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The Biochemistry of Rice

Lipids and Fats

The Story of Rice

Rice (Oryza sativa L.) is one of the most important cereal crops cultivated in the world; it feeds more than half of the world's population. Metabolome analysis, the investigation of all cellular metabolites, has become an important strategy for gaining insight into functional biology around understanding the flavor, health benefits, aroma and cultivation processes in rice production.

Japanese rice contains well-balanced nutritional elements. It has an ample supply of vegetable proteins, calcium and vitamins. While rice also contains an abundant supply of dietary fiber, the level of saturated fats, whose over-consumption is thought to be linked to lifestyle-related illnesses, is relatively modest. Cooked rice is composed of about 60% water. Eating a portion of about 200 grams of prepared rice means you are eating only about 80 grams of actual rice. The level of water content in rice relative to the water content in other comparable foods means that the level of calories is less. Rice is a food that encourages not only health, but beauty.

The commitment to improving quality in Japanese rice continues unabated. This includes improving the quality of rice itself, as well as, striving for cultivation that follows environmentally sustainable practices. Rice grain quality is an important economic trait that influences rice production in many rice-producing areas. Although the fat in rice grain is low (2–3%) and is concentrated in the germ and bran fractions, it is a key determinant of the processing and cooking quality of rice.

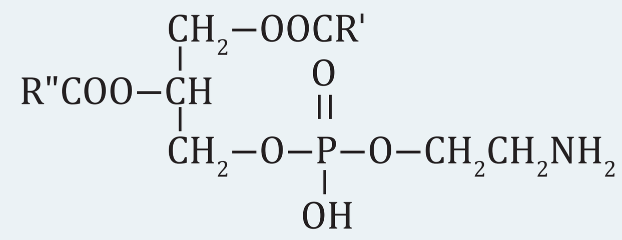
Oryza sativa, or Asian rice, contains two broad groups: indica (long-grain) and japonica (short-grain). Other types of Asian rice include glutinous rice and aromatic rice. All varieties of rice can be processed post-harvest as either white or brown rice, affecting flavor, texture and nutritive value. In short-grain rice varieties, including japonica varieties of Asian rice, grains tend to stick together when cooked. This is not to be confused with glutinous (or 'sticky') rice.

The stickiness of Japanese rice—the way the individual grains cling together—is due to its high proportion of starch. Starch is itself composed of amylose and amylopectin. Their proportions can vary according to the variety of rice, but in general if the level of amylose is low and amylopectin is high, you get sticky rice—the kind of rice grown in Japan.

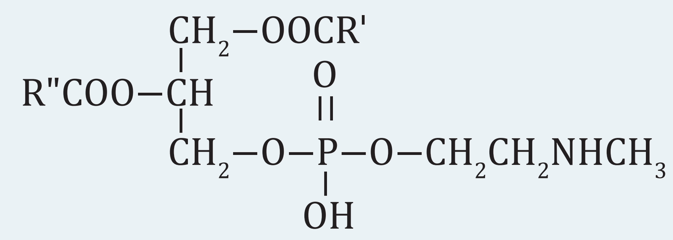
Lipid Content

A number of studies have shown that rice bran oil reduces the harmful cholesterol (LDL) without changing good cholesterol (HDL). On the other hand, reports showed that the hydrolysis and oxidation of rice fat are responsible for rice aging and deterioration of grain flavor during storage, and low-oil rice cultivars are more suitable for grain storage The lipids of these rice brans comprised mainly triacylglycerols (TAG) and phospholipids (PL) (Graph Lipid Distribution). The PL components included phosphatidyl choline (PC), phosphatidyl ethanolamine (PE) and phosphatidyl inositol (PI) (**Figure B: Lipid Structures**). Comparison of the different cultivars showed, with a few exceptions, there is no substantial difference in total lipid content.

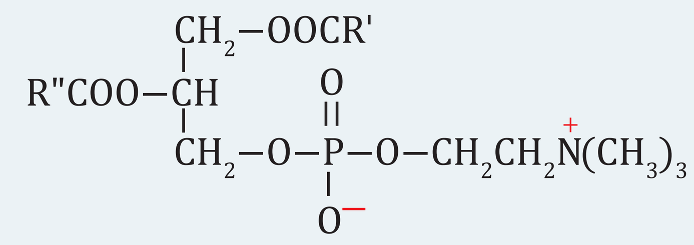
Phosphatidylethanolamine



Phosphatidylmonomethylethanolamine



Phosphatidylcholine



Phosphatidyldimethylethanolamine

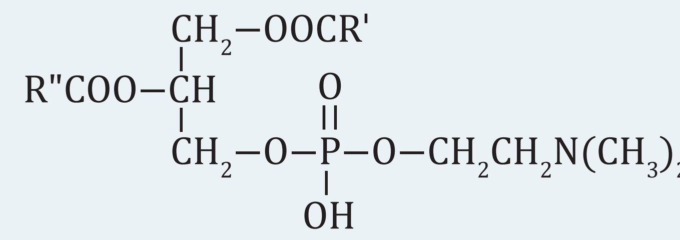
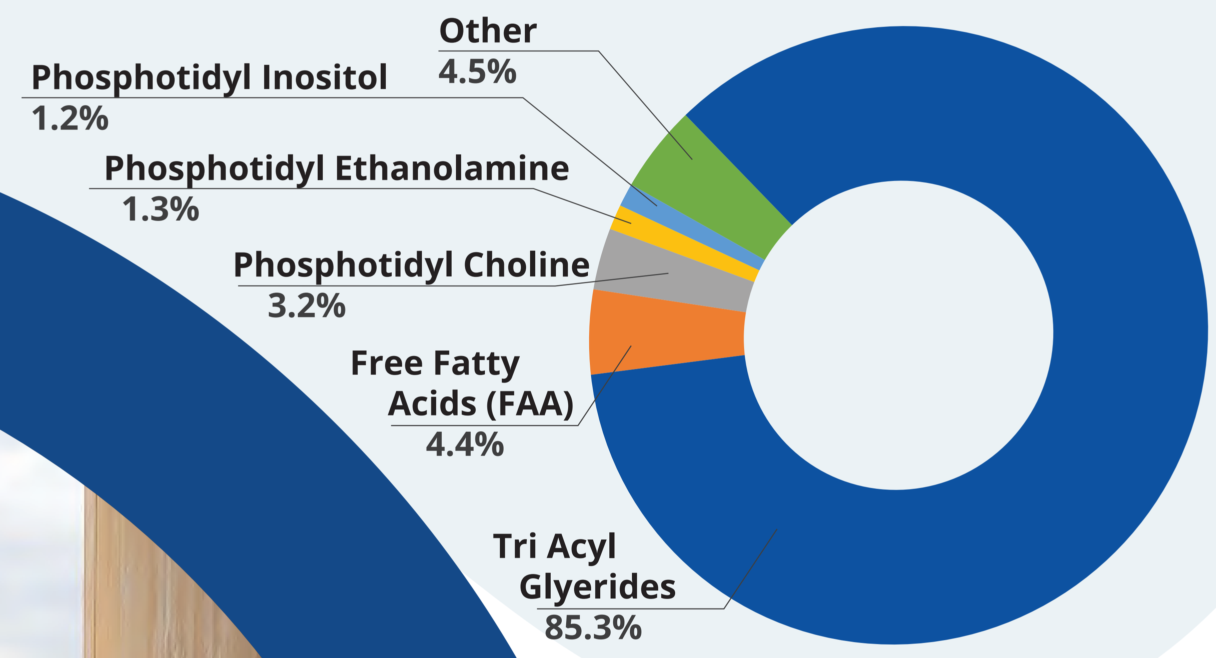
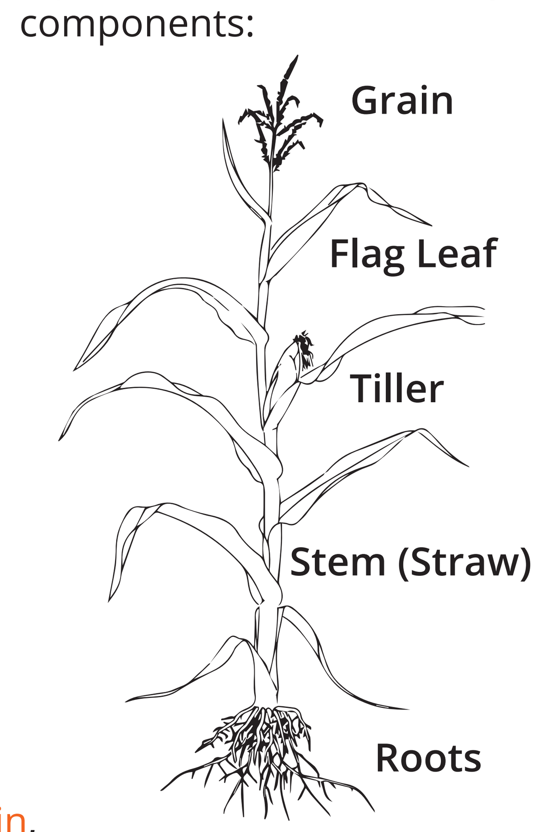


Figure B: Lipid Structures Acyl glyceride lipids consist of a glycerol core, a charged terminus of ethanolamine, monomethylethanolamine, dimethylethanolamine or trimethylethanolamine (Choline) with two long chain or very long chain fatty acids that can be saturated or unsaturated R' or R".



Cross Section Rice Plant

Oryza sativa L. rice plant is separated into 5 major components:



the grain,
the flag leaf,
the tiller,
the stem (straw),
and the roots.

Upon harvest, the grain contains the edible kernel that is polished rice.

Fatty Acid Content

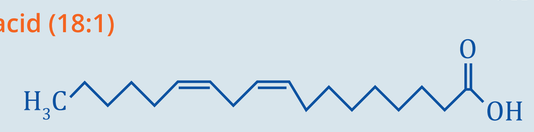
Free fatty acids (FFA) released by hydrolysis of the lipid during storage exert influences flavor and cooking quality of rice. To reduce risk of atherosclerosis, obesity, and maturity-onset diabetes, people are recommended that edible fat should have a reduced saturated fatty acid content and a linoleic acid (unsaturated fat) content amounting to at least one third of the total fatty acids (Graph Unsat vs Sat FFA). FFAs contribute significantly to the overall acceptability of rice grains by serving as sensory active flavor agents in cooked rice. Rice generally contains a majority of unsaturated fats (Graph % fatty acids). Edible oil is important as source of energy, essential fatty acids for cell structure and prostaglandins, and a vehicle for oil-soluble vitamins and for cell structure and membrane functions and control of blood lipids.

Lipid content and stearic acid, oleic acid, and linoleic acid contents can be significantly affected by variety and cropping year with palmitoleic acid and linolenic acid contents can be affected by cropping year (Figure A: Long Chain Fatty Acids).

Palmitic acid (16:0)

Stearic acid (18:0)

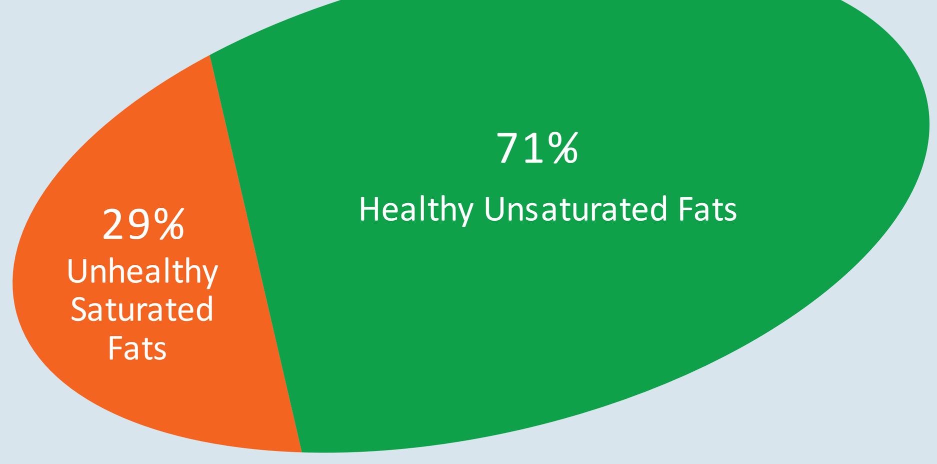
Oleic acid (18:1)



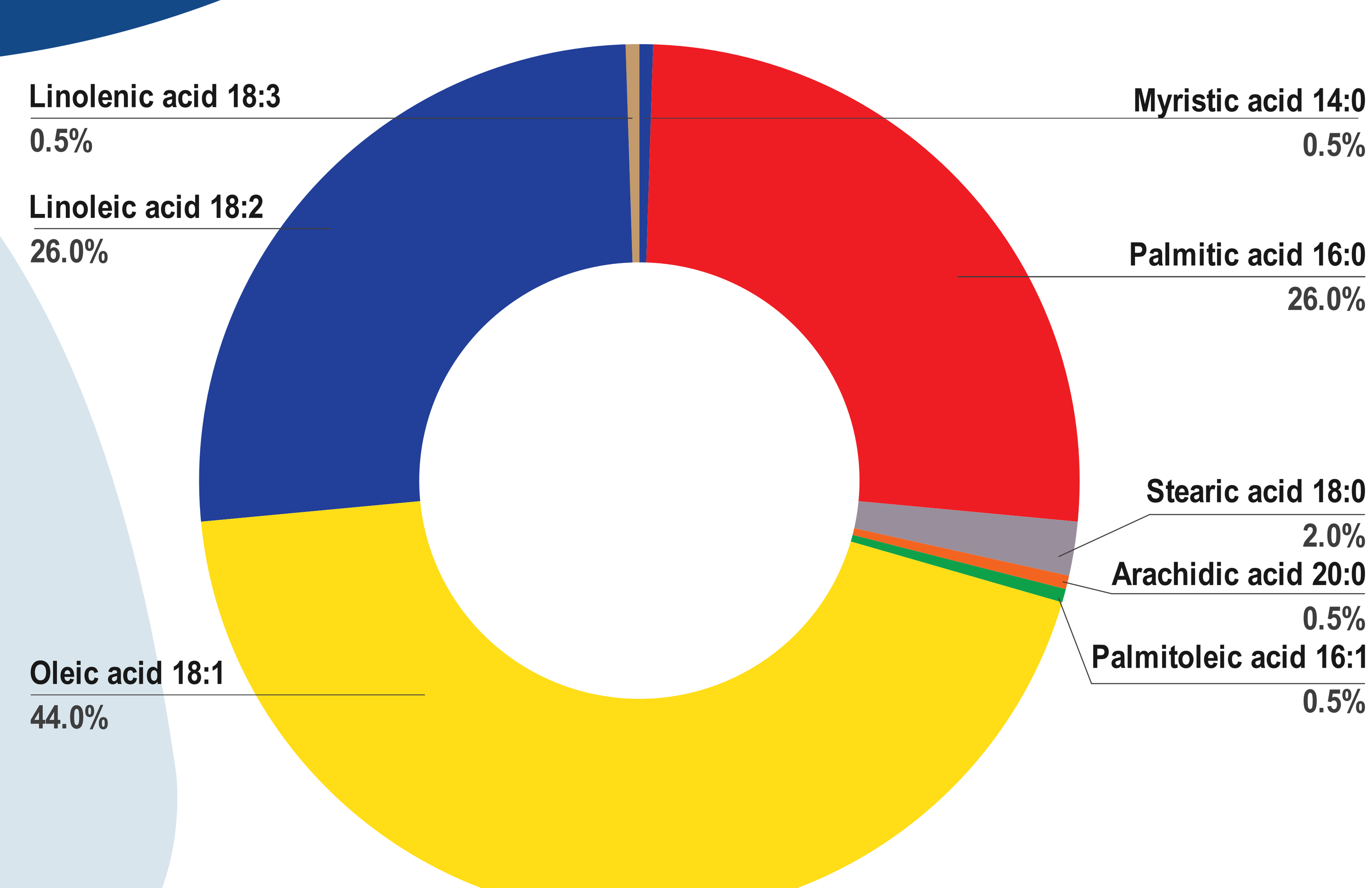
Linoleic acid (18:2)

Linolenic acid (18:3)

Figure A: Long Chain Fatty Acids The major long chain fatty acids in rice plants include more abundant unsaturated fatty acids like Oleic and Linoleic acids compared to the less abundant and less healthy saturated fatty acids like Palmitic acid.



Fat Content White Rice



Did You Know? (Statista.com, Ricepedia.org)

- Estimated Rice Revenue Japan JP Yen 808.5 Billion in 2020.
- In Japan, the on average per person consumption is around 43 kg of rice per year, or around 117 grams a day.
- Volume rice produced in Japan is 1,822 mKg / year.

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*Capillary-Electrophoresis Mass Spectrometry Based Metabolomics

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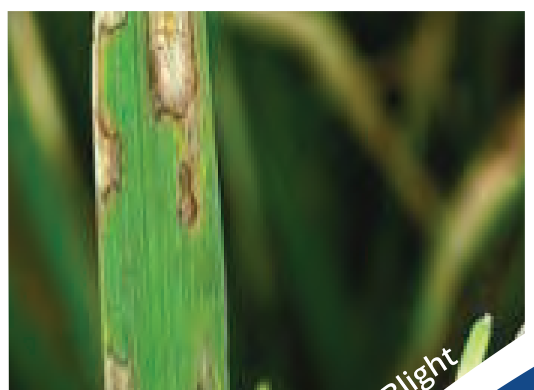
The Biochemistry of Rice

Amino Acids and Polar Metabolites

Improving Rice Production

Rice is one of our most important food crops and provides an essential part of the daily dietary intake for nearly half of the world's population. However, rice production worldwide is affected by various biotic and environmental stresses. Among all biotic stresses, pathogen infections are considered as major constraints for rice production as 10 to 30 per cent of the annual rice harvest is lost due to disease infection. Of many different infections, a common and severe disease in rice is sheath blight. Rice sheath blight disease is caused by Rhizoctonia solani and has led to large scale crop losses, especially in Japan. Rhizoctonia solani is a fungus that can affect rice production by reducing crop production through the inhibition of germination.

However, genetic breeding has successfully introduced species resistant varieties. Infection resistance strains (32R) have shown different physiological responses than infection susceptible rice lines (29S). Several key enzymes and metabolites in the phenylpropanoid phenylalanine ammonia lyase enzyme and shikimate pathways are observed to have increased after R. solani infection. Phenylpropanoid, amino acid and shikimate pathways are involved in plant defense mechanisms during pathogen infection. Plant metabolites, especially amino acids and phenols that are involved in plant defense to R. solani infection include glutamate, GABA, glycine, histidine, phenylalanine, serine, tryptophan, tyrosine, and pipecolic acid that are abundant in 29S (susceptible) species and influenced by the presence of R. solani. The enhancement of specific amino acids in 29S may increase the plant susceptibility as host response to necrotrophic pathogens. On the other side, chlorogenic acid was primarily higher in 32R (resistant) strains. These metabolomic results suggest that the accumulation of chlorogenic acid could be related to the resistance to pathogen as Chlorogenic acid levels are maintained high in 32R resistant strains perhaps to prepare for defense against a pathogen infection in advance (Figure A: Chlorogenic pathway).



Flavor and Aroma

The flavor of rice differs by type of rice and depends on if it has been polished (i.e. brown or white rice) and, of course, cooking methods. Those considerations are obvious to most of us. But flavor may also vary by genetics, the growing environment, type of fertilizer and cultural practices, the timing of draining and harvesting the field, harvest moisture content, rough rice drying conditions, final moisture content, storage conditions, degree of milling, and also finally also washing and soaking practices and serving temperature of the cooked rice. There are over a dozen different aromas and flavors in rice. Analyses have found

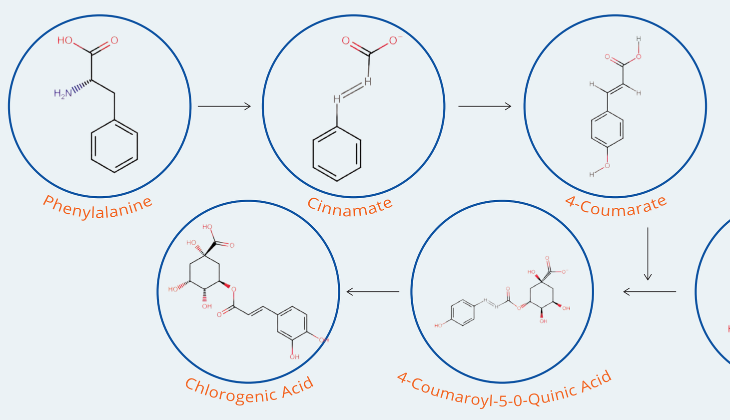
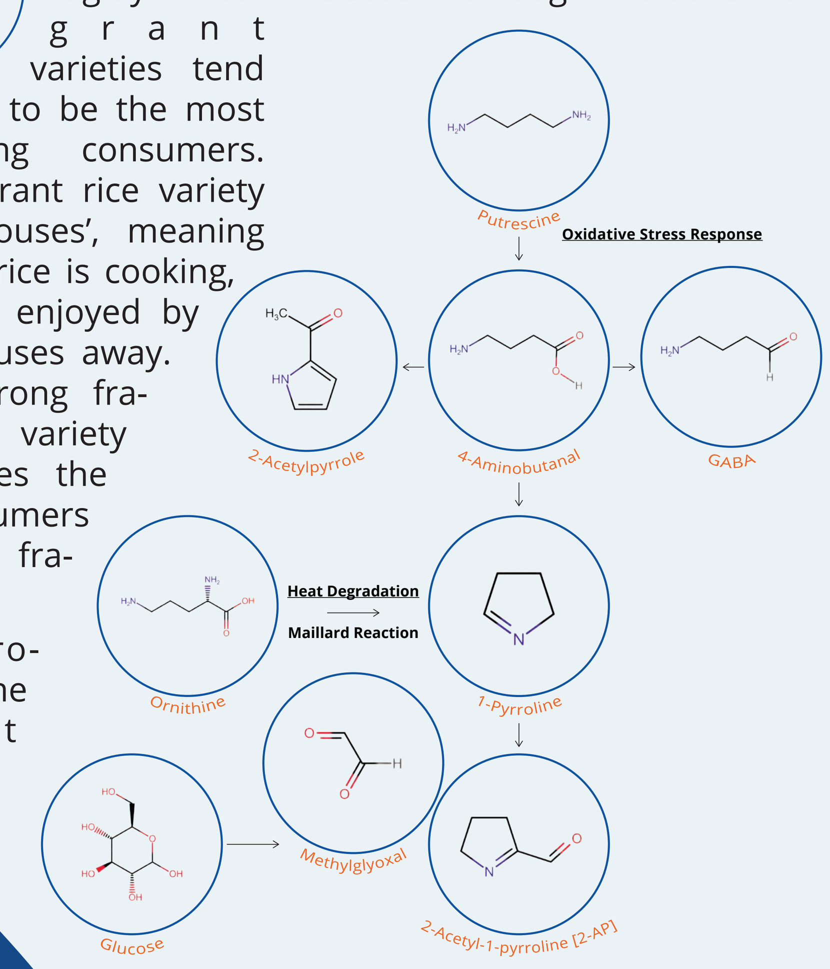


Figure A: Chlorogenic acid is biosynthesized from the amino acid Phenylalanine and maybe a chemical that provides pathogen resistance to riceplants.

over 200 volatile compounds present in rice. However, after over 30 years of research, little is known about the relationships between the numerous volatile compounds and aroma/flavor. Fragrant (or aromatic) rice commands the highest prices in the global rice market. The strength of fragrance differs between varieties and the most highly fragrant varieties tend to be the most popular among consumers. There is a fragrant rice variety called 'Four Houses', meaning that when this rice is cooking, its fragrance is enjoyed by people four houses away. Emphasizing strong fragrance through variety naming indicates the value that consumers place on highly fragrant rice.

2-acetyl-1-pyrroline (2AP) is the most important aroma compound in rice. However, three other amine heterocycles: 2-acetylpyrrole, pyrrole and 1-pyrroline also correlate strongly with the production of aromaticity and related through biochemical



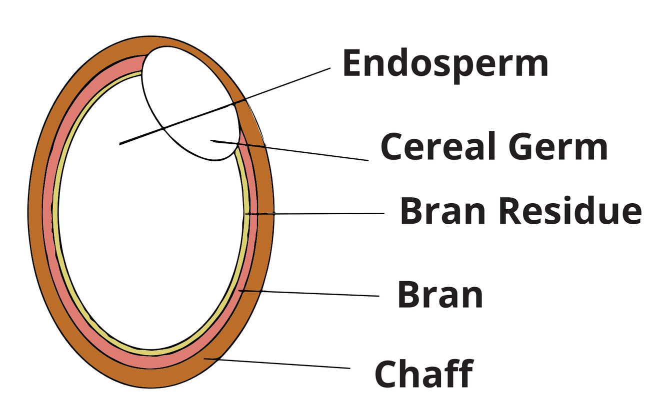
The aroma of rice can originate from a major metabolie, 2-AP, that is biosynthesized from polyamines by oxidative stress or through sugar (glucose) or amino acid (ornithine) by heat degradation. Other chemical intermediates including 2-acetylpyrrole and 1-pyrroline may contribute to oder.

pathways. Oxidative stress transforms putrescine to 4-aminobutanal (4-ABA), 4-ABA can then further convert to γ-aminobutyric acid (GABA), 2-acetylpyrrole or 1-pyrroline. GABA is a signaling metabolite while 2-acetylpyrrole can contribute to aroma. 1-pyrroline can combine with methylglyoxal to from 2-AP. In addition, 1-pyrroline can be formed from the heat denaturation by a maillard reaction from amino acids proline and ornithine. Methylglyoxal can be formed from the heat decomposition of glucose. Together, these metabolomic pathways provide new insights into the production of 2AP, and evidence for understanding the pathways leading to the accumulation of aroma in fragrant rice.

Polar Metabolites

The metabolites in rice can be categorized into two groups, primary and secondary. Primary metabolites include polar metabolites, glucose, sugars, lipids, vitamins, free amino acids and free fatty acids, those needed to provide fuel and energy for cellular growth, while secondary metabolites include complex metabolites that include flavonoids and terpenes that adjust to environmental stress (water, salt, temperature), as well as, providing additional health benefits for human consumption. Among these primary metabolites, the concentrations of certain free amino acids (FAA) have been linked directly to the taste scores of rice. This apparent relationship between the palatability of cooked rice and the FAA profile of rice grains has generated a growing interest in research on the physiological basis of FAA accumulation in rice grains. FAAs contribute significantly to the overall acceptability of rice grains by serving as sensory active flavor agents in cooked rice. FAA accumulation is a complicated process involving a complex of biochemical networks and control mechanisms. Metabolites existing in glycolysis, the tricarboxylic acid cycle, the pentose phosphate pathway (oxidative and reductive), photorespiration, and amino acid biosynthesis, can be classified into four groups. Group A contained amino acids, amines, and purine bases; group B included organic acids and sugar phosphates; group C included nucleotides and coenzymes; and group D containing neutral sugars (Chart A: Prominent Concentrations of Polar Metabolites nmol/g (wt)).

Cross Section Rice Grain



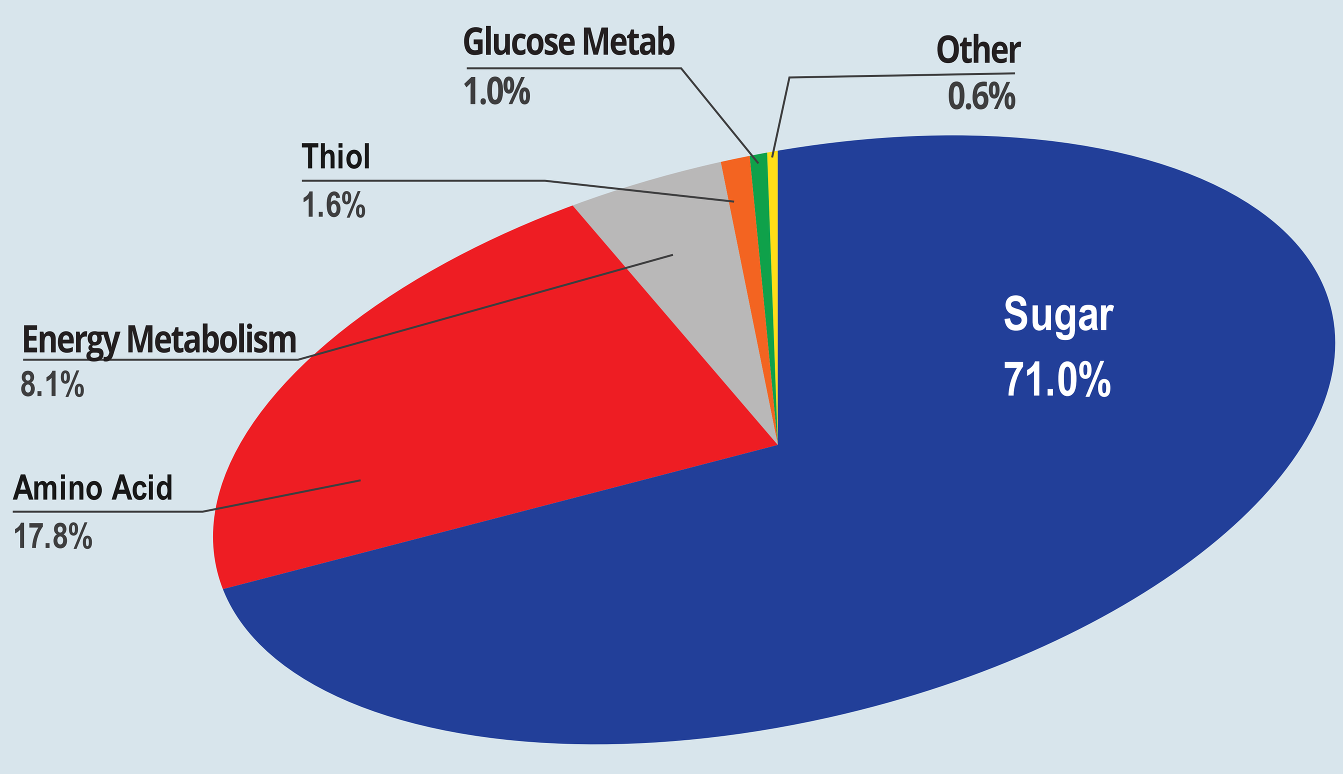
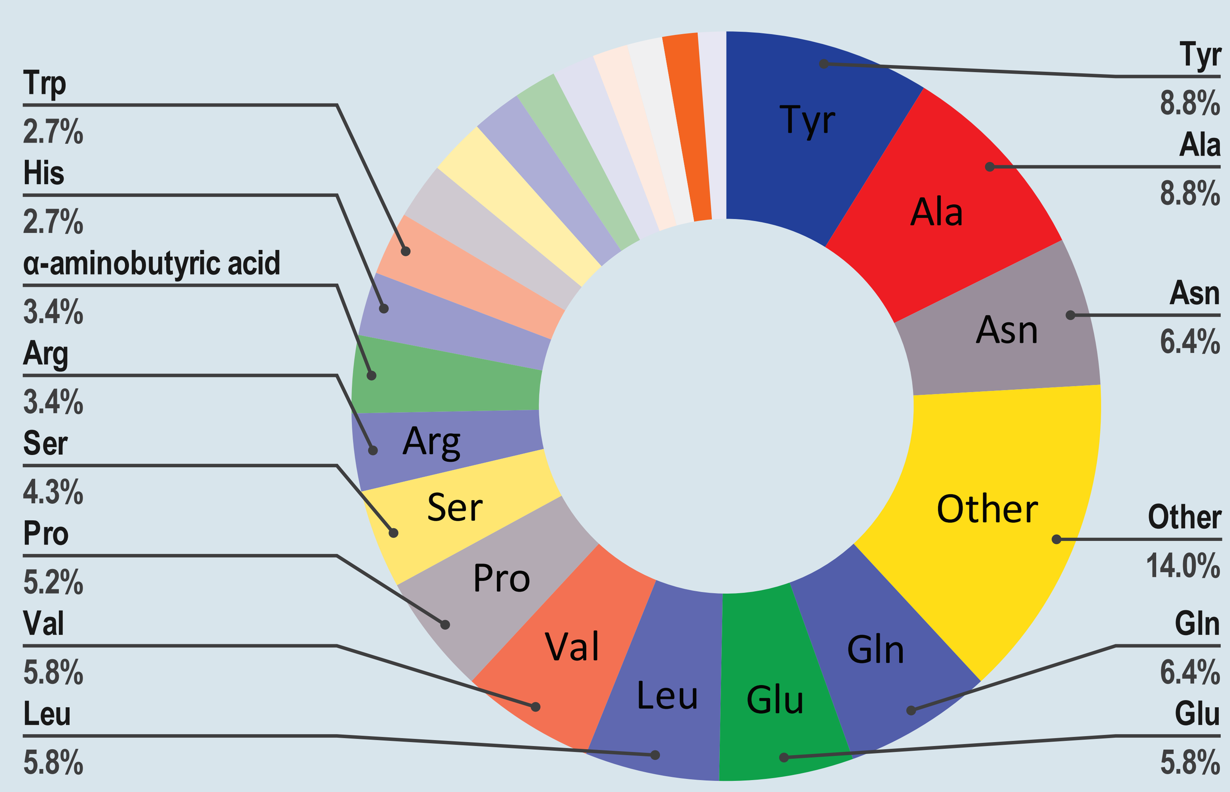


Chart A: Prominent Concentrations of Polar Metabolites nmol/g (wt)



Graph B: Dry Weight Japonica Rice (mg/100g)

Did You Know? (Statista.com, Ricepedia.org)

- Japan is 100% self-sufficient in rice, but only 14% wheat and 8% beans.
- 85% of the 2.3 million farmers in Japan produce rice.
- The average rice farmer works only 1.65 acres.

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