

librium rotation and mutarotation constant would be the same as in the case of either component. A quantity of 2.047 g. of such a mixture would contain enough of the alpha form to initially saturate 25 cc. of water at 0° with respect to α -lactose [Hudson, THIS JOURNAL, 30, 1771 (1908)]. In an experiment, 25 cc. of water at 0° was added to three grams of the new form of lactose. All but a trace dissolved within two minutes. Then 0.25 g. of pure alpha lactose monohydrate was added and the mixture shaken for five minutes. By rapid filtration, 0.26 g. was recovered unchanged. In a control experiment, 0.25 g. of alpha lactose monohydrate was nearly completely dissolved by 25 cc. of water at 0° in one and one-half minutes and no trace remained after five minutes. It is necessary to conclude that by dissolving the new form the water became saturated with respect to the ordinary hydrated alpha form. The former consequently must be considered either a mechanical mixture or a molecular compound of the usual alpha and beta forms of lactose. Because the crystals of the new substance are characteristic and homogeneous and because the same substance (as indicated by its initial rotation) was obtained in many preparations under varied conditions of acid strength and time of reaction, we regard the substance as a molecular compound of definite composition (5α -lactose- 3β -lactose) analogous to the double salts of inorganic chemistry. It is noteworthy that the new compound is anhydrous whereas one of its components (α -lactose) has never been obtained anhydrous when crystallizing from a solvent; this fact is a further proof that the new form of lactose is not a mechanical mixture of the two older modifications.

Apparently, this is the first case to be observed where two chemical isomers of a free reducing sugar combine to form a molecular compound of the general type previously found among the methylxylosides, as described in the preceding communication. Its isolation may serve to illustrate that extreme caution is necessary in characterizing a homogeneous crystalline form of a reducing sugar as a pure chemical individual.

DIVISION OF CHEMISTRY
NATIONAL INSTITUTE OF HEALTH
WASHINGTON, D. C.

R. C. HOCKETT
C. S. HUDSON

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THE REACTION OF SEVERAL METHYLPENTOSIDES AND OF ALPHA-METHYLMANNOSE WITH TRIPHENYLMETHYL CHLORIDE¹

Sir:

In numerous researches of recent years it has been assumed that triphenylmethyl chloride will attack readily only *primary* hydroxyl groups by direct action in pyridine solution [Helferich and Becker, *Ann.* 440, 1

¹ Publication approved by the Surgeon-General, U. S. Public Health Service.

(1924); Josephson, *ibid.*, **472**, 230 (1929); Pacsu, *THIS JOURNAL*, **53**, 3099 (1931), etc.]. Using this assumption as a premise we inferred that such methylpentosides as contain a 1,5-ring structure and consequently no primary hydroxyl group, should be inactive toward this reagent unless there can occur during reaction a ring shift in such glycosides, which is contrary to the views of most, though not all, investigators. Conversely, any methylpentoside containing the 1,4-ring should be free to react directly with this reagent because of its possession of an unprotected primary hydroxyl on carbon number five. This reaction consequently appeared to us as a promising possible means of distinguishing between the ring types among the five-carbon sugars and thus of settling the controversy regarding the ring assignment for α -methyl-*d*-lyxoside.

We found to our surprise that solutions of α -methyl-*d*-xyloside, β -methyl-*d*-xyloside, α -methyl-*d*-lyxoside and β -methyl-*d*-arabinoside, respectively, in dry pyridine, react with triphenylmethyl chloride. In each case a polarimetric change in the levo direction has been observed to occur at 20°, amounting to from 5 to 12 saccharimeter degrees in a 12% solution in a 100-mm. tube and completing its course in from 100 to 360 hours. When the rotations ceased to change, the solutions were poured in a thin stream into large volumes of water to dissolve out the unchanged portions of the glycosides, which were then recovered in a crystalline condition. The maximum yield which could be obtained in each case indicated that a substantial proportion of the original sample (from 45 to 80%) must have reacted with the triphenylmethyl chloride and thus have become insoluble in water. Although crystalline products have not yet been obtained, our efforts are being concentrated toward that end with the assistance of Dr. E. L. Jackson of this Laboratory.

It is evident from these results that one of the three assumptions adopted by most investigators in this field must be incorrect and it becomes apparent that (1) triphenylmethyl chloride is not specific in action toward primary hydroxyls, or (2) none of these methylpentosides has a 1,5-ring or (3) ring shifts can occur. Further experimental work will be required before a choice among these possibilities can be made.

Similar experiments with α -methyl-*d*-mannoside have led to the isolation of a crystalline condensation product which is being studied more fully by Dr. A. J. Watters of this Laboratory. One would of course expect from Helferich's studies with the triphenylmethyl sugar derivatives that α -methylmannoside would combine with the reagent.

DIVISION OF CHEMISTRY
NATIONAL INSTITUTE OF HEALTH
WASHINGTON, D. C.

R. C. HOCKETT
C. S. HUDSON

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