Chapter 6

Physicochemical Properties of Peanuts

By WILLIAM Y. COBB[1] AND BOBBY R. JOHNSON[1]

Introduction

Peanuts (*Arachis hypogaea* L.) are self-pollinated, one to six seeded, annual herbaceous plants belonging to *Papilonaceae,* a suborder of *Leguminoseae.* The oil from these seeds is of high quality and a large percentage of the world production of peanuts is utilized as an edible oil source. In the United States approximately 65% of the production goes into the cleaned and shelled trade, the end product being roasted and/or salted peanuts, peanut butter, and confections. As with many other foods, interest in the composition and chemistry of peanuts is largely a result of their use for human food. Peanuts are continually utilized for preparation of new and improved products; thus a more complete knowledge of their physiochemical properties is desirable.

Botanically, *Arachis hypogaea* may be divided into three main types—Virginia, Spanish, and Valencia—based on plant branching order, pattern of branching, and number of seed per pod. Runner peanuts, the fourth type sold commercially, are genetically related to Virginia-type nuts and are grown extensively in the Southeast and Southwest areas.

The most distinguishing characteristic of the peanut is the yellow papilionate flowers which are borne above ground on the vines. Following fertilization the flower

[1]Adj. Asst. Professor and Assistant Professor respectively. Food Science Department. North Carolina State University, Raleigh, N. C. 27607

wilts and after a period of 5-7 days a positively geotropic peg (ovary) emerges, grows downward to the soil and penetrates to a depth of 2-7 cm. Subsequently, the peg orients to a horizontal position and the pod begins to form. The pod is a single-loculed, dehiscent legume which splits along a longitudinal ventrae suture. Pod size varies from approximately 0.5 x 1 cm to 2 x 8 cm, while seed weight varies from ca. 0.2 to 5 grams (g). The pericarp (cortex, hull, shell) material of the pod comprises 20-30 wt. % of the pod and is easily removed from properly cured nuts. The number of seed per pod is usually two for Virginia, two to three for Spanish, and three to six for Valencia. The seed consists of two cotyledons and the germ (embryonic axis, embryo, heart) covered by a thin skin called the testa, which may range in color from a red-brown through purple to white.

Woodroof (1a) estimated that Spanish-type peanuts consist of approximately 20% shells, 72.4% cotyledons, 4.1% skins, and 3.3% hearts.

Factors Affecting Composition And Properties Of Peanuts

At the outset it should be pointed out that several factors will effect variation in the compositional makeup of peanuts:

Variety. As early as 1942 Guthrie *et al.* (2) reported variations in gross composition among Spanish, Runner and Virginia peanuts. Holley and Hammons (3) demonstrated definite genotype differences in such characteristics as protein, oil content, and oil stability.

Individual seeds within an aliquot. Herein would be reflected such conditions as maturity of the individual seed, its microenvironment in the soil, and/or postharvest treatment. Carotenoids, sugars, amino acid content, and roasted flavor development have been linked to these factors (4, 5, 6).

Year-to-year climatic variations. Holley and Hammons (3) found some extreme year-to-year effects on constituents of 26 strains and varieties. Eheart and coworkers (7) also noted seasonal variations in composition of Virginia-type peanuts.

The portion of the seed tissue analyzed, i.e., testa, heart, cotyledon, etc. Several groups (2, 8) have demonstrated differences in lipid composition of morphologically distinct fatty tissues of the peanut.

Abnormalities of the seed, including disease, insect infestation, or damage from harvest. Fungal growth on the surface of peanuts has been shown to grossly affect sugars, as well as the total quantity and unsaturation of free fatty acids (9, 10). The well-known effects of *Aspergillus flavus* in producing aflatoxin need not be elaborated upon here.

Lack of accuracy and precision in testing methods. Numerous procedures exist for determining the physicochemical properties of peanuts. Variations in results between two distinct methods, as well as between different laboratories using the same method is not uncommon. The problem was well illustrated in the 1965 report of the Instrumental Methods Committee of the American Oil Chemists Society (11) wherein it was noted that the same peanut oil sample analyzed in fourteen different laboratories produced such ranges as 0.9-5.7% for stearate, 34.2-49.3% for oleate, and 21.6-41.1% for linoleate.

Gross Composition

The gross composition of peanut cotyledons (full and partially defatted), defatted peanut flower, shells, testa, and germ is given in Table 1. Additional data on composi-

tion and the nutritive value of peanuts and peanut products may be obtained from data of Watt and Merrill (20) and others (21-24).

Freshly-harvested peanuts have moisture contents approaching 40%. Upon drying this content is lowered to 10% or less, usually in the range of 5-8%. The moisture must be less than 10% to prevent mold spoilage during storage. Young and Holley (25) found that peanuts dried at 75% relative humidity attained hygroscopic equilibrium in the range of 7.5-8.0% whether dried at room temperature or 160°F, while at 43% relative humidity a final moisture content of 5.0-5.5% was achieved. Peanuts attain moisture equilibrium much more rapidly at elevated temperatures and air flow rates but off-flavors may develop from the former (26). Woodroof (1b) found that cured, shelled peanuts (initial moisture 6.29%) stored in burlap bags at 35°F and 89% relative humidity attained a moisture range of 6.8-12.0%, depending upon the position at which the bag was sampled. Karon and Hillery (27) noted that moisture in skins is approximately twice that of the meats, and in general the relative moisture content in cured peanuts is: skins > shells > hearts > meats. Uncured or "green" peanuts will attain equilibrium at approximately 5.5% moisture following 35 days storage at 35°F and 50% relative humidity. When stored at 35°F and 70% relative humidity, equilibrium of approximately 10% moisture is attained in 60 days (28).

Peanuts will have a moisture content of less than 2% following roasting (1c). When used in candies and baked goods, they will absorb moisture in a manner closely related to the package and storage conditions. It has therefore been recommended that peanuts and peanut products be stored at a relative humidity not exceeding 60% (29). The hygroscopic nature of peanuts has also prevented their use in ice cream, as the nut texture becomes soggy within a short period of storage.

Generally speaking, peanuts are considered a rich source of both oil (44-56%) and protein (25-34%). Holley and Hammons (3) found a negative correlation between protein and oil contents for 69 varieties and strains of varied genetic background. Differences of 22% in the high-low range for oil, 28.5% for protein, 122% for sucrose and 217% for linolein were noted.

The gross compositions of raw and roasted cotyledons are similar. Defatted cotyledons and flour have higher percentages of protein, carbohydrate and minerals due to the lipid removal.

Some rather striking differences are noted in the makeup of various morphological structures of the peanut. The shells are extremely low in oil and protein, but high in crude fiber. The pentosan content of hulls is relatively high and xylose has been obtained from hydrolysis of same (2). Fernandez and Lara (18) reported that the shells contain 27.98% lignin with a methoxyl content of 4.3%.

The testa is considerably lower in protein and oil than the cotyledons, but much higher in total carbohydrates and crude fiber. The embryo (germ), center of germination in the seed, approximates the cotyledons in protein and lipid content; the concentration of reducing sugars and disaccharides, however, is considerably higher than in the cotyledons.

In a society which is becoming increasingly weight-conscious, the importance of caloric content cannot be overlooked. As indicated in Table 1, blanched full-fat raw peanuts contain about 568 calories per one hundred grams. The caloric value with skins intact, 564/100 g, is essentially the same. Full-fat roasted peanuts with and without skins are also of approximately the same caloric value, 582 and 585/100 g, respectively. Development of the reduced fat peanut by the Southern Utilization laboratories of

Table 1. Gross Composition of Peanuts[a]

	Blanched, Full Fat Raw Cotyledons		Shells	Testa	Germ	Blanched Defatted Cotyledons	Defatted Flour	Blanched Full Fat, Roasted Cotyledons
	Range	Avg.						
Moisture	[b]	[b]	[b]	9.01%	—	2.7%	7.3%	1.6%
Protein	25.4-33.8%	27.6%	4.8-7.2%	11.0-13.4	26.5-27.8	43.2	47.9-56.8	26.0
Lipid (Oil)	44.5-56.3	52.1	1.2-2.8	0.5-1.9	39.4-43.0	16.6	8.6-9.2	49.8
Total Carbohydrates	6.0-24.9	13.3	10.6-21.2	48.3-52.2	—	31.2	21.3-31.5	18.8
Reducing Sugars	0.1-0.4	0.2	0.3-1.8	1.0-1.2	7.9	—	—	—
Disaccharides (as Sucrose)	2.9-6.4	4.46	1.7-2.5	—	12.0	—	—	—
Pentosans	2.2-2.7	2.5	16.1-17.8	—	—	—	—	—
Starch	0.9-5.3	4.0	0.7	—	—	—	—	—
Hemicellulose	—	3.0	10.1	—	—	—	—	—
Crude Fiber	1.6-1.9	—	65.7-79.3	21.4-34.9	1.6-1.8	—	2.7-4.0	2.4
Ash	1.8-2.9	2.44	1.9-4.6	2.1	2.9-3.2	6.3	4.1	3.8
Calories	—	564/100g	—	—	—	415.8/100g	371/100g	585/100g

[a]Compiled from References 2, 3, 7, 12-20.
[b]Varies with curing and storage technique; usually 5-8%.

USDA has opened a new area for the weight-watching peanut eater (15). Table 1 indicates a caloric content of approximately 416/100 g for this product. However, when considered on a *calories per seed* basis, the reconstituted low fat peanut has less than one-half the calories of a full-fat peanut.

Protein

The history of isolation, identification and characterization of peanut protein is attended in a succeeding chapter.

Lipids

General Properties of the Oil (Table 2)

Peanut oil is composed of mixed glycerides of approximately 80% unsaturated and 20% saturated fatty acids (2, 14). As will be discussed in a succeeding section, the exact fatty acid composition may vary with genotype and cultural conditions. At ordinary temperatures peanut oil is a slightly viscous, light yellow liquid with a slightly nut-like aroma and taste. When submitted to refrigeration temperatures (0°C) solidification occurs.

Table 2. General Properties of Peanut Oil[a]

Melting Point	0-3°C
Iodine Value	82-106
Thiocyanogen Value	58-75.5
Saponification Value	188-195
Acetyl Value	8.5-9.5
Reichert-Meissl Value	< 0.5
Polenske Value	< 0.5
Free Fatty Acids	0.02-0.6%
Unsaponifiable Matter	0.3-0.7%
Refractive Index (N_D^{20})	1.4697-1.4719
Density at 15°C	0.917-0.921
Density at 25°C	0.910-0.915
Mean Viscosity, 20°C	71.07-86.15 centipoise
Titer	26-32°C
Heat of Fusion	21.7 cal/g (unhydrogenated)
	24.7 cal/g (hydrogenated)
Color: Visual	Light yellow
Lovibond, 1 in.	Yellow: 16-25; Red: 1-2
Taste and Odor	Slightly nut-like

[a]Compiled from References 2, 3, 14, 30-35.

Peanut oil may be easily hydrogenated, and small quantities of this product have been used to prevent "oiling-off" in peanut butter for some years. Lutton (36) has indicated that hydrogenated peanut oil (iodine value = 8) may exist in three crystalline forms: α (m.p. 51.5°C), β_1 (m.p. 63°C), and β (m.p. 67.8°C). The lower melting forms are characterized by finely-divided crystals, and are generated by rapid chilling (37, 38). Transformation between forms to a more stable entity may occur without melting. The establishment of proper crystal structure through rapid cooling is of considerable importance in producing a peanut butter of proper texture and appearance. The formation of the lower-melting crystalline forms results in a smoother final product with a minimum of "tallowy" or "unctuous" textural sensation in the mouth.

Magne and coworkers (39) have reported on solubility properties of hydrogenated peanut oil in peanut oil, a factor of considerable import in stabilizing peanut butter. The solubility temperature rose sharply with increases in quantity of "hardened" oil up to 9%, at which concentration the observed temperature was 55°C. Results suggested that mixtures with more than 2% "hard fat" would stabilize peanut butter from separation under average storage conditions.

The iodine value (40a) is a measure of the relative degree of unsaturation of the fatty acids appearing in an oil, as measured by the uptake of halogen. This value is a reflection of melting point or hardness of a fat, as well as the resistance of the oil to oxidation. The higher the iodine value, the greater is the unsaturation of the fat and, generally speaking, the susceptibility to oxidation. Peanut oil, with a range in IV of 82-107, is more saturated than corn (IV 103-128), cottonseed (IV 99-113), or linseed (IV 155-205) oils, but considerably less saturated than coconut (IV 7.5-10.5), palm (IV 44-54), or butter (IV 25-42) oils (30).

While investigating peanut oils from such widely divergent areas as China, Argentina, and Africa, Seitz (32) found iodine values ranging from 87.1-106.8. Williams (35) noted that oils from South America customarily have high unsaturation. Iodine values as high as 107 for oils from this source have been observed, and values of 105 are common. Holley and Hammons (3) reported values of 93.5-98.6 for oil from 24 strains of nondormant Spanish-Valencia types, 86.8-98.7 for 23 strains of dormant Virginia-type, and 81.3-95.5 for 22 strains of dormant Jumbo-type peanuts grown at Tifton, Georgia in 1964. A high statistical correlation was noted between iodine value and such variables as oil content, refractive index, keeping time, and olein-linolein content.

The thiocyanogen value (40b) is a measure of the amount of this reagent, expressed as centigrams of iodine equivalents, absorbed by one gram of fat. Thiocyanogen reagent $(CNS)_2$ adds to double bonds somewhat differently from the halogenating agents, and together with the iodine value can be used to roughly estimate percentages of oleic, linoleic and linolenic acid present in an oil. The thiocyanogen value for peanut oil (58 to 64) is moderate when compared with corn (TV 75-80), cottonseed (TV 60-70), coconut (TV 6.5-7), palm (TV 45) and linseed (TV 95-120) oils.

The saponification value is a measure of the milligrams of potassium hydroxide needed to hydrolyze one gram of fat. This value is inversely proportional to the mean molecular weight of the glycerides of a fat. Peanut oil, which is comprised almost exclusively of glyceryl esters of fatty acids containing 16 or more carbons, exhibits a lower saponification value than butterfat or coconut fat, both of which contain a significant amount of fatty acids with ten carbon atoms or less.

The acetyl value is an assay of the number of milligrams of potassium hydroxide required to neutralize the acetic acid obtained from saponifying one gram of an *acetylated* fat. It is a measure of free hydroxyl groups present in the oil, whether from hydroxy fatty acids, sterols and other high molecular weight alcohols, or possibly free hydroxyl groups of mono- and diglycerides. Peanut oil contains no measurable quantity of hyroxy acids; the low acetyl value is attributed to sterols and other unsaponifiables present.

The Reichert-Meissl value is an index of steam-volatile, water-soluble fatty acids (primarily butyric) in a fat. The companion assay—Polenske value—indicates steam-volatile water-insoluble fatty acids. These values are concerned with fatty acids of ten carbons or less, hence peanut oil exhibits an extremely low value.

Present oils are generally very low in free fatty acids. Freeman *et al.* (14) reported values of 0.1-0.6% from 20 batches of oil, the average being 0.33%. Free acid content

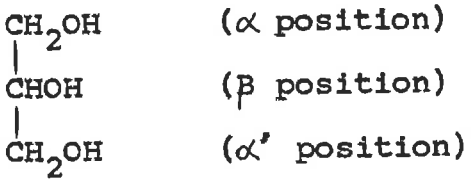
of nuts processed for peanut butter dropped slightly, probably due to removal of germs, testa and other material. The mean acid value of oil removed from germs was 0.38%, with a range of 0.2-0.6%, while that from testa averaged 1.6%, with a range of 0.8-3.1%.

The titer value of oils is a measure of the temperature range for solidification of the purified fatty acids making up the glyceride structure. In comparison to the value for peanut oil, 26-32°C, cottonseed oil has a value of 30-37°, while corn and linseed oils have ranges of 14-20° and 19-21°C, respectively.

As mentioned previously, Holley and Hammons (3) observed some extreme year and genotype effects on the oil content of peanuts. Very little seasonal variation in oleic and linoleic acid content of oils had been observed in earlier studies (41).

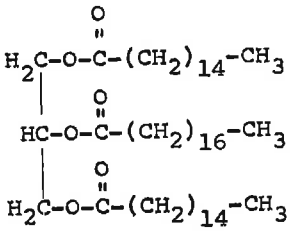
Saponifiable Lipids.

Occurrence of Fatty Acid Esters. The compounds comprising this group would be the glycerol esters of fatty acids. Glycerol is a trihydroxy alcohol which can be esterified with a molecule of fatty acid at each alcohol grouping:



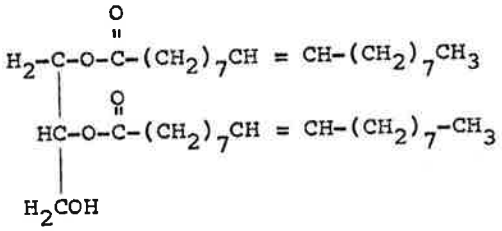
Glycerol

Most of the glyceride material in fats and oils exists in the form of triglycerides, i.e., all hydroxyl groups of the glycerol molecule are esterified. Small amounts of di- and monoglycerides also occur, however. The glycerol portion of these structures is not completely esterified; hence, the prefix names:



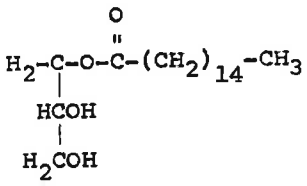
Triglyceride

(β-stearyl-α, α'-dipalmitin)



Diglyceride

(β-diolein)



Monoglyceride

(α-monopalmitin)

Pohle and coworkers (42) reported 0.8% monoglyceride in peanut oil. No study pertaining to diglyceride content was encountered in the present literature review.

Since peanut oil is derived from a vegetable source, the fatty acids are composed primarily of even-carbon number from C16 to C24. The major fatty acids (>1%) of peanut oil are (Table 3): palmitic (hexadecanoic, 16:0); stearic (octadecanoic, 18:0); oleic (*cis* 9-octadecenoic, 18:1); linoleic (*cis* 9, *cis* 12-octadecadienoic, 18:2); arachidic (eicosanoic, 20:0); *cis* 11-eicosenoic (20:1); behenic (docosanoic, 22:0); and lignoceric (tetracosanoic, 24:0). Minor acids (<1%) which have been reported include: caprylic (octanoic, 8:0); capric (decanoic, 10:0); lauric (dodecanic, 12:0); myristic (tetradecanoic, 14:0); palmitoleic (*cis* 9-hexadecenoic, 16:1); 9-heptadecenoic (17:1); *cis* 11-octadecenoic; linolenic (*cis* 12, *cis* 15-octadecatrienoic, 18:3); hexacosanoic (26:0); and a series of odd-carbon number saturated fatty acids ranging from C13-C27 (43-48).

Table 3. Fatty Acid Composition of Total Saponifiable Peanut Lipids

Acid[a]	Inverson *et al.* (43) Avg.	Inverson *et al.* (43) Range	Worthington and Holley (44) Avg.
Caprylic (8:0)	0.3%		
Capric (10:0)	0.03		
Lauric (12:0)	0.1		
Tridecanoic (13:0)	0.004		
Myristic (14:0)	0.09	0.01-0.23	
Pentadecanoic (15:0)	0.01		
Palmitic (16:0)	11.1	8.42-14.0	7.48-12.45%
Palmitoleic (16:1)	0.1		0.08-0.14
Heptadecanoic (17:0)	0.03		0.05-0.11
9-Heptadecenoic (17:1)			0.01-0.07
Stearic (18:0)	2.6	1.75-3.20	2.77-4.92
Oleic (18:1)	47.8	33.3-61.3	41.35-67.44
cis-11 Octadecenoic (18:1)	0.9[b]		
Linoleic (18:2)	30.7	18.5-47.5	13.90-35.13
Linolenic (18:3)			0.02-0.04
Nonadecanoic (19:0)	0.002		
Arachidic (20:0)	1.1	1.0-1.7	1.25-1.88
11-Eicosenoic (20:1)	1.3	0.74-2.27	0.84-1.45
Heneicosanoic (21:0)	0.004		
Behenic (22:0)	3.0	1.7-3.78	2.16-3.59
Tricosanoic (23:0)	0.02		
Lignoceric (24:0)	1.2	0.46-2.6	0.98-1.67
Pentacosanoic (25:0)	0.007		
Hexacosanoic (26:0)	0.4		
Heptacosanoic (27:0)	0.004		

[a]First figure in parentheses refers to number of carbons; the second figure to number of double bonds.
[b]Reference 45 and 46.

Iverson *et al.* (43) and Sekhon *et al.* (49) noted little difference in the fatty acid composition of oil from raw and roasted peanuts. The ranges for major fatty acids of Valencia, Spanish, Runner, and Virginia-types were established via gas chromatography of methyl ester preparations. The methyl esters from ten sources were combined for isolation and identification of the minor fatty acids. Values for these acids in Table 3 thus reflect a cross-type average.

Oleic and linoleic acids are the major components of the glyceride fraction. Holley and Hammons (3) demonstrated a high reciprocal relationship (-0.988) between these two acids in varietal studies. The proportion of linoleic acid in the oil is important to the processor, for as the degree of unsaturation rises, keeping quality decreases. Thus, peanut butter manufacturers have over the years attempted to utilize peanuts with oils of a lower iodine value to optimize shelf life of the final product. Norden and Block (50) have investigated blending of peanut varieties at planting to influence the properties of the oil obtained from the mature crop.

Fore *et al.* (51) reported differences in linoleic acid content of Spanish, Virginia and Runner types. However, the large number of genetic crosses in recent years has made classification of types via chemical properties a hazardous proposition. One may cross a Spanish and a Virginia-type peanut, obtaining a Virginia-type reflecting Spanish chemical composition (or *vice versa).*

There has been much conjecture over the presence of linolenic acid in peanut lipids. Until gas chromatography arrived on the analytical scene, the problem could not be solved. Iverson and coworkers (43) examined numerous urea adduct fractions from peanut oil, but were unable to confirm the presence of the triunsaturate. Observance of their published gas chromatograms does not preclude the existence of small levels of linolenate, as has since been reported by Worthington and Holley (44). These latter researchers found levels of 0.02-0.04%. French (52) has reported linolenate concentrations of 1.1-1.6%, which would appear to be rather high.

It is interesting to note that *cis* 11-eicosenoic acid (20:1) appears in peanut lipids, whereas the *cis*-9 monounsaturated isomer would commonly be expected in natural systems.

Fatty Acids of Morphological Distinct Tissues. Developmental changes in fatty acids of various tissues of the Virginia Bunch 67 variety have been followed (53). Cotyledon and germ composition roughly paralleled one another during maturation, as did testa and shells. Triglycerides predominated the lipid makeup of the cotyledons and germ, while complex lipids comprised a large percentage of testa and shell lipids. At maturity shells contained 0.6% crude lipid, the testa 2.9%, embryos 51.3% and the cotyledons 52.2%. In Table 4 is presented the fatty acid composition of these tissues. Oil from the shells (pericarp) was analyzed only once, this being 2-3 weeks after soil penetration by the peg. At this time, a very high content of palmitic and linolenic acids was observed.

Table 4. Fatty Acid Composition of Morphologically Distinct Tissues of the Peanut

	Worthington (53)				Fedeli *et al.* (8)		
Acid	Cotyledon	Embryonic Axis	Testa[a]	Pericarp[a-b]	Cotyledon	Embryonic Axis	Pericarp
16:0	9.21%	15.55%	16.81%	25.24%	9.2%	16.2%	11.9%
18:0	2.50	1.70	3.43	2.39	3.7	2.7	3.5
18:1	52.71	38.38	28.26	13.28	62.7	45.5	55.1
18:2	29.45	36.20	32.27	38.19	16.2	26.6	20.0
18:3	0.04	0.60	5.90	13.59	1.6	2.0	1.9
20:0	1.27	0.90	1.57	1.06	2.0	1.6	1.8
20:1	1.26	1.77	1.10	0.59	—	—	—
22:0	2.46	3.02	3.92	1.92	2.7	2.8	3.2
24:0	1.10	1.90	2.79	1.35	1.5	2.0	1.8

[a] Determinations made on crude lipid extract.
[b] 2-3 weeks after soil penetration by peg; highly immature.

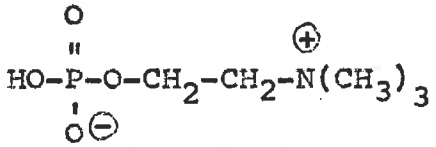
During maturation of the cotyledons, palmitic, linoleic, linolenic, eicosenoic, behenic, and lignoceric acids declined in concentration while oleic acid increased. The other acids present did not change appreciably. The maturation pattern for palmitate, linoleate and linolenate in the embryo was similar to cotyledons. Behenate, lignocerate and eicosenoate showed little change (Table 4). At maturity the triglyceride fraction of the embryo contained 70% more palmitate, approximately 23% more linoleate, and fifteen times the linolenate of the cotyledons. The cotyledons contained higher levels of oleic and stearic acids.

Hartzook (54) observed a reciprocal relationship between oleic and linoleic acid content in mature and immature seeds. The linoleic acid level dropped from 43.9% in the immature to 38.2% in the mature while the oleic increased from 45.6% to 48.8%, respectively.

The fatty acid composition of the crude testa lipids reflected higher levels of palmitate, linoleate and linolenate than the cotyledons. During maturation, stearic, oleic, arachidic, eicosenoic, behenic, and lignoceric acids increased in concentration, while palmitic, linoleic and linolenic decreased.

Fedeli and coworkers (8) also examined the fatty acid composition of peanut tissues, but did not state the genetic origin of the sample(s). The acid composition of mature hulls more nearly resembled the cotyledons in their study (Table 4). The value reported for linolenic acid in the cotyledons (1.6%) appears high, although it is possible that the particular variety of peanuts under study may have reflected this degree of unsaturation.

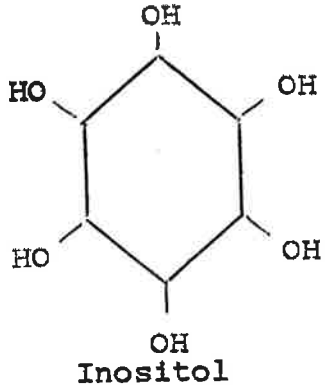
Phospholipids. Several phosphatide forms exist in nature. The following is a brief description of each. Lecithins are a type of glyceride consisting of two fatty acids plus one molecule of phosphatidylcholine linked to the glycerol molecule.



Phosphatidylcholine

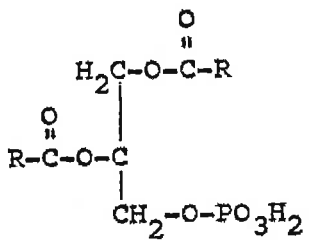
Cephalins are of the same structure except ethanolamine, $HO\text{-}CH_2\text{-}CH_2\text{-}NH_2$, replaces choline on the phosphoryl moiety. The phosphate may be esterified either at α or β positions of the glyceride. Phosphatidylserines consist of having the grouping, $HO\text{-}CH_2\text{-}\overset{\overset{NH_2}{|}}{C}\text{-}COOH$, linked to the glyceride through phosphate.

Lysolecithin is lecithin minus one fatty acid molecule. Phosphatidylinositol consists of the hexahydroxy alcohol inositol joined through phosphate to the glyceride.

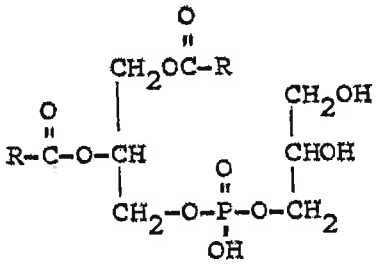


Inositol

As will be discussed, the so-called phosphatidylinositol fraction from peanut lipids contains other material as well. Phosphatidic acid is composed of glycerol, two esterified fatty acids and a phosphate grouping alone at the third hydroxyl grouping. Phosphatidylglycerol involves a second molecule of glycerol linked to the terminal end of the phosphate grouping.



Phosphatidic Acid



Phosphatidylglycerol

Rewald (55) has shown that "cold-pressed" oil contains less than one-half of the total phosphatides of the seed. These complex lipids exist in "bound" as well as "free" form in the seed, and a polar solvent must be utilized along with the common lipid solvents for complete isolation.

Osman and coworkers (56) reported Egytian peanut oil as containing measurable quantities of phosphatidylinositol, lysolecithin, phosphatidylcholine (lecithin), phosphatidylethanolamine (cephalin), and phosphatidylglycerol. Phosphatidic acid and phosphatidylserine were not detected. Malkin and Poole (57) noted that phosphatidylinositol constituted about 38% of the total phospholipids isolated from peanut oil. Acid hydrolysis of the inositol phosphatide fraction yielded glycero- and inosito-phosphoric acids (1:1), ethanolamine, ethanolamine phosphate, L-arabinose and a disaccharide composed of L-arabinose and D-galactose.

Osman *et al.* (56) perceived some rather striking differences in fatty acid composition among the glyceride, lecithin and cephalin isolates of Egyptian peanut oil. Arachidic acid was overwhelmingly predominant in the latter two fractions (55.6 and 71.3%, respectively), whereas the content in glycerides was only 2.4%. Palmitate was two to three times as high in phosphatide fractions as in the glycerides. In contrast, oleic acid content was much lower in the phosphatides, and while linoleate was present at a level of 18.6% in the "total" phospholipid isolate, this acid was not detected in either the lecithin or cephalin subfractions.

Senn (58) isolated and purified three phosphatide fractions and the triglycerides from cold-pressed oil of Virginia-type peanuts (undetermined origin). In contrast to the results of other researchers (56), a phosphatidylserine fraction was obtained. The results of fatty acid determinations on this fraction as well as triglycerides, lecithins, and cephalins are reported in Table 5. Since a portion of the phosphatides in peanuts are complexed, it is not known whether the values reported for cold-pressed oil (Table 5) would be reflective of the total phosphatides.

Senn (58) found palmitate at noticeably higher levels in the phosphatides, as did the Egyptian researchers (56). With certain exceptions the composition of the phosphatidylserine fraction resembled the triglycerides. Stearic and lignoceric acids were slightly higher in lecithin and cephalin fractions than in glycerides, but oleic and linoleic acids were much lower. A higher content of arachidic acid in glycerides than

in either lecithin and cephalin may reflect the difference in oil extraction technique between Senn (58) and Osman's group (56).

Sreenivasan (59) reported that a "crude lecithin" fraction obtained from degummed peanut oil (Indian origin) was higher in palmitate and oleate but lower in linoleate, arachidate, behenate, and lignocerate than the source oil. This "crude lecithin" fraction contained both cephalin and lecithin, as well as some of the source oil.

Table 5. Comparison of the Fatty Acid Composition of Purified Triglyceride and Phospholipid Fractions from Cold-Pressed Peanut Oil (Senn, 58)

Fatty Acid	Triglycerides	Phosphatidyl-ethanolamines	Phosphatidyl-cholines	Phosphatidyl-serines
16:0	8.1%	24.7%	33.9%	12.9%
16:1	Tr	0.1	0.2	Tr
17:0	Tr	0.2	—	Tr
18:0	1.5	2.6	4.7	2.8
18:1	49.9	39.5	30.9	47.0
18.2	35.4	28.2	27.5	35.6
18:3	Tr	0.1	Tr	Tr
20.0	1.1	0.1	0.2	0.3
20:1	0.9	1.0	0.2	0.4
22:0	2.1	0.5	0.5	0.3
22:1	—	—	—	0.1
24:0	1.0	3.0	2.0	0.5
24:1	—	—	—	0.1

Phytosphingolipids. A complex glycolipid, constituting approximately 5% of the phospholipids, appears in peanuts and other plant seed (60,61). On hydrolysis this fraction from peanut lipids was found to contain phytosphingosine, fatty acids, inositol, glucosamine, a hexuronic acid, galactose, arabinose, mannose, and phosphate. Phytosphingosine has the structure:

$$CH_3\text{-}(CH_2)_{12}\text{-}CHOH\text{-}CHOH\text{-}CHNH_2\text{-}CH_2OH$$

Nothing is known about the synthesis of this organic base in higher plants.

Glyceride Composition. The position and type of fatty acids making up individual triglyceride molecules has been studied by several groups. Van der Wal (62) made the following calculations pertaining to triglyceride structure in peanut lipids (S = saturated. U = unsaturated acid):

S, S, S	S, S, U	S, U, S	S, U, U	U, S, U	U, U, U
0.1%	0.6%	9.3%	41.8%	0.7%	47.5%

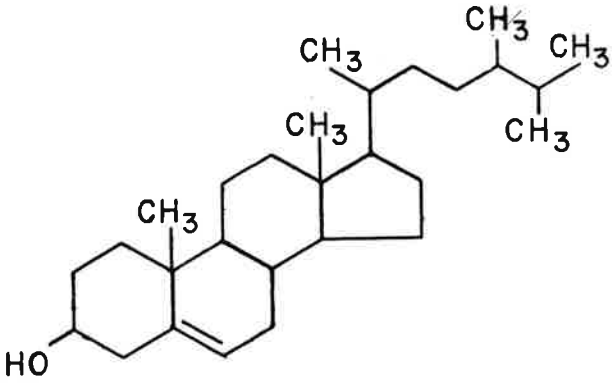
With oleic and linoleic acids occupying a major role in triglyceride constitution, it is not difficult to understand why glycerides with two or three unsaturated acid moieties would dominate.

Jurriens and Kroesen (63) found that oleate (18:1) in the β-position of peanut triglycerides fell from 75.7% to 10.6% as the total unsaturation of purified triglyceride fractions rose from 1 to 5 double bonds. Linoleate (18:2) showed a direct correlation, rising from 34.5% in the 2-position of a glyceride fraction with two total double bonds to 84.5% in the 2-position of a fraction with five total double bonds. Linolenate (18:3) also showed a rather high percentage in the 2-position of a five double bond triglyceride fraction.

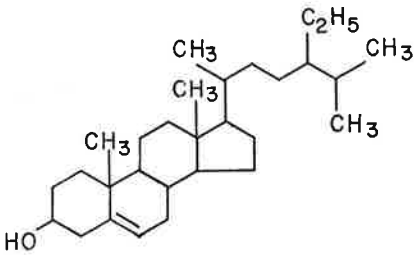
Employing lipase hydrolysis and gas chromatographic data, Subbaram and Young (64) estimated that peanut oil contained 11% triolein, 21% dioleolinolein, 22% saturated oleolinolein, 12% dilinoleoolein, 15% saturated diolein, and 6% saturated dilinolein.

Unsaponifiable Lipids

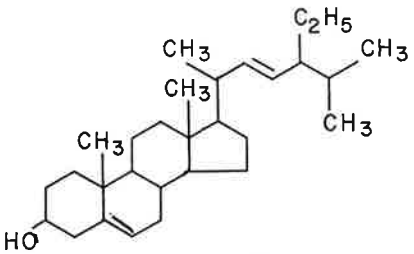
Sterols. Thin layer chromatographic analysis of peanut unsaponifiables indicated that sterols constituted 17.5% of this fraction in cotyledons, 22.0% of the total in germs, and 7.1% of the unsaponifiables in hulls (8). Fedeli *et al.* (8) related the higher percentage of embryo sterols to germination of the seed. β-sitosterol, campesterol, and stigmasterol have been identified as the main components of the sterol fraction (8, 65). A fourth compound appearing in gas chromatograms of the sterol fraction has not been identified (8).



Campesterol



β-sitosterol

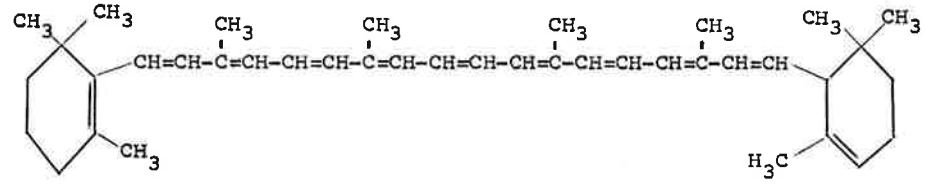


Stigmasterol

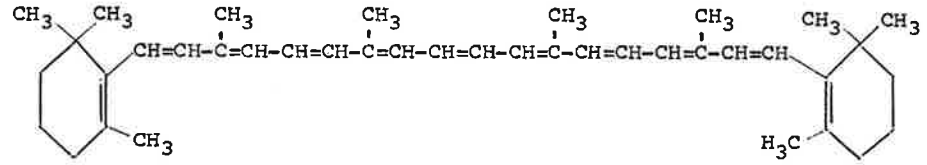
β-sitosterol appears to be the major sterol in germs, cotyledons, and hulls (8). Concentrations of stigmasterol and campesterol have been shown to approximate one another in cotyledons, with both occurring at significantly lower levels than β-sitosterol. Campesterol was present in significantly smaller quantities than stigmasterol in both

germs and hulls. The unidentified compound in the sterol fraction roughly paralleled the concentration of stigmasterol in each of the tissues investigated by Fedeli and co-workers (8). In contrast to the study of Fedeli, Eisner and Firestone (65) found the sterol fraction of domestic peanut oil to be composed of 84% β-sitosterol, 12% campesterol, 3% stigmasterol, and < 1% minor components. Sterol glycosides appear in commercial plant phospholipid samples (66). β-sitosterol-D-glucoside, a stigmasterol glucoside, and an unidentified saturated sterol glucoside constituted 1-3% of such samples investigated. β-sitosterol-D-glucoside has been isolated from fat-free peanut flour (67).

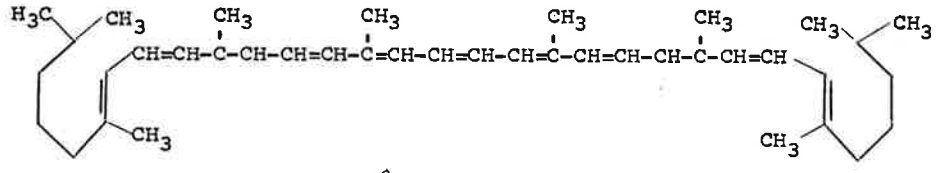
Pigments. Since oil color may be used as a rough index of seed maturity (68, 69, 70), Pattee and Purcell initiated an investigation of the pigments responsible (4, 71). As full maturity of the seed approaches, the color of expressed oil becomes noticeably lighter. This phenomenon was demonstrated as a dilution effect which is brought about by the rapid increase in seed oil content near maturation. Carotenes characterized in oil from immature peanuts included alpha (trace), beta (60 μg/l oil), zeta (0.088 μg/l), and an unknown (12 μg/l). Xanthophylls present included lutein (138 μg/l), zeaxanthin (11 μg/l), and flavoxanthin (5.4 μg/l). Pigments were at exceedingly low concentrations in oil expressed from mature nuts (< 1 μg/l). Structures for the isolated pigments are given below. Striking similarities may be noted, several differing only in the position of a double bond or the presence of hydroxyl groups.



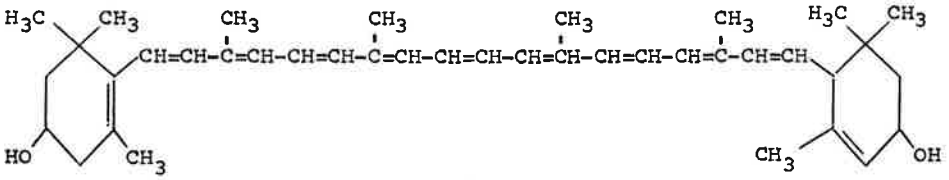
α-carotene



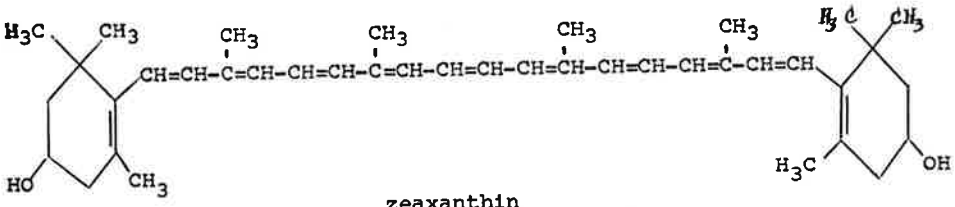
β-carotene



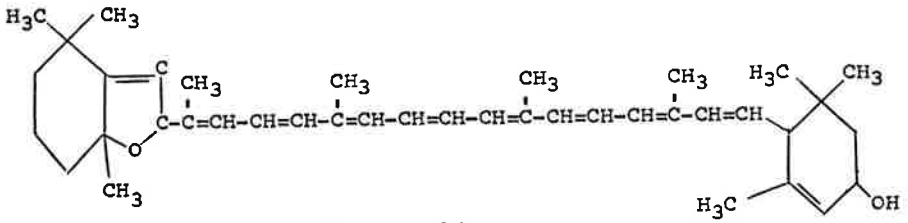
γ-carotene



Lutein
(3,3'-dihydroxy-α-carotene)



zeaxanthin
(3,3'-dihydroxy-β-carotene)



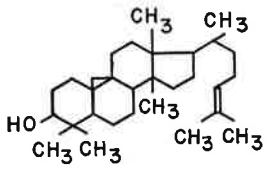
flavoxanthin

Evidence has been presented to the effect that these pigments do not exist within the oil-bearing spherosomes of the seed.

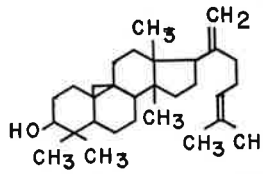
Fedeli *et al.* (8) have shown that phytol is an artifact produced from chlorophyll during saponification. Relating phytol concentration to chlorophyll in the intact seed, the following relation ship was postulated: hulls > seed > germ.

Tocopherols. A series of tocopherols (Vitamin E) have been demonstrated in the unsaponifiable fraction of peanut lipids. These will be discussed in subsequent sections (see "Stability of Peanut Oils" and "Vitamins").

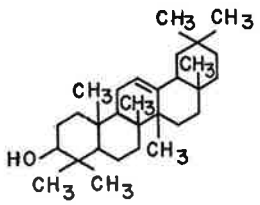
Terpenes. Densitometric measurement of thin-layer chromatograms demonstrated that triterpenes comprise approximately 2.9% of the unsaponifiable matter of cotyledons, 6.8% of the germ unsaponifiables, and 2.4% of this fraction from hulls (8). Three terpene alcohols have been positively identified: β-amyrin, cycloartenol, and 24-methylene cycloartenol (8, 72). An unidentified fourth component constituted the major portion of the triterpene alcohol fraction from hulls. Cycloartenol and 24-methylene cycloartenol were present in about equal quantities in both seed and embryo.



Cycloartenol



24-methylene cycloartenol



β-amyrin

Hydrocarbons. Squalene, $C_{30}H_{50}$, is the most important hydrocarbon present (8). Numerous other hydrocarbons have been found in the deodorization distillates of pea-

nut oil (73). Those identified include hexacosane, docosane, eicosane, saturated and unsaturated C18 compounds, and C20, C22, and C26 compounds with terminal *gem*-dimethyl groupings.

Miscellaneous. Jasperson and Jones identified 2-undecanone and 2-undecanol as components of the unsaponifiable constituents of deodorization distillates of peanut oils (74). Inasmuch as ketones and certain lactones are formed under influence of moisture and heat in lipids known to contain keto – and hydroxy fatty acids (75, 76), these results may indicate trace quantities of such precursors in peanut lipids.

Stability of Peanut Oil

Although peanut oil is relatively stable in relation to many other vegetable oils, nevertheless it is susceptible to the development of oxidative or hydrolytic rancidity. Oxidative rancidity is the more serious problem in most lipids. The chemical changes resulting are directly due to the reaction of oxygen with the unsaturated fatty acid structure of the glycerides. The higher the degree of total unsaturation in the oil, the lower is oil stability. This can be related simply to linoleic acid content or to an oleate-linoleate ratio, the monounsaturate being considerably more stable than the diunsaturate (3, 51, 77-79). In keeping with these observations, Roy and Guha (80) have noted increased oxidative stability in hydrogenated peanut oil. No correlation has yet been demonstrated between keeping quality and the rather low content of linolenic acid in peanut lipids (44), although linolenic acid and its esters are known to oxidize approximately ten times as rapidly as linoleate in model systems.

Young (81) reported a rapid microanalytical technique whereby the oleic/linoleic acid (methylester) ratio can be determined from a portion of a peanut kernel with the remainder being planted for genetic evaluation. This information is useful in speeding the development of peanut varieties with a lower linoleic acid content and hence greater oil stability.

An increase in oleic/linoleic acid ratio with increasing maturity was shown to be correlated with higher oxidative stability of the oil and a higher CLER score (organoleptic value for peanut butter samples (81).

Freeman *et al.* (14) noted that the AOM stability of oils from freshly prepared peanut butter was about 35 hours. Following three months storage of the butter, this stability time had dropped approximately one-third. Salt, stabilizers, and variation of the extent of roast affected the stability very little.

It has been proposed that flavor deterioration in peanut oil is the result of factors not significantly affected by added antioxidants (82). The isolated products of off-flavor were found to be aldehydic in nature, however; hence the problem is indeed oxidative. Hexanal, *cis, trans* and *trans, trans* decadienals were specifically mentioned as being involved.

Gaddis and Ellis (83) isolated and identified the volatile carbonyls produced in oxidized peanut oil (peroxide value = 26). The compounds obtained from unheated oxidized oil were: *n*- alkanals—C2, C6, C8, C9; *n*- alk-2-enals—C7 to C11; *n*- alk-2, 4-dienals—C7, C9, C10. From oxidized oil heated to degrade peroxides was obtained the following: *n*-alkanals—C6, C9; *n*-alk-2-enals—C7 to C11; *n*-alk-2,4-dienals—C7, C9, C10, C12.

Alumina refining will impart greater stability to refined peanut oil than does active earth bleaching (84). The improved stability was attributed to lack of side reactions which are stimulated by the bleaching earths, and to removal of proxidants and oil degradation components. Adsorbed glycerides recovered from spent alumina contained

saturated and α, β unsaturated carbonyl groups, possibly as aldehydoglycerides. Keto, epoxy-, and hydroxy fatty acids were present in gas-liquid chromatograms of methyl ester preparations of this material.

A heme-containing lipoprotein was isolated from peanut lipids by Butler and Baker (85). Insoluble in common lipid solvents, it was dispersed only in digitonin solution (slightly) and 4M urea. The hematin compound was proposed as either a pro- or an antioxidant, depending upon its concentration in lipid systems. Its ultraviolet absorption properties were similar to those of catalase, peroxidase and methemoglobin.

A rather interesting, though puzzling, phenomenon was reported by Salatore and Gavai (86), who noted an increase in the nitrogen content of peanut oil during autoxidation. The rise occurred from an initial value of 70 mg/100 g oil to 109 mg/100 g during a 42-day exposure period.

Tocopherols (Vitamin E) have been found to exert weak antioxidative properties when present at low concentrations in oils. In relation to other oilseeds, peanuts exhibit a uniformly high level of tocopherols, and it has been suggested that any differences among varieties will not be appreciably evident in oil stability variations (87). The level of tocopherols in peanut oil may run to as high as 600 mg/kg or more. Two of the tocopherols taken from peanut oil—gamma and delta—behaved in a similar manner when used as antioxidants in lard. Both were significantly better than α-tocopherol in preventing or impeding lipid oxidation. Tocopherols will be further discussed under "Vitamins."

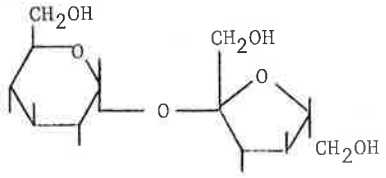
Various synthetic antioxidants have been evaluated for their effects on peanut lipids. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) have been used most successfully in cooking oil and on salted nuts (88, 89). Other agents affording various degrees of effectiveness have included nordihydroguaiaretic acid (NDGA), lecithin, ascorbic acid, citric acid, tartaric acid, and oat flour (89, 91). A metal chelator such as citric acid and/or propylene glycol in combination with BHA or BHT will exhibit synergistic effects (88, 91).

Hydrolytic rancidity can become a problem under certain conditions. Naudet and Baisini (92) reported acidification taking place in peanut oil stored unsealed at 20°C. but only in the presence of water and organic matter. This proceeded non-specifically and released considerable amounty of gylcerol.

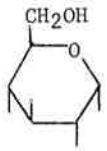
Carbohydrates

Sugars

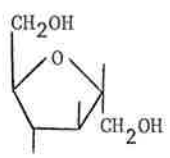
The saccharide in greatest abundance in the peanut seed is sucrose, although small quantities of glucose, fructose, and galactose have been detected (3, 5, 93). Holley and Hammons (3) found sucrose to vary from 2.86-6.35% depending upon genotype. Newell and coworkers (5) noted fructose appeared in the range of 4.18-6.24 μM/gm (0.08-0.11 wt. %) in raw, fat-free peanut meal, with glucose at 3.27-6.90 μM/gm (0.06-0.12%) and sucrose at 236-312 μM/gm (8.07-10.67%).



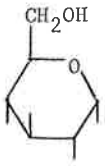
Sucrose
(α-D-glucopyranosyl-β-D-fructofuranoside)



Glucose
(α-D-glucopyranose)



Fructose
(β-D-fructofuranose)

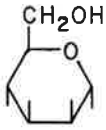


Galactose
(α-D-galactopyranose)

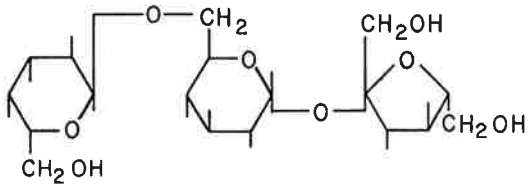
Ho and Cheng (94) isolated from peanuts two previously-unknown oligosaccharides, one of which was a trisaccharide. Both unknowns were composed of glucose and galactose. The trisaccharide consisted of the sequence glucose → galactose → glucose, but the configurations and linkages were not determined. The second unknown was calculated to contain glucose to galactose in a 1:4 ratio.

Aylward and Nichols (95) found that staychose, sucrose, arabinose, mannose and raffinose constituted about 0.86% of that portion of peanut phospholipids which was insoluble in alcohol. Sucrose and stachyose were also associated with the alcohol-soluble phospholipid material. Some of these sugars were later reported in peanut sphingolipids (66).

Arabinose
(β-L-arabinopyranose)



Mannose
(α-D-mannopyranose)



Raffinose
(α-D-galactopyranosyl-(1→6)-α-D-glucopyranosyl-(1→2)-β-D-fructofuranoside)

Stachyose is a tetrasaccharide consisting of the combination galactose → galactose → glucose → fructose.

Sterol glucosides have been previously discussed (see Lipids).

Non-Sugars

Phytin, inositol hexaphosphate, was reported at a concentration of 0.5% in germs and 3.2% in peanut flour (2, 96). The nutritional significance of this compound in the peanut is not known, but phytin will complex calcium, magnesium, and iron into forms which will pass through digestive tract without absorption (20). Sharma (97, see "Subcellular Particulate Bodies") has noted that aleurone grains are the primary

site of phytin in the resting cotyledon. Other inositol phosphates have been discussed under "Lipids."

Pinitol, a monomethyl ether of D-inositol was characterized in peanut flour by Lee and Morris (98).

Polysaccharide nomenclature of such fractions as pectin, protopectin, hemicellulose A, hemicellulose B, and cellulose A is based on solubilities of organic components in aqueous solutions of varying acidity (99). Thus, whether the chemical properties of such fractions represent a discrete chemical component within the intact cell is highly questionable. These fractions are obtained by rupturing covalent bonds; when sufficient bonds are broken a portion of the polysaccharides is solubilized. Starch, which occurs in discrete, easily-isolated granules, would be an exception.

Hirst and Jones (100, 101) observed starch, cellulose, and a peptic acid-araban complex in the polysaccharide fraction of peanut cotyledons. The starch comprised about 4% of the total composition of the peanut (102), cellulose about 2% and the araban-pectic acid complex approximately 4%. Further purification of the araban complex produced a hygroscopic powder, $(\alpha)_D$-160° in water, which quantitatively yielded L-arabinose upon hydrolysis.

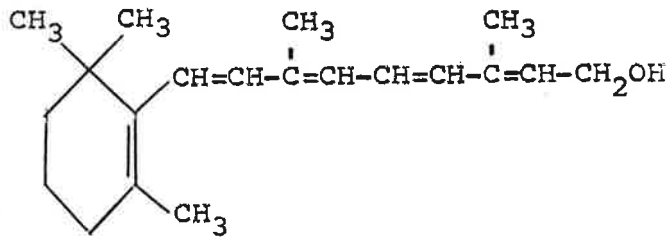
The following data have been reported for peanut shells: uronic acids — up to 6.94% (2); hemicellulose B_1 — 2% (18); starch — 0.74% (16).

Studies on the hemicellulose B_1 fraction of shells have demonstrated the presence of D-xylose, L-arabinose, and D-glucuronic acid (103, 104). A structure was proposed for the hemicellulose fraction consisting of a linear chain of 1, 4 linked β-D-xylopyranose residues. It was further hypothesized that arabinose is attached to glucuronic acid which is in turn linked to the xylose polymer as a branched chain (1-D-glucuronysl-(4 → 1)-L-arabofuranose).

Vitamins

Data for the vitamins in peanuts are tabulated in Table 6.

Fat-Soluble



Vitamin A alcohol

Vitamin A. In the human this vitamin is necessary for growth, reproduction, and maintenance of health. It exists partially as a component of visual purple, which is a protein-carotenoid complex in the light receptors of the human eye.

Table 6. Vitamin Content of Peanuts (Units per 100 g dry weight)

Fat-Soluble[a]	*Cotyledons*	*Defatted Flour*
Vitamin A	26 I.U.	
Carotene (provitamin A)	Trace (< 1 μg)	
Vitamin D	(c)	
Vitamin E[b]	26.3-59.4 mg (avg 41.6)	
α — tocopherol	11.9-25.3 mg (avg 17.1)	
γ — tocopherol	10.4-34.2 mg (avg 22.9)	
δ — tocopherol	0.58-2.50 mg (avg 1.62)	
Vitamin K	(c)	
Water-Soluble[a]		
B-Complex		
Vitamin B_1 — Thiamine	0.99 mg	0.75 mg
Vitamin B_2 — Riboflavin	0.13 mg	0.35 mg
Vitamin B_6 — Pyridoxine	0.30 mg	
Vitamin B_{12} — Cyanocobalamine	(c)	
Niacin — Nicotinic Acid	12.8-16.7 mg	2.5 mg
Choline	165-174 mg	252 mg
Folic Acid	0.28 mg	
Inositol	180 mg	
Biotin	0.034 mg	
Pantothenic Acid	2.715 mg	
Vitamin C	5.8 mg	

[a]Compiled from References 2, 4, 12, 14, 20, 87, 105-110.
[b]Results expressed as mg/100 g oil.
[c]No evidence for presence.

Peanuts have little or no vitamin A activity (111). The presence of carotenes (provitamin A) in mature peanuts was established by Pattee and Purcell (4), but the level is too small to be of significance.

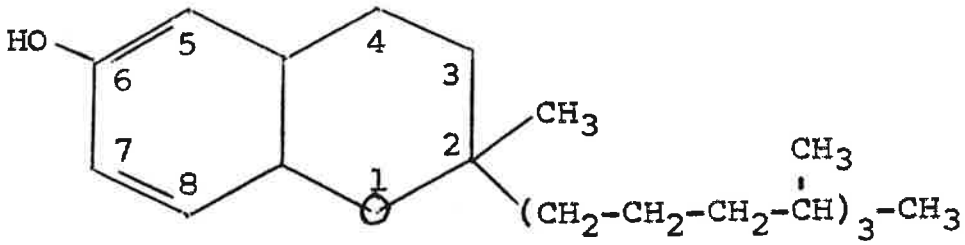
Various attempts have been made to fortify peanut butter with vitamin A (14, 112). It has been noted that 93-95% of that incorporated during continuous peanut butter manufacture was retained (112). Some small loss occurred over six months storage and the loss was not significantly inhibited by the added antioxidants NDGA and citric acid.

Roy (113) has investigated the effect of added vitamin A acetate on stability of crude and refined peanut oil. Hydrogenated peanut oil retained the maximum amount of vitamin A during storage, while refined oil retained the least. Loss of tocopherols during deodorization may partially account for the behavior of the latter. A small increase in stability of the vitamin was noted from addition of ethyl gallate to samples.

Vitamin D. No evidence of vitamin D activity in the peanut was encountered in this review.

Vitamin E. This vitamin includes a broad class of chemically related compounds called tocopherols (see Lipids). The biochemical function of these compounds is not

clear, but they appear to be associated with the physiology of muscular and vascular tissue and may be involved in electron transport. Vitamin E is also related to fertility and reproduction in some species. Tocopherols function as weak antioxidants in expressed peanut oil (114), and may also serve a similar *in vivo* function in the metabolizing seed. Of the several chemical forms, only α, γ, and δ-tocopherols have been demonstrated in the peanut (87, 109, 110). The three forms differ in the number and position of methyl groups on the chroman ring of tocol:



Tocol

α-tocopherol = 5,7,8-trimethyltocol

γ-tocopherol = 7,8-dimethyltocol

δ-tocopherol = 8-methyltocol

Peanut oil exhibits a total tocopherol range of 26.3-59.4 mg/100 g of oil after chromatographic purification of saponified oil fractions (87). It will be noted that the results in Table 6 are presented on an oil basis. The individual isomers have shown the following ranges (mg/100 g oil): α - 11.9 to 25.3, γ - 10.4 to 34.2, and δ- 0.58 to 2.50. Skinner, *et al.,* noted that genotype will effect tocopherol content (87). Argentine, Spantex, Florida 416 and Virginia Bunch 67 genotypes were characterized as low-tocopherol producers, while Georgia 186-28, Early Runner, Southeastern Runner 56-15, and Florida 393-7 appeared to be high-tocopherol types. High storage temperatures (70° vs. 100°F) were generally destructive to tocopherols in stored nuts, possibly due to their accelerated oxidative degradation (87). The higher temperature was responsible for a loss of about 25% of the α-form over four months storage. Oil from overmature seeds contained slightly higher tocopherol content than that from mature seeds. Geographic location also appeared to affect the total Vitamin E content. Certain genotypes (Argentine, Georgia 186-28, Southeastern Runner 56-15) produced higher tocopherols when grown at Holland, Virginia, while others (Florida 416 and Early Runner) yielded higher levels at the Tifton, Georgia location.

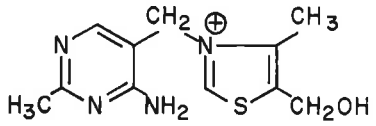
γ- and δ-tocopherols were found to be significantly better antioxidants than the α-form, in that either of the former two would protect an oil approximately twice as long as a similar concentration of the latter (110).

The recommended daily intake of Vitamin E for adults is 25-30 mg, making peanuts a good source (115).

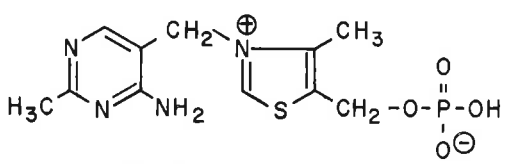
Vitamin K. No evidence has been encountered for the presence of this agent in peanuts.

Water-Soluble

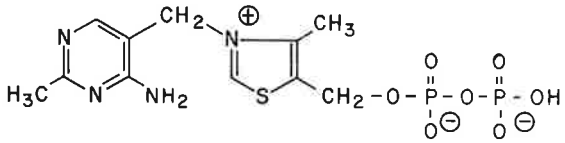
Vitamin B_1. This vitamin (thiamine, aneurin) is involved as a coenzyme in several general biochemical reactions: (a) nonenzymatic decarboxylations of α-keto acids; (b) oxidative decarboxylation of α-keto acids; (c) and formation of α-ketols, or acyloins (116a). Vitamin B_1 has been found to exist in at least three forms in the peanut: thiamine, thiamine monophosphate, and thiamine pyrophospate (cocarboxylase), in the ratio of about 33:10:1, respectively (117).



Thiamine



Thiamine Monophosphate

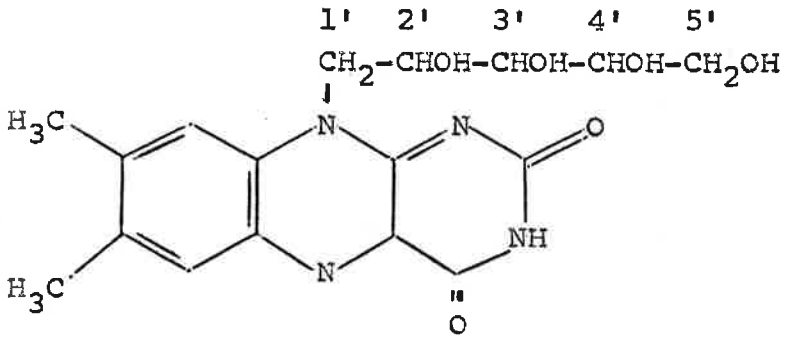


Thiamine pyrophosphate
(Cocarboxylase)

Thiamine occurs to the extent of about 10 μg/g in cotyledons. The content in skins (testa) is considerably higher, having been reported in excess of 36 μg/g (118). The recommended daily intake of thiamine for adults is about 1.0-1.4 mg (115).

Dougherty and Cobb (117) have demonstrated that at least a portion of the thiamine in cotyledons migrates inward from the testa during curing, and is probably due to solute equilibration on loss of moisture. Intracellular thiamine does not appear to any great extent in subcellular particulate bodies in the resting seed (117). There may exist some weak associations with non-particulated proteins. A very small portion of thiamine is tightly bound to protein, possibly as cocarboxylase.

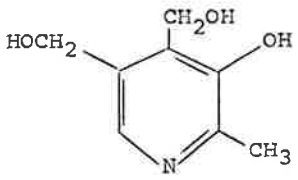
Vitamin B_2—Riboflavin. This vitamin occurs most frequently in combined form, either as the 5′-phosphoric acid derivative (flavin mononucleotide, FMN), or in combination with adenylic and phosphoric acids (FAD). As FMN or FAD, the vitamin serves as a coenzyme in oxidation-reduction reactions of dehydrogenases and oxidases. It is therefore involved in the metabolism of carbohydrates, fats, and protein in the body.



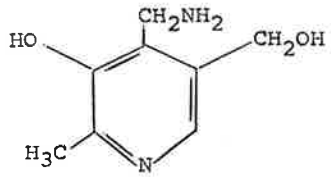
Riboflavin

Peanuts are a moderate source of B_2 (19, 20, 119) yielding a content of 0.105-0.157 mg/100 g nuts. The recommended daily dietary allowance for adults is 1.5-2.0 mg (115).

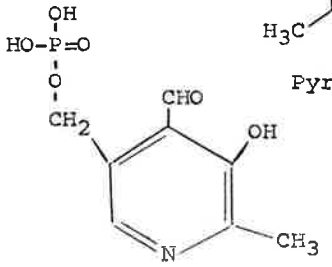
Vitamin B_6—Pyridoxine. There are three biologically active forms of this vitamin (116b): pyridoxine, pyridoxal, and pyridoxamine, all three of which occur in tissues as phosphate esters. The active form is believed to be pyridoxal phosphate, which functions as coenzyme for amino acid decarboxylases, transaminases, racemases, cystathionase, and certain enzymes involved in tryptophane metabolism. Vitamin B_6 is also required for normal fat metabolism. It has been assayed at a level of 0.3 mg/100 g in peanuts (120-122). Normal adult daily intake should approach 2 mg (115).



Pyridoxine



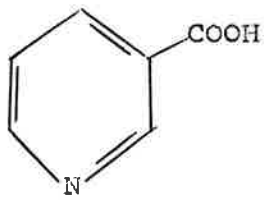
Pyridoxamine



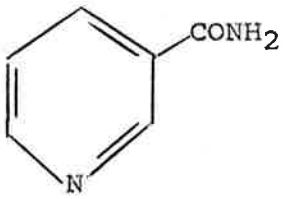
Pyridoxal Phosphate

Vitamin B_{12} (cyanocobalamin). No information was encountered relative to the presence of this vitamin in peanuts.

Niacin (nicotinic acid). There are two biologically active forms of niacin, nicotinic acid itself and nicotinamide (116).



Nicotinic acid

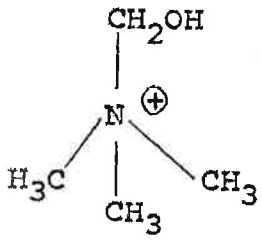


Nicotinamide

The vitamin is an integral part of triphosphopyridine nucleotide (TPN) and diphosphopyridine nucleotide (DPN), so is biochemically implicated in some forty or more oxidation-reduction reactions involving dehydrogenases. The reactions in question include: synthesis of "high energy" phosphate bonds, pyruvate metabolism, glycolysis, pentose metabolism, photosynthesis, lipid metabolism, and oxidative degradation of amino acids.

Niacin has been reported by Daniel and Norris to range from 12.8-16.7 mg/100 g in peanuts (106), and 2.5 mg/100 g in peanut flour (12). Watt and Merrill (20) list an average value of 15.8 mg/100 g nuts. The daily intake of this vitamin should approximate 13-18 mg for adults (115).

Choline. The biological function of choline involves phospholipid (lecithin) and acetylcholine production. The vitamin is considered as a methyl group donor in biochemical reactions. Choline also enhances fatty acid transport from the liver.

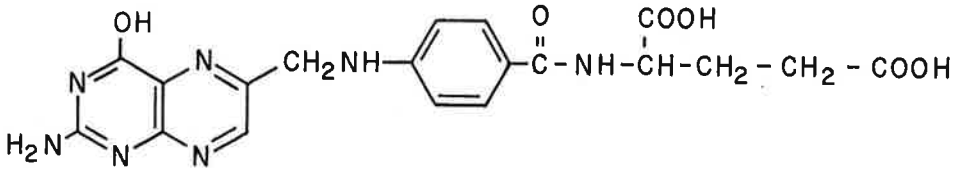


Choline

Engel (123) pointed out the nutritional significance of choline and found the following concentrations in peanut products (mg/100 g dry weight): peanut meal—252, peanut meal with 6% fat—244, Spanish peanuts—174, Runner peanuts—165, and peanut butter—148.

Boudreau and associates have identified choline or one of its esters as the hemostatic factor occurring in peanut skins (124, 125). Bisordi (126) reported a clinical benefit in hemophiliacs treated by inclusion of peanut flour in the diet. Moreover, Brüster (127, 128) noted increased thrombokinase activity in hemophiliacs treated with alcoholic extracts of peanut oils.

Folic Acid (pteroylglutamic acid). The transfer of one-carbon fragments constitutes an important class of metabolic reactions. These reactions are associated with biosynthesis of purines, pyrimidines, and certain amino acids. Generally, coenzymes derived from tetrahydrofolic acid, the active form of folic acid, are intimately involved (99b):

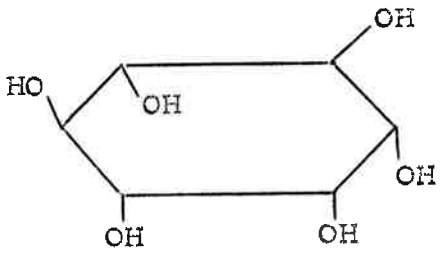


Folic Acid

In addition to the structure shown above containing one glutamic acid residue, biologically active triglutamate and heptaglutamate forms have been found linked to proteins. Folic acid is required in the human body for normal red blood cell formation.

Folic acid has been assayed at a level of 0.28 mg/100 g peanuts (2). The normal adult daily requirement is about 0.4 mg (115).

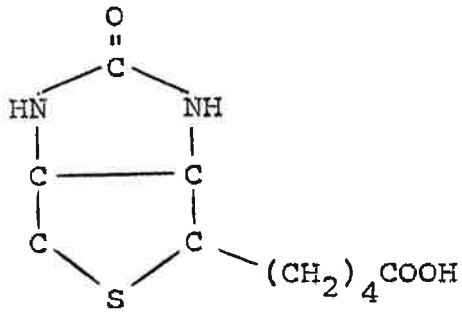
Inositol. The biochemical function of this cyclic alcohol has not as yet been established. It occurs as inositol phosphates, including the hexaphosphate phytin, and may be involved in protein complexes.



myo-inositol

Inositol is present in peanuts at a concentration of approximately 180 mg/100 g (2).

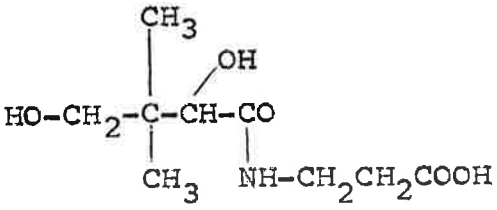
Biotin. This vitamin serves as a coenzyme for two general types of biochemical reactions: carboxylations and decarboxylations (or transcarboxylations).



Biotin

Biocytin, the lysyl amide of biotin, also exhibits biological activity. Biotin has been reported at a concentration of 0.034 mg/100 g in peanuts (2).

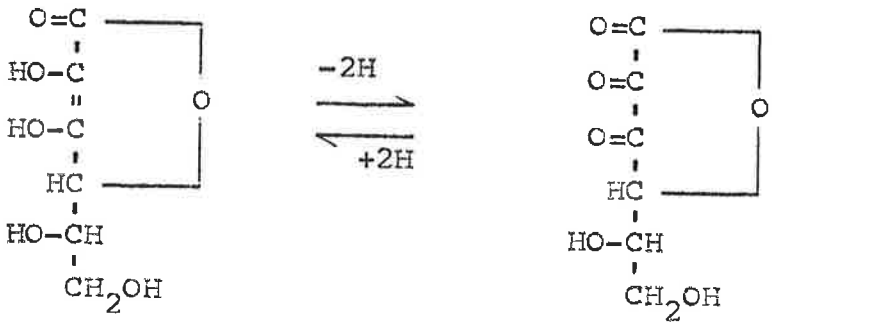
Pantothenic Acid. This compound occurs naturally as part of the coenzyme A molecule. It is thus involved biochemically in transfer and donor reactions: acetyl transfers, benzoyl transfers, succinyl transfers, fatty acid synthesis and oxidation. Pantothenic acid is required for proper maintenance of nerve tissues.



Pantothenic Acid

Dunn and Goddard (105) noted an average concentration of 2.715 mg of pantothenic acid per 100 g peanuts.

Vitamin C (ascorbic acid). There is some conjecture over vitamin C in peanuts. While an early report (108) indicated ascorbic acid at a concentration of 5.6 mg/100 g of nuts, Watt and Merrill (20) list no concentration of the vitamin.



L-ascorbic acid Dehydro-L-ascorbic acid

Vitamin C exists in two active forms: ascorbic and dehydroascorbic acids. Either form may be utilized in the body. Vitamin C is thought to be involved in synthesis of steroid hormones, as large quantities of ascorbate appear in the adrenal cortex. Ascorbate may also be involved in hydroxylation of other aromatic compounds.

A daily adult requirement of 55-60 mg has been established (115).

Enzymes

Little has been reported in the chemical literature pertaining to the enzymes in dormant peanut seeds. As enzymes are the life control agents of the metabolizing seed, certainly one would expect many of the enzymes necessary for active metabolism to be present in the dormant seed and, consequently, at germination.

Swaisgood and Pattee (129, 130) have characterized alcohol dehydrogenase from dormant seed. The active unit was found to have a molecular weight of 112,000 and a sedimentation coefficient of 5.465 in aqueous salt solution. The enzyme contained zinc as a cofactor and was inactivated by 1,10 phenanthroline, ethylenediamine tetra-acetate, 8-hydroxyquinoline-5-sulfonic acid, and iodoacetate. When compared to yeast and liver alcohol dehydrogenases, the peanut enzyme more nearly resembled the yeast dehydrogenase in physicochemical properties.

Several researchers have investigated lipoxidase activity in peanuts. Siddiqi and Tappel (131) noted that the activity was approximately 1% of that from soybeans at pH 7.0. Such antioxidants as NDGA, propyl gallate, and hydroquinone were effective in inhibiting the enzyme. Dillard *et al.* (132) found lipoxidase activity highest at pH 8.1 when using linoleic acid as substrate. Employing trilinolein pH 5.5 became the point for optimum activity, followed by a second maximum at pH 7.5. Peanut lipoxidase exhibited approximately 40% of the activity of its soybean analog on trilinolein at pH 5.5, but only 10% at pH 8.1. Peanuts were thus concluded to have low lipoxidase activity.

Bronisz *et al.* (133) studied the lipase activity of peanut seed and oil press cake; at pH 8.0 the seed exhibited approximately one-third and the press cake about one-

fifth the activity of soybean lipase. Hartzook *et al.* (134) observed a higher amylotytic activity in immature seed-protein extracts than in mature seeds. Lipase activity was noted in Spanish type and in immature seeds of all types but not in mature seeds protein extracts of Virginia and Valencia types.

Giri (135) reported the presence of glycerophosphatase and pyrophosphatase activity in dormant seed.

A large number of enzymes have been isolated from the germinating or actively-metabolizing peanut seed. Among those reported are amylase (136), fumarase (137), isocitric lyase (138, 139), catalase (140), phosphoenol pyruvate carboxylase (141), ATPase (142), allantoicase (143, 144), acetaldehyde dehydrogenase (145), malate synthetase (139), ascorbic acid oxidase (146), phosphoric monoester hydrolases (147), adenosine-5-phosphatase (148), a fatty acid β-oxidation system (149), a fatty acid α-oxidation system (150), phytase (151), a glucosidase (152) and a phospholipase D (153).

Several anti-enzyme factors have also been demonstrated in peanuts. Tixier (154) identified a polypeptide which effectively functioned as a protease inhibitor (trypsin and chymotrypsin). The basic molecule consisted of 154 amino acid residues. Those acids in high concentration included cystine-cysteine, aspartic acid, glutamic acid, threonine, proline and arginine. Tryptophane was totally absent. Zimmerman *et al.* (155) and Werle (156) also have discussed antitryptic substances from peanuts. Zimmerman's group noted that the antitryptic activity in fractionated cotyledons does not invariably follow the protein-distribution pattern.

Narayanan *et al.* (157) found in testa an agent which will inhibit lipoxidase activity. Werle (156) also detected anti-thyroid activity in peanuts.

Inorganic Constituents

The reported ash content for peanuts is relatively low, on the order of 2-3% in full fat cotyledons (Table 1). As shown in Table 7, peanuts may contain as many as 26 trace elements. Potassium content is relatively high and sodium is low, which is usual for plant ash (2). The peanut is nutritionally deficient in calcium, iodine and iron, but is fairly adequate in phosphorous and magnesium.

It has been previously mentioned (see Carbohydrates) that phytic acid will bind calcium, magnesium and iron in forms which can pass through the body without absorption. Oxalic acid may cause the same phenomenon (20). Thus, the actual concentrations of these metals in peanuts may not reflect their nutritional availability.

There is good evidence to indicate that all metals nutritionally required in trace quantities by the human participate on a molecular level either as cofactors for enzymes or as structural components of enzymes (161).

Upon spectrochemical analysis of peanut meal extracts (162), the following elements were found to be nonexistent or below the assayable threshold: thallium, lithium, cesium, tungsten, lanthanum, cobalt, zirconium, silver, beryllium, bismuth, antimony, arsenic, mercury, gold, and cadmium.

Table 7. Inorganic Constituents of the Peanut

Element	(mg/100 g dry weight)[a] Blanched, Full Fat Cotyledons	Shells	Testa	Germ	Defatted Flour
Potassium	500-890	36		750-890	
Phosphorous	250-660	39-678	57-61	540-650	800
Sulfur	190-240		150-220		
Aluminum	100	97.7			
Magnesium	90-340	100		170-230	
SiO_2	80				
Titanium	30-80				
Calcium	10-80	127-316	380-385	50-80	127
Vanadium	10-50				
Barium	8-30				
Sodium	5	16			
Nickel	3-8				
Boron	2.6-50	1.3			
Iron	1.8-100	2.8-303	0.48-0.75	0.34-0.36	3.5
Zinc	1.7-80	1.9			
Chromium	1-30				
Manganese	0.8-50	3.8			
Strontium	0.8-5				
Molybdenum	0.8-3	0.17			
Copper	0.7-30	1.14			
Fluorine	0.14				
Cobalt	0.03				
Iodine	0.02				
Chlorine	Trace		10-20		
Lead	0-50				
Tin	0-5				

[a]Compiled from References 2, 12, 20, 111, 158-160.

Jodidi (163) found considerable variation in the amount of ash from peanuts raised on different types of soil. Hallock and coworkers (159) noted slight genotype variations in content of potassium, calcium, magnesium, boron, manganese and zinc.

Shells are higher in calcium and sodium than cotyledons, but considerably lower in potassium. Testa are much higher in calcium, but lower in phosporus and iron than are cotyledons. Germs are quite high in potassium, phosphorus, and magnesium.

Color

Color in raw peanuts is basically concerned with two parts, the testa and the oil.

Pigments of the testa have been studied by several groups (164-166). Tannins and related compounds of the catechol-type are responsible for this color. This tannin-like material was found to represent about 7% of the testa weight. Small quantities

of phlobaphene, a "leuco-anthocyanic chromogen," and a flavonone were also characterized. Further study of the pigments in light of added literature information and newer instrumental methods would seem to be in order.

Observing the internal surface color of the hull is a common subjective method to determine maturity and thus the harvest date of peanuts (1). Miller and Burns (167) objectively determined internal hull color and found it significantly related to other indices of maturity and quality (kernel density and light transmittance of the oil at 480 nm). With appropriate instrumentation, this method appears to be a good non-destructive technique for determining peanut maturity.

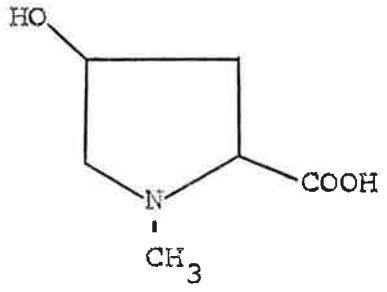
As mentioned previously (see Lipids), the color in peanut oil is primarily a result of the carotenoids which are present. A series of these compounds have been identified in oil from immature peanuts with leutein and β-carotene predominating (4). As maturity ensues, the pigment content is diluted due to rapid oil production (70). Holley and Young (67) showed the color reduction as being highly correlated with maturity, but noted that upon slow curing pigmentation fades in all types of peanuts. Others have confirmed this curing variability (69, 168, 167). Emery *et al.* (68, 69) suggested using oil coloration as a maturity index and genetic marker of maturity inheritance.

The bulk of brown color development upon roasting of peanuts is most likely due to sugar-amine reactions with subsequent production of melanins (170). The temperature of roasting does not preclude caramelization of sugars; yet the small quantities of sugar degradation products in roasted peanut flavor distillates, while sugar-amine interaction products abound, suggests caramelization as a secondary route for color development (171). Additionally, the heat of activation for sugar-amine reactions in model systems is much lower than for caramelization reactions (170).

The brown color formation during roasting has been objectively measured by means of reflectance spectrophotometry and expressed as CIE (ICI) designations (172). In general, the x-trichromatic coordinate—the redness factor—increases with the amount of roasting accorded peanuts.

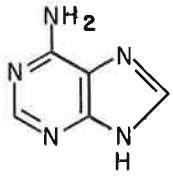
Miscellaneous

While investigating flavor precursors in mature and immature peanuts, Newell *et al.* (5) noted the presence of nineteen amino acids plus the amides of aspartic and glutamic acids. Raw samples were highest in glutamic acid, alanine, phenylalanine, asparagine and glutamine. The significance of these components will be discussed further under "Roasted Flavor." Lee and coworkers (173) isolated 4-hydroxy-N-methylproline from peanut flour, the first instance of this compound having been found in an edible product.

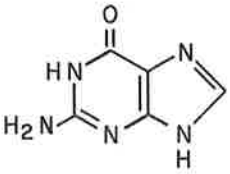


4-hydroxy-N-methylproline

Reeves and Guthrie (174) identified several nitrogenous bases in peanut protein extracts. Included were adenine, guanine and xanthine, all of which are important constituents in nucleotides:



Adenine
(6-aminopurine)



Guanine
(2-amino-6-oxypurine)

Xanthine
(2,6-dioxypurine)

Additionally, these workers demonstrated the presence of oxalic acid. It has since been found that peanuts will contain from 200-400 mg/100 g of this organic acid (20). Glutathione, a three-unit peptide (glutamyl-cysteinyl-glycine) has also been shown in peanut protein extracts (174).

Six nucleic acid and four polynucleotide fractions have been isolated from germinating peanuts (175, 176). RNA content was found to increase twofold during early germination (2 to 6 days), then subsequently decrease with time. DNA content of peanuts did not change significantly during germination.

Some evidence has been advanced for the presence of auxin and gibberelin-like substances in peanuts (177). Auxins are indole-substituted aliphatic acids, while gibberelins are terpene or isoprenoid-related compounds. Both are growth hormones and may have some effect on dormancy and "after-ripening" of peanut seed.

A thiamine-destroying factor was localized in the testa by Wada and Takahaski (178). A tannin, this factor was heat stable with an optimum actively at pH 7 and 60°C.

Peanuts have been adapted to a variety of non-food applications including using the protein in plywood glues (179, 180), paint (181), and paper coatings (182), the cellulose in manufacture of rayon (183), and the hulls as activated charcoal (184, 185).

Subcellular Particulate Bodies

Dieckert *et al.* (186) obtained several relatively discrete subcellular fractions by utilizing nonaqueous differential centrifugation of peanut homogenates. Among those characterized were two protein-rich fractions, a starch grain fraction, one of "fines" material, one of cell wall fragments, and a fraction composed largely of vascular tissue. The two protein fractions differed in content of phytic acid and globoids within the particulates. On this basis one of the protein fractions was designated as aleurone grains. Sucrose was found predominantly in the "fines" and starch granules. The "fines" fraction also contained small fragments of the reticulate matter of the cell, as well as ribonucleic acid. In subsequent research, Phillips (187) obtained ribonucleoprotein particles via high-speed centrifugation of this RNA-rich fraction. The properties of these particles were similar to ribosomes isolated from other sources.

Yatsu and coworkers (188, 189) have characterized the oil-bearing spherosomes of the cotyledon. On a dry weight basis the spherosomes averaged 98.1% total lipid,

0.77% phospholipid, and 1.27% protein. These particles, 1.0-2.0 μ in diameter, are bounded by a limiting membrane, which is most likely accounted for by the protein and phospholipid. Spherosomes amply accounted for all the lipid in peanut cotyledons. Lipase and fatty acylcoenzyme A activity were not associated with these bodies, suggesting that their primary function is lipid storage and not lipid degradation during germination.

Kmetec demonstrated the presence of mitochondria in germinated cotyledons (190), but attempts to show these particles in resting seed have resulted in few positive identities (118, 191, 192).

Sharma has reported on the metal stores in aleurone grains (97). These bodies were shown to be the major depositary for magnesium, potassium, manganese and copper, as well as phytic, oxalic, and citric acids. Of the magnesium present, 34-40% was bound by the latter two acids. Phytic acid was thought to bind the remainder of this metal. About 30% of the mass of the globoids of aleurone grains was accounted for as mixed salts of phytic acid, oxalic acid, magnesium and potassium. Of the compounds investigated in aleurone grains, 50% of the magnesium, 80% of the calcium, 13% of the potassium, 50% of the phytic acid, and 50% of oxalic acid were present in the globoids.

Peanut Flavor And Aroma

Raw Peanuts

The typically sweet, slightly "green" flavor and aroma of raw peanuts arises from the relatively high sucrose content (ca. 5%) and certain volatile organic components. Ten of the volatile components have been identified (193). These include pentane, octane, methyl formate, acetaldehyde, acetone, methanol, ethanol, 2-butanone, pentanal, and hexanal. A low temperature distillate fraction highly reminiscent of raw peanut aroma was found to contain hexanal as the major component. It was thus suggested that this compound is the "backbone" aroma component, aided by pentanal and possibly other compounds. The bulk of volatile aldehydes from raw peanuts are produced upon rupture of the tissue in a neutral aqueous environment of high oxygen tension (194, Table 8). This suggests an enzyme mechanism for formation of at least a portion of raw peanut aroma, as has been observed in onions and cucumbers (195-197). On this basis one might hypothesize that unless a type of peanuts is lacking in certain enzyme systems, similar qualitative patterns of volatile aroma components would be obtained among varied genotypes. In a subsequent study relating the changes in the volatile profiles and their relationship to enzyme levels during maturation, the results suggested two enzymes were associated with four of the five major volatiles produced (198). Lipoxidase activity during maturation closely followed concentrations of pentane and hexanal. Alcohol dehydrogenase activity, acetaldehyde and ethanol concentrations were maximal at 7-8 weeks. The ethanol and acetaldehyde concentrations then decreased steadily during the remaining maturation, whereas the enzyme activity remained high.

Twenty-nine carbonyl compounds were identified in cold pressed raw peanut oil (199). These are listed in Table 9, along with some of their concentrations and corresponding threshold concentrations in oil (200). Hexanal and octanal concentrations were the only ones that exceeded their flavor threshold values. These two compounds

Table 8. Carbonyl Production in Raw Peanuts Disintegrated under Various Conditions (194)

Blending Conditions	Unsaturated Monocarbonyls (μm/g Lipid)	Saturated Monocarbonyls (μm/g Lipid)
Laboratory atmosphere, aqueous environment	42.4	22.0
Nitrogen, aqueous environment	0.24	1.02
Laboratory atmosphere, HCl:H_2O (1:4)	0.18	0.32
Laboratory atmosphere, following 15 seconds blanch in boiling water	0.30	1.06

Table 9. Carbonyl Compounds Identified in Cold Pressed Oil from Raw Peanuts and Their Relative Concentrations (199)

Compounds	Concentration in Oil[a]	Compounds	Concentration in Oil[a]
Alkanals		2-Octanone	S
Ethanal	S	2-Nonanone (tentative)	S
Propanal	S	2-Decanone (tentative)	S
Butanal	S		
Pentanal	M	*2-Enals*	
Hexanal	L (0.34; 0.08)[b]	2-Pentenal (tentative)	S
Heptanal	S	2-Hexenal	S (0.2; 0.60)[b]
Octanal	M (0.06; 0.08)[b]	2-Heptenal	S
Nonanal	M (0.12; 0.20)[b]	2-Octenal	S (0.04; 0.15)[b]
Decanal	M (0.10; 0.71)[b]	2-Nonenal	S (0.03; 0.05)[b]
Dodecanal (tentative)	S	2-Decenal	S (0.02; 0.15)[b]
2-Alkanones		2-Undecenal (tentative)	S
2-Propanone[c]	VL	*2, 4-Dienals*	
2-Butanone	S	2, 4-Heptadienal	S
2-Pentanone	S	2, 4-Octadienal (tentative)	S
2-Hexanone	S	2, 4-Nonadienal	S
2-Heptanone	S	2, 4-Decadienal	S

[a]S = small; M = medium; L = large; VL = very large.
[b]First value indicates concentration found in raw peanut oil; second value is the threshold concentration in oil (200).
[c]Present primarily as an artifact.

were reported as being probably responsible for the characteristic "green or beany" flavor and aroma of raw peanuts which is in agreement with Pattee *et al.* (193). The other alkanals, 2-alkanones, 2-alkenals or 2,4-alkadienals were considered as probably unimportant to the flavor of raw peanuts.

Rapid curing at temperatures exceeding 95°F. will adversely affect the flavor quality of raw peanuts (201, 202). The off-flavor developed is more pronounced in immature peanuts than in mature nuts. A number of the volatile components present in high temperature cured off-flavor peanuts have been characterized (203). Compounds not present in normal-flavored peanuts but detected in off-flavor nuts included: 2-me-

thylpropanal, butanal, 3-methylbutanal, 2-methylpentanal, and 2-hexanone. Furfural and either 2-methyl- or 3-methyl- 1-butanol were also tentatively identified. Levels of all volatile compounds typical of normal flavored raw nuts were significantly increased in off-flavor samples. The volatile profiles produced by peanuts cured at 22°, 35°, 45°, and 50°C. have been determined by gas-liquid chromatography (204). These profiles, in conjunction with taste panel evaluation of flavor and aroma, indicated that acetaldehyde, ethanol and ethylacetate were compounds which might indicate flavor deterioration. The taste panel preferred peanuts cured at lower temperatures and indicated the 50°C. cured peanuts to be most objectionable. Since the ethylacetate concentration was high in the 50°C. cured peanuts and only trace in the 35° and 45°C. samples, it alone could be an indicator of flavor deterioration due to elevated temperature curing.

Uncured or "green" peanuts may be stored for 60 days or longer at refrigeration temperatures (35°F.) without noticeable loss of quality (28). The flavor after 60 days storage was bland and somewhat lacking in the "green" quality, but no off-flavor was present. Moisture content, free fatty acids, peroxides and carbonyl compounds all showed major declines during storage. Volatiles of peanuts during storage exhibit primarily quantitative rather than qualitative changes (205). Peanuts stored under simulated warehouse storage conditions produced the largest quantity of volatiles—80-98% present being comprised of pentane, acetaldehyde, and methanol. Pectin methylesterase and lipoxidase were indicated as enzymes which may be responsible for producing these volatiles.

Maturity has a definite effect on flavor in raw peanuts. Kramer *et al.* (206) noted that flavor panels could usually pick out samples with high indications of immaturity. Thomas *et al.* (207) and Young (81) found that peanut products produced from mature kernels were scored significantly higher than identical products from immature nuts.

The typical volatile profile of raw peanuts (193) was greatly reduced immediately after a high temperature blanching of the peanuts (208). The term "blanching" refers to the process of removing the testa of the peanuts. The components were apparently volatilized during the heating process or entered into a chemical reaction, but were restored qualitatively during storage. This suggested enzymatic action by lipoxidase and alcohol dehydrogenase, as well as autoxidative reactions. Blanched peanuts were found to develop undesirable flavor characteristics in a direct relationship to the heat treatment used and length of storage before processing into final products (208).

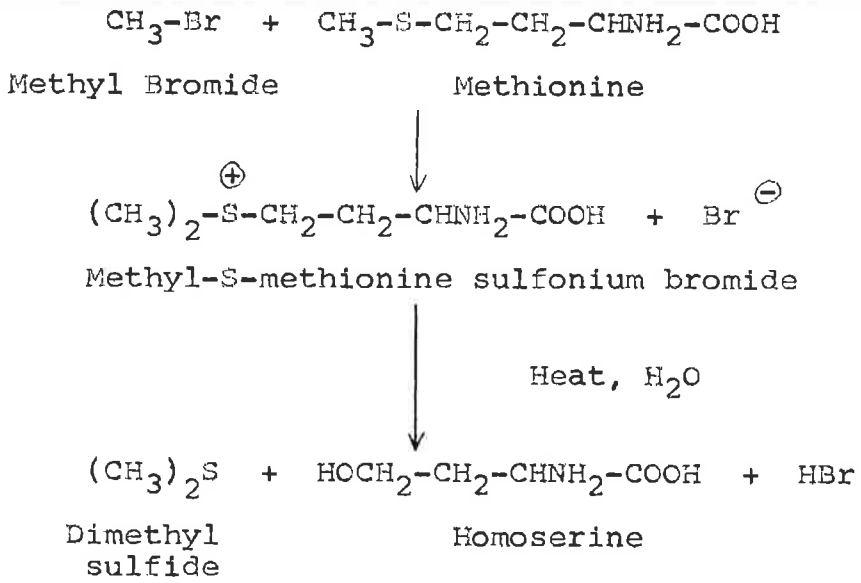
A bitter principle which appears in peanuts is particularly concentrated in the hearts. Dieckert and coworkers (209, 210) noted that a purified extract of the principle possessed the general properties of saponins. Saponins (Latin:*sapo,* soap) are, as a general rule, glycosides in which the C3-hydroxyl group of terpenoid or steroidal aglycones is combined with a chain of sugars. At least four distinctly bitter fractions were resolved from the purified peanut extract. Upon hydrolysis of the total extract, glucose, xylose, rhamnose, and glucuronolactone were identified in the glycone fraction, while at least six chromatographically separable components were found in the aglycone fraction. None of the latter were identified. Applebaum *et al.* (211) found a saponin preparation (CaO precipitable) in peanuts which inhibited development of the Azuki bean beetle *(Callosobruchus chinensis* L.), a major pest of stored legume seeds.

With the advent of broad pesticide usage, some concern naturally centered around the effect of these chemical agents on flavor quality. One of the first pesticides to come under scrutiny was benzene hexachloride (BHC) and its various isomers, in particular

the γ-isomer. A definite off-flavor resulted in peanuts grown in rotation with cotton which was dusted with heavy applications of BHC (212-214). Measurable quantities of BHC were detected in the peanuts, but technical BHC produced no off-flavor when incorporated directly into peanut butter at a level several times that found in peanuts with definite mustiness. The musty odors observed were attributed variously to heptachlorocyclohexanes (215) and/or polychlorocyclohexenes (216). Later tests (217) indicated that the total dosage of BHC isomers applied to the field is important in determining whether off-flavors will arise.

Aldrin, toxaphene, chlordane, dieldrin, and heptachlor were found to cause little or no off-flavor problems (218). Soil treatment with pentachloronitrobenzene (PCNB) as a pre-emergence fungicide resulted in improved organoleptic quality of peanuts in 9 of 10 tests (207).

Cured peanuts fumigated with methyl bromide may develop a very unpleasant aroma and taste upon heating (219). Dimethyl sulfide has been postulated as the compound primarily responsible, since it was found in off-flavored nuts at 50 times the level in acceptably-flavored nuts. It has been hypothesized that methyl bromide reacts with methionine, forming methyl-S-methionine sulfonium bromide which in turn degrades to homoserine and dimethyl sulfide upon heating:



Roasted Peanuts

The roasted aroma and flavor of peanuts is unique among all foods. Nowhere is this character reproduced, although the chemical makeup of the flavors of potato chips, coffee, and cocoa have been found somewhat similar (220-224). Early investigations of peanut aroma (225) indicated that the bulk of gases evolved during roasting is comprised of carbon dioxide and water. A later extension of this work (226) established the presence of carbonyls, hydrogen sulfide and mercaptans. Ballschmieter and Germishuizen (227) indicated the presence of ethanal, propanal, butanal, 2-methylpropanal, 3-methyl-2-butanone, and butylacetate in roaster gases. A correlation was shown between 2-methylpropanal concentration and the degree of roast given the peanuts, the compound increasing in concentration with higher roast temperatures.

An intense research effort at Oklahoma State University pertaining to chemistry of roasted peanut flavor and aroma has elucidated much of the mystery concerning the flavor components, their precursors, and the mechanism of formation during roasting. Mason and Waller (228) established that the precursors are compartmentalized in the aleurone grains. Flavor was found not to arise from the large globular proteins contained in these sacs, nor from any interactions with starch grains, but from simple micromolecules undergoing Maillard sugar-amine type browning (5). Glucose and fructose, the primary monosaccharides of peanuts, were implicated as the reducing sugar reactants. These two sugars occur in very limited concentration, however. Thereafter, it was found that sucrose is hydrolyzed during roasting to provide a high concentration of reducing sugar reactants (Table 10). Amino acids serve as the nitrogenous reactant, and a correlation was shown between optimum roasted flavor and the concentrations of aspartic acid, glutamic acid, glutamine, asparagine, histidine, and phenylalanine in the peanuts (Table 11). Similarly, threonine, tyrosine, lysine, and arginine were correlated with off-flavor (5, 6). The change in arginine content during maturation was demonstrated to be a particularly good index of subsequent roasted flavor. As arginine decreased, maturation and organoleptic quality of roasted samples increased. Young (81) reported similar results and developed a method for establishing the degree of immaturity in freshly harvested or cured peanuts by determining arginine content. A modified Sakaguchi procedure was used and found to be an accurate measure of immaturity under field conditions.

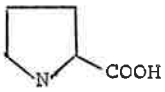
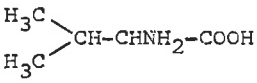
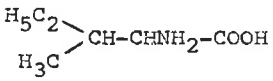
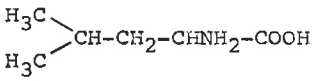
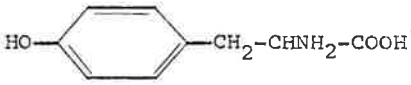
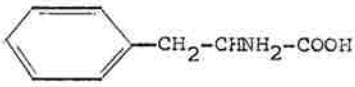
The concentrations of free amino acids were found insufficient for the nitrogenous portion of the total roasted flavor principle. Two peptides which virtually disappear during roasting were subsequently found in the aleurone grains. These peptides are apparently hydrolyzed and serve as the source of the necessary amine precursors for proper flavor development. The approximate amino acid composition of these peptides from Spanish-type peanuts is given in Table 12, along with a more highly purified preparation peptide 2 recently reported by Young (81). The importance of the peptides as a flavor precursor may have been overemphasized; however, the increase in concentration of peptide 2 with increasing maturity, its high percentage of glutamic acid (glutamine) and phenylalanine which were in the group positively correlated with optimum flavor (5, 6), and its relative concentration all point to an important role as a flavor precursor.

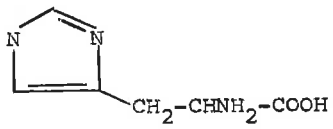
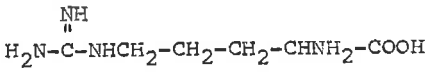
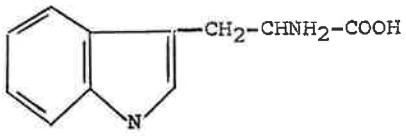
Table 10. Sugar Content [a] of Spanish Peanuts Before and After Roasting (6)

	Mean Values and Ranges for Five Samples			
Sugar	Raw Mean	Raw Range	Roasted Mean	Roasted Range
Fructose and/or Mannose (unresolved by GC)	2.7	1.6-3.3	1.8	1.4-2.0
Glucose	1.9	1.7-2.1	1.3	0.9-1.5
Inositol	1.3	1.0-1.6	1.1	0.7-1.6
Sucrose	149.0	109-197	125.3	107-161

[a] mg/g fat-free peanut meal.

Table 11. Correlation of the Free Amino Acids of Peanuts to Roasted Flavor Quality (5, 6)

Amino Acid	Structure	Correlation[a]
Aspartic Acid	$HOOC-CH_2-CHNH_2-COOH$	T
Threonine	$CH_3-CHOH-CHNH_2-COOH$	A
Serine	$HOCH_2-CHNH_2-COOH$	X
Asparagine	$H_2NOC-CH_2-CHNH_2-COOH$	T
Glutamine	$H_2NOC-CH_2-CH_2-CHNH_2-COOH$	T
Proline		D
Glutamic Acid	$HOOC-CH_2-CH_2-CHNH_2-COOH$	T
Glycine	H_2NCH_2-COOH	X
Alanine	CH_3-CHNH_2-COOH	X
Valine		D
Isoleucine		X
Leucine		D
Tyrosine		A
Phenylalanine		T
Lysine	$H_2NCH_2-CH_2-CH_2-CH_2-CHNH_2-COOH$	A

Amino Acid	Structure	Correlation[a]
Histidine		T
Arginine		A
Tryptophan		X

[a] T = precursor of typical flavor; A = precursor of atypical flavor; X = borderline; D = insufficient data for prediction.

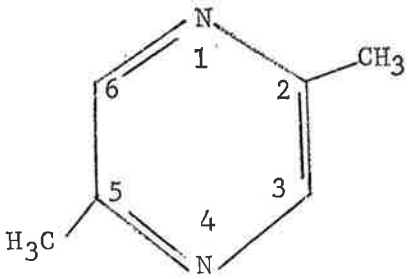
Table 12. Approximate Amino Acid Content[a] of Peptides Isolated from Aleurone Grains of Peanuts (6, 81)

Amino Acid	Crude Peptide 1	Crude Peptide 2	Partially Purified Peptide 2
Glutamic acid (Glutamine)	16	25	50
Aspartic acid (Asparagine)	6	4	1
Phenylalanine	6	17	58
Glycine	14	11	[b]
Serine	11	6	[b]
Alanine	7	3	1
Threonine	1	2	[b]
Leucine	1	2	[b]
Isoleucine	1	1	[b]
Valine	1	1	1
Tyrosine	1	1	1
Unknown			1
Hydroxy-Proline			1

[a] Number of residues.
[b] denotes a detection but in very small amounts.

Peanut oil is not a precursor *per se* but functions as a valuable medium for the flavor-generating reactions to occur (228). Removal of oil from raw peanuts and replacement with other oils resulted yet in the typical roasted aroma upon heating. When water was substituted, pyrazines were much less conspicuous and the total aroma was not typical of roasted nuts.

A total of 36 substituted pyrazines were demonstrated in the aroma distillate from roasted peanuts (229, 230, 231, 234).



2,5 dimethylpyrazine

Those compounds which have been tentatively or positively identified are included in Table 13. An open tubular gas chromatogram representative of this fraction of the volatiles is shown in Figure 1. Due to the close structural similarity of these substituted pyrazines, chromatographic separation was extremely difficult to attain, and it can be noted that the resolution of several compounds is not optimum even with a 500 ft. open tubular column coated with a polar stationary phase.

The role of pyrazines in roasted peanut aroma is not yet clear, but by virtue of their abundance, they are of significance. These compounds were considered by the Oklahoma group to be the "backbone" of roasted peanut aroma. However, Johnson (230) describes the aroma as "nut-like," but not "pea-nutty" *per se*. Acidification of the total aroma distillate from roasted peanuts destroyed the characteristic aroma. Immediately upon increasing the pH to alkaline conditions the aroma potency was restored.

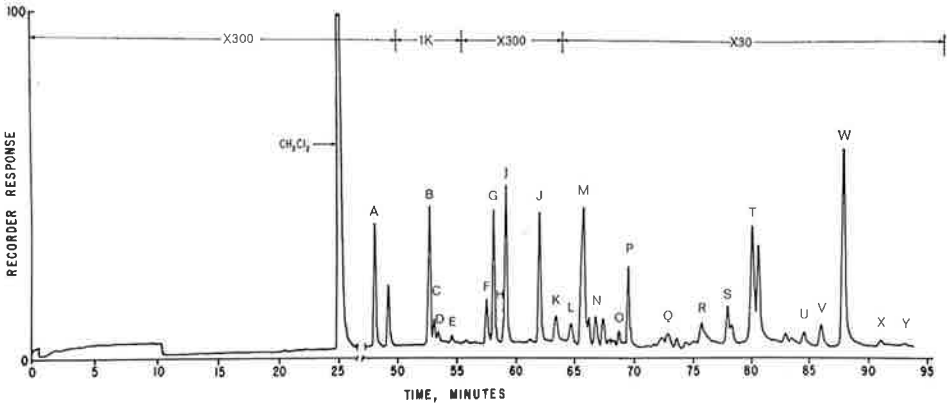


Figure 1. Capillary Gas-Liquid Chromatogram of the "Basic Fraction" of Roasted Peanut Volatile Distillate. Column 500′ x 0.02″ stainless steel coated with Carbowax 1540 + KOH. Column temperature: 65°-165° C at 2°/minutes (230).

Table 13. Compounds Identified from Roasted Peanuts

Pyrazines	*References*
Pyrazine	234, 235
Methylpyrazine	229, 234
2, 5-Dimethylpyrazine	229, 234
2, 6-Dimethylpyrazine	231, 234
Ethylpyrazine	231, 234

	References
2, 3-Dimethylpyrazine	231, 234
Isopropylpyrazine	234
2-Ethyl-6-methylpyrazine	231, 234
2-Ethyl-5-methylpyrazine	221, 234
Trimethylpyrazine	229, 234
2-Ethyl-3-methylpyrazine	234
Methyl isoproprylpyrazine	234
Propylpyrazine	234
Vinylpyrazine	234
2-Ethyl-3, 6-dimethylpyrazine	231, 234
2-Ethyl-3, 5-dimethylpyrazine	234
Methyl propylpyrazine	231, 234
Diethylpyrazine	234
Tetramethylpyrazine	234
Isopropenylpyrazine	234
2-Methyl-6-vinylpyrazine	234
2-Methyl-5-vinylpyrazine	234
2, 3-Diethyl-5-methylpyrazine	231, 234
2-Ethyl-3, 5, 6-trimethylpyrazine	231
Diethyl methylpyrazine	234
Methyl propenylpyrazine	234
Diethyl dimethylpyrazine	234
Acetylpyrazine	234
5-Methyl-6, 7-dihydro-5*H*-cyclopentapyrazine	234
6, 7-Dihydro-5H-cyclopentapyrazine	234
2 (or 3), 5-Dimethyl-6, 7-dihydro-5H-cyclopentapyrazine	234
6-Acetyl-2-methylpyrazine	234
5-Acetyl-2-methylpyrazine	234
2-Methyl-6, 7-dihydro-5*H*-cyclopentapyrazine	234
6-Acetyl-2-ethylpyrazine	234
5, 6, 7, 8-Tetrahydroquinoxaline	234
Quinoxaline	234
Alkanals	
Acetaldehyde	199, 233, 234
Propanal	199
Butanal	199
Isobutyraldehyde	199, 233, 234
2-Methyl butanal	199, 233
3-Methyl butanal	199, 233
Pentanal	199, 233, 235
Hexanal	199, 232, 234, 236
Heptanal	199, 232, 234
Octanal	199, 234
Nonanal	199, 234
Decanal	199
Undecanal	199
Dodecanal	199
Benzaldehyde	233, 234
o-Tolualdehyde	234
Phenylacetaldehyde	233, 234
o-Ethylbenzaldehyde	234
p-Ethylbenzaldehyde	234

	References
2-Alkenals	
2-Methyl-2-butenal	234
2-Methyl-2-pentenal	234
2-Pentenal	199
2-Hexenal	199
2-Heptenal	199
2-Octenal	199
2-Nonenal	199
2-Decenal	199
2-Undecenal	199
2-Dodecenal	199
2-Phenyl-2-butenal	199, 232, 234
5-Methyl-2-phenyl-2-hexenal	232, 234
Cinnamaldehyde	234
Alk-2, 4-Dienals	
2, 4-Pentadienal	199
2, 4-Hexadienal	199
2, 4-Heptadienal	199
2, 4-Octadienal	199
2, 4-Nonadienal	199
2, 4-Decadienal	199, 234, 236
2, 4-Undecadienal	199
Ketones	
Acetone	199, 234
2-Butanone	199, 232, 234
2, 3-Butanedione	234
2-Pentanone	199, 234
3-Methyl-2-butanone	199, 232
4-Methyl-2-pentanone	234
2, 3-Pentanedione	234
2-Hexanone	**199**
4-Heptanone	234
4-Methyl-3-penten-2-one	232, 234
3-Penten-2-one	234
2-Heptanone	199, 234
Cyclopentanone	234
2-Octanone	199, 234
Cyclohexanone	**234**
2-Nonanone	199
Cyclopentenone	**234**
2-Decanone	**199**
2-Undecanone	199, 234
Acetophenone	234
Ethyl phenyl ketone	**234**
Benzyl methyl ketone	**234**
2-Hydroxy-3-methyl-2-cyclopenten-1-one	**234**
Pyridines	
Pyridine	234, 235
2-Methylpyridine	234
2-Pentylpyridine	**234**
Methyl 2-pyridyl ketone	**234**
Methyl nicotinate	**234**

Pyrroles	*References*
1-Methyl pyrrole	229, 234
Pyrrole	234
Methyl-1-pyrrolyl ketone (1-acetyl pyrrole)	232
Methyl-2-pyrrolyl ketone (2-acetyl pyrrole)	234
2-Methyl pyrrole	234
Pyrrole-1-carboxaldehyde	234
1-Ethyl pyrrole-2-carboxaldehyde	232, 234
2-Methyl pyrrole-1-carboxaldehyde	234
1-Methyl pyrrole-2-carboxaldehyde	232, 234
5-Methyl pyrrole-2-carboxaldehyde	232, 234
1-Furfuryl pyrrole	232, 234
Methyl-2-pyrrolyl ketone (2-acetyl pyrrole)	232, 234
Pyrrole-2-carboxaldehyde	232, 234
2-Propionyl pyrrole	234
1-Furfuryl pyrrole-2-carboxaldehyde	234
Furans	
3-Methyl furan	233
2-Pentyl furan	232, 234
2-Furaldehyde	232, 234
Furyl methyl ketone	232, 234
Furfuryl alcohol, acetate	234
5-Methyl furfural	232, 234
Furoic acid, methyl ester	234
Furoic acid, ethyl ester	234
Methyl 5-methylfuryl ketone	234
Furfuryl alcohol	232, 234
3-Phenyl furan	232, 234
α-Methyl furanacrolein	234
Esters	
Acetic acid, ethyl ester	233, 234
Butyric acid, ethyl ester	234
Acetic acid, butyl ester	234
Acetic acid, isopentyl ester	234
Acetic acid, 2-ethoxy ethyl ester	234
Acetic acid, phenyl ester	234
Acetic acid, methylphenyl ester	234
Propionic acid, phenethyl ester	235
Lactones	
4-Hydroxy valeric acid, γ-lactone	234
4-Hydroxy butyric acid, γ-lactone	234
4-Hydroxy octanoic acid, γ-lactone	234
Alcohols	
Methanol	237
Ethanol	237
Propyl alcohol	237
Isopropyl alcohol	234, 237
Isobutyl alcohol	234, 237
2-Pentanol	234, 237
3-Pentanol	234
Butyl alcohol	234, 237
1-Penten-3-ol	234

Alcohols	*References*
4-Methyl-2-pentanol	234
2-Methyl-1-butanol	234
2-Hexanol	234
Pentyl alcohol	234
Hexyl alcohol	234
3-Hexene-1-ol	234
Cyclohexanol	234
Heptyl alcohol	234
α-Methylbenzyl alcohol	234
Benzyl alcohol	234
Phenethyl alcohol	234
1-Octanol	237
1-Dodocanol	237
Thiazoles	
Thiazole	234
4-Methylthiazole	234
Benzothiazole	234
Sulfur Compounds	
Methyl disulfide	232, 234
Propyl disulfide	234
3-Methylthiopropionaldehyde	234
2-Methyl dihydro-2(H)-thiophen-3-one	234
Dihydro-2(H)-thiophen-3-one	234
Thiophene-2-carboxaldehyde	232
Methyl-2-thienyl ketone (2-acetyl thiophene)	233, 234
5-Methylthiophene-2-carboxaldehyde	234
Benzyl methyl disulfide	234
Phenols	
o-*sec* Butyl phenol	234
2, 6-Di-*tert*- butyl-*p*-cresol	234
o-Methoxy phenol	234
Phenol	234
p-Ethyl phenol	234
2-Methoxy-4-vinyl phenol (4-vinyl guaiacol)	234
4-Vinyl phenol	234
Terpenes	
2(10)-Pinene (β-pinene)	234
4(10)-Thujene (sabinene)	234
Myrcene	234
p-Mentha-1, 8-diene (limonene)	234
1-Isopropyl-4-methyl benzene (8 terpiene)	234
p-Mentha-1, 4-diene (*p*-cymene)	234
4, 8-Epoxy-*p*-menth-2-ene (4-terpineol)	234
p-1-Menthen-8-ol (α-terpineol)	234
p-Mentha-6, 8-dien-2-one (carvone)	234
Aromatic Hydrocarbons	
Benzene	234
Toluene	233, 234
Ethyl benzene	234
p-Xylene	234
M-Xylene	234

Aromatic Hydrocarbons	*References*
o-Xylene	234
Propyl benzene	234
Mesitylene	234
Styrene	234
1, 2, 4-Trimethyl benzene	234
Butyl benzene	234
Indene	234
Methyl-2, 3-dihydroindene	234
1, 2, 3, 4-Tetrahydronaphthalene	234
Naphthalene	232, 234
Methyl naphthalene	234
Aromatic Hydrocarbons	
Ethyl Naphthalene	234
Dimethyl Naphthalene	234
Biphenyl	234
Dimethyl Naphthalene (Isomer)	234
Miscellaneous	
Pentane	234
Acetaldehyde, Dibutyl Acetal	234
1-Chloro-2-methyl Benzene	234
Hexadecane	234
$C_{17}H_{36}$	234
Tolunitrile	234
Benzonitrile	234
Tridecane	234
Thiacyclohexane	233
3-Methylthiacyclohexane	233
4-Methylthiacyclohexane	234

In addition to the 36 pyrazines, 187 additional components have have been reported (Table 13), making a total of 223 volatile components from roasted peanuts. The short-chain alkyl aldehydes were proposed as the main contributors to "harsh aroma" emanating from peanuts immediately after roasting (233). Phenylacetaldehyde, in particular, was cited for its evident contribution to the "sweet" characted of the aroma, i.e., an enrichment of the overall "bouquet" (233). Certain multicarbonyl compounds appeared in isolates but were not identified.

The extensive number of components in Table 13 were reported predominantly by three research groups. The techniques of isolation employed largely determined the number and types of compounds obtained from the roasted peanuts. Determination of the aldehydes and ketones in roasted Southeastern Early Runner peanuts was one of the objectives of Brown *et al.* (199). They obtain 40 carbonyl 2, 4-dinitrophenylhydrazone components from the oil of freshly roasted peanuts by passing it through a Celite column impregnated with 2, 4-dinitrophenylhydrazine and phosphoric acid. Many of the compounds reported were also found in the raw peanut oil. It was suggested that heptanal, nonanal, decanal, four alkenals and 2, 4- decadienal all contribute to the "fatty" and "deep-fried" notes in the overall olfactory sensation of freshly roasted peanuts (199, 200). The Oklahoma group reported some 56 compounds in an effort to identify all of the aroma-contributing components of roasted Spanish (Argentine variety) peanut flavor (228, 229, 231, 232, 235). Vacuum degassing of the oil from roasted peanuts was felt by this group to yield the most representative qualitative volatile gas chromatographic

profile. Walradt and coworkers (234) reported 187 volatile components of roasted Spanish peanuts (Starr variety), employing a steam distillation technique which permitted isolation and identification of minute quantities of volatiles which were previously tentatively or incorrectly identified.

Ballschmieter and Dercksen (237) reported nine alcohols isolated from a steam distillate of the peanut variety Natal Common. Brown and coworkers (236) resolved extracts from roasted peanuts into various fractions via classical chemical techniques. A number of acids were found including acetic, propionic, isobutyric, isovaleric, valeric, heptanoic, decanoic, lauric, myristic, phenylacetic and dihydroxynaphthaleneacetic. Carbonyl compounds reported were hexanal, 2, 4-decadienal, and 2-oxooctanal. Tentative evidence was presented of aliphatic lactones, which are powerful flavoring agents.

Data on the qualitative appearance of a compound in aroma extracts is only one step in establishing its impact in the flavor-aroma system. Only by quantitation of the compound and comparison with the average flavor threshold of the authentic can one begin to elucidate its role in a flavor. A small amount of information along this line is becoming available. Concentrations of some volatile components found in roasted peanuts and their aroma thresholds in oil are given in Table 14. Those pyrazine concentrations listed all occur below their threshold. Cobb (240) recently introduced an isotope dilution technique for quantitation of flavor components in roasted peanuts. Two flavorful aldehydes, benzaldehyde and phenylacetaldehyde, were found to vary in their contributions to the aroma of roasted peanuts (241). Benzaldehyde was shown to occur usually within a range of 0.2-3.0 ppm, while phenylacetaldehyde was present at levels from 2 to over 10 ppm. The average aroma thresholds for the authentics in mineral oil were 9.0 and 0.07 ppm, respectively. Flavor thresholds in similar media were not greatly different. Thus, benzaldehyde occurs below its threshold value, while phenylacetaldehyde is present at approximately 20 to 100 times threshold.

Table 14. Concentrations of Some Volatile Components Found in Roasted Peanuts and Their Aroma Thresholds

Compound	*Concentration in Peanuts (ppm)*	*Aroma Threshold in Oil (ppm)*
2-Methylpyraine[a]	6	27
2, 5 Dimethylpyrazine[a]	[c]	17
2, 6 Dimethylpyrazine[a]	[c]	8
2-Ethylpyrazine[a]	[c]	17
Trimethylpyrazine[a]	—	27
Tetramethylpyrazine[a]	—	38
2-Ethyl-3, 6-dimethylpyrazine[a]	—	24
2-Ethyl-3, 5-dimethylpyrazine[a]	—	24
Benzaldehyde[b]	0.2-3.0	9
Phenylacetaldehyde[b]	2-10	0.07
Butanal + 2-methylpropanal[e]	1.6	0.04
Pentanal + 3-methylbutanal[e]	1.8	0.06
2-Methylbutanal[e]	1.7	0.04
Hexanal[e]	1.1	0.1
Heptanal[e]	0.08	0.06
Octanal[e]	0.43	0.05
Nonanal[e]	0.7	0.2
Decanal[e]	0.28	0.7

[c] 11 (1.1)[d]

		References *References*
2-Hexenal[e]	0.04	0.6
2-Octenal[e]	0.23	0.15
2-Nonenal[e]	0.63	0.05
2-Decenal[e]	0.2	0.12
Dodecanal[e]	0.07	0.04
2-Heptenal[e]	0.23	0.2
2, 4-Decadienal[e]	0.32	0.1
Phenyl-2-butanal[e]	—	0.25

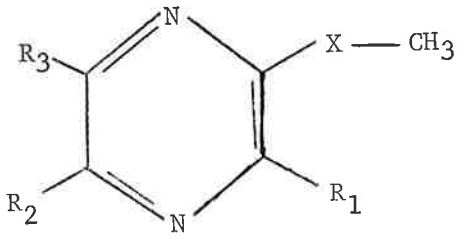
[a]Ref. 239
[b]Ref. 241
[c]Concentration reported includes all three components.
[d]Ref. 235 — value obtained from roasted peanut oil passed through molecular still.
[e]Ref. 200.

Brown and coworkers (200) found 14 aldehydes in concentrations above their threshold values in oil.

Contributions of the quantitated compounds to roasted peanut aroma must in the case of the pyrazines and benzaldehyde be synergistic. This effect, between two or more components can reduce the threshold of detection of a flavor mixture significantly below that of any of its components. The possibility of an entirely different aroma characteristic from mixtures of this sort cannot be overlooked. There is no doubt that, barring masking or physical adsorption, phenylacetaldehyde strongly contributes to peanut aroma, confirming the earlier postulation of Mason *et al.* (214).

It becomes clear that the character of roasted peanut flavor and aroma is quite complex. Pyrazines play an integral role, as do carbonyls. The fact that the aroma has not been exactly duplicated may lie in the presence of some extremely potent, as yet unidentified component(s) or simply to a lack of proper blending of the identified material. In respect to the former postulation, certain dihydropyrazines possess very "nut-like" aroma qualities but are unstable (220). Such compounds have not been identified in peanuts, but may not survive the rigorous pH treatment for extraction and gas chromatography described by the Oklahoma group.

Some unusual and interesting alicyclic and oxygenated pyrazines were identified by Walradt and coworkers (234). There is no information available on aroma thresholds of the alicyclic compounds but certain oxygenated pyrazines are extremely potent flavor components. 2-Isobutyl-3-methoxypyrazine has been reported as a major characteristic aroma component of bell peppers (242). Its odor threshold in water is two parts in 10^{12} parts H_2O. The compound is being used commercially as a flavor ingredient (243). A recent patent has been obtained indicating that foodstuffs can be given nut-like flavors from compounds having the general structure:



Where X is sulfur or oxygen, one of the R groups is methyl, and the other R groups are

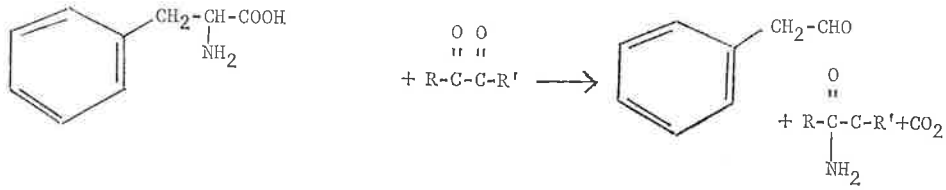
hydrogen (244). Also acetylpyrazine and methylacetylpyrazine have been patented for addition to foods as "popcorn" flavor (245).

Studies have been conducted pertaining to mechanism of formation of the pyrazines during roasting. Newell *et al.* (246) utilized a nonaqueous reaction medium with glucose and the free amino acids found in peanuts. When a mixture of all amino acids was present, concentrations of major pyrazines and phenylacetaldehyde approached those levels obtained from roasted peanuts. When individual amino acids were heated with glucose, quantitative differences were noted in total amount of pyrazine formed. It thus was suggested that donor amino acid structure controls the type and concentration of pyrazine formed during roasting.

Koehler *et al.* (247), utilizing ^{14}C-labeled glucose and amino acids, showed that the carbon atoms of the pyrazines arise from the sugar moiety, while the amino acids contribute only the nitrogen atoms. Ammonium ions were not the common intermediate through which the nitrogen entered the pyrazine ring. The data indicated that fragmentation of the glucose molecule involved cleavage at C2-C3 and C3-C4 linkages, with the latter type predominating. Interestingly enough, the label from glucose-1-^{14}C and glucose-6-^{14}C was incorporated about equally into dimethylpyrazine indicating that either of the three carbon fragments from C3-C4 cleavage may be utilized. However, incorporation of the label from glucose-1-^{14}C into methylpyrazine was higher than that from glucose-6-^{14}C, indicating the C2-C3 split occurs primarily at the anomeric end of the aldose.

Wang *et al.* (248) proposed a mechanism explaining the formation of methyl substituted pyrazines. According to this mechanism, α-dicarbonyls may induce Strecker degradation of amino acids yielding an amino-reductone. This in turn may convert to pyrazines by a series of subsequent steps such as self-condensation and oxidation. The resultant pyrazine would be dependent on the α-dicarbonyl structure and independent of the amino acid. Walradt *et al.* (234) suggested possible formation routes for acetyl, methyl acetyl, the branched chain alkyl, alkenyl and alicyclic pyrazines.

The short chain aliphatic aldehydes (including phenylacetaldehyde) are most likely formed from Strecker degradation of amino acids during roasting, i.e.,



phenylalanine — bis carbonyl (sugar degradation) — phenylacetaldehyde

The origin of benzaldehyde is unknown but may well be a glucoside such as amygdalin.

Pyrroles are known to be products of the Maillard reaction. Kato and Fujimaki (249) identified a number of pyrrole-2-aldehydes from reaction of D-xylose and amines. Furans, as well as pyrroles, have been reported in roasted cocoa beans and coffee (250, 251). Furans are formed during roasting by degradation reactions of sugars.

Roasted peanuts and their headspace vapors were exposed directly to light and compared to similar peanuts where the vapors only were irradiated (252). The odor

of the peanuts exposed to light, whether peanuts and vapors or vapors only, was generally characterized as slightly objectionable or stale. At light levels up to 32 ft.-candle-hours, there was no carryover of objection to the odor of the peanuts.

A compositive analysis of the basic volatile aroma constituents (primarily pyrazines) of roasted peanuts was conducted involving standard varieties, different fertilizer treatments, times of planting and harvesting and different storage conditions (235). Two Spanish varieties, Argentine and Starr, were used and no qualitative differences in the GC profile of the basic volatiles were observed. However, four of the 19 peaks showed a significant quantitative difference. The effect of length of growing time on the relative volatile concentrations was not significant for peanuts harvested at different dates after 120 days from planting. Quantitative differences in the GC profile was observed in peanuts fertilized with boron and those not so treated. Peanuts stored in a mixture of SO_2 and N_2 exhibited an off-flavor and the relative volatile concentrations and seed appearance were different from peanuts stored in either N_2, CO_2 or dry air alone.

Cobb and Swaisgood (253) initiated a study relating growth environment and roasted peanut flavor. Amino acid and sugar levels were determined and related to flavor scores, soil types and rainfall. No definite conclusions could be reached but the effect of soil type appeared in evidence.

A recent survey of vegetable volatiles includes a table on the volatile compounds identified in peanuts and peanut oil (254). The table includes many of the compounds listed in Table 13 and a large number of fatty acids reflecting peanut glyceride composition.

Swenson and Martin (255) have noted that a superior-flavored peanut butter ice cream mix resulted from incorporation of the butter to the mix prior to pasteurization rather than immediately before the freezing process. A chromatographic investigation of headspace vapors from mix prepared both ways indicated 2-methylpropanal and 2-methylbutanal as likely "harsh-flavor" components. When the butter was added prior to pasteurization, these compounds and possibly others were apparently volatilized, such that no off-flavor occurred in the ice cream subsequently prepared.

Other Physicochemical Changes Due to Heat

It has not been determined whether water is needed to initiate the browning reaction during roasting. Pickett and Holley (225) noted that dry amino acid-sugar mixtures evolved no carbon dioxide when heated at 140°C for three hours, concluding that, at least for CO_2 production, water is a necessary catalyst. Water is also chemically evolved during roasting, probably due to sugar degradation and partial destabilization of proteins.

The hydrogen-ion concentration of peanuts has been found to increase upon roasting (225). Raw nuts ranged from pH 6.7-7.0. Commercial peanut butters varied from pH 6.2-6.5. Upon extended periods of heating the pH of peanuts was observed to drop below 6.0. Higher roasting temperatures caused a more rapid drop in pH.

Pickett (256) determined that peptizable nitrogen decreased with increasing internal temperature and time of roasting. Roasting apparently affects the digestibility of proteins in small manner, however, unless the nuts are subjected to very severe roasting temperatures (257, 258). The effect of dry roasting on the proteins of peanuts was investigated more recently by Neucere *et al.* (259). Solubility of the proteins in phosphate buffer was found to be reduced to less than one-half that of raw nuts due either to ir-

reversible denaturation, a change in the isoelectric point, or both. The major reserve protein, α-arachin, increased in electrophoretic mobility but its antigenic structure was maintained. Sedimentation analyses indicated that association-dissociation had occurred. Proteins other than α-arachin, exhibited modified physiochemical properties, some with changes in primary and/or secondary structures.

Autoclaving peanuts at 121°C for 4 hours destroyed much of the cystine present and reduced their value as a source of lysine for chicks while there was little change in their value as a source of methionine and threonine (260). Losses in available lysine in heat-treated peanuts appears due to reactions involving the α-amino groups forming linkages which are not hydrolyzed by digestive enzymes (261). Model experiments with peanut isolates and different sugars indicated the lysine losses were related to reactions involving the proteins and sucrose.

Bensabat and coworkers (262) have shown that maximum lysine preservation during processing of peanuts into flour can only be accomplished with low heat treatment.

The formation of dextrins from starch during roasting is apparently very low (256). A dextrin content of 0.1-0.2% has been reported in raw peanut flour. In contrast, crude fiber decreased during roasting (225), especially during a heavy roast. Whereas a value of 4.38% crude fiber was found in raw nuts, only 2.77% was found after roasting for 40 minutes at 150°C.

It is now well-documented that thiamine is heavily degraded by roasting temperatures. Pickett (119) reported that whereas no thiamine loss occurred after 5 hours at 76°C, 90% was lost by heating peanuts at 146°C for 2 hours. Oven studies of a large number of samples (263) indicated that a long roast at relatively low temperatures was best for thiamine preservation but was difficult for making peanut butter. Dark color formation was closely correlated with thiamine loss. Several groups have confirmed Pickett's results (264-266).

Roasting at 160°C destroyed no riboflavin and only about one-fourth of pantothenic acid, while 180°C roast temperatures destroyed about 25% of riboflavin and all of the pantothenic acid (267). The niacin and choline contents of peanuts are affected in small manner by normal roasting techniques (268, 269).

Roasting apparently changes the character of peanut oil to a very slight extent, if at all. Pickett (225) noted no change in iodine number, saponification number, acetyl value or free fatty acid content. Iverson *et al.* (43) noted little difference in the fatty acid composition of glycerides from raw and roasted samples.

During heating certain changes occur in the gross structure (228). Protein bodies maintain their gross structure (228), but some clumping of subcellular particulates occurs, and a lightening of inclusion bodies is perceived. Starch granules tend to rupture, forming small circular holes, presumably due to water vapor release.

List Of References

1. Woodroof, J. G. "Peanuts: Production, Processing, Products," (a) p. 18, (b) p. 118, (c) p. 119, Avi Publishing, Westport, Conn. (1966).
2. Guthrie, J. D., C. L. Hoffpauir, M. F. Stansbury and W. A. Reeves. USDA *AIC-61* (1949).
3. Holley, K. T. and R. O. Hammons. Ga. Agr. Expt. Sta. Res. Bul. *32* (1968).
4. Pattee, H. E. and A. E. Purcell. J. Am. Oil Chem. Soc. *44*:328 (1967).
5. Newell, J. A., M. E. Mason and R. S. Matlock. J. Agr. Fd. Chem. *15*:767 (1967).

6. Mason, M. E., J. A. Newell, B. R. Johnson, P. E. Koehler and G. R. Waller, J. Agr. Fd. Chem. *17*:728 (1969).
7. Eheart, J. F., R. W. Young and A. H. Allison. Food Res. *20*:497 (1955).
8. Fedeli, E., G. Favini, E. Camurati and G. Jacini. J. Am. Oil Chem. Soc. *45*:676 (1968).
9. Ward, H. S., Jr. and U. L. Diener. Phytopathology *51*:244 (1961).
10. Pattee, H. E. and S. L. Sessoms. J. Am. Oil Chem. Soc. *44*:61 (1967).
11. O'Connor, R. T., E. M. Sallee, R. R. Allen, W. J. Coleman and J. R. Chipault. J. Am. Oil Chem. Soc. *42*:347 (1964).
12. Greve, E. Food Res. 10:28 (1945).
13. Pickett, T. A. Pl. Physiol. *25*:210 (1950).
14. Freeman, A. F., N. J. Morris and R. K. Willich. USDA *AIC-370* (1954).
15. Vix, H. L. E., J. Pominski, H. M. Pearce, Jr. and J. J. Spadaro. Peanut J. and Nut World *46*(3):10, *46*(4):10, *46*(6):10 (1967).
16. Fraps, G. S. Tex. Agr. Expt. Sta. Bul. *222* (1917).
17. White, H. C. Ga. Agr. Expt. Sta. Bul. *13* (1891).
18. Fernandez, O. and M. D. Lara. Rev. Real acad. cienc. exact. fis. y Nat. Madrid *50*:135 (1956), as in Chem. Abstr. *50*:16104c (1956).
19. Hoffpauir, C. L. J. Agr. Fd. Chem. *1*:668 (1953).
20. Watt, B. K. and A. L. Merrill. Agriculture Handbook No. 8, ARS, USDA (1963).
21. Roberson, S., J. E. Marion and J. G. Woodroof. J. Am. Diet. Assoc. *49*:208 (1966).
22. Willard, C., R. D. Englert and L. M. Richards. J. Am. Oil Chem. Soc. *31*:131 (1954).
23. Bernfeld, P. Am. J. Clin. Nutr. *11*:554 (1963).
24. Smith, H., W. Horwitz and W. Weiss. J. Ass. Off. Anal. Chem. *45*:734 (1962).
25. Young, C. T. and K. T. Holley. Proc. *3rd* Nat. Peanut Res. Conf. Auburn, Ala. (1964), p. 99.
26. Beasley, E. O. and J. W. Dickens. N. C. State Coll. Tech. Bul. *155* (1963).
27. Karon, M. L. and B. E. Hillery. J. Am. Oil Chem. Soc. *26*:16 (1949).
28. Cobb, W. Y., S. E. Gilliland and E. B. Williams. Food Tech. *23*:1586 (1969).
29. Woodroof, J. G., S. R. Cecil and H. H. Thompson. Ga. Agr. Expt. Sta. Bul. *241* (1945).
30. Archer-Daniels-Midland Company, Minneapolis, Minn. "Composition and Constants of Fatty Acids" (wall chart).
31. Morris, N. J., R. K. Willich and A. F. Freeman. Food Tech. 7:366 (1953).
32. Seitz, F. G., Fette, Seifen, Anstrichmittel 63:1063 (1961).
33. Rabari, L. F., R. D. Patel and J. G. Chohan. J. Am. Oil Chem. Soc. *38*:4 (1961).
34. Ward, T. L. and W. S. Singleton. J. Am. Oil Chem. Soc. *27*:423 (1950).
35. Williams, K. A. "Oils, Fats and Fatty Foods: Their Practical Examination," *4th* edition, pp. 307-309, American Elsevier, New York (1966).
36. Lutton, E. S. J. Am. Chem. Soc. 67:524 (1945).
37. Bailey, A. E., "Melting and Solidification of Fats," *2nd* edition, p. 22, Interscience, New York (1950).
38. Ibid. *1st* edition, p. 277.
39. Magne, F. C., E. L. Skau and A. F. Freeman. J. Am. Oil Chem. Soc. 31:113 (1954).
40. Triebold, H. O. and L. W. Aurand. "Food Composition and Analysis," (a) p. 168, (b) p. 173, D. Van Nostrand, Princeton, N. J. (1963).
41. Pickett, T. A. and K. T. Holley. J. Am. Oil Chem. Soc. 33:650 (1956).
42. Pohle, W. D., V. C. Mehlenbacher and J. H. Cook. Oil and Soap *22*:115 (1945).
43. Iverson, J. L., D. Firestone and W. Horwitz. J. Assn. Off. Anal. Chem. *46*(4):718 (1963).
44. Worthington, R. E. and K. T. Holley. J. Am. Oil Chem. Soc. 44:515 (1967).

45. Kuemmel, D. F. J. Am. Oil Chem. Soc. *41*:667 (1964).
46. Zorzut, C. M. and P. Capella. Riv. Ital. Sost. Grasse *46*:66 (1969).
47. Longenecker, H. E. J. Soc. Chem. Ind. *56*T:310 (1937).
48. Wikoff, H. L., J. M. Kaplan and A. L. Berman. J. Biol. Chem. *153*:227 (1944).
49. Sekhon, K. S., K. L. Ahuja and R. S. Sandhu. The Ind. J. Nutr. & Dietet. 7:243 (1970).
50. Norden, A. J. and D. H. Block. Proc. *5th* Nat. Peanut Res. Conf., Norfolk, Va. (1968), p. 61.
51. Fore, S. P., N. J. Morris, C. H. Mack, A. H. Freeman and L. E. Compton. J. Am. Oil Chem. Soc. *30*:298 (1953).
52. French, R. B. J. Am. Oil Chem. Soc. *39*:476 (1962).
53. Worthington, R. E. Proc. *5th* Nat. Peanut Res. Conf., Norfolk, Va. (1968), p. 87.
54. Hartzook, A. Curr. Sci. *38*:176 (1969).
55. Rewald, B. Biochem. J. *36*:822 (1942).
56. Osman, F., A. E. Ashour and A. M. Gad. Fette, Seifen, Anstrichmittel *71*:264 (1969).
57. Malkin, T. and A. G. Poole. J. Chem. Soc. (London) *1953*:3470, as in J. Sci. Fd. Agr. Abstr. *i*:253 (1954).
58. Senn, V. J. J. Am. Oil Chem. Soc. *46*:476 (1969).
59. Sreenivasan, B. J. Am. Oil Chem. Soc. *45*:259 (1968).
60. Carter, H. E., W. D. Celmer, D. S. Galanos, R. H. Gigg, W. E. M. Lands, J. H. Law, K. L. Mueller, T. Nakayama, H. H. Tomizawa and E. Weber. J. Am. Oil Chem. Soc. *35*:335 (1958).
61. Wagner, H., W. Zofesik and I. Heng. Z. Naturforschg. *246*:922 (1969).
62. Van der Wal, R. J. J. Am. Oil Chem. Soc. *37*:18 (1960).
63. Jurriens, G. and A. C. J. Kroesen. J. Am. Oil Chem. Soc. *42*:9 (1965).
64. Subbaram, M. R. and C. G. Youngs. J. Am. Oil Chem. Soc. *44*:425 (1967).
65. Eisner, J. and D. Firestone. J. Assn. Off. Anal. Chem. *46*:542 (1963).
66. Aylward, F. and B. W. Nichols. J. Sci. Fd. Agr. *13*:86 (1962).
67. Morris, N. J. and L. S. Lee. J. Agr. Fd. Chem. *9*:401 (1961).
68. Holley, K. T. and C. Young. Proc. PIWG, Stillwater, Okla., (1963), p. 52.
69. Emery, D. A., C. L. Gupton and R. O. Hexam. Proc. *4th* Nat. Peanut Res. Conf., Tifton, Ga., (1966), p. 25.
70. Emery, D. A. and C. L. Gupton. Oleagineux *23*:99 (1968).
71. Pattee, H. E., A. E. Purcell and E. B. Johns. J. Am. Oil Chem. Soc. *46*:629 (1969).
72. Walbecq, M. J. Am. Oil Chem. Soc. *43*:396A (1966).
73. LeFort, D. and J. Sorba. Bull. Soc. Chim. France 1956:69, as in Chem. Abstr. *50*:17484i (1956).
74. Jasperson, H. and R. Jones. J.S.C.I. *66*:13 (1947).
75. Tharp, B. W. and S. Patton. J. Dairy Sci. *43*:475 (1960).
76. Patton, S. and B. W. Tharp. J. Dairy Sci. *42*:49 (1959).
77. Fisher, G. S., W. G. Bickford and F. G. Dollear. Oil and Soap *24*:478 (1951).
78. Morris, N. J. and A. F. Freeman. Food Tech. 7:227 (1953).
79. Pickett, T. A. and K. T. Holley. J. Am. Oil Chem. Soc. *28*:478 (1951).
80. Roy, B. R. and B. C. Guha. J. Sci. Ind. Res. (India) *15*C:192 (1956), as in Chem. Abstr. *51*:4028b (1957).
81. Young, C. T. "Biochemical Studies of Peanut *(Arachis hypogaea* L.) Quality," Ph.D. dissertation, Oklahoma State University, Stillwater, (1970).
82. Paul, S. and A. Roylance. J. Am. Oil Chem. Soc. *39*:163 (1962).
83. Gaddis, A. M., R. Ellis and G. T. Currie. J. Am. Oil Chem. Soc. *38*:371 (1961).

84. Crossley, A. and A. Thomas. J. Am. Oil Chem. Soc. *41*:95 (1964).
85. Butler, W. L. and J. E. Baker. Nature *209*(4978):1319 (1965).
86. Salatore, S. A. and V. N. Gavai. J. Sci. Ind. Res. *21*D:86 (1962), as in Chem. Abstr. *56*:15623g (1962).
87. Skinner, W. A., R. M. Parkhurst and P. A. Sturm. Final Report. Contract No. 12-14-100-7745(34), USDA, OICRB, Beltsville, Md., July 24, 1967.
88. Cecil, S. R. and J. G. Woodroof. Ga. Agr. Expt. Sta. Bul. *265* (1951).
89. Dugan, L. R., H. R. Kraybill, L. Ireland and F. C. Vibraus. Food Tech. *4*:457 (1950).
90. Woodroof, J. G., H. H. Thompson and S. R. Cecil. Ga. Agr. Expt. Sta. Bul. *247* (1946).
91. Roy, B. R. J. Ind. Chem. Soc., Indus. News Edn. *17*:135 (1954), as in J. Sci. Fd. Agr. Abstr. *i*:210 (1955).
92. Naudet, M. and S. Biasini. Rev. fse Corps gras *16*:185 (1969).
93. Traetta-Mosca, F. Portici R. Scuola Super. di Agr. Ann. *3*:164 (1929).
94. Ho, H. K. and T. C. Cheng. Chin. Agr. Chem. Soc. J. *4*:45 (1966).
95. Aylward, F. and B. W. Nichols. J. Sci. Fd. Agr. *12*:645 (1961).
96. Balley, D. S. and R. H. McCormack. J. Am. Oil Chem. Soc. *29*:470 (1952).
97. Sharma, C. B. Diss. Abstr. *26*:6355 (1966).
98. Lee, L. S. and N. J. Morris. J. Agr. Fd. Chem. *11*:321 (1963).
99. Bonner, J. and J. E. Varner. "Plant Biochemistry," 1*st* edition, 4*th* printing, (a) p. 299, (b) p. 417, Academic Press, New York (1969).
100. Hirst, E. L. and J. K. N. Jones. J. Chem. Soc. (London) *1938*:496.
101. Hirst, E. L. and J. K. N. Jones. J. Chem. Soc. (London) *1939*:452.
102. Steiner, E. T. and J. D. Guthrie. Ind. Eng. Chem., Anal. Ed., *16*:736 (1944).
103. Radahakrishnamurty, B. and V. R. Srinivasan. Proc. Ind. Acad. Sci. *49*A:98 (1959), as in Chem. Abstr. *53*:17912e (1959).
104. Radahakrishnamurty, B. and V. R. Srinivasan. J. Sci. Ind. Res. (India) *16*C:59 (1957), as in Chem. Abstr. *51*:14014d (1957).
105. Dunn, K. R. and V. R. Goddard. Food Res. *13*:512 (1948).
106. Daniel, L. and L. C. Norris. J. Nutr. *30*:31 (1945).
107. Fisher, G. S. Ind. Eng. Chem., Anal. Ed., *17*:224 (1945).
108. Giral, F. and L. M. de la Torre. Ciencia *6*:252 (1945).
109. Lambertson, G., H. Myklestad and O. R. Braekkan. J. Sci. Fd. Agr. *13*:617 (1962).
110. Parkhurst, R. M., W. A. Skinner and P. A. Sturm. J. Am. Oil Chem. Soc. *45*:641 (1968).
111. Schwimmer, S. Cer. Chem. *24*:70 (1947).
112. Willich, R. K., N. J. Morris, R. T. O'Connor and A. F. Freeman. Food Tech. *8*:381 (1954).
113. Roy, B. R. J. Sci. Ind. Res. (India) *13*B:496 (1954), as in Chem. Abstr. *49*:645g (1955).
114. Oliver, G. D., W. S. Singleton and A. E. Bailey. Oil and Soap *21*:188 (1944).
115. Food and Nutrition Board, National Academy of Sciences — National Research Council. Recommended Dairy Dietary Allowances, Revised 1968.
116. Mahler, H. P. and E. H. Cordes. "Biological Chemistry," (a) p. 348, (b) p. 355, (c) p. 370, Harper and Row, New York (1966).
117. Dougherty, R. H. and W. Y. Cobb. J. Agr. Fd. Chem. *18*:921 (1970).
118. Dougherty, R. H. and W. Y. Cobb. J. Sci. Fd. Agr. *21*:411 (1970).
119. Pickett, T. A. Ga. Agr. Expt. Cir. *128* (1941).
120. Booker, L. E. Proc. 1*st* Ann. Meeting Nat. Peanut Council *1*:24 (1941).
121. Cheldelin, V. H. and R. J. Williams. Tex. Univ. Pub. *4237*:105 (1942).
122. Sherwood, F. W. and J. O. Halverson. J. Agr. Res. *44*:849 (1932).

123. Engel, R. W. J. Nutr. *25*:441 (1943).

124. Boudreaux, H. B. and V. L. Frampton. Nature (London) *185*:469 (1960).

125. Jackson, B., W. Owen and H. B. Boudreaux. Thrombos. Diathes. Haemorrh. (Stuttgart) *16*:257 (1966).

126. Bisordi, M. Lancet *II*:476 (1964).

127. Brüster, H. Klin. Wschr. *21*:1145 (1961).

128. Brüster, H. Z. Kinderheilk. *8*:462 (1962).

129. Pattee, H. E. and H. E. Swaisgood. J. Fd. Sci. *33*:250 (1968).

130. Swaisgood, H. E. and H. E. Pattee. J. Fd. Sci. *33*:400 (1968).

131. Siddiqi, A. M. and A. L. Tappel. J. Am. Oil Chem. Soc. *34*:529 (1957).

132. Dillard, M. G., A. S. Henick and R. B. Koch. Fd. Res. *25*:544 (1960).

133. Bronisz, H., M. Arbatowska and H. Leszczynska. Roczniki Panstworwego Zakladu Hig. *9*:29 (1958), as in Chem. Abstr. *52*:13020d (1958).

134. Hartzook, A., B. Yehudith and S. Hurwitz. Agrochimica *14*:365 (1970).

135. Giri, K. V. Ann. Biochem. Expt. Med. *1*:297 (1941).

136. Vyas, D. N. and K. C. Patel. Starke. *20*:114 (1968).

137. Shih, D. S. and L. B. Barnett. Arch. Biochem. Biophys. *123*:558 (1968).

138. Marcus, A. and J. Freely. Biochem. et Biophys. Acta. *84*:359 (1964).

139. Longo, C. B. Pl. Physio. *43*:660 (1968).

140. Sreeramulu, N. and I. M. Rao. Andhra Agr. J. *14*:173 (1967).

141. Maruyama, H. Diss. Abstr. *25*(11):6200 (1965).

142. Brown, H. D., N. J. Neucere, A. M. Altschul and W. J. Evans. Life Sci. *4*:1439 (1965).

143. Singh, R. Phtochem. 7:1503 (1968).

144. Singh, R., A. J. St. Angelo and N. J. Neucere. Phytochim. *9*:1535 (1970).

145. Oppenheim, A. and P. A. Castelfranco. Pl. Physiol. *42*:125 (1967).

146. Vyas, D. N., K. C. Patel and R. D. Patel. Naturwissenschaften *52*:166 (1965).

147. Duda, C. T., A. E. Richmond and J. H. Cherry. Phytochem. 6:171 (1967).

148. Barzoni, N. and A. Luzzati. Atti. Accad. Nazl. Lincei Rend., Classe Sci. fis., mat. e nat. *21*:450 (1956), as in Chem. Abstr. *51*:8894g (1957).

149. Rebeiz, C. and P. Castelfranco. Pl. Physiol. *39*:932 (1964).

150. Humphreys, T. E. and P. K. Stumpf. J. Biol. Chem. *213*:941 (1955).

151. Fontaine, T. D., W. A. Pons, Jr. and G. W. Irving. J. Biol. Chem. *164*:487 (1946).

152. Leoncini, G. Boll. regio. ist. super. agrar. Pisa 7:603 (1931).

153. Heller, M. and R. Arad. Biochem. Biophys. Acta *210*:276 (1970).

154. Tixier, R. Compt. Rend. Acad. Sci., Paris, Ser. D *266*:2498 (1968).

155. Zimmerman, G., S. Weissmann and S. Yannai. J. Fd. Sci. *32*:129 (1967).

156. Werle, E. Voeding *30*:312 (1969).

157. Narayanan, K. M., G. S. Bains and D. S. Bhatia. Chem. and Ind., Sept. 38, 1963, p. 1588.

158. Ohio Agricultural Experiment Station, Wooster, Ohio, March, 1965. Tests for Franklin Peanut Co., Inc.

159. Hallock, D. L., D. C. Martens and M. W. Alexander. Agron. J. *61*(1):81 (1969).

160. Adolph W. H. and H. Liu. Chin. Med. J. *55*:337 (1939).

161. Conn, E. E. and P. K. Stumpf. "Outlines of Biochemistry," *2nd* edition, p. 191, John Wiley, New York (1967).

162. Allison, R. V. and T. Whitehead, Jr. Fla. Grower *51*:4 (1943).

163. Jodidi, S. L. J. Agr. Res. 57:301 (1938).

164. Robinson, G. M. and R. Robinson. Biochem. J. *27*:206 (1933).
165. Toyeau, F. and J. Masquelier. Compt. Rend. Acad. Sci., Paris *227*:602 (1948).
166. Masquelier, J. and P. Blanquet. Compt. Rend. Acid. Sci., Paris *227*:614 (1948).
167. Miller, O. H. and E. E. Burns. J. Food Sci. *36*:669 (1971).
168. Beasley, E. O. and J. W. Dickens. Trans. Am. Soc. Ag. Eng. *11*:689 (1968).
169. Kramer, H. A., J. E. Gates, K. D. Demaree and A. P. Sidwell. Food Tech. *17*:90 (1963).
170. Hodge, J. E. J. Agr. Fd. Chem. *1*:928 (1953).
171. Mason, M. E., B. Johnson and M. Hamming. J. Agr. Fd. Chem. *14*:454 (1966).
172. Morris, N. J., I. W. Lohmann, R. T. O'Connor and A. F. Freeman. Fd. Tech. 7:393 (1953).
173. Lee, L. S., N. J. Morris and V. L. Frampton. J. Agr. Fd. Chem. *13*:309 (1965).
174. Reeves, W. A. and J. D. Guthrie. Arch. Biochem. *26*:316 (1950).
175. Cherry, J. H. Biochem. Biophys. Acta. *68*:193 (1963).
176. Chroboczek, H. and J. H. Cherry. J. Mol. Biol. *19*:28 (1966).
177. Gordin-Sharir, A. and P. F. Waring. Nature *204*:1308 (1964).
178. Wada, S. and H. Takahaski. Eiyo to Shokuryo *9*:185 (1956), as in Chem. Abstr. *55*:19062c (1961).
179. Hogan, J. T. and J. C. Arthur, Jr. J. Am. Oil Chem. Soc. *28*:272 (1951).
180. Hogan, J. T. and J. C. Arthur, Jr. J. Am. Oil Chem. Soc. *29*:16 (1952).
181. Sastry, G. M. and J. G. Aggarwal. Paintindia *9*(7):19 (1959), as in Chem. Abstr. *54*:16861f (1960).
182. Arthur, J. C., Jr., T. W. Mason, Jr. and M. E. Adams. J. Am. Oil Chem. Soc. *25*:338 (1948).
183. Govil, R. S. Textil-Rundschau *15*:485 (1960), as in Chem. Abstr. *53*:1959h (1959).
184. Vilbrandt, F. C. and S. M. Gano. VPI Eng. Expt. Sta. Series No. 95, Vol. *47*(11), (1954).
185. Narasimha Rao, T. L. and D. S. Datar. J. Ind. Chem. Soc., Ind. and News Ed. *20*:75 (1957), as in Chem. Abstr. *53*:611f (1959).
186. Dieckert, J. W., J. E. Snowden, Jr., A. T. Moore, D. C. Heinzleman and A. M. Altschul. J. Fd. Sci. *27*:321 (1962).
187. Phillips, M. Biochem. Biophys. Acta *91*:350 (1964).
188. Yatsu, L. Y. Proc. Seed Protein Conf., SURDD, USDA, New Orleans (1963), p. 240.
189. Jacks, T. J., L. Y. Yatsu and A. M. Altschul. Pl. Physiol. *42*:585 (1967).
190. Kmetec, E. P. Diss. Abstr. *17*:1890 (1957).
191. Yatsu, L. Y. SURDD, USDA, New Orleans. Personal Communication (1967).
192. Cherry, J. H. Pl. Physiol. *38*:440 (1963).
193. Pattee, H. E., J. A. Singleton and W. Y. Cobb. J. Fd. Sci. *34*:625 (1969).
194. Cobb, W. Y. Unpublished data (1969).
195. Stoll, A. and E. Seebeck. Adv. Enzymol. *11*:377 (1951).
196. Schwimmer, S. and W. J. Weston. J. Agr. Fd. Chem. *9*:301 (1961).
197. Fleming, H. P., W. Y. Cobb, J. L. Etchells and T. A. Bell. J. Fd. Sci. *33*:572 (1968).
198. Pattee, H. E., J. A. Singleton, E. B. Johns and Beth C. Mullin. J. Agr. Food Chem. *18*:353 (1970).
199. Brown, D. F., V. J. Senn, J. B. Stanley and F. G. Dollear, submitted to J. Agr. Food Chem., (1972).
200. Brown, D. F., V. J. Senn, F. G. Dollear and J. B. Stanley. American Peanut Research and Education Association J. *3*:208 (1971).
201. Bailey, W. K., T. A. Pickett and J. G. Futural. Peanut J. and Nut World *33*(8):17 (1954).
202. Beasley, E. O. and J. W. Dickens. N. C. Agr. Expt. Sta. Tech Bul. *155* (1963).

203. Pattee, H. E., E. O. Beasley and J. A. Singleton. J. Fd. Sci. *30*:388 (1965).

204. Singleton, J. A., E. Pattee and E. B. Johns. J. Agr. Food Chem. *19*:131 (1971).

205. Pattee, H. E., J. A. Singleton and E. B. Johns. J. Agr. Food Chem. *19*:134 (1971).

206. Kramer, H. A., J. E. Gates, K. D. Damaree and A. P. Sidwell. Food Tech. *17*:1044 (1963).

207. Thomas, M. C., C. M. Lyman, B. C. Langley and V. J. Senn. Food Tech. *22*:1442 (1968).

208. Pattee, H. E. and J. A. Singleton. American Peanut Research and Education Association J. *3*:189 (1971).

209. Dieckert, J. W. and N. J. Morris. J. Agr. Fd. Chem. *6*:930 (1968).

210. Dieckert, J. W., N. J. Morris and A. F. Mason. Arch. Biochem. Biophys. *82*:220 (1959).

211. Applebaum, S. W., S. Marco and Y. Birk. J. Agr. Food Chem. *17*:618 (1969).

212. Reynolds, H., G. L. Gilpin and I. Hornstein. J. Agr. Fd. Chem. *1*:772 (1953).

213. Gilpin, G. L., E. H. Dawson, E. L. Geissenhainer and H. Reynolds. Food Tech. 7:132 (1953).

214. Reynolds, H., G. Gilpin and I. Hornstein. USDA Cir. No. *952* (1954).

215. Wilson, J. K. and R. S. Chondric. J. Agr. Res. *77*:25 (1948).

216. Reimschneider, R. Anz. Schädlingskunde *26*:37 (1953).

217. Hornstein, I., H. Reynolds and G. Gilpin. J. Agr. Fd. Chem. *2*:776 (1954).

218. Gilpin, G., R. A. Redstrom, H. Reynolds and F. W. Poos. J. Agr. Fd. Chem. *2*:778 (1954).

219. Reddy, M. C., D. D. Bills and R. C. Lindsay. Manufacturing Confectioner *49*(9):39 (1969).

220. Bondarovich, H. A., P. Friedel, V. Krampl, J. A. Renner, F. W. Shepard and M. A. Gianturco. J. Agr. Fd. Chem. *15*:1093 (1967).

221. Deck, R. E. and S. S. Chang. Chem. Ind. *1965*, 1343.

222. Goldman, I. M., J. Seibl, I. Flament, F. Gautschi, M. Winter, B. Willholm and M. Stoll. Helv. Chim. Acta *50*:694 (1967).

223. Marion, J. P., F. Muggler-Chavan, R. Viani, J. Bricout, D. Raymond and R. H. Egli. Helv. Chim. Acta *50*:1509 (1967).

224. Rizzi, J. P. J. Agr. Fd. Chem. *15*:549 (1967).

225. Pickett, T. A. and K. T. Holley. Ga. Agr. Expt. Sta. Tech Bul. *1* (1952).

226. Young, C. T., and K. T. Holley. Ga. Agr. Expt. Sta. Bul. N. S. *41* (1965).

227. Ballschmieter, H. M. and P. J. Germishuizen. Fette, Seifen, Anstrichmittel *70*(8):571 (1968).

228. Mason, M. E. and G. R. Waller. J. Agr. Fd. Chem. *12*:274 (1964).

229. Mason, M. E. and B. Johnson. J. Agr. Fd. Chem. *14*:454 (1966).

230. Johnson, B. R. "Chemical Characterization of Roasted Peanut Armoa," Ph.D. dissertation, Oklahoma State University (1970).

231. Johnson, B. R., G. R. Waller and A. L. Burlingame. J. Agr. Fd. Chem. *19*:1020 (1971).

232. Johnson, B. R., G. R. Waller and R. L. Foltz. J. Agr. Fd. Chem. *19*:1025 (1971).

233. Mason, M. E., B. Johnson and M. C. Hamming. J. Agr. Fd. Chem. *15*:66 (1967).

234. Walradt, J. P., A. D. Pittet, T. E. Kinlin, R. Muralidhara and A. Sanderson. J. Agr. Food Chem. *19*:972 (1971).

235. Shu, C. K. and G. R. Waller. J. Food Sci. *36*:579 (1971).

236. Brown, B. A., K. S. Konigsbacher, F. E. Ellison and G. E. Mann. J. Fd. Sci. *33*:595 (1968).

237. Ballschmieter, H. M. B. and A. W. Dercksen. Fette Seifen Anstrichmittel *72*(8):719 (1970).

238. Koehler, P. E. "Formation of Alkylpyrazine Compounds and Their Role in the Flavor of Roasted Foods." Ph.D. dissertation, Oklahoma State University (1969).

239. Koehler, P. E., M. E. Mason and G. V. Odell. J. Food Sci. *36*:816 (1971).

240. Cobb, W. Y. J. Fd. Sci. *34*:466 (1969).

241. Cobb, W. Y. and E. B. Williams. Manuscript in preparation (1973).

242. Buttery, R. G., R. M. Seifert, D. G. Guadagni and L. C. Ling. J. Agr. Fd. Chem. *17*:1322 (1969).

243. French, R. T. Co. Product Data Sheet, Green Bell Pepper Flavor 1, Mustard St., Rochester, New York (1970).

244. Firmenich, E. T. Japanese Patent 5189/67, as in Fd. Tech. *21*:1118 (1967).

245. Roberts, Donald L., R. J. Reynolds Tobacco Co., Winston-Salem, N. C., U. S. Pat. 3,402,051 (1968).

246. Newell, J. A., M. E. Mason and R. S. Matlock. J. Agr. Fd. Chem. *15*:767 (1967).

247. Koehler, P. E., M. E. Mason and J. A. Newell. J. Agr. Fd. Chem. *17*:393 (1969).

248. Wang, P.-S., H. Kato and M. Fujimaki. Agr. Biol. Chem. (Japan) *33*:1775 (1969).

249. Kato, H. and M. Fujimaki. J. Fd. Sci. *33*:445 (1968).

250. van Praag, M., H. S. Stein and M. S. Tibbetts. J. Agr. Fd. Chem. *16*:1005 (1968).

251. Stoffelsma, J., G. Sipma, D. K. Kettenes and J. Pypker. J. Agr. Fd. Chem. *16*:1000 (1968).

252. Powers, J. J., R. J. Cox, M. C. Elland and P. A. Kelly. The Flavour Industry (1971), p. 87.

253. Cobb, W. Y. and H. E. Swaisgood. J. Fd. Sci. *36*:538 (1971).

254. Johnson, A. E., H. E. Nursten and A. A. Williams. Chem. and Ind. (1971), p. 556.

255. Swenson, P. E. and J. H. Martin. J. Dairy Sci. *52*:38 (1969).

256. Pickett, T. A. Ga. Agr. Expt. Sta. Circ. *142* (1943).

257. Holmes, A. D. USDA Bul. *717* (1918).

258. Buss, L. W. and V. R. Goddard. Fd. Res. *13*:56 (1948).

259. Neucere, N. J., R. L. Ory and W. B. Carney. J. Agr. Fd. Chem. *17*:25 (1969).

260. Anantharaman, K. and K. J. Carpenter. J. Sci. Fd. Agric. *22*:412 (1971).

261. Anantharaman, K. and K. J. Carpenter. J. Sci. Fd. Agric. *20*:703 (1969).

262. Bensabat, L., V. L. Frampton, L. E. Allen and R. A. Hill. J. Agr. Fd. Chem. *6*:778 (1958).

263. Pickett, T. A. Ga. Agr. Expt. Sta. Cir. *146* (1944).

264. Fournier, S. A., J. F. Beuk, F. W. Chornock, L. C. Brown and E. E. Rice. Food Res. *14*:413 (1949).

265. French, R. B., O. D. Abbott and R. O. Townsend. Fla. Agr. Expt. Sta. Bul. *482* (1951).

266. Willich, R. K., M. D. Murray, R. T. O'Connor and A. F. Freeman. Food Tech. *6*:199 (1952).

267. Dunn, K. R. and V. Z. Goddard. Fd. Res. *13*:512 (1948).

268. Pickett, T. A. Peanut J. and Nut World *25* (March) :25 (1946).

269. Higgins, B. B,. K. T. Holley, T. A .Pickett and C. D. Wheeler. Ga. Agr. Expt. Sta. Bul. *213* (1941).