Habit Modification of Sucrose Crystals

A Lecture

Andrew VanHook *

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, pyra-
mids, 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 dis-
course 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 be-
cause 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 inter-
rupt 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 dis-
proportinately 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 conglome-
rates 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 communica-
tions.

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 ½a: 1b: 1c 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 arbitarily selected "normal" crystals, for in-
stance, (.45±07) : 1: (.56±.06) was realized. Other in-
vestigators report similar ratios and dispersons.
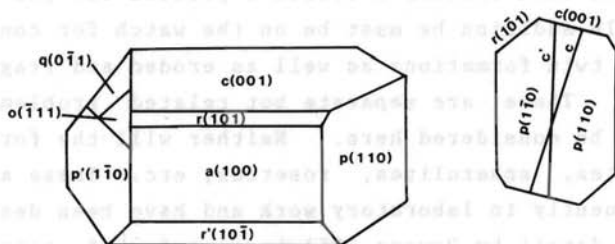
Unit Cell	Right Pole, ac, View
$a = 10.80\text{Å}$, $b = 8.70\text{Å}$, $c = 7.74\text{Å}$	c^1 = lengths of prism intersection
1.25 :1 :0.89	c = perpendicular to c(100) pinacoids
$\beta = 103°$ $Z = 2$	$c = 1.0284C^1$

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).

     - : 1: 1.50   in the presence of dextran (28)

    .2 : 1: .05   " "   "   " invert, etc (21)

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 elangation is horizontal.
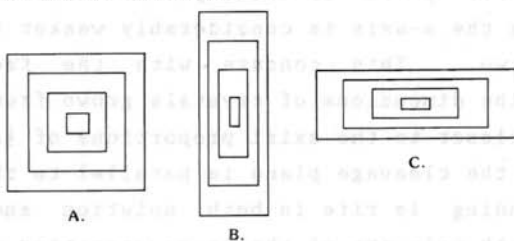

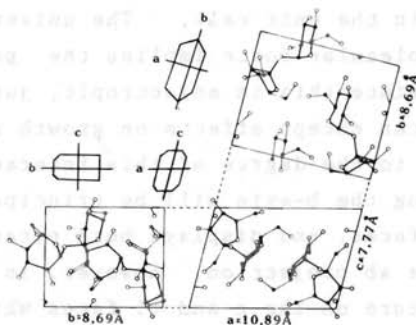Figure 2. The slow growing crystal face prevails.

Figure 3. Molecular structure of the sucrose crystal.

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 ½a : 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 except 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 occurence 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 occurence 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, Oba (22) had likewise observed some asterim 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 thr 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).
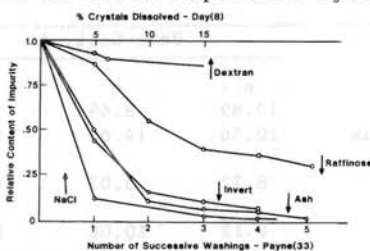

Figure 4.   Distribution of impurities through sucrose crystals.

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 interstitually 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 condi-
tions). 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.

	Unit Cell, A				
	a	b	c	β	Z
Sucrose-monoclinic	10.89	8.69	7.77	103°	2
-D-glucose-anhydrous orthorhombic	10.36	14.69	4.97	90°	4
"-monohydrate monoclinic	8.72	5.03	9.59	97°	2
D-fructose orthorhombic	9.12	10.06	8.06	90°	4
Raffinose pentahydrate orthorhombic	8.97	12.33	23.84	90°	4

such as reported by McCleery (21), develop. These pat-
terns may very well be the result of the different orien-
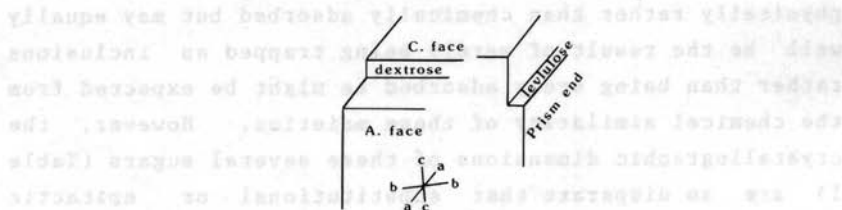tation of these moieties within the crystal. In the model

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 im-
purities are present in the mother liquor although con-
siderable 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.
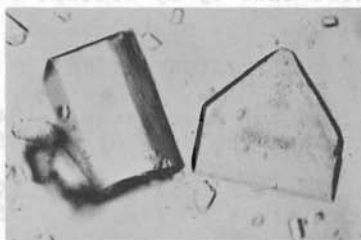

Figure 6.   Triangles and elongated sucrose crystals deposited simultaneously from a fortified corn syrup.

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.

Latic acid stems from excessive alkalinity and tem-
peratures 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.

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