NOTES

Composition of Coconut Shells

BY REGINALD CHILD AND S. RAMANATHAN

L. C. Fleck and co-workers recently have reported the results of standard analytical determinations carried out on coconut shells.[1] We have had in hand since 1935 a study of the development of the coconut fruit involving the analysis of husks, shells and endosperm of fruits at various stages of maturity.[2] Since this study will not be complete for some time, we are placing on record the results of our determinations on mature coconut shells, which are in general agreement with those of L. C. Fleck and his colleagues, except for the somewhat higher figure for cellulose determined by a different method.

The only figures on record before those referred to above seem to be those of A. L. Winton,[3] who in 1901 applied the usual methods of Food and Drug analysis to the detection of powdered coconut shells in spices, which adulteration he stated to be a very common practice in the United States. His figures are not otherwise of particular interest. A figure of 56.19% was recorded for "crude fibre," but A. G. Norman[4] has emphasized the unreliability of this determination, since the "crude fibre" fraction obtained bears no definite relationship to the structural constituents of the original material.

J. B. Boswell[5] has investigated the composition of certain nut-shells, and has reported that of the seed coat of Brazil nuts (*Bertholletia excelsa*). In this material lignin appears to be present in larger and cellulose in lesser proportion than in coconut shells. It is of interest, however, to note that the cellulose in Brazil nut shells was found to be associated largely with xylan, and we have been able by suitable hydrolysis to isolate crude xylose in considerable amount from coconut shells, and from the "cellulose" fraction thereof. R. W. Tromp de Haas and B. Tollens[6] obtained "a satisfactory yield" of crystalline xylose by hydrolysis of coconut shells with 4% sulfuric acid, and stated that this appeared to be the only product of the hydrolysis. The residue gave dextrose on hydrolysis with stronger acid.

We propose to investigate further the xylan fraction of coconut shells and the nature of its association with cellulose.

Experimental

The shells were ground to pass a 100-mesh sieve and the determinations tabulated below were carried out. Pentosans were estimated by the method of A. W. Schorger,[7] cellulose by the method of A. G. Norman and S. H. Jenkins[8] and lignin by a modification of the method of H. Schwalbe,[9] whereby 2 g. of material was treated with a mixture of 10 cc. of 18% hydrochloric acid and 50 cc. of 72% sulfuric acid, the mixture kept cool for two hours and then boiled for thirty minutes after dilution with 300 cc. of water.

TABLE I

COMPOSITION OF COCONUT SHELLS

	On air-dried material, %	On dry weight (at 105°) %	Figures of Fleck, *et al.*,[a] based on weight of oven-dry (105°) shells, %
Moisture	8.78	...	6.07
Cold water soluble	0.19	0.20	1.43
Hot water soluble	3.25	3.57	2.67
Alcohol soluble	2.29	2.51	...
Benzene soluble	0.25	0.27	0.19 (Ether soluble)
1% alkali soluble	17.15	18.80	20.53
Ash	0.56	0.61	0.23
Lignin	33.30	36.51	33.30
Cellulose	48.40	53.06	44.98
Total pentosans	26.70	29.27	30.28
Pentosans in cellulose	...	20.54	17.67
Pentosans in cellulose (on basis of cellulose)	...	38.69	39.30

[a] Fleck and others also record % methoxyl. "Hydrolysis no." (loss in cellulose due to 15% H_2SO_4 hydrolysis), % cellulose stable to 15% H_2SO_4 hydrolysis, acetic acid by hydrolysis, and loss in weight of shells due to 2.5% H_2SO_4 hydrolysis from acetic acid determination.

The hot water extract contained 0.160% K_2O calculated as a percentage of the original shells. Potash is the major constituent of the ash.

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(1) L. C. Fleck, W. G. van Beckum, and Geo. J. Ritter, THIS JOURNAL, **59**, 2279 (1937).

(2) See "Report and Accounts of the Coconut Research Scheme for 1936" (Ceylon Government Sessional Paper X, 1937, page 5).

(3) A. L. Winton, *Am. J. Pharm.*, **73**, 552 (1901).

(4) A. G. Norman, *J. Agr. Sci.*, **25**, 529 (1935).

(5) J. B. Boswell. *Biochem. J.*, **30**, 971 (1936).

(6) R. W. Tromp de Haas and B. Tollens, *Ann.*, **286**, 303 (1895).

(7) As adopted by the Cellulose Division of the American Chemical Society; see *Ind. Eng. Chem.*, **15**, 748 (1923).

(8) A. G. Norman and S. H. Jenkins, *Biochem. J.*, **27**, 818 (1933).

(9) H. Schwalbe, *Papier-Fabr.*, **23**, 174 (1925).

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
LUNUWILA, CEYLON
RECEIVED JANUARY 4, 1938

The Preparation of Diacetone Sugars

BY H. VAN GRUNENBERG, C. BREDT AND WERNER FREUDENBERG

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 acid[1] 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 sulfate[3] 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*-sorbose 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 diacetonesorbose (ascorbic acid synthesis) has been considered.

The following yields of diacetone sugars were obtained: *l*-sorbose 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.

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.

Acknowledgment is made to the Works Progress Administration of the City of New York for assistance rendered under Project 465-97-3-120.

DEPARTMENT OF CHEMISTRY
FORDHAM UNIVERSITY
NEW YORK, N. Y.
RECEIVED MAY 5, 1938

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[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**, 503 (1931).

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

BY WM. D. KENNEDY, C. HOWARD SHOMATE AND GEORGE S. PARKS

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 Kistiakowsky[1] 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-

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[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).