Effects of Storage Time and Conditions on Peanut Volatiles

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Quantitative changes in the volatiles of unshelled peanuts stored under simulated warehouse conditions and of shelled peanuts stored under controlled environmental conditions have been determined using gas-liquid chromatography. Under both storage conditions, total volatile content reached a maximum after 90 to 120 days of storage and then declined. The largest quantity of volatiles was found in peanuts stored under the simulated warehouse storage conditions. Three compounds—pentane, acetaldehyde, and methanol—accounted for 80 to 98% of the volatiles present and were primarily responsible for the changes found in the total volatile pattern during the storage period. Lipoxidase and pectin methyl esterase are discussed as enzymes possibly responsible for the production of these volatiles.

Peanuts are considered semiperishable. They may be held up to 5 years under optimum conditions, but under unsuitable storage conditions become inedible within a month due to mold, insects, discoloration, absorption of foreign flavors, staleness, or rancidity (Woodruff, 1966). All peanuts which are processed into peanut products pass through a storage period which may vary from a few weeks to over a year. The affect and value of this storage period seems to be open to some question among peanut processors. Some processors in the peanut industry have suggested that peanuts which have been mechanically cured do not have the same flavor potential as those which have been field-cured on stackpoles. Cecil (1969) indicated that this lack of flavor potential could be overcome by storage for 4 to 6 months. He conducted taste-panel evaluations on freshly shelled, mechanically dried and stack-cured peanuts and found a preference for the stack-cured sample. From this he suggested that a minimum "aging" period may be required for development of the "typical" cured flavor. Peanuts in the stack-cured sample by Cecil had a somewhat higher free fatty acid value than the mechanically cured sample, and roasting tests showed they were also higher in volatile carbonyls and volatile sulfur compounds (Young and Holley, 1965).

Woodruff (1966) indicated that peanuts are generally at a quality peak when they go into storage. However, Woodruff's definition of quality does not consider such factors as roasting-flavor potential. How well the initial quality level is maintained depends upon storage conditions. Woodruff and Heaton (1961) found that peanuts placed in refrigerated storage as soon as properly cured were more suitable for long-term storage than those held at variable temperatures during the winter and placed in refrigerated warehouses in the spring.

Although studies have been conducted on the volatiles of roasted peanuts (Mason *et al.*, 1966; Young and Holley, 1965), changes in the raw peanut volatiles during maturation (Pattee *et al.*, 1970a), and on the effect of curing temperature on the volatiles of raw peanuts (Pattee *et al.*, 1965; Singleton *et al.*, 1970), little if any information is available on the changes which take place in the volatiles of peanuts during storage. However, work has been conducted on the effect of storage on several fruits and vegetables in both the raw and processed forms. Norman *et al.* (1967) studied the volatiles emanating from injured and uninjured oranges at different holding temperatures and suggested that care must be used in interpreting the aromagrams as a complete objective measurement of quality. Bengtsson and Bosund (1964) studied the formation of volatiles in stored peas and suggested that enzyme-catalyzed reactions were responsible for major volatile changes and that hexanal could be used as an indicator of off-flavor development in cooked peas. Storage effects on the volatiles of apples were studied by Angelini and Pflug (1967) and Brown *et al.* (1968), while Nelson and Hoff (1969) studied the effect of variety, processing, and storage time on tomato volatiles. All of these studies have in common the assessment of quality through analysis of volatiles and the determination of volatile changes as a means of understanding the mechanism by which quality is affected.

The purpose of this study was to determine changes both qualitative and quantitative in the volatiles of stored peanuts and to accumulate information on the variables which would influence the use of the peanut volatile profile as a quality indicator for raw peanuts. The conditions selected represent the two major storage conditions to which peanuts are subjected between harvesting and processing.

EXPERIMENTAL PROCEDURE

Sample Treatment. Freshly harvested peanuts (Variety NC-2) were cured for good quality according to the procedures recommended by Beasley and Dickens (1963). The moisture content at the end of curing was approximately 6%. Immediately after curing, a 50-lb sample was placed in a 55-gal drum with the top removed. A small-mesh wire screen was placed on the top of the drum to keep out small animals. The drum of unshelled peanuts was placed in an isolated, partially enclosed shelter to simulate warehouse storage and avoid extraneous volatile contamination. A third sample, of sufficient size to provide duplicate analyses, was shelled and analyzed within 7 days; until analysis the sample was kept at 45° F and 60% RH.

Stored peanuts were sampled after 45, 90, 120, and 195 days of storage. Samples were drawn on the day of analysis and 10 days were required for a sampling-analysis cycle.

Preparation of Samples of Glc and Mass Spectral Analysis. Volatiles were collected for glc and mass-spectral analysis by subjecting a slurry, consisting of 500 g of peanuts and 1 l. of distilled water, to a vacuum of 5×10^{-3} Torr for 3 hr with a distilling-pot temperature of 25° C. Volatiles were collected in a trap cooled with liquid nitrogen (−196° C). To minimize enzymatic formation of volatile components during grinding and vacuum-extraction procedures, certain precautionary measures were used. Peanuts were separated into five 100-g lots which were ground individually in a small blender for 1

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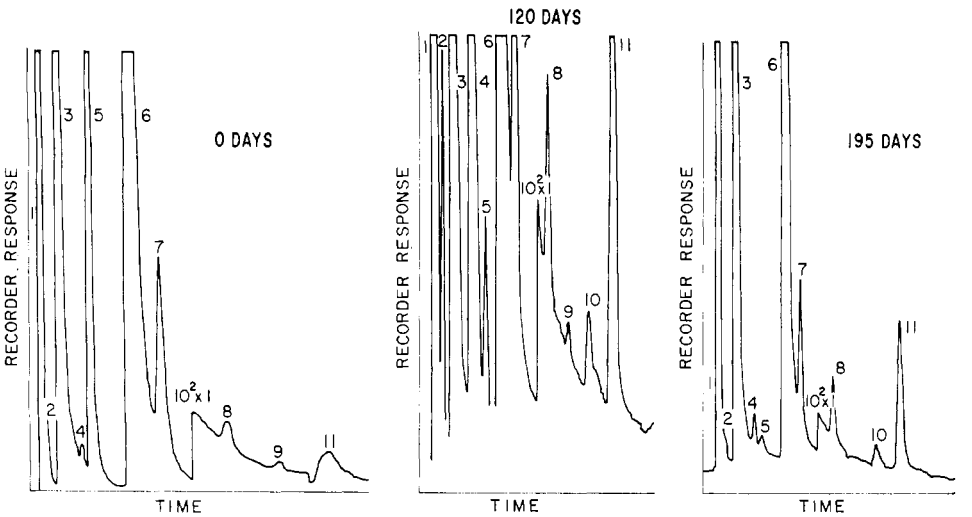

Figure 1. Influence of warehouse storage on the volatile profile of unshelled peanuts

min. After grinding, the five 100-g samples were immediately placed into the distilling pot which had been previously evacuated and flushed with nitrogen. Duplicate distillations were made for each storage treatment and subsequent glc analysis. A previous paper describes the apparatus and techniques used, along with the incorporated modifications (Pattee *et al.*, 1970a).

Volatile components were separated on a Micro-Tek 2000R Research gas chromatograph equipped with dual flame ionization detectors. Columns and the operating parameters were as follows: a $^1/_8$ in. × 12 ft stainless steel column packed with 15% Carbowax 20M on 60 to 80-mesh acid washed DMCS treated Chromosorb W and programmed from 70° to 140° C at 2° per min, a $^1/_4$ in. × 6 ft stainless steel column packed with 60 to 80-mesh Chromosorb 102 programmed from 125° to 200° C at 2° per min. These two columns differ greatly in degree of polarity.

Identification of the volatile components was confirmed by mass spectral analysis using a Time-of-Flight mass spectrometer (Pattee *et al.*, 1969).

Volatile Profile Data Collection and Analysis. Aroma profiles were integrated using a digital readout system. Output from the glc electrometer was fed directly into the integrator, and the retention times and their corresponding peak areas were punched onto paper tape by a Teletypewriter paper-tape-punch system. Data were read from the paper tapes by a paper-tape reader and stored in a computer. Techniques for collection, storage, and computer handling of the data are described elswhere (Pattee *et al.*, 1970b).

RESULTS

Typical chromatograms of volatiles from unshelled peanuts stored under simulated warehouse conditions illustrate the quantitative changes which occurred during the storage period (Figure 1). Similar chromatographic patterns were found for the shelled peanuts stored at 45° F and 60% RH. Components identified in this study are listed as follows with the respective peak number as shown in Figure 1: (1) pentane, (2) ethyl ether, (3) acetaldehyde, (4) methyl formate, (5) acetone, (6) methanol, (7) ethanol, (8) pentanal, (9) chloroform, (10) unknown, and (11) hexanal. Ethyl ether and chloroform are contaminants in the system.

Total volatile content of peanuts stored under both conditions peaked between 90 and 120 days (Figure 2); however, storage conditions did influence the total amount of volatiles present at any given sampling period. The increase in total

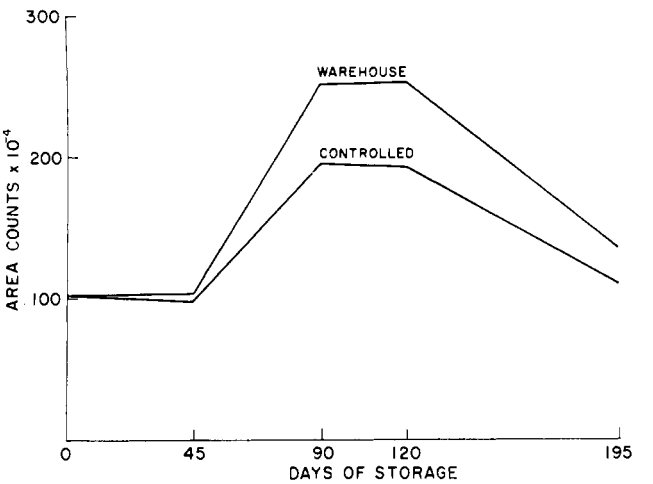

Figure 2. Changes in the total volatile content of peanuts stored under simulated warehouse (unshelled) and controlled (shelled) conditions

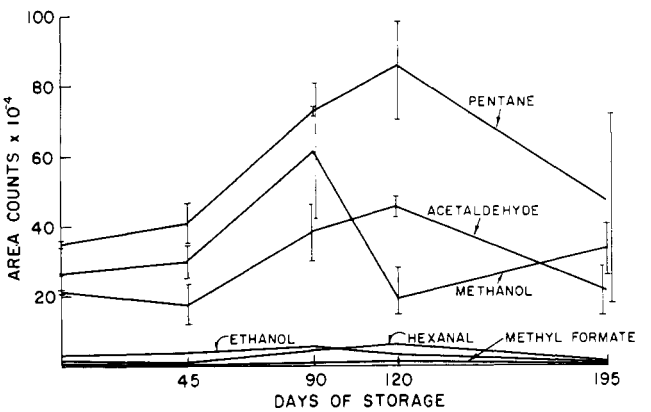

Figure 3. Effect of controlled storage on the major peanut volatiles

volatile content is largely accounted for by the increase in pentane, acetaldehyde, and methanol (Figures 3 and 4). These three components accounted for 80 to 98% of the volatiles isolated, and pentane and acetaldehyde together accounted for 55 to 75%. The results and chromatograms given are from the second crop year of a 2-year study. Lack of an integrator during the first crop year prohibits combining

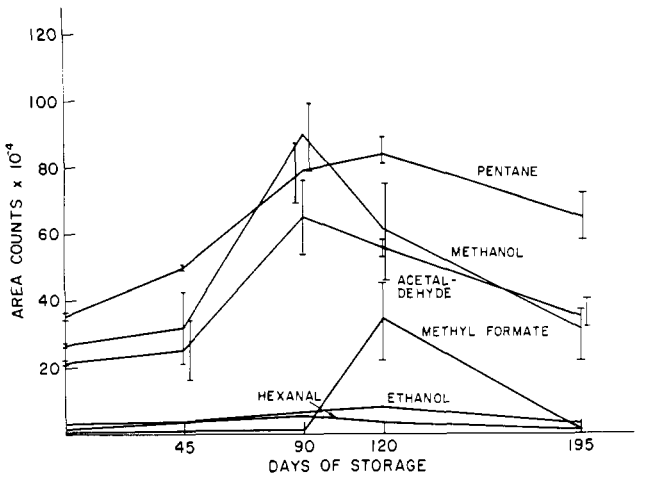

Figure 4. Effect of simulated warehouse storage on the major peanut volatiles

the data. However, the general trends for total volatiles and individual components for the first crop year were the same as the results given.

Under controlled conditions fluctuations of pentane and acetaldehyde were generally similar, while methanol underwent a substantial loss between 90 and 120 days of storage (Figure 3). While the degree of loss of methanol between 90 and 120 days may not be significant, its maximum at about 90 days is supported by the data from the warehouse storage conditions (Figure 4). Under warehouse storage conditions, similarities exist between the respective patterns for acetaldehyde and methanol. Acetaldehyde is also noted to reach its maximum at 90 days rather than at 120 days, as found under the controlled storage conditions. The pattern for pentane is similar under both storage conditions. However, the amount present at 195 days is somewhat greater under the warehouse storage conditions.

Ethanol and hexanal underwent two- and three-fold changes but did not exert a major influence upon the total volatile pattern. However, because hexanal has been reported to be the "backbone" component of raw peanut flavor (Pattee *et al.*, 1969), these changes could influence peanut flavor significantly.

The methyl formate content of peanuts in storage was generally less than 0.5% of the total volatiles, but between 90 and 120 days of warehouse storage methyl formate markedly increased to nearly 14% of the volatiles isolated (Figure 4). Immediately after this observation on the chromatograms, mass spectral analysis confirmed that the component responsible for this increase was indeed methyl formate. This substantial increase in methyl formate in the warehouse stored peanuts was found in both crop years of this study. The mechanism by which this increase occurs is not known. However, it is characteristic of our climatic conditions to undergo a warming trend during this time period. This change may have been responsible for activating the factors responsible for the methyl formate production, and also explain why a substantial change was observed under warehouse storage conditions.

Under controlled environment conditions at 0 time, acetone accounted for about 12% of the volatiles present. Early in storage this value dropped to about 3.5, increased to 6.2 at 120 days, and dropped to 2.2% at 195 days. The amount found under warehouse conditions at all times was approximately one-seventh of the values found for controlled conditions. The pentanal content was nearly constant at about 0.2% under all conditions except for an increase to 0.8% at 120 days under controlled storage conditions.

DISCUSSION

Although the conditions for maintaining peanuts at a quality peak in storage have been specified (Woodruff, 1966), very little is known concerning changes in the volatiles under optimum controlled-environment conditions or under uncontrolled warehouse storage. This paper shows that significant changes do occur in the volatiles with storage time and that storage conditions do affect the quantities of the volatiles present.

Peanut volatiles are thought to arise through two principal mechanisms: autoxidative and enzymatic. Autoxidation may give rise to carbonyls, hydrocarbons, and esters (Ellis *et al.*, 1968; Hawkins *et al.*, 1968). Hawkins *et al.* (1968) reported methyl formate, pentane, acetone, pentanal, and hexanal among other compounds as products of autoxidation of methyl linoleate with a peroxide value of 100 to 150. The above mentioned components are of interest here since most of them are present in the peanut volatile profile. The relative percentages generally found for methyl formate, acetone, pentanal, and hexanal indicate, however, that the degree of autoxidation was very low. The amount of autoxidation could be limited, primarily by two factors—oxygen diffusion rate into the peanuts and temperature of storage. Although no direct information is available on oxygen diffusion rates into dried peanuts, the rapidity with which they rancidify at room temperature suggests that oxygen is not the limiting factor and that storage temperature is primarily responsible for limiting the rate of autoxidation in this study.

Enzyme reactions do occur in low-moisture seeds (Acker, 1962a,b; Blain, 1960). Acker (1962b) has indicated these reactions are mainly hydrolyses, but oxidations involving lipoxidase and phenoloxidase are known to occur. When considering changes produced by endogenous enzymes, the possibility of microbiological production must be eliminated. In our study this was done by using a seed moisture content below 10% and a relative humidity of 65% (Acker, 1962a). Although the warehouse conditions could not be controlled, there were no extended periods of high relative humidity, *i.e.*, above 75%.

We previously suggested that changes found in the volatile profile of peanuts with increasing maturity could be related to changes in the activity of lipoxidase and alcohol dehydrogenase (Pattee *et al.*, 1970a). Lipoxidase activity was related to changes in pentane and hexanal, while alcohol dehydrogenase activity was related to changes in acetaldehyde and ethanol. Johns and Pattee (1968) also showed that curing increases the level of extractable lipoxidase in peanuts. This suggests that lipoxidase is more available for metabolic activity in cured mature than in the green, mature peanuts.

Methanol production in plant tissues is thought to arise by the action of pectin methyl esterase on methylated pectins (Reed, 1966). Although pectin methyl esterase has not been demonstrated in peanuts, this must be considered as a possible source of methanol.

Since acetaldehyde, pentane, and methanol can arise as products of lipoxidase and pectin methyl esterase activity, and because these compounds constitute 80 to 98% of the total volatiles present, these enzymes might be primarily responsible for the changes in the peanut volatile profile during storage.

Lipoxidase in peanuts is found in the soluble fraction

(Johns and Pattee, 1968; Siddiqui and Tappel, 1957). In pears, apples, and cherries, most of the pectin methyl esterase is firmly bound to the cell wall (Davignon, 1961), while in oranges there are both free and bound forms (Jansen *et al.*, 1960). Although the functioning sites of these enzymes within the cell are not known, it is significant that the primary sources of substrate for the enzymes are at the interfaces of the spheresomes and cytoplasm for lipoxidase, and cell wall and cytoplasm for pectin methyl esterase. Because there are also the sites of bound water and films of water several layers thick (Craft, 1968), an aqueous environment necessary for the functioning of these enzymes could be present. Acker (1962b), using the relationship between sorption isotherms and phospholipase B activity levels, also has suggested that the enzymatic activity in dried material occurs in the capillary regions of the material where water can be readily absorbed or bound.

Other workers have indicated that the volatile profile of fruits and vegetables may be used as a quality indicator (Aylward and Haisman, 1969). Singleton *et al.* (1971) have shown that qualitative changes occur in the volatile profile of peanuts during curing at selected temperatures and that these changes may be related to high-temperature curing off-flavor. Results of this study show that the volatiles of peanuts during storage exhibit primarily quantitative rather than qualitative changes. The appearance of other volatile components might suggest poor quality, improper curing and handling processes, or contaminating substances. Quantitative changes in the volatile profile during storage of peanuts as related to quality have not been determined, but they may be a reflection of metabolic processes which affect flavor quality of raw peanuts and their roasting potential.

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