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17-Ketosteroids condense with o-nitrobenzaldehyde to yield steroidal indoxyls (1).

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In continuation of our studies of synthesis of steroidal nitrogen compounds with pharmacological interest (2-4), we investigated the condensation of o-nitrobenzaldehyde with 3-aza-A-homo- $4\alpha$ -androstene-4,17-dione.

We used as starting material 3-aza- $17\beta$ -hydroxy-Ahomo- $4\alpha$ -androsten-4-one (5), which by oxydation is transformed to the corresponding ketone. The latter with o-nitrobenzaldehyde under basic conditions in the dark produces 3-aza-A-homo-16, 17-seco-16-nor- $4\alpha$ -androsten-4-one-15-(2'-indoxyliden)-17-oic acid. The structure was determined from spectral data.

$$\begin{cases} \begin{array}{c} OH \\ I \end{array} \\ \\ II \end{array} \qquad \begin{array}{c} OH \\ III \end{array}$$

## **EXPERIMENTAL**

## 3-Aza-A-homo-4α-androstene-4,17-dione (II).

Jones reagent (2.6 ml) was added dropwise with stirring to a cool suspension of 3-aza-17 $\beta$ -hydroxy-A-homo-4 $\alpha$ -androsten-4-one (0.9 g) in 200 ml of acetone. After 24 hours the reaction mixture was diluted with water and extracted with chloroform. The chloroform extract was washed

with water, dried and the solvent was removed under reduced pressure. The residue was taken up in chloroform and passed through a column of silica gel. The product so obtained was crystallized from ethyl acetate to give 0.65 g, mp 219-221°; ir (potassium bromide):  $\nu$  max = 1740 cm<sup>-1</sup> (C = 0).

Anal. Calcd. for C<sub>19</sub>H<sub>27</sub>NO<sub>2</sub>: C, 75.74; H, 8.97; N, 4.65. Found: C, 75.48; H, 9.00; N, 4.48.

3-Aza-A-homo-16,17-seco-16-nor- $4\alpha$ -androsten-4-one-15-(2'-indoxyliden)-17-oic acid (III).

3-Aza-A-homo-4α-androstene-4,17-dione (410 mg) was dissolved in 10 ml of methanol. A solution of 500 mg of potassium hydroxide in 1 ml of water was added followed by a solution of 250 mg of freshly steam-distilled o-nitrobenzaldehyde in 2.5 ml of methanol. The mixture was refluxed for 90 minutes and allowed to stand in the dark over night. The solution was concentrated under reduced pressure, diluted with water and acidified with dilute hydrochloric acid. The yellow solid was collected by filtration, washed with water and dried (400 mg). On recrystallization from methanol-water produced mp 250° dec; ir (potassium bromide): ν max = 3350, 1700, 1640, 1615, 890, 750 cm<sup>-1</sup>; mr (DMSO): δ 1.1 (18-CH<sub>3</sub>), 1.190 (19-CH<sub>3</sub>), 5.487 (s, 5-CH), 5.609 (d, 15-CH, J = 11.5 Hz), 7.240 (aromatic protons), 7.40 (NH-lactam) 9.571 (NH-indoxyl); ms: M\* 434.

Anal. Calcd. for C<sub>26</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>: C, 71.88; H, 6.91; N, 6.45. Found: C, 71.53; H, 6.93; N, 6.35.

## REFERENCES AND NOTES

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