

publish, very strong evidence that adsorption isothermals given by charcoal-aqueous solution systems may also show discontinuous structure.

The more homogeneous nature of the surfaces of finely divided metals and of silica gel as compared with charcoal, together with the complications due to the gradual elimination of gas from the surface of the latter during adsorption, is presumably responsible for the more regular and uniform results obtained with the former adsorbents.

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#### A NOVEL MODIFICATION OF METHYL-*D*-XYLOSIDE<sup>1</sup>

*Sir:*

During a recent preparation of the methylglycosides of *D*-xylose, a novel modification was isolated. Having condensed thirty-five grams of the sugar with methyl alcohol by refluxing for two hours under the usual conditions [Hudson, *THIS JOURNAL*, **47**, 265-268 (1925)], and having removed a 6-g. crop of the  $\beta$ -methyl-*D*-xyloside, we concentrated the filtrate to a thick sirup which was then dissolved in four volumes of amyl alcohol. Overnight 20 g. of crystals of a new substance separated. After one recrystallization from methyl ethyl ketone, its  $[\alpha]_D^{21}$  value was  $+104.4^\circ$  in water (concn. 2%) and this rotation was not changed by two subsequent recrystallizations. The m. p. is  $89-91^\circ$ . The crystals are exceptionally clear and well-formed prisms with pyramid faces at one end, quite different from the crystals of the well-known  $\beta$ -methyl-*D*-xyloside ( $[\alpha]_D^{20} -65.5^\circ$ ) or  $\alpha$ -methyl-*D*-xyloside ( $[\alpha]_D^{20} + 154.5^\circ$ ).

The properties so far described might well lead one to the conclusion that this substance is probably a new chemical isomer of the known methylxylosides, but this view proved erroneous on further test. Acetylation of the substance with acetic anhydride and pyridine in the cold gave a product which was resolved into the tetra-acetates of the known  $\alpha$ - and  $\beta$ -methylxylosides, the former predominating. Moreover, a determination of the rate of hydrolysis of the new substance by 0.05 *N* hydrochloric acid (approximately 1 g. in 25 cc.) gave  $k = 0.00121 \pm 2 \times 10^{-5}$  at  $99^\circ$  (min. and dec. logs). Redeterminations of the rates for the ordinary alpha and beta forms under identical conditions gave  $k = 0.00151 \pm 2 \times 10^{-5}$  and  $k = 0.00286 \pm 4 \times 10^{-5}$ , respectively. Since the two latter substances have opposite signs of rotation and the rotation of xylose lies between these values, a mixture of them would have a rate of hydrolysis apparently smaller, when determined polarimetrically, than that of either component. An actual mixture of the ordinary alpha and beta forms in the ratio of seven to two, gives a specific rotation of  $+105.4^\circ$  and shows an

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

apparent rate of hydrolysis corresponding to  $k = 0.00125 = 3 \times 10^{-5}$ . 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.

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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.