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On the relations between morphological and structural modifications in sucrose crystals grown in the presence of tailor-made additives: effects of mono- and oligosaccharides

G. Sgualdino [a,*], D. Aquilano [b], E. Tamburini [a], G. Vaccari [a], G. Mantovani [a]

[a] *Dipartimento di Chimica, Università, via L. Borsari, 46, I-44100 Ferrara, Italy*

[b] *Dipartimento di Scienze Mineralogiche e Petrologiche, Università, via Valperga Caluso, 35, I-10125 Torino, Italy*

Abstract

A survey is given on morphological modifications induced on sucrose crystals by some tailor-made additives (mono- and oligosaccharides). Special attention is paid to a critical discussion of our analysis of the structure compatibility between additive molecules and surface sites of the crystals, and further of its developments concerning incorporation of additives in the crystal lattice. Finally, it is shown as X-ray powder diagrams of sucrose crystals grown in the presence of these additives, coupled with chromatographic analysis of crystal sectors, proved to be a promising sensitive tool, chiefly to associate the different lattice spacing variations to the absorption anisotropy.

Keywords: Sucrose crystal; Growth morphology; Tailor-made additives; Monosaccharides; Oligosaccharides; X-ray powder diffractometry

1. Introduction

The influence of additives and impurities in growth media has been recognised for a long time as a relevant matter in crystallisation processes. As far as sucrose crystals are concerned, the effects of both inorganic and organic additives on the growth kinetics and morphology have been extensively studied, also due to the commercial interest in improving the product quality. Sucrose crystals (Space Group $P2_1$) are polar, with the polar axis along the [0 1 0] direction. The growth morphology of sucrose, which is strongly dependent on the anisotropy of the growth rate of complementary forms (R_{hkl} and $R_{\bar{h}\bar{k}\bar{l}}$), reflects this property (Fig. 1a). Growth rate anisotropy is enhanced even by the presence of chiral additives in growth media and strongly affects habit and quality of commercial crystals. Monosaccharides (MS) and oligosaccharides (OS) are both technologically relevant chiral impurities in sucrose processing. Raffinose is the OS most extensively studied, due to the marked modifications induced on the sucrose crystal habit, when it is present even at low concentration (0.5–1 g/100 g H_2O) in the growth solutions [1–3]. However, other OS have been recognised as efficient habit-modifiers: gentianose [2], stachiose [1,2], the kestoses [2,4,5], theanderose [6]. Glucose and fructose (by-products of industrial sucrose) raise a peculiar question about the fact that their morphological effects, even if never as severe as that of raffinose, become macroscopically evident only if their concentrations in growth solutions are two order of magnitude higher than those of raffinose.

In this paper we will show as the correct development of the analysis of structure compatibility between the additive molecules and the surface sites of sucrose crystal may satisfactorily explain the habit-modifications induced by saccharides.

2. Adsorption and absorption models

The first step of our analysis was to consider the adsorption of additive molecules on the most significant polar and non-polar flat (F) forms of sucrose crystals, having adopted the classical TLK (surface, ledges, kinks) surface model and the atomic interactions confined to the nearest neighbours (H-bonding). The adsorption energies were estimated by the broken bond method. In the growth models, adsorption on such a surface affects generally both thermodynamic (specific surface or edge energy, γ or ρ) and kinetic (step advancing rate, v_s) parameters of the displacement rate, R_{hkl}, of the (*hkl*) face of a crystal [7,8]. Both kink poisoning and 2D-coverage of the terraces with ad-molecules reduce v_s; the same molecules adsorbed on edges decrease ρ, so increasing R_{hkl} [7,8]. From the above, it follows

* Corresponding author. Tel.: +39-532-291171; fax: +39-532-240709.
E-mail address: vcg@ifeuniv.unife.it (G. Sgualdino).

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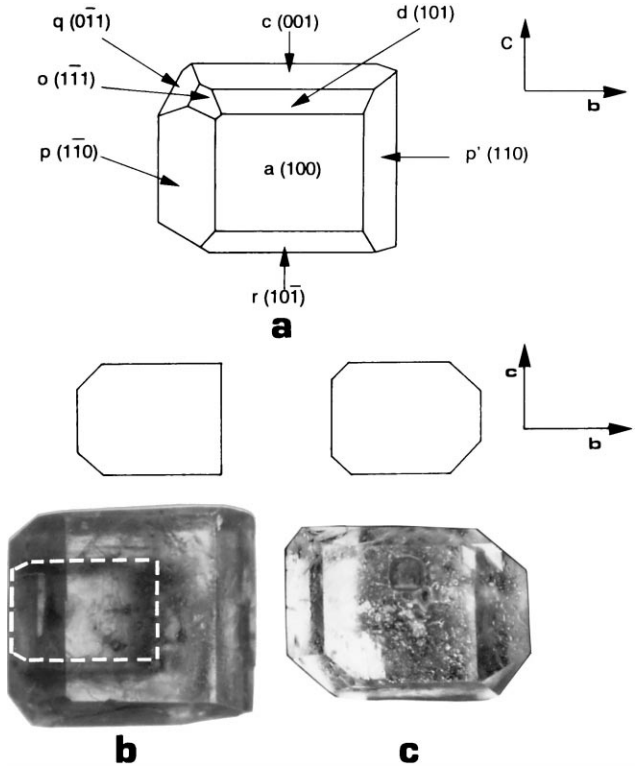

Fig. 1. Growth habits of sucrose crystals: (a) schematic drawing of the "standard" habit, showing important forms; (b) crystal grown in the presence of 150 g glucose/100 g H_2O, dashed white lines define the seed — $\{\bar{1}\,\bar{1}\,0\}$ form is stopped; (c) crystal grown in the presence of 150 g fructose/100 g H_2O — the habit is more symmetrical with respect to the (*ac*) plane, because of the slowing down of the growth rate of $\{0\,1\,1\}$ and $\{1\,1\,1\}$ forms.

that the theoretical growth models predict opposite effects for the impurity adsorption on growth kinetics. However, a highly non-equilibrium process, like crystal growth, is much more affected by kinetic factors than thermodynamic ones.

The second step was to examine the behaviour of additive molecules entered into sucrose lattice, distinguishing between disruption and blocking tailor-made additives [9,10] for MS and OS, respectively. Finally, the results of our analysis were evaluated through the discussion of planar chromatographic densitograms and/or X-ray powder diffractograms (XRPD) of sucrose crystals grown in the presence of saccharides.

2.1. Monosaccharides

Experimental evidences [11,12]: (i) Glucose mainly slows down the growth rate of the left pole faces, until stopping the $\{\bar{1}\bar{1}0\}$ forms (Fig. 1b). (ii) Fructose cannot stop the growth of any form, but reduces very strongly the kinetics of $\{0\,1\,1\}$ and $\{1\,1\,1\}$ (Fig. 1c). (iii) All effects become evident at very high concentration of both MS (>50 g/100 g H_2O) and increase with concentration.

Structures and conformations: (i) Glucose: α-D-glucopyranose ring with $^4C_1$ chair conformation and gauche–gauche orientation of the primary hydroxyl group O(6)-H (for adsorption and absorption analysis). (ii) Fructose: β-D-fructofuranose ring with $^4T_3$ conformation and gauche–gauche orientation of primary hydroxyl group O′(6)-H, while the O′(1)-H is *trans*-gauche (for adsorption analysis); β-D-fructofuranose ring with $^2C_5$ chair conformation (for absorption analysis). Hence, about adsorption, we referred to two molecular model similar to the α-D-glucose and β-D-fructose residues, separately maintaining the same H-bonds with the substrate as when they are combined in the sucrose molecule [13]; these conformations assure the lowest potential energy for ad-molecules because the highest number of H-bonds is formed. Since the configuration inversion on the anomeric carbon atoms of MS (mutarotation) does not offer new H-bond with the substrate, we can correctly speak of glucose and fructose without further specifications.

Results of the adsorption analysis: On the whole, fructose shows more affinity with the substrate with respect to glucose, due to the higher number of H-bonds formed, but its selectivity is lower. However, for the pair of complementary $\{0\,1\,1\}$ and $\{0\,\bar{1}\,\bar{1}\}$ forms only, the kink selectivity of fructose is very high, because three kinks out of four can be poisoned on $\{0\,1\,1\}$, whereas no poisoning occurs on $\{0\,\bar{1}\,\bar{1}\}$. Energetic competitions between the molecules of sucrose and MS entering a kink follow the sequence: sucrose, fructose, glucose, owing to the different number of H-bonds linking up with the substrate.

The kink poisoning and the hindrance to the spreading of the growth step on the substrate faces from the ad-molecules were proposed to be the mechanisms involved in changing the growth habits. Model and results are deeply discussed in [14,15]. They show that the adsorption analysis, accounting for both geometry and adsorption energy of the different sites of specific crystallographic forms, satisfactorily agrees, in spite of its roughness, with experimental growth habit of impure sucrose crystals. Notwithstanding, it cannot answer three fundamental questions at least:

- why so high MS concentrations are necessary to induce macroscopic habit-modifications?
- why growing is not stopped even if 75% of $\{0\,1\,1\}$ kinks are poisoned by fructose?
- how so high MS concentrations can be consistent with a kink poisoning mechanism?

Absorption model: Temporarily setting aside the simple adsorption model, we considered the behaviour of MS incorporated in the sucrose crystal (absorption model) [14,15]. With this approach, we tried an extension of the classical morphology modelling techniques (based on the correlation between bulk structure and crystal morphology) to impure sucrose crystal too. To do that, we considered MS as disruption tailor-made additives. These are habit-modifiers, the molecules of which are slightly different and smaller than those of the host crystal. When they are adsorbed, during

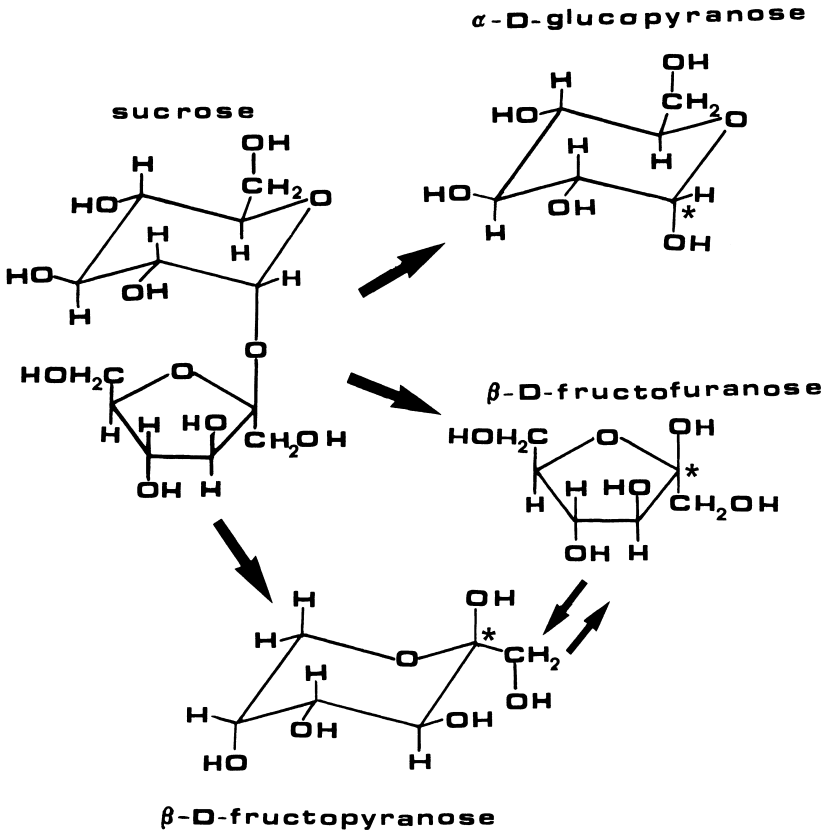

Fig. 2. Schematic drawing of the splitting of sucrose into α-D-glucose and β-D-fructose; the equilibrium in solution between the two most important fructose forms is represented; stars stay for anomeric carbons.

the growth, onto specific surface sites and then incorporated, they are able to modify the proper intermolecular bond sequence within the crystal lattice. In this way the additive molecules can affect both attachment (E_{att}) and slice (E_{sl}) energies, thus working as habit-modifiers. Then we evaluated, by means of the PBC analysis [16], the stability of the $\{\bar{1}\,\bar{1}\,0\}$ and $\{0\,1\,1\}$ slices of sucrose crystal containing a molecule of glucose and fructose, respectively, instead of a sucrose molecule. The results obtained in the two cases were different. The strong F character of $\{\bar{1}\,\bar{1}\,0\}$ is only little weakened by glucose, maintaining the slice flat. The layer by layer growth can go on, unless the fraction of poisoned sites becomes sufficient to disrupt the lattice, thus hindering the regular incorporation of sucrose molecules coming from solution. First, the growth of $\{\bar{1}\,\bar{1}\,0\}$ form is slowed, then stopped. Such a condition needs a glucose concentration, in the growth solution, much higher than that determining the simple kink poisoning mechanism. The history of fructose inside $\{0\,1\,1\}$ slice is different. Both PBCs [1 1 1] and [1 0 0], determining the flat profile of $\{0\,1\,1\}$, are interrupted by the absorption of a fructose molecule in fructofuranose form: hence, the absorption of few fructose molecules should be sufficient to induce a flat → rough profile transition, so that the $\{0\,1\,1\}$ forms should disappear from the growth habit, quite the opposite of the experimental evidences. On the contrary, these are consistent with an adsorption mechanism where a couple of fructose molecules enter a kink, the former as fructofuranose, the second as fructopyranose. Both forms are available in the impure growth solution, where they are in equilibrium (Fig. 2). This couple replaces rather well a sucrose molecule in the same kink site; indeed the $\{0\,1\,1\}$ slice gains four H-bonds for each couple of kinks A (+) and B (−) filled by fructose. The value of E_{sl}, in the sense of Hartman-Perdok [10], increases, while that of E_{att} decreases: $R_{0\,1\,1}$ is lowered with respect to that in the pure sucrose solution and then its morphological importance is enhanced. This absorption model accounts clearly for both the experimental high values of fructose concentration needed for the appearance of $\{0\,1\,1\}$ on the growth habit and the fact that it cannot be stopped. Moreover, the former fructose as fructofuranose assures the adsorption anisotropy, according to the simple adsorption model.

2.2. Oligosaccharides

Here, we discuss chiefly some isomer trisaccharides (raffinose, 1-kestose and *neo*-kestose), the effects of which are well described [1–5,17].

Experimental evidences: (i) Raffinose strongly affects the kinetics of all the most important F forms of the sucrose

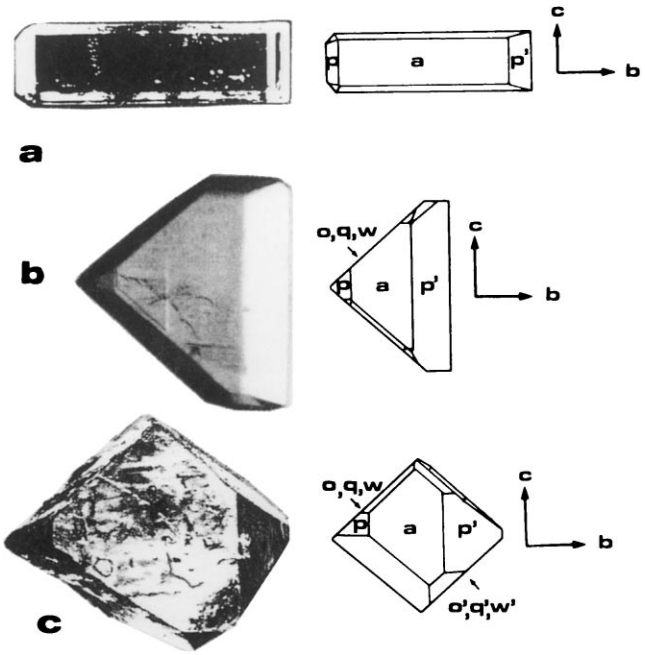

Fig. 3. Sucrose crystals grown in the presence of: (a) raffinose; (b,c) *Actilight*® (see text).

crystal, but the polar $\{\bar{1}\,\bar{1}\,0\}$, even at low concentrations, so that the simple growth habit of Fig. 3a can be obtained; moreover, it causes rounding of the polygonised spiral macrosteps on $\{1\,0\,0\}$ forms of sucrose [1,3,17]. (ii) We observed that a commercial mixture of 1-kestose, *neo*-kestose together with other fructo-oligosaccharides (*Actilight*® [1]) induced the quite unusual "rhombic" growth habit showed in Fig. 3c, when it is present in the growth solutions [4,5]. Strong effects promoted on $\{\bar{1}\,\bar{1}\,0\}$, $\{0\,1\,1\}$ forms by 1-kestose and on $\{1\,0\,0\}$, $\{1\,1\,0\}$, $\{0\,\bar{1}\,\bar{1}\}$ forms by *neo*-kestose alone were already documented during the 1960s [2] (Fig. 4).

Structures and conformations: The three trisaccharides contain a sucrose moiety, linking an α-D-galactose unity or a β-D-fructose unity through an O-glycosydic (6→1) bond in raffinose and *neo*-kestose, respectively, whilst a β-D-fructose unity is linked through an O-fructosydic (1→2) bond in 1-kestose (Fig. 5). The conformation of the glucopyranosyl (1→2) O-β-D-fructofuranosyl bond, which determines the overall shape of the sucrose component within the OS molecules, is characteristic for each of them [18]. We did not carry out however the adsorption analysis making use of real OS structures, but of models of OS molecules, the sucrose moieties of which had the same conformation as that of the true sucrose molecule. When such ideal molecules were adsorbed onto a surface site of the sucrose crystal, their sucrose moieties can wholly replace a sucrose molecule, whilst the MS rings, emerging from the surface, prevented the adsorption of new growth molecules arriving from solution. Hence, OS behaved as "blocking tailor-made additives".

Results of the analysis: Summarising, the structure compatibility, coupled with ex- and in-situ kinetic measurements during the sucrose growth from impure solutions [3,17], improved the previous knowledge on the raffinose effects [1,2]. Indeed, progressive adsorption in the kinks of the most important F forms, but $\{\bar{1}\,\bar{1}\,0\}$, as well as the shape transition of growth spirals, were shown to be consistent with experimental evidences. Minor complementary F forms $\{0\,1\,1\}$, $\{0\,\bar{1}\,\bar{1}\}$ and $\{1\,1\,\bar{1}\}$, but $\{\bar{1}\,\bar{1}\,1\}$, can adsorb raffinose in their kinks too. Unfortunately, the disappearance of $\{0\,\bar{1}\,\bar{1}\}$ from the growth morphology of sucrose crystals grown in the presence of raffinose seems testify against the kinetic poisoning mechanism. However, *neo*-kestose, where the fructofuranose unity replaces galactose, does work as habit-modifier just as foreseen by adsorption analysis, i.e. it stops the growth of $\{0\,\bar{1}\,\bar{1}\}$ too (Fig. 4a). Finally, the structural compatibility well explains the inversion of the distribution of the active surface adsorption sites in the case of 1-kestose, which modifies the growth morphology (as drawn in Fig. 4b), because of the fructofuranosyl (1→2) O-β-fructofuranoside bond location (Fig. 5).

The evidences during the growth process of sucrose crystals in solutions containing *Actilight*® [4,5] raised a deeper discussion. Just to begin with, we remark that the rhombic habit showed in Fig. 3c was the end-form of a sequence of intermediate growth shapes. At first, small

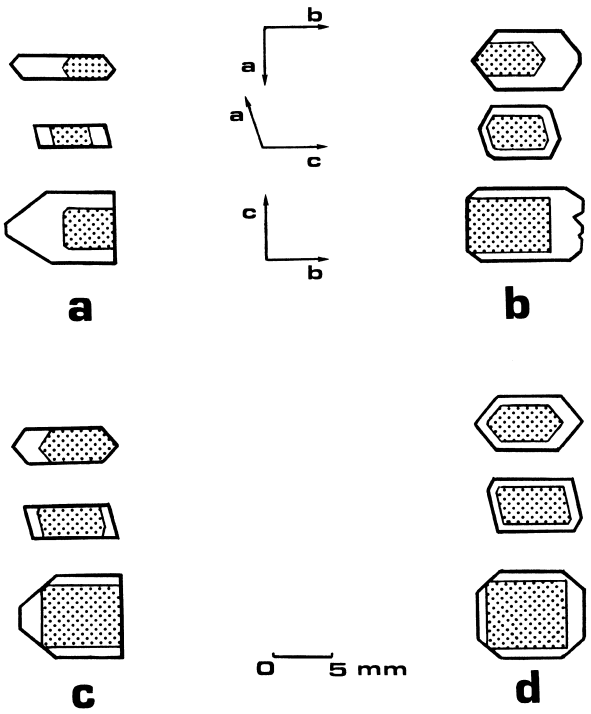

Fig. 4. Schematic drawings illustrating growth habits of sucrose crystals modified by: (a) *neo*-kestose (20 g/100 g H_2O); (b) 1-kestose (20 g/100 g H_2O); (c) *neo*-kestose+1-kestose (1:1); *neo*-kestose+1-kestose (1:5).

[1] *Actilight*® composition: nystose 50%, 1-kestose 35%, *Fructosyl*-nystose 10%, *neo*-kestose 3%.

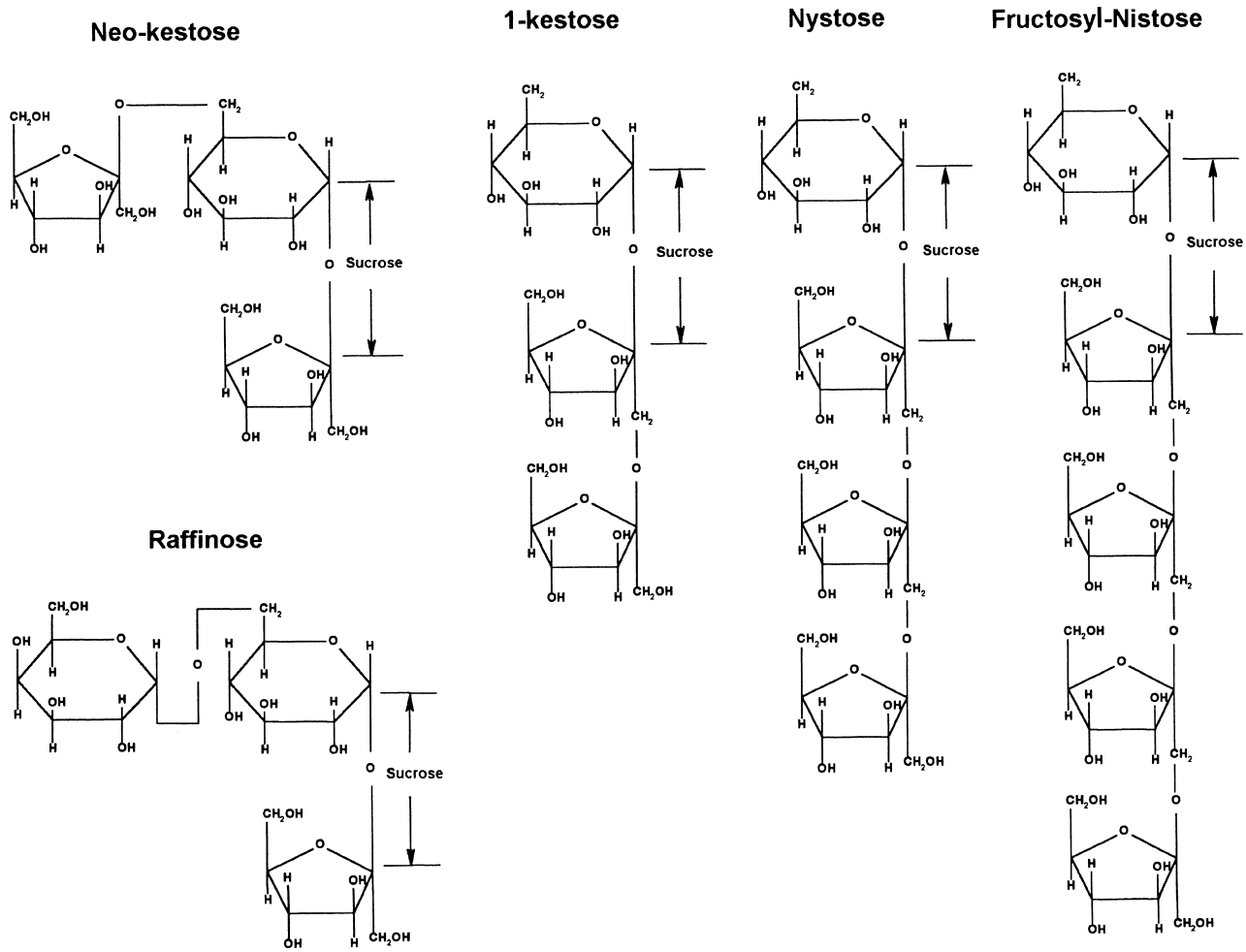

Fig. 5. Structure formulas of the oligosaccharides considered in this paper (see text).

crystals (≈100 μm in size) nucleated and grown in the presence of *Actilight*® (80 g/100 g H_2O) showed a triangular habit, characterised by very large $\{0\,\bar{1}\,\bar{1}\}$, $\{1\,\bar{1}\,\bar{1}\}$, $\{\bar{1}\,\bar{1}\,\bar{1}\}$ forms and small $\{\bar{1}\,\bar{1}\,0\}$ (Fig. 3b). Both sucrose single crystals and twins, grown under controlled conditions from well prepared seeds, showed a similar behaviour, even at *Actilight*® concentrations one order of magnitude lower [4]. These very strong habit-modifications can be explained on the ground of combined selective adsorption of 1-kestose and *neo*-kestose in the aforementioned way, if we postulate for both the kestoses a synergistic effect on the $\{0\bar{1}\bar{1}\}$ form and a competition on the right pole forms, the latter effect becoming effective only when 1-kestose is in large excess (Fig. 4c and d). Besides we believe *neo*-kestose to be the most powerful habit-modifier in *Actilight*®, where its concentration is only one tenth of that of 1-kestose. Then, in growth solutions containing 8.0 g/100 g H_2O of mixture, the concentration of *neo*-kestose is about 0.25 g/100 g H_2O , or rather 5×10^{-4} mol/100 g H_2O, value at which a kink adsorption mechanism allows so strong morphological effects. On the other hand, the triangular transient habit of the smallest growing crystals can be justified by the fast slowing down of the rate of the involved forms, which is consistent once more with a very effective kink poisoning from *neo*-kestose. Another consideration at least supports our hypotheses. Careful chromatographic analyses on whole impure sucrose crystals or sections cut from their right and left poles showed clearly preferential incorporations of *neo*-kestose with respect to 1-kestose from the whole crystal and in particular from the right pole forms: here, the value of the 1-kestose/*neo*-kestose ratio changes from 10 in solution to 0.7. As a matter of fact, the crystal also incorporated a low quantity of nystose, while it rejected *fructosyl*-nystose. Since such incorporation was nearly isotropic, this tetrasaccharide cannot work as habit-modifier. Now it is worth noting that all the OS, aforementioned in the introduction as powerful habit-modifiers of the sucrose crystal, are incorporated in the host lattice at higher concentrations than in the growth solutions, so that a positive segregation always occurs. Furthermore, their molecules always contain the sucrose nucleus linking one or more MS unities through the O-glycosidic (6→1) α or β bond. Relations between incorporation and habit-modification power were already suggested for ionic species [19]. Finally, we point out that we observed rounded

growth spirals on $\{1\,0\,0\}$ forms, just like those spreading on the same forms of sucrose crystals grown in the presence of raffinose. From the above, *neo*-kestose is seen fitting well into the behaviour of the strongest habit-modifiers.

At the moment we are not able to propose well-founded mechanisms to elucidate either the OS incorporation in the lattice of sucrose crystal, or the competition between *neo*-kestose and 1-kestose on its right pole forms. We limit ourselves to point out the peculiar character of the (6→1) linkage in raffinose allowing a relatively open structure, with the galactose moiety directed away from sucrose group; in this way both ends of the molecule can form H-bonds with other molecules [20].

Since raffinose appeared to be inefficient on the kinetic of $\{0\,\bar{1}\,\bar{1}\}$ form, two possibilities can be now suggested:

1. the heavy water adsorption on such form, due to the high surface density of polarisable fructose moieties, enables the dominance of the surface diffusion growth mechanism [21]. Hence, the desolvation of a raffinose molecule entering the 2D-growth layer could be so slow (at room pressure and temperature raffinose crystallises with five water molecules) that sucrose molecules competing with it are the winners during the surface diffusion. Such a competition on the right pole forms turns in favour of raffinose, because it occurs within the framework of a growth dominated by volume diffusion;
2. steric and/or energetic conditions could allow the growth of the $\{0\,\bar{1}\,\bar{1}\}$ form with incorporation of raffinose within its growth sector, made easier by the (6→1) linkage.

3. X-ray analysis: modification of the bulk structure of doped sucrose crystals

We obtained some X-ray powder diagrams from sucrose crystals grown in the presence of MS and OS with the aim both to check our conclusion about the anisotropy of impurity absorptions and to attain experimental insights into the nature of the host lattice changes [4,5,14,15]. On the whole, both asymmetry and splitting of the profiles corresponding to important diffraction peaks were observed in the XRPD spectra; tail drifts and new maxima were always shifted towards lower 2θ values. Then, to understand the structure of the modified peak profiles, they were decomposed in symmetric elementary curves: the profile corresponding to the expected equidistance d_{hkl} can be generally fitted by a couple of elementary curves, the component at lower d_{hkl} corresponding to the diffraction from the pure crystal, the other at $(d_{hkl}+\Delta d_{hkl})$, larger and less intense, to the diffraction from the *hkl* planes population deformed by the additive inclusion in the $\{hkl\}$ growth sector (Fig. 6). The volume change of the elementary cell was inhomogeneous with respect to its edges, and hence, we can exclude absorption of the additives as components of a solid solution. However, differences between XRPD patterns of sucrose crystals incorporating *Actilight*® components and those incorporating MS components need to be highlighted. In the former case, we found $\Delta d_{0\,1\,1} = \Delta d_{\bar{1}\,1\,1} = 0$, i.e. no splitting for $0\,1\,1$ and $\bar{1}\,1\,1$ reflections. Hence, the distance $d_{0\,1\,1}$ and $d_{\bar{1}\,1\,1}$ was constant despite of fructo-oligosaccharides incorporated into the crystal during the growth. $1\,1\,1$ reflection showed on the contrary $\Delta d_{1\,1\,1}\neq 0$, as a consequence of the incorporation into growth sectors of $\{1\,1\,1\}$ form. Since the forms which are not sensitive to incorporation were strongly affected by *neo*-kestose and 1-kestose, we deduced that we dealt with a mechanisms of temporary adsorption for such forms, whereas adsorption and further absorption of OS occurred for $\{1\,1\,1\}$ form. The reasons of such a different behaviour is not clear, but it can probably be related to the stepped (S) character of $\{1\,1\,1\}$ form. On the other hand, in the case of MS, Δd_{hkl} can roughly be divided into two classes centred around two mean values, the higher of which corresponds to F forms, whilst the lower to S forms.

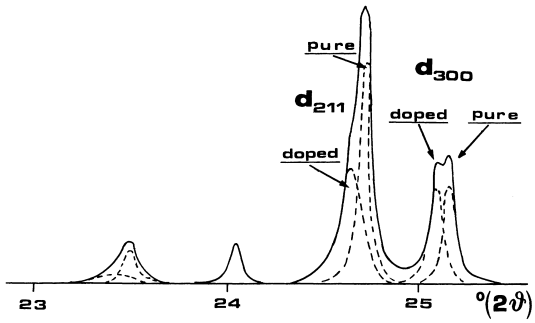

Fig. 6. Decomposed X-ray powder pattern (λ=Cu Kα_1) of sucrose grown in the presence of *Actilight*® (0.83 g/100 g H_2O), in the range $23^\circ<2\theta<25.5^\circ$. Diffraction peaks of spacing $d_{2\,1\,1}$ and $d_{3\,0\,0}$ show the profile splitting due to contributions of both pure and doped crystal regions.

4. Conclusions

The improved analysis of additive adsorption at kinks, edges and terraces, considered in the framework of surface and volume diffusion theories of crystal growth from solutions, correlates rather well much of the morphological and structural modifications induced by tailor-made additives as MS and OS. However it would be little realistic to claim that the foregoing discussion may offer a quantitative proof of the general validity of this approach, but it is undoubtedly attractive in its physical simplicity and plausibility. Another significant aspect of this method is that it is able to suggest guide-lines for its own improvement without rejecting the bases on which it is founded. For instance, to get over the open questions previously raised, we have to deal with quantitative aspects such as proposing a model for the adsorbed layer (ad-sucrose, ad-water, ad-MS and ad-OS molecules) which considers water interactions, as well as obtaining relationships between supersaturation and growth rates in the

impure solutions (growth isotherms), which are an unavoidable tool for investigations on the rate determining kinetic processes [21].

Finally, XRPD patterns proved to be a promising sensitive tool not only to measure variations in elementary cell volumes induced by the incorporation of impurities, but also chiefly to associate the absorption anisotropy to the different lattice spacing changes.

Acknowledgements

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