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ARTICLE

Peanut Seed Maturation, Quality, and Nutritional Composition

L.L. Dean[*1]; C.M. Eickholt[2]

[1]First author: Research Food Technologist, Food Science and Market Quality and Handling Research Unit, USDA, ARS, SEA, Raleigh, NC 27695-7624; Second author: Graduate Student, Dept. of Food, Bioprocessing and Nutrition Sciences, North Carolina State University, Raleigh, NC 27695

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Corresponding Author:
L.L. Dean
Lisa.Dean@usda.gov

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ABSTRACT

Due to the indeterminant flowering nature of the peanut plant, at harvest, a range of seed maturities are found. Although sorting by size does produce seed lots of consistent maturity, some quantity of immature kernels may be present as it has been reported that a peanut pod may grow to its final size before the seed inside is fully mature. This review discusses the physical and chemical changes that occur with peanut seed maturation. The effects on the peanut composition and resulting quality of the components and roasted peanut flavor and lipid quality are presented.

Introduction

The unique nature of the peanut as a "fruit" that grows below the ground's surface does not lend itself readily to the study of its maturation. Unlike related legumes such as soybeans and peas, or tree nuts, with their similar flavors and end-product uses, peanuts cannot be observed in their development without destroying the growing plant. In addition to their underground development, investigating peanut seed maturity is further complicated by an indeterminate growth habit. As peanut size and maturity are not correlated, peanuts of different maturation levels are found in all commercial sizes (Sanders *et al.,* 1995). The landmark publication on peanut development was produced over 65 years ago (Schenk, 1961). Since then, cultivars have come and gone. Changes have occurred in peanut composition, such as the development and extensive proliferation of lines with high levels of oleic acid. This review will rely on those pioneering studies of the development of the peanut and newer reports using more modern methods of scientific analysis to provide a current evaluation of peanut seed maturity as it pertains to the production of peanut as a source of human nutrition.

Physical Development of the Seed

Like most legumes, the peanut is an angiosperm plant in that the seed is produced in a "capsule" or pod. The plant is unique in that flowering occurs above ground as with other plants, but then a peg (gynophore) forms after fertilization, which moves below the soil surface to bear fruit (Zhu *et al.,* 2014). Although seed development can begin above ground, such seeds cannot form a pod or are not at all viable (Feng *et al.,* 1995). It has been determined that not only is the lack of light necessary for proper growth and seed production, but there is also a need for calcium that is only made possible by the actual contact of the peg with moist soil (Schenk, 1961; Pathak *et al.,* 2013). After five weeks, once the peg is set, the pod has grown to full size with a fleshy interior that is very high in moisture at approximately 40% (Schenk, 1961).

As the other components within the seed develop further, the seed becomes drier and the shell firmer. The testa or skin has also formed, and the protein percentage of the dry weight is at

a maximum. By nine weeks, most of the seeds are close to fully mature, and if left unharvested, many of the seeds will become detached, as the peg stem has decayed (Schenk, 1961). This timeline changes slightly with market type as Spanish-types are generally faster to mature than runner or Virginia-types (Boote, 1982; Davis *et al.,* 2017).

Once formed within the pod, the peanut seed consists of two cotyledons compromising up to 96 % of the total seed weight and the embryo, which compromises the radicle and plumule (Schadel *et al.,* 1983). Figure 1 illustrates the development of the seed (Okada *et al.,* 2021).

The outer hulls or shells of the peanut pods also undergo significant development. These changes have been found to be very useful in that they allow for the determination of the maturity stage of the seed within the shell (Henning, 1983; Williams and Drexler, 1981). When the very exterior layer of the shell, also known as the exocarp, is scraped away at the midpoint of the pod, where the shell begins to constrict between the two seeds inside, the mesocarp layer of the shell will be found to be colored. When initially formed, the pod is watery and easily deformed and the mesocarp is white. As the pod matures, the color of the mesocarp becomes increasingly brown and darker. The pod itself becomes harder and drier and the surface becomes more pitted. As the pod matures, the mesocarp color changes from white to yellow, then to a light orange that becomes increasingly darker. This color change is referred to as the maturity classes of White, Yellow, Orange A, and Orange B, respectively. The mesocarp completely darkens to brown and finally to black at the most mature stage. These are maturity classes of Brown and Black that are found when the peanuts are ready to be harvested. There are a variety of methods suggested as possible ways to determine maturity such as seed size, chemical composition, and the "hull scrape" method described above (Hinds *et al.,* 1992; Holaday *et al.*, 1979; Sanders *et al.,* 1980; Sanders *et al.,* 1982b; Henning, 1983; Williams and Drexler, 1981). This review will refer to the hull scrape colors described above to delineate maturity phases in peanuts, as this is the method most often used. During maturity, the kernels increase in size to fill the pod and change in chemistry as will be described in the following sections.

Figure 1. Physical development of Virginia type peanut seeds and pods. Numbers represent the days after flowering. Illustration reproduced from Okada et al., 2021 under copyright terms of the Creative Commons Attribution License.

Carbohydrate

During the initial stages of development, the peanut seed relies primarily on carbohydrate compounds for energy storage. Simple sugars (mono and disaccharides) are formed by the action of photosynthesis in the leaves. They are subsequently transported by the phloem or vascular tissue to the seeds where they are converted into different energy-containing compounds such as lipids and proteins (Pattee *et al.,* 1974a). Initially, the sugars serve as the energy source for rapid cell division for the developing pod with sucrose, the main sugar that the plant transfers, acting as both a nutrient and a developmental signal (Waterworth and Bray, 2007). As growth slows and cell division stops, less energy is needed. The sucrose is converted to starch for energy storage, but as the seed forms inside the pod, the sugars are converted to fatty acids. The seed needs only a small part of the energy provided by the sugars transferred from the plant above during development, and the remainder is stored (Zamsi, 2017). It has been seen in a study of individual plant parts performed by this author, that as the plant grows, both the seeds and the pegs increase in sugar content and then drop back as the seeds mature (Dean, unpublished data) (Figure 2). Although the pegs are significantly higher in sugars than the seeds until the seeds start converting carbohydrates to triglycerides, the levels decrease and become nearly equal to the seeds at harvest. This suggests that the plant has slowed the transfer rate of sugars from the leaves to the pods. As the seed is the storage organ for the plant, the purpose it serves is to ensure long-term survival of the plant (Zamsi, 2017). The movement of sugars into the seed cannot be reversed. The plant is unable to use this material for growth once it has been deposited in the seed.

Peanuts contain notable amounts of myo-inositol, a sugar alcohol. As this compound has not been proven to be involved in flavor production in roasted peanuts, there is not much discussion in the literature about its possible role in peanut development. During seed growth, the cell walls undergo rapid division and subsequent differentiation. To maintain the cell signalling during growth, a source of myo-inositol is needed (Lott *et al.,* 1995). In addition, phytic acid (inositol hexaphosphoric acid) is the storage compound for phosphorus and minerals such as calcium, magnesium, and potassium and will be discussed in a later section (Fontaine *et al.,* 1946).

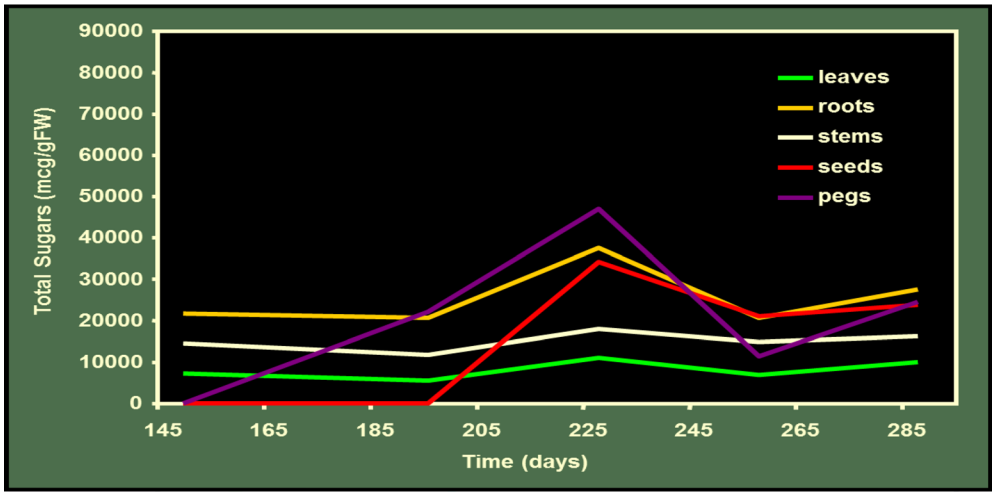

Figure 2. Sugar content (mcg/g fresh weight) of peanut plant parts during the growth cycle. (Dean, unpublished results).

Sucrose is the main sugar transported to the seed from the plant during development. Other sugars identified in peanut seeds are fructose and glucose, raffinose, and stachyose (Pattee *et al.,* 2000). Levels of sucrose are reported to range from 20320 to 42282 mcg/g (dw) across a range of genotypes at harvest and represent at least 90% of the total carbohydrates found. The trisaccharide, raffinose and tetrasaccharide, stachyose ranges were 253 mcg/g to 917 mcg/g and 1156 mcg/g to 4177 mcg/g, respectively. Much lower levels of the monosaccharides, fructose, and glucose were found at 15 mcg/g to 309 mcg/g for fructose and 17 mcg/g to 342 mcg/g for glucose. Small amounts of verbascose (a pentasaccharide) and ajugose (a hexasaccharide) have also been tentatively identified in some reports (Pattee *et al.,* 2000). Pattee and coworkers (2000) also listed several unknowns at various levels in their study. Using total sugar means to compare across market types, they also reported the highest levels (35057 mcg/g) in Virginias, followed by runners (28971 mcg/g) and Spanish (28842 mcg/g).

During seed growth, the seed converts carbohydrates to lipids, and the amount of carbohydrates being transferred from the plant to the seed eventually slows, as discussed above (Waterworth and Bray, 2007). This would indicate that the amount of total sugars present in peanut seeds would remain constant or be slightly reduced with maturity. In a study of normal oleic runners grown in Texas, this was found as seen in Figure 2. In older work, using residue weights from aqueous extractions, this same pattern was seen for peanut seeds (Pattee *et al.,* 1974a). Another study of the sugar levels in runner peanuts sorted into maturity classes did not show a decrease in the more mature seeds, but rather a slight increase in the fully mature ones (Da Conceicao Neta, 2010). A more systematic study is needed using modern cultivars to determine how carbohydrate chemistry in peanuts changes with maturity.

Raffinose oligosaccharides are present as carbohydrate reserves in peanuts as opposed to starch. Previously, starch levels in mature peanuts were found at levels much less than the sugar on the order of a ten-fold difference (30 to 50 mg/g compared to 400 to 600 mg/g) (Isleib *et al.,* 2004). The starch becomes polymerized to function as part of the cell wall structure. The lignin formed makes the seed less permeable as the seed matures which controls the flow of gases, water, and solutes, allowing it to regulate growth and metabolism, and gives structural protection against the environment, fungal, and insect attack and pathogens (Boesewinkel and Bouman, 1995).

Lipid

At maturation, peanut seeds are comprised of approximately 49% lipid. Lipids are the primary energy storage compounds in mature peanut seeds. The biosynthesis of lipids in peanut begins by the conversion of soluble sugars to fatty acids (Pattee *et al.,* 1974b). Within 3 weeks after the plant first flowers, the enzymes needed for lipid synthesis become active (Wang *et al.,* 2016). Acetyl-CoA carboxylase and fatty acid synthase are the major enzymes for lipid synthesis (Ohlrogge and Jaworski, 1997). Sucrose serves as the original source of the Acetyl Co A (Bewley and Black, 1978). In the simplest of terms, the fatty acids are synthesized in the plastids and transported as fatty acids to the endoplasmic reticulum where they are combined with glycerol to form triacylglycerides (TAG). During synthesis from Acetyl CoA, 2 carbon units are added to this compound initially forming palmitic (C 16:0) and stearic (C 18:0) acids. Both are converted to oleic acid (C 18:1) as evidenced by their decrease from the initial levels. Very low levels (<0.5%) of linolenic acid (C 18:3) are also initially present but quickly disappear. Oleic is then further desaturated to linoleic (C 18:2) acid. As the moisture content of the seed drops with seed maturity, the production of total lipids slows and eventually stops (Mohapatra and Pattee, 1973). Their study also showed that the free fatty acids present at this stage are due to the inability of the seed to form monoacyl glycerides (MAG), which are subsequently converted to TAG rather than decomposition of TAG. Once mature, the seeds store most of the lipid in oil bodies (oleosomes) as TAG. These oleosomes are comprised of TAG surrounded by a monolayer of phospholipids with proteins embedded in the phospholipid layer. The negative charge of these proteins at neutral pH prevents the oleosomes from aggregating or coalescing and thus, they remain distinct (Miquel and

Browse, 1995). In other pathways, fatty acids combine with phosphate to form membrane lipids (Rajasekharan and Nachiappan, 2010). Once the seeds mature, the levels of free fatty acids will be negligible as they will all be incorporated into the various lipid compounds (McKillican, 1966; Sangwan *et al.,* 1986). Along with carbohydrates, lipids provide carbon skeletons for later construction of other components and serve as a source of energy for the peanut seed (Boesewinkel and Bouman, 1995).

High-oleic (HO) peanut cultivars have a ratio of oleic acid to linoleic acid (O/L) of nine or greater. The introduction of HO peanut cultivars into commercial production resulted from the identification of a HO mutant within the University of Florida breeding program (Gainesville, FL) in the 1980s (Norden *et al.*, 1987). Developmental factors have been implicated in the ability of a peanut seed to obtain an O/L ratio great enough to be considered as high oleic (Andersen and Gorbet, 2002; Klevorn *et al.,* 2016). Pod maturity is a developmental factor that has been shown to impact many compositional characteristics of the peanut seed. Specifically, advanced pod maturity has been linked to increased levels of oleic acid and decreased levels of palmitic and linoleic acid (Hinds, 1995; Sanders *et al.,* 1982a). Determination of pod maturity was done in those studies through use of the hull-scrape method (Williams and Drexler, 1981).

Investigation of the four commercially produced market types in the United States, runner, Virginia, Spanish, and Valencia, demonstrated that a clear relationship exists between seed maturity and development of O/L ratio. This relationship was established by discovering that the most immature seeds (those with a white mesocarp) had O/L ratios almost entirely below the HO threshold of an O/L ratio of nine or greater. As the mesocarp colors darkened, the range of O/L ratios present was higher. Pods with white, yellow, and orange A mesocarp colors were considered to be immature. Those with orange B, brown, or black mesocarp colors were considered to be mature (Williams and Drexler, 1981). Additionally, the phenomenon of increased O/L ratio with increased maturity was observed within the normal oleic (NO) control cultivars included in the study.

From a study of the two major market types, runner and Virginia, the average lipid composition within the peanut seed has implications on the stability of peanut seeds as well as on the expressed peanut oil during storage (Klevorn *et al.,* 2016). A strong relationship was observed between increased O/L ratios and more advanced maturity. Increased O/L ratio with increased maturity was present for all four market types, yet the extent of this relationship appeared to differ among the market types (Dean *et al.,* 2020). When modeling the development of the O/L ratio using mesocarp color and market type as predictors, a significant interaction between mesocarp color and market type was observed (Table 1). A significant interaction term confirmed the visually observed variability in the relationship between O/L ratio development with darker mesocarp colors between the four market types.

Table 1. Average O/L Ratio by mesocarp color for high-oleic (HO) and normal-oleic (NO) samples from each market-type (Dean *et al.,* 2020).

	Average O/L Ratio by Mesocarp Color					
Market Type	White	Yellow	Orange A	Orange B	Brown	Black
Runner HO	9.3	20.5	27.7	33.8	42.4	47.2
Runner NO	1.2	1.9	1.7	2.2	1.9	2.4
Virginia HO	2.5	10.4	17.0	25.0	39.0	49.0
Virginia NO	0.9	1.2	1.3	1.5	1.8	2.0
Spanish HO	2.1	6.4	10.7	16.3	21.9	23.9
Spanish NO	0.6	0.9	1.0	1.1	1.2	1.3
Valencia HO	1.3	6.3	12.5	18.1	20.8	24.6
Valencia NO	0.6	0.9	1.0	1.1	1.2	1.2

Changes in O/L ratio with increased maturity were most evident in Virginia-type samples with an average O/L of 2.5 in white pods to an average of 49.0 in black pods, which were the most mature. Spanish and Valencia-type peanuts followed a similar trend moving from average O/L ratios of 2.1 and 1.3 in white pods to 23.9 and 24.6 in black pods, respectively. Runner-type peanuts also increased from an average O/L ratio of 9.3 in white pods to 47.2 in black pods. Runner-type peanuts had an average O/L ratio greater than the HO threshold of 9.0 even in the most immature pods. This phenomenon was not observed in any of the other market types. Virginia-type peanuts achieved average HO O/L ratios higher than the other market types.

Although TAGs, with their associated fatty acids comprise the largest part of the lipids in peanuts, other components are present, including phospholipids, phytosterols, and tocopherols. Due to their action in both the seed and in human nutrition, tocopherols will be discussed in the section on vitamins. Phospholipids represent approximately 1% of the total lipid in the mature seed. As they are such a minor portion, little study has been dedicated to their presence in peanuts. The forms most commonly found are phosphatidic acid (PA), phosphatidylglycerol (PG), phosphatidylethanolamine (PE), phosphatidylinositol (PI), and phosphatidylcholine (PC) (Dean *et al.,* 2011). Structurally, they all contain two fatty acids linked to a phosphate moiety, with differing functional groups that define them. They give structure to lipid cell membranes but are also involved in cell signalling. The movement of lipids between membranes and organelles in response to temperature is one of the primary functions of these compounds (Dörmann, 2005). Phospholipids can chelate metal ions which allows them to serve as antioxidants. However, this function is more dependent on the length of

the fatty acids present in the molecule rather than the makeup of the moiety attached to the phosphate (Nwosu *et al.,* 1997). Higher levels of palmitic and linoleic acid are found in phospholipids (Soler *et al.,* 1988). The actual fatty acid composition may be subject to environmental conditions. For example, in soybeans, it has been reported that low temperatures favor incorporating linoleic acid, but more oleic acid is incorporated at higher temperatures (Slack and Roughan, 1978). The phospholipids present in peanut lipids are also affected by seed maturity (Singleton and Stikeleather, 1995). Immature peanuts have higher amounts of phospholipids (700 mg/100g dry weight basis (dwb)) compared to mature ones (500 mg/100g dwb). In addition, when immature, the levels of PA and PC are higher than in mature peanuts because PA and PC are the precursors to the other forms. It has also been found that the highest levels of phospholipids are in heat-cured peanuts (900 mg/100g dwb). This increase is greater than could be attributed to loss of moisture emphasizing the role of these compounds in cell function. Once mature, the relative amounts of the different phospholipids are not significantly different from each other regardless of cultivar or fatty acid profiles (Jonnala *et al.,* 2006a; Jonnala *et al.,* 2006b).

Phytosterols or plant sterols are membrane lipids that are analogous to cholesterol in animal fats (Figure 3). Like phospholipids, they are found as parts of the cell membrane and can be either free or esterified to fatty acids. They provide stability to the membrane and allow for permeability (Grossman *et al.,* 1985). The hydroxyl group on the first ring interacts with phospholipids also present in the membrane as it is able to fit into the phospholipid cavity due to the very planar structure produced by the multiple carbon rings present (Grunwald, 1975). The need for phytosterols is high when cells are actively growing and reproducing during seed maturation. Once mature, the plant sterols are at their highest levels in the oldest parts of the plants such as stems and lower stalks (Grunwald, 1975). There has been no systematic study on peanut seeds to date to determine if this is the case for peanut seed oil. As with other lipids in peanuts, the starting point for phytosterol synthesis is Acetyl CoA. Condensation with aceto acetyl-CoA results in the formation of melvalonic acid, which is then sequentially phosphorylated and then dephosphorylated, and decarboxylated to form isopentnylpyrophosphate. Through a series of condensations between similar molecules and isomerization, the main precursor, squalene is formed (Ponsinet and Ourisson, 1968). From there, molecular rearrangements occur, mainly to form carbon-carbon bonds that result in the closed rings. However, some squalene continues to exist in the mature seed and is considered to have antioxidant properties due to its ability to quench singlet oxygen (Esche *et al.,* 2013; Kohno *et al.*, 1995). Modifications at the ends of the side chains occur to produce the different phytosterols. This consists of the addition of ethyl and methyl groups contributed by methionine (Wojciechowski *et al.,* 1973). Each phytosterol is likely formed individually as there is insufficient evidence to show that one serves as a precursor to the others, despite the similarities (Grunwald, 1975). Total reported phytosterol levels range from 55 mg/100g (fresh weight) in the Virginia market type to 127 mg/100g in the Valencia market type (Awad *et al.,* 2000). This may indicate that maturity plays a role in sterol content as the Valencia cultivars are often overall more mature than other market types at harvest.

As these components change with maturity, the lipid color also changes. When the oil is expressed from the seeds, it changes from a distinct yellow color in the most immature to a lighter, paler color in the mature seeds. However, some cultivars still display the darker yellow colors at maturity (Dean, unpublished data). The color change has been attributed to loss of carotenoid pigments or dilution of the levels as the amount of oil in the seed increases (Pattee *et al.,* 1969a).

In addition to seed development, lipids play the largest role in the deterioration of the peanut seed quality, especially during storage. Oxidation of unsaturated fatty acids can be induced by a variety of factors. While the tocopherols present can offer some protection, autooxidation occurs due to simple seed aging. Hydroperoxides form then decompose into aldehydes, which propagate the reaction (Wilson and McDonald, 1986). This leads to loss of the unsaturated fatty acids and the production of fatty acid alcohols. In roasted peanuts, this problem can be confounded by the presence of Maillard compounds produced by heat induced polymerization of free amino acids and reducing sugars (Shi *et al.,* 2016). These compounds can also act as pro-oxidants. In roasted peanuts, this leads to the production of off-flavor, and the loss of roast peanut flavor (Williams *et al.,* 2006). In raw seed, lipid oxidation reduces the ability of the seed to germinate due to the loss of membrane lipids and certain enzymes needed for development.

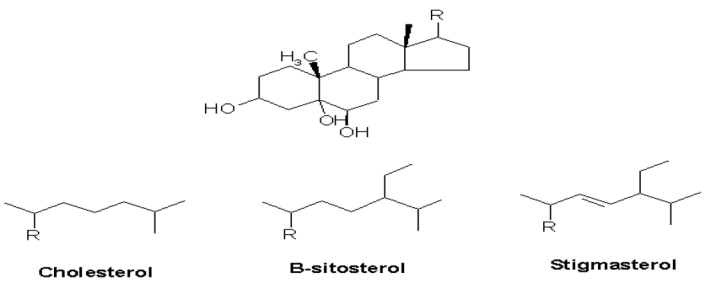

Figure 3. Chemical structures of sterols showing variations in the side chain that differentiate the forms.

Protein

One of the major advantages of peanuts as a human food is their high protein levels compared to other plant foods. Like other legumes, peanuts contain about 25% protein (Davis and Dean, 2016). In the initial development of the peanut, free amino acids are produced which are then incorporated into proteins as maturation progresses (Basha *et al.,* 1976). These amino acids can be translocated from the plant leaves via vascular bundles or phloem that connect the developing seed to the rest of the plant as the testa develop. In general, the amounts of free amino acids decrease with maturation (Figure 4). However, some remain unchanged or actually increase, as seen with glutamic acid and phenylalanine, the dominate amino acids in the intact proteins. Of the total amino acids, the most abundant at the onset of kernel formation are arginine, glutamine/glutamic acid and asparagine/aspartic acid (Jones *et al.,* 1994). At maturity, glutamine/glutamic acid is increased, arginine is decreased, asparagine/aspartic acid content is roughly the same, while glycine is greatly increased (Jones *et al.,* 1994). The free amino acids also serve as the nitrogen source for the developing seed (Bewley and Black, 1978). The involvement of amino acids in flavor development will be discussed in another section.

Thousands of proteins are thought to be involved in peanut pod development (Wang *et al.,* 2016). Proteins serve as a connection between the genome where genetic information is coded and the phenotype, and as such, they are very involved with the development and maturation of the peanut seed (Zhu *et al.,* 2013). Most of the proteins are synthesized during the expansion phase of development (Bewley and Black, 1978). The field of proteomics has served to identify the proteins involved in peanut development. For instance, 31 different proteins were present during the initial swelling of pods once the peg penetrated the soil (Zhu *et al.,* 2014). Throughout seed growth, proteins are formed, transported, and decayed as needed for various aspects of growth and development.

The seed storage proteins make up the largest portion of the proteins present. These proteins are glycosylated to enable them to move across the membranes of the protein bodies for sequestration (Bewley and Black, 1978). The protein bodies appear as distinct rounded structures within the cell walls of the peanut seeds when viewed using electron microscopy (Young and Schadel, 1990). The peanut seed storage proteins are the most important sources of dietary protein and can represent as much as 30 % of the total fresh weight of the seed (Dean *et al.,* 2009). They are stored in vacuoles and consist of proteases and glycosidases needed for degradation during germination (Vitatle and Bollini, 1995).

Once the seed starts to germinate, many proteins are hydrolysed quickly to provide a source of reduced nitrogen for the early stages of growth of the plant seedling (Higgins, 1984). Other proteins are lectins, which provide binding sites for calcium, magnesium, and carbohydrates. The major types are globulins, albumins, and oleosins. These are further broken down into fractions based on their sedimentation coefficients and their secondary structures and formation have been described (Shewry *et al.,* 1995). The storage proteins are also involved in allergenic responses to peanut consumption (Mueller *et al.,* 2014; Zhuang and Dreskin, 2013). Attempts to relate specific proteins to maturity have had limited success (Bland and Lax, 2000). It has been difficult to associate them with compounds that are flavor precursors.

As with cereals, another primary seed source of plant protein to the human diet, peanuts are deficient in lysine, which lowers the protein quality. Since the majority of the proteins are present as globulins, they are also deficient in the sulfur-containing amino acids, cysteine, and more importantly, methionine (Shotwell and Larkins, 1991). Attempts to increase levels of certain amino acids through conventional genetic manipulation may not necessarily lead to improved products. For example, high concentrations of lysine found in specific maize mutants were associated with undesirable textures in the endosperm, poor yields, higher insect infestations, and processing problems (Mertz, 1992). Sulfur-containing amino acids are linked to off-flavors in dairy products. Increasing the sulfur-containing amino acids might also be problematic, as was found in a study with French beans where an oligonucleotide containing 6 methionine codons was inserted into a globulin gene (Hoffman *et al.,* 1988). The proteins were found to be less stable and degrade more rapidly, leading to reduced germination. Phytic acid or phytate is a major impurity in protein isolated from peanuts and is discussed in the next section (Fontaine *et al.,* 1946).

Minerals

The mineral content of peanuts is an important part of their value in human nutrition. They provide significant amounts of calcium (Ca), magnesium (Mg), and phosphorus (P) but also contain iron (Fe) and zinc (Zn) among other minor minerals (Davis and Dean, 2016). The literature on plant growth is primarily concerned with soil applications to maximize the growth of the plant (Cox *et al.,* 1976; Howe *et al.,* 2012; Nicholaides and Cox, 1970). In addition, some studies discuss the need for specific minerals to prevent defects in the mature seed such as “pops” or empty pods from insufficient Ca and “hollow heart” from insufficient soil boron (B) (Harris and Gilman, 1957; Beringer and Tekete, 1979; Rerkasem *et al.,* 1993). Minerals have a role in many of the reactions involved in cell development and their role in peanut growth and maturation is important. The pod consists of the shell and the developing seed inside. During the initial stages of its development, the shell is the first pool of minerals for the developing seed (Pattee *et al.,* 1974a). Studies that isolated the root zone from the developing pods when treating the soil with minerals proved that certain minerals such as calcium (Ca) are absorbed through the pods and are necessary for the maturation of the enclosed seed (Brady *et al.,* 1948; Inanaga *et al.,* 1988). In addition, the anion of the Ca salt did not have an effect, proving that the cation is necessary. The Ca cation is the center for many cell-signaling pathways including those needed for pod development (Yang *et al.,* 2017). Field studies have verified the increase in pod shell calcium over that of Ca in the seed but also indicated sufficient moisture was needed to ensure the added Ca was solubilized for translocation (Pathak *et al.,* 2013; Skelton and Shear, 1971;

Sorensen and Butts, 2008). Using gypsum as the source of Ca did not increase the sulfur (S) content of either the seeds or the shells (Pathak *et al.*, 2013). Ca deficiency was associated with a depression in lipid biosynthesis but not protein production. Insufficient potassium (K) resulted in lower-weight seeds with decreased starch contents in the shells but not the seeds. It was hypothesized that K ions become associated with phytic acid and are not translocated into the rest of the pods, producing lower seed levels.

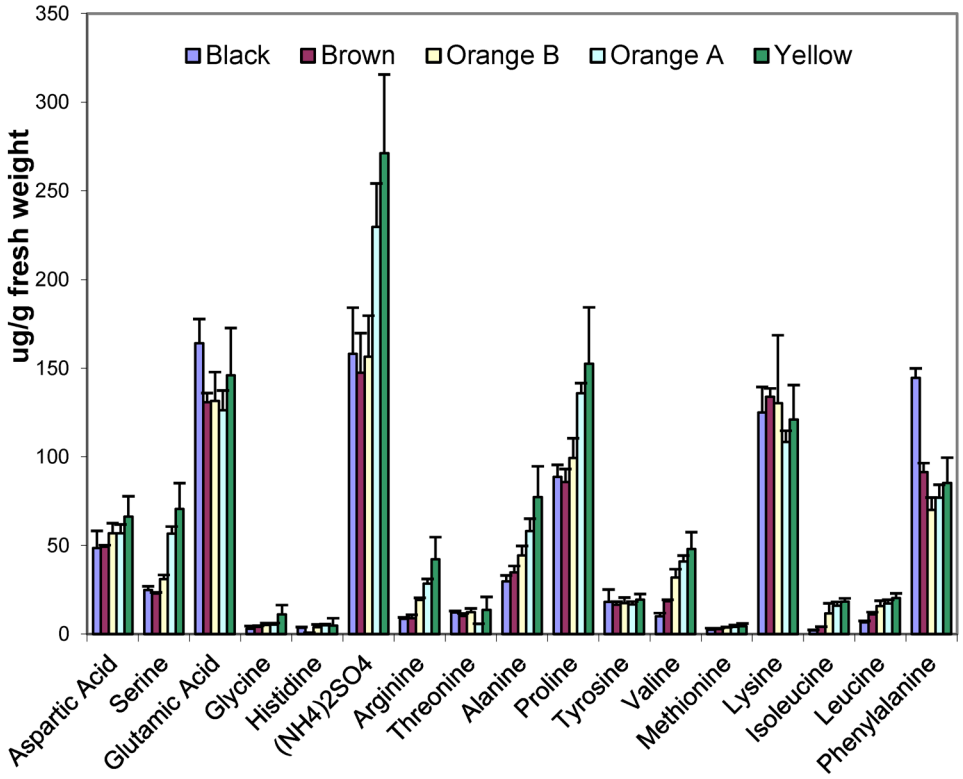

Figure 4. Free amino acid content (µg/g fresh weight) in peanuts at different maturity stages (Da Conceicao Neta, 2010).

Once mature, market type was a determining factor in the levels of some minerals present in peanut seeds (Hallock *et al.,* 1971). As all the experimental samples were harvested at the same time, the maturity of the lines was considered to have a role in the final mineral contents. When soil nutrients were available without any deficiencies, phosphorus (P) was higher in the Spanish and Valencia lines than in the Virginia or runner ones. Ca, boron (B), and K were higher in the Virginia lines. Most runner samples were higher in magnesium (Mg) and manganese (Mn). Copper (Cu) was similar in all lines but at lower levels than any of the other minerals. The early maturation of the Spanish and the Valencia types was given as the primary reason for the differences.

In the reactions discussed above, the inorganic ions serve as enzyme cofactors, structural components, and as electrolytes in cells (Hunt and Groff, 1990). They also are complexed with phytic acid (Seo and Morr, 1985). Phytic acid, present in the protein bodies (Bewley and Black, 1978) is the principal storage form of P in most plants and serves as a source of energy and cations. The structure consists of an inositol ion complexed through oxygen bonding with six phosphates that can be complexed to inorganic cations depending on the pH. Levels in peanuts are 0.17 g/100g (fresh weight) equal to or slightly lower than levels in tree nuts (Venkatachalam and Sathe, 2006). Phytic acid is considered to be an antinutrient as the chelation of mineral ions, in particular, Ca, iron (Fe), and zinc (Zn) makes them unavailable as nutrients to non-ruminant animals that cannot produce phytase to digest it. Roasting peanuts does reduce the levels of phytic acid slightly (Seo and Morr, 1985).

Vitamins

Peanuts are known to be the source of specific vitamins to the human diet however, the peanut has not been the subject of research for the formation of water-soluble vitamins during maturation. As vitamins play a role in seed development, their presence in the growing and germinating seed is expected. In work on other legumes and cereal grains, thiamine (Vitamin B1) was identified as being generated as part of carbohydrate metabolism (Asensi-Fabado and Munné-Bosch, 2010). In the plastid, the precursors are glycine and L-cysteine, which combine with ribose to form thiamine, which is then phosphorylated. In this form, thiamine serves as a cofactor to enzymes that are part of the metabolic pathways that generate energy for growing peanut kernels including the skins (Golda *et al.,* 2004). Thiamine content in seeds is higher in the starch portion and the embryo. In peanuts, the high tannin content of the skins results in the binding of thiamine there (Ball, 2005a). In

legumes, once the seed starts to germinate, thiamine is metabolized, and levels drop in legumes by 50% within days. Therefore, the highest levels are expected to be present in mature dry, dormant seeds. In peanuts, these levels supply the human diet with about 10% of Daily Reference Value (DRV) per serving (USDA, 2015).

Of the water-soluble B vitamins, niacin is found at the highest levels. It functions as a cofactor in the coenzymes NAD and NADPH which are proton and electron carriers in a range of oxidation and reduction reactions that are responsible for the release of energy from carbohydrates, fatty acids, and free amino acids as well as for the synthesis of these compounds (Ball, 2005b). Pyridine nucleotide synthesis increases NAD, so there may be stress-related effects that require Ca^{2+}signalling increases. These are theorized to be a plant defence mechanism that results in increased levels of niacin being produced (Gallais *et al.,* 2000). As tryptophan serves as the source of the synthesis of niacin in the peanut, this constant need for niacin may be the reason tryptophan levels are low in peanut (1.5 g/100g fresh weight). There is also some concern that the storage of niacin in seeds to maintain its production of proteins and polysaccharides limits the nutritional availability of this vitamin, which may be as low as 46 % (Carter and Carpenter, 1982).

Peanuts are thought to be a source of naturally occurring folates, which are referred to collectively as folate or Vitamin B9 (USDA, 2015). These compounds exist in nature as tetrahydrofolate and its many derivatives. They are essential to human nutrition as they serve as co-factors in single carbon transfers for synthesis of nucleic acids and some amino acids (Castorena-Torres *et al.,* 2014).

There are many forms of folate which differ by the addition of methyl or formate groups to the basic pteridine structure of the molecule and the number of glutamate groups which form the tail of the molecule. In pea plants, folate has been found to be present in the leaves of the plant and as the seed develops, initially in the embryo (Gambonnet *et al.,* 2001). The folate biosynthetic pathway is initiated early as folate is needed for nucleic acid synthesis and can be the limiting factor in seed growth if not sustained. The cotyledons of the pea were not found to be large reservoirs of folate (Gambonnet *et al.,* 2001). In wheat and other cereal grains, the folate is partitioned into the endosperm and bran layers once the seed matures (McIntosh *et al.,* 2008). This work also found that folate in the leaves was high due to the need for light to express or activate enzymes involved in tetrahydrofolate biosynthesis. No studies are available on folate levels in peanuts at different stages of maturation. In wheat, total folates decreased from 0.9 µg/g to 0.6 µg/g or 30% over 40 days of maturation (McIntosh *et al.,* 2008). It would be important to determine if folate levels in peanuts are higher in germinating seed compared to mature, dormant seed. The measurement of folates in peanuts has proven to be problematic. Values in the literature have been obtained using enzymatic methods, which consist of digesting the matrix using an excess of enzymes such as amylases and proteases and then removing the side chains using a conjugase (DeVries *et al.,* 2005; Chen and Eitenmiller, 2007). The resulting solution is then used to inoculate a culture of a specific *Lactobacillus,* and the growth is compared to that of a culture inoculated with a known amount of folic acid. The results can only be quantified as total folates with no information as to the forms present in the food. In addition, the assay is sensitive to other compounds present in the matrix and falsely high values have been reported (Chen and Eitenmiller, 2007). Attempts to use chromatography to identify individual folates based on assays for blood, urine, and very low protein food matrices have failed due to binding of the folates to the protein present in peanuts (Dean, unpublished results; Selhub, 2016 unpublished results; Schwartz, 2016 unpublished results).

As the peanut is an oilseed, it is logical that the bioactive compounds found at the largest concentration would be the tocopherols known collectively as Vitamin E. Only α-tocopherol has found to have activity in vivo based on its ability to be absorbed and retained and is labelled as "Vitamin E" for human nutritional labels. Of the four major forms, α-, β-, γ-, and δ-tocopherol, the ones found at the highest levels in peanut are α-tocopherol and γ-tocopherol. The levels of these forms were determined to range from 5.9 to 14.7 mg/100g of α-tocopherols in the seed and 2.5 to 11.4 mg/100 of γ-tocopherol with the β-form ranging from 0.6 to 1.1 mg/100g and the δ-form found at 0.1 to 1.5 mg/100g (Dean *et al.,* 2009). While this study could not define the effects of seed maturity, it provided an overview of a representative set of the available peanut germplasm. Differences have been found between cultivars at maturity, but the levels of the various forms of tocopherols change with maturity (Hashim *et al.,* 1993). Vitamin E is synthesized in the plastids from pyruvate (Hunter and Cahoon, 2007). The amino acid, tyrosine is needed which is present in adequate levels in peanuts. During growth, α-tocopherol is synthesized initially and is converted to the γ-form by demethylation as the seed matures and the amounts of the fatty acids in the seed increase. The γ-form has been found to have more antioxidant activity in plant oils (Wagner and Elmadfa, 2000). Seeds such as peanuts may accumulate significant amounts of the γ- form to protect against oxidative damage and damage from nitrous oxide (Cooney *et al.,* 1993). In contrast, sunflower seeds naturally produce more than 90 % α-tocopherol in their oil. Conventional breeding with mutants has produced oil with high levels of γ-tocopherol to take advantage of the greater oil stability (Hass *et al.,* 2006). The amount of α-tocopherol was positively correlated with the oleic acid content of peanuts, which may indicate that high O/L cultivars would be better sources of this nutrient (Klevorn *et al.,* 2019).

Seed Coat

Within the developing pod, the seed coat or testa, is the first part of the kernel to appear in the white, soft, spongy interior (Pattee *et al.,* 1974a). The texture is rather fibrous and waxy but has very little, if any color. At first, the seed develops the embryo and the seed coat. There is almost no lipid present at this point, as there is no developing tissue available to create the appropriate enzymes for lipid synthesis (Bewley and Black, 1978). Sugars, upon being transported from the leaves of the plant to the pod are initially incorporated into the seed coat (Patee *et al.,* 1974b). The skins store carbohydrates and are higher in starch than the shell during initial development (Schenk, 1961). The shell walls are

relatively thick, which help retain moisture inside for the developing seed. The stored nutrients then shift to the growing seed as it develops. The functions of the seed coat are to protect the seed from environmental hazards such as pathogen or insect attack as well as to provide structure and mechanical support (Boesewinkel and Bouman, 1995). Similar to the cotyledons, the skin levels of sugars and free amino acids decreased with increasing maturity. Sugars decreased from 12% to 5% and free amino acids from 4% to less than 0.5%. Protein contents increased from 20% to 40% (defatted basis). The proteins present in the skins were not the same types as those present in the cotyledons. The total amino acid contents varied with much larger ranges at maturity than the rest of the seed with the largest proportion being serine, glycine, and proline (Jones *et al.,* 1994). Also, when the polypeptides are isolated from the skins, their amino acid composition is very different in that the main amino acid present is proline which accounts for the astringent mouthfeel of peanut skins as proline is known to bind to the surface of the tongue (Constanza *et al.,* 2012). As the embryo and the cotyledons form, the seed coat takes on color in most cases and becomes thinner. A range of seed coat colors are known in peanuts, but most cultivars are predominately dark red or reddish brown (Shem-Tov *et al.,* 2012). The colors have been related to a range of compounds, but for the most part, they have been found to be polyphenolic, of which A-type procyanidins and catechins make up the major portion by weight. These types of compounds as a group are usually referred to as tannins and are chemical protectants against fungi, molds, and other microbes (Boesewinkel and Bouman, 1995). They are biosynthesized from phenylalanine and can also protect the seed from light damage due to their opacity and delay decomposition of the seed while in the soil (Sobolev *et al.,* 2010). Peanut kernels themselves contain polyphenols such as *p*-coumaric acid, *p*-hydroxybenzoic acid, and 5-hydroxymethyl furfural (Talcott *et al.,* 2005). Using these types of compounds as precursors, 3-malonyl-Co A and a series of flavonoid hydroxylases and reductases can act to increase the size of the molecules and add additional hydroxyl groups to form catechin molecules and ultimately form procyanidins. This has been documented in tea leaves but no similar study in known in developing peanuts (Punyasiri *et al.,* 2004). These enzymes also operate optimally at elevated temperatures which may also be slowed by colder soils as are other enzymes responsible for plant maturity. In addition, the color development due to the production of these compounds could be an indicator of the maturity of those cultivars with darker-colored testa. In general, extraction of the skins results in a mixture of compounds of relatively low molecular weights that have anti-inflammatory effects on challenged cells in culture (Lewis *et al.,* 2013). The procyanidins isolated from peanut skins have been found to be beneficial in lowering harmful oxygen species generated by oxidative stress in humans and thus may reduce incidences of onset of diseases and syndromes related to them, such as cardiovascular, diabetic and hypotensive events (Yu *et al.,* 2005; Dudek *et al.,* 2017). Resveratrol has also been found in peanuts and peanut skins, but since its production is a plant stress response, the concentration can vary widely (Sobolev and Cole, 1999).

Roast Peanut Flavor

As peanut flavor is the most important driver of peanut consumption, the impact of maturity on the flavor of roasted peanuts must be considered. The overall flavor of peanuts is a combination of many different attributes with their own compositional origins, with optimum flavor resulting when desirable flavors are at the highest intensity and undesirable ones at the lowest (Sanders and Bett, 1995). There have been studies devoted to understanding the compounds responsible for roasted peanut flavor, but their absolute identity remains uncertain. Those compounds most associated are products of thermal reactions such as the degradation of sugars or caramelization, oxidation of lipids, the Maillard reaction, and Strecker degradations. A review of the topic discusses the mechanisms involved and describes the importance of free amino acids, sugars, and lipids in flavor formation (Neta *et al.,* 2010). The content of these factors has been shown to change as peanuts mature and thus will have an impact on roast peanut flavor. A study of the volatile compounds produced by raw peanuts was related to biochemical changes occurring during maturation (Pattee *et al.*, 1970). The production of total volatiles, which were identified as alcohols and aldehydes, increased rapidly until 9 weeks after the initial formation of the pegs after which production slowed and then decreased. Correspondingly, the activities of the enzymes, alcohol dehydrogenase and lipoxygenase followed the same pattern. Alternatively, the activity of the lipoxygenase could be related to the small amounts of linolenic acid present in very immature peanuts that is not found in the mature seed (Dean *et al.*, 2020). The depletion of the volatiles was suggested as the transition time for the end of peanut maturation and the preparation for germination. The actual intensity of roast peanut flavor attribute is impacted by the maturity of the peanuts. As the peanuts become more mature, it increases. In lots of Virginia type peanuts with high amounts of larger seed, more immature seeds maybe present, resulting in lower roast peanut flavor scores (McNeill and Sanders, 1998). The major compounds that have been identified with roasted peanut flavor are pyrazine and carbonyl compounds that are created by Maillard reactions that involve amino acids and sugars. Heating is also thought to break down proteins into free amino acids for this reaction. Work to explore which proteins are involved has determined that lipoproteins may be the most logical (Basha *et al.,* 1998).

Maturity and curing have the most significant effects on flavors. When separated into maturity classes, immature runner peanuts had higher levels of off-flavors and lower levels of the desired flavors, “roast peanutty” and sweet aromatic when cured at high temperatures (Sanders *et al.,* 1989). The presence of some aldehydes in peanuts was attributed as being a source of off-flavors (Pattee *et al.,* 1969b). The source of these compounds is usually the oxidation of unsaturated fatty acids, which is enhanced at higher moisture contents, as would be seen in the more immature seeds. One flavor defect described as “fruity” has been found most often in immature peanuts. Free valine is thought to serve as a precursor for the formation of 2-methylpropanal, a compound associated with this off-flavor (Sanders and Greene, 1989). Levels of this compound were found to decrease with maturity and with seed size. More

recent work on the origins of this flavor defect identified a series of esters formed by reaction of ethanol with oxidized fatty acids as the source of "fruity" off flavors (Didzbalis *et al.*, 2004; Greene *et al.*, 2008). Immature peanuts are often higher in sugar than mature ones, which leads to the production of ethanol with high-temperature curing. They are also higher in moisture, which leads to lipid oxidation, making oxidized fatty acids more available in immature rather than mature peanuts. As the pyrazines formed during roasting due to the Maillard reaction and Strecker degradation are stable, the loss of roast peanut flavor or "flavor fade" in peanuts is due to other compounds from lipid oxidation masking their flavors. Lipid oxidation during storage produces a series of aldehydes from oxidized fatty acids that are responsible (Warner *et al.,* 1996). These lipid oxidation compounds are most associated with rancid or stale off flavors.

Summary

The goal of peanut production is to produce sound mature seeds that will have maximum roast peanut flavor intensity. The indeterminate flowering pattern of the peanut plant results in peanuts with a range of maturities at harvest. Sorting by size can have a major effect on the final product by eliminating a large portion of the immature seeds present, but seeds at all ranges of maturity are found within any commercial size. Many chemical changes occur during the maturation to the major components of protein, lipid, and carbohydrate. These components, in addition to moisture, have the greatest impact on the nutrition, texture, and flavor of the finished, roasted product. While the impact of the development of high oleic peanuts cannot be underestimated as a contributor to higher quality peanuts, especially in their role in extending the shelf life of stored peanuts due to resistance to oxidation and resulting flavor changes, it is still necessary that peanuts be as mature as possible to ensure an optimal final product. The chemistry of peanut maturation needs more research to determine how the changes occur to better allow for association of specific compounds to genetic markers for crop improvement.

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