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.

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

THE CRYSTALLOGRAPHY OF MELEZITOSE.

BY EDGAR T. WHERRY.

Received September 16, 1919.

Crystallography.

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

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[1] *Compt. rend.*, **84**, 37 (1877); *Bull. soc. chim.*, **27**, 100 (1877).

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

front and side pinacoids, *o* and *a*, prism, *m*, and front and side domes, *od* and *ga*, although he recorded no measurements at all. In both cases the dihydrate is supposed to have been represented, but no information has been available to indicate whether this was a case of dimorphism or whether the two authors were in fact not dealing with the same substance.

The recent discovery by Hudson and Sherwood[1] of this sugar in relatively large quantities from two widely separated regions in the United States[1] has given an opportunity to study the matter further.

A sample of material from Pennsylvania was dissolved in an excess of water and filtered into a small beaker, which was covered with filter paper and allowed to stand at ordinary temperature for several days. The crystals which separated attained a diameter of a millimeter, but were crowded together to such an extent as to make them unsuitable for crystallographic measurements. A few minute simple ones were picked out, and the balance redissolved by addition of a little water and warming. The liquid was then allowed to cool and the crystals previously picked out were introduced, the vessel being allowed to stand in a room kept at a constant temperature of 20° for several days. The same procedure was followed, using 50% alcohol as the solvent.

The crystals which separated proved to be rhombic, those from water being broader than those from alcohol; and both types showed the same forms as those described by Alekhine. In the following description his orientation is retained, although the lettering of the forms is changed so as to bring it into accord with modern practice. The faces are somewhat rounded as well as distorted by subparallel intergrowth, so that the measurements vary as much as ±30′, but the general features of the crystallography can be readily established. The average angular values and the derived axial ratio are presented in Table I.

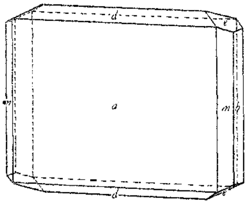

Fig. 1.—Melezitose crystal.

TABLE I.

Angle-Table for Melezitose Dihydrate, $C_{18}H_{32}O_{16}.2H_2O$.

System, rhombic; seemingly holohedral, but no doubt bisphenoidal.

Axes: $a:b:c = 1.216:1:0.496$.

No.	Form.	Symbol. Gdt.	Symbol. Mill.	Description.	Observed. φ ° ′	Observed. ρ ° ′	Calculated. φ ° ′	Calculated. ρ ° ′
1	*b*	0 ∞	010	Narrow, somewhat dull	0 00	90 00	0 00	90 00
2	*a*	∞ 0	100	Prominent, brilliant	90 00	90 00	90 00	90 00
3	*m*	∞	110	Narrow, but good	38 05	90 00	.. ..	90 00
4	*e*	01	011	Small, somewhat rounded	0 00	26 30	0 00	26 24
5	*d*	10	101	Prominent, brilliant	90 00	21 15	90 00	.. ..

Many crystals showed only the forms *b*, *a*, and *d;* and it is possible that Villiers' measurements were made on greatly distorted crystals of this

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[1] THIS JOURNAL, 40, 1456–60 (1918). See also the preceding article.

development, *b* being his *p*, *a* his g_1, and *d* his *m*. The complete set of forms observed is shown in Fig. 1.

Optical Properties.

Under the microscope melezitose presents the form of plates and rods, in part rectangular in outline and in part terminated by faces inclined at large angles (see Fig. 2). On crushing the crystals, irregular flakes are produced.

The rectangular plates yield on immersion in oily liquids of known refractive index the values of β and γ, but crushed fragments usually show values intermediate between α and β in one direction. Observations were made in light of variable wave length, obtained by a monochromatic illuminator, at 20°. The dispersion relations were found to be as stated in Table II.

TABLE II.

Refractive Indices of Melezitose for Different Wave Lengths.

	Wave length.					
Index.	450.	500.	550.	D, 589.	600.	650.
α	1.550	1.546	1.542	1.540	1.540—	1.538
β	1.558	1.553	1.550	1.548	1.547	1.545
γ	1.561	1.556	1.552	1.550	1.549	1.547
γ-α	0.011	0.010	0.010	0.010	0.009+	0.009

The refractive indices for sodium light are thus $\alpha = 1.540$, $\beta = 1.548$, and $\gamma = 1.550$, all ±0.001. The total double refraction is 0.010 but that usually seen is the difference between γ and β, or 0.002.

In parallel polarized light the double refraction of the plates is seen to be weak, and the colors are mostly brilliant grays of the first order. Rod-like fragments may show white or yellowish colors, corresponding to the maximum double refraction. The extinction is straight and the sign of elongation usually +.

In convergent polarized light, on thick plates, a good biaxial interference figure is obtained, the axial angle $2E_D$ being large, 85°, and the character, —. The orientation is $X = a$, $Y = b$ and $Z = c$.

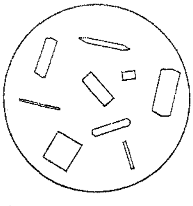

Fig. 2.—Melezitose under the microscope.

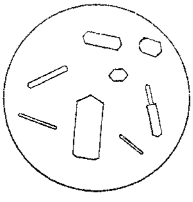

Fig. 3.—Glucose under the microscope.

Certain of these properties, especially the habit and the weak, double refraction, may be turned to account in the identification of this sugar in honeys or honey-dews. The *d*-glucose which frequently crystallizes out in honeys is in rods terminated at one end by planes lying 60° apart and rounded at the other end (Fig. 3); and in parallel polarized light showing at least in the centers of the grains brilliant colors of the second order, with — elongation. If the sirupy honey is removed from around these crystals by glacial acetic acid and the refractive indices are determined by the immersion method, the α of *d*-glucose is found to be about one unit in the second decimal place lower than that of melezitose, and the γ a like amount higher. Sucrose can also be readily distinguished from melezitose by its much greater double refraction, α being 1.45 and γ 1.57, and by breaking into irregular fragments with oblique extinction.

It is believed that this method of examination of the crystals which develop in honeys will be of much aid in the systematic search for the occurrence of melezitose.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE PREPARATION OF PARA-UREIDO-PHENYLACETYLUREA, AND RELATED COMPOUNDS.

BY MARY RISING.[1]

Received October 20, 1919.

A study of the preparation of ureido-phenylacetylurea was begun by the author, with the aid and advice of Professor Stieglitz, following the publication some time ago of the work upon the synthesis of phenylethyl-barbituric acid.[2] Phenylethyl-barbituric acid (luminal), widely used in the treatment of epilepsy, has hypnotic and sedative properties. Under certain conditions, the drug is known to have a toxic effect, and for this reason its use cannot be prescribed in all cases. With time of peace at hand, when there is leisure to work along lines of theory, rather along those laid down by the imperative demands of war needs, the building up of a new series of compounds, related chemically to phenylethyl-barbituric acid, was undertaken. The effort has been made to retain in these compounds the excellent hypnotic properties of phenylethyl-barbituric acid, avoiding meanwhile those properties which are harmful. The compounds prepared in this way are to be thoroughly tested physiologically, in the hope of discovering a hypnotic of even greater value than is phenylethyl-barbituric acid.

The fact that phenylethyl-barbituric acid possesses toxic properties which are not possessed by the closely related compound, diethyl-barbituric acid, suggested the toxicity of the phenyl group. For the modification of the phenyl group, we have first tried the introduction in the phenyl radical of a urea group, which might at the same time enhance the hyp-

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[1] The material given in this report will be included in the dissertation of the author in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

[2] Rising and Stieglitz, THIS JOURNAL, 40, 4, 725 (1918).