

OXIDATION OF ALLIOGENIN AND  $\beta$ -CHLOROGENIN  
WITH N-BROMOSUCCINIMIDE

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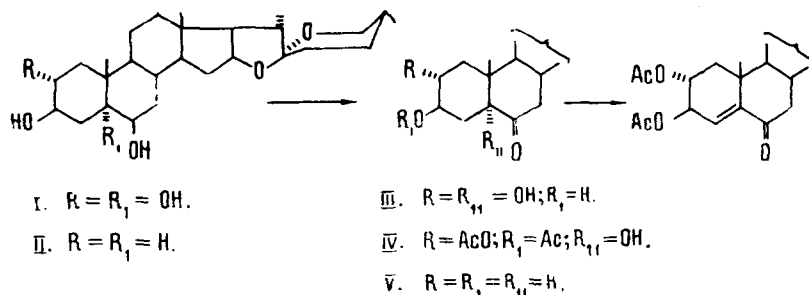
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It is known that some 6-oxosteroids inhibit the molting and metamorphosis of insects [1] and are also effective chemosterilants for them [2]. From the readily accessible steroid 6-hydroxysapogenins allioigenin (I) [3] and  $\beta$ -chlorogenin (II) [4] we have obtained their 6-oxo analogs.

The oxidation of allioigenin (I) with bromosuccinimide in aqueous dioxane [5] gave the oxo compound (III),  $C_{27}H_{42}O_6$ , with mp 273-275°C,  $[\alpha]_D^{20} - 93.9^\circ$  (c 1.32; pyridine). The nature of the optical rotatory dispersion curve with a negative Cotton effect (c 0.06; methanol;  $[M]_{321} - 6570^\circ$ ,  $[M]_{283} + 2820^\circ$ ) shows [6] that the compound formed (III) was 2 $\alpha$ ,3 $\beta$ ,5 $\alpha$ -trihydroxy-(25R)-5 $\alpha$ -spirostan-6-one. The acetylation of (III) under the usual conditions gave the diacetate (IV),  $C_{31}H_{46}O_8$ , mp 303-305°C,  $[\alpha]_D^{20} - 145.0^\circ$  (c 1.71; chloroform). With thionyl chloride in pyridine, substance (IV) formed a spirost-4-ene (VI),  $C_{31}H_{44}O_7$ , with mp 233-235°C,  $[\alpha]_D^{20} - 169.4^\circ$  (c 1.57; chloroform),  $\lambda_{\max}^{C_2H_5OH}$  235 nm (log  $\epsilon$  3.94).

$\beta$ -Chlorogenin (II) was also oxidized by N-bromosuccinimide in aqueous dioxane; the previously known sapogenin laxogenin (V) [7] was isolated with mp 211-214°C,  $[\alpha]_D^{20} - 81.9^\circ$  (c 1.22; chloroform).

The insecticidal action of these compounds will be described later.



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