

or water; slightly soluble in benzene or ether; and insoluble in ligroin. These solubilities differ somewhat from those of the 2-benzyl-semicarbazide. In cold chloroform very little of the product dissolves and hence a means of separating the two semicarbazides is afforded. This semicarbazide begins to reduce Fehling's solution even in the cold and reduces it readily upon warming, as recorded by Busch *et al.* A sample of this semicarbazide and an equal quantity of 2-benzyl-semicarbazide melted as low as  $120-4^{\circ}$ , hence an explanation of the indefinite results obtained by other investigators.

#### Action of Isocyanic Acid upon N-Amino Derivatives of Carbimino Nucleus.

As previously stated, the compounds here subjected to the action of isocyanic acid failed to condense with the latter at low temperatures either in glacial acetic or propionic acid. Benzylidene-*as*-diphenylhydrazone ( $C_6H_5.CH : N.N : (C_6H_5)_2$ ) was brought into reaction under these conditions and also in a mixture of benzene and acetic acid in order to increase somewhat its solubility. No reaction could be detected. In a similar manner benzylidene-phenylhydrazone ( $C_6H_5.CH : N.NH.C_6H_5$ ) was found to be unreactive toward isocyanic acid, but as discussed in our theoretical considerations, this compound does condense with phenyl isocyanate at high temperature. 1-Benzylidene-2-benzyl-semicarbazone as also previously discussed, failed to condense further with isocyanic acid. Though the carbimino nucleus is a favored complex for condensation with isocyanic acid, we note further that certain substituents on the nitrogen atom may considerably retard this tendency for condensation.

MIDLAND, MICH.

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[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,  
U. S. DEPARTMENT OF AGRICULTURE.]

### THE OCCURRENCE OF MELEZITOSE IN HONEY.

BY C. S. HUDSON AND S. F. SHERWOOD.

Received September 16, 1919.

We recently<sup>1</sup> called attention to the abundant occurrence of the rare trisaccharide melezitose in a manna that forms upon Douglas fir trees in British Columbia during summer droughts. Since bees often collect manna and honey-dew in times of drought when the preferred floral nectar is scarce it would appear to be possible that honey from the particular region of British Columbia where this Douglas fir manna occurs would contain melezitose. An occurrence of melezitose in honey would not only be of general scientific interest but would require the attention of the food analyst because melezitose may readily be confused with cane sugar,

<sup>1</sup> THIS JOURNAL, 40, 1456-60 (1918).

one of the recognized adulterants of honey. While we were discussing this matter along these lines and were planning to obtain honey from the wilds of British Columbia there came an answer to the question in a most unexpected way. A sample of honey was received from central Pennsylvania, accompanied by a statement that it had proved unfit winter food for bees and a request that a chemical analysis be made in the hope of disclosing why the bees had died. Bees do not winter well upon honey-dew honey in general, as they seem unable to digest or assimilate such honey fully; but this material had caused even more difficulty than ordinary honey-dew honey. This sample of honey had thoroughly crystallized in the comb and the appearance of the crystals was different from that of *d*-glucose, the sugar that frequently crystallizes from honey. It was soon determined that the crystals were pure *melezitose*.<sup>1</sup> Subsequently we have obtained samples of comb honey from two localities in Maryland, near the District of Columbia, one produced in 1917, and the other in 1918, both of which also contain much *melezitose* in crystalline form. The sample from Pennsylvania was from the crop of 1917, and in the summer of 1918 similar honey, rich in crystalline *melezitose*, was produced in the same locality. It can hardly be doubted, therefore, that *melezitose* occurs not infrequently in honey, and it seems indeed remarkable that its crystals, which can be readily distinguished from those of glucose, have never before been observed in honey. We have at least not been able to find any record of such an observation in the extensive literature that deals with the composition of honey. The mode of origin of the three samples of honey that have been found to contain *melezitose* will be described after the presentation of the chemical data on the identification of the sugar.

#### Identification of Melezitose in Three Samples of Honey.

*Comb Honey from Port Royal, Juniata County, Pennsylvania.*—In one section of this honey the contents of 90% of the cells had crystallized thoroughly and solid masses having the shape of the cells could be removed from the wax of the comb. In two other sections the crystallization was slightly less pronounced. A quantity of the honey was removed mechanically with a knife blade from the wax, ground in a mortar with glacial acetic acid, which is miscible with the sirupy portion of honey but does not dissolve crystalline *melezitose* or glucose, and the crystals were separated from the liquid by filtration. They were washed with glacial acetic acid, then with absolute alcohol and were dried at 70°.

The specific rotation of this material in aqueous solution was +89.9°. After one recrystallization from hot aqueous alcohol and drying at 70° the crystals showed  $[\alpha]_D^{20} = +88.2^\circ$ . Their melting point was 148°. The acetyl derivative of the sugar,

<sup>1</sup> The identification by chemical means was confirmed by optical-crystallographic measurements made by Dr. Edgar T. Wherry, as described in the following article, p. 125.

prepared by the use of acetic anhydride and sodium acetate, crystallized readily from alcohol on the addition of water and showed the melting point  $117^{\circ}$  and  $[\alpha]_D^{20} = +110.7^{\circ}$  in benzene and  $+103.8^{\circ}$  in chloroform.

These data agree completely with previously recorded measurements<sup>1</sup> by other observers and by ourselves on melezitose and its hendeca-acetate. The crystals of melezitose from the honey did not reduce Fehling's solution until after hydrolysis by acids, a property by which melezitose may be distinguished readily from the crystals of glucose that are commonly present in honey.

In the subsequent separation of larger quantities of melezitose from comb honey a more convenient method has been followed. Fifty g. of the comb honey was macerated in a mortar with 50 cc. of cold 80% alcohol, which thins out the sirupy portion but does not dissolve the crystals to any great extent, and the crystals and solid beeswax were filtered off through cloth and washed with cold 80% alcohol. The mixture of crystals and wax was then heated with a small quantity of water to dissolve the melezitose and melt the wax. After cooling, the upper layer of congealed wax was removed, and the solution was filtered with the aid of infusorial earth and evaporated to a sirup under reduced pressure. Some alcohol was mixed with the sirup and the melezitose rapidly crystallized. The crystals were washed with alcohol and dried at  $70^{\circ}$ . The yield from one section of the Port Royal comb honey was 20% melezitose, from another section 10%.

*Comb Honey from Drummond, Montgomery County, Maryland.*—Some two weeks after the isolation of melezitose from the Port Royal honey Dr. E. F. Phillips of the Bureau of Entomology, U. S. Department of Agriculture, who had become much interested in the subject, called our attention to the occurrence of a peculiar crystallization in honey combs that were being filled by bees at that time (July, 1918) in the vicinity of Drummond, Maryland. The crystallization formed in the comb with unusual rapidity, a phenomenon which had also arrested the attention of the producer of the Port Royal honey. Examination by the methods that have been described showed conclusively that the crystals in the Drummond honey were melezitose.

*Comb Honey from Riverdale, Prince George's County, Maryland.*—Dr. Phillips has also supplied a sample of crystallized comb honey from this locality, made during the 1917 season. It was found to contain about 16% of crystalline melezitose. Like the Port Royal honey it had also proved unwholesome winter food for bees.

#### The Source of the Melezitose in the Pennsylvania Honey.

In July, 1917, the bee-keepers at several places in central Pennsylvania noted that their honey was crystallizing shortly after the bees

<sup>1</sup> THIS JOURNAL, *Loc. cit.*

placed it in the hives. Not only did this render the honey difficultly salable, but also when the honey was stored by the bees to be used as winter food, it proved to be unsuited to their requirements, and this, in connection with the unusual severity of the following winter, led to the loss from indigestion of many bee colonies. Coming as it did at a time of sugar shortage, when every effort was being made to increase the production of honey, this situation had a rather serious aspect; for it was not known but that it might be connected with some disease which would spread over a wide area, and lead to serious diminution in the honey supply. Mr. Charles N. Greene, Chief Apiary Adviser to the Pennsylvania Bureau of Economic Zoölogy—now the Bureau of Plant Industry—investigated the matter and obtained evidence that the honey in question was derived not from floral nectar but from honey-dew, the sweet fluid which collects on plants as the result of the activities of aphids and other insects. As far as could be determined at the time, the bees obtained this honey-dew from some species of pine tree, several of which are abundant in the region. Mr. Greene sent a sample of this honey to the Bureau of Entomology, U. S. Department of Agriculture, and that Bureau transmitted it to the Bureau of Chemistry with a request that its composition be studied. It was in this sample that the melezitose was first recognized.

At our request Dr. Edgar T. Wherry, Crystallographer of the Bureau of Chemistry, made a visit to Port Royal in June and August, 1918, and again in August, 1919, to obtain data on the origin of the melezitose in the Port Royal honey. On two of these trips he was accompanied by Mr. Greene, who aided in many ways the working out of the origin of the sugar. Information as to the occurrence of the material was obtained from H. L. Bowers of Port Royal and J. S. Colyer of Perulack, both in Juniata County; Prof. H. C. Klinger of Liverpool, Perry County; the Merrill Bee and Honey Co. of Muncy and C. Y. Lorson of Williamsport, both in Lycoming County, Pennsylvania. Data as to the distribution of the various pines was obtained from Prof. J. S. Illick of the Pennsylvania Bureau of Silviculture; from the staff of the Pennsylvania Forest Academy at Mont Alto; and from Mr. Harold W. Pretz of Allentown. To all these gentlemen and others who coöperated in the investigation thanks are hereby extended. Dr. Wherry has submitted the following report of the results of his investigations:

“Five species of pine trees are common throughout the region studied: the white pine, *Pinus strobus* L., the table-mountain pine, *Pinus pungens* Michx. f., the yellow pine, *Pinus echinata* Mill., the pitch pine, *Pinus rigida* Mill., and the scrub pine (or jack pine as it is commonly called there), *Pinus virginiana* Mill. It was soon found that only the last of these was of significance in connection with the development of the melezitose. At a few localities, trees of this species, especially 4 or 5-year old

seedlings, were infested with a reddish brown soft-scale insect, which has been identified by the Bureau of Entomology as *Toumeyella parvicorne* Ckll.<sup>1</sup> As a matter of record the following specific places where it was observed in 1918 are listed: on hillside just back of Rockville, north of Harrisburg; on small ridge about 4 miles north of Liverpool; and in ravine about 2 miles south of Port Royal. At the Liverpool locality the honey-dew produced by this insect was being actively collected by bees identifiable by their color and direction of flight to be those belonging to Prof. Klinger, whose place lies about half a mile away. Another point of interest about this locality was the fact that in one instance the same insect occurred on a young tree of *Pinus rigida*, which happened to be surrounded by numerous individuals of *P. virginiana*. It is also noteworthy that the water extract of honey-dew-covered branches collected from these trees yielded on evaporation a quantity of nondescript gummy material, in which microscopic examination showed the presence of crystals, identifiable by their optical properties as melezitose. This indicates that the bees merely collect this sugar as it occurs, and do not synthesize it.

"Far more widespread than the above mentioned insect in all the localities in central Pennsylvania visited by the writer was a large gray to reddish aphid which has also been found at Drummond, Maryland, by Mr. Jacob Kotinsky of the Bureau of Entomology, U. S. Department of Agriculture; there are records on file of its occurrence also in Ohio, Virginia, and the District of Columbia. This insect was provisionally identified by Dr. A. C. Baker, of the Bureau of Entomology, as *Lachnus pineti* (Fab.) Koch. In the majority of the cases observed by the writer, and presumably in the others noted, the host plant was *Pinus virginiana*; occasionally a few insects were noted on *P. echinata* and *P. rigida*. This insect or a closely related species is said to be found in Europe more or less commonly, though never abundantly, on the Scotch pine, *Pinus sylvestris* L. This tree has been used in this country in considerable quantity for the purpose of reforesting some denuded hills, especially in central Pennsylvania, and the insects may have been introduced into this country on young trees of this species and spread from them to the native pine, *Pinus virginiana*; none could be found, however, on the numerous Scotch pine trees examined by the writer at several localities.

"In a grove of trees of *Pinus virginiana* in a ravine about 2 miles south of Port Royal, Pa., these insects were found to be common in 1918, and it was to the vicinity of this grove that Mr. Bowers, whose place is about a mile away, was able to trace his bees, which could easily be recognized by their color. What a large quantity of the melezitose must have been produced here is indicated by the results of the working up by the Bureau

<sup>1</sup> See Mr. Kotinsky's report on page 122.

of Chemistry of some honey obtained from Mr. Bowers. From 40 sections, which had been withdrawn from the hive before they were completely filled, we were able to extract over 5 kg. of the pure melezitose. Similar observations were made at every other place where melezitose formed; the producers had seen their bees working in or near colonies of this species of pine. One producer found his bees to collect honey-dew from a large tree of Norway maple, *Acer platanoides* L., at the time the melezitose appeared, but the relatively minute amounts of this sugar developed in his honey in 1918 may well have come from pines, which grow within a mile, and on which the aphid was found to occur.

"Only in exceptional seasons does melezitose-honey-dew appear to be collected by the bees. During the early part of July they obtain honey extensively from white clover, and about the first of August change over to buckwheat, which comes into bloom at that time. But if the weather is dry in mid-July the yield of white clover honey becomes scanty, and then the bees seek other sources of supply. The dry weather likewise permitting the accumulation of the honey-dew on the pine trees, they soon discover that this material is sweet, and collect it in large quantities. In both 1917 and 1918 there were long dry spells at the critical period, and large amounts of melezitose appeared in the honey. In 1919, however, the weather was wet during the greater part of July, and, although aphids and scales flourished, no melezitose whatever appears to have been collected, the clover honey lasting over until the buckwheat began to yield, and the rain keeping the honey-dew from collecting on the pine branches.

"In order to complete the identification of *Pinus virginiana* as the source of the melezitose it seemed worth while to ascertain whether the development of this sugar in honey is, in fact, limited to the region in which this tree occurs. This pine may be classed as a southern species, as its range is rather sharply limited on the north at about latitude  $41^{\circ} 30'$ . It occurs rarely on Long and Staten Islands, New York; thence it appears sporadically in the Highlands of northern New Jersey. It is present in the Wyoming Valley up to a short distance north of Wilkes-Barre, Pa.; further west it has been found to reach a northern limit in the hills several miles north of Williamsport, in the Susquehanna valley. From here the northern boundary of its range swings southwestward to Pittsburgh, Pa., and it enters the southeastern part of Ohio, being included in lists of the plants of that state. As far as known it is bounded on the west by a line running thence southward to the Gulf states; and between this line and the coast it occurs at many places. It appears to be limited, however, to soils considered by the agriculturist as sterile and barren, the reaction of which is decidedly acid; thus it occupies old, "worn-out" fields throughout its range; it occurs on dry shale and sandstone soils throughout the Appala-

chian mountains, and on the sands of the Coastal Plain. In no case has melezitose been found in any honey produced outside of the area described, at least east of the Rocky Mountains, reports of crystallization in honey further north and west having proved on examination to be due to glucose and not to melezitose. The tracing of the source of the melezitose in the honey to this species of pine, therefore, seems justified."

Mr. Jacob Kotinsky, Entomological Assistant in the Bureau of Entomology, U. S. Department of Agriculture, has transmitted the following report on the identity of the scale insect found on the scrub pines, on the way such insects produce honey-dew, and on the possibility of preventing the development of melezitose:

"The insect on the pine twigs that were collected near Liverpool, Pa., by Dr. Wherry late in June, 1918, was identified by Mr. H. Morrison, a Bureau specialist on the classification of the group, as *Toumeyella parvicorne* (?) Ckll. (Order, Homoptera: Family Coccidae.) The insects were immature, which accounts for his query on the specific identity. *T. parvicorne* is one of the group of scale insects known as 'soft' or 'brown' scales, and is confined to pine trees. True to its affiliations, it feeds on sap, which it procures by means of a slender proboscis forced into the plant tissue and used as a conveyance of the substance pumped by muscles located at the proximal end of the organ. The developmental stage of the insect on the date that the specimens were brought to this office (July 2) indicates that *T. parvicorne* produces but one generation annually in the latitude and altitude of Liverpool and hibernates in the larval form, though these facts still remain to be determined definitely by observation. The family of scale insects (Coccidae) is closely allied to the Aphidae, the most common and best known honey-dew producing insects, and, like them, various 'brown' or 'soft' scales and mealy bugs, when in large colonies, are sometimes capable of producing prodigious quantities of honey-dew. In the 'brown' or 'soft' scales, to which *Toumeyella parvicorne* belongs, production of honey-dew is the work of females only, is heaviest in the pre-adult stage and is doubtless further conditioned by the part of the plant inhabited and by meteorological conditions. A young, growing shoot, itself favored by liberal precipitation, yields its sap more readily in such weather. Normally, honey-dew is washed off by rains and, therefore, accumulates more readily in dry weather. The presence or absence of ants, which usually accompany honey-dew producing insects, and other honey-dew gathering insects, especially aculeate (stinging) Hymenoptera, as well as the growth of the sooty fungus (*Meliola* sp.) obviously gage the quantity of honey-dew available for hive bees. A suggestive peculiarity of many species of these insects is that their feeding tends to produce deformities in the host tissues which, in some cases, become galls.<sup>1</sup>

"Three methods of preventing the development of melezitose suggest themselves, *i. e.*, to kill the honey-dew producing insects by encouraging their natural enemies, by spraying the infested trees with an insecticide, or by cutting out the trees subject to infestation. But, when it is realized that normally bees range two miles or more, the impracticability of the last two suggestions is obvious. The first one may likewise be dismissed for the reason that there is no way known to encourage the natural enemies of the insects in question.

"Dr. E. F. Phillips suggests that the control of this condition resolves itself, therefore, into disposing of the product as 'honey-dew honey' and providing for winter

<sup>1</sup> A. C. Baker, U. S. Dept. Agr., *Rept.* 101, 34 (1915), records finding unusually high sugar and low starch content in galls produced by the woolly apple aphid.

stores of each colony a supply of digestible sugar, so placed that this material will be first used during wintering. This is readily done, for example, by feeding sugar sirup or good honey to each colony after brood rearing has ceased. If it is stored below all other stores it will be first used."

**Analytical Data on Honey Containing Melezitose.**

It may be useful in connection with the general subject of the chemical analysis of honey to record the analytical data on the Port Royal honey. Two sections of it were examined, denoted as Samples 1 and 2. Sample 1 contained only a small quantity of crystalline melezitose but Sample 2 had crystallized solidly. The comb honey was dissolved in water, the insoluble wax, etc., filtered off, and the filtrate evaporated under reduced pressure to the consistency of honey. Polarizations and estimations of reducing sugars both before and after the Clerget (cold) inversion, using both hydrochloric acid and invertase as hydrolysts, were made on the liquid honey. All polarizations are calculated to the basis of 26 g. of liquid honey in 100 cc. of solution, read in a 200 mm. tube in a saccharimeter with the Ventzke scale. The percentage of solids in the liquid honey was determined by the refractometer, Sample 1 showing 75.5% and Sample 2, 77.1%. The reducing sugars are calculated as invert sugar. The measurements on the inverted solutions were made after 24 hours standing and also after 5 days and agreement was obtained for the two sets, proving that the hydrolyses were complete in 24 hours.

ANALYSIS OF THE PORT ROYAL, PENNSYLVANIA, HONEY OF HONEY-DEW TYPE.

Sam- ple No.	Polarization.						Reducing sugars.				
	Direct.		HCl inversion.		Invertase inv.		Sucrose invertase Clerget %.	Direct.	Invert.	Sucrose by inver- tase.	
	21°.	87°.	21°.	87°.	21°.	87°.		%.	HCl.	Inver- tase.	tase.
1.	-9.5	+12.6	-12.50	+11.00	-11.75	+11.20	1.71	67.58	69.35	68.96	1.31
2.	+27.9	+43.8	+17.60	+35.64	+27.05	+44.00	0.65	42.00	63.08	42.73	0.69

What is probably a close approximation to the percentage of melezitose present in the samples may be calculated in the following manner from the data of the table. In Sample 2 the percentage of sucrose that is shown by the Clerget method, using invertase as the hydrolyst, is 0.65%, and by the increase in reducing sugars after inversion with invertase 0.69%. These values agree well and it is probable that the action of invertase, which hydrolyzes sucrose but not melezitose, furnishes the most reliable estimation of sucrose in such products.<sup>1</sup> Using the average, 0.67%, the weight of sucrose in the normal weight of honey, 26 g., is (26) (0.0067) = 0.17 g. The change of rotation that is caused by the inversion of 26 g. of sucrose, readings being made at 21°, is known to be 142.7 — (21 ÷ 2) = 132.5°, hence the change due to 0.17 g. is 0.86°. Now the acid inversion of the honey causes a change in rotation towards the negative side of 10.3° and if the change that is known to be due to the sucrose, 0.86°, be

<sup>1</sup> Hudson, *J. Ind. Eng. Chem.*, 2, 143-6 (1910).



subtracted, the difference,  $9.4^\circ$ , may be used as a basis for estimating the amount of melezitose that is present. Since<sup>1</sup> 26 g. of melezitose in 100 cc. of solution rotates  $+134^\circ$  V. before hydrolysis and  $+95.5$  afterwards, the quantity of melezitose present in 26 g. of the honey is calculated to be  $(9.4)(26) \div (134 - 95.5) = 6.3$  g., and the percentage of melezitose is  $6.3 \div 26 = 24.2\%$ . A similar calculation can be based upon the increase in reducing sugars after the hydrolysis of the honey by invertase and by acid. The increase through the action of invertase is  $42.73 - 42.00 = 0.73\%$  invert sugar, while the acid hydrolysis shows an increase of  $63.08 - 42.00 = 21.08\%$ , calculated as invert sugar. Attributing the difference,  $21.08 - 0.73 = 20.35$ , to the hydrolysis of melezitose, it is noted first that this much invert sugar is equivalent in reducing power to  $20.35(0.95) = 19.3\%$  of *d*-glucose, and second that 100 g. of melezitose is known<sup>1</sup> to have the same reducing power after hydrolysis as 69 g. of *d*-glucose. Hence the percentage of melezitose present in the honey is  $19.3 \div 0.69 = 27.9\%$ . Similar calculations indicate that Sample 1 contained 1.96% melezitose, according to the polarization data, and 0.54% according to the reducing sugar estimations. While these methods of analysis leave much to be desired in the way of accuracy, they are nevertheless fairly satisfactory approximations in a case where all methods of analysis that have been employed in the past in the examination of honey fail completely. In the future when a honey is found by the analyst to show a large increase in reducing sugars by acid inversion, but a much smaller increase by invertase hydrolysis, the presence of melezitose should be suspected. On the other hand, no honey should be condemned as being adulterated with sucrose on the sole basis of an increase in reducing sugars by acid hydrolysis because the presence of melezitose can equally well cause such an increase. The quantity of sucrose in a honey should be estimated by inversion with invertase.

Honey which contains so much melezitose as does Sample 2, over 20%, will deposit crystals of this sugar readily, but if the honey is in liquid form, through heating, for example, the melezitose may best be crystallized by fermenting away the other sugar with baker's yeast. Forty g. of Sample 2 was diluted with water to a solution of about 20% solids and fermented several days with baker's yeast. When no further gas bubbles were observed the solution was clarified by filtration through a little infusorial earth and evaporated to a thick sirup, which soon crystallized and yielded 8.3 g. of melezitose or 20.7% of the weight of the honey, a very good yield. Possibly this method of crystallizing melezitose from honey may prove useful in detecting the sugar in cases where its presence in honey is suspected from analytical data.

<sup>1</sup> THIS JOURNAL, 40, 1456-60 (1918).

### Summary.

It has been known since ancient times that bees collect mannas during droughts because floral nectar is not then abundant. Turkestan manna and likewise a manna from the European larch tree have long been known to contain the rare sugar melezitose, and recently we have found over 70% melezitose in a manna from the Douglas fir of British Columbia. Might not melezitose be present, therefore, in some kinds of honey and have escaped detection in the past? While considering this question we received a sample of comb honey, of honey-dew type, from Port Royal, Pennsylvania, which had crystallized solidly in nearly all the cells. The crystals were not *d*-glucose, the sugar that frequently crystallizes from honey, but were pure melezitose. Two samples of honey-dew honey from Maryland have also been found to contain crystals of melezitose. An investigation by Dr. Edgar T. Wherry of the origin of these 3 lots of honey discloses that the bees collect a sweet fluid deposited on the young twigs of the Virginia pine (*Pinus virginiana*) by a soft scale insect (*Toumeyella parvicorne* (?) Ckll.), or at other times by an aphid (*Lachnus pineti* (Fab.) Koch), and store away this material in place of floral nectar. The fluid itself was found to contain melezitose. Analytical data on this type of honey are recorded, and a way for the approximate estimation of melezitose in such products is described. Since melezitose has already been identified in mannas from two conifers, namely the European larch and the Douglas fir, and is now found in an exudation from a third, the scrub pine, the question naturally arises, whether melezitose may not be present in the sap of most coniferous trees. In making this query it is assumed that the insects that produce these mannas and exudations do not synthesize the melezitose; this assumption seems quite probable, though it remains to be established.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

## THE CRYSTALLOGRAPHY OF MELEZITOSE.

By EDGAR T. WHERRY.

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### Crystallography.

The existing data as to the crystallography of the trisaccharide melezitose is not only incomplete but contradictory. Villiers<sup>1</sup> described it as monoclinic, bounded by a prism, *m*, the base *p*, and the side pinacoid *g*<sub>1</sub>; he obtained the angles  $g_1 : m = 136^\circ 38'$  and  $m : p = 92^\circ 40'$ . On the other hand Alekhine<sup>2</sup> found it to be rhombic, his crystals showing

<sup>1</sup> *Compt. rend.*, 84, 37 (1877); *Bull. soc. chim.*, 27, 100 (1877).

<sup>2</sup> *J. Russ. Soc. Phys. Chim.*, 21, 411 (1889); *Ann. chim. phys.*, [6] 18, 538-9 (1889).