

H<sub>2</sub>O, 4.35; Br, 38.63. The alkaloid regenerated from a portion of the salt showed  $n_D^{25}$  1.5259 and yielded a picrate, m. p. 206°.

The methyl iodide was readily prepared by mixing the original fraction with excess of methyl iodide and allowing to stand in the cold. After a half-hour the whole solidified to a mass of white crystals. Sparteine usually shows no such behavior. A mixture of sparteine and methyl iodide remains liquid for weeks, unless warmed, but eventually deposits crystals. In our preparation the second alkaloid appears to catalyze the reaction.

The methyl iodide so prepared was recrystallized several times from alcohol. Dried in a desiccator the purest crop melted at 239–240°. Found: N, 7.51; I, 33.72, 33.63. C<sub>15</sub>H<sub>26</sub>N<sub>2</sub>CH<sub>3</sub>I requires N, 7.45; I, 33.75. Moureu and Valeur<sup>3</sup> give the melting point "about 240°." Further crops of crystals obtained in the above preparation gave 6.91 and 7.19% N, indicating admixture with the second alkaloid.

These data establish the presence of sparteine in *L. barbiger*. Two or three other alkaloids are present but are not sufficiently characterized at present for identification. No evidence indicating the presence of lupinine has as yet been obtained.

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## OXIDATION OF THE ALPHA AND BETA FORMS OF THE SUGARS

*Sir:*

In the course of studies on the oxidation of the sugars with bromine water experimental conditions have been developed by means of which it is possible to follow the oxidation of a single form of a sugar. The crystalline sugar is added to a suspension of barium carbonate in bromine water saturated with carbon dioxide, and the reaction is allowed to continue while stirring the mixture and holding the temperature constant. At intervals samples of the solution are taken and the amount of oxidation is determined by analysis. Through the buffer action of the barium carbonate and carbon dioxide the solution is maintained in a slightly acid condition (*P<sub>H</sub>* 6). As a result the mutarotation of the sugar is relatively slow and the oxidation is relatively rapid. Equilibrium between the various forms of the sugar is not established prior to oxidation and consequently the reaction rates depend largely on the particular forms of the sugars used. There are marked differences in the rates obtained with various sugars and in the rates obtained with different forms of a given sugar.

Thus the oxidation of a sample of beta lactose is about 95% complete in three minutes, while under like conditions the reaction of alpha lactose is

only about 50% complete. This marked difference in the reaction rates affords a new method for ascertaining the approximate amounts of the alpha and beta isomers in solution. Such data should be of value in the study of the mechanism of the oxidation reactions and also for determining whether a given crystalline form of a sugar consists of a single isomer or whether it is a mixture of the alpha and beta forms. The oxidation of the sugar containing a single isomer progresses uniformly, while the oxidation of a mixture of the alpha and beta forms progresses rapidly until one form, usually the beta, is used up, and then more slowly as the oxidation of the other form is continued. Inasmuch as homogeneous crystalline compounds containing the alpha and beta forms of a single sugar have been discovered recently by Hockett and Hudson [THIS JOURNAL, 53, 4455 (1931)] it is necessary to determine whether or not the known crystalline sugars are substances of this type. This problem may be attacked by determining the rates at which they are oxidized by bromine water.

Since a large number of the sugars are being studied under strictly comparable conditions, the results may be used also in correlating the rate of oxidation with the stereomeric structure of the sugars.

The writer is being assisted in this work by W. W. Pigman.

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### THE NATURE OF ACTIVATED ADSORPTION

*Sir:*

In a recently published article [THIS JOURNAL, 54, 602 (1932)] Taylor and Sickman presented data on the low- and high-temperature adsorption of hydrogen by zinc oxide, from which some information on the two types of adsorption can be secured by statistical methods. From their Fig. 3 on page 612, it is found that equal amounts are adsorbed at 125°K. and 580°K. and 400 mm. pressure, while the heats of adsorption are 1100 and 21,000 cal., respectively. Writing statistical expressions for exp.  $(-f/kt)$  ( $f$ : free energy at constant pressure in  $\mu$  space), setting free energy of gas equal to that of adsorbate at each temperature and dividing the square of the expression for 125°K. by that for 580°K. the following equation results

$$e^{(2\Delta a_1/KT_1) - (\Delta a_1/KT_2)} = \frac{T_1^3 h^3}{T_2^{7/2} P^{1/2} \pi^{3/2} m^{1/2} k^{1/2} J} \frac{\Omega_{v_2}^3 N^2}{\Omega_{v_1}^2 S^2}$$

The assumptions underlying this expression are that in low temperature adsorption hydrogen molecules have freedom of motion over the surface (two dimensional ideal gas) and that their rotation is unchanged by