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Influence of growth temperature on the structure and thermodynamic parameters of barley starches

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Abstract

Barley starches grown at different temperatures were investigated using high sensitivity differential scanning microcalorimetry and X-ray diffraction. By applying physico-chemical approaches, thickness of crystalline lamellae, thermodynamic and structural characteristics (such as gelatinisation) of cooperative units and parameters characterising thermodynamic properties of crystal surfaces were determined. It was established that a difference of growth temperature experienced by plants during development does not lead to changes in the thickness of amylopectin crystalline lamellae and hence constituent double helix length. The role of defects in structural organisation of native barley starches is discussed. It is suggested that not all fatty acids necessarily form crystalline inclusion complexes.

Keywords: Starch; Gelatinisation; Melting; Crystallinity

1. Introduction

Within Europe and America barley as well as wheat, rye and pea are considered as perspective sources of starch for industry (Andreev, 2001; Banks & Muir, 1980; Batchelor et al., 1996; De Baere, 1999; Shannon & Garwood, 1984; Vasanthan & Bhatty, 1996; Wang, Bogracheva, & Hedley, 1998). Naturally occurring barley starch typically contains around 26% amylose although a broad range of amylose and amylopectin contents are known in mutant lines of diploid species (Andreev, 2001; Banks & Muir, 1980; Morrison, Scott, & Karkalas, 1986; Tester, 1997; Tester, South, Morrison, & Ellis, 1991; Vasanthan & Bhatty, 1996; Yuryev, Kalistratova, Soest, & Niemann, 1999). In particular, barley starches can be obtained with amylose contents in the range of 1–10% (waxy) to 35–40% (high amylose). Irrespective of amylose content, barley starch granules are comparable in dimension and size distribution as wheat and rye starches (Andreev, 2001; Contado & Dondi, 2001; Farmakis, Sakellarali, Koliadima, Gavrili, & Karaiskakis, 2000; Vasanthan & Bhatty, 1996). The functional properties of the starches depend on the amylose content and the size distribution of granules (Andreev, 2001; Tester, 1997; Vasanthan & Bhatty, 1996; Zobel, 1988a,b). Additionally, at present it has been found that an environment and soil temperature in particular, also influences functional properties (Tester, 1997; Tester & Karkalas, 2001)—especially the gelatinisation (melting) temperature of starches (Tester, 1997). The exact nature of the phenomenon remains incompletely understood.

Existing concepts concerning an influence of growth temperature on the structure and the properties of starches are based, in general, on the analysis of the thermodynamic data by means of different physical and physico-chemical approaches (Bershtein & Egorov, 1994; Privalov & Khechinashvili, 1974; Yuryev, Wasserman, Andreev, & Tolstoguzov, 2002). It is apparent that the ‘two-state’ model of Privalov and Khechinashvili (1974) that describes the melting process of biopolymers and especially waxy and normal starches (Andreev, Kalistratova, Wasserman, & Yuryev, 1999; Matveev et al., 2001; Protserov, Karpov, Kozhevnikov, Wasserman, & Yuryev, 2001; Yuryev et al., 2002). The application of the model allows for the determination of the cooperative melting unit of starches and the thickness of crystalline lamellae. In addition, the Thomson–Gibbs' equation (Bershtein & Egorov, 1994)

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Table 1
Amylose content and thermodynamic (melting) parameters of barley starches grown at different temperatures

Genotype	Growth temperature (°C)	Total amylose content (%)	T_{crl} (K)	ΔH_{crl} (kJ mol^{-1})	ΔH^{vH} (kJ mol^{-1})	ΔT_{crl} (K)	T_{alc} (K)	ΔH_{alc} (kJ mol^{-1})
Waxy Oderbrucker (waxy)	7	nd	316.8	1.9	29.6	10.4	363.0	0.8
	10	3.6–4.9	324.3	2.5	31.9	12.7	366.3	0.3
	13	nd	327.5	2.7	36.2	10.7	365.3	0.4
	15	2.3–5.7	328.0	2.6	38.1	9.3	365.0	0.4
	16	nd	329.7	2.8	40.6	8.8	366.2	0.3
	20	5.1–6.7	333.0	2.8	39.5	7.1	366.8	0.3
Golden Promise (normal)	7	nd	314.7	1.2	22.5	12.7	362.6	0.9
	10	25.9–28.2	320.9	1.9	26.6	14.2	365.9	0.7
	13	nd	323.5	2.1	29.3	13.1	366.8	0.7
	15	26.6–27.4	325.5	2.0	30.8	11.2	366.8	0.8
	16	nd	327.2	2.2	37.3	8.96	367.4	0.7
	20	24.9–28.0	330.9	2.1	37.4	9.0	367.6	0.8
Triumph (normal)	7	nd	315.0	2.3	–	21.9	361.4	0.5
	10	24.8–28.2	320.8	2.4	28.9	16.9	365.2	0.3
	13	nd	325.0	2.8	34.1	11.8	365.1	0.4
	15	24.7–27.7	326.1	2.6	35.7	9.8	365.3	0.4
	16	nd	327.7	3.0	39.4	9.6	366.3	0.3
	20	24.7–27.5	332.0	3.2	42.9	9.1	366.7	0.4
Glacier Pentlandfield (high amylose)	7	nd	–	1.3	–	30.0	363.4	0.9
	10	53.3–54.7	320.7	1.8	–	26.7	364.6	0.7
	13	nd	323.6	2.1	–	24.0	366.4	0.5
	15	36.1–40.0	325.0	2.0	–	22.0	367.0	0.6
	16	nd	332.1	2.1	24.2	19.6	367.2	0.7
	20	37.0–40.9	334.3	2.3	27.8	16.3	366.8	0.5

nd, not determined.

allows researchers to estimate the contributions from the polymorphic structure, the thickness of crystalline lamellae and the free surface energy of face sides of crystalline lamellae to the melting temperature of starches and to express the data with respect to a role of defects in a structural organisation of starch granules (Protserov et al., 2001, 2002; Wasserman et al., 2001).

At present it is believed that the increase of melting temperature as a function of increasing growth temperature (which parallels annealing mechanisms in vitro) may be caused by: (i) changes in double helix length and, most importantly, (ii) registration optimisation within crystalline lamellae (Tester, 1997; Tester, Debon, Davies, & Gidley, 1999; Tester & Karkalas, 2001). Indeed, it has been shown recently (by some of these authors and co-workers) that an increase of growth temperature during biosynthesis of sweet potato starches, i.e. C-type (mixed A + B) starches, is accompanied by an elevation of the cooperative melting unit of starches and, correspondingly, the thickness their crystalline lamellae. Additionally the analysis of the DSC and X-ray data has shown that elevation of growth temperature leads to the change of the starch polymorphic structure. For sweet potato starches grown at soil temperature of 15 °C, they contain C-type structure while starches grown at higher temperature contain the A-type structure.

In contrast to sweet potato starches, for potato starches (containing B-type polymorphs), the thickness of crystalline lamellae remains constant as a function of growth temperature (Protserov et al., 2002). It has been proposed that a decrease of the melting temperature of potato starches with decreasing of growth temperature is caused by the accumulation of defects (amylose tie chains and F2 or F1 amylopectin sub-fractions) located in crystalline and amorphous lamellae and acting as destabilisers on the structural organisation of starch granules (Protserov et al., 2002).

Analysis of previously published data shows that for B- and C-type (mixed A- and B-type) starches there are established views describing the influence of growth temperature on the gelatinisation (melting) temperature of starches based on knowledge about the structural organisation of native granules; although such inferences are generally lacking for A-type starches. Rice, maize and barley starches are useful models to study in relation to cereal starch A-type polymorphic structure (Gallant, Bouchet, Buleon, & Perez, 1992; Vasanthan & Bhatty, 1996), with different amounts of amylose and amylose–lipid complexes (Tester, 1997; Yuryev et al., 1999). However, in contrast to rice and maize starches for which there is observed a reduction in the proportion of amylopectin short chains and the molecular size of amylose due to an increase in the growth temperature (Asaoka, Okuno, & Fuwa, 1985a,b, Asaoka, Okuno, Hara, Oba, & Fuwa, 1989; Asaoka, Okuno, Konishi, & Fuwa,

Table 2
Values for the melting of cooperative units (ν_{crl}), thickness (L_{crl}), free surface energy (γ_i), enthalpy (q_i) and entropy (s_i) of crystalline lamellae faces

Genotypes	Growth temperature (°C)	ν_{crl}	L_{crl} (nm)	$\gamma_i \times 10^7$ (J cm^{-2})	$q_i \times 10^7$ (J cm^{-2})	$s_i \times 10^7$ (J cm^{-2} K^{-1})
Waxy Oderbrucker (waxy)	7	16.01	5.6	17.83	71.25	0.169
	10	13.57	4.7	15.14	59.41	0.137
	13	13.07	4.6	13.99	55.74	0.127
	15	14.67	5.1	13.80	57.57	0.133
	16	14.49	5.1	13.19	53.75	0.123
	20	14.11	4.9	12.07	54.40	0.127
Average value		14.6 ± 0.5	5.1 ± 0.4			
Golden Promise (normal)	7	18.74	6.6	21.16	94.75	0.234
	10	14.00	4.9	18.63	80.18	0.192
	13	14.16	5.0	17.57	76.67	0.183
	15	15.88	5.6	16.75	79.30	0.192
	16	16.86	5.9	16.06	73.76	0.176
	20	17.54	6.1	14.54	75.52	0.184
Average value		16.2 ± 0.8	5.7 ± 0.3			
Triumph (normal)	7	–		–	–	–
	10	12.04	4.2	14.73	55.12	0.126
	13	12.19	4.3	13.39	48.11	0.107
	15	13.72	4.8	13.02	51.81	0.119
	16	13.10	4.6	12.52	45.23	0.099
	20	13.39	4.7	11.14	41.61	0.092
Average value		12.9 ± 0.3	4.5 ± 0.1			
Glacier Pentlandfield (high amylose)	7	nd	–	–	–	–
	10	nd	–	–	–	–
	13	nd	–	–	–	–
	15	nd	–	–	–	–
	16	11.54	4.0	10.11	55.39	0.136
	20	12.07	4.2	9.46	51.70	0.126
Average value		11.8 ± 0.3	4.1 ± 0.1			

1987; Asaoka, Okuno, Sugimoto, Kawakami, & Fuwa, 1984; Inouchi, Ando, Asaoka, Okuno, & Fuwa, 2000; Lu, Jane, Keeling, & Singletary, 1996), for waxy, normal and high amylose barley starches no major differences of amylopectin fine structure have been identified (Tester et al., 1991). The biochemistry underlying this variation is not understood.

Starch lipid content is very sensitive to environmental effects, although less literature has been published on lipid compared to amylose content. In barley and wheat starch, elevated growth temperatures increase the amount of starch lipids (Myllärinen, Schulman, Salovaara, & Poutanen, 1998; Shi, Seib, & Bernardin, 1994; Tester, 1997; Tester et al., 1991; Tester et al., 1995). The situation is less well researched and is less clear for rice starch (Morrison & Azudin, 1987). The proportion of lipid complexed amylose (in cereal starches) increases with increasing growth temperature (Morrison, 1995).

This work was conducted to provide a better understanding of the molecular basis for variation in the gelatinisation (melting) temperature of barley starches grown at different temperatures. The starches discussed here contained different amylose contents, cooperative melting unit parameters, thickness of crystalline lamellae, polymorphic structure and associated defects in the structural organisation of the starch granules.

2. Materials and methods

2.1. Materials

Barley cultivars (waxy Oderbrucker, Golden Promise, Triumph and Glacier Pentlandfield were grown in constant environment chambers as previously described and total (lipid extracted) amylose contents (Table 1) have similarly been reported previously (Tester et al., 1991).

2.2. Methods

Calorimetric investigations of starch dispersions in water (0.3–0.5% dry matter, sample volume 0.5 cm^3 in sealed cells) were performed using a high sensitivity differential scanning microcalorimeter DASM-4 (Puschino, Russia) from 10 to 130 °C with a heating rate of 2 K min^{-1} and excess pressure of 2.5 bar. The term ‘melting’ is used in preference to gelatinisation in the text to describe this quantification because of the thermodynamic approach. However, it is recognised that true melting of starch occurs

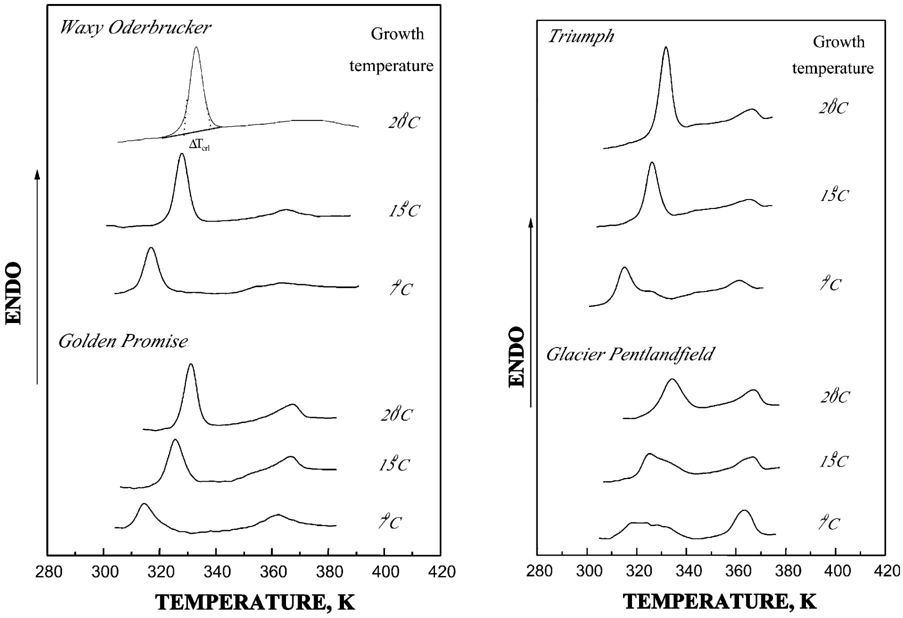

Fig. 1. DSC endotherms obtained in excess water for some barley starches (waxy Oderbrucker, Golden Promise, Triumph and Glacier Pentlandfield) grown at different growth temperatures.

above 150 °C. Deionised water was used as a reference material. The heat capacity scale was calibrated using the Joule–Lenz effect for each run. Corrections for dynamic lag and residence of the samples in calorimetric cell were not necessary under these conditions (Andreev et al., 1999; Danilenko, Shikova, & Yuryev, 1994). The average values of the thermodynamic parameters were determined as described elsewhere (Andreev et al., 1999; Danilenko et al., 1994; Matveev et al., 2001), using five measurements at 95% significance level and converted to dimensions per mole anhydroglucose unit (162 g mol^{-1}).

Values for van't Hoff enthalpy (ΔH^{vH}) were calculated according to others (Andreev et al., 1999; Danilenko et al., 1994; Matveev et al., 2001; Privalov & Khechinashvili, 1974). Values for the melting cooperative unit (ν) and the thickness of crystalline lamellae (L_{crl}.) for starches with symmetrical DSC endotherms were calculated according to published approaches (Andreev et al., 1999; Danilenko et al., 1994; Matveev et al., 2001; Protserov et al., 2001, 2002; Wasserman et al., 2001), and are presented in Eqs. (1) and (2) as follows:

$$\nu = \Delta H^{\mathrm{vH}}/\Delta H_{\mathrm{m}} \tag{1}$$

where ΔH_{m} is the experimental melting enthalpy of crystalline lamellae;

$$L_{\mathrm{crl}} = 0.35\nu \tag{2}$$

where according to Gernat, Radosta, Anger, and Damaschun (1993), there is pitch height of 0.35 nm per anhydroglucose residue in double helices.

To calculate the thermodynamic parameters characterising surfaces of crystalline lamellae of the starches, symmetrical DSC endotherms were used applying the Thomson–Gibbs' Eq. (3) (Bershtein & Egorov, 1994):

$$T_{\mathrm{m}} = T_{\mathrm{m}}^{0}[1 - 2\gamma_i/(\Delta H_{\mathrm{m}}^{0}\rho_{\mathrm{crl}}L_{\mathrm{crl}})] \tag{3}$$

where T_{m}^{0} and $\Delta T_{\mathrm{m}}^{0}$ are the melting temperature and the melting enthalpy, respectively, of a hypothetical crystal with unlimited size (a perfect crystal), γ_i is the free surface energy of faces of crystalline lamellae, while ρ_{crl} and L_{crl} are, respectively, the density and the thickness of the crystal. Also, the parameter q_i may be calculated where Eqs. (4) and (5):

$$q_i = [(\Delta H_{\mathrm{m}}^{0} - \Delta H_{\mathrm{exp}})L_{\mathrm{crl}}]/2.5 \tag{4}$$

and

$$\gamma_i = q_i - T_{\mathrm{m}}s_i \tag{5}$$

where q_i is the surface enthalpy of crystalline lamellae.

Since the specific values of the melting temperature (T_{m}^{0}) and the melting enthalpy ($\Delta H_{\mathrm{m}}^{0}$) for a perfect crystal are not available, for calculations of the thermodynamic parameters the values of T_{m}^{0} (366.5 K) and $\Delta H_{\mathrm{m}}^{0}$ (35.5 J g^{-1}) for A-type spherolitic crystals (Whittam, Noel, & Ring, 1991) were used. In addition, values of ρ_{crl} for A-type structures (1.48 g cm^{-3}) (Wasserman et al., 2001; Whittam et al., 1991) as well as L_{crl}, ΔH_{m} and T_{m} values for the starches investigated (Table 2) were used. Because of the occurrence of asymmetrical melting endotherms for some normal and high amylose starches, a peak fit programme (AISN Software Incorporated, Version 4) was used for the deconvolution of the melting endotherms and for the calculation of the thermodynamic parameters obtained as a result of the deconvolution. The procedure for deconvolution has been described previously (Matveev et al., 2001).

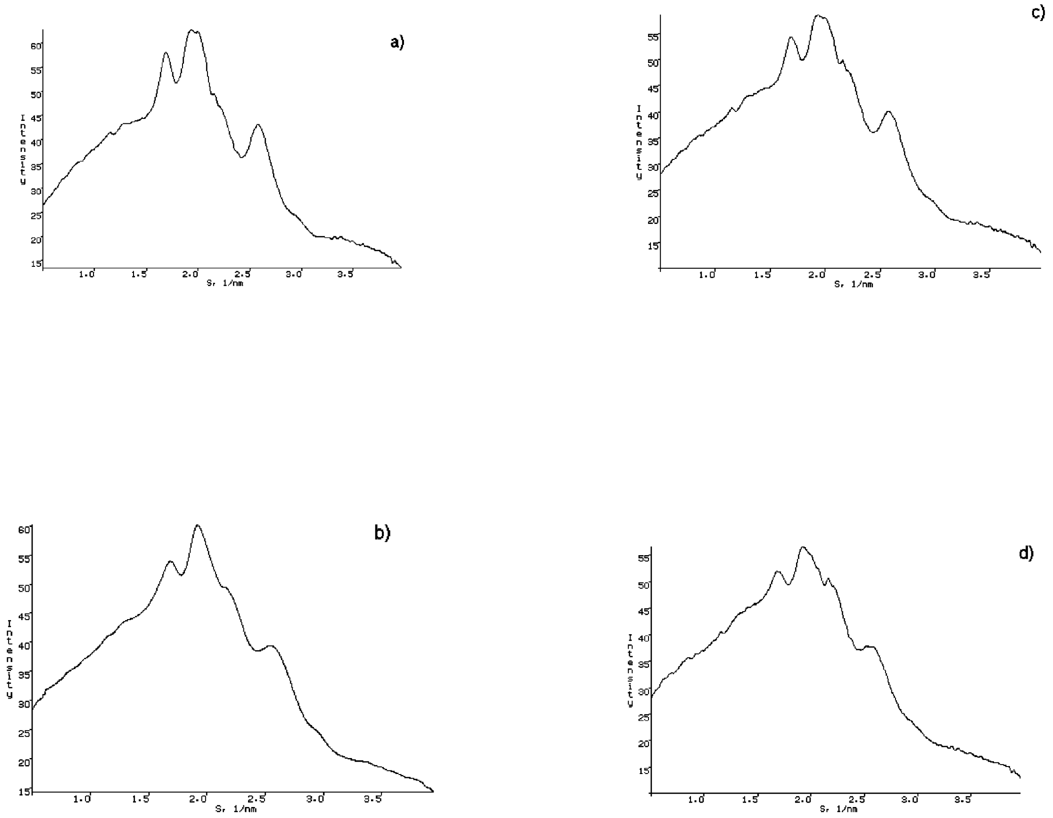

Fig. 2. X-ray diffraction patterns of some barley starches (Triumph (a) and (b)) and Glacier Pentlandfield (c) and (d) varieties) grown at different growth temperatures ((a) and (c), 20 °C; (b) and (c), 7 °C)).

X-ray diffraction measurements were performed in transmission geometry on an X-ray diffractometer of local (Russian) design. Ni-filtered radiation from Cu X-ray tube was line focused with glass mirror collimator. Diffraction patterns were recorded with a gas-filled one-dimensional position-sensitive detector, constructed in JINR (Dubna, Russia). Sample-to-detector distance was 140 mm. Diffraction patterns were corrected for background scattering and plotted as function of $S = (2\sin\theta)/\lambda$, where λ is Cu Kα-wavelength (0.1542) and θ is a half of scattering angle.

3. Results and discussion

Original thermograms obtained for the gelatinisation/-melting (referred to as melting in the context of this discussion) of 0.3% of some barley starch dispersions are presented in Fig. 1. The thermograms show typical endothermic transitions (Matveev et al., 1998; Yuryev et al., 1999; Zobel, 1988a,b). The low-temperature endotherm (circa 330 K or 57 °C) is attributed to the melting of the crystalline lamellae, while the high-temperature peak (circa 365 K or 93 °C) is defined as dissociation of amylose–lipid complexes and the melting of single-helical type (such Vh-type) crystallites (Buleon, Le Bail, Ollivon, & Bizot, 1998; Matveev et al., 1998; Yuryev et al., 1999). Amylose–lipid complexes do occur in native starch granules (Morrison, 1995). Because of the low amylose content in the waxy barley starches, the second transition is (almost) absent for these type of starches. The thermodynamic melting parameters for both crystalline lamellae and amylose–lipid complexes are in broad agreement with published data (Tester, 1997; Yuryev et al., 1999).

The change of the shape of DSC endotherm at decreasing of soil temperatures may be caused by three factors:

1. A change in the ratio of small to large granules since it is well known that granular size distribution of starches influences the breadth of DSC type endotherms (Liu & Lelievre, 1993). However, this is unlikely because as can be seen from Table 1, the values of ΔT (endotherm peak width) decreases with increasing growth temperature while the ratio of small to large granules does not change proportionally (Tester et al., 1991).
2. A change in starch polymorphic structure.
3. A decrease in starch defects (increase in perfection) within crystalline lamellae as a function of increasing growth temperature.

In Fig. 2, X-ray diffractograms of the different starches are shown where typical A-type crystalline structure (Gallant et al., 1992; Vasanthan & Bhatty, 1996) is found irrespective of growth temperature. Some broadening of crystalline reflexes can be observed due to the appearance of

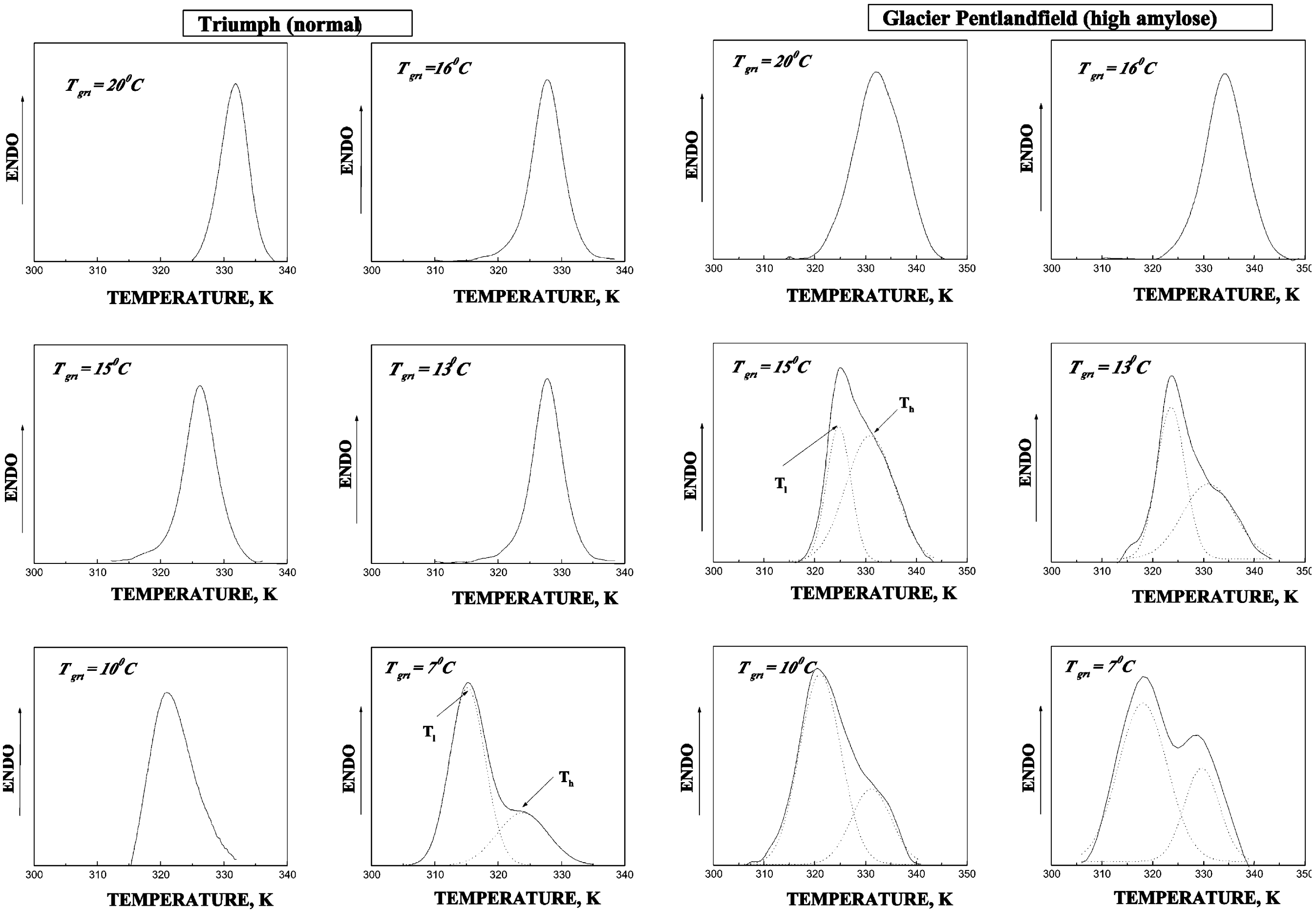

Fig. 3. Excess water DSC endotherms (—) and results of their deconvolution (– – –) for starches (Triumph and Glacier Pentlandfield) grown at different growth temperatures. T_l and T_h are the melting temperature of low- and high-temperature structures, respectively.

defects in crystalline domains. Additionally, some changes in the ratio of crystalline reflexes may be observed, although it is unlikely that an increase in the width of calorimetric peaks (Fig. 1; Table 1) is as a consequence in the change of polymorphic structure of starches. Another feature to note is the decrease in the intensity of the crystalline reflexes as a function of decreasing amylose content or decreasing growth temperature and hence a decrease in the crystallinity of starches while the polymorphic structure of starches remains constant. The decrease of the crystallinity with an increase in amylose content as found here for barley starches (Fig. 2) is typical of maize starches (Matveev et al., 2001). As can be seen from Figs. 1 and 2 and Table 1 the changes of starch crystallinity are in agreement with the changes in the gelatinisation (melting) enthalpy of the starches as a function of amylose content and growth temperature.

The biosynthesis of potato and wheat starch granules is accompanied by accumulation of defects (Protserov et al., 2001; Wasserman et al., 2001; Yuryev & Wasserman, 2001). Also, it has been reported that a decrease of the gelatinisation/melting temperature of potato starches with decreasing growth temperatures is caused by the accumulation of defects (including amylose tie chains and F2 or F1 amylopectin sub-fractions) located in crystalline and amorphous lamellae acting as destabilisers on the structural organisation of starch granules (Protserov et al., 2002; Yuryev & Wasserman, 2001). It might be expected that both a decrease of T_m and an increase of the width of calorimetric peaks (Fig. 1; Table 1) may be caused by an accumulation of defects and the formation of defective crystalline structures. If the supposition is valid, we should observe an increase in the s_i values with decreasing growth temperature. The s_i values can be estimated by means of Eq. (3)–(5), however, using Eqs. (1) and (2) both ν and L_{crl} values may be calculated. Although such an approach is really applied only to starches with symmetrical calorimetric melting peaks, its a use allows for the determination of trends with respect to the formation of starch granules with respect to growth temperature.

Calculations of crystalline parameters show (Tables 1 and 2) that for a decrease of growth temperature the values of the cooperative melting unit and the thickness of crystalline lamellae remain constant whereas the values of the surface entropy have a tendency to a decrease irrespective of barley variety. In other words, a decrease

Table 3
Thermodynamic characteristics and proportions of low- and high-temperature structures in Triumph and Glacier Pentlandfield barley starches

Cultivar	Growth temperature (°C)	Low temperature structure			High temperature structure		
		T_l (K)	ΔH_l (kJ mol^{-1})	Amount (%)	T_h (K)	ΔH_h (kJ mol^{-1})	Amount (%)
Triumph	7	315.2	1.6	69.9	323.9	0.7	30.1
Glacier Pentlandfield	7	314.9	0.8	63.7	326.6	0.5	36.3
	10	321.1	1.3	72.2	331.1	0.5	27.8
	13	323.6	1.1	52.6	331.0	1.0	47.4
	15	324.7	0.7	34.8	330.9	1.3	65.2

of growth temperature leads to a decrease in the melting temperature and an increase in the width of the calorimetric peaks of investigated starches due to an accumulation of defects. This conclusion is in agreement with the data obtained for potato starches (Protserov et al., 2002). Unfortunately it is not possible to calculate values of s_i for starches with asymmetric calorimetric peaks. However, the totality of the data obtained here (Tables 1 and 2) infers that starches with asymmetric calorimetric peaks contain most defects.

It is conceivable (Yuryev & Wasserman, 2001) that starch defects may be considered as a origins of 'canals' in native starch granules that easily filled by water (Tang, Godward, & Hills, 2000). The existence of such canals in barley starch granules is well established. It is relevant to note that a decrease in growth temperature leads both to an increase of swelling factor (Tester, 1997; Tester et al., 1991) and to the amount of defects in granules (Table 2). According to Donovan (1979) starch granules contain two types of crystallites distinguishing by their hydration/swelling properties. These differences can be observed on DSC-thermograms of B- and A-type starches at intermediate water content (Biliaderis, 1992; Donovan, 1979) although there may rearrangements of dislocations (essentially registration) between double helices as a primary event (Waigh, Gidley, Komanshek, & Donald, 2000; Waigh et al., 2000). However, as shown in Figs. 1 and 3, asymmetry and doubling within endotherms can be observed (even for excess water) when starches originate at low temperatures. It must be taking into consideration that (i) there are more defects in crystalline growth rings located nearer to a surface of granules (Protserov et al., 2001; Wasserman et al., 2001; Yuryev & Wasserman, 2001) and, (ii) such defects accumulate at low growth temperature. As the proportion of defects in crystallites located within different crystalline growth rings is not great, dual calorimetric peaks are observed only at intermediate water contents whereas if there were large differences this feature would be apparent for excess water systems. Assuming that these crystalline structures are gelatinised (melt) independently, using deconvolution applied to the asymmetric calorimetric peaks provides relative enthalpic contributions (percent) of each structure for the overall gelatinisation (melting) enthalpy of the starches.

Deconvolution of the calorimetric peaks (Fig. 3) shows that the melting process of starches can be described as the melting of two independent structures. The low-temperature endotherms are attributed to the melting of the crystalline lamellae containing the greatest proportion of defects and having largest swelling factor whilst the high-temperature endotherms can be related to crystalline lamellae with the smallest proportion of defects and correspondingly smallest swelling factors. The melting temperatures of these structures and their proportion are presented in Table 3. Analysis of data presented in Fig. 3 and Table 3 shows that the asymmetry of DSC endotherms for barley starches in water excess represents the difference between the proportion of the low- and high-temperature crystalline structures and is approximately 30–40%.

Analysis of data regarding dissociation of amylose–lipid complexes together with the results data published by Tester (1997) and Tester et al. (1991) allows interpretation of the influence of growth temperature on the formation of amylose–lipid complexes. Taking into consideration that:

(i) an increase of growth temperature leads to an increase of lipid content and a decrease of amylose content in barley starches (Tester, 1997; Tester et al., 1991),
(ii) the magnitude of ΔH_{alc} (Table 1) is proportional to the content of amylose–lipid complexes in starches,
(iii) the magnitude of T_{alc} (Table 1) is the characteristic of thermostability for amylose–lipid complexes.

It can be deduced that in spite of an increase of total lipid content in starches, a decrease of growth temperature leads to an increase in the content of amylose–lipid complexes in starches, apparently in part due to a decrease of amylose content, and a decrease thermostability of complexes. Taking into account that the T_{alc} of amylose–lipid complexes depends bookon a nature of fatty acids (Akuzawa, Sawayama, & Kawabata, 1995) and decreases in a number of: linoleic acid $<$ myristic acid $\sim$ oleic acid $<$ stearic acid $\sim$ palmitic acid, it is possible that at lower of growth temperature not all fatty acids form complexes. This is not necessarily in accord with other authors (Morrison, 1995) where it is assumed that the lipid fraction in cereal starches is essentially all complexed with amylose.

4. Conclusions

The application of different physico-chemical approaches to describe the gelatinisation (melting) process of starches grown under various temperature conditions with X-ray analysis, has provided an estimate for the thickness of crystalline lamellae, an understanding of thermodynamic parameters characterising the surface of starch crystalline lamellae as well as an overview of influence of growth temperature and amylose content on the proportion of defects barley starches. It is apparent that a decrease in growth temperature during development of barley starch granules (A-type crystalline structures) in common with B-type potato starches (Protserov et al., 2002), leads to the formation of starch crystals with decreased melting temperature whereas the thickness of crystalline lamellae is constant with respect to dimensions. Such behaviour can be explained by the accumulation of defects located in crystalline and amorphous lamellae. The amount of defects increases both with decreasing growth temperature and with increasing amylose content. The asymmetry of calorimetric peaks for DSC-thermograms of barley starches in water excess is observed as the difference between the proportion of the low- and high-temperature crystalline structures and is approximately 30–40%. In addition, in spite of an increase of total content of lipids in starches at lower growth temperature (Tester, 1997; Tester et al., 1991), not all fatty acids necessarily form crystalline complexes.

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