Microbiological Transformations of 3α-Acetoxy-17a-aza-D-homo-5α-androstan-17-one and of 3α-Acetoxy-5α-androstan-17-one with the Fungus *Cunninghamella elegans*

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3α-Acetoxy-17a-aza-D-homo-5α-androstan-17-one is hydroxylated by *Cunninghamella elegans* to 3α-acetoxy-6β-hydroxy-, 3α-acetoxy-7α-hydroxy-, 3α,11α-dihydroxy-, and 3α,11β-dihydroxy-17a-aza-D-homo-5α-androstan-17-one, in contrast to the near carbocyclic analogue, 3α-acetoxy-5α-androstan-17-one, which is hydroxylated to 3α-acetoxy-6β,11β-dihydroxy-5α-androstan-17-one, 1β,3α-dihydroxy-5α-androstan-17-one, and 3α-acetoxy-6β-hydroxy-5α-androstane-11,17-dione.

In contrast to the large amount of work published on the microbial transformation of steroids [1,2] very little information is available concerning the transformation of aza-steroids. Accordingly 3α-acetoxy-17a-aza-D-homo-5α-androstan-17-one (1), synthesised [3] by Beckmann rearrangement of the oxime of 3α-acetoxy-5α-androstan-17-one, was incubated with *Cunninghamella elegans* Lendner (C.B.S.167.53), selected for study after screening of (1) against a variety of micro-organisms.

From the amide (1), 36% of compound (2), 16% of (3), and 2% of (4) and (5) in addition to 16% of unchanged (1) were obtained. Yields are based on the amount of substrate transformed by the fungus and separations were achieved by a combination of column chromatography (Al_2O_3), preparative layer chromatography (silica gel), and recrystallisation.

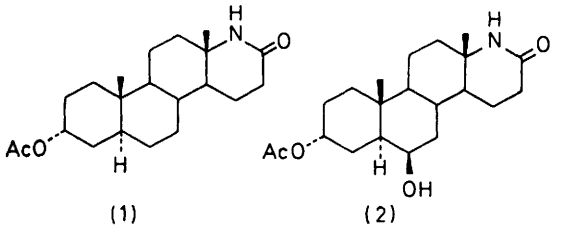
The n.m.r. spectrum ($CDCl_3$) (Table 1) of the major product (2) shows hydroxylation to have occurred in an axial position: the C*H*OH signal is a broadened singlet

[1] W. Charney and H. L. Herzog, ' Microbial Transformations of Steroids,' Academic Press, New York, 1967.

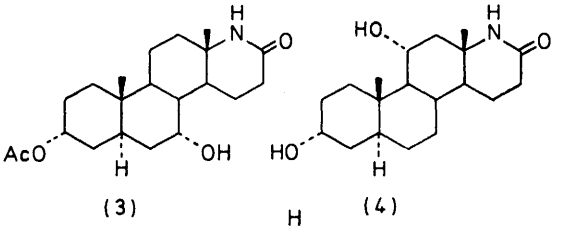
[2] L. L. Smith in ' Terpenoids and Steroids,' ed. K. H. Overton, Chem. Soc. Specialist Periodical Report, 1974, vol. 4, p. 394.

[3] B. M. Regan and F. N. Hayes, *J. Amer. Chem. Soc.*, 1956, **78**, 639.

with $W_{\frac{1}{2}}$ 8 Hz.[4] Comparison with literature values [4,5] for the chemical shifts due to substituent hydroxy-groups in steroids suggests 6β-hydroxylation, the large



(1) (2)



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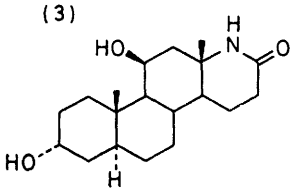
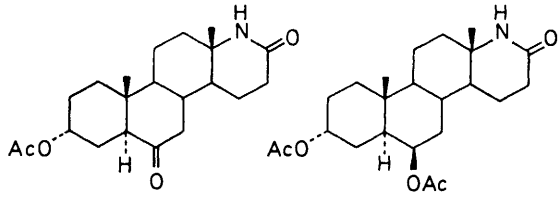


(5)

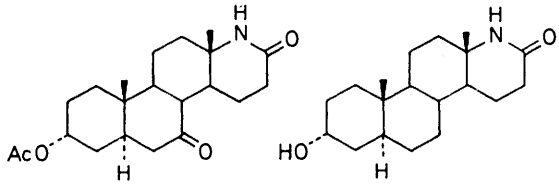
deshielding relative to (1) of the C-19 methyl protons arising from the 1,3-*syn*-axial interaction between the 6β-hydroxy-group and the C-19 methyl. The alternative 2β- or 4β-hydroxylation, consistent with a large deshielding of the C-19 methyl protons, is ruled out by analysis of the C*H*OAc signals.

androstane-6,17-dione (6). The methyl resonances of the C-18 and C-19 protons relative to those in (1) showed an upfield shift of the latter and a downfield shift of the former, similar to the literature values [5] for the shifts of the C-18 and C-19 protons arising from a C-6 oxo-function in steroidal systems. Acetylation of (2) gave 3α,6β-diacetoxy-17a-aza-D-homo-5α-androstan-17-one (7). The large deshielding of the C-19 protons relative to (1) is evidence for a 1,3-*syn*-axial interaction between the acetoxy-function and the C-19 protons.

The axial orientation of the introduced OH group in the product (3) was shown by the C*H*OH resonance



(6) (7)



(8) (9)

(δ 4.06, $W_{\frac{1}{2}}$ 12 Hz).[4] The δ values of the C-18 and C-19 methyl protons in (1) were unaffected by the introduction

TABLE 1

^{1}H N.m.r. spectra ($CDCl_3$) of 17a-aza-D-homo-5α-androstan-17-one derivatives

Compound	C-19 (δ)	C-18 (δ)	Obs. methyl shifts (Δδ) [a] C-19	Obs. methyl shifts (Δδ) [a] C-18	Lit. methyl shift (Δδ) [b] C-19	Lit. methyl shift (Δδ) [b] C-18	C-3 (δ) [c]	C-*n* (δ) [c]	CH_2 adjacent to C=O centred at (δ)
(2)	1.00	1.18	+0.22	+0.03	+0.23	+0.04	5.11 m (8)	3.78 m (8)	2.42
(3)	0.78	1.15	0.00	0.00	0.00	+0.01	5.04 m (10)	4.06 m (12)	2.45
(4)	0.79	1.18	+0.10	+0.11	+0.12	+0.03	4.09 m (9)	3.54 sx (10, 10, 6)	2.42
(5)	0.99	1.25	+0.30	+0.18	+0.23	+0.25	4.21 m (10)	3.82 m (10)	2.42
(6)	0.74	1.17	−0.04	+0.02	−0.05	+0.02	5.11 m (8)		2.50
(7)	0.97	1.20	+0.19	+0.05	+0.16	+0.06	5.06 m (9)	4.93 m (9)	2.46
(8)	1.07	1.16	+0.29	+0.01	+0.28	+0.01	5.03 m (11)		2.42

[a] For compounds (2), (3), (6), (7), and (8), Δδ values are relative to (1); for (4) and (5) values are relative to (9). A positive value denotes a downfield shift. [b] See ref. 5. [c] The multiplicity of the C*H*OR signal is followed in parentheses by the coupling constants (*J*/Hz); for an unresolved multiplet (m) the half-height width ($W_{\frac{1}{2}}$/Hz) is given.

These structural assignments were confirmed by Jones oxidation [6] of (2) to 3α-acetoxy-17a-aza-D-homo-5α-of the hydroxy-group, suggesting α-axial hydroxylation. α-Hydroxylation at position 16 would cause an unobserved simplification of the CH_2·CO splitting pattern and a 12α-hydroxy-group would cause a small downfield shift (Δδ +0.05) [5] of the C-18 methyl signal. Consequently 1α- or 7α-hydroxylation must have occurred.

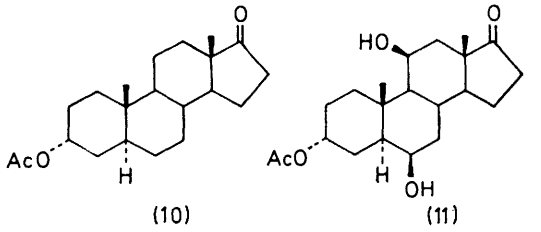
[4] K. Tori and E. Kondo, *Steroids*, 1964, **6**, 713.

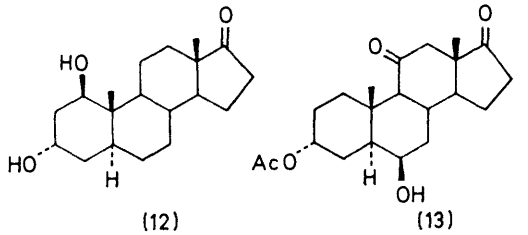
[5] J. E. Bridgeman, P. C. Cherry, A. S. Clegg, J. M. Evans, E. R. H. Jones, A. Kasal, V. Kumar, G. D. Meakins, Y. Morisawa, E. E. Richards, and P. D. Woodgate, *J. Chem. Soc.* (*C*), 1970, 250.

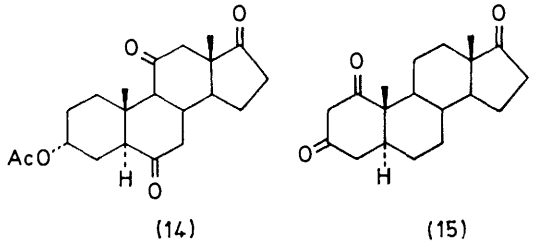
[6] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.

Oxidation of (3) to 3α-acetoxy-17a-aza-D-homo-5α-androstane-7,17-dione (8) with 8N-chromic acid provided evidence for 7α-hydroxylation. The large downfield shift (Δδ +0.29) of the C-19 methyl signal of (8) is less than that expected for a carbonyl at C-1 (Δδ +0.38).[5]

Repeated recrystallisations of the mixture of (4) and (5) gave (4) as the major product. In the n.m.r. spectrum of (4) the 3β-C*H*(OH) signal occurs at δ 4.09 as a broad singlet ($W_{\frac{1}{2}}$ 9 Hz), and the microbiologically introduced hydroxy-group is characterised by a broad multiplet (δ 3.54) for C*H*(OH). The spin–spin coupling between the O*H* and vicinal C*H*(OH) was removed by deuteriation, with consequent simplification of the C*H*(OH) multiplet into a triplet of doublets. Analysis







of this gave two $J_{ax,ax}$ (10.6 Hz) and one $J_{ax,eq}$ (5.3 Hz) vicinal couplings. Of the splitting patterns possible for axial protons in the steroid nucleus, only four positions (C-6, C-7, C-11, and C-15) are consistent with the observed splittings, and of these only a 11α-hydroxy-group would deshield the C-19 methyl protons relative to 3α-hydroxy-17a-aza-D-homo-5α-androstan-17-one (9) by as much as observed (Table 1).

The n.m.r. spectrum ($CDCl_3$) of the minor component (5) again showed no C*H*OAc or OCOC*H*$_3$ signals, indicating hydrolysis of the acetate function during incubation. The 3β-proton absorbed at δ 4.21 ($W_{\frac{1}{2}}$ 9 Hz) and the C*H*(OH) proton geminal to the introduced hydroxy-group absorbed as a broad singlet at δ 3.82 ($W_{\frac{1}{2}}$ 10 Hz) consistent with axial hydroxylation.[4] The magnitudes of the downfield shifts of both angular methyl group protons relative to (9) indicate 11β-hydroxylation.

For comparison purposes the near carbocyclic analogue (10) of (1) was incubated under the same conditions as employed for (1), and the three products isolated in yields of 22, 8, and 1% were assigned the structures (11)—(13) respectively.

TABLE 2

^{1}H N.m.r. spectra ($CDCl_3$) of 5α-androstan-17-one derivatives

Compound	Obs. methyl frequencies (δ) C-19	C-18	Calc. methyl frequencies [a] (δ) C-19	C-18	C-3 (δ) [c]	C-*n* (δ)
(11)	1.28	1.15	1.26	1.12	5.15 m (8)	3.8m (8)—6β 4.45 m (8)—11β
(12)	0.83	0.85	0.85	0.87	4.08 m (9)	3.78 d of d (11, 6)
(13)	1.26	0.86	1.27	0.88	5.10 m (10)	3.8 m (9)
(14)	1.02	0.87	0.99	0.86	5.13 m (8)	
(15)	1.26	0.89	1.26 [b]	0.90 [b]		

[a] See ref. 5. [b] See ref. 7. [c] The multiplicity of the C*H*OR signal is followed in parentheses by the coupling constants (J/Hz); for an unresolved multiplet (m) the half-height width ($W_{\frac{1}{2}}$/Hz) is given.

The n.m.r. spectrum of (11) ($CDCl_3$) (Table 2) showed two broadened singlets at δ 3.80 and 4.45 with $W_{\frac{1}{2}}$ 8 Hz indicating the presence of two axial secondary OH groups. The downfield shifts of the C-18 and C-19 methyl signals are consistent with 11β-hydroxylation together with β-hydroxylation at C-2, -4, or -6. Hydroxylation at C-2 or -4 would result in simpler C*H*OAc signals than observed; accordingly β-hydroxylation must have occurred at C-6 and -11. The spectrum of (11) (Table 3) in C_5D_5N showed the C-18 and C-19

TABLE 3

^{1}H N.m.r. spectra (C_5D_5N) of 17a-aza-D-homo-5α-androstan-17-one and 5α-androstan-17-one derivatives

Compound	Obs. methyl frequencies (δ) C-19	C-18	Obs. methyl shifts [a] (Δδ) C-19	C-18	Lit. methyl shifts [b] (Δδ) C-19	C-18
(1)	0.67	1.07				
(2)	1.20	1.11	+0.53	+0.04	+0.49	+0.06
(3)	0.74	1.14	+0.07	+0.07	+0.04	−0.04
(10)	0.71	0.77				
(11)	1.80	1.35	+1.09	+0.58	+1.06	+0.57
(12)	1.08	0.82	+0.28	+0.02	+0.33	+0.05
(13)	1.62	0.78	+0.91	+0.01	+0.92 [c]	+0.01 [c]

[a] The shifts of compounds (2) and (3) are relative to (1), of compounds (11) and (13) relative to (10), and of compound (12) relative to 3α-hydroxy-5α-androstan-17-one (C-18 δ 0.80, C-19 δ 0.80). A positive value represents a downfield shift. [b] See ref. 4. [c] See ref. 8.

signals to have undergone large downfield shifts, similar to the literature values[4] for β-hydroxylation at C-6 and -11.

Oxidation of (11) with 8N-chromic acid gave 3α-acetoxy-5α-androstane-6,11,17-trione (14), with chemical shifts for the C-18 and C-19 methyl protons of δ 0.87

and 1.02, respectively (*cf.* calculated values [5] of 0.86 and 0.99).

The n.m.r. spectrum ($CDCl_3$) of compound (12) showed the acetoxy-function to have been hydrolysed during incubation [C(3)*H*OH δ 4.08, $W_{\frac{1}{2}}$ 9 Hz]. A doublet of doublets centred at δ 3.78 showing $J_{ax,ax}$ 11 Hz and $J_{ax,eq}$ 6 Hz indicated equatorial hydroxylation either at C-1 or -12: only in these positions is the C*H*OH vicinal to only two protons. The deshielding of the C-19 protons expected from literature values [4,5] for a β-hydroxy-function in the 1-position is observed.

The n.m.r. spectrum (Table 2) of the product (15) from oxidation of (12) with 8N-chromic acid showed a large downfield shift of the C-19 signal relative to (12), the methyl resonance frequencies agreeing with the observed values [7] for a 1,3-dione system. The isolated AB quartet (δ 3.64 and 3.24, J — 16.6 Hz) was entirely consonant with the presence of a C-2 methylene group in the 1,3-dione.

The n.m.r. spectrum of the minor product (13) showed two broadened singlets at δ 5.10 ($W_{\frac{1}{2}}$ 10 Hz) and 3.8 ($W_{\frac{1}{2}}$ 9 Hz) attributable to the 3β-proton in the 3α-acetoxy-steroid and to C*H*OH geminal to an axial OH. The i.r. spectrum showed absorption for three carbonyl groups at $\nu_{max.}$ 1 740, 1 728, and 1 710 cm^{-1}, indicating in addition to the C-17 and ester carbonyl groups the presence of a carbonyl in a six-membered ring. The C-18 and C-19 methyl frequencies (δ 0.86 and 1.26, respectively) are similar to literature values [5] (C-18 δ 0.88, C-19 δ 1.27) for steroids carrying a 6β-hydroxy-function and a C-11-carbonyl, and the large deshielding of the C-19 methyl protons is consistent with 6β-hydroxylation. The carbonyl group must be located in ring C: no simplification of the signals from C*H*OAc and C*H*OH in rings A and B, respectively, was observed. The n.m.r. spectrum in C_5D_5N of (13) (Table 3) showed very large deshielding of the C-19 protons with a very small effect on the C-18 protons, in agreement with the literature values [8] for a C-6 axial hydroxy-function and a C-11 carbonyl group. The product was therefore assigned the 3α-acetoxy-6β-hydroxy-5α-androstane-11,17-dione structure, (13), being the result of further oxidation of the 11β-hydroxy-function in (11) by *C. elegans*.

Conclusion.—Most reported transformations by *C. elegans* utilise polyfunctional substrates, particularly pregn-4-ene-3,20-diones,[1] and in these cases 11β-hydroxylation,[9] 11α-hydroxylation,[9] 6β-hydroxylation,[9] 6β,11α-dihydroxylation,[10] and 6β,14α-dihydroxylation [11] have been recorded. 7β-Hydroxylation has been achieved on some cardenolides.[10] In the present work on (10) the previously unrecorded 6β,11β-dihydroxylation was observed and an unusual 1β-monohydroxylation. For the 17a-aza-steroid (1) the major position of hydroxylation was C-6(β) with only a small amount of 11α- and 11β-hydroxylation. The inactivity of C-11 appears to be attributable to the presence of an amide function in ring D.

EXPERIMENTAL

M.p.s were determined for samples in sealed tubes. I.r. spectra were measured for 0.2M-solutions in deuteriochloroform (0.2 mm path length) with a Perkin-Elmer 457 spectrometer. ^1H N.m.r. spectra were obtained with Varian T60 and JEOL JMN 4H 100 spectrometers for solutions in deuteriochloroform with tetramethylsilane as internal standard. Optical rotations (chloroform solutions at 25 °C) were measured on a Bellingham and Stanley polarimeter. Mass spectra were recorded with an A.E.I. MS20 spectrometer. Merck pre-coated silica gel 60_{254} plates (20 × 20 cm, 5 × 20 cm) were used for analytical purposes. Preparative layer chromatography plates (thickness 1.25 mm) were prepared from a 1 : 2 suspension of Merck silica gel 60 $PF_{254+366}$ in distilled water and left to dry in air for 4 days.

General Microbial Procedure.—The cultures, obtained from the Centraalbureau Voor Schimmelcultures, Baarn, Holland, were grown at 25 °C on slopes, inoculated from master slopes, of Oxoid nutrient-agar made up to manufacturer's specifications. The liquid nutrient medium was inoculated with the fungus grown in petri dishes on nutrient-agar, which had been inoculated from the slopes, after sufficient growth had occurred.

The liquid nutrient medium was prepared as specified by Jones *et al.*[12] Beef extract (1 g), corn steep liquor (1 g), yeast extract (1 g), malt extract (1 g), and glucose (5 g) were dissolved in distilled water (1 l) and the pH was adjusted to 5.5. Sucrose (2 g) was added to the resultant solution. The liquid nutrient medium was divided into 200 ml portions in wide-neck 500 ml flasks which were stoppered (cotton wool) and autoclaved at 121 °C (15 lb in^{-2}) for 15 min. The media were inoculated with the fungus and swirled (*ca.* 120 rev. min^{-1}) on a rotary shaker at 25 °C for 3 days. The steroidal substrate, dissolved in ethanol, was added to the fungus in nutrient media at 0.2 mg ml^{-1} and swirled with the fungus for 3 days at 25 °C.

After incubation, the contents of the flasks were combined and filtered. The filtrate was saturated with NaCl and extracted with dichloromethane (1 vol. of CH_2Cl_2 to 4 vol. of filtrate), and the organic layer was dried (Na_2SO_4). Removal of the solvent gave the ' broth extract.' The residue from filtration of the nutrient media was extracted by soaking in acetone followed by decantation. Removal of acetone left an aqueous residue which was extracted with chloroform. The organic layer was dried (Na_2SO_4) and evaporated to give the ' mycelial extract.'

3α-Acetoxy-17a-aza-D-homo-5α-androstan-17-one (1).—The synthetic procedure used was based on that described.[3] The work-up was modified such that the solvent used for extraction was completely removed, leaving a solid residue which was triturated with n-hexane. Recrystallisation

[7] A. M. Bell, I. M. Clark, W. A. Denny, E. R. H. Jones, G. D. Meakins, W. E. Müller, and E. E. Richards, *J.C.S. Perkin I*, 1973, 2131.

[8] K. Tori and K. Aono, *Ann. Reports Shionogi Res. Lab.*, 1964, **14**, 136.

[9] A. Capek and O. Hanc, *Folia Microbiol. (Prague)*, 1961, **6**, 237.

[10] Y. Nozaki, E. Masuo, H. Ishii, T. Okumura, and D. Satoh, *Ann. Reports, Shionogi Res. Lab.*, 1961, **11**, 9.

[11] A. Schubert, K. Heller, D. Onken, K. Zetsche, and G. Langbein, *Naturwiss.*, 1958, **45**, 264.

[12] J. W. Blunt, I. M. Clark, J. M. Evans, E. R. H. Jones, G. D. Meakins, and J. T. Pinhey, *J. Chem. Soc. (C)*, 1971, 1136.

from methanol gave a white crystalline solid, m.p. 285—287°, $[\alpha]_D$ +16.9° (Found: C, 72.3; H, 9.7; N, 4.2. Calc. for $C_{21}H_{33}NO_3$: C, 72.6; H, 9.6; N, 4.0%).

Incubation of 3α-*Acetoxy*-17a-*aza*-D-*homo*-5α-*androstan*-17-*one* (1) *with* C. elegans.—The aza-steroid (4.40 g), dissolved in ethanol (500 ml), was incubated with *Cunninghamella elegans Lendner* (C.B.S. 167.53) grown in the nutrient media (110 flasks) for 3 days. Extraction gave the mycelial and broth extracts (2.25 and 3.35 g, respectively). Chromatography of the mycelial extract on Al_2O_3 (10% deactivated, 100 g) gave starting material (473 mg). The broth extract was chromatographed on Al_2O_3 (10% deactivated; 300 g). Ether eluted starting material (224 mg) and ether–methanol (19 : 1) eluted 3α-*acetoxy*-6β-*hydroxy*-17a-*aza*-D-*homo*-5α-*androstan*-17-*one* (2) (1.396 g), m.p. (Me_2CO) 144.5—146.5°, $[\alpha]_D$ +1.8°, $\nu_{max.}$ 3 660, 3 610, 3 382, 1 722, and 1 640 cm^{-1} (Found: C, 69.1; H, 9.0; N, 4.0. $C_{21}H_{33}NO_4$ requires C, 69.4; H, 9.15; N, 3.85%). Further elution gave 3α-*acetoxy*-7α-*hydroxy*-17a-*aza*-D-*homo*-5α-*androstan*-17-*one* (3) (630 mg), m.p. (Me_2CO) 122—124°, $[\alpha]_D$ +9.6°, $\nu_{max.}$ 3 665, 3 604, 1 727, and 1 642 cm^{-1} (Found: C, 69.35; H, 9.2; N, 3.9. $C_{21}H_{33}NO_4$ requires C, 69.4; H, 9.15; N, 3.85%). Ether–methanol (4 : 1) eluted a mixture of 3α,11α-*dihydroxy*- and 3α,11β-*dihydroxy*-17a-*aza*-D-*homo*-5α-*androstan*-17-*one* (5) (66 mg). Repeated recrystallisation of the mixture from methanol gave 3α,11α-dihydroxy-17a-aza-D-homo-5α-androstan-17-one (4) (5 mg), *m/e* 321 (M^+), $\nu_{max.}$ 3 622, 3 382, and 1 640 cm^{-1}.

Chemical Transformations.—Oxidation of 3α-acetoxy-6β-hydroxy-17a-aza-D-homo-5α-androstan-17-one (2) and 3α-acetoxy-7α-hydroxy-17a-aza-D-homo-5α-androstan-17-one (3) with 8N-H_2CrO_4 gave respectively 3α-*acetoxy*-17a-*aza*-D-*homo*-5α-*androstane*-6,17-*dione* (6), m.p. (Me_2CO) 273—275°, $\nu_{max.}$ 3 384, 1 732, 1 711, and 1 646 cm^{-1} (Found: C, 72.95; H, 9.2; N, 4.0. $C_{21}H_{31}NO_3$ requires C, 73.0; H, 9.05; N, 4.05%), and 3α-*acetoxy*-17a-*aza*-D-*homo*-5α-*androstane*-7,17-*dione* (8), m.p. (Me_2CO–hexane) 239—241° (decomp.), $\nu_{max.}$ 3 382, 1 726, 1 708, and 1 645 cm^{-1} (Found: C, 73.2; H, 9.2; N, 4.1. $C_{21}H_{31}NO_3$ requires C, 73.0; H, 9.05; N, 4.05%). Acetylation of 3α-acetoxy-6β-hydroxy-17a-aza-D-homo-5α-androstan-17-one (2) with acetic anhydride and pyridine (2 : 1) overnight at ambient temperature gave the *diacetate* (7), m.p. (Me_2CO–hexane) 219—221° (decomp.), $\nu_{max.}$ 3 381, 1 729, and 1 646 cm^{-1} (Found: C, 70.8; H, 9.3; N, 3.5. $C_{23}H_{35}NO_4$ requires C, 70.9; H, 9.1; N, 3.6%).

Incubation of 3α-*Acetoxy*-5α-*androstan*-17-*one* (10) *with* C. elegans.—The steroid (4.44 g), dissolved in ethanol (400 ml), was incubated with *C. elegans* grown in the nutrient media (111 flasks) for 3 days. Extraction gave the mycelial and broth extracts (5.18 and 3.15 g, respectively). The mycelial extract was chromatographed on Al_2O_3 (6% deactivated; 150 g) to give starting material (591 mg). The broth extract was chromatographed on Al_2O_3 (6% deactivated; 300 g). Ether eluted material which was purified by p.l.c. (2 × $CHCl_3$) to give 3α-*acetoxy*-6β-*hydroxy*-5α-*androstane*-11,17-*dione* (13) (25 mg), *m/e* 362 (M^+), $\nu_{max.}$ 3 610, 1 738, 1 729, and 1 710 cm^{-1}. Further elution with ether and ether–methanol (98 : 2) gave 3α-*acetoxy*-6β,11β-*dihydroxy*-5α-*androstan*-17-*one* (11) (836 mg), m.p. (Me_2CO) 202—204°, $[\alpha]_D$ +93° (*c* 1.0), *m/e* 364 (M^+), $\nu_{max.}$ 3 160, 3 500vbr, and 1 730br cm^{-1} (Found: C, 69.3; H, 8.9. $C_{21}H_{35}O_5$ requires C, 69.3; H, 8.85%). Ether–methanol (1 : 1) eluted 1β,3α-*dihydroxy*-5α-*androstan*-17-*one* (12) (289 mg), m.p. (Me_2CO) 211—213°, $[\alpha]_D$ +137.5° (*c* 0.8), $\nu_{max.}$ 3 600, 3 450vbr, and 1 720br cm^{-1} (Found: C, 74.55; H, 9.8. $C_{19}H_{30}O_3$ requires C, 74.5; H, 9.9%).

Chemical Transformations.—Oxidation of 3α-acetoxy-6β,11β-dihydroxy-5α-androstan-17-one (11) and 1β,3α-dihydroxy-5α-androstan-17-one (12) with 8N-H_2CrO_4 gave, respectively, 3α-*acetoxy*-5α-*androstane*-6,11,17-*trione* (14), m.p. (Me_2CO) 269—271° (Found: C, 69.8; H, 8.0. $C_{21}H_{28}O_5$ requires C, 70.0; H, 7.8%), and 5α-androstan-1,3,17-trione (15), m.p. (Me_2CO) 196—198° (lit.,[13] 198—199°).

[7/923 *Received*, 30*th May*, 1977]

[13] J. J. Schneider, P. Crabbé, and N. S. Bhacca, *J. Org. Chem.*, 1968, **33**, 3118.