Solvent.	Chloroform.			Benzene.		Methyl alcohol.	Glacial acetic acid.
Grams pentacetate per 100 cc. soln.	3.2500	3.3376	4.0084	1.6816	2.2412	3.9480	3.3732
$[\alpha]_D^{20}$	+106.7°	+106.9°	+106.1°	+94.8°	+92.3°	+113.6°	+114.0°

The second galactose pentacetate was crystallized also from the products of the acetylation of galactose with acetic anhydride and zinc chloride but the yield was so small that this method is not recommended.

Our thanks are expressed to Mr. A. S. Eastman, who has kindly verified some of the work.

WASHINGTON, D. C.

THE EXISTENCE OF A THIRD CRYSTALLINE PENTACETATE OF GALACTOSE.

BY C. S. HUDSON.[1]

Received April 10, 1915.

The acetylation of an aldose sugar with acetic anhydride and sodium acetate (the Liebermann method) has yielded the fully acetylated β-derivative in all cases in which a crystalline product was obtained. If one acetylates either the α- or β-form of glucose by this reaction, substantially the same product is obtained, namely, β-glucose pentacetate, mixed with a small proportion of sirupy acetylation products. It would seem probable in these cases that at least a small proportion of the isomeric alpha acetate is produced along with the larger amount of the beta derivative, and some months ago the writer undertook a careful search for the presence of the second pentacetate of galactose as a side product in the preparation of the first pentacetate[2] of this sugar by the Liebermann reaction. The acetates of galactose were chosen for the experiments because of the fact that the one which must be removed from the mixed products in order to permit the possible crystallization of the second pentacetate is a decidedly crystalline substance of low solubilities. On this plan, 400 g. of very pure galactose, prepared in the laboratory from lactose, were acetylated in the manner indicated and poured into cold water. About 275 g. of the first pentacetate of galactose (m. p. 142°) were obtained after one recrystallization from 95% alcohol of the crude crystalline product which did not dissolve in the water. The water was extracted with chloroform and this solution was mixed with the mother liquor from the crystallization of the first pentacetate and the chloroform allowed to evaporate slowly at room temperature. The sirupy residue crystallized somewhat in the course of several days, and these crystals proved to be more of the first pentacetate. The mother liquor from them later crystallized

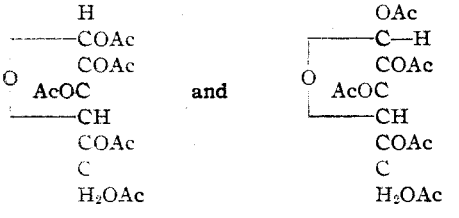
[1] Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

[2] See the preceding article in regard to the existence of these first and second pentacetates.

further, and after recrystallization from alcohol about 15 g. of a substance was obtained which melted at 96°. It was supposed that this was the product sought, namely, the second galactose pentacetate, which had been found to melt at 95–6°.[1] Later, an occasion arose to examine the specific rotation of this substance, which had not been done before because it was believed that its melting point characterized it sufficiently, and to my surprise it showed levorotation, $[\alpha]_D^{20} = -41°$ in chloroform solution. The first pentacetate of galactose, melting at 142°, has $[\alpha]_D^{20} = +25$, the second, melting at 95–6° shows $[\alpha]_D^{20} = +107$, both being of dextrorotation. The levorotatory substance must therefore be considered a new acetate of galactose. At this stage Dr. J. M. Johnson undertook the further examination of these three acetates of galactose, an investigation which is now in progress, and I am much indebted to him for the following data which show that the new acetate is in reality a third pentacetate of galactose. From 175 g. of galactose he obtained by the method which has been described above, except with the improvement of neutralizing the aqueous solution with sodium bicarbonate before extracting it with chloroform, 163 g. of the first pentacetate of galactose (m. p. 142°), and sufficient of the new levorotatory acetate to yield 20 g. of it after several recrystallizations from alcohol to bring it to a constant rotation. This pure material showed $[\alpha]_D^{20} = -41.6°$ in chloroform and melted at 98°. This temperature is thus quite distinct from that at which the second pentacetate melts, 95–96°, though of course the specific rotation of the latter, +107°, fully distinguishes it from the new acetate. Saponification of the levorotatory acetate with alcoholic potash yielded crystalline galactose, which was recrystallized and identified by its initial and final specific rotations.

Acetyl determinations made by boiling half-gram samples with 100 cc. of 0.25 *N* H_2SO_4 during three hours, indicated 54.6 and 54.8% acetyl (CH_3CO). Theoretical value for a galactose pentacetate, 55.1. The value for a tetracetate is only 49.4%. Mol. wt. determinations in benzene solution by the freezing-point method gave values between 386 and 404. Theoretical for a galactose pentacetate, 390.

These data show that the substance is a third crystalline pentacetate of galactose. From a theoretical standpoint the existence of three such isomers is noteworthy because, while two of them may be assigned the usual stereomeric structures,



[1] See the preceding article by Hudson and Parker.

the existence of a third isomer must be accounted for on other grounds. It is possible of course that the third form may have the oxygen ring linkage on some other than the gamma carbon atom. This is the suggestion which Fischer[1] has recently made in connection with his discovery of a third modification of methyl glucoside which he obtained in the form of a distillable sirup. As mentioned, Dr. Johnson and myself are continuing the investigation of the isomerism of the three galactose pentacetates.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE NORTHWESTERN UNIVERSITY MEDICAL SCHOOL.]

ON THE COMBINATION OF PROTEIN WITH HALOGEN ACIDS.[2]

BY J. H. LONG AND MARY HULL.

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Certain classes of combinations between protein bodies and halogen acids, and, in particular, hydrochloric acid, have been studied and frequently described. Before the full recognition of the fact that the proteins may act as basic bodies and hold these acids in salt forms, the distinction between such salts and substitution compounds was not clearly made. Hydriodic acid, for example, forms salts with egg albumin, but it forms also substitution products in which the iodine replaces hydrogen in nucleus groups. In this manner relatively large amounts of iodine may be added, but the products lose the properties of proteins.

In the production of these compounds and in the determination of the proportions in which proteins and halogen acids unite, a number of quite different processes have been employed. The results vary with the process and we are still without a satisfactory answer to some phases of the general question. Among the earliest papers describing definite combinations between proteins and acid those of Paal[3] may be referred to. Paal produced compounds which he considered as definite salts of peptones, containing from 10 to 15% of HCl. These were made by treatment of egg albumin with diluted acid and also by digestion of the protein by acid and pepsin. In these cases the salts were separated in comparatively pure form, but in most inquiries on the subject the aim has been to determine the ratio of combination between protein and halogen, rather than the isolation of the actual compounds. This has been done, usually, by finding the amount of acid held by a given weight of protein, when an excess is added and this excess measured by the aid of an appropriate indicator. In this manner, for example, Osborne[4] showed, by use

[1] *Ber.*, **47**, 1980 (1914).

[2] Presented at the New Orleans meeting of the American Chemical Society, April 2, 1915.

[3] C. Paal, *Ber.*, **25**, 1202 (1892); **27**, 1827 (1894).

[4] THIS JOURNAL, **21**, 477 and 486 (1899).