greater as the concentration of the alcohol or acetone increases, in this respect also differing from the behavior of neutral salts. The addition of sugar reduces the rate of fading, but this is probably due to a diminution of the hydroxyl ions caused by combination of the base with the sugar molecules to form glucosates. It is possible practically to stop the progress of the fading reaction by the addition of sufficient sugar.

Summary.

1. The temperature coefficient for the conversion of a triphenylmethane carbinol into the quinoid form, in the presence of an acid, is independent of the concentration of the acid and between 25° and 40° independent also of the temperature. For crystal violet the increase in the velocity of the change is 66% for every five degrees. Changes of the same order of magnitude were observed in the case of diamino derivatives but comparatively few measurements were made with these dyes and the results have not been tabulated in this paper.

2. The temperature coefficient for the fading of a triphenylmethane dye in the presence of an alkali is independent of the concentration of the base and independent of the temperature (between 25–40°). For crystal violet the increase in velocity is 43% for five degrees.

3. For all concentrations of acid below 0.024 N the speed of the color development in crystal violet is an inverse function of the concentration of the hydrogen ions. For all concentrations of acid above this value the velocity is a direct function of the hydrogen ion concentration.

4. The rate of fading of a triphenylmethane dye is a direct function of the concentration of the hydroxyl ions and in the case of basic dyes, such as crystal violet, is exactly proportional to such concentration.

5. Neutral salts retard the rate of fading and also retard the rate of development of color in all the basic triphenylmethane dyes but accelerate the rate of fading of acidic dyes.

6. All uniunivalent neutral salts in equivalent concentrations are equally effective in modifying the catalytic influence of the acid or base. They behave like acids in their effect upon basic dyes and like bases in their influence upon acid dyes.

BERKELEY, CAL.

CONVERSION OF GALACTOSE PENTACETATE TO AN ISOMERIC FORM.

BY C. S. HUDSON AND H. O. PARKER.[1]

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Crystalline galactose pentacetate was prepared by Erwig and Koenigs[2]

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

[2] *Ber.*, **22**, 2207 (1889).

by the acetylation of galactose with acetic anhydride and sodium acetate. They found that the substance melts at 142°, and their analysis shows that its percentages of carbon, hydrogen and acetyl agree closely with the theoretical values for a galactose pentacetate. Fischer and Armstrong[1] found the specific rotation of the substance to be +7.48° in benzene solution. We have prepared a considerable quantity of this pentacetate by the indicated method, using the proportions 4 parts of sugar, one of anhydrous sodium acetate and 16 of acetic anhydride, have purified it without difficulty by recrystallization from alcohol, and have confirmed the quoted data on the melting point and the specific rotation in benzene. In chloroform solution (*chloroformum purificatum*, U. S. P.) we find dextrorotation of the value $(\alpha) = +25°$.

Erwig and Koenigs[2] mention that the boiling of this pentacetate with acetic anhydride and a little zinc chloride yields a sirupy product. We have investigated this change and find that there is produced a second galactose pentacetate which may be readily crystallized.

Fifty grams of the first pentacetate (m. p. 142°) were heated on the steam bath with 150 cc. of acetic anhydride containing 10 g. zinc chloride until the specific rotation changed from +28° to the constant value of +105°, the reaction being complete within about fifteen minutes. The mixture was then poured into 500 cc. ice water, neutralized with sodium bicarbonate, and the solution extracted with chloroform, in which the acetates of the sugars are very soluble. The greater part of the chloroform was removed by distilling under reduced pressure, followed by evaporation in a strong air current. The residue was mixed with 95% alcohol to form a thick sirup and it was not difficult to bring about crystallization by scratching the wall of the glass container. The crystals were purified by several recrystallizations from alcohol until the specific rotation became constant.

The yield was about 70% of the weight of the first acetate. The substance, which we would designate for the present the second pentacetate of galactose,[3] melts sharply at 95.5°.

On combustion, 0.2631 and 0.2746 g. subs. yielded 0.4727 and 0.4945 g. CO_2 and 0.1325 and 0.1385 g. H_2O.

Found: C = 48.99 and 49.10%; H = 5.52 and 5.60%. Theoretical, 49.23 and 5.64 for a hexose pentacetate.

The saponification of several half-gram samples of the substance by boiling 3 hours with 0.25 *N* sulfuric acid gave values ranging between 54.3 and 54.9% CH_3CO. Theory, 55.1. The saponification of the substance with alcoholic potash yielded crystalline galactose, which was identified by its specific rotation.

The specific rotations of the new pentacetate (m. p. 95.5°) in several solvents, all the rotations being in the right-hand direction, are recorded in the table.

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[1] *Ber.*, **35**, 838 (1902).

[2] *Loc. cit.*

[3] In the following article a third crystalline pentacetate of galactose is described, and on account of its existence it appears preferable to avoid the designations *α*, *β* and *γ* until the relationship of these acetates to the *α*- and *β*-forms of galactose is established.—C. S. H.

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
$[\alpha]^{20}_{D}$	+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]

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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

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[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.