Starch Molecular Characteristics and Digestion Properties

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Presentation Outline

• Background on starch digestion
• Slowly digestible/low glycemic starch – is it a defined material?
• What kind of starch structures are digested slower?
• Implications
Glycemic Index

A measure of carbohydrate (starch) digestion rate

Area under the glycemic curve after consumption of 50 g CHO from test food divided by area under curve after 50 g CHO from control food

Source: D. Ludwig

Soy beans
White bread
Soy beans

Area under the glycemic curve after consumption of 50 g CHO from test food divided by area under curve after 50 g CHO from control food
GI and GL concepts now being studied fairly intensively

• In a recent review “Glycemic index and load – dynamic dietary guidelines in the context of diseases” by P.C. Colombani, Swiss Federal Institute of Technology (2004, Physiology and Behavior 83:603)
  – 90 of the 115 references were published since 2000
• In a Medline search for “glycemic or glycaemic”
  – 2005 – 1097 hits
  – 2006 – 1186 its
Starch

- Amylopectin (AP)
  - Highly branched
  - MW >10^7 daltons
  - Slow reassociation on cooling
  - Gelatinization and retrogradation thermal transitions related to AP
- About 5-6 x 10^7 amylopectin molecules in a single starch granule

Cluster model for rice AP structure, CL denotes chain length (Hizukuri, 1986)
Amylopectin Fine Structure

(Hizukuri 1986)
Starch Digestion

- In the human, by the action of 3 enzyme types:
  - \( \alpha \)-Amylase (salivary and pancreatic)
  - Small intestinal brush border enzymes
    - Maltase-glucoamylase (MGAM)
    - Sucrase-isomaltase (SI)
- In vitro assays use (generally):
  - Porcine pancreatic \( \alpha \)-amylase or pancreatin
  - Fungal amyloglucosidase (glucoamylase)
α-Amylase

- Endoenzyme
- Hydrolyzes α-1,4 linkages
- Unable to cleave α-1,6 and neighboring α-1,4 linkages
- Final products:
  - Maltose, maltotriose, and maltotetraose
  - α-Limit dextrins (amylopectin)
**α-Limit Dextrins**

- Heterogeneous mixtures
- DP: 4 - more than 10
- Contains 1,6 and two or more adjacent 1,4 linkages
- Smallest is tetrasaccharide
- Generally though to be processed to glucose rather rapidly

(French 1970)
Classification of Starch

• Nutritionally
  • Rapidly Digestible Starch (RDS)
  • Resistant Starch (RS)
  • Slowly Digestible Starch (SDS)
• RDS: Digested within 20 min
• RS: Not digested and absorbed in the small intestine
• SDS: Digested between 20 and 120 min

(Englyst 1992 & 1996)
How to get to the slowly digestible starch/low GI state?

G. Zhang, WCCR
Starch and Its Digestion Property

• Uncooked native starch is inherently more difficult to digest
  – Uncooked corn starch has high slowly digestible property, however has somewhat limited use in foods

• Cooked starches
  – Amylose
    • Retrogrades quickly
    • Known to relate to resistant starch property
  – Amylopectin
    • Retrogrades slowly, though variably depending on structure
    • Responsible for slowly digestible characteristic of native starches (e.g., maize starch)
How Does Amylopectin Fine Structural Variability Influence Digestion Property?

Questions:

1. Are there structures that inherently differ in digestion rate? (that is – independent of retrogradation)

2. Are there structures that are more prone to retrogradation, and how does that influence digestion property?

3. Broader question – how much change is needed to elicit a physiological effect?
Are there structures that inherently differ in digestion rate?

- Increase in branching and shortening of chains does slow starch digestion rate, as is shown in the following example.
- Does variability in amylopectin fine structures seen within varieties and mutants demonstrate the same thing?
Shortening the Chain-Length

Amylose and amylopectin

Maltogenic α-amylase

β-Amylase

Maltodextrin

Maltose
Enzyme-treated shortened amylopectin retards digestion rate

BA=β-amylase, NV=maltogenic α-amylase, TG=transglucosidase
Corn Starch Study

- 60 lines analyzed consisting of normal and starch mutants (single and double mutants)
  - Englyst test conducted after cooking to a paste and cooled overnight
- RS and amylose content were correlated ($r=0.763$) indicating that SDS relates to amylopectin structure
- 18 lines selected based on a range of SDS and RS and were investigated for amylopectin fine structure
- 2 groups appeared:
  1. High ratio of short chains (DP<13) to long chains (DP>13)
  2. Low ratio of short chains (DP<13) to long chains (DP>13)
Size-exclusion chromatography of debranched starch

• Dotted line = DP13
Relationship between proportion of SDS and the weight ratio of the short chain fraction (SF, DP < 13) to the long chain fraction (LF, DP ≥ 13) of debranched amylopectin

R² = 0.7147
The correlation matrix of amylopectin structure with digestibility for varieties with low SF/LF ratios (Group I)

<table>
<thead>
<tr>
<th>Fraction (AP)</th>
<th>SDS</th>
<th>P-value</th>
<th>RS</th>
<th>P-value</th>
<th>RDS</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP5-9</td>
<td>-0.779</td>
<td>0.0133</td>
<td>-0.546</td>
<td>X*</td>
<td>0.832</td>
<td>0.0053</td>
</tr>
<tr>
<td>DP9-13</td>
<td>-0.855</td>
<td>0.0033</td>
<td>-0.455</td>
<td>X</td>
<td>0.807</td>
<td>0.0086</td>
</tr>
<tr>
<td>Total SF</td>
<td>-0.830</td>
<td>0.0056</td>
<td>-0.495</td>
<td>X</td>
<td>0.823</td>
<td>0.0064</td>
</tr>
<tr>
<td>DP13-30</td>
<td>-0.636</td>
<td>X</td>
<td>-0.398</td>
<td>X</td>
<td>0.648</td>
<td>X</td>
</tr>
<tr>
<td>DP30-69</td>
<td>0.752</td>
<td>0.0193</td>
<td>0.502</td>
<td>X</td>
<td>-0.786</td>
<td>0.0119</td>
</tr>
<tr>
<td>DP &gt; 69</td>
<td>0.721</td>
<td>0.0284</td>
<td>0.413</td>
<td>X</td>
<td>-0.703</td>
<td>0.0344</td>
</tr>
<tr>
<td>Total LF</td>
<td>0.829</td>
<td>0.0057</td>
<td>0.497</td>
<td>X</td>
<td>-0.824</td>
<td>0.0063</td>
</tr>
<tr>
<td>SF/LF</td>
<td>-0.795</td>
<td>0.0104</td>
<td>-0.525</td>
<td>X</td>
<td>0.827</td>
<td>0.0059</td>
</tr>
<tr>
<td>Amylose</td>
<td>0.157</td>
<td>X</td>
<td>0.852</td>
<td>0.0035</td>
<td>-0.732</td>
<td>0.0249</td>
</tr>
</tbody>
</table>
Relationship between proportion of SDS and the weight ratio of the short chain fraction (SF, DP < 13) to the long chain fraction (LF, DP ≥ 13) of debranched amylopectin.
The correlation matrix of amylopectin structure with digestibility for varieties with high SF/LF ratios (Group 2)

<table>
<thead>
<tr>
<th>Fraction (AP)</th>
<th>SDS</th>
<th>P-value</th>
<th>RS</th>
<th>P-value</th>
<th>RDS</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP5-9</td>
<td>0.689</td>
<td>0.0275</td>
<td>0.298</td>
<td>X*</td>
<td>-0.639</td>
<td>0.0467</td>
</tr>
<tr>
<td>DP9-13</td>
<td>0.279</td>
<td>X</td>
<td>0.447</td>
<td>X</td>
<td>-0.345</td>
<td>X</td>
</tr>
<tr>
<td>Total SF</td>
<td>0.803</td>
<td>0.0051</td>
<td>0.538</td>
<td>X</td>
<td>-0.820</td>
<td>0.0037</td>
</tr>
<tr>
<td>DP13-30</td>
<td>0.123</td>
<td>X</td>
<td>0.237</td>
<td>X</td>
<td>-0.149</td>
<td>X</td>
</tr>
<tr>
<td>DP30-69</td>
<td>-0.715</td>
<td>0.0202</td>
<td>-0.751</td>
<td>0.0122</td>
<td>0.843</td>
<td>0.0022</td>
</tr>
<tr>
<td>DP &gt; 69</td>
<td>-0.563</td>
<td>X</td>
<td>-0.144</td>
<td>X</td>
<td>0.430</td>
<td>X</td>
</tr>
<tr>
<td>Total LF</td>
<td>-0.803</td>
<td>0.0051</td>
<td>-0.538</td>
<td>X</td>
<td>0.820</td>
<td>0.0037</td>
</tr>
<tr>
<td>SF/LF</td>
<td>0.801</td>
<td>0.0054</td>
<td>0.519</td>
<td>X</td>
<td>-0.810</td>
<td>0.0045</td>
</tr>
<tr>
<td>Amylose</td>
<td>-0.264</td>
<td>X</td>
<td>0.394</td>
<td>X</td>
<td>-0.010</td>
<td>X</td>
</tr>
</tbody>
</table>
Amylopectin molecules with more proportion of long chains (A), and more proportion of short chains (B)

Lower branching,
long internal chains,
faster retrograding,
higher SDS

High branching,
very short chains,
slow to no retrogradation,
higher SDS
Chromatograms of products resulted from the action of α-amylase on amylopectins for 4 hrs

High proportions of short side chains and high branching density

High proportion of long B chains and low branching density

S. Maghaydah
Digestion profiles of α-amylase degraded products incubated with amyloglucosidase enzyme for 1 hour
Rice Study

• A similar trend was found among a range of normal US rice varieties
• Followed the correlation of the group with the lower short to long chain ratio
  – Rice amylopectin with higher long chains correlated to more SDS in cooked rice flour stored overnight at 4°C
Small variations in rice amylopectin structure affect digestion properties

M. Benmoussa
<table>
<thead>
<tr>
<th>Fraction</th>
<th>RDS</th>
<th>SDS</th>
<th>RS</th>
</tr>
</thead>
<tbody>
<tr>
<td>FrI</td>
<td>-0.87**</td>
<td>0.79**</td>
<td>NS</td>
</tr>
<tr>
<td>FrII</td>
<td>-0.81**</td>
<td>0.77**</td>
<td>NS</td>
</tr>
<tr>
<td>FrIII</td>
<td>0.79**</td>
<td>-0.76**</td>
<td>NS</td>
</tr>
</tbody>
</table>

**Correlation is significant at 0.01 level.**

**NS not significant.**
Conclusions

- SDS is related to the amylopectin fraction
  - Amylopectin with higher amount of branches and very short chains do not retrograde well and are inherently slower to digest
  - Amylopectin with higher amount of internal long chains do retrograde more and, for this reason, are slower to digest
    - When stored at 4°C, SDS amount peaked ~24 hours and began to diminish at 4-5 days with concomitant increase in RS
Digestion Prediction Using RVA?

- In both studies (corn and rice), RVA breakdown viscosity showed high correlation with amount of SDS from Englyst assay.
- Based on relationship with amylopectin fine structures.
- A previous study (Han and Hamaker, 2001, J. Cereal Science) showed good relationship between RVA breakdown viscosity and proportion of amylopectin long chains.
SDS content and the ratio of breakdown to peak viscosity

Group I - high proportion of long chains
Group II - high proportion of short chains