

group is as great as this figure, the nearest being the " $\frac{3}{4}$ white" mean.

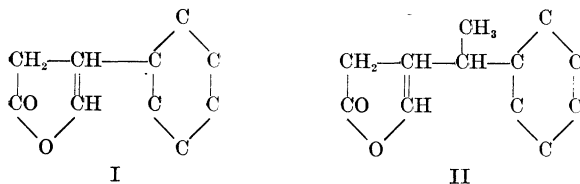
(6) The relative variability of the Negro brain weight (as measured by the coefficient of variation) appears to be slightly greater than that in the whites, though the difference can not be asserted to be significantly greater than might arise from fluctuations of random sampling, so far as concerns any of the comparisons that can be instituted on the basis of the present material.

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THE DIGITALIS GLUCOSIDES. VIII. THE DEGRADATION OF THE LACTONE SIDE CHAIN OF DIGITOXIGENIN

DEGRADATION studies with a number of derivatives of strophanthidin and of the digitalis aglucones have been in progress since the reports of our earlier work.¹ Because of the possible significance of recent results which we have obtained, in particular in degradation experiments with the digitalis aglucones, we wish to present a preliminary report of this phase of the work before its completed presentation can be made elsewhere.

Our previous observations have suggested that the unsaturated lactone side chain of the cardiac aglucones may be attached directly on the β -carbon atom to a six-membered ring as in formula I, or by an intermediate carbon atom as in formula II.² The latter



possibility, however, would be excluded if the presence of the sterol ring system as indicated by the formation of methyl cyclopentanophenanthrene on dehydrogenation of strophanthidin³ could be substantiated by other means. For further information we have attempted the graded degradation of the lactone side chain in a number of selected substances. The present preliminary report deals with the experience with a previously described digitoxigenin derivative, γ -digitoxanoldiacid.⁴ On oxidation of its secondary hydroxyl group with chromic acid this was converted into the keto acid, *digitoxanondiacid*, $\text{C}_{23}\text{H}_{34}\text{O}_5$. On reduction by the Clemmensen method, *digitoxandiacid*,

¹ W. A. Jacobs and R. C. Elderfield, *Jour. Biol. Chem.*, 102: 237, 1933.

² W. A. Jacobs and R. C. Elderfield, *Jour. Biol. Chem.*, 100: 676, 1933; R. C. Elderfield and A. Rothen, *Jour. Biol. Chem.*, 106: 71, 1934.

³ R. C. Elderfield and W. A. Jacobs, *SCIENCE*, 79: 279, 1934.

⁴ W. A. Jacobs and E. L. Gustus, *Jour. Biol. Chem.*, 86: 211, 1930.

$\text{C}_{23}\text{H}_{36}\text{O}_4$, resulted. The *dimethyl ester* was converted with Grignard reagent into the bis-diphenyl carbinol which on oxidation with chromic acid was degraded with the loss of three of the original carbon atoms of the lactone side chain to the *monobasic acid*, $\text{C}_{20}\text{H}_{32}\text{O}_2$.

At this point the striking property of this acid of forming very sparingly soluble salts which made manipulation somewhat difficult recalled a similar experience reported by Wieland, Schlichting and Jacobi⁵ in the case of aetiocholanolic acid of the same formula. On further study other resemblances appeared. Our acid melted at 219–219.5°. The melting point given for aetiocholanolic acid is 219°. The methyl ester of our acid melted at 97–98°. Wieland, Schlichting and Jacobi reported 98–99° for aetiocholanolic methyl ester. The ethyl ester of our acid melted at 76.5–77.5°. Aetiocholanolic ethyl ester melts at 78–79°.

The striking similarity of the two series of substances thus suggests the possible identity of our degradation product from digitoxigenin with aetiocholanolic acid. Final check of such identity, however, must await the results of a direct comparison of physical constants, mixed melting points, etc. We are attempting to procure the material for such comparison.

Should the identity of these substances be verified, the conclusions are obvious which can be drawn in regard to the structure of the cardiac aglucones.

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⁵ *Zeits. physiol. Chem.*, 161: 102, 1926.

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