This relationship is shown in the following partial formulas:

\[
\begin{align*}
\text{digitoxigenin} & \quad \text{gitoxigenin} \\
\text{CH}_2\text{-C-H} & \quad \text{CH}_2\text{-C-OH} \\
\text{CO} & \quad \text{CO} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

In all other respects the two aglucones are structurally identical. These conclusions have been reached from the study of the following series of substances.

Gitoxigenin on isomerization by alkali is converted into isogitoxigenin.\(^1\) On saponification of the lactone group of the latter substance, the salt of isogitoxigenic acid results, which can be oxidized by hypobromite to isogitoxigenic acid. When the latter is treated with concentrated hydrochloric acid, the remaining tertiary hydroxyl is replaced by chlorine with the formation of chloroisogitoxigenic acid. Simultaneously stereo-isomerization occurs under the influence of the reagent on some center of asymmetry in the molecule. The chlorine atom in this acid can be removed under certain conditions as hydrochloric acid with the production of anhydro isogitoxigenic acid.

It was hoped that on catalytic hydrogenation this anhydroacid (as the ester) would absorb one mol of hydrogen with the formation of a substance identical, or at least isomeric, with the previously described isodigitoxigenic acid obtained from isogitoxigenin. The reaction, however, took an abnormal course in that two mols of hydrogen were consumed. Investigation showed that not only was the double bond hydrogenated but the lactone group was cleaved with the formation of a saturated acid in accordance with the following scheme:

\[
\begin{align*}
\text{CH}_2\text{-C-H} & \quad \text{CH}_2\text{-C-CH}_2 \\
\text{COOH} & \quad \text{COOH} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

On saponification this half ester readily yielded the dibasic acid.

Following a number of unsuccessful attempts the identical dibasic acid was obtained also from digitoxigenin through the following steps. Isodigitoxigenin\(^2\) after saponification was oxidized by hypobromite to isodigitoxigenic acid. On treatment with concentrated hydrochloric acid the latter was isomerized to \(\gamma\)-isodigitoxigenic acid. When treated with acetic anhydride and acetyl chloride a reaction occurred, which involved cleavage of the lactone group and formation of a substituted succinic anhydride while simultaneously the newly uncovered hydroxyl group was removed as water.\(^3\) The secondary hydroxyl group elsewhere in the molecule was also acetylated. When this anhydro anhydride acetate (acetate of anhydro-\(\gamma\)-digitoxenoldiacid)

\[
\begin{align*}
\text{CH}_2\text{-CH--CH} & \quad \text{CH}_2\text{-CH--CH} \\
\text{COOH} & \quad \text{COOH} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

was treated with methyl alcohol containing one percent of hydrochloric acid, the succinic anhydride group was converted into the half ester. Catalytic hydrogenation of the resulting unsaturated half ester gave rise to the saturated substance, the acetate and half ester of \(\gamma\)-digitoxanoldiacid. On saponification \(\gamma\)-digitoxanoldiacid was produced and this substance proved to be identical with the above described dibasic acid obtained from gitoxigenin. This conclusion was substantiated by the comparison of the neutral dimethyl esters prepared from both acids as well as of the stable half esters which resulted on partial saponification of the latter.

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