using benzene–hexane (4 : 1, v/v) as eluant to give the *thioacetal* (14) (62 mg, 76.2%) as needles, m.p. 163—165 °C (from benzene–hexane) (Found: C, 64.25; H, 6.65. $C_{23}H_{28}O_3S_2 \cdot 0.5H_2O$ requires C, 64.50; H, 6.85%); $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1} (C=O); δ($CDCl_3$), 0.93 (3 H, s, Me), 2.10 (3 H, s, OCOMe), 3.82 (3 H, s, OMe), 4.93—5.40 (2 H, m, 15- and 17-H), 6.67—6.90 (2 H, m, ArH), and 8.80 (1 H, d, *J* 10 Hz, ArH); *m/e* 416 (M^+).

17-*O*-*Acetyl*-14,15-*didehydro*-3-O-*methylestradiol*-17β (15).—A mixture of the thioacetal (14) (62 mg) in ethanol (15 ml) and an excess of Raney nickel in ethanol was refluxed overnight. The mixture was filtered and the solids washed with ethyl acetate. The combined filtrate and washings were evaporated to give a crystalline solid which was recrystallised from methanol to yield the *acetate* (15) (27 mg, 55.6%) as needles, m.p. 109—110 °C (Found: C, 76.55; H, 7.95. $C_{21}H_{26}O_3 \cdot 0.1H_2O$ requires, C, 76.85; H, 8.05%); $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1} (C=O); δ($CDCl_3$), 1.03 (3 H, s, Me), 2.10 (3 H, s, OCOMe), 3.83 (3 H, s, OMe), 5.00—5.40 (2 H, m, 15- and 17-H), 6.70—7.00 (2 H, m, ArH), and 7.40 (1 H, d, *J* 10 Hz, ArH); *m/e* 326 (M^+).

Estra-1,3,5(10)-*triene*-3,14α,17β-*triol* 3-*Methyl Ether* (18).—To a stirred solution of compound (17) (3 mg) in methanol (1 ml) at 0 °C was added sodium borohydride (5 mg). After stirring at 0 °C for 1.5 h and adding water (3 ml), the reaction mixture was extracted with ethyl acetate. This extract was washed with saturated aqueous sodium chloride and dried (Na_2SO_4). Evaporation afforded (18) as pale yellow *crystals* (2.7 mg, 89.4%); $\nu_{max.}$ ($CHCl_3$) 3 625 cm^{-1} (OH); δ($CDCl_3$) 0.90 (3 H, s, Me), 3.82 (3 H, s, OMe), and 6.60—7.48 (3 H, m, ArH); *m/e* 302 (M^+).

14,15-*Didehydro*-3-O-*methylestradiol*-17β (16).—(*a*) A mixture of the acetate (15) (21 mg) in ethanol (5 ml) and 2M-aqueous potassium hydroxide (4 drops) was stirred for 2.5 h at room temperature. After addition of water (5 ml), the reaction mixture was extracted with ethyl acetate. The extract was washed with saturated aqueous sodium chloride and dried (Na_2SO_4). Evaporation afforded pale yellow crystals which were recrystallised from benzene–hexane to yield (16) (17 mg, 92.9%) as *needles*, m.p. 127.5—128 °C (Found: C, 76.75; H, 8.95. $C_{19}H_{24}O_2 \cdot 0.6H_2O$ requires C, 77.0; H, 8.6%); $\nu_{max.}$ ($CHCl_3$) 3 625 cm^{-1} (OH); δ(CCl_4) 0.98 (3 H, s, Me), 3.71 (3 H, s, OMe), 4.00 (1 H, t, *J* 8 Hz, 17-H), 5.14br (1 H, s, 15-H), and 6.42—7.11 (3 H, m, ArH); *m/e* 284 (M^+).

(*b*) To a stirred solution of compound (18) in acetone (2 ml) at 0 °C was added 5N-hydrochloric acid (2 drops) and the mixture was stirred for 10 h at 0 °C. After addition of saturated aqueous sodium hydrogencarbonate, the solution was extracted with ethyl acetate. The extract was washed with saturated aqueous sodium chloride and dried (Na_2SO_4). Evaporation afforded an oily product which was chromatographed on silica gel (2.5 g) using benzene–ethyl acetate (9 : 1 v/v) as eluant to give (16) as needles, m.p. 127.5—128.0 °C (from benzene–hexane), identical (mixed m.p.) to the sample prepared in (*a*).

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