discrepancy between the two methods, it is recommended that method II be used in conjunction with method I, and not as the sole determinant of digestibility.

The *in vitro* digestibility data in the present study provided a criterion for evaluating the relative digestibility of stored soybean LPC. Although Buchanan (1969a) showed favorable agreement between papain digestibility and true digestibility, the recent report of Saunders *et al.* (1973) advises that values obtained by papain digestibility are poorly correlated with *in vivo* data. It is of interest that the values obtained by Saunders *et al.* (1973) were considerably lower (in general, 40–60% digestible) than values reported by the authors and others (Buchanan, 1969; Byers, 1971). Since there are conflicting reports regarding the correlation of papain digestibility with *in vivo* digestibility, *in vitro* digestibility by papain should be viewed as providing comparative data within experiments, but should not be viewed as having direct implications for *in vivo* digestibility.

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Parameters Affecting the Binding of Volatile Flavor Compounds in Model Food Systems. I. Proteins

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The binding of a homologous series of aldehydes and methyl ketones by various food proteins was studied in model systems by headspace analysis using gas chromatography. The amount of flavor bound depended on the type, amount, and composition of the protein, and the presence of solvents such as water and lipids. The addition of water to proteins, *i.e.*, α-lactalbumin, bovine serum albumin, leaf protein concentrate, single-cell protein, and various soy protein preparations, decreased the volatilities *via* increased adsorption or solubilization of flavors by the protein–water mixture. The concentration of headspace volatiles in model systems containing flavor and leaf protein concentrate increased upon removal of lipids. Flavor binding by the concentrate, isolate, and textured forms of soy protein was influenced by their compositions. The effect of proteins on volatility was similar in systems containing either dilute or concentrated flavors.

The problem of flavoring foods, excessive flavor binding by specific food components, and loss of flavor is assuming increasing importance because of the growing use of fabricated foods. Desirable organoleptic qualities are required for the eventual large scale utilization of new food proteins including leaf proteins, single-cell protein, and fish protein concentrate. In developing artificial flavoring systems and modifying or enhancing natural ones, a knowledge of the parameters influencing flavor volatility, binding, and the interaction of flavoring compounds with different food constituents is necessary.

Foods are complex mixtures of proteins, carbohydrates, lipids, water, and other organic compounds which can interact with and bind flavors. Nawar (1966) listed the factors affecting the headspace concentration of a volatile flavor compound, *i.e.*, vapor pressure and temperature, type of medium, degree of solubility, concentration, miscibility with other organic compounds, and the presence of salts or sugars. Sodium chloride increased the volatilities of dilute ester solutions (Jennings, 1965), and saturated aqueous sodium sulfate solutions increased the vapor pressures of aldehydes, ketones, esters, and alcohols (Nelson and Hoff, 1968). Unlike salts, carbohydrates and proteins either increase or decrease the volatility of flavor compounds. Wientjes (1968) found that the addition of glucose, sucrose, fructose, or invert sugar to dilute aqueous flavor solutions increased the volatility of a number of compounds while it decreased the volatility of other compounds. Sucrose increased the headspace volatility of aqueous acetone solutions; however, it decreased the volatility of 2-heptanone and heptanal solutions (Nawar, 1971). Maier (1970) investigated the influences of casein, gelatin, ovalbumin, and various carbohydrates on the headspace concentrations of acetone, ethanol, acetalde-

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Table I. Components of Dilute Flavor Model Systems

Vial 1	Control, 200 ppm of flavor in oil (a 0.5-ml aliquot of a standard flavor solution)
Vial 2	Control + 20 mg of α-LA
Vial 3	Control + 20 mg of BSA
Vial 4	Control + 0.5 ml of water
Vial 5	Control + 0.5 ml of water + 20 mg of α-LA
Vial 6	Control + 0.5 ml of water + 20 mg of BSA

hyde, ethyl acetate, and diethyl ether. These solids increased the headspace responses of some of the flavors, but decreased those of others. Significantly, Nawar (1971) found that the effect of aqueous solutions of sucrose, gelatin, and glycerol on the headspace volatilities of methyl ketones was influenced by the order of addition of the ingredients of the model systems.

Because of the increasing use of novel and refined proteins and because of the paucity of information concerning the effects of novel food protein on flavor compounds, the interaction of some common carbonyl flavor compounds with several food grade proteins was studied in an attempt to define reaction conditions which minimize flavor binding in foods. The binding of homologous series of aldehydes and methyl ketones by α-lactalbumin, bovine serum albumin, leaf protein concentrate, single-cell protein, and some of the different forms of soy protein was investigated in model systems. Gas chromatography was used to quantify flavor concentration in the headspace above these model systems.

EXPERIMENTAL SECTION

Materials. Pure aldehydes and methyl ketones were obtained from Eastman Organic Chemicals (Rochester, N. Y.) and Aldrich Chemical Co., Inc. (Milwaukee, Wis.). Several proteins were used: α-lactalbumin (α-LA) (Nutritional Biochemicals, Cleveland, Ohio); bovine serum albumin (BSA), crystallized and lyophilized (Sigma Chemical Co., St. Louis, Mo.); alfalfa leaf protein concentrate (LPC) prepared by the technique of Betschart and Kinsella (1973); single-cell protein (SCP) extracted from yeast (*Saccharomyces fragilis*), grown on deproteinized whey (Vananuvat and Kinsella, 1973); soy protein concentrate (Griffith Lab, Inc., Chicago, Ill.); soy protein isolate (Promin D, Central Soya, Chicago, Ill.); and beef-flavored textured vegetable protein (TVP) (Swift Co., Chicago, Ill.).

Gas Chromatography. Flavor volatiles were separated using a Perkin-Elmer Mk II gas chromatograph (Model F11) equipped with a flame ionization detector and a Speedomax W recorder. A coiled glass column (6 ft × 4 mm i.d.) packed with 15% Apiezon L on Gas Chromosorb P (Applied Science, State College, Pa.) was used to quantify the carbonyls in the headspace samples. A column temperature of 225° and a detector temperature of approximately 230° were maintained. The flow rates of the nitrogen carrier gas, hydrogen, and air were 38.5, 38.5, and 300 ml/min, respectively. Peaks were quantified by triangulation.

Chromatographic response was calibrated using a standard solution of each flavor. The headspace peak area ratio is the ratio of the peak areas in square millimeters of the experimental treatment and the appropriate control.

Methods. The model systems were contained in cone-shaped glass reaction vials (5 ml) (Regis Chemical Co.) sealed with silicone rubber septa and screw caps. The reaction mixtures were agitated at 25° for 1 min by a mechanical shaker before sampling. Fifty-microliter headspace samples were withdrawn from the sealed vials and injected into the gas chromatograph using a gas-tight Hamilton glass syringe. Controls, used in every experiment, lacked the protein.

To measure the effects of moisture on flavor volatility, 1 ml of distilled water was added to reaction vials containing 0.2 ml of flavor and 40 mg of each of the proteins (α-LA, BSA, LPC, SCP, and soy) studied. The effects of fat were observed by adding 1 ml of corn oil to the model systems containing 0.2 ml of flavor and 40 mg of α-LA or BSA. In addition, the effects of endogenous lipids were studied by measuring changes in headspace response following extraction of lipids with acetone.

A solution (200 ppm) of each volatile compound was prepared to study the effects of water and protein on the headspace volatility of dilute flavor systems. The protocol, summarized in Table I, was repeated for each flavor compound.

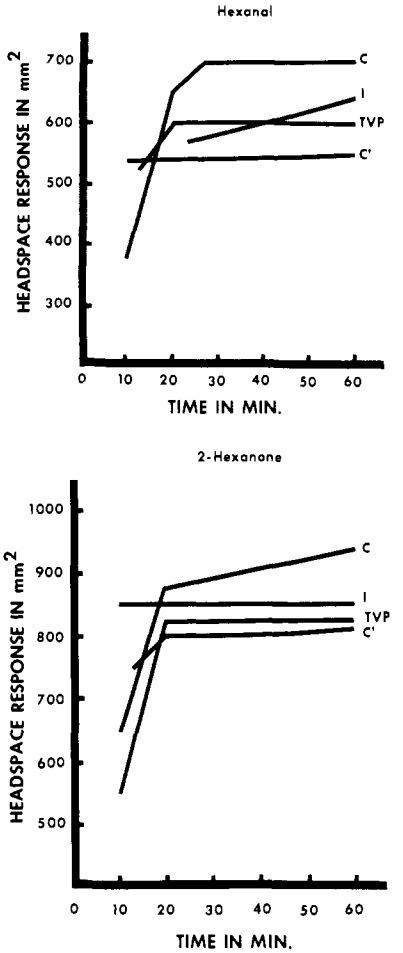

Figure 1. The headspace responses of hexanal and 2-hexanone in model systems containing water and different forms of soy protein. The treatments are denoted by C = control, I = isolate, TVP = textured vegetable protein, and C′ = concentrate.

RESULTS

Equilibration of the headspace concentration was attained after 20 min following agitation for 1 min at 25° (Figure 1). This equilibration time was repeatedly observed for all of the model systems; hence, only the data from the model systems containing various soy protein forms are used as an example.

The addition of protein to model systems containing water and flavor consistently caused a decrease in the concentration of headspace volatiles (Table II). The effect varied with each protein and flavor compound, and no consistent magnitudes of flavor release or binding were observed. The soy protein bound most of the six flavor compounds, and the magnitude was influenced by the composition of the soy proteins. The amount of flavor bound by the isolate and TVP was similar since they do not contain preponderant amounts of carbohydrates and

Table II. Effects of Different Proteins and Moisture on the Headspace Peak Area Ratios of Various Carbonyls

Flavor compd	Ratio of headspace response (treatment[a]/control) for protein						
	α-LA	BSA	LPC	SCP	Soy isolate	TVP	Soy concn
Hexanal	0.78	0.79	0.77	0.89	0.90	0.91	0.79
Heptanal	0.90	0.92	0.90	0.79	0.95	0.98	0.92
Octanal	0.78	0.67	1.08	1.11	0.88	0.80	0.96
2-Hexanone	0.82	0.89	1.05	1.03	0.92	0.91	0.89
2-Heptanone	0.86	0.90	0.98	0.99	1.07	0.96	0.95
2-Octanone	0.99	1.10	0.92	0.74	0.74	0.83	0.79

[a] The control lacked the protein being studied.

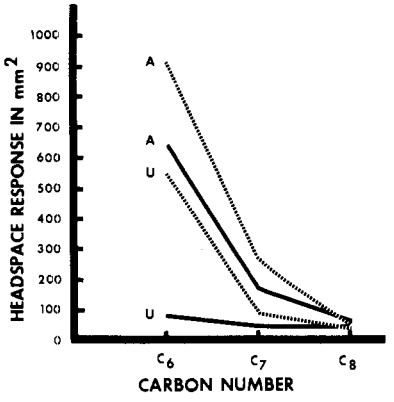

Figure 2. The headspace responses of the carbonyls in model systems containing leaf protein concentrate and acetone-treated leaf protein concentrate. The untreated LPC is denoted as U and the acetone-treated LPC as A: (—) aldehydes; (- - -) methyl ketones.

fats that bind flavors. Soy concentrate bound the most flavor because it contains 70% protein and 20% carbohydrate. Examples of the magnitude of binding of hexanal and 2-hexanone by the various soy proteins are shown in Figure 1.

The reduction in headspace volatility in the aqueous model systems is most likely attributed to surface area phenomena. In the presence of water, the surface areas of the protein–flavor mixtures were reduced, and volatilities were reduced. The proteins apparently aided solubilization of the flavor in water although they did not contain lipophilic agents. Less flavor floated on the aqueous surface and more bound to the protein so volatility decreased.

The effect of endogenous lipids on flavor binding was exemplified using LPC. Removal of lipids, *i.e.*, 20–30% of LPC, increased the concentration of volatiles in the headspace presumably because of the reduced binding of the lipophilic carbonyls to the protein (Figure 2).

Unlike the aqueous systems, the addition of α-LA or BSA to vials containing flavor and corn oil did not produce binding of all of the flavors (Table III). This was probably the result of lower volatility of the flavor in oil or of lower solubility of the protein in the oil.

Because the total flavoring content of foods is between 1 and 1000 mg/kg (Maier, 1970), the effect of proteins, *i.e.*, α-LA and BSA, on the volatility of dilute (200 ppm) flavor solutions in corn oil was investigated (Table IV). The headspace responses were greater than those of the controls for hexanal, heptanal, and 2-heptanone upon the addition of α-LA and BSA to reaction vials containing the volatile flavor compound in corn oil. This was attributed to an increase in volatile surface area as the protein–flavor mixture coated the sides of the vials. The addition of water to these systems decreased the headspace responses by decreasing the surface area and solubilizing the flavor with the protein. Hence, the behavior of the protein and water was essentially the same in both concentrated and dilute model systems although the individual magnitudes of flavor release or binding were different in both systems.

Table III. Effects of Oil and Proteins on the Headspace Peak Area Ratios of the Carbonyls

	Ratio of headspace response for	
	α-LA	BSA
Hexanal	1.19	1.12
Heptanal	0.94	1.06
Octanal	0.83	0.92
2-Hexanone	1.11	1.19
2-Heptanone	0.98	0.87
2-Octanone	0.83	1.06

Table IV. Effects of Proteins on the Headspace Peak Area Ratios of Dilute Carbonyl Solutions in Various Model Systems

Flavor compd	Protein		Protein + water	
	α-LA	BSA	α-LA	BSA
Hexanal	1.08	1.14	1.06	0.98
Heptanal	1.08	1.12	0.65	0.60
Octanal	0.90	0.90	0.79	0.59
2-Hexanone	0.89	0.83	0.89	0.81
2-Heptanone	1.14	1.07	0.83	0.97
2-Octanone	0.91	0.97	1.01	1.11

DISCUSSION

Many factors affect the flavor of a food and the intensity of its perception (Kinsella, 1969). These include flavor volatility (*i.e.*, molecular weight and structure), antagonism and synergism between the flavor compounds per se, and interactions of the flavors with various food components such as carbohydrates, lipids, and salts. In addition, the present data reveal that protein–water and protein–lipid mixtures affect the volatility of common food flavors. In order to enhance or change the flavor response, either the flavor or its carrier can be modified. However, the quality and intensity of a flavor change when its chemical structure is altered; hence, it may be more expeditious to manipulate the carrier substrate in order to control flavor volatility.

The effects of proteins on the headspace volatilities of the carbonyls observed in these studies are in keeping with the findings of Maier (1970) and Nawar (1971). The proteins decreased the concentration of headspace volatiles in aqueous systems. The proteins showed no consistent or predictable effects with regard to the magnitude of flavor binding, and no one flavor was preferentially bound by all of the proteins. Thus, the flavor–protein interactions depend on the protein source, the flavor compound, the presence of moisture, and the presence of endogenous components (lipids) or contaminants. If these parameters are carefully controlled, it may be possible to predict flavor release or binding in fabricated foods and also alter these parameters so that the optimum flavor re-

sponse is achieved. The effects of moisture on flavor release are especially critical in drying operations (Flink and Karel, 1972; Flink and Labuza, 1972; Rulkens and Thijssen, 1972a,b) and in the development of intermediate moisture foods. In addition, flavor microencapsulation techniques would benefit from a knowledge of these interactions.

The observed results are attributed to surface area and solubility effects, but they could be the result of molecular interactions between the flavor and the protein. Hence, flavor binding by protein in these model systems merits further study. Lipids and carbohydrates bind flavors (Maier, 1970; Nawar, 1966, 1971) which was demonstrated in this work by the direct correlation between the magnitudes of flavor binding by the various soy protein forms and their carbohydrate and lipid compositions. The headspace volatility of the flavors also increased upon the removal of the lipids from the LPC. The proteins did not bind the carbonyls in the corn oil solvent. This could be the result of the solubility of the lipophilic flavors in the oil so that they were less accessible to the protein whose solubility in oil was reduced compared to that in water.

Thus, in this study the effects of protein on the headspace volatilities of aldehydes and methyl ketones depended upon the amount, type, and composition of the protein, and the presence of solvents such as water and lipids. These results, however, should be more precisely quantified to aid in establishing the molecular mechanisms of flavor release or binding by proteins.

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Composition and Nutritive Value of Cashew Nut to the Rat

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The proximate composition, amino acids, and protein quality of good grade and discarded cashew nut meals were studied. The crude protein in both sources was high and on oil extraction produced meals with comparable protein levels to those of peanut and soybean meals. The total amount of sulfur amino acids in the good grade meal was higher than in soybean, while these amino acids in both meals were higher than in peanut. The lysine and threonine levels were, however, lower than in soybean but comparable to those in peanut. The good grade meal was better digested and showed superior quality to the discarded kernel meal. Rats fed the good grade meal did not respond to methionine supplementation, but showed significant response to lysine, indicating an adequacy of the sulfur amino acids but a low available lysine level. Lysine but not methionine supplementation significantly improved the quality of the discarded kernel meal.

The desire for improved animal productivity, as well as better nutrition of the vast and fast-increasing population of the tropical and sub-tropical areas of the world, has given considerable impetus to evaluatory tests aimed at finding uses for some of the minor oilseeds and oilseed residues, quite distinct from the soybean, peanut, and cottonseed, which have long attained commercial importance, and for which nutritive values are fairly well documented. The cashew nut (*Anacardium occidentale*) is one oilseed with great potential and increasing commercial value, capable of joining the ranks of those mentioned above. The processing of the raw nut is now being carried out in many of the producing countries. In many of those only 60–65% are of commercial value while 35–40% of the nuts reaching the factory would be discarded either as broken kernels or as kernels scorched in the roasting process.

There has been limited work done on the nutritional qualities of cashew nuts. One study (Piva *et al.*, 1971) showed the extracted meal of some Tanzanian commercial grade kernel to be of high nutritive value and comparable to soybean meal. The work reported here was carried out to evaluate the discarded broken and scorched nuts in comparison with the good grade nuts, bearing in mind that while the good grade nuts and their extraction meal may find use in human nutrition, the discarded nuts could be a cheap source of protein in livestock feeding.

EXPERIMENTAL SECTION

Two grades of cashew nut meals were employed in these studies. A good grade kernel meal and a discarded kernel meal were both obtained as the unextracted kernels from the Western Nigeria Development Corporation (WNDC) processing factory in Ibadan, Western Nigeria. The processing treatment at the factory involved roasting of the whole nuts for 90 sec in cashew nutshell liquid (a caustic, vesicant liquid, primarily made up of mono- and dihydroxyalkylbenzenes and alkylphenolic acids (Kaufmann and Barve, 1967) obtained from the spongy mesocarp of the cashew nutshell) at 185°. The nuts were then cracked and the kernels dried at 105–110°. Manual peeling and final roasting in peanut oil for 5 min was carried out. Following roasting at 185°, in cashew nutshell liquid, the nuts that were scorched or heat damaged were separated from the undamaged nuts. The kernels from the scorched nuts together with broken pieces of the good grade kernel

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