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MOLECULAR STRUCTURE AND PHYSICO-CHEMICAL PROPERTIES OF PSEUDO CEREAL STARCHES

Abstract

Glucans of pseudo cereal starches with significant differences in their branching pattern – amaranth, quinoa and buckwheat – were investigated upon the correlation of their molecular characteristics with technological properties. Consistency of glucan conformation, in particular persistance against elevated temperature, acidic pH and mechanical stress was investigated with respect to consequences on molecular and supermolecular structures of starch/DMSO-solutions.

For analytical purposes starch glucans were separated by semi-preparative size-exclusion chromatography (SEC) and obtained fractions were tested upon their iodine-complexing potential. Amaranth was found to be short chain branched (scb ≡ amylopectin type); quinoa to be scb-type, but consisting of longer branches than amaranth; buckwheat was found to be a mixture of scb-glucans with approx. 24% of long-chain branched (lcb ≡ amylose-type) glucans.

Molecular weight (degree of polymerization) for DMSO-dissolved starches was determined absolutely by means of aqueous SEC. Weight average molecular weights (M_w) were found close to $12 \cdot 10^6$ g/M for the investigated samples. Dimensions of starch glucan coils were estimated from SEC-data combined with universal calibration: values between 2–40 nm were found without significant differences for the three starches. However, in spite of these minor differences, the investigated starches differ significantly in their inter- and intramolecular interaction potential. Thus, obviously interaction potentials are strongly controlled by branching patterns, glucan-coil packing densities and by the ability to form supermolecular structures.

Introduction

Although diversity of technological qualities of cereal starches is as widespread as the variety of basic cereals, this list continuously is expanded by newly breeded and technologically modified species.

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As starch is strongly determined by the biological history of the starch containing system a systematic analysis of technological qualities needs information from different levels: history of biological conditions, macroscopic granula-level characteristics, information about molecular dimensions and about conformation on molecular and supermolecular level. Whereas granule-characteristics such as composition (percentage of glucans, proteins, lipids, salts), size and geometry of granules, degree of cristallinity and water content ever have been considered to be important, the influence of molecular-level characteristics such as degree of polymerization (mean values, mass and molar distributions), branching pattern and interactive potential of starch glucans often is ignored or, at least, underestimated [1, 2]. Nevertheless, it is well known that in particular kind and percentage of amylose-type non/long-chain branched (nb/lcb) and amylopectin-type short-chain branched (scb) glucan fractions strongly influence macroscopic starch qualities [3, 4]. Starches of pseudocereals amaranth, quinoa and buckwheath, which differ in these molecular qualities, are investigated upon the consequences of these differences on technological properties [5-12]. 5,,,,,,,12

Experimental

Material

Starch of buckwheat was isolated from *Fagopyrum esculentum* (Nestelberger/ Austria); starches of amaranth and quinoa were prepared from *Amaranthus cruentus* and from *Chenopodium quinoa* (Posch/Austria), respectively.

Molecular characteristics

Dissolution

DMSO/starch glucan solutions were prepared for semi-preparative low pressure SEC-system in the range between 0.5–2 mg/mL for high pressure SEC analysis. To ensure elimination of supermolecular associates, dissolution was extended up to 100 hours with permanent stirring at 80°C. To avoid interfering phenomena by exergonic mixing energies in SEC-matrix, DMSO/starch solutions were mixed 1:1 with aqueous eluent (0.005 M Na_2CO_3) before chromatographical analysis.

Molecular weight distribution and glucan dimensions

For absolute molecular weight analysis, estimation of glucan coil dimensions and packing densities within occupied volumina, the SEC system (TSK PWM, PW 6000G, PW 5000G, PW 4000G, PW 3000 G; each 300 mm, ID 7.5 mm, ToyoSoda / J) was connected to dual-detection of mass (interferometric refractometer: Optilab 903, Wyatt Technology/US) and scattering intensity (low angle laser light scattering instrument

(KMX-6, TSP/US; injected sample volume: 260 µL of approx. 0.5 mg/mL solutions; eluent: 0.005 M aqueous Na_2CO_3). Estimation of glucan coil dimensions was achieved by universal calibration of SEC-chromatograms. For branching analysis of separated components, 1 mL fractions were stained with iodine reagent.

For these experiments data acquisition with integrated data reduction was managed by software package CODAwin32 and data processing with software package CPCwin32 (both: a.h group/Austria).

Branching analysis by iodine staining

The percentage of amylose-type nb/lcb-glucans was obtained from iodine-complexing potential (stock solution: 125 mg suspended with 400 mg KJ in 1000 mL H_2O; before application an equivalent of the stock solution was diluted 1:1 with 0.1 M acidic acid to provide pH 4.6). 1 mL of this reagent was added to 1 mL starch solution (100 µg glucan/mL) either from the bulk or from SEC-obtained fractions. Non-complexed scb-glucans were monitored by extinction at 525 nm (E_{525}), iodine-complexed nb/lcb-glucans at 640 nm (E_{640}).

Amylose-content of investigated starch solutions (10 mg glucan in 1 mL DMSO, diluted with 0.005 M Na_2CO_3 to a final concentration of 100 µg glucan/mL) were determined by referring to amaranth (0% amylose) and phosphorylase-synthezised non-branched $\alpha(1\rightarrow4)$ glucan (100 % amylose).

Finally, a ratio of amylose-type non/long-chain branched and amylopectin-type short-chain branched glucans was obtained by computing the extinction-ratio E_{640}/E_{525}.

Branching analysis by enzymatic fragmentation and subsequent fragment analysis

Starch samples were dissolved in DMSO (31 h, 80°C) and mixed with acetatbuffer (0.5 mL starch suspension + 1.5 mL buffer; final pH 5.3); debranching was achieved by incubating 5 µL Isoamylase (Hayashibara, EN 102) and stirring for 17 h at 38°C. Enzyme was denaturated by heating (5 min 95°C) and the sample solution was desalted with DOWEX mixed bead ionexchanger.

Analysis of debranched glucans was done by means of SEC (Pharmacia Superose 12 (l = 300 mm, ID = 10 mm) + Merck Fractogel TSK-HW 40 (S) (l = 150 mm, ID=10 mm); eluent 0.06M sodium-acetate pH 5.5; injection volume: 300 µL; flowrate: 0.42 mL/min) and HPAEC-PAD system (Dionex: Bio LC Modell 4000i System, working electrode: gold, reference electrode: Ag/AgCl, column: Carbo-Pac PA 100; injected volume: 20 µL; flowrate: 1,2 mL/min; gradient profile: 0 min 90% A/10% B to 90 min 10% A/90% B: A = 150 mM NaOH, B = 150 mM NaOH + 500 mM $NaOOCCH_3$).

Preparation of ß-limit dextrin: starch samples (1% in DMSO) were mixed with sodium-acetat buffer (1 mL starch suspension + 3 mL buffer; final pH 5.3) and incubated with 4.55 µL ß-Amylase (SIGMA, A-7005) for 2 h at room temperature. Enzyme

was denaturated by heating (5 min 95°C) and the sample solution was desalted with DOWEX mixed bead ionexchanger.

Technological Qualities

Gelatinization behaviour and resistance against mechanical, chemical and thermal stress

Gelatinization behaviour of aqueous starch suspensions was investigated with a cone/plate-Rheometer (Physica/Germany; system MK 250; 5% (w/w), 50°C, shear rate of 100 s^{-1} and a heating rate of 2°C/min up to 95°C).

Paste viscosity was determined with a Brabender Viscoamylograph E (Brabender, Duisburg/Germany, 10% (w/w), temperature program 30–90°C with a heating rate of 1.5°C/min, 75 rpm, holding period: 30 min, cool to 30°C).

Shear stability was determined in a cylinder-geometry rheometer (Physica/ Germany; system cylinder Z3 DIN, smooth spindle; 5% (w/w) aqueous starch suspension; shear rates: 5 min at 100 s^{-1}, 5 min 1000 s^{-1} and again 5 min at 100 s^{-1}). Shear stability is computed as the similarity between viscosity at the end of first period (η_{before}) and viscosity after second period (η_{after}) of shear stress in terms of shear stability percentage.

Acid resistance was determined for aqueous starch suspensions (5% (w/w), pH 3.0, 2 M citric acid, viscosity at 95°C before and after acidification at 100 s^{-1}. The degree of resistance was determined as the ratio of viscosity before ($\eta_{initial}$) and after ($\eta_{pH\ 3}$) acidification.

Freeze/thaw stability was determined according a modified method of Schoch [13,14]. For a freeze/thaw cycle the resulting suspensions were stored overnight at -7°C and thawed the next day in a 30°C water bath. The amount of liberated water was determined after centrifugation. For a next freeze/thaw cylce the starch pastes were resuspended with the liberated water, homogenized and once again stored overnight at -7°C. Freeze/thaw-stability is computed as the percentage of liberated water in a series of six freeze/thaw-cycles. Each freeze/thaw-cycle is assumed to be equivalent to a three week storage at 4°C.

Results and discussion

Molecular characteristics

With dual detection of mass (DRI) and scattering intensity (LALLS) absolute information about molecular weight and degree of polymerization for SEC-separated starch glucan fractions, and thus, about degree of polymerization distribution for the investigated starches could be achieved (Fig. 1).

The maximum value of degree of polymerization was found for all of the investigated starches in the range of 150 000 ± 20 000 glucose units – a surprising fact, as no significant difference was found for scb-type starch glucans (amaranth, quinoa) and scb/lcb-mixed-type (buckwheat) starch.

Minimum dp-values however, differ significantly for the different starch: the applied dissolving-process obviously reduced supermolecular structures of amaranth, and quinoa but left supermolecular structures buckwheat. As mean values of degree of polymerization, for instance weight average degree of polymerization (dp_w), strongly depend on the width of degree of polymerization distribution, dp_w-values for the investigated starches differ significantly. Resulting molecular weight distributions in Fig. 1 are normalized to unity-area to enable fast identity-checks via matching/ mismatching areas.

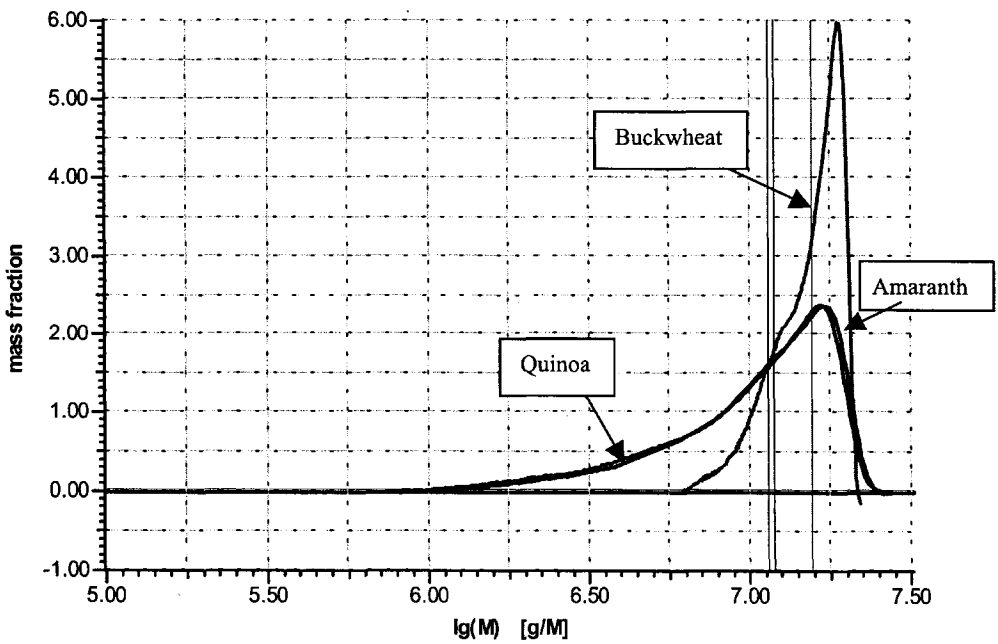

Fig. 1. Amaranth (M_w=11.8·10^6 g/mol ≡ dp_w=72500 Glc), Quinoa (11.3·10^6 g/mol ≡ dp_w=70000 Glc) and Buckwheat (15.4·10^6 g/mol ≡ dp_w=94900 Glc).

Tab. 1 lists the values for computed dimensions and packing densities of glucan-coils. All of the investigated starches consisted of glucan coils which occupied volumina with sphere-equivalent radii (R_e) between 2–40 nm. Different to the fluctuating dp_w-values, R_e-values for maximum-mass fraction (R_ep(Max)) were found very similar for all investigated samples.

Tabela 1

Mean values of degree of polymerization and dimensions of DMSO-dissolved glucan coils of investtigated starches from universal calibrated SEC-data.

Molecular characteristics	amaranth	quinoa	buckwheat
dp(Min) [Glc]	5 000	4 600	38 000
dp(Max) [Glc]	167 000	161 000	134 000
dp_w [Glc]	72 500	70 000	94 900
sphere equivalent radius of glucan coils			
R_e(Min) [nm]	2	2	2
R_e(Max) [nm]	40	40	40
R_ep(Max) [nm]	27	28	29
relative packing density of glucan coils			
molecules, corresponding to dp_w	ref = 1.0	0.9	1.3
R_e = 2-5 nm molecules	ref = 1.0	0.9	7.6
R_e = 35-40 nm molecules	ref = 1.0	0.9	0.8
average	ref = 1.0	0.9	3.2

ref: reference; Min: minimum value; Max: maximum value; dp: degree of polymerization; dp_w: weight average degree of polymerization; R_e: sphere equivalent radius of occupied volume by a dissolved glucan molecule; R_ep(Max): R_e for maximum mass glucan-fraction;

Referring to amaranth, relative packing densities for each glucan fraction was estimated with determined molecular weight (degree of polymerization) and corresponding occupied volumina: the fraction containing the largest molecules dp(Max), the fraction of smallest molecules dp(Min) and the fraction in the vicinity of weight average degree of polymerization (dp_w). Whereas no significant difference in the packing densities of the most voluminous molecules between the investigated starches could be found, differences were significant for the small molecules, in particular for buckwheat. Glucan coils of buckwheat were 7 times higher in packing density than amaranth and quinoa.

For investigation of branching characteristics the starch samples in a first approach were investigated upon their iodine-complexing potential in bulk solution. Minimum interaction was found for amaranth, resulting in a value of 0.46 for the E_{640}/E_{525}-ratio and thus, indicating that amaranth consists of scb-glucans only. Amylose-percentages for quinoa and buckwheat were determined from observed E_{640}/E_{525}-ratio-values referring to E_{640}/E_{525}-values obtained for mixtures of scb-glucan amaranth mixed with increasing percentages of synthetic nb-glucans (Tab. 2).

For more detailed information, the starches then were separated on SEC-system (Fig. 2). Similar to results of bulk-investigations, the E_{640}/E_{525}-profiles classify amaranth as scb-glucan starches with comparable uniform E_{640}/E_{525}-values close to 0.5. Likewise for quinoa a quite uniform E_{640}/E_{525}-elution profile was found, but with sig-

nificantly higher iodine-complexing characteristics. But although significantly higher in terms of E_{640}/E_{525}-values, quinoa glucans even were classified as scb-type but consisting of longer branches than amaranth. Buckwheat obviously contain two populations with respect to iodine-complexing potential: a scb-fraction of large molecules with minor iodine complexing potential and a fraction of midrange-size molecules with significantly higher iodine complexing potential and thus, with longer branches.

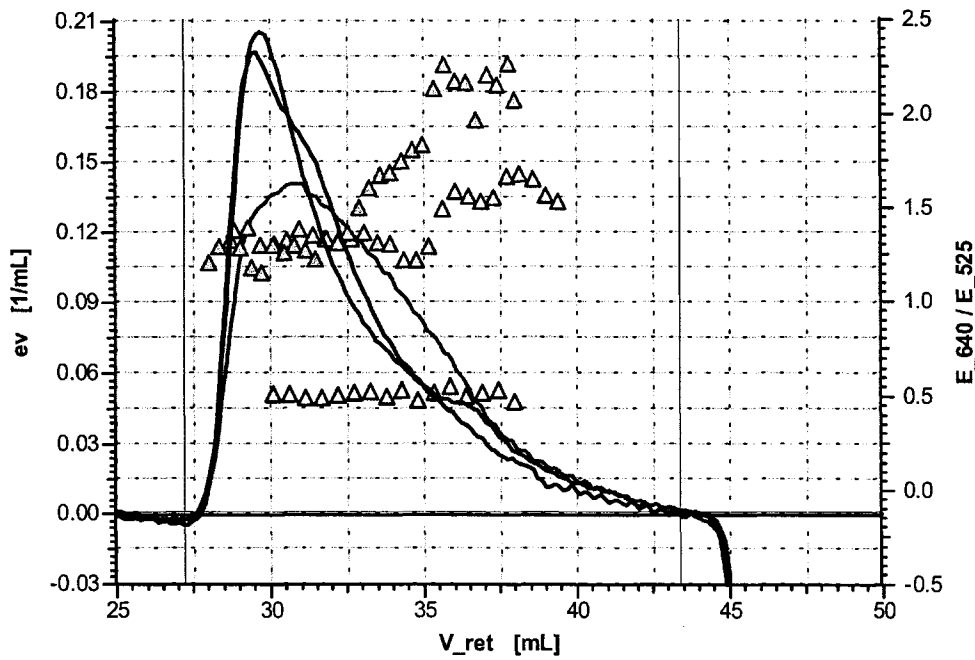

Fig. 2. Normalized elution profiles (area = 1.0) of SEC-separated starch samples (amaranth, quinoa, buckwheat) with superimposed iodine (E_{640}/E_{525}) ratio.

Supplementary to iodine staining, enzymatically catalyzed debranching and subsequent fragment analysis by means of chromatography was performed to investigate the mean branching patterns of the three starch glucans.

Tabela 2

Iodine/glucan-complexing potential E_{640}/E_{525} and correlated percentages of amylose-type nb/lcb glucans and amylopectin-type scb glucans and arithmetic population analysis of nb/lcb and scb-contributions.

Type of glucan	amaranth	quinoa	buckwheat
bulk solution:			
E_{640}/E_{525}	0.46	1.40	1.51
amylose-type nb/lcb-glucans [%]	ref.=0	20	25
SEC + E_{640}/E_{525}-fraction analysis:			
amylopectin-type scb-glucans: E_{640}/E_{525} 0-1.5 [%]	100	80	76
amylose-tpe nb/lcb-glucans: $E_{640}/E_{525} > 1.5$ [%]	ref.=0	20	24
SEC + population analysis:			
selective SEC-elution section (k_{av} 0.0-0.5): 1-4 [%]	72	68	56
selective SEC-elution section (k_{av} 0.5-1.0): 5-7 [%]	28	32	44
amylose-type nb/lcb-glucans (k_{av} 0.5-1.0): [%]	ref.=0	4	16

E_{640}: extinction at 640 nm; E_{525}: extinction at 525 nm; k_{av}: SEC-separation coefficient (selective separation range: 0.0-1.0);

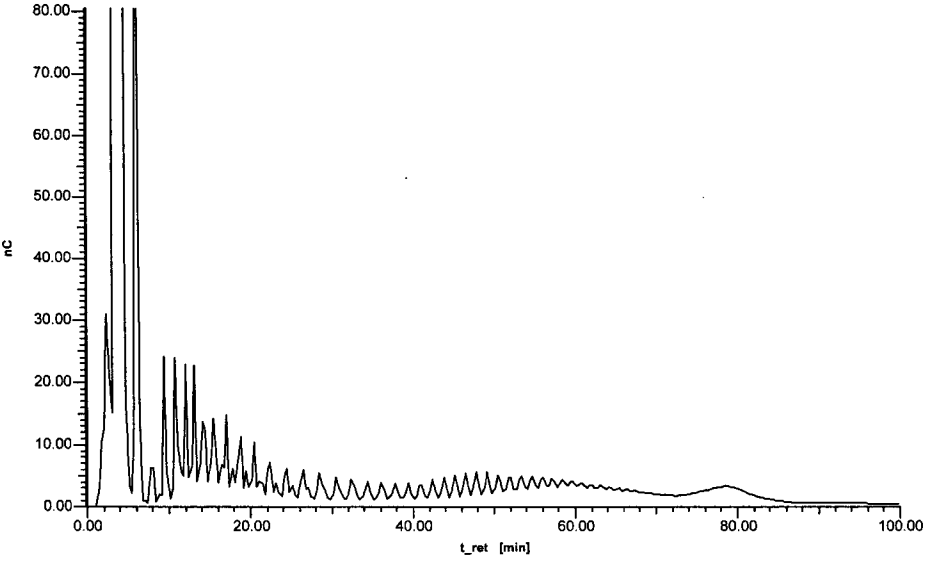

Fig. 3a. HPAEC-PAD analysis after application of ß-Amylase and Isoamylase for amaranth.

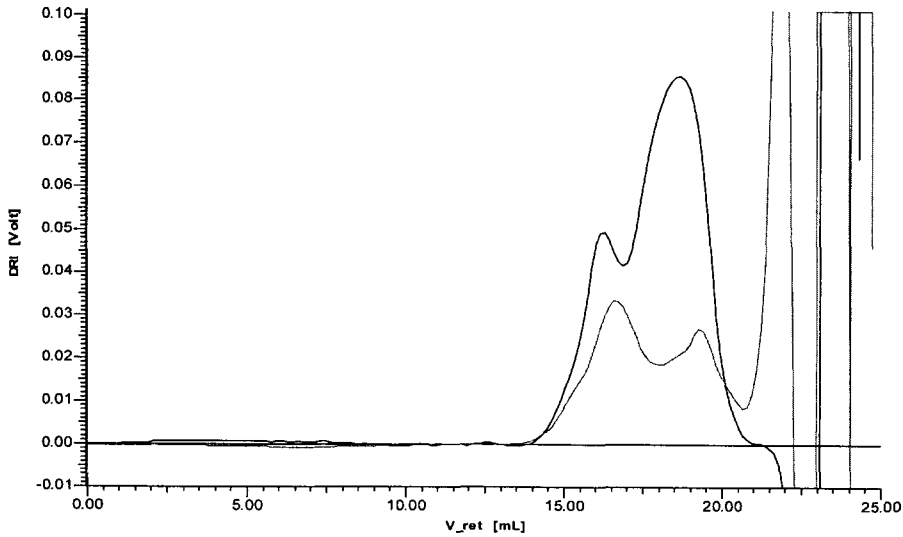

Fig. 3b. SEC-analysis of amaranth glucans: debranched native starch; debranched ß-limit dextrin.

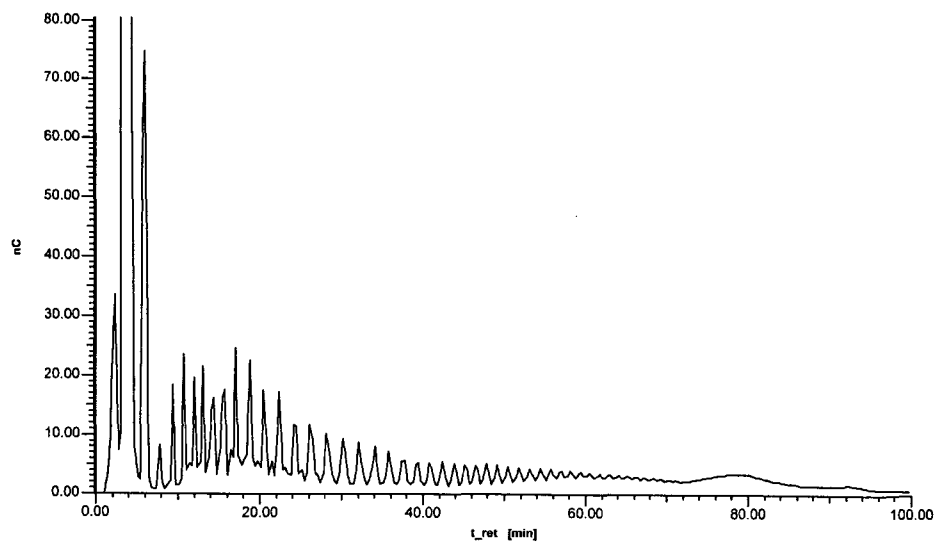

Fig. 4a. HPAEC-PAD analysis for debranched ß-limit dextrin of quinoa starch.

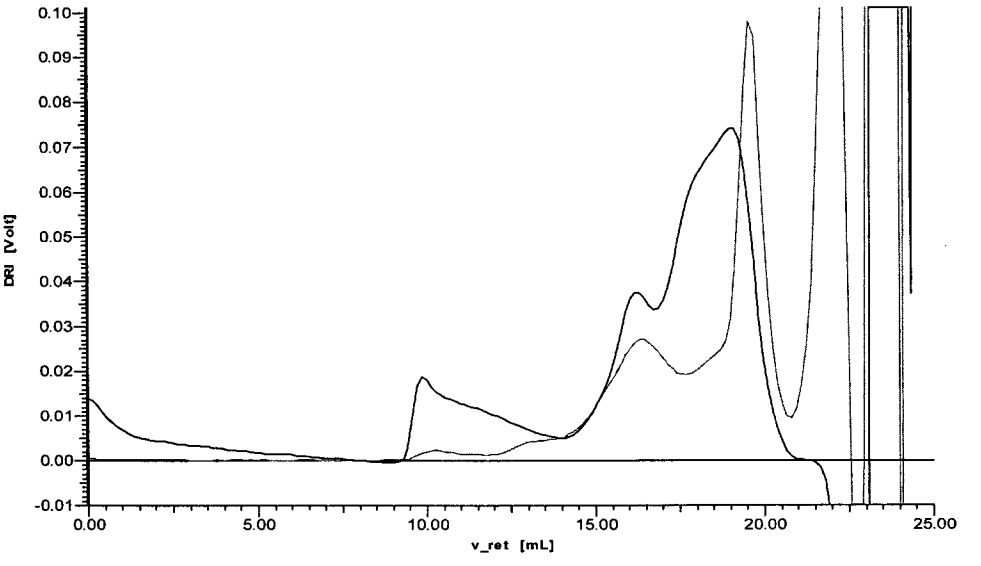

Fig. 4b. SEC-analysis of quinoa starch: debranched native starch; debranched ß-limit dextrin.

HPAEC-PAD-chromatograms of debranched ß-limit dextrin and SEC-elution profiles of debranched native starches and ß-limit dextrins for amaranth and quinoa are displayed in Fig. 3a-b and Fig. 4a-b, respectively. HPAEC-PAD-data of quinoa indicate the higher amount of glucan-dps exceeding 13 compared to amaranth. However, the SEC-elution profiles of debranched native starches show that quinoa but not amaranth consist of molecule fragments with dps exceeding 13 (approx. 20% of total mass of glucans elute between 9–15 mL). This again confirms, that quinoa is formed by longer glucan chain lenths than amaranth.

Technological qualities

Gelatinization / Temperature Dependence of Viscosity

Dependence of viscosity on temperature was determined for 5% (w/w) starch-suspensions in the range between 55–95°C (Fig. 5). Amaranth shows a maximum of disintegration at 75°C; quinoa, although uniform but with longer branches, starts disintegration at comparably lower temperatures and keeps this process without significant maximum over the observed temperature range till 95°C.

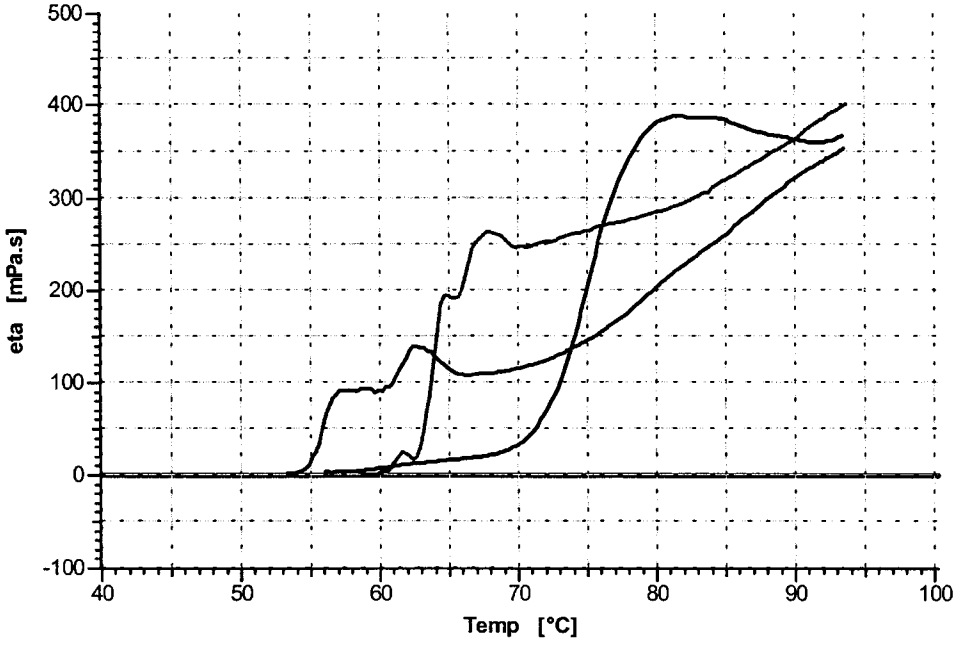

Fig. 5. Amaranth, Quinoa, Buckwheat - temperature dependence of viscosity.

Compared to quinoa glucans, which become continously disintegrated, the performance of amaranth rather is a phase-transition than a destruction phenomenon. Analysis buckwheat results in loose stabilized supermolecular glucan-structures which break up comparably easily. However, increasing viscosity with increasing temperature indicates an initial transition kind of cracking the glucan-packing at 65°C, followed by a continous disintegration of components beyond 65°C.

To monitor disintegration behaviour upon controlled energy input and accompanied tendencies to re-constitute supermolecular glucan structures, Brabender viscosity was determined for 10% (w/w) aqueous starch suspensions (Fig. 6). Although determination of Brabender viscosity for 10%-suspension is a-typical, such high concentrations were applied because for amaranth a minimum of such concentrations were required to obtain reasonable responses.

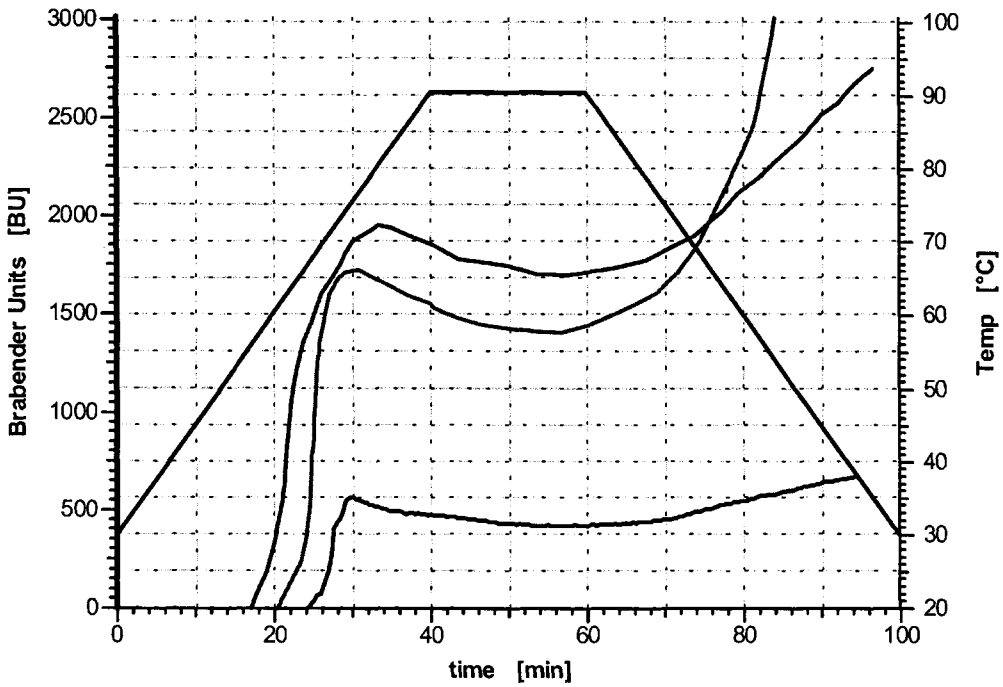

Fig. 6. Amaranth, Quinoa, Buckwheat - Brabender viscosity.

Amaranth forms the most stable structures which stand the applied temperature program significantly better than quinoa: after comparable minor disintegration in the initial temperature raising period, no further significant increase of viscosity was observed. Disintegration of quinoa glucans starts at lower temperatures than for amaranth, but is of similar magnitude. However, different to amaranth, disintegrated glucan/glucan interaction potential of quinoa glucans is high. Such a performance matches with results obtained from iodine-complexation: significantly longer branches for quinoa than for amaranth. The performance of buckwheat in the initial temperature rising period and the subsequent holding period is very similar to quinoa: supermolecular glucan structures of buckwheat are seriously disintegrated, but exhibit a high glucan/glucan-interaction potential. In the cooling period these interactions exceed the detectable scale, indicating a pronounced tendency to re-constitute supermolecular structures.

Resistance against mechanical, chemical and thermal stress

The three 5% (w/w) aqueous starch suspensions were found to be thixotropic. Viscosity decreases if shear stress is applied and regenerates or even exceeds the initial value after shearing is stopped.

In general, the applied shear stress of 1000 s^{-1} for 5 min didn't affect the investigated starches completely (Tab. 3): only loose-stabilized components within the supermolecular glucan-structures became disintegrated. An observed slight increase of viscosity for amaranth and quinoa should be due to a slightly increased reconstitution-tendency of supermolecular structures after shearing. The slightly decreased viscosity of buckwheat suspensions after shearing should be caused by destruction of loose-stabilized supermolecular structures.

Tabela 3

Molecular and technological characteristics of amaranth, quinoa and buckwheat.

	amaranth	**quinoa**	**buckwheat**
molecular characteristics			
iodine complexing potential of high molecular components: E_{640}/E_{525} E_{640}/E_{525} -correlated branching characteristics	0.4 - 0.55 scb	1.3 - 1.4 scb	1.2 - 1.4 scb
iodine complexing potential of low molecular components: E_{640}/E_{525} E_{640}/E_{525} -correlated branching characteristics lcb-glucans [%]	0.5 - 0.55 scb -	1.5 - 1.7 scb -	1.6 - 2.2 lcb 24
weight average molecular weight: M_w [g/M]	$11.8x10^6$	$11.3x10^6$	$15.4x10^6$
relative packing density of molecules	ref = 1.0	0.9	2.6
technological characteristics			
isolated from / provided by	*Amaranthus cruentus*	*Chenopodium quinoa*	*Fagopyrum esulentum*
moisture [%]	12.4	13.2	11.0
glucan content [% dry matter]	97.0	97.9	95.8
Brabender visc. 90→30°C: $[BE]_{30°C}/[BE]_{90°C}$	1.6	1.5	2.7
visc.of 5% aqu.suspension at 95°C [mPas]	122	187	230
stability against shear stress	high	high	medium
acid resistance	non	medium	low
status of starch-suspensions after the first freeze/thaw cycle	pasteous: thin-liquid	pasteous: gelous	gel: stiff
freeze/thaw stability	high	non	high

scb: amylopectin-type short-chain branched glucans; nb/lcb: amylose-type non-branched/long-chain branched glucans; E_{640}: extinction at 640 nm; E_{525}: extinction at 525 nm; M_w: weight average molecular weight;

Different to the applied shear stress, citric acid of pH 3 causes significant changes. Stability of scb-starches amaranth and for the mixed-type scb/lcb-glucans buckwheat was found to be bad. However, glucans of quinoa performed surprisingly well and kept more than half of the initial viscosity.

Consistency of aqueous starch suspensions after an initial freeze/thaw-cycle range from: scb-glucan amranth 'thin-liquid paste', quinoa 'gelly paste' and buckwheat 'stiff gel'. Quinoa liberates water already in the first freeze/thaw cycle of 20%. Quite different in their molecular characteristics, amaranth and buckwheat perform similarly well in a sequence of seven freeze/thaw cycles. These starches obviously form supermolecular structures, which are not collapsing at the applied conditions.

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STRUKTURA MOLEKULARNA I WŁAŚCIWOŚCI FIZYKOCHEMICZNE SKROBI PSEUDOZBOŻOWYCH

Streszczenie

Zbadano glukany skrobi pseudozbożowych o istotnych różnicach w ich rozgałęzieniach (amarantus, chinoa i gryka). Ich charakterystykę molekularną skorelowano z właściwościami technologicznymi. Niezmienność konformacji glukanów, zwłaszcza pod wpływem wzrastającej temperatury, odczyn kwaśny i naprężenia mechaniczne rozważano pod kątem wpływu tych parametrów na strukturę molekularną i supramolekularną roztworów skrobi w DMSO.

Skrobiowe glukany wydzielono przez półpreparatywną chromatografię na sefadeksach (SEC) a uzyskane frakcje charakteryzowano za pomocą reakcji z jodem. Amarantus miał krótkie rozgałęzienia (sbc = typ amylopektynowy), chinoa również należała do typu sbc, ale jej rozgałęzienia były dłuższe niż u amarantusa, a gryka była mieszaniną glukanów sbc z 24% domieszką długich rozgałęzień (lcb = typu amylozy).

Ciężar cząsteczkowy (stopień polimeryzacji) skrobi w DMSO został wyznaczony metodą absolutną za pomocą SEC. Badane próbki miały średni ciężar cząsteczkowy bliski 1,2·106 g/M. Rozmiar heliksów glukanów skrobiowych wyznaczony za pomocą SEC w połączeniu z uniwersalną kalibracją wynosił 2–40 nm bez istotnych różnic dla wszystkich trzech skrobi. Mimo tego badane skrobie różniły się istotnie ich miedzy- i wewnątrzcząsteczkowym potencjałem. Wynika stąd, że potencjał oddziaływań zależy w znacznym stopniu od rodzaju rozgałęzienia i upakowania w heliksach od czego zależy struktura supramolekularna.