

Summary.—The results of standard analytical determinations on coconut shells agree well with those recorded by Fleck and colleagues except for the higher value found for cellulose.

It is proposed to investigate further the nature of the association of xylan and cellulose in coconut shells.

COCONUT RESEARCH SCHEME OF CEYLON
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The Preparation of Diacetone Sugars

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The use of concentrated sulfuric acid as catalyst and dehydrant for acetonizations of carbohydrates has found general acceptance. Several disadvantages of this method are well known; while high (4–5%) concentration of sulfuric acid¹ brings about rapid condensation of acetone, less catalyst leaves considerable quantities of sugar undissolved and favors formation of monoacetone derivatives instead of diacetone sugars. Furthermore, the neutralization of sulfuric acid with anhydrous solid carbonate is time consuming. Other catalysts, zinc chloride,² copper sulfate³ or phosphoric anhydride,⁴ among others, have been suggested; much lower yields however have been obtained as compared to the sulfuric acid method.

In studying the acetonization of *l*-sorbitose we have obtained by using zinc chloride in combination with a mixture of ortho- and metaphosphoric acids very satisfactory results and have developed the method given below which seems to be generally applicable to the preparation of diacetone sugars and superior to older methods in yield, speed and simplicity. The application of this process to the commercial preparation of diacetonesorbitose (ascorbic acid synthesis) has been considered.

The following yields of diacetone sugars were obtained: *l*-sorbitose 85%, *d*-arabinose 90%, *d*-galactose 78%, *d*-mannose 92% and *d*-glucose 75%. In all cases the products isolated were practically pure as checked by analysis and rotation. The yields are based on crystallized or distilled products. Due possibly to the acidic acetonization medium the same diacetone products are obtained which are formed by the use of sulfuric acid as catalyst.

(1) Bell, *J. Chem. Soc.*, 1874 (1935); Ohle, *Ber.*, **71**, 562 (1938); Reichstein and Grüssner, *Helv. Chim. Acta*, **17**, 311 (1934).

(2) Fisher, *Ber.*, **60**, 485 (1927).

(3) Ohle and Koller, *ibid.*, **57**, 1566 (1924).

(4) Smith and Lindberg, *ibid.*, **64**, 505 (1931).

Procedure.—One hundred grams of the very finely powdered sugar is suspended in two liters of dry acetone to which is added in rapid succession 120 g. of fused zinc chloride (sticks) and a homogeneous mixture of 20 g. of phosphorus pentoxide and 40 g. of phosphoric acid (85%). The whole is shaken mechanically until solution is complete, which lasts about two hours. Then, in order to bring the reaction to completion the solution is allowed to stand overnight at room temperature. The mixture is then made alkaline by adding an aqueous suspension of sodium carbonate, the precipitate of zinc carbonate is filtered, washed with acetone, and the combined filtrate and washings are distilled *in vacuo* until most of the acetone is removed.

The resulting aqueous residue is extracted with three 150-cc. portions of benzene or ether, which, after removal of the solvent *in vacuo*, leaves the diacetone product in practically pure form.

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Thermal Data on Organic Compounds. XVIII. The Heat Capacity and Entropy of *t*-Butylethylene

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The combination of constancy of freezing point and constancy of boiling point serves as an excellent criterion of the purity of a chemical compound. This criterion has been used frequently by Kistiakowsky¹ and his collaborators in their extremely accurate determinations of the heats of organic reactions. Recently in the case of *t*-butylethylene,^{1b} however, they failed to find a constant freezing point by their methods, although otherwise they had every reason to believe in the extreme purity of the material; and accordingly they invited us to study the fusion behavior of a sample of their material by our calorimetric method.

We have now measured the heat capacities of this olefin between 80 and 298°K. From the temperature change during the fusion of the crys-

(1) (a) Kistiakowsky, Ruhoff, Smith and Vaughan, *THIS JOURNAL*, **58**, 137, 146 (1936); (b) Dolliver, Gresham, Kistiakowsky and Vaughan, *ibid.*, **59**, 831 (1937); (c) Dolliver, Gresham, Kistiakowsky, Smith and Vaughan, *ibid.*, **60**, 440 (1938).