

## Dehydrogenation of Lactones using Benzeneseleninic Anhydride. X-Ray Crystal Structure of $3\beta$ -Acetoxy-14 $\alpha$ -hydroxy-17 $\alpha$ -oxa-D-homo-5 $\alpha$ -androst-15-en-17-one

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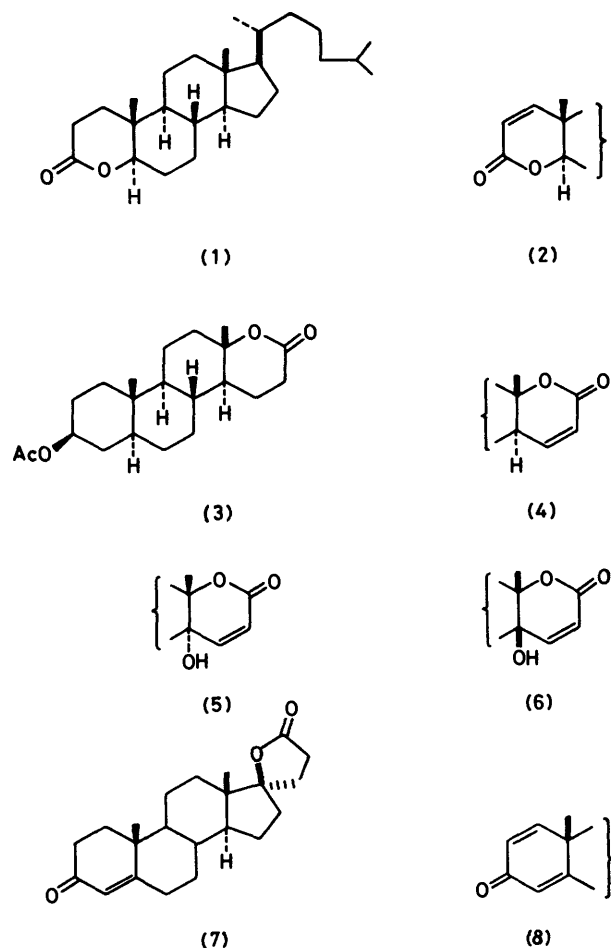
$\delta$ -Lactones such as 4-oxa-5 $\alpha$ -cholestan-3-one (1) and  $3\beta$ -acetoxy-17 $\alpha$ -oxa-D-homo-5 $\alpha$ -androst-17-one (3) undergo smooth dehydrogenation using benzeneseleninic anhydride in chlorobenzene at 100–130 °C. Reaction of compound (3) for longer periods of time additionally leads to the formation of C-14 hydroxylated derivatives. Similar reaction of a  $\gamma$ -lactone, 3-oxo-17 $\beta$ H-pregnane-21,17-carbolactone (7), afforded only ring A dehydrogenation and no dehydrogenation of the spiro- $\gamma$ -lactone ring. The structure of compound (5) was confirmed by a single-crystal X-ray analysis.

THE use of benzeneseleninic anhydride, PhSe(O)·O·Se(O)Ph, as an effective dehydrogenating reagent for ketones<sup>1</sup> is now well recognised. However, its use as a dehydrogenating reagent for lactones<sup>2,3</sup> and lactams<sup>4</sup> has been less well studied. Here we report a brief investigation of the reaction of the anhydride with some steroidal lactones.

Thus, oxidation of 4-oxa-5 $\alpha$ -cholestan-2-one (1) with 0.5 molar equivalent of benzeneseleninic anhydride in chlorobenzene at 100 °C under nitrogen gave the  $\alpha\beta$ -unsaturated lactone (2) in 90% yield after 42 h. Although the reaction time is noticeably longer than the corresponding dehydrogenation of steroidal ketones,<sup>1</sup> the above preparation of compound (2) compares favourably with either dichlorodicyanobenzoquinone (DDQ) dehydrogenation methods<sup>5</sup> for similar  $\delta$ -lactones or with other indirect procedures.<sup>6</sup>

Similar reaction of the D-homo-lactone (3) with the anhydride in boiling chlorobenzene for 16 h afforded three products. The first of these, from its spectral data was clearly the unsaturated  $\delta$ -lactone (4) (16%). The other two more-polar products (A) and (B), were isolated after careful chromatography in 19 and 23% yields respectively. From their i.r. spectra these compounds were obviously related since both showed absorption bands corresponding to a hydroxy-group and an  $\alpha\beta$ -unsaturated six-ring lactone. The mass spectral and microanalytical properties suggested a molecular formula of C<sub>21</sub>H<sub>30</sub>O<sub>5</sub>. These results together with their <sup>1</sup>H n.m.r. spectra indicated that the compounds were the novel 14-hydroxy- $\alpha\beta$ -unsaturated lactones (5) and (6). The optical rotation [ $\alpha$ ]<sub>D</sub> of the slightly less-polar isomer (A) was +17° in CHCl<sub>3</sub> while that of (B) was -18°. These values may be interpreted as indications of the isomeric relationship between (A) and (B), but in the absence of literature analogies no definite inferences can be drawn as to the relative configuration of the C-14 hydroxy-groups in (A) and (B).

Although from the t.l.c. and <sup>1</sup>H n.m.r. properties of (A) and (B) an indication as to which isomer is which can be made, definitive proof was only obtained from an X-ray crystallographic analysis. In this manner the



isomer (A) was shown to correspond to the 14 $\alpha$ -hydroxy-derivative (5) (Figure) and therefore (B) must be structure (6). In addition, the X-ray study of compound (5) showed that, in the solid state, the carbonyl group is not co-planar with the neighbouring double-bond, a feature in accord with the relatively low extinction coefficient shown in the u.v. spectrum.

In an effort to improve the yield of the unsaturated

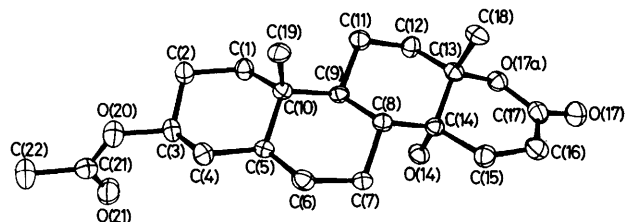
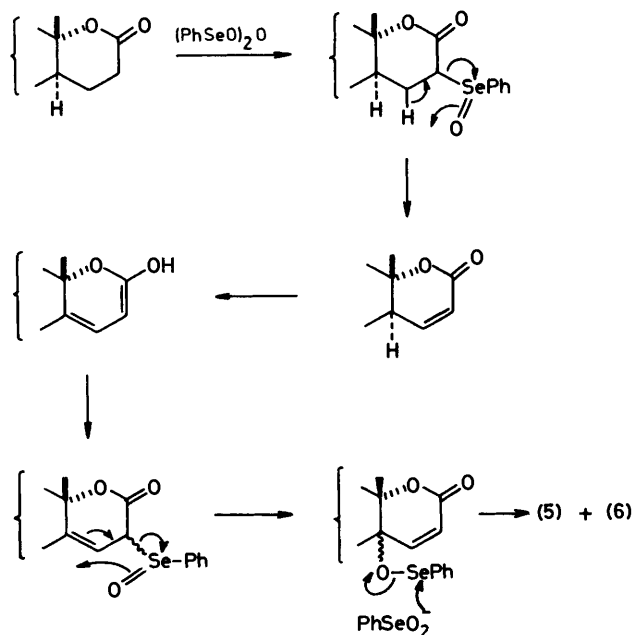


FIGURE Perspective view of the hydroxy unsaturated lactone (5) and the crystallographic numbering

$\delta$ -lactone (4) from compound (3) it was found that by reducing the reaction time to 2.5 h an 80% yield could be realised with only small amounts (*ca.* 4% each) of (5) and (6) also being formed. By way of contrast, dehydrogenation of compound (3) to the unsaturated lactone (4) using DDQ required a reaction period of 240 h and gave only a 25% yield of product.

The mechanism for the benzeneseleninic anhydride oxidation of compound (3) is shown in the Scheme. It



SCHEME

is comparable to that proposed recently by Khôi and Polonsky.<sup>3</sup> It is thought that initial benzeneseleninylation at C-16 followed by rapid *syn*-elimination yields compound (4). Further benzeneseleninylation at C-16 and rapid 2,3-sigmatropic rearrangement then yields the hydroxylated unsaturated lactones, after fission of the intermediate benzeneselenenyl species with an appropriate nucleophile. Other examples of angular hydroxylation using the anhydride have been reported recently.<sup>7</sup>

Finally, an attempt was made to dehydrogenate the spiro lactone (7) using the anhydride. However under a variety of conditions the only isolable product from the reaction was that of dehydrogenation of the ring A ketone, namely compound (8). Indeed using molar equivalents of the anhydride at 120 °C for 1.7 h an 84%

yield of compound (8) could be obtained. This high yield can be compared with a related dehydrogenation reaction using selenium dioxide where the corresponding ring A dienone was only produced in poor (13%) yield.<sup>8</sup>

The above results indicate that it is possible to dehydrogenate  $\delta$ -lactones in one step using benzeneseleninic anhydride, but that  $\gamma$ -lactones are essentially unreactive. The method compares favourably with other direct lactone dehydrogenating reagents such as DDQ.

#### EXPERIMENTAL

M.p.s were determined using a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded (in Nujol unless otherwise stated) on Perkin-Elmer 157 and 198 spectrometers; n.m.r. spectra were recorded using a Varian EM 360A machine for solutions in  $CDCl_3$  using  $SiMe_4$  as internal standard. Optical rotations were measured with a Perkin-Elmer polarimeter at ambient temperatures. Mass spectra were recorded on A.E.I. MS9 and V.G. Micromass 7070 instruments. All solvents and reagents were purified by standard methods. Petroleum refers to light petroleum (b.p. 60–80 °C) throughout.

*Oxidation of 4-Oxa-5 $\alpha$ -cholestan-3-one (1) with Benzeneseleninic Anhydride (BSA).*—To compound (1) (40 mg) in dry chlorobenzene (1 ml) was added BSA (40 mg, 1.1 mol equiv.) and the stirred mixture heated at 100 °C under nitrogen for 42.5 h. P.l.c. (petroleum–20%  $Et_2O$ ) then gave 4-oxa-5 $\alpha$ -cholest-1-en-3-one (2) (36 mg, 90%), m.p. (from MeOH) 88–89 °C (lit.,<sup>6</sup> 85.5–86.5 °C),  $\nu_{max}$  ( $CCl_4$ ) 1740s and 1710sh  $cm^{-1}$  [lit.,<sup>6</sup>  $\nu_{max}$  (KBr) 1740 and 1708  $cm^{-1}$ ];  $\delta$  ( $CCl_4$ ) 6.85 and 5.75 (1 H + 1 H, ABq,  $J$  10 Hz), 3.95 (1 H, dd,  $J$  5, 10 Hz, 5 H), and 2.3–0.5 (complex m) [lit.,<sup>6</sup>  $\delta$  ( $CDCl_3$ ) 4.0 (1 H, q, 5 $\alpha$ -H), 5.80 (1 H, d), and 6.96 (1 H, d)];  $m/e$  386 ( $M^+$ ), 371, and 273;  $[\alpha]_D^{29}$  ( $CHCl_3$ ) (lit.,<sup>6</sup>  $[\alpha]_D^{28}$ ).

*Oxidation of the D-Homolactone (3) with BSA.*—(a) To compound (3) (50 mg, 0.144 mmol) in dry chlorobenzene (1 ml) was added BSA (52 mg, 1 mol equiv.) and the stirred mixture was heated at 130 °C under nitrogen for 16 h, the reaction being monitored by t.l.c. The resulting mixture was directly subjected to p.l.c. (PhH–50%  $Et_2O$ ) to give small quantities of minor products and, in order of increasing polarity, (i) diphenyl diselenide (40 mg, 89%), m.p. 62–63 °C (lit.,<sup>9</sup> 63 °C); (ii) the unsaturated lactone 3 $\beta$ -acetoxy-17 $\alpha$ -oxa-D-homo-5 $\alpha$ -androst-15-en-17-one (4) (8 mg, 16%), m.p. (from petroleum–ethyl acetate) 147–149 °C (lit.,<sup>5</sup> 149–150 °C),  $\nu$  ( $CCl_4$ ) 3050w, 1735vs, 1730vs, shoulder, and 1240s  $cm^{-1}$  [lit.,<sup>5</sup>  $\nu_{max}$  (KBr) 1750 and 1240  $cm^{-1}$ ];  $\delta$  (100 MHz,  $CDCl_3$ ) 6.84 (1 H, dd,  $J$  2, 10 Hz, 15-H), 6.07 (1 H, dd,  $J$  3, 10 Hz, 16-H), 4.70 (1 H, br, 3-H), 1.98 (s, OAc), 1.28 (s, 18-Me), 0.78 (s, 19-Me), and 2.4–0.7 (complex m) [lit.,<sup>5</sup> 6.91 (d) and 6.75 (d) (15-H), 6.09 (d) and 5.93 (d) (16-H) ( $J_{15,16} = 10$  Hz,  $J_{14,15} = 2$  Hz,  $J_{14,16} = 3$  Hz), 1.32 (19-Me), and 0.82 (18-Me)];  $m/e$  346 ( $M^+$ );  $[\alpha]_D^{29} -56^\circ$  ( $CHCl_3$ ,  $c$  0.076 [lit.,<sup>5</sup>  $[\alpha]_D^{29} -52^\circ$  ( $CHCl_3$ )]); and (iii) two just overlapping bands, the material in which was re-subjected to careful p.l.c. (petroleum–50%  $Et_2O$ , double elution) to give (iv) the less-polar product (A) 3 $\beta$ -acetoxy-14 $\alpha$ -hydroxy-17 $\alpha$ -oxa-D-homo-5 $\alpha$ -androst-15-en-17-one (5) (10 mg, 19%) as white crystals, m.p. (from petroleum–ethyl acetate) 204–208 °C (subl. from 180 °C);  $\lambda$  (MeOH) 216 ( $\epsilon$  4000) nm;  $\nu$  ( $CCl_4$ ) 3600sharp, 3650–3100br, 3060w, 1735vs, 1720s, shoulder, 1703m, 1620w, and 1240s,  $cm^{-1}$ ;  $\delta$  (100 MHz,  $CDCl_3$ ) 7.08 (1 H,  $J$  10 Hz, 15-H) and 6.10 (1 H,

d,  $J$  10 Hz, 16-H) (ABq), 4.70 (1 H, br, 3 $\alpha$ -H), 2.02 (s, OAc), 1.46 (s, 18-Me), 0.82 (s, 19-Me), and 2.5–0.8 (complex m);  $m/e$  362 ( $M^+$ ), 302, 284, and 244;  $[\alpha]_D^{+17}$  (CHCl<sub>3</sub>,  $c$  0.2); accurate  $M^+$  at  $m/e$  362 ( $M^+$ ) (Found: C, 69.35; H, 8.4%;  $M^+$ , 362.2089 C<sub>21</sub>H<sub>30</sub>O<sub>5</sub> requires C, 69.59; H, 8.34%;  $M$ , 362.2093); and (v) the more-polar product (B) 3 $\beta$ -*acetoxy-14 $\beta$ -hydroxy-17 $\alpha$ -oxa-D-homo-5 $\alpha$ -androst-15-en-17-one* (6) (12 mg, 23%) as white crystals, m.p. (from petroleum-ethyl acetate) 222–225 °C (subl. from 215 °C),  $\lambda_{max}$  (MeOH) 218 ( $\epsilon$  4 050);  $\nu_{max}$  (CCl<sub>4</sub>) 3 590sharp, 3 650–3 100br, 3 060w, 1 735vs, 1 715s, 1 700m, shoulder, 1 630w, and 1 240s cm<sup>-1</sup>;  $\delta$  (100 MHz, CDCl<sub>3</sub>) 7.02 (1 H, d,  $J$  10 Hz, 15-H) and 6.04 (1 H, d,  $J$  10 Hz, 16-H) (ABq), 4.70 (1 H, br, 3 $\alpha$ -H), 2.02 (s, OAc), 1.53 (s, 18-Me), 0.81 (s, 19-Me), and 2.2–0.8 (complex m);  $m/e$  362 ( $M^+$ ), 302, 284, 244, 219, and 193;  $[\alpha]_D^{-18}$  (CHCl<sub>3</sub>,  $c$  0.18) (Found: C, 69.32; H, 8.39%;  $M^+$ , 362.2089. C<sub>21</sub>H<sub>30</sub>O<sub>5</sub> requires C, 69.6; H, 8.35%).

(b) Experiment (a) was repeated but with heating at 130 °C for only 2.25 h. The cooled (room temp.) reaction mixture was filtered free from white crystals of benzene-seleninic acid (24 mg, 44%) (identical with authentic material) and the yellow filtrate was subjected to chromatographic

TABLE 1

Fractional co-ordinates ( $\times 10^4$ ) for the non-hydrogen atoms with estimated standard deviations in parentheses

| Atom   | $x$       | $y$       | $z$        |
|--------|-----------|-----------|------------|
| C(1)   | 9 486(4)  | 8 759(2)  | -1 431(8)  |
| C(2)   | 10 426(4) | 9 078(3)  | -1 890(8)  |
| C(3)   | 10 384(4) | 9 780(3)  | -1 277(9)  |
| C(4)   | 10 158(4) | 9 846(2)  | 1 014(9)   |
| C(5)   | 9 221(3)  | 9 540(2)  | 1 419(8)   |
| C(6)   | 8 888(4)  | 9 659(2)  | 3 624(8)   |
| C(7)   | 7 900(4)  | 9 430(2)  | 3 924(8)   |
| C(8)   | 7 758(3)  | 8 724(2)  | 3 246(8)   |
| C(9)   | 8 158(3)  | 8 603(2)  | 1 079(8)   |
| C(10)  | 9 178(3)  | 8 815(2)  | 870(8)     |
| C(11)  | 7 984(4)  | 7 905(2)  | 406(9)     |
| C(12)  | 6 959(4)  | 7 730(3)  | 533(9)     |
| C(13)  | 6 581(3)  | 7 842(2)  | 2 689(8)   |
| C(14)  | 6 727(3)  | 8 553(2)  | 3 281(8)   |
| O(14)  | 6 300(2)  | 8 958(2)  | 1 779(7)   |
| C(15)  | 6 235(4)  | 8 652(2)  | 5 344(9)   |
| C(16)  | 5 443(4)  | 8 350(3)  | 5 680(9)   |
| C(17)  | 5 029(4)  | 7 915(2)  | 4 132(10)  |
| O(17)  | 4 234(3)  | 7 746(2)  | 4 187(7)   |
| O(17a) | 5 580(2)  | 7 722(2)  | 2 583(6)   |
| C(18)  | 6 984(4)  | 7 362(2)  | 4 248(9)   |
| C(19)  | 9 834(4)  | 8 413(2)  | 2 230(9)   |
| O(20)  | 11 289(3) | 10 066(3) | -1 697(9)  |
| C(21)  | 11 312(4) | 10 611(3) | -2 801(11) |
| O(21)  | 10 632(4) | 10 853(2) | -3 503(9)  |
| C(22)  | 12 255(5) | 10 866(4) | -2 977(15) |

TABLE 2

Bond lengths with e.s.d.'s in parentheses

|              |          |              |          |
|--------------|----------|--------------|----------|
| C(1)–C(2)    | 1.541(8) | C(1)–C(10)   | 1.558(7) |
| C(2)–C(3)    | 1.521(8) | C(3)–C(4)    | 1.524(8) |
| C(3)–O(20)   | 1.462(6) | C(4)–C(5)    | 1.518(7) |
| C(5)–C(6)    | 1.526(8) | C(5)–C(10)   | 1.557(6) |
| C(6)–C(7)    | 1.516(7) | C(7)–C(8)    | 1.554(7) |
| C(8)–C(9)    | 1.537(7) | C(8)–C(14)   | 1.530(7) |
| C(9)–C(10)   | 1.543(7) | C(9)–C(11)   | 1.543(7) |
| C(10)–C(19)  | 1.542(7) | C(11)–C(12)  | 1.526(8) |
| C(12)–C(13)  | 1.515(8) | C(13)–C(14)  | 1.549(7) |
| C(13)–O(17a) | 1.469(6) | C(13)–C(18)  | 1.536(8) |
| C(14)–O(14)  | 1.429(6) | C(14)–C(15)  | 1.526(8) |
| C(15)–C(16)  | 1.324(8) | C(16)–C(17)  | 1.479(8) |
| C(17)–O(17)  | 1.201(6) | C(17)–O(17a) | 1.341(7) |
| O(20)–C(21)  | 1.344(7) | C(21)–O(21)  | 1.195(7) |
| C(21)–C(22)  | 1.467(9) |              |          |

TABLE 3

Bond angles (°) with e.s.d.'s in parentheses

|                    |          |
|--------------------|----------|
| C(2)–C(1)–C(10)    | 113.8(4) |
| C(2)–C(3)–C(4)     | 110.4(4) |
| C(4)–C(3)–O(20)    | 109.6(4) |
| C(4)–C(5)–C(6)     | 111.9(4) |
| C(6)–C(5)–C(10)    | 111.1(4) |
| C(6)–C(7)–C(8)     | 112.8(4) |
| C(7)–C(8)–C(14)    | 110.3(4) |
| C(8)–C(9)–C(10)    | 113.1(4) |
| C(10)–C(9)–C(11)   | 113.7(4) |
| C(1)–C(10)–C(9)    | 109.5(4) |
| C(1)–C(10)–C(19)   | 109.2(4) |
| C(9)–C(10)–C(19)   | 112.3(4) |
| C(11)–C(12)–C(13)  | 111.1(4) |
| C(12)–C(13)–O(17a) | 106.5(4) |
| C(12)–C(13)–C(18)  | 111.6(4) |
| O(17a)–C(13)–C(18) | 107.0(4) |
| C(8)–C(14)–O(14)   | 105.7(4) |
| C(8)–C(14)–C(15)   | 115.7(4) |
| O(14)–C(14)–C(15)  | 108.2(4) |
| C(15)–C(16)–C(17)  | 122.0(5) |
| C(16)–C(17)–O(17a) | 116.8(5) |
| C(13)–O(17a)–C(17) | 119.9(4) |
| O(20)–C(21)–O(21)  | 122.8(5) |
| O(21)–C(21)–C(22)  | 125.4(6) |
| C(1)–C(2)–C(3)     | 109.4(4) |
| C(2)–C(3)–O(20)    | 108.1(4) |
| C(3)–C(4)–C(5)     | 108.7(4) |
| C(4)–C(5)–C(10)    | 114.0(4) |
| C(5)–C(6)–C(7)     | 111.4(4) |
| C(7)–C(8)–C(9)     | 111.3(4) |
| C(9)–C(8)–C(14)    | 109.9(4) |
| C(8)–C(9)–C(11)    | 110.5(4) |
| C(1)–C(10)–C(5)    | 106.2(4) |
| C(5)–C(10)–C(9)    | 107.3(4) |
| C(5)–C(10)–C(19)   | 112.1(4) |
| C(9)–C(11)–C(12)   | 111.7(4) |
| C(12)–C(13)–C(14)  | 109.1(4) |
| C(14)–C(13)–O(17a) | 107.9(4) |
| C(14)–C(13)–C(18)  | 114.4(4) |
| C(8)–C(14)–C(13)   | 110.7(4) |
| C(13)–C(14)–O(14)  | 110.0(4) |
| C(13)–C(14)–C(15)  | 106.5(4) |
| C(14)–C(15)–C(16)  | 118.8(5) |
| C(16)–C(17)–O(17)  | 123.1(5) |
| O(17)–C(17)–O(17a) | 120.1(5) |
| C(3)–O(20)–C(21)   | 117.8(4) |
| O(20)–C(21)–C(22)  | 111.8(5) |

purification as before to yield the following: diphenyl diselenide (24 mg, 53%), m.p. 62–63 °C (lit.,<sup>9</sup> 63 °C); the unsaturated lactone (4) (40 mg, 80%); the 14 $\alpha$ -hydroxy unsaturated lactone (5) (2 mg, 4%); and the 14 $\beta$ -hydroxy unsaturated lactone (6) (2 mg, 4%); all the products were identical with previous samples.

*Oxidation of the Steroidal Spirolactone (7) with BSA.*—To compound (7) (50 mg, 0.146 mmol) in dry chlorobenzene (1 ml) was added BSA (53 mg, 1 mol equiv.), and the stirred mixture was heated at 120 °C under nitrogen for 1.7 h. The reaction mixture was directly subjected to p.l.c. (CHCl<sub>3</sub>–10% Et<sub>2</sub>O) to give diphenyl diselenide (53 mg, 76%), m.p. 62–64 °C (lit.,<sup>9</sup> 63 °C); and as the major product, 3-oxo-17 $\beta$ H-pregna-1,4-diene-21,17-carbolactone (8) (42 mg, 84%), m.p. (from MeOH) 134–135 °C (lit.,<sup>10</sup> 134–136 °C),  $\lambda$  (MeOH) 244 nm ( $\epsilon$  14 500) [lit.,<sup>10</sup>  $\lambda$  (MeOH) 245 ( $\epsilon$  14 900 nm)];  $\nu$  (CCl<sub>4</sub>) 3 040w, 1 780s (5-ring saturated lactone), 1 665s ( $\alpha\beta\alpha'\beta'$  unsaturated ketone), 1 630w, and 1 605w cm<sup>-1</sup>;  $\delta$  (CCl<sub>4</sub>) 6.85 (1 H, d,  $J$  10 Hz), 6.05 and 5.85 (together 2 H, m), and 2.6–0.7 (complex m) (18-Me at  $\delta$  0.98, 19-Me at  $\delta$  1.25);  $m/e$  340 ( $M^+$ ), 322, and 267.

*Crystal Data.*—(5), C<sub>21</sub>H<sub>30</sub>O<sub>5</sub>,  $M = 362.47$ , crystallises as fine clear needles elongated along  $c$ , orthorhombic, space

group  $P2_12_12_1$ ,  $a = 14.435(1)$ ,  $b = 20.896(1)$ ,  $c = 6.469(1)$  Å,  $U = 1951$  Å<sup>3</sup>,  $Z = 4$ .

Data for a crystal mounted along its  $c$  direction were measured on a Siemens off-line four-circle diffractometer using Ni-filtered Cu- $K_\alpha$  radiation. A total of 1708 independent reflections were measured ( $\theta \leq 60^\circ$ ) using the  $\theta$ - $2\theta$  scan technique with the 'five value' measuring procedure. Of these 161 had  $I < 2.58 \sigma(I)$  and were classed as unobserved. The net count of the 1110 reflection, measured as a reference every 50 reflections, did not alter significantly during the data collection (3 days) indicating that no deterioration of the crystal had occurred. The data were brought to a uniform arbitrary scale by use of this reflection, and Lorentz and polarisation corrections were applied.

The structure was solved by direct methods by the application of the program MULTAN to 200 reflections with normalised structure factors ( $E$ 's)  $\geq 1.48$ . An  $E$ -map computed for the phase solution with the highest 'combined figure of merit' gave plausible positions for all the non-hydrogen atoms in the molecule.

The non-hydrogen atoms were refined anisotropically. The hydrogen atoms, with the exception of that of the C(14) hydroxy which was clearly located in a different map, were placed at calculated positions. Refinement was terminated at  $R = 0.051$ .

Computations were carried out on the Imperial College CDC Cyber 174 and the University of London CDC 7600 computers, using, in the main, programs belonging to the X-ray 72 system.

Table 1 lists the fractional co-ordinates for the non-hydrogen atoms in the molecule. Tables 2 and 3 give the bond lengths and bond angles respectively. Tables of the

\* For details of the Supplementary publications Scheme, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

temperature factors, hydrogen atom co-ordinates, and observed and calculated structure factors are deposited as a Supplementary publication [SUP No. 23305 (13 pp)].\*

The C(15)-C(16)-C(17)-O(17) torsion angle is  $-163.4(6)^\circ$ . There is a hydrogen bond ( $2.822(6)$  Å) between the 14-hydroxy-group and the acetate oxygen of a screw-related molecule.

We thank Dr. Judith Polonsky (I.C.S.N.) for kindly informing us of her related work<sup>3</sup> with the quassinoid chapparrinone. We thank Dr. B. A. Marples (Loughborough University) and Professor P. D. Magnus (University of Indiana, U.S.A.) for generous gifts of compounds (1) and (7) respectively.

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