grade II of activity on a funnel with a No. 3 porous filter. The solvent is removed from filtrates not containing the impurity of I (R_f 0.6), and 4.2 g of II are obtained. A 2.5-g portion of II is dissolved in 2 ml of chloroform and the solution is placed on a column (1.5 × 30 cm) filled with Sephadex LH-20 (about 20 g). Chloroform is used as the eluent. Fractions of 5 ml are collected and analyzed by GLC. Yield, 0.5 g of colorless II. UV spectrum (C_2H_5OH), λ_{max}, nm: 285. $E^{1\%}_{1cm}$ 43. n_D^{20} 1.4975.

Trimethylphytylbenzoquinone (VII). n_D^{20} 1.5000. Found, %: C 81.16; H 11.38. $C_{29}H_{48}O$. Calculated, %: C 81.26; H 11.29. IR spectrum, ν, cm^{-1}: 1650 (C=O). UV spectrum (C_2H_5OH), λ_{max}, nm: 258, 266 (log ε 2.61; 2.60).

Diacetyltrimethylphytylhydroquinone VIII. n_D^{20} 1.4912. Found, %: C 76.91; H 10.65. $C_{33}H_{54}O_4$. Calculated, %: C 76.99; H 10.57. IR spectrum, ν, cm^{-1}: 1770, 1200 (—OAc).

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IMPROVED METHOD OF OXIDATIVE CLEAVAGE OF THE DIHYDROXYACETONE SIDE CHAIN IN CORTICOSTEROIDS

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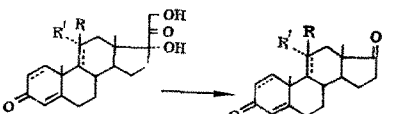
The oxidative cleavage of the side chain of corticosteroids (I) with the formation of 17-ketoandrostanes (II) is used to establish the structure of compounds I, and also as a path for the preparation of compounds II. However, the existing methods [1, 2] for carrying out this transformation are not always satisfactory as a preparative method: The yields of products II vary depending on the structure of the starting compounds I, and do not usually exceed 50%. The process is also accompanied by oxidation reactions at C^6, formation of a Δ^6 bond, etc.



Ia-f IIa-f

a: $R = R^1 = H$; b: $R = H$, $\Delta^{9(11)}$ bond; c: $RR^1 = O$; d: $R = OH$, $R^1 = H$; e: $R = OH$, $R^1 = H$, Δ^1 bond; f. $RR^1 = O$, Δ^1 bond

The oxidation of compounds Ia, c, d by active MnO_2 [4] into 17-ketones IIa, c, d in yields of 34, 65, and 52%, respectively has been described in [3]. When studying this reaction by TLC, we noticed that in the course of prolonged (25 h) heating, 6-ketones are formed, and oxidation of the hydroxy group at C^{11} takes place, which hinders the isolation and purification of compounds II. We therefore increased the amount of MnO_2 so that the time of the reaction could be shortened and the formation of side products could be avoided. The proposed method consists in boiling compound I with a 20-fold excess of MnO_2 in chloroform for 3-4 h. At the end of the oxidation (TLC test), MnO_2 is filtered, and a solution of chromatographically almost pure compound II is obtained. The experimental results are listed in Table 1.

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TABLE 1. Results of Oxidation of Corticosteroids Ia-f by Active MnO_2

Reaction product	Yield, %	mp, °C	Solvent for recrystallization
IIa	67,6	169—172 [3]	MeOH—water
IIb	72,6	203—205 [5]	Acetone—hexane
IIc	64,9	218—220 [3]	Alcohol
IId	76,8	196—200 [2]	Acetone—hexane
IIe	74,5	185—187* [2]	As above
IIf	55,3	192—196 [6]	" "

*Solvate with acetone, melts at 100-105°C, solidifies and melts again at 185-187°C.

Table 1 shows that the oxidation of corticosteroids Ia-f leads to the formation of the corresponding compounds IIa-F in yields of 55-77%. The method is suitable for preparation of various 3,17-diketo-Δ^4-androstenes II: unsubstituted at C^{11} (IIa), containing an 11-keto- (IIc, f) and 11-β-hydroxy groups (IId, e), and also additional bonds at Δ^1 (IIe, f) and $\Delta^{9(11)}$ (IIb).

We thus propose a general method for the preparation of androst-4-ene-3,17-dione (IIa) and its substituted derivatives (IIb-f) which is convenient from the preparative point of view

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