Habit Modification of Sucrose Crystals

A Lecture

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INTRODUCTION

Variations in the shapes of sugar crystals must have been noticed since the earliest days of sugar boiling. Differences in form were probably more pronounced then than now since the progress of crystallization was certainly less carefully controlled. The differences can be demonstrated readily by evaporation on a microscope slide or by slow cooling of still stronger syrups. In such preparations there appears to be a normal shape but, aside from differences in size, closer scrutiny usually reveals deviates in the form of platelets, needles, pyramids, etc. Contact with the container surfaces, modified procedures and especially additives cause such variations to a marked degree.

Harold Powers (24) has amply developed this theme for pure sugar solutions as well as the pronounced influence of non-aqueous solvents and other added components. Buckley (6) treats the subject exhaustively for the general case in a lengthy chapter in his book on Crystal Growth and, most, recently, Berkovitch-Yellin (3) at the Weizmann Institute has inaugurated a significant series of papers on the Sterospecific Habit Modifications on Chiral Crystals. Gabor Vavrinecz in his Atlas of Sugar Crystals has (37) compiled a virtual Bible for the sugar crystallographer while Max Smythe (30), Frank Kelly (15), George Mantovani (18), Harold Powers (24), Kamoda (14) and Delavier (9) are only a few of the many sugar technologists who have turned their attentions to this subject in recent years. Its importance is further attested by having been included in the agenda of ICUMSA*

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since 1966. This especially has served to focus attention on the subject and one of the purpose of the present discourse will be to mention what the writer considers some of the major unsolved problems in the field.

At the factory level such matters are important because habit modifications frequently occur when growth rates are impeded by impurities; which same impurities may enhance viscosity with its problems. Altered shapes behave awkwardly in purging and packaging and such factors interrupt normal smooth production and thus shape as well as size becomes important.

CLASSIFICATION

While most of the crystals in any particular strike may look alike, aside from differences in size, there are usually individuals which appear to differ in being disproportionately elongated, thinner, etc. The properties of such irregularities may differ considerably in repeated trials and when excessive create a problem for the sugar boiler. In addition he must be on the watch for conglomerates and twin formations as well as eroded and fragmented crystals. These are separate but related problems but will not be considered here. Neither will the formation of dendrites, spherulites, rosettes, etc. These are met more frequently in laboratory work and have been described in great detail by Powers (25) in a series of communications.

Aside from this, Vavrinecz classifies single sucrose crystals morphologically as follows:

A. Simple or normal of stout-prismatic form.
B. Needles, elongated along the b-axis.
C. Those elongated along C.
D. Platelets on a, (100)
E. " on c, (001)
F. " on d, (101)
G. " on r, (101)
H. Biphenods
I. Triangles and pentangular shapes.

Most of the examples illustrated in his Atlas were se-
lected from factory product but there are some laboratory specimens from syrups of designated composition.

The thickness (a), length (b), and width (c) of the crystal depicted in Fig. 1 describe the essential features of form. Day (8), amongst others (17), points out that five measurements are necessary to completely account for the shapes but the three depicted here are satisfactory for most ordinary purposes.

Real, normal crystals from pure syrups are more apt to have axial ratios closer to $\frac{1}{b}a: \frac{1}{c}b: \frac{1}{c}c$ rather than the ideal unity. Actual lineal dimensions are, in the writer's experience, $(.4-5) : 1 : (.5-7)$. This spread covers a large variety of single and batch crystals but often still higher or lower values are observed. In one set of 25 arbitrarily selected "normal" crystals, for instance, $(.45\pm0.07) : 1 : (.56\pm0.06)$ was realized. Other investigators report similar ratios and dispersions.

![Figure 1. The normal sucrose and its unit cell.](image)

Unit Cell

- $a = 10.80\AA$, $b = 8.70\AA$, $c = 7.74\AA$
- $c' = 1.0284c$
- $a' = 1.25 \cdot a$
- $b' = 0.89 \cdot b$
- $\beta = 103^\circ$
- $Z = 2$
- $c' = 1.0284c$

Right Pole, ac, View

- $\ell = \text{lengths of prism intersection}$
- $c = \text{perpendicular to } c(100)$
- $c = \text{pinacoids}$

Figure 1. The normal sucrose and its unit cell.

In pronounced cases of modified crystals, considerable differences from these ratios are noted as, for instance, $06 : 1 : .50$ in the presence of raffinoise (13)\(^*$

\(^*$Hungerford and Nees 13 point out that unless growth is extensive these ratios should be computed from the increases in dimensions of a crystal growing from a seed rather than the demensions themselves (36).
It is these and other aberrations that will be considered here.

MECHANISM

Some basic information is first needed:

I. In the continued growth of a crystal it is the slow growing face which prevails. This is illustrated in the following simple 2-dimensional scheme (Figure 2) using an ordinary square. If the several faces progress at the same pace, as in (a), the form is preserved, but if the vertical faces advance slower than the horizontal ones, the vertically elongated rectangle (b) results. When the opposite is the case, as in (c), the elongation is horizontal.

Figure 2. The slow growing crystal face prevails.

II. The structure of a sucrose molecule as it appears in the crystal is represented in Figure 3. This structure was first worked out by Beevers and
Cochran (2) and the figure is adapted from their original paper and the projections offered by Prof. Mantovani to CITS in 1967. It shows not only the configuration of the atoms within the molecule but also their alignment in the unit cell.

The five membered ring in the lower right corner is the fructose (furanose) moiety of the molecule and the glucose (six membered pyranose) counterpart is immediately above it in this projection. The work of Beevers (2) has been refined to a high degree by Brown and Levy (5) as well as others (11). Equivalent presentation can be found in the writings of Max Smythe (30), Frank Kelly (16), George Cossairt (7) and many others.

It is immediately evident from the models that the right and left poles of the crystal differ and that packing along the a-axis is considerably weaker than along the other two. This concurs with the facts that ordinarily the dimensions of crystals grown from pure solutions are closer to the axial proportions of $\frac{a}{c} : 1b : 1c$ and that the cleavage plane is parallel to the a face. Hydrogen bonding is rife in both solution and crystal (5, 20, 30) with only one of the seven operating across the bc plane. This may also be correlated to the occurrence of 2 molecules in the unit cell. The universal nature of this type of molecular force implies the possibility of adsorption and since this is anisotropic, just as in crystal itself, we can expect effects on growth rate and hence habit according to the degree of this interaction. The ac projection along the b-axis will be principally the prism ends, p(100), faces, and displays both pyranose and furanose ring. The ab projection, however, is predominately pyranose in nature on the c and rl faces while bc, or a faces, are more furanose in nature than pyranose—all suggestive of different polarities in the three major directions.

**SOME PARTICULAR CASES**

I. Raffinose
The ability of raffinose to promote needle grain is well known and documented (33). Its similarity to sucrose chemically, as d-galactosido sucrose, and to some extent structurally (5) both suggest the possibility of uniting with the host crystal, at least in part. Kelly (16) shows quite clearly how raffinose could stack most economically along the b-axxis, thus impeding growth transversally and leading to the familiar acicular crystals with enhanced girdle faces. The occurrence of raffinose throughout the doped crystal (see Figure 4) definitely indicated a strong chemisorbed condition in spite of overall crystallographic incompatibility (Table 1). Careful x-ray examination of slowly grown doped crystals did (33) not reveal any raffinose, and neither, with reservation, was special distortion noted in analogously dextran modified cases (26). However, "the occurrence of a few additional spots in the doped case indicated some distortion of the unit cell in the c-direction" (26). At an earlier data, Obá (22) had likewise observed some asterism in the Laue spots of commercial sugars and rock candy and these he attributed to strain and mosaic structure which could lead to changes in structural arrangement of the crystal lattice. Hence, reconsideration of this problem should be undertaken with more refined methods. The following rough calculation indicates that it will be a challenging, yet possible, task.

A typical doped crystal contains 0.3% raffinose on sucrose. At densities of 1.48 and 1.58, respectively, the latter corresponds to 7.1111Å per molecule in cubic array. If the volumes in the doped case are additive 7.1143Å would be the effective lattice distance. The difference of three thousands Å is just within reach of the standard error of 0.001 to 0.002Å in modern x-ray measurements.

The possibility of a hexamer arrangement of sucrose molecules in both crystal and solution could readily afford an openness in structure within which large molecules such as raffinose and dextran would easily be included.
Raffinose slows up the rate of advance of most all the faces of the sucrose crystal (10) but most strongly the r'(101) planes. A very revealing experiment would then be to grow a single crystal specimen in the presence of tagged raffinose (when it becomes available) and note any spatial distribution by means of radiautography. When this was done with tagged glucose, many years ago (34), preferential adsorption on the a-pinacoid faces was recorded.

As far as I know, galactose, like glucose and fructose in amounts equivalent to the raffinose from which they may be derived, does not exhibit the strong mellassigenic nature of its progenitor. Hence, the elimination of raffinose by selective fermentation ameliorates its obnoxious performance in beet processing.

II. Dextran

The influence of this material on the habit of sucrose has been studied about as assiduously as raffinose. It, too, causes crystal elongation but in the c direction rather than b-wise. This is the result of adsorption on the prism faces and this is understandable since as a polyglucoside with 1-4 carbon linkages it will attach differently than raffinose with 1-6 links. Kelly (16) discusses this difference in detail.

As already noted, Day (8), in Queensland, found dextran to be adsorbed throughout the crystal (Figure 4) but Robinson (20) did not find any special lattice distortion.

Another interesting thing about dextran is that its effect appears to be aggravated by other components as yet unknown. The group at the Audubon Sugar School have particularly noted this altho McCleery (21) many years ago suggested similar synergistic behavior in the formation of needle grain by high glucose content. Dextran alone caused only mild elongation but when added to molasses yields needle grain (28). Mantovani (19) reports a similar behavior when dextran with and without KCl is employed. It will be interesting to track down the culprit in the present instance.
Like raffinose, dextran can be eliminated by selective enzymatic hydrolysis.

III. Hexoses

Oddly enough, the influence of hexoses and their combination as invert on the crystallizing behavior of sucrose has not been completely described in detail and much remains to be done on these important systems (25).

Figure 4. Distribution of impurities through sucrose crystals.

When growth is slow invert is effectively rejected by the growing crystal, as illustrated in Figure 4, but as higher temperature and supersaturation lead to faster growth more and more invert is contained within the growing crystal. This may be the result of being physically rather than chemically adsorbed but may equally well be the result of merely being trapped as inclusions rather than being truly adsorbed as might be expected from the chemical similarity of these moieties. However, the crystallographic dimensions of these several sugars (Table 1) are so disparate that substitutional or epitactic growth would seem improbable in all these cases. On the other hand, the dimensions of these separate monosaccharides are quite compatible with the moieties as they occur in the sucrose unit cell (5). But again, on the same score, the uniform distribution of raffinose suggests its incorporation interstitially or a s-s solution in spite of its high degree of disregistry. Why this is not so with the simpler monosaccharides is an enigma to the writer. Maybe calculations of intermolecular faces such as Michael Suska has been doing at LSU (27) may throw light on this question.

At low concentrations and temperatures the effect of
hexosis on habit is minimal but at higher levels (---200I/100W) and temperatures (60-70°) dextrose tends to favor plate like growth (especially under quiscent conditions). Fructose, under these conditions definitely forms (1) triangles due to right end prism enlargement. At room temperature, and high glucose content, needles along c., Table 1. Crystallographic architecture of some sugars.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Unit Cell, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose-monoclinic</td>
<td>a: 10.89, b: 8.69, c: 7.77, β: 103°, Z: 2</td>
</tr>
<tr>
<td>D-glucose-anhydrous</td>
<td>a: 10.36, b: 14.69, c: 4.97, β: 90°, Z: 4</td>
</tr>
<tr>
<td>&quot;-monohydrate</td>
<td>a: 8.72, b: 5.03, c: 9.59, β: 97°, Z: 2</td>
</tr>
<tr>
<td>D-fructose</td>
<td>a: 9.12, b: 10.06, c: 8.06, β: 90°, Z: 4</td>
</tr>
<tr>
<td>Raffinose</td>
<td>a: 8.97, b: 12.33, c: 23.84, β: 90°, Z: 4</td>
</tr>
</tbody>
</table>

such as reported by McCleery (21), develop. These patterns may very well be the result of the different orientation of these moieties within the crystal. In the model

Figure 5. Sucrose crystal - schematic.

the dextrose component of sucrose lies essentially in the ab plane while the levulose half is approximately at right angles in the ac lane. If the corresponding faces advance by means of steps on these planes we would then expect dextrose impurity if adsorbed to impede extension in the a direction, with enlargement of this face, and levulose likewise regarding the c face (Figure 5). These are exactly the habit modifications observed when these impurities are present in the mother liquor although considerable amounts are needed to bring out marked changes.
It also seems not unlikely that this orientation may have something to do with the pronounced difference in ratios of advance of the right and left poles. This seems to be aggravated especially by the presence of fructose which overall appears to have more effect than glucose (9, 29).

High invert and corn syrups as well as honey are usually reluctant to crystallize even when seeded. If, however, the sucrose content is increased by saturation at a higher temperature they will then throw down all sorts of sucrose crystals including needles, blades, triangles, etc. Figure 6 is just one illustration of this unusual combination of triangles and elongated crystals caused from a fortified dark colored corn syrup. No doubt, the synergistic behavior referred to in Part II is operating here.

Figure 6. Triangles and elongated sucrose crystals deposited simultaneously from a fortified corn syrup.

Invert sugar is much more common in cane juices than beet and many attempts to avoid and reduce it, as well as utilize it for desugarizing molasses, have been proposed. However, I must confess I am unacquainted with the problem.

IV. Lactic Acid

I was recently asked if lactic acid had any special habit modifying effects. Not finding any reference to this substance in the voluminous literature on the subject I tried it out at a concentration of 1M., sodium lactate, which is about 3 times the extreme that may be expected. Nothing unusual was observed in the crop of crystals obtained. Neither did its addition to a cane molasses on hand exert any influence so, presumably, no synergistic
behavior was invoked, although it must be admitted that this is only a singular case.

Lactic acid stems from excessive alkalinity and temperatures in the early stages of juice treatment, so that careful monitoring these should minimize its formation as well as that of related derivatives.

V. Glycerol

When sucrose crystals are nucleated and grown in 10 to 30% aqueous glycerol no special habit modifications are noted. There is, though, about a 25% elongation of $b$ with respect to $c$ when the development is carried out in stronger glycerol, say 80-90%. This is similar to the needles grown by Bjerager (4) from seeds formed from supersaturated glycerol solutions.

ACKNOWLEDGMENT

The figures were made by my friends in the Biology Department; Susan Berman, the Madhavans and Joel Villa.

LITERATURE CITED


(17) Kelly, F.H.C., Sucrose Crystal Elongation. Z. Zuckerind. 27(3) 128.


