THE RELATIVELY INERT OXYGEN ATOM OF DIGOXIGENIN, SARMENTOGENIN AND THE STEROID COMPOUNDS OF THE ADRENAL CORTEX

Sir:

We have recently described [THIS JOURNAL, **60,** 1493, 2566 (1938)] a series of *etio*-cholanic acids and esters with oxygen atoms at C-3 and C-12. Steiger and Reichstein [*Helv. Chim. Acta,* **21,** 828 (1938)] have prepared from digoxigenin a similar series of acids which were thought to have oxygen atoms at C-3 and C-11. Since the 3,*x*-diketo-4-*etio*-cholenic acids derived from digoxigenin and from corticosterone proved to be different, they considered it doubtful that an oxygen atom occupied C-11 in the acids derived from digoxigenin. Through the courtesy of Professor Reichstein we have been able to compare directly the methyl diketo-*etio*-cholanates and the methyl diketo-4-*etio*-cholenates from the two sources. The results given in the table show that the properties of the esters from the two sources are identical. We conclude that Reichstein's acids are identical with those derived from desoxycholic acid and that the inert oxygen atom of digoxigenin, which was assigned to C-11 by Tschesche and Bohle [*Ber.* **69,** 793 (1936)], is actually at C-12.

	Acid or ester	From digoxigenin M. p., °C.	From digoxigenin $[\alpha]^{19}_D$	From desoxycholic acid M. p., °C.	From desoxycholic acid $[\alpha]^{25}_D$
1	Methyl diketo-*etio*-cholanate	171–172[a]	138.3 ± 2	169–170[a]	142 ± 3
2	Methyl diketo-4-*etio*-cholenate	236–238[b]	185 ± 2	236–238[b]	190 ± 6
3	Diketo-*etio*-cholanic acid	170		178	
4	Dihydroxy-*etio*-cholanic acid	280–286		283–286	
5	Methyl dihydroxy-*etio*-cholanate	180–183		145–146	

[a] Mixtures melted at 169–170°.

[b] Mixtures melted at 236–237°.

The other comparisons of the table are less satisfactory since the specific rotations of these compounds of Reichstein were not known and specimens were not available for mixed melting point determinations. The melting points of the diketo-*etio*-cholanic acids are in reasonable agreement, since we have found, as has Reichstein, that the acid is very difficult to purify. The methyl dihydroxy-*etio*-cholanates appear to be different since the melting point of our ester was sharp and could not be raised by distillation or recrystallization. Accepting this difference, epimerism at C-12 is indicated since the configuration of both esters at C-3 is α (no precipitation with digitonin). This difference is not certain, however, since the corresponding acids melt at the same point.

It has been generally accepted since the work of Tschesche and Bohle [*Ber.* **69,** 2497 (1936)] that digoxigenin and sarmentogenin differ only in the configuration at C-9. Inasmuch as some of the adrenal steroids contain an oxygen atom which corresponds in almost all respects with the inert oxygen atom of sarmentogenin, it has been assumed [Marker, THIS JOURNAL, **60,** 1725 (1938)] that they had a configuration at C-9 like that of sarmentogenin which was supposed to have a *cis* linkage of rings B and C instead of the normal or *trans* linkage. Marker [THIS JOURNAL, **60,** 1061 (1938)] has made the same assumption for his urane compounds. There is now no need to assume such a configuration at C-9 for sarmentogenin to explain its difference from digoxigenin, although such a possibility is by no means excluded. Consequently, such an assumption for the adrenal compounds has no basis. Indeed, all the evidence [Reichstein, *Helv. Chim. Acta,* **19,** 402 (1936); **20,** 978 (1937); **21,** 161 (1938)] points to a normal steroid skeleton with an oxygen atom at C-11.

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ABSENCE OF COMBINED FATTY ACID IN CEREAL STARCHES

Sir:

The common cereal starches contain fatty material which cannot be extracted by solvents such as petroleum ether, ethyl ether or carbon tetrachloride. From this behavior, T. C. Taylor and his co-workers assumed that the fatty acid must be present as an ester of the carbohydrate substance. His later work indicated that the α-amylose fraction of the starch was characterized by—and owed its insolubility to—this esterification with fatty acid.

Recent investigations in these Laboratories show that the fatty acids in corn, wheat and rice starches can be removed completely by Soxhlet extraction with certain water-miscible fat solvents, particularly methanol, the cellosolves, and 80% dioxane. The de-fatted starch retains its characteristic granule structure and optical birefringence, and gelatinizes in hot water to give a paste of normal high viscosity. By treatment