# ANALOGS OF ECDYSONES BASED ON STEROID SAPOGENINS

## II. 3β,5,14α-TRIHYDROXY-(25R)-5α-SPIROST-7-EN-6-ONE

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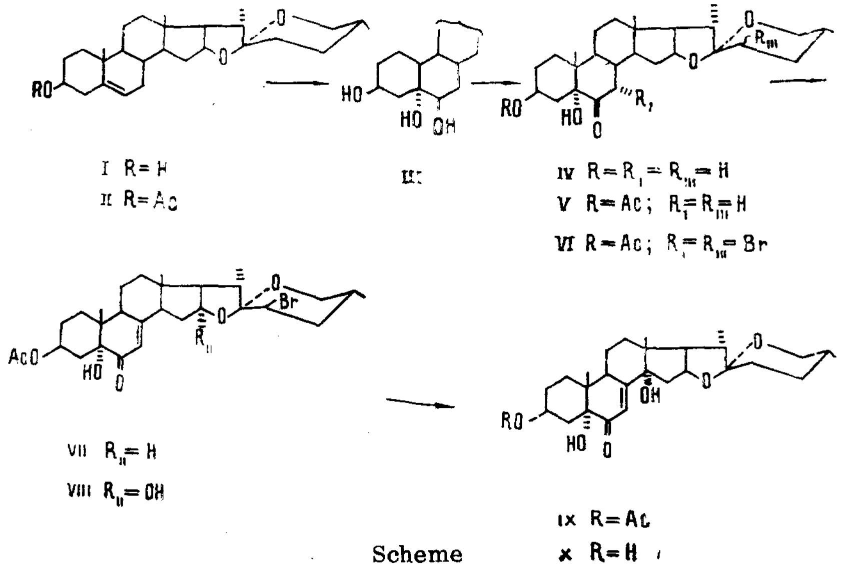
Continuing an investigation of the synthesis of ecdysone analogs [1], from diosgenin (I) we have obtained the 3β,5,14α-trihydroxy-5α-spirost-7-en-6-one (X). By a known method [2], diosgenin (I) was converted into the triol (III), which, on oxidation with N-bromosuccinimide in dioxane solution for seven days formed the spirostan-6-one (IV) [3] with mp 269-272°C, $[\alpha]_D^{20}-111.4°$ (c 1.92; $CHCl_3$). Yield of (IV) calculated on (I)−78%.

The acetylation of (IV) gave the acetate (V), with the composition $C_{29}H_{44}O_6$, mp 265-267°C, $[\alpha]_D^{20}-121.7°$ (c 1.84; $CHCl_3$). Compound (V) can also be obtained by the direct oxidation of diosgenin acetate (II) with tert-amyl hydroperoxide [4].

The bromination of (V) in glacial acetic acid [5, 6] with two moles of $Br_2$ at 15°C led with 61% yield to the 7α,23-dibromide (VI), with the composition $C_{29}H_{42}O_6Br_2$, mp 208-209°C, which is obviously a mixture of the 23S- and 23R-bromo derivatives [5].

The splitting off of HBr from (VI) under the action of $Li_2CO_3$ and LiBr in dimethylformamide [6] gave a 57% yield of the spirostene (VII), with the composition $C_{29}H_{41}O_6Br$, mp 182-185°C; $[\alpha]_D^{20}-96.4°$ (c 1.90; $CHCl_3$); $\lambda_{max}^{C_2H_5OH}$ 246 nm, log ε 4.20.

The presence in the NMR spectrum of (VII) of a one-proton singlet at 4.09 ppm ($W_{1/2}=6$ Hz) corresponding to an equatorial proton at $C_{23}$, and also a downfield shift in the signal of the $C_{21}$ methyl group (1.15 ppm) by 0.22 ppm [7] as compared with the corresponding signal (0.93 ppm) of the acetate (V) shows that compound (VII) is (23R)-bromo-(25R)-spirostene.



Scheme

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The introduction of the 14α-hydroxy group was effected by oxidizing (VII) with $SeO_2$ in dioxane [6]. From the reaction products was isolated a 75% yield of the 14α-hydroxyspirostene (VIII) with the composition $C_{29}H_{41}O_7Br$, mp 236-238°C; $[\alpha]_D^{20}$ −55.7° (c 1.67; $CHCl_3$).

The reduction of (VIII) with zinc dust in ethanol gave a 71% yield of 3β,5,14α-trihydroxy-5α-spirost-7-en-6-one acetate (IX) with the composition $C_{29}H_{42}O_7$, mp 274-276°C, $[\alpha]_D^{20}$ −12.8° (c 2.00; $CHCl_3$). The saponification of (IX) with an aqueous methanolic solution of $K_2CO_3$ yielded 3β,5,14α-trihydroxy-(25R)-5α-spirost-7-en-6-one (X) with the composition $C_{27}H_{40}O_6$, mp 261-263°C; $[\alpha]_D^{20}$ −5.4° (c 2.23; $CHCl_3$).

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