LEVULOSE, *the* SUGAR *of the* FUTURE

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The very common, yet unfamiliar sugar, levulose, is destined to take its place along with cane, beet, and corn sugar in the food supply of the nation. Its intrinsic value is unparalleled in the realm of sugars. A study of the unique properties and resultant uses of this sweet holds promise of many possible benefits, even to improving the health of mankind. Levulose is widely distributed in many humble plants, including a prolific native weed, the Jerusalem artichoke or wild sunflower. The successful operation of a semicommercial factory at Iowa State College leads to the prediction that levulose can be produced at a cost comparable to that of cane and beet sugar on the same large scale of production.

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THE word "sugar" by common usage has become synonymous with the term sucrose, leaving the somewhat general impression that the sources of sweetening agents are limited. The properties of sucrose (cane and beet sugar) have been so long accepted that dextrose (corn sugar) has not been rapidly recognized as a sugar. The chemist is familiar with many other sugars, all possessing in varying degrees the properties which make sucrose and dextrose valuable articles of commerce. With such a large number of sugars from which to choose, why are only two of them in common use? The majority of them are either inaccessible in commercial quantities or possess the desirable qualities to a very limited extent. Levulose, however, is widely distributed in nature and offers many attractive qualities. It is the sweetest (*1*) and most soluble (*2*) of all the sugars. It has a unique and delightful flavor distinguishing it from other sugars and it possesses certain physiological properties which cause it to be more easily and quickly assimilated (*3*) to supply the necessary energy for the human system.

While the name, levulose, may be unfamiliar to the layman, the substance itself is no stranger. Sucrose when digested is first converted into equal amounts of levulose and dextrose. The inimitable delicate flavor of many fresh fruits is partially dependent upon the levulose present. The Germans have named the sugar fructose (fruit sugar) because of its occurrence in fruits. The characteristic flavor of honey is due in part to the high percentage of levulose. The sugar has long been used as a constituent of infant foods, of cough medicines, and other therapeutic preparations. This sugar, although widely used by nature and by man in improving the flavor and food value of food products, has rarely been separated from the other sugars with which it is commonly found. The high cost of this separation has heretofore prevented levulose from becoming a popular food and sweetening agent.

Sucrose and glucose have so successfully filled many of the requirements for sweets that it may seem unnecessary to add a third member to the group. However, as a greater knowledge of the individual properties of these three sugars becomes available, important and specific uses for each become apparent. In the preparation of food products it is sometimes desirable to increase the "body" and carbohydrate content without producing undue sweetness. These conditions are adequately met by the present sugars. Other types of foods would undoubtedly be improved by the correct blending with less weight of the sweeter sugar, levulose. There is a class of products which are consumed primarily for enjoyment. Most beverages, pastries, cakes, candies, and other confectionery are of this type. Levulose, with its greater sweetness, is ideal for the preparation of these delicacies. The average diet is overbalanced with carbohydrates. It is possible to make candies using less than one-half pound of levulose for each pound of candy, yet securing all of the desired sweetness and flavor. By selecting the remainder of the ingredients to include wholesome substances of low calorific value the danger of harmful overindulgence is greatly lessened. Attempts have been made to meet this condition by utilizing a synthetic organic preparation reputed to be many times sweeter than the sugars. The resulting loss in flavor and possible harmful effect make these preparations somewhat undesirable.

Many additional uses which are best supplied by levulose are developing. Its high solubility tends to prevent the crystallization of other sugars in its presence. Thus, the quality of jams, jellies, marmalades, and similar products is greatly improved if prepared with levulose. Sandiness in ice cream may be prevented by including the proper amount of levulose. The granulation of honey which causes loss and inconvenience to the honey producer can be absolutely prevented by increasing the levulose content. The characteristic flavor of levulose makes it desirable for improving the flavor of many canned foods. Preliminary experiments indicate that this is especially true in the canning of fruits since it seems to bring out markedly the pleasant flavor.

The use of levulose would give a uniform and permanent flavor to carbonated beverages. When sucrose is used there is a change of sweetness in the bottled product as it becomes older, due to inversion.

The use of dextrose (corn sugar) could be greatly increased by mixing it with crystalline levulose thus raising its sweetening power. Levulose and dextrose sirups may be mixed to produce "invert" sirup or imitation honey.

Among the therapeutic uses for levulose is claimed its application as a food for the consumptive where the production of carbon dioxide in abundance is important (*3*). It has also been found effective in the prevention of hyperacidity of the gastric juice (*4*).

DIABETES

Perhaps the most important potential use is the possibility of its application in the treatment or prevention of diabetes. Joslin (*5*) states that one person in seventy-five has diabetes or will develop it. The total estimated number of cases in the United States in 1931 was 1,800,000. It is of interest to note that the words, "diabetes" and "rohrzucker" (sugar), occur very early in historical writings, 490 B.C. There seems to be a direct correlation between the increase per capita consumption of sugar (cane and beet), and the increase in the number of deaths per 100,000 population, from diabetes. This is shown in Figure 1, the data being taken

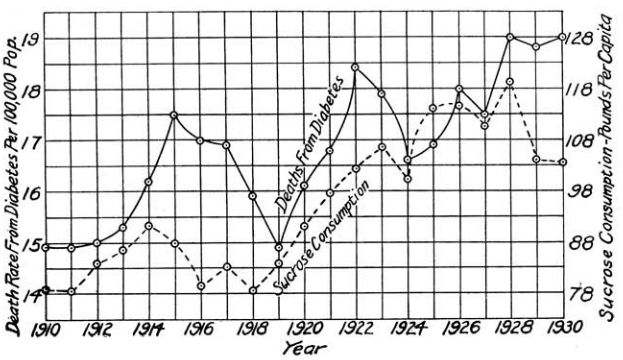


FIGURE 1

Diabetic death-rate and sucrose available for consumption in the United States, plotted for a twenty-year period. The two curves show a striking correlation.

from the *Statistical Abstracts of the United States* (*6*). The sugar curve in Figure 1 is based on the pounds of raw sugar available for consumption. These data may be coincident to the increased accuracy in keeping records and in diagnosis of disease. However, it is of interest to note the decrease in the death rate in 1924 and the corresponding decrease in the consumption of sugar, followed in 1925 and 1926 by a correlating increase in each. The methods of recording and diagnosing would not be expected to vary appreciably over this period of time. Sugar (sucrose) has never been shown to *cause* diabetes. However, if the condition is present, the fact is well known that it is greatly aggravated by the prolonged use of sucrose. This fact, together with the knowledge that numerous persons are unknowingly afflicted with diabetes, makes the data of Figure 1 seem reasonable, if not to be expected. These considerations seem sufficient to merit a very thorough investigation into the effect of replacing sucrose in the diet with levulose, not only for the diabetic but for the normal person as well.

There is no general agreement in the medical profession as to the value of levulose in the diet of the diabetic. Joslin (*7*) made extensive investigations with levulose and summarized his results as follows:

> Fifty-one observations upon the effect of levulose were made. As a rule the quantities ingested were well utilized (the levulose utilized, as computed from the carbohydrate balance was—mild cases 100%, moderate cases 99%, severe cases 88%), though of 41 experiments with 19 severe cases, in only 9 did the urine remain sugar-free . . . . The increase in metabolism following the ingestion of levulose with severe cases was greater than with moderate or mild cases or with normal individuals.

More recently, Dr. Joslin (*8*) has given the following opinion:

> Tentatively we are inclined to the opinion that levulose can be used with advantage in the diabetic diet in very small amounts daily for intermittent periods. It will raise the respiratory quotient in a diabetic more than dextrose and the heat production as well. Levulose seems to cause a different type of metabolism from dextrose, possibly due to the conversion of levulose in part into fat by the diabetic or to a more active stimulation of insulin production. Similarly inulin and lower polymers of levulose in the form of Jerusalem artichokes have been used by our patients with pleasure and benefit.

The literature is abundant with notes on levulose assimilation but the actual number of diabetic cases which have been scientifically studied, using levulose as a part of the diet, is surprisingly low. The experimental work has undoubtedly been retarded by the previous excessive price of the sugar, and also by a certain faction of scientists who have dismissed the suggestion of using levulose for diabetics as ridiculous in the face of an old and accepted theory that all carbohydrate, regardless of kind, meets a like fate in the digestive system, being converted to glycogen and thus to dextrose. Dogged adherence to this contention fails to explain the experimental results of Joslin (*7*), Folin and Berglund (*9*), and many others, (*10*), (*11*), (*12*), (*13*), (*14*), (*15*), (*16*).

Hale (*17*) states that:

> Levulose is an excellent glycogen (animal fat) producer and yet does not cause a rise in hyperglycemia (blood sugar). This characteristic of levulose, distinguishing it above other sugars, is no doubt due to its slow rate of absorption and high rate of conversion into glycogen; in four hours time, 16% of the glucose absorbed in the human system is deposited in the liver as glycogen, whereas with levulose likewise absorbed, 40% is so converted and deposited.

Regardless of theories, the greater sweetness of levulose gives it a unique position in the carbohydrate-restricted diet since pleasure and benefit can be derived from small amounts. With levulose becoming available in more generous quantities, the study of the metabolism of the three major sugars becomes a challenge to the medical profession.

OCCURRENCE

Levulose occurs either free or combined in the form of disaccharides and polysaccharides in many varieties of plants. The levulose-yielding plants include the dahlia, chicory, camas, burdock, dandelion, Canadian thistle, goldenrod, Jerusalem artichoke, and wild onion. It is very interesting to find nature's hardiest and most abundant weeds thriving upon this highly prized carbohydrate. However, the difficulty of propagating, cultivating, and harvesting, or in some cases the low levulose content, of some of these plants eliminates them from serious consideration. The most promising of those named are the dahlia, chicory, and Jerusalem artichoke. The dahlia and chicory possess the higher levulose content but this advantage is overshadowed by the agricultural difficulties encountered in their large-scale production. During the drought summer of 1931 the Horticulture Department of Iowa State College had under cultivation several varieties of dahlia, chicory, and the Jerusalem artichoke. Only the latter survived to produce a reasonable quantity of levulose and the yield (13 tons tubers per acre) was most gratifying under the conditions.

Levulose is very rarely found pure in nature. An interesting incident is recorded by Lippmann (*18*) who found half-ripe tomatoes with peculiar excrescences consisting of a mucilaginous nucleus permeated with a multitude of pointed needles, which proved to be pure crystalline levulose. It is commonly found as a component of saccharides such as sucrose, inulin, raffinose, lupeose, melezitose, gentianose, and similar carbohydrates. These saccharides may be broken down into their component parts by acid or enzyme treatment, thus yielding their share of levulose. The prospective producer of levulose needs but to select from this bountiful supply of raw materials one most suited to the climate and proposed method of preparation.

THE JERUSALEM ARTICHOKE

Because of the ease of cultivation and the large yields obtainable, the Jerusalem artichoke (*Helianthus tuberosus*) has come to be regarded as a very remarkable plant and one of the most outstanding possibilities as a source of large quantities of levulose. It is described in Iowa as a noxious weed. It is well known to the corn farmer. Shoemaker (*19*), however, states that its reputation is undeserved and points to the annual plantings of more than 300,000 acres in France which are mostly in rotation. He suggests that the proper time to attempt the destruction of this plant is when the mother tubers are exhausted and before the new crop is formed. That is, if after free growth, the plant is cut in midsummer, it will be largely destroyed at one operation. He considers it strange to count as a disadvantage the tendency of a valuable plant to grow too well. This characteristic at least promises well for the ease and certainty of a crop when wanted. The Jerusalem artichoke, rapidly becoming valuable as an important source of sugar, will be elevated from the class of weeds.

A native of America, the Jerusalem artichoke was carried back to Europe by early explorers, cultivated for nearly three centuries, and finally reintroduced into this country in a number of improved varieties. Shoemaker (*19*) states that the wild types to be found in the native range of the plant could be listed by the hundred thousands. Among the cultivated varieties, the Mammoth French White, Portland, United States Department of Agriculture seedlings, and the Purple are probably the best known. In 1927, the variety plantings at the Arlington Farm of the United States Department of Agriculture included over 160 numbers, some of which were undoubtedly duplicates.

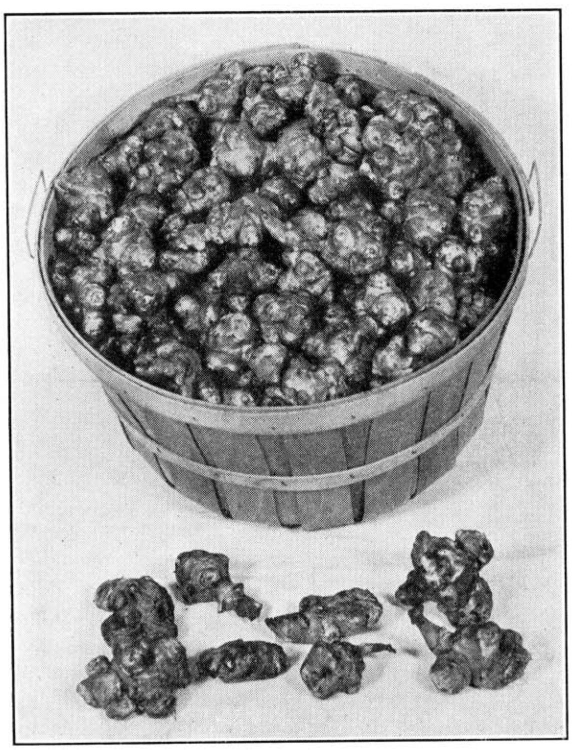
The first published record of the Jerusalem artichoke is given by Champlain (*20*) who speaks of seeing it in the gardens of the Indians at Nauset Harbor, Cape Cod, Massachusetts, on July 21, 1605. According to Shoemaker the plant seems to have reached England in 1616 or 1617. Some 200 years later (1824), the Frenchman, Braconnot (*21*), succeeded in isolating the starch-like substance, inulin, from the Jerusalem artichoke, and in 1843 Crookewitt (*22*) hydrolyzed inulin and obtained an "uncrystallizable" sugar. The "uncrystallizable" sugar was later crystallized by Jungfleisch (*23*) and others, and it is known today as levulose. Willaman (*24*) (1920) seems to have been the first to propose the Jerusalem artichoke as a source of levulose in commercial quantities, and his suggestion has been followed by the studies of the United States Bureau of Standards and other investigators.

THE WILD SUNFLOWER, AN IOWA WEED

One of the many wild varieties of Jerusalem artichoke native to the middle west. The tubers of this plant have a levulose content sometimes as high as 24%.

The levulose content of the Jerusalem artichoke varies within wide limits. Shoemaker reports values ranging from 8.64% to 19.47% for the different varieties. The average of several years production by the Department of Horticulture at Iowa State College is about 14%. Traub, Thor, Zeleny, and Willaman (*25*) at the Minnesota Agricultural Experiment Station analyzed four varieties grown on sandy loam at the University Farm, St. Paul, Minnesota, and found only 6.72% to 10.3% levulose. Since these same varieties were found to yield considerably higher percentages of the sugar at Ames, Iowa, it is possible that the more severe climate of the northern state is somewhat detrimental to the levulose content of the Jerusalem artichoke. The fact that this plant is very slow in maturing, the tubers generally trebling in size soon after the first frost, would seem to support this contention. Some of the wild varieties analyzed at Ames have shown a levulose content as high as 24%. It is impossible to predict the outcome of studies in plant breeding but considering that the sugar beet has been bred from an initial sugar content of less than 6% to the present 12% to 20%, it would seem quite reasonable to expect similar results from the artichoke. The development of a variety containing 30% levulose, giving large yields per acre, and producing fairly smooth tubers in a compact hill, should be within the realm of possibility. What an opportunity for workers in the field of plant breeding!

Johnson (*26*) has made an extensive study of the storage of Jerusalem artichokes and his work shows that storage at a temperature near the freezing point is the only successful method of keeping a large percentage of the tubers free from rot and shriveling for any length of time after they are dug. The principal reason for this is the very thin skin which permits the tubers to lose moisture rapidly when they are exposed to the air at room temperatures. The poor storage qualities of the tubers have an important bearing upon any plan contemplating their use in an industrial process and will be referred to in this connection in a later portion of the paper.



JERUSALEM ARTICHOKE (*Helianthus tuberosus*) TUBERS

Mammoth French White variety, grown by the Department of Horticulture, Iowa State College. Yields for the past four years have averaged about 14 tons of these tubers per acre.

Dr. William J. Hale, director of research for the Dow Chemical Company (*27*), in his address to the Manufacturing Chemists Association at Absecon, New Jersey, on June 4, 1931, said:

> The Jerusalem artichoke for western lands requires little cultivation, and yet is capable of tremendous yields per acre. Aside from utilization in the form of new foods, the tubers will supply levulose, that sugar 50% sweeter than sucrose, or ordinary sugar, and far better than sucrose for the human system. The engineering problems necessary to insure the successful operation of a levulose plant on a commercial scale are still to be worked out; a few month's time and a few thousand dollars will guarantee the success of the enterprise. The result is staggering to the imagination; it means the utter banishment from our tables of all cane and beet sugar, and the directed efforts of thousands upon thousands of our farmers toward the supply of our entire needs for sugars—not alone levulose, but its counterpart, dextrose derivable from corn.

HISTORY

The history of the discovery and methods of preparation of levulose and its parent substance, inulin, has been presented by Harding (*28*). Therefore the present sketch will include only the more important chronological developments. As was previously mentioned, Crookewitt (*22*), in 1843, was the first to prepare levulose. He heated inulin in a water solution for fifteen hours and hydrolyzed it to a sweet sirup. Later (1847) Dubrunfaut (*29*) selected the one-hundredth anniversary of Marggraf's successful separation of sucrose from the sugar beet to announce the separation of levulose from glucose as an insoluble lime salt. This discovery was to become the basis for the preparation of levulose for many years, and at the present time still holds the most promise of becoming the successful commercial method.

The Crookewitt and Dubrunfaut methods have been repeatedly imitated and re-discovered.

It was necessary to consider levulose as a "liquid" sugar, since all attempts to crystallize it failed, until 1880 when Jungfleisch and Lefranc (*23*) prepared levulose sirup by Dubrunfaut's method, washed it repeatedly with absolute alcohol, abandoned it, and returned later to find long silky needles of levulose. This proved to be a banner year for levulose, marked by intense interest and the publication of several valuable treatises. Kiliani (*30*) gave a long historical review of previous work on inulin. He succeeded in preparing crystalline levulose by hydrolysis of inulin, claiming a 96.7% conversion. Girard (*31*) displayed rare ingenuity in his method for concentrating levulose sirups by freezing and was able to crystallize very white levulose from the concentrated sirup without the aid of expensive organic reagents.

Browne (*32*), in 1912, published a method for preparing levulose on a laboratory scale, in which crystallization from aqueous solutions was described.

Fernbach and Schoen (*33*), in 1912, described a method for the production of levulose by biochemical methods. They discovered an anaërobic bacillus, called "gommobacter," which in nutritive medium attacks sucrose and gives a gum. This gum may be precipitated by alcohol, acetone, or barium hydroxide and hydrolyzed by acid treatment to the same weight of levulose.

DESICCATED ARTICHOKE SLICES
This material may be handled and stored like grain without loss of sugar content, and provides the levulose factory with raw material for all-year operation.

In 1922 Harding (*34*) published "the first real departure from the much-imitated technic of Dubrunfaut." His method was based upon the use of glacial acetic acid as a solvent in the separation of glucose from levulose. The method included the recovery of the glucose. Sucrose was the raw material used and levulose was obtained in yields of 25.5% to 28% of the weight of sucrose taken, and the dextrose in yields of 36% to 37.5%. Harding stressed that the method was successful on a laboratory scale only, and that any attempt to enlarge the scale of operation was likely to result in the production of confusion and profanity rather than levulose.

The same year Willaman (*35*) gave specific directions for the preparation of inulin from the Jerusalem artichoke. He stated that the tubers are not a satisfactory material for the preparation of true inulin, although they are good for a study of the whole group of inulin substances. He suggested the following as a possible procedure for the manufacture of levulose sirup: extraction of juice by diffusion, clarification by means of lime, phosphoric acid, and carbon, acid hydrolysis of all inulin bodies, precipitation of lime-levulate, the decomposition of lime-levulate, and evaporation of the levulose solution to sirup.

The researches of the United States Bureau of Standards were first reported by Jackson, Silsbee, and Proffitt (*36*) in 1924. These authors (*2*) presented a more complete report in 1926. They used both the dahlia and the Jerusalem artichoke as raw materials. They separated levulose from the converted artichoke juices by the old Dubrunfaut lime-precipitation method, using revised technic to produce larger and more filterable particles of lime-levulate. Their procedure followed very closely that suggested by Willaman with the exception that hydrolysis was accomplished before clarification. The Crookewitt method was applied to the dahlia. The inulin was obtainable directly from the dahlia juices by freezing, and converted to levulose sirups of 86% to 90% purity. They made a study of the solubility of levulose in water and decided it was feasible to crystallize from aqueous solutions.

The Crookewitt method was also tried on a factory scale in 1926 by Hoche (*37*). Chicory was the raw material used. The levulose was crystallized from water solutions also in these experiments. Solutions of 84° to 88° Brix crystallized on seeding and holding at 40°C.

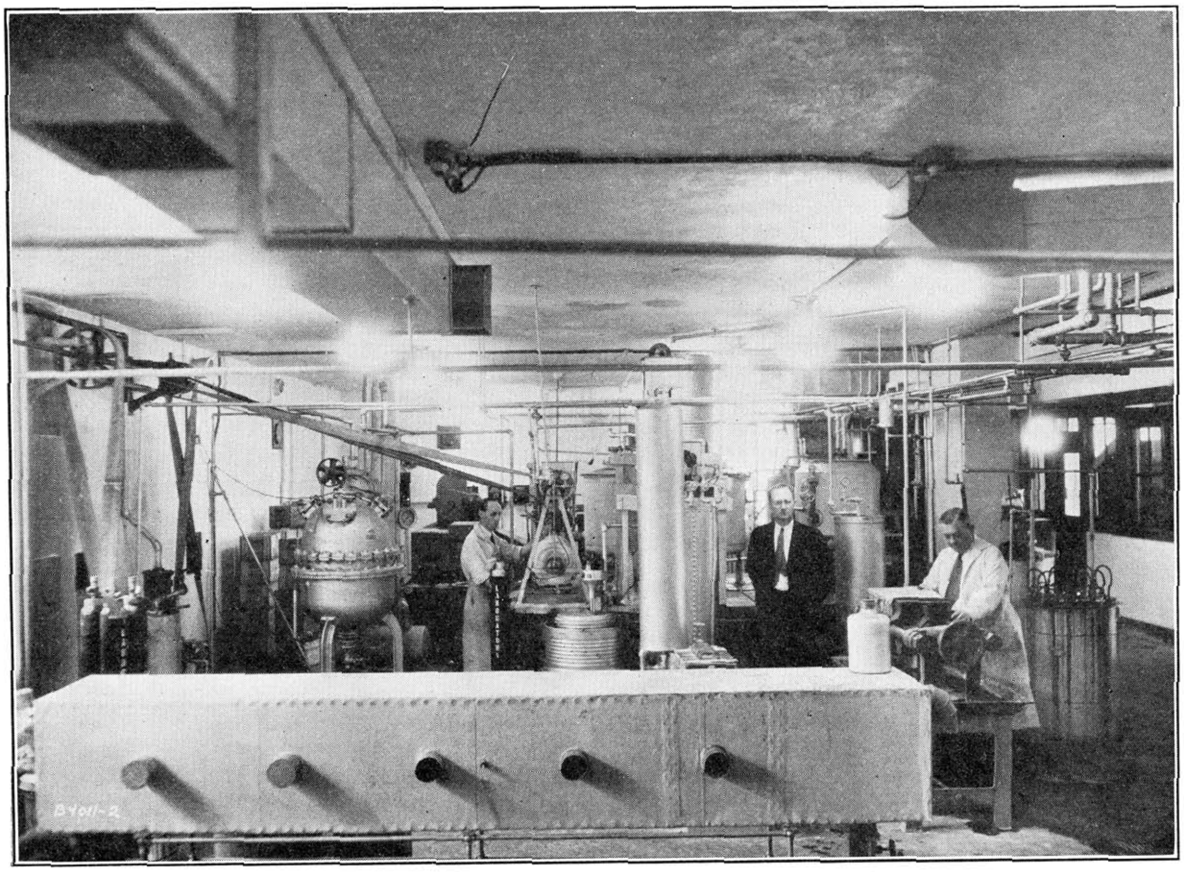
In the ninety-year interim since the discovery of levulose the information accumulated has been chiefly concerned with three basic methods of preparation, those of Crookewitt, Dubrunfaut, and Harding. That these methods are insufficient is evidenced by the fact that levulose is not yet available in commercial quantities.

The Harding method is unsuitable for commercial purposes by the originator's own testimony. Even though the expense of handling might be decreased by refined technic the cost of glacial acetic acid would have to be markedly lower before levulose could compete with other sugars.

The use of Crookewitt's method, consisting of the isolation and purification of inulin, and its subsequent hydrolysis to levulose, requires a raw material, such as dahlia or chicory, which is high in inulin and low in other levulose-yielding polysaccharides. The agricultural difficulties encountered in the raising of large quantities of these roots is a serious problem. Furthermore, Jackson (*38*) has shown that levulose is not the sole product of the hydrolysis of inulin. Certain dilevulose anhydrides are formed which reduce the purity of the sirup and interfere with the crystallization of the sugar. The separation of inulin from the defecated juices is not nearly as quantitative as would be indicated by its low solubility. Jackson (*2*) found that the quantity of inulin recoverable was extremely variable and depended not only on the condition and variety of dahlias, but upon the method employed to induce crystallization. Thus, if the juice was cooled by standing on ice overnight frequently as low as 60% of the inulin crystallized, while by freezing the entire mass and allowing it to thaw amounts varying from 66% to

85% were recovered. The expense of refrigeration is a handicap to commercial development.

An advantage claimed for the Crookewitt method is the fact that a sirup with extremely low ash content can be prepared by hydrolysis of the inulin with a volatile acid, such as carbon dioxide or sulfur dioxide, under pressure. Kleiderer and Englis (*39*) reported that with carbon dioxide at a pressure of 70 to 80 atmospheres, conversion of inulin was complete in one hour at 160°C. The sirups obtained were very satisfactory in taste and appearance. Almost no caramelization occurred in the experiments.



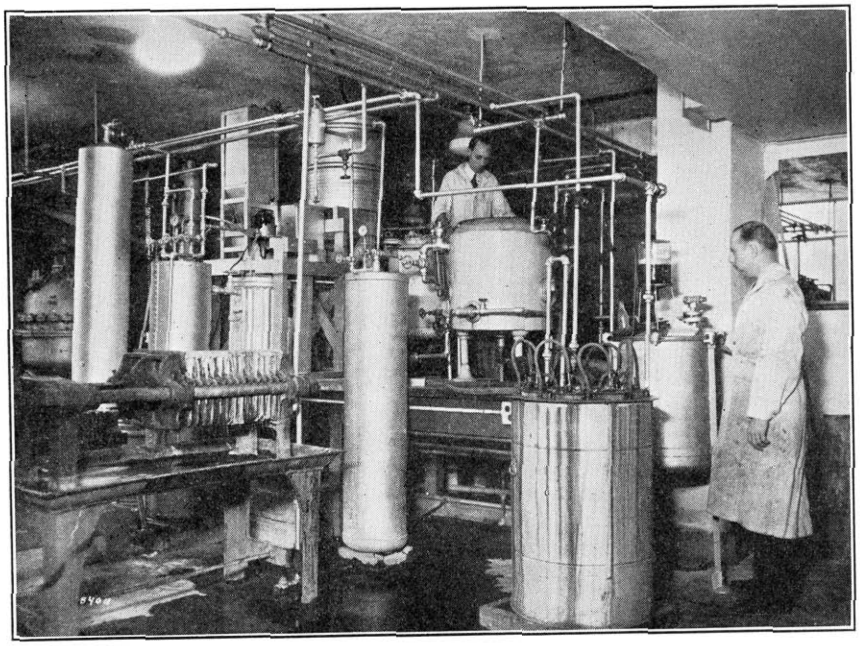
GENERAL VIEW OF PILOT PLANT FOR LEVULOSE PRODUCTION AT IOWA STATE COLLEGE

THE PROCESS

The Dubrunfaut method has the advantage that it can be applied to any levulose-yielding raw material. The process for the production of levulose as developed at Iowa State College (*40*) is an adaptation of this method, but differs from previous practice in a number of respects. These differences become of tremendous importance when large-scale production is contemplated. Many raw materials have been studied, including sucrose (cane and beet), molasses, dahlia, chicory, and the Jerusalem artichoke.

It has been pointed out that Jerusalem artichoke tubers, because of their thin periderm, are subject to rot and withering during storage. Since the operation of a levulose factory by seasonal campaigns would require the storage of some of the tubers for at least three months, this becomes a serious problem. If the tubers are allowed to freeze solidly they must thaw out very gradually or they become black and mushy. Such tubers are undesirable since they are difficult to wash, lose a part of their sugar content to the wash water, tend to crush as they are handled, and much juice is expressed in the slicer. As the period of freezing is lengthened the levulose-glucose ratio steadily decreases. The standard practice used for beets is therefore not adaptable to artichoke tubers. Tubers that are "stored" by leaving them in the ground until spring show a progressive decrease in the levulose-total-sugar ratio. Tubers that are stored under optimum conditions in root cellars lose an appreciable amount of their levulose content.

The Iowa process solves the storage problem and gains many other decided advantages by desiccating the tubers. The dried material may be stored indefinitely without loss of sugar content (*41*) and the factory is able to operate throughout the year. This eliminates the expensive nine-month shutdown of the present sugar factories and enables a quarter-sized plant to equal the annual production of a full-sized one. Many efficiencies of this mode of operation are apparent.



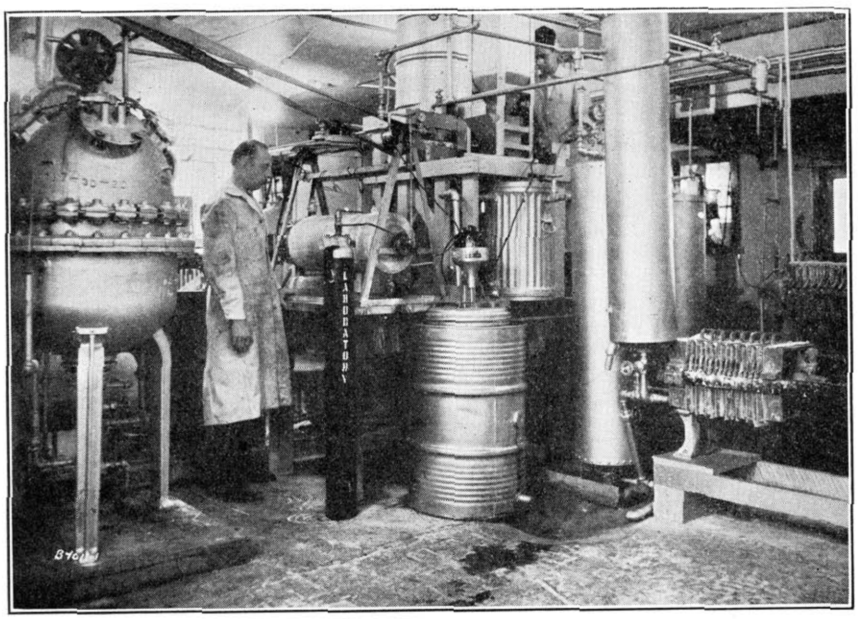
PARTIAL VIEW OF PILOT PLANT. I

The diffusion battery is shown in the foreground. Above it and to the left is the jacketed conversion vessel. Following conversion and neutralization, the juice is filtered in the press on the left and delivered to the storage tank at the top of the picture.

By the use of inexpensive local drying stations only the dried material need be shipped to the factory and the artichoke growing area for an individual plant can be greatly extended. One can conceive of a huge levulose factory drawing its raw material from a vast area, with resulting centralization economies.

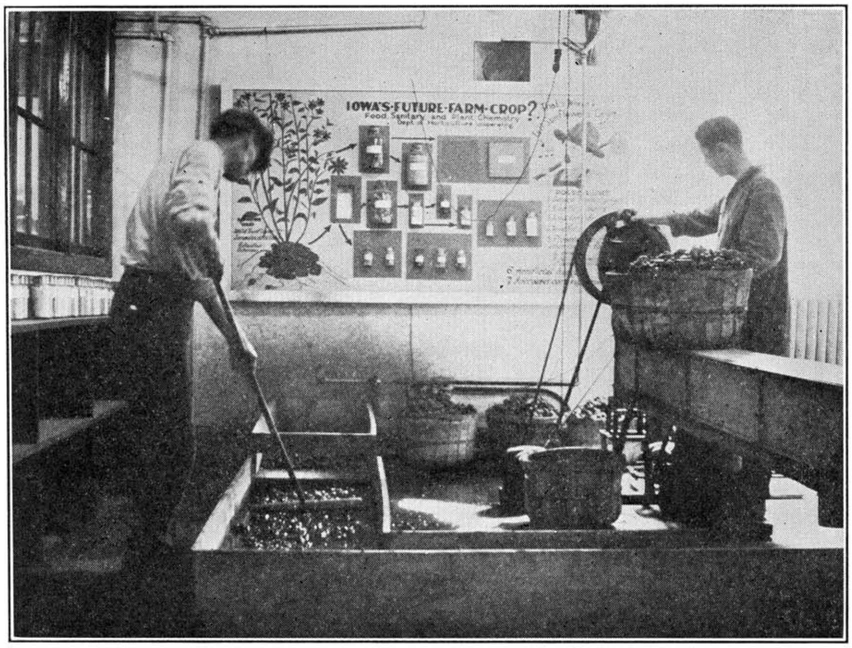
Jerusalem artichokes can be dried without harming the carbohydrates present provided proper precautions are observed. The temperature during the first stages of drying may be as high as 125°C. without injury to the chips and as the drying continues should be progressively dropped until the final temperature does not exceed 80°C. The chips should be white when dry. Any formation of caramel will, of course, decrease the sugar content and cause difficulty later in the clarification of the extract. The drying coagulates the albuminous matter and causes an increase of about 5% of the total albuminoids to be retained by the pulp upon extraction. It also renders the soluble albuminous matter more easily coagulable, and thus simplifies the clarification of the extract. The drying breaks down the cell structure and makes diffusion more easily accomplished. The levulose-total-sugar ratio remains unchanged in dried tubers when stored.

The desiccation of beets has frequently been proposed as an improvement in the beet-sugar industry. In recent years the experimental factory at Eynsham, England, has been making an intensive study and the Oxford modification of the De Vecchis process developed (*42*). Many startling claims have been made



PARTIAL VIEW OF PILOT PLANT. II

The round tank at the top of the picture contains the converted artichoke juice and the square tank to the right front, the lime. The materials are fed continuously into the precipitator tank directly below, and the lime-levulate overflows into the pressure tank attached to the filter press at the right. After filtration, the lime-levulate is treated in the carbonator (foreground). The vacuum evaporator is shown at the extreme left.



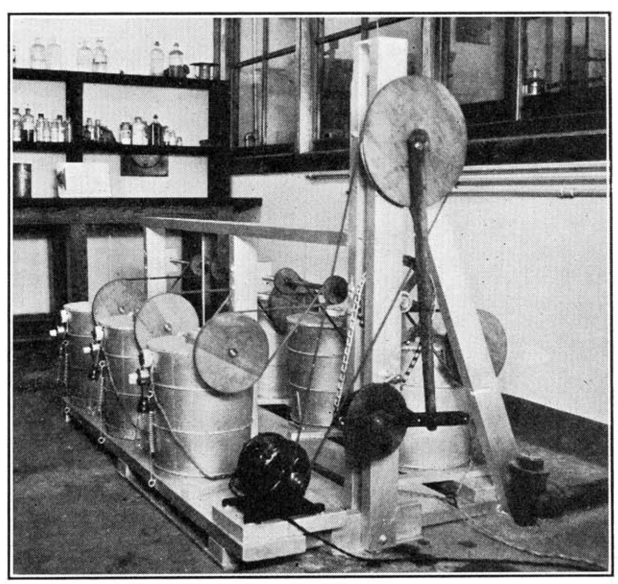
WASHING AND SLICING JERUSALEM ARTICHOKE TUBERS PREPARATORY TO DRYING

and denied concerning this process. Browne (*43*) has listed the chief objections to the process that have been advanced by foreign technologists. It is possible that the Oxford process would have greater appeal to the beet-sugar producers if the present large factories, designed to accommodate the entire beet production in a short time, were not already established. However, the problems of drying beets are not entirely comparable to the desiccation of artichokes and therefore the criticisms are not applicable to the production of levulose from the dehydrated tubers. The care required in beet drying to prevent inversion and resulting loss of sucrose can be neglected entirely in artichoke drying since inversion is necessary to the production of levulose. The levulose factories have not yet been built and therefore the possible loss and cost of a change of equipment to handle a modified process is of no concern. The levulose process is actually improved, the yields increased, and the cost lessened as a result of the desiccation.

The desiccated tubers are extracted in the usual type of diffusion battery with hot water. The use of dried tubers permits a high concentration of solids in this solution, values from 30% to 50% being easily obtainable. The levulose is present in the extract in the form of inulin and lower polymers called levulins (*44*). In order to convert these substances to levulose the solution is subjected to acid treatment. Since levulose is sensitive to acids, it is very important to control carefully the concentration of acid, the temperature and time of reaction during this hydrolysis. These factors must also vary with the concentration of solids in the extract. Incomplete hydrolysis would cause losses in the process to follow. The correct treatment for the complete hydrolysis of the inulin and levulins to levulose with a minimum of loss has been carefully worked out (*45*). This produces a solution of levulose contaminated with glucose and other soluble extractives of the plant cells, some of which are albuminous in character. The albumins are largely precipitated upon neutralization of the excess acid and the solution is ready for the separation of the levulose.

The Dubrunfaut method is dependent upon the insolubility of the levulosate of calcium, or other alkaline earth metals. The corresponding salts of glucose are quite soluble. Calcium levulosate dissolves in 137 parts water at 15°C. and at 0°C. is almost insoluble (*46*). Levulose is easily decomposed in the presence of alkali and the rate of decomposition increases with the temperature. For these reasons all previous workers have formed the levulose salt at very low temperatures, ranging from below freezing to 5°C. The instructions warn that great care must be taken with this step, otherwise an unfilterable, gelatinous precipitate results. Obviously such conditions involve untold difficulties in commercial production. If it were necessary that this precipitate be formed, filtered, washed, and the levulose regenerated from it at these low temperatures, a vast amount of expensive refrigeration would be required in a large plant.

An extensive study of this precipitation has been made with a view to making the process more applicable commercially. A method has been developed whereby the precipitation and the subsequent operations may



BATTERY OF EXPERIMENTAL CRYSTALLIZERS

be carried out at temperatures easily obtainable by the circulation of water. The reaction chamber is a water-jacketed vessel equipped with a high-speed agitator. The levulose solution and lime are added continuously, in the proper proportions, to a suspension of the insoluble levulosate previously formed which acts as "seed" for the crystal growth. The product is removed continuously from the reaction chamber and an easily filterable precipitate is the result. Filtration may be accomplished by the use of a filter press equipped for washing or a continuous drum filter.

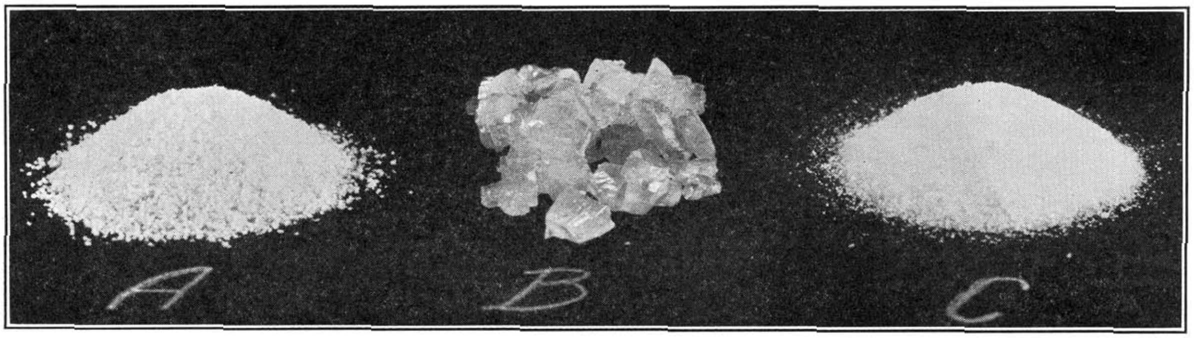
The high concentration of the levulose extract obtainable from desiccated artichokes keeps the losses, due to the increased solubility of lime-levulosate at the higher temperatures, at a minimum. The loss of levulose due to decomposition by the strong alkali is prevented by the very rapid manipulation made possible by the technic of the continuous operation.

The insoluble levulose compound is suspended in pure water and treated with carbon dioxide gas. This gas combines with the alkaline earth metal, forming the insoluble carbonate and leaving the liberated levulose dissolved in the water. When the carbonation is complete, the mixture may be heated to a moderate temperature for a short period of time to decompose any bicarbonates which may have formed. The insoluble carbonate is removed by filtration and the resulting levulose sirup is concentrated by vacuum evaporation.

The proper crystallization of levulose from the sirup requires all of the technic developed through years of experience in the crystallization of sucrose and glucose, with added skill necessary to handle this more highly soluble and sensitive sugar. The crystallization may be conducted in the vacuum pan following the regular sugar-house practice, provided the sirup is of sufficiently high purity and a somewhat longer time is allowed for crystal growth. Sirups of lower purity may be handled with advantage in the familiar crystallizers equipped with slow-moving stirrers and temperature regulators for gradually lowering the temperature as crystallization progresses. The experimental crystallizer used at Iowa State College consists of a battery of ice-cream freezers equipped with adjustable heating elements and geared to revolve very slowly. The concentrated sirup, usually about 90% solids, is placed in the crystallizer at a temperature of 50° to 60° C., seeded with levulose crystals, and the temperature lowered automatically, by a mechanical arrangement, to about 25° C. before spinning. The process requires from 24 to 36 hours. An ordinary sugar centrifuge is used to remove the crystals from the adhering molasses. Due to the high solubility of levulose, it is sometimes desirable to wash the crystals with a solution of pure levulose rather than to attempt this operation with water. If the crystals have been allowed to grow to a larger size than is desired, the washing may be conducted to advantage with water.

As a result of several years of experience in the crystallization of levulose and a study of the optimum pH, temperature, rate of crystallization, and other factors, it is now possible to control the crystal size at will.

Levulose crystallizes in at least two distinct forms, long silky needles and almost perfect cubes which become distorted as they increase in size. The needles, which are commonly formed when a concentrated levulose solution is allowed to stand at room temperature, are said to be levulose hydrate containing one-half molecule of water of crystallization (*47*). The cubes or prisms are formed at the higher temperatures as described above or when more dilute levulose solutions are allowed to stand at room temperature.



SUGAR CRYSTALS

(*A*) Shows crystalline levulose as produced by the pilot plant. The large levulose crystals in (*B*) are an answer to those who believe that levulose must resemble "powdered" sugar. Commercial beet sugar is shown in (*C*) for comparison of crystal size.

The levulose molasses may again be concentrated to 90% solids and a second crop of white crystals obtained. As many as three crystallizations have been successfully performed upon a single batch of sirup. The first crystallization yields an average of 40% of the weight of massecuite as crystals, and the second and third crystallizations about 35%.

The levulose produced by the above-described process is pure white, very low in ash (less than 0.05%), and has an average specific rotation of $-91°$ to $-92°$.

BY-PRODUCTS

By-products are a very important phase of modern industry and the levulose industry will be no exception to this rule. Some of the possibilities are along lines already pioneered by the beet-sugar producers, while others are somewhat more unique.

The Jerusalem artichoke yields a tremendous tonnage of tops, averaging from 10 to 15 tons per acre. If these tops are harvested while green, they produce a very satisfactory ensilage. Unfortunately, when this is done, the yield of tubers is low. It is necessary, at least with the present varieties, to delay harvesting until after the first frost, and the tops at this time are dry and hard like cornstalks. No figures are available for the cost of harvesting the tops, but estimates based upon work with cornstalks (*48*) indicate that the cost should not exceed $1.00 per ton. At this low cost, it is possible that Jerusalem artichoke tops may become a valuable cellulosic raw material. The fibers are longer and stronger than those of the cornstalk, and very satisfactory wallboard has been made from the material by the Chemical Engineering Department of Iowa State College. The material would seem to be as satisfactory for paper pulp as cornstalks. Another possibility, as yet untested, is the utilization of this material in fermentation processes. An average analysis of the dried matured tops is as follows:

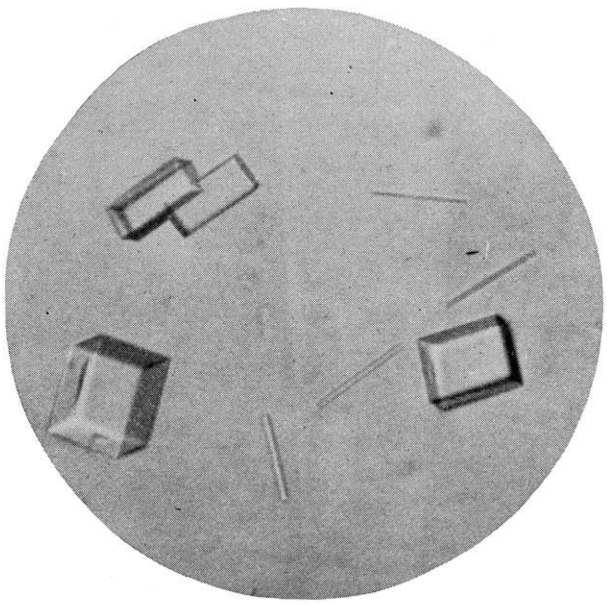
Reducing sugars	6.22%
Non-reducing sugars	14.79
Total sugars	21.01
Starch	13.91
Pentosans	3.59
Protein	6.87
Ash	6.21

The diffusion process yields an extracted pulp composed of the cellulosic plant tissues and other water-insoluble components of the original Jerusalem artichoke tuber. The sugar-beet industry disposes of a similar material by mixing it with molasses and drying, thereby producing a valuable stock food. The artichoke pulp could be utilized in this manner or fermented to yield volatile acids such as acetic. In the latter case, yields as high as 50% to 55% acetic acid, based on the weight of dry material, are obtainable.

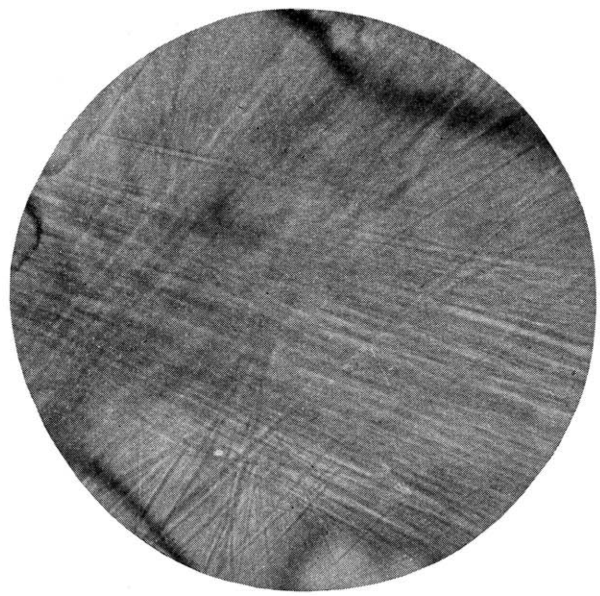
The filter cake obtained following the conversion and neutralization of the extracted juice contains the albuminous protein materials of the artichoke tubers. If sulfuric acid and lime were used, it also contains a quantity of calcium sulfate. This material could probably be used as a fertilizer because of its high nitrogen content. If a fermentation process were operated in connection with the levulose plant, the filter cake could profitably be used as a protein nutrient. For this purpose, it would be desirable to eliminate the calcium sulfate content by converting the artichoke juice with an acid such as hydrochloric, which forms no insoluble compounds with the lime used for neutralization.

The filtrate from the lime-levulosate precipitation contains the glucose originally present in the artichoke together with a small amount of levulose. By the use of concentrated juices obtainable from dried tubers, the sugar content of this filtrate can be made as high as 12% making it an ideal medium for fermentation. Tests conducted by the Biophysical Division of the Chemistry Department yielded 40% to 45% ethyl alcohol. With increasing demand for industrial alcohol and its eventual widespread use in blended motor fuels, this may become an important source of revenue for the levulose factory.

Because of the high purities obtained in the levulose sirup, the molasses resulting from the separation of the crystals is likewise very pure and is in no way com-



Cubical levulose crystals obtained by proper control of the crystallization process.



Hydrated needle-shaped levulose crystals obtained by low-temperature crystallization. The spreading, fanlike formation is clearly shown.

PHOTOMICROGRAPHS OF LEVULOSE CRYSTALS

parable to beet or cane molasses. Levulose molasses will, therefore, be handled in an entirely different manner. As many as three crops of white levulose crystals have been obtained from a single batch of sirup. Each crop removes from 35% to 40% of the levulose present. A relatively high proportion of the material is thus obtained in crystalline form, and the remaining molasses may still have a purity as high as 80%. Several possibilities are open for the utilization of this material. It has none of the bitter taste of beet or cane molasses, and this fact together with its high levulose content and sweetness make it suitable for a table sirup and for use in confectionery and preserving. These fields will probably absorb the entire output, but the levulose manufacturer will be independent of this market. He may, if he wishes, simply add the molasses to the raw artichoke juice and start it back through the process again. Since levulose is precipitated as an insoluble compound and washed free of all impurities including soluble salts, there is little danger of trouble provided the process is carefully controlled. Other alternatives include the use of the molasses with the extracted pulp to produce stock food, and the preparation of various organic materials by fermentation and synthetic processes, for example, the production of mannite by a process of electrolytic reduction (*49*).

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