

apparent rate of hydrolysis corresponding to  $k = 0.00125 \approx 3 \times 10^{-5}$ . These values agree well with the constants determined directly for the new modification and we conclude that this substance contains both the previously known methylxylosides in combination. Because of the homogeneity of the crystals and their stability on recrystallization from methyl ethyl ketone, we regard the substance as a molecular compound of definite composition ( $7\alpha$ -methyl-*d*-xyloside- $2\beta$ -methyl-*d*-xyloside)<sup>2</sup> analogous to the double salts of inorganic chemistry and to the double compounds of certain sugars with salts. The new methylxyloside can be separated into its components by crystallization from ethyl acetate, though with difficulty.

These observations illustrate the extreme care which is necessary in the task of identifying new isomers in the sugar group and also suggest the possibility that some carbohydrates now considered to be pure chemical individuals may eventually be resolved into components.

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

R. C. HOCKETT  
C. S. HUDSON

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#### A NOVEL MODIFICATION OF LACTOSE<sup>1</sup>

*Sir:*

We have observed that when finely powdered milk sugar ( $\alpha$ -lactose monohydrate) is shaken at room temperature with ten times its weight of methyl alcohol containing from one to five per cent. of anhydrous hydrogen chloride, an interesting change takes place. The characteristic crystals of milk sugar gradually disappear while tiny needles soon begin to crystallize. Simultaneously the solid phase increases much in bulk and if shaking is interrupted it tends to cake. The reaction is heterogeneous and at no time is any large proportion of the sugar in solution.

When the change was complete, so that only the needle type of crystals was to be observed on examination with a hand-lens, the substance was filtered, washed free of acid with methyl alcohol and dried at  $50^\circ$ . It had an initial specific rotation in water, as obtained by extrapolation of its mutarotation curve, of  $[\alpha]_D^{20} + 67.9^\circ$ . Anhydrous  $\alpha$ -lactose has an initial rotation of  $+90^\circ$ . The new substance showed the accepted final specific rotation of anhydrous lactose ( $+55.2^\circ$ ) and its mutarotation coefficient is likewise the value accepted for lactose.

A mixture of the alpha and beta forms of lactose in the ratio of five to three would have an initial specific rotation of  $+67.5^\circ$ , while the equi-

<sup>2</sup> It seems possible to us that the accepted rotation of  $\alpha$ -methylxyloside may be somewhat low and that consequently the new methylxyloside may contain the  $\alpha$  and  $\beta$  isomers in the ratio of 3 to 1 rather than 7 to 2.

<sup>1</sup> Publication approved by the Surgeon-General, U. S. Public Health Service.

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  $\alpha$ -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 ( $5\alpha$ -lactose- $3\beta$ -lactose) analogous to the double salts of inorganic chemistry. It is noteworthy that the new compound is anhydrous whereas one of its components ( $\alpha$ -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.

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THE REACTION OF SEVERAL METHYLPENTOSIDES AND OF ALPHA-METHYLMANNOSE WITH TRIPHENYLMETHYL CHLORIDE<sup>1</sup>

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

<sup>1</sup> Publication approved by the Surgeon-General, U. S. Public Health Service.