Cereal Grains Structure & Composition

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Topics of Discussion

• Structure of Corn Kernel
  – Hand dissection exercise
• Starch
• Protein
• Oil
• Fiber
• Other Constituents
• Corn Composition
Structure of Cereal Grains

- Cereals are members of grass family
- Produce dry, one-seeded fruit, called caryopsis
- Caryopsis is also called kernel or grain
- Caryopsis consists of
  - Fruit coat or pericarp, which surrounds seed and is tightly adhered to seed coat
  - Seed, which consists of germ or embryo and endosperm enclosed by a nucellar epidermis and a seed coat
- All cereal grains have these same parts in approx. same relationship to each other

Structure of Corn Kernel

Pericarp
Endosperm
Germ
Tip Cap
Scanning Electron Micrograph (SEM) of Dissected Steeped Corn Kernel

Pericarp

- 5 to 6% of kernel dry weight

- Cells in pericarp: hollow tubes, channels for water absorption via tip cap
- Seed coat: semipermeable
- Walls of pericarp contain cellulose and pentosans, no lignin.
Aleurone layer

- Aleurone layer beneath seed coat
- Aleurone layer cells contain protein bodies (good amino acid profile), oil bodies, and no starch. It is rich in minerals (phytin)
- Removed with pericarp in wet milling

Germ

- 10 to 12% of kernel dry weight
- Stores nutrients and minerals
- Contains 81 to 85% of total kernel oil (mostly triglycerides)
- Composed of embryo and scutellum
- Scutellum contains oil bodies
**Corn Germ: Phytic Acid (Phytate)**

- Phytate is principal storage form of phosphorus in many plant tissues
  - Yellow Dent Corn
    - Whole Corn (0.89%)
    - Endosperm (0.04%)
    - Germ (6.25%)
    - Pericarp (0.07%)

![Inositol hexakisphosphate, IP6](image)

**Endosperm**

- 82 to 84% of kernel dry weight, 86 to 89% starch by weight
- In corn both translucent and opaque endosperm are found with a single kernel
**Endosperm**

- Translucent endosperm (Hard endosperm)
  - Tightly packed with few or no air spaces
  - Polygonal shaped starch granules
  - Starch granules are held together by a matrix protein
  - Protein bodies are zein
- Opaque Endosperm (Soft endosperm)
  - Starch granules are spherical
  - Starch granules covered with protein matrix that does not contain protein bodies
- True density is measure of endosperm hardness

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**SEMs of Corn Endosperm**
**SEM of Cells in Soft Endosperm**

Air space, loosely packed starch granules, thin protein matrix and exposed starch granules

*Source*: USDA/ARS/ERRC

**SEM of Corn Endosperm**

Cells in corn endosperm containing tightly bound starch granules

*Source*: USDA/ARS/ERRC
SEM of Cells in Hard Endosperm

Tightly packed starch granules with adhering protein matrix and few exposed starch granules

Source: USDA/ARS/ERRC

Corn Hand Dissection Exercise
Corn Kernel Hand Dissection

Starch, Protein, Oil, Fiber and Other Minor Constituents
Starch

• Primary source of stored energy in cereal grains
• 60-75% weight of grain
• Used in several food and industrial applications

Starch Physical Structure

• Found in form of granule in cereal grains
• Granules are formed inside plastids
• In wheat, rye, barley, sorghum inside a plastid there is a single starch granule
• In rice and oats there are several or compounds starch granules
• Starch granules grow in layers
**Growth of Starch Granule**

**Starch Chemical Composition**

- Starch is a polymer of a six-carbon sugar D-glucose
- The structure of D-glucose can be shown in ring form or open chain
Starch Chemical Composition

- Starch consists primarily of D-glucopyranose polymers linked together by alpha 1,4 and alpha 1,6 glycosidic bonds
- Polymer are of two kinds
  - Amylose, smaller linear polymer, alpha 1,4 bonds
  - Amylopectin, larger branched polymer, branching at alpha 1,6 bonds
### Starch Chemical Composition

- The molecular size of polymer (degree of polymerization, DP) for
  - Amylose is 1,500-6,000
  - Amylopectin is 300,000-3,000,000
- Dent corn typically has 23-25% Amylose and 75-77% Amylopectin
- Waxy corn has less than 1% Amylose and more than 99% Amylopectin
- High-amylose corn has 55-70% Amylose and 30-45% Amylopectin

### Starch Chemical Composition

- Amylose molecules due to their long and linear nature form complexes with chemical compounds
  - For example with iodine amylose molecules give blue color
  - Test for determination of waxy corn hybrids
Crystallinity Emerges From Amylopectin Structure

Jenkins et al., 1994

Amylopectin superhelical structure.
Oostergetel and van Bruggen, 1993

100% amylopectin: 40% crystalline
High-amylose: 15% crystalline

Hairy Billiard Ball Model

Robertson et al 2006
Channels from Surface to Hilum

Amylopectin Structure

- Non reducing ends
- Alpha A attack
- Gluco A attack
- A-Chains
- C-Chain
- B-Chains
- Reducing end
- Granule Surface
- Granule Center
Amylopectin Structure

- Non reducing ends
- A-Chains
- C-Chain
- B-Chains
- Granule Surface
- Granule Center
- Reducing end

Amylose Structure: Helix

- Six anhydrous glucose units per helix turn
- Reducing end
- Non reducing end
Properties of Starch

- Crystallinity
  - Packing of amylose and amylopectin within starch granule is not random but is very organized
  - A, B and C X-ray patterns
  - Most cereal starches give the A pattern

- Birefringence
  - Under polarized light, starch granules show birefringence in form of a “maltese cross”

Starch X-ray Diffraction Pattern

- Corn and most cereals exhibit A-pattern, but amylomaize are closer to B-pattern (exhibited by most tubers like potato)

Robyt, 1998
Characteristics of Starch in Cereal Grain

- The size, shape and structure of starch granules varies among botanical sources
- Size of granules range from less 1 \( \mu m \) to 100 \( \mu m \)
- Shapes can be spherical, ovoid or angular
### Characteristics of Starch in Cereal Grain

<table>
<thead>
<tr>
<th>Cereal Grain</th>
<th>Gelatinization Temperature (°C)</th>
<th>Shape</th>
<th>Granule Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barley</td>
<td>51-60</td>
<td>Elliptical</td>
<td>20-25</td>
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<tr>
<td></td>
<td></td>
<td>Spherical</td>
<td>2-6</td>
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<tr>
<td>Wheat</td>
<td>58-64</td>
<td>Lenticular</td>
<td>25-35</td>
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<tr>
<td></td>
<td></td>
<td>Round</td>
<td>2-10</td>
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<tr>
<td>Corn</td>
<td>62-72</td>
<td>Round/Polyhedral</td>
<td>15</td>
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<tr>
<td>Rice*</td>
<td>68-78</td>
<td>Polygonal</td>
<td>3-8</td>
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<tr>
<td>Sorghum</td>
<td>68-78</td>
<td>Round</td>
<td>15</td>
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<tr>
<td>Oats*</td>
<td>53-59</td>
<td>Polyhedral</td>
<td>3-10</td>
</tr>
<tr>
<td>Rye</td>
<td>57-78</td>
<td>Round/Lenticular</td>
<td>28</td>
</tr>
</tbody>
</table>

*Individual not compound granules

### Starch Granular Changes in Relationship to Viscosity

- **Fully Swollen**: Intact granules, polymer begins to leach
- **Granules Begin to Break**: polymer continue of solubilize (drop in viscosity)
- **Solubilized polymers begin To reassociate (rise in Viscosity)**

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Proteins

Structure of Protein

- Proteins are built from a repertoire of 20 amino acids

General Structure of Amino Acid.
The R group is the side chain. Amino Acids are commonly grouped by their type of R groups.

<table>
<thead>
<tr>
<th>Amino Acids</th>
<th>Three letter Abbreviation</th>
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</thead>
<tbody>
<tr>
<td>Alanine</td>
<td>Ala</td>
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<tr>
<td>Arginine</td>
<td>Arg</td>
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<tr>
<td>Asparagine</td>
<td>Asn</td>
</tr>
<tr>
<td>Aspartic Acid</td>
<td>Asp</td>
</tr>
<tr>
<td>Asparagine or</td>
<td>Asx</td>
</tr>
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<td>Aspartic Acid</td>
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<td>Cysteine</td>
<td>Cys</td>
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<td>Glutamine</td>
<td>Gln</td>
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<tr>
<td>Glutamic acid</td>
<td>Glu</td>
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<td>Glutamine or</td>
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<td>Gly</td>
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<td>Histidine</td>
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<td>Isoleucine</td>
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<td>Leucine</td>
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<tr>
<td>Lysine</td>
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</tr>
<tr>
<td>Methionine</td>
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<tr>
<td>Phenylalanine</td>
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<tr>
<td>Proline</td>
<td>Pro</td>
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<td>Serine</td>
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<tr>
<td>Tyrosine</td>
<td>Tyr</td>
</tr>
<tr>
<td>Valine</td>
<td>Val</td>
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</table>
Structure of Protein

- A protein is a polypeptide with a specific sequence of amino acids and tridimensional structure
- The acid and amino group of each amino acid are involved in the peptide bonds and form the backbone of protein

![Amino-terminal residue](image)

Structure of Protein

- Primary Structure
  - Sequence of amino acids
- Secondary Structure
  - R group on amino acid can react with other R groups (one of the factors)
  - Hydrogen bonds

![Sulphydryl Group](image)

![Disulfide Bond](image)
Structure of Protein

- Tertiary Structure
- Quaternary structure

Three dimensional structure of protein determines its properties
- e.g. whether protein is soluble in water or not
- Heat or alteration of pH can denature proteins
Classification of Protein

• Generally classified into four types according to their solubility (work by T. B. Osborne)
  – Albumins: soluble in water e.g. egg white
  – Globulins: soluble in dilute salt solutions
  – Prolamins: soluble in 70% alcohol
  – Glutelins: soluble in dilute acid or base
• This classification is widely used but the fractions obtained are not clear cut
  – e.g. prolams have limited solubility in water at low ionic strength
  – better classification can be done by several analytical techniques such as electrophoresis, isoelectric focusing, gel filtration etc.

Albumins & Globulins

• Most of the physiologically active proteins (enzymes) are present in albumins and globulins
• These proteins in cereal grains are mainly in aleurone layer, bran & germ fractions
  – Very low in endosperm
• Good amino acid balance
• High in Lysine, Tryptophan and Methionine
Prolamins & Glutelins

- These are storage proteins
- In cereal grains mainly founds in endosperm
- Low in nutritionally important amino acids
  - Lysine, Tryptophan and Methionine

Variation in Protein Content
Protein Content Determination

- Protein content of cereal grains is estimated as the nitrogen content times 6.25
  - This factor is used for all cereals except for rice and wheat

Corn Proteins

- Protein in Corn Endosperm
  - 5% Albumins and Globulins
  - 44% Zein
  - 28% Glutelin
  - 17% is not classified by Osborne technique
- Protein not classified by Osborne technique is mainly zein fraction cross linked by disulfide bonds
Oils

Oil in Corn Kernels and Corn Germ?

% Extractable Oil

- Corn Kernels: 3-4
- Corn Germ, from wet mills: 44-50
- Corn Germ, from dry mills: 18-22
Chemical Composition of Vegetable Oils

- 98-99% triacylglycerols, triglycerides, TAG

Triacylglycerols, Fatty Acids, Saturation, and Physical Properties of Oils

Triacylglycerols (triglycerides), each is comprised of one glycerol molecule esterified to three fatty acids.

- Saturated FA: Palmitic Acid, 16:0
- Monounsaturated FA: Oleic Acid, 18:1
- Polyunsaturated FA: Linoleic Acid, 18:2
Lipids In Vegetable Oils

- Saponifiables (>99%) (Acyl Lipids, TAG)
- Unsaponifiables (<1%)
  - Phytosterols
    - Free
    - acyl esters
    - OH-cinnamate esters
  - Tocols
    - Tocopherols
    - Tocotrienols
  - Carotenoids
    - carotenes (w/o OH)
    - xanthophylls (with OH)
  - Others (squalene, phospholipids, glycolipids)

Fibers
Cellulose

- Structural polysaccharide
  - D-glucose molecules (Beta 1, 4 bonds)

Cellulose

- Large polymer, partially crystalline, insoluble
  - makes it resistant to many organisms and enzymes
  - Cellulose is usually found associated with lignin and other nonstarchy polysaccharides
- Mainly found in hull of cereal grains (rice, barley and oats)
  - Pericarp is rich in cellulose
  - Very little cellulose in endosperm
Hemicellulose and Pentosans

- Make up cell walls and cementing material that holds cells together
- Chemically
  - Simple sugars (Beta-glucans)
  - Complex polymers (pentoses, hexoses, proteins and phenolics)
- Can or cannot be soluble in water
- Water soluble pentosans form viscous solutions in water (oxidative gelation)

Other Minor Constituents
Other Minor Constituents

- Sugars
- Lipids
- Enzymes
- Vitamins and Minerals

Lipids

- Five most abundant fatty acids found in TAGs of corn oil are palmitic, stearic, oleic, linoleic and linolenic acid.
- Corn oil has high linoleic acid, essential polyunsaturated fatty acid
- Corn oil is fairly stable to oxidation
- Has low levels of saturated fatty acids, palmitic and stearic
- Contains high levels of antioxidants, tocols and other phenolic compounds
- Phytosterols
Vitamins and Minerals

Vitamin and Mineral Composition (mg/100 g) for a Number of Cereal Grains

<table>
<thead>
<tr>
<th>Vitamin or Mineral</th>
<th>Wheat</th>
<th>Rye</th>
<th>Barley</th>
<th>Oats</th>
<th>Rice</th>
<th>Corn</th>
<th>Sorghum</th>
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<tr>
<td>Vitamins</td>
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<td>Thiamine</td>
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<td>Riboflavin</td>
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<td>0.09</td>
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<td>Niacin</td>
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<td>4.9</td>
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<td>Pantothenic acid</td>
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<td>1.4</td>
<td>1.2</td>
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<td>6</td>
<td>6</td>
<td>1.5</td>
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Yellow Dent Corn Proximate Analysis

- **Fiber (NDF)**: 10%
- **Fat**: 4%
- **Protein**: 10%
- **Starch**: 72%
- **Others**: 4%
- **Others**: 10%

**Fiber Composition**

- Oil, 3%
- Hemicellulose, 40%
- Cellulose, 12%
- Starch, 25%
- Protein, 10%
- Others, 10%

**Others**

- Sugars, 2.5%
- Ash, 1.4%
- Minor Compds, 0.1%