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17α-HYDROXYSTROPHANTHIDIN

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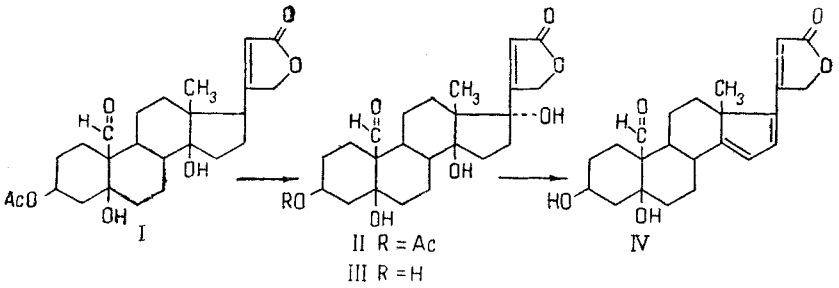
In addition to the obligatory hydroxy groups at C-3 and C-14, many natural cardenolides have additional alcoholic groups in positions 1β, 2α, 5β, 11β, 12α, 12β, 15β, 16β, and 19 of the steroid nucleus [1]. However, in contrast to the vegetable pregnanes and the corticosteroid hormones, cardiac aglycones substituted by a hydroxy group at C-17 are not found in nature.

We have effected the synthesis of 17α-hydroxystrophanthidin (III). For this purpose, strophanthidin acetate (I) was oxidized with selenous acid [2, 3] in boiling dioxane solution for 25 hr; the reaction products yielded II, $C_{25}H_{34}O_8$, with mp 272–275° C (from methanol), $[\alpha]_D^{25}$ −9.9°(c 1.2: pyridine), $[\alpha]_D^{24}$ +17.0°(c 0.1; dioxane); UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 218, 303 mμ (log ε 4.10, 1.61). With Raymond's reagent the substance gives a pink coloration. Compound II is not acetylated under the usual conditions.



When the tetraol III was boiled with methanol containing 5% hydrochloric acid for 5 hr, it gave a mixture of substances from which, after separation on a thin-layer chromatogram, product IV was isolated; it was identified chromatographically and also by its UV spectrum [$\lambda_{max}^{C_2H_5OH}$ 338 mμ (log ε 4.20)] as 14, 16-dianhydrostrophadogenin [4].

In biological tests on cats, 17α-hydroxystrophanthidin acetate (II) possessed fairly pronounced activity (LD 1.0 mg/kg), although this was a fifth of the activity of the initial strophanthidin acetate (I) (LD 0.20 mg/kg). All this indicates that the newly introduced hydroxy group occupies the 17α-position.

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