temperature of the work it decomposes only very slowly. However, I have found the mono-sodium or potassium salt of this acid just as efficient and much more stable.

Within the last few months a French patent has been issued to F. Lanza for the separation of solid and liquid fatty acids. Stearosulphuric acid, called in the specifications sulpho-oleic acid, is the reagent used in his process, which is very similar to the one described in this paper.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF FOODS. SENT BY H. W. WILEY.]

STUDY OF APPLE MARC.[1]

BY W. D. BIGELOW AND H. C. GORE.

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GENERAL DISCUSSION.

APPLE marc, or the insoluble matter of the flesh of the apple, is composed mainly of parenchymous tissue, containing besides this only the somewhat lignified vascular bundles in small quantity, and a little albuminoid matter. For this reason apple marc affords a convenient material for study of parenchymous tissue, such tissue being, of course, much easier of study in the nearly pure form in which it occurs in the apple, than in the grains and grasses in which it occurs together with more complex tissue. Parenchymatous tissue has been very little worked with *per se*, notwithstanding the fact that it is the first tissue formed in plant growth, and therefore of extreme importance physiologically.

In our work with apple marc[2] we found that about 40 per cent. of the product was rendered soluble by boiling with water. This method of treatment, which has been used by Weisburg[3] and Wohl and Van Niessen[4] in their work with beet marc, is well adapted to the study of such products, because after the treatment not only the undissolved tissues, but the dissolved portions, can be readily recovered nearly unchanged and further examined. Acid or alkali treatment of course alters the composition of the dissolved material to a very much greater extent than water.

[1] Read before the Agricultural Section of the American Chemica Society, June 23, 1905.

[2] U. S. Dept. Agr., Bur. Chem., Bull. 94, p. 87.

[3] Neue Z. Rübenz, 21, 325 (1888).

[4] Z. Ver. Zucker-Ind. 39, 924 (1889).

The present work was undertaken in order to determine whether the portion of the marc made soluble by boiling with water, consists of one carbohydrate complex or of several. Two methods were proposed in our early work,[1] *viz.*, fractional extraction with boiling water whereby the portion first removed can be compared with those removed later; and fractional precipitation of the soluble product with alcohol. The first-named method has been employed in the work here recorded. The criteria used have been the yields of pentosans, of galactans, and the yield of reducing sugars calculated to starch when treated with hydrochloric acid as in the method for starch. The results show that one complex, a galacto-araban, is being gradually made soluble by the action of boiling water. This is shown in Table I. Since the sum of the yield of pentosans and the yield of galactans is considerably greater than that of reducing sugars calculated to starch, it is evident that the three-hour treatment with hydrochloric acid, as prescribed by the method for starch, does not give the maximum of reducing sugars.

TABLE I.—ANALYSES OF HOT WATER EXTRACTS OF APPLE MARC.

	Time of boiling.	Original dry marc. Per cent.	Protein (N × 6.25). Per cent.	Pentosans. Per cent.	Galactans. Per cent.	Hydrolyzable carbohydrates calculated as starch. Per cent.	Ratio of galactans to pentosans.
First extract.....	½ hr.	17.32	3.16	38.8	31.6	53.4	0.81
Second extract.....	1 "	13.23	3.86	42.1	35.4	55.0	0.84
Third extract.....	1 "	5.53	5.26	36.1	29.9	48.8	0.83
Fourth extract.....	1 "	3.75	6.38	32.3	30.4	44.6	0.94

The must of apples, when treated with several volumes of alcohol, invariably gives a gummy precipitate. Preliminary experiments indicated that it would be worth while to collect a considerable quantity of such precipitate and determined therein the relation between the pentosan, galactan, and hydrolyzable carbohydrate contents for comparison with those found for the soluble portions of apple marc. The results are shown in Table II. It will be noted that the ratio of galactans to pentosans is much higher in this product than in the hot water extract of apple

[1] Loc. cit.

marc. If the alcohol precipitate of the must be supposed to be formed from some change in the cell wall whereby the less resistant portions of the tissue are partially resolved, it would seem that during the change a greater portion of the galactans is converted into compounds precipitable with alcohol than of the pentosans.

TABLE II.—ANALYSIS OF ALCOHOL PRECIPITATE OF APPLE MUST.

Protein ($N \times 6.25$). Per cent.	Pentosans. Per cent.	Galactans. Per cent.	Hydrolyzable carbohydrates calculated as starch. Per cent.	Ratio of galactans to pentosans.
23.50	13.10	23.5	23.4	1.79

At this time in our work the high pentosan content relative to the total solids of "second pressing" ciders[1] was called to our attention by Messrs. Tolman and LeClerc. These were found to yield considerable quantities of precipitate when treated with alcohol. This precipitate contained from 39 to 65 per cent. of the pentosan content in case of the three samples of "second pressing" cider which we examined. One of these samples was converted into vinegar by one of the rapid process methods and examined at intervals during acetification. The alcohol precipitate remained practically unchanged in quantity and character during the acetification of the cider. These results are shown in Table III. It will be noted from Table IV that the ratio of galactans to pentosans is also higher in this product than in our preparations of hot water extracts of apple marc. In fermentation in heaps it is probably the wild yeasts which occur on the apples which attack the cell walls, breaking them down in such manner that a further yield of juice is obtained on a second pressing. The results are interesting in showing that possibly the action of yeasts on the cell walls of the apple marc in the pomace is similar to that of the life forces on the wall, an alcohol precipitate in which the galactan to pentosan ratio is high, being found in both cases.

[1] Prepared from apple pomace which had been allowed to ferment in large heaps for considerable periods of time. The pomace is again pressed, and a cider is obtained which is sometimes used for vinegar stock.

TABLE III.—PENTOSANS IN "SECOND PRESSING" CIDERS.

Serial number.	Date of analysis.	Pentosans. Grams per 100 cc.	Alcohol precipitate. Grams per 100 cc.	Pentosans in alcohol precipitate. Per cent. of precipitate.	Pentosans in alcohol precipitate. Per cent. of cider.	Precipitable pentosans. Per cent. of pentosans.
11533	April 22, '05	0.80	1.50	31.1	0.466	58.1
11533	May 1, '05	0.66	1.43	29.9	0.426	64.9
11533	" 17, '05	0.79	1.49	33.2	0.495	62.7

TABLE IV.—ANALYSIS OF ALCOHOL PRECIPITATE OF "SECOND PRESSING" CIDER.

Date of analysis.	Pentosans. Per cent.	Galactans. Per cent.	Hydrolyzable carbohydrates, calculated as starch. Per cent.	Ratio of galactans to pentosans.
May 17, '05	33.2	46.5	55.0	1.40

Aside from the study of the hot water extracts of apple marc, and the relations of other products of the apple to them, *viz.*, the alcohol precipitate of the must, and the alcohol precipitate of "second pressing" ciders, the effect of the treatment with boiling water on the residual cellular material is of interest in showing to what extent the hot water treatment will affect the amount and character of the residues which are obtained by applying the method for crude fiber and the method for cellulose[1] after the treatment with hot water.

The percentages of crude fiber and of cellulose were determined in the marcs and in the insoluble residues left after extraction with hot water, the results being calculated in terms of the original marc. These results are given in Table V. It will be seen that the results obtained with the untreated marc are higher than those obtained with the residue from the hot water extraction. The products separated as crude fiber and cellulose from the original marc were found to be considerably richer in pentosans than those separated from the residue from the hot water extraction, a purer fiber and a purer cellulose being obtained. It is therefore evident that the methods employed for the determination of crude fiber and of cellulose do not separate cleanly the resistant from the non-resistant constituents of parenchymous tissue.

[1] "Cellulose," 2nd Ed., 1905, p. 95.

TABLE V.—CRUDE FIBER AND CELLULOSE IN APPLE MARC BEFORE AND AFTER HOT WATER TREATMENT. BASIS OF ORIGINAL DRY MARC.

	Crude fiber.	Pentosans in crude fiber.	Cellulose.	Pentosans in cellulose.
Untreated marc.....	30.90	2.92	40.19	5.51
Treated marc[1].....	27.34	2.21	34.82	4.20

METHODS EMPLOYED.

The methods of the Association of Official Agricultural Chemists were used for the analytical work—save that for the pentosan determinations the latest modifications of the method and the factors of Kröber[2] were used.

We were unsuccessful in applying the method for galactan to apple marc. No separation of mucic acid crystals was obtained, although the analysis of the hot water extracts of apple marc showed nearly 13 per cent. of galactan calculated on the marc. See Table VI. We did not, however, try the procedure of Wohl and Van Niessen.[3]

The material required for the work has been (*a*) hot water extracts from apple marc; (*b*) alcohol precipitate of fresh apple must; and (*c*) alcohol precipitate of "second pressing" ciders.

The methods of preparation of the above products were as follows:

(*a*) *Preparation of Hot Water Extracts from Apple Marc.*—A large sample of Rhode Island Greening apples was employed. These apples by March 30, 1905, the date at which the work was begun, were about at the end of their life history. They were free from starch, and many of the larger individuals were mealy. Some were browned about the core, indicating that physiological death was setting in. Such fruits were rejected. The remaining apples were cored and pared, all decayed and bruised places removed, and the sample ground in a meat grinder. The ground pulp was received in cloth bags from which the juice was pressed out. The marc remaining in the bag was thoroughly washed until free from sugar in the cloth bags by repeatedly adding water and pressing. It was then scraped from the bags, spread out on a large glass plate and dried over night at room temperature in a current of air from an electric fan. It was then ground

[1] 39.83 per cent. of original marc removed by hot water treatment.

[2] U. S. Dept. of Agr., Bur. of Chem., Bull. 73, 173.

[3] Z. Ver. d. Zucker-Ind. 39, 932 (1889); abst. in U. S. Dept. Agr., Bur. of Chem., Bull. 94, p. 74.

and passed through a 1 mm. sieve. The analysis of the product is given in Table VI.

TABLE VI.—ANALYSIS OF APPLE MARC. WATER-FREE BASIS.

	Per cent.
Pentosans	24.51
Extracted pentosans[1]	15.50
Extracted galactans[1]	12.96
Cellulose[2]	40.19
Crude fiber[3]	30.90
Reducing sugar	1.67
Protein	3.43
Ether extract	0.74
Ash	0.95

After preliminary trials which indicated the quantities of marc and water which could be successfully used, 100 grams of marc prepared as above were added to fifty times their weight of boiling water and the whole boiled for one-half hour under return condensers. Three flasks were used, two holding one and one-half liters each, and the third, two liters. Thirty grams of marc were accordingly added to each of the first two flasks, and 40 grams to the last.

At the end of the half hour's boiling, the flasks and their contents were rapidly cooled, the contents poured into clean cloth bags, and the bags squeezed to remove as much of the liquid as possible. The residues in the bags were washed by repeatedly soaking with water and pressing out. The filtrates and washings were combined and evaporated on the steam-bath, dried at 100°, weighed, ground, passed through bolting-cloth of about 0.5 mm. mesh, and again dried at 100°. The residues in the bags were then roughly weighed, the flasks charged with the original quantity of water less that held in the marc, the water heated to boiling, and the residue added. The time of the second, third and fourth boiling was one hour each. The extracts were treated as in the case of the product from the first boiling. The analyses of the hot water extracts are given in Table I.

(*b*) *Preparation of Alcohol Precipitate from Fresh Apple Must.*—The fresh juice from the above sample of apple pulp was whirled in a centrifugal machine which removed the small quantity of

[1] Sum of constituent in hot water extracts.

[2] Contains 5.51 per cent. of pentosans.

[3] Contains 2.92 per cent. of pentosans.

suspended materials, chiefly albuminous in character, which began to separate from the juice on standing in the air. On whirling, these were thrown down as a brown slimy sediment. To the supernatant liquors which were still turbid, but in which no more sediment would collect on whirling, was added with stirring an equal volume of 95 per cent. alcohol and the whole well shaken. A flocculent precipitate resulted equal to 0.3 per cent. of the original juice. The precipitate was settled in the centrifugal machine, and washed by repeated stirring with successive portions of alcohol and settling until no more yellow color and only traces of sugar were removed. The precipitate was then washed on to a filter with alcohol, allowed to drain (keeping the funnel covered with a watch-glass to prevent drying at the edges and consequent sticking to the filter-paper), separated from the filter-paper (it separates easily if kept moist with alcohol), and dried and weighed in a tared dish. It was then ground, passed through bolting-cloth, and dried at 100° C. The analysis of this product is given in Table II.

(*c*) *Preparation of Alcohol Precipitate from Second Pressing Ciders.*—The "second pressing" cider employed was obtained through Mr. Tolman of this laboratory. It had been made from apple pomace which had been fermented in heaps for fourteen days. To the clear cider four volumes of 95 per cent. alcohol were added, and the mixture well shaken. A finely divided white precipitate formed equal to 1.5 per cent. of the cider. This was separated from the mother-liquors by means of the centrifugal machine and washed by repeated stirring with alcohol and sedimentation. It was finally thrown on a filter, allowed to drain, transferred to a tared dish, dried and weighed. It was then passed through bolting-cloth, and dried at 100°.

CHARACTERISTICS OF PRODUCTS.

The hot water extracts from apple marc dry down as nearly transparent leaflets. The first extract was of a tough character but this property disappeared with successive extractions, the last extract being easily pulverized. They possess a slight acid taste, and dissolve in water to form viscid cloudy liquids. Alcohol precipitates the product from its solution in water as a jelly.

The alcohol precipitate from apple must appears as an opaque yellow-brown jelly-like mass. It dries down to a hard, easily pulverized dark brown product.

The alcohol precipitate of "second pressing" cider dries down to hard readily pulverized white masses. It is easily soluble in water, forming opalescent solutions very difficult to clarify. It possesses a marked acid taste.

SUMMARY.

The following points are determined.

(1) The hot water extract amounting to 40 per cent. of apple marc consists of one carbohydrate complex, a galacto-araban.

(2) The carbohydrate complexes in case of the alcohol precipitate of apple must, and in case of the alcohol precipitate of second pressing ciders, are both higher in galactan, relative to the pentosan content, than the hot water extracts of apple marc.

(3) The treatment with boiling water lessens the yield of crude fiber and cellulose, and at the same time gives a purer fiber and a purer cellulose.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 117.]

ON 5-AMINO-4-KETODIHYDROQUINAZOLINE AND 5-AMINO-2-METHYL-4-KETODIHYDROQUINAZOLINE.[1]

BY MARSTON TAYLOR BOGERT AND VICTOR JOHN CHAMBERS.

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THE authors have prepared 5-amino-4-ketodihydroquinazoline and 5-amino-2-methyl-4-ketodihydroquinazoline by reducing the corresponding nitro compounds with stannous chloride and hydrochloric acid. The 5-amino-4-ketodihydroquinazoline is much more easily obtained than its 2-methyl derivative, since it is soluble in hot water and can thus be readily separated from the tin, hence most of the reactions carried out were with this quinazoline. Its hydrochloride, chlorplatinate, bibrom, acetyl, benzoyl and phenyluramino derivatives, were prepared and studied, as well as its reactions with nitrous acid, chloroform and potassium hydroxide, and with benzaldehyde. The phenyluramino derivative breaks up at high temperatures into carbanilide and what appears to be the diquinazolylurea. The 5-amino-2-methyl-4-ketodihydroquinazoline was more troublesome to obtain, and only its hydrochloride and chlorplatinate were prepared.

[1] Read at the General Meeting of the American Chemical Society, June 22, 1905.