4. When mixtures of the sulfamic acids, which are formed by the action of sodium bisulfite on 3-nitro-4-hydroxyphenylarsonic acid, and 3-amino-4-hydroxyphenylarsonic acid are reduced with sodium hydrosulfite, the rate of formation of insoluble reduction products is much less than when the amino acid is reduced to arsphenamine base in the usual way, and the products separate from the solution in a different condition from that of arsphenamine base. The behavior of these bases in methyl alcoholic hydrochloric acid is also quite different from that of arsphenamine base. These products are more toxic and contain more sulfur than arsphenamine prepared from the amino acid.

5. When 3-nitro-4-hydroxyphenylarsonic acid is reduced with sodium hydrosulfite to 3-amino-4-hydroxyphenylarsonic acid, two by-products are formed which may be isolated and separated by means of their barium salts. Reduction of a mixture of one of these by-products and the pure amino acid yields a product which is much more toxic and contains more sulfur than arsphenamine prepared from the amino acid.

6. Barium bromide is recommended for the preparation of barium salts when alcoholic solvents are employed. The preparation of this bromide is described in detail.

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THE PREPARATION OF RAFFINOSE FROM COTTONSEED MEAL

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The occurrence and methods for the preparation of raffinose have been recently reviewed[1] and need no extended comment here. It has been shown by Hudson and Harding[2] that cottonseed meal is the cheapest and most convenient source, and the method of preparation which they worked out has made this rare sugar accessible, their yield of pure raffinose being about 2.5%. While their method gives good results with an experienced operator, it has been our experience that the rapid manipulations in the aqueous extraction of the meal and the intermediate formation and decomposition of the barium raffinosate, although a step of safety tending to make the method dependable, can cause difficulty. Recognizing a need for improvement, Harding[1] has suggested a new procedure consisting in extraction of the sugar with dil. aluminum sulfate, concentration to a small volume, precipitation of the aluminum sulfate with alcohol, clarification with basic lead acetate and finally separation of the raffi-

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[1] Harding, *Sugar*, **25**, 308 (1923).

[2] Hudson and Harding, THIS JOURNAL, **36**, 2110 (1914).

nose without recourse to the formation of the raffinosate. Clark[3] utilizes an aqueous extraction by percolation.[4] The rest of the process is very similar to that of Hudson and Harding. In 1844, Ritthausen[5] extracted raffinose from cottonseed meal with 80% ethyl alcohol. He then removed the alcohol, extracted with ether, dissolved in water, clarified with basic lead acetate and finally crystallized the sugar from alcoholic solution. The method was rejected by Hudson and Harding as expensive and inconvenient. Ritthausen merely mixed the meal with alcohol and then drew off the liquid. However, since the meal does not become slimy when treated with alcohol as it does with water, it is possible to continue the extraction for a long period and, by adopting a device of the continuous-extraction type, to minimize the quantity of solvent and obtain more complete removal of the sugar. An attempt to use 80% ethyl alcohol in this connection would lead to distillation of a fraction with a higher percentage of alcohol and one in which the raffinose becomes very much less soluble. Fortunately, strong methyl alcohol, in contrast to strong ethyl alcohol, has a high solvent action for raffinose[6] and can be used without difficulty. Thus a somewhat simpler method for the preparation of the sugar seems possible.

Procedure

A stopper is inserted in the tubulature of a 6-liter bottle and 2 kg. of cottonseed meal is introduced. This is followed by sufficient cotton to form a layer and soft plug at the outlet of the inverted bottle. When the meal is acid a small amount of powdered calcium carbonate may be mixed with it. The assembled apparatus differs somewhat from that previously described by Sando.[7] The bottle is inverted to secure better extraction by central drainage. The vapor from the flask is discharged into a 500mm. Liebig condenser which empties into the bottle through a 2-hole stopper in the upper tubulature. Through this stopper a Hopkins condenser is also connected to the bottle to act as a safety tube and prevent loss of solvent during active boiling. Four liters of methyl alcohol and a few small pieces of pumice are placed in the 5-liter flask and the flask is heated on a steam cone. At the beginning of the extraction it is best to pull the siphon tube forward to a horizontal position until the meal has been thoroughly wet, after which it may be raised to the vertical. The heat should be adjusted so that the rates of distillation and percolation are equal and the extraction allowed to continue two or three days. When the heat is shut off, the siphon tube is bent down and as much of the alcohol as possible is allowed to drain from the meal. The exhausted meal can be removed from the bottle most easily by adding water and stirring to form a thin mush, then rinsing out. The alcohol in the flask is removed under diminished pressure until the volume is reduced to about 600 cc. The residual solution is poured into a 3-liter florence flask with a large neck, and the original flask is rinsed with hot water. Sufficient hot water is now

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[3] Clark, *Bur. Standards Sci. Papers*, 432, **1922**.

[4] A very coarse meal is necessary for this procedure. With the type of meal which we have had, percolation was never successful.

[5] Ritthausen, *J. prakt. Chem.*, [II] **29**, 351 (1844).

[6] Lippmann, "Chemie der Zuckerarten," Braunschweig, **1904**, vol. 2, p. 1634.

[7] Sando, *Ind. Eng. Chem.*, **16**, 1125 (1924).

added to the florence flask to bring the liquid almost to the neck and to float the oil to the top of the solution. A 50–75cc. portion of petroleum ether is added and the flask rotated at a slight angle to the vertical, then allowed to stand for a few minutes. The petroleum ether layer is blown off in the manner employed in the Werner-Schmidt method[8] for the determination of fat in milk. The process is repeated until the major portion of the oil is removed. A large separatory funnel may be used to better advantage if care is taken to avoid emulsions. The mixture should never be shaken. The usual precipitation with basic lead acetate[9] follows, about 1 cc. of the reagent being used for every 20 g. of the meal. There appears to be no definite cessation in the precipitation of the impurities, and in general when the mass commences to settle and give a clear supernatant layer near the surface the reaction can be assumed to be complete. The precipitate is filtered on an 8cm. Büchner funnel through a thin layer of Norite on a hardened filter paper. Use of larger quantities of the lead salt usually gives a better looking product but decreases the yield. According to Svoboda,[10] raffinose in 5-20% solution is almost quantitatively precipitated by basic lead acetate if allowed to stand eight hours or longer. Even under the conditions of the clarification described above in a more dilute solution an appreciable quantity of raffinose is precipitated, part of which can be recovered by washing. This can be done most effectively by removing from the filter, macerating in water and again filtering. The excess of lead is precipitated with hydrogen sulfide, Norite is added and the solution filtered through a thin layer of Norite as before. It is then concentrated under diminished pressure to a sirup of about 70–80% of solids, transferred to a beaker and crystallization is carried out as directed by Hudson and Harding.[2] The yield varies from 2 to 4% with an average of about 2.5% for the recrystallized product. The variation may be due to the degree of completeness of extraction, loss by precipitation and by hydrolysis. The use of a large excess of lead acetate brings about the development of a considerable quantity of acetic acid in the solution during the removal of the excess of lead with hydrogen sulfide, and during the process of concentration hydrolytic action is increased. Promptness in carrying out each step in the process is very desirable and contributes much to its success.

Summary

A modification of Ritthausen's extraction of raffinose from cottonseed meal, using methyl instead of ethyl alcohol to effect a saving in solvent, is described. The crystallization of the raffinose from the extract, following the directions of Hudson and Harding for crystallizing from purified raffinose solutions, can be made directly with the yield obtained by them (2.5% of pure recrystallized sugar). The present directions should be useful in simplifying the preparation of raffinose.

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[8] Leach, "Food Inspection and Analysis," John Wiley and Sons, New York, 4th ed., **1920**, p. 126.

[9] "Methods of Analysis," Association of Official Agricultural Chemists, p. 74, **1920**.

[10] Ref. 6, p. 1649.