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Characterization of Poultry Byproduct Meal Flavor Volatiles

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The vacuum distillate of poultry byproduct meal (PBPM), a pet food ingredient, has been analyzed by WCOT glass capillary gas–liquid chromatography–mass spectrometry. A total of 41 components were identified in this volatile oil. Major components were hexanal, 3-octen-2-one, 1-pentanol, pentanal, heptanal, octanal, 1-heptanol, 1-octanol, and 1-octen-3-ol. Other important odor compounds were 2-(*n*-pentyl)furan, 3,5-octadien-2-one, 3,5-undecadien-2-one, and 2-octenal. These compounds contribute to the notes characteristic of PBPM which may play a role in the acceptance of PBPM-containing pet foods by pet and pet owner.

Poultry byproduct meal (PBPM) is a relatively inexpensive protein source that was first reportedly used in pet foods by Morris (1946) and in the diets of other fur-bearing animals by Bassett and Wilke (1948). It is also used in poultry diets as described by Potter and Fuller (1967). PBPM is prepared out of head, legs, viscera, feathers, lungs, etc. which are waste materials of poultry processing plants. The processing and utilization of PBPM have been the subject of reviews by Rao and Mahadevan (1976) and McNaughton et al. (1977a,b).

The composition of PBPM has been reviewed by McNaughton et al. (1977a) and Doty (1969). These authors found PBPM to contain 54–63% protein, 14–25% crude fat, and 6–11% moisture. Amino acid composition studies indicated that glutamic acid and aspartic acid were the most abundant amino acids. Most of the sulfur amino acids were in the form of methionine and cystine. The flavor chemistry of PBPM or other meat by products which are utilized in pet foods has not been reported in the literature. This is in contrast to the flavor chemistry of prime meats which are used in human consumption and to a limited extent in pet foods. For example, studies of the flavor chemistry of prime meats have been reviewed by Dwivedi (1975) and more recently by Wasserman (1979) and Shibamoto (1980). The flavor of specific meats such as chicken have been reviewed by Wilson and Katz (1972).

It is the objective of this study to identify key flavor components in PBPM. A discussion of how these PBPM components may be formed and how they differ from volatiles of prime meats which have been reported on in the literature will also be presented.

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EXPERIMENTAL SECTION

Materials. PBPM was obtained from a major supplier (Rockingham Poultry Market Cooperative Inc., Broadway, VA). The meal was refrigerated within 1 week after purchase. The PBPM was used "as is" during the isolation procedures.

Authentic chemical reference compounds were obtained from reliable commercial sources (e.g., Aldrich Chemical Co. and Alpha Chemical Co.).

Isolation of the Volatile Flavor: Vacuum Degassing. The volatile flavor components were isolated from a total of 28 lb of Rockingham Poultry By Product Meal by using a vacuum degassing technique.

Each isolation involved degassing 1600 g of poultry byproduct meal at room temperature with a pressure of 0.02 mmHg and collecting the volatiles in a series of coiled traps as those described by Chang et al. (1977) which were immersed in dry ice–2-propanol. At the end of 6 h the volatiles were taken up in diethyl ether. The ether was dried over anhydrous sodium sulfate, concentrated to 0.5 mL by using a Kuderna-Danish concentrator, and concentrated to a final volume of 0.3 mL under a nitrogen stream.

Capillary GLC–Mass Spectral (GLC–MS) Analysis. The two GLC columns used were 50 m × 0.50 mm i.d. Pyrex WCOT glass capillary coated with SE-30 or OV-225. A number of different GLC-MS runs were made with the two columns by using a Hewlett-Packard 5840A gas chromatograph.

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Table I. Compounds Identified in Volatile Oil of PBPM

peak no.	compd[a]	characteristic mass spectral ions[b]	Kovats GLC index[c] measd	Kovats GLC index[c] std	rel concn, %
		Alkanals			
1	3-methylbutanal	29, 41, 43, 44, *86*	638	638	0.2
4	1-pentanal	29, 41, 44, 57, 58, *86*	686	684	3
7	1-hexanal	29, 41, 43, 44, 56, 82, *100*	785	787	40
13	1-heptanal	44, 57, 70, 81, 86, 96, *114*	888	889	2
19	1-octanal	44, 56, 57, 84, 100, *128*	991	992	1
29	1-nonanal	44, 57, 98, 114, *142*	1095	1097	0.9
		Alkenals			
5	(*E*)-2-pentenal	29, 41, 44, 55, *84*	744	743	0.1
8	(*E*)-2-methyl-2-pentenal	29, 39, 41, 55, 69, 83, *98*	818	820	0.1
23	(*E*)-2-octenal	39, 41, 55, 70, 97, *126*	1040	1040	0.3
		Aliphatic Ketones			
9	4-hydroxy-4-methyl-2-pentanone	43, 58, 98, 101, *116*	836		0.1
12	2-heptanone	39, 43, 58, 71, *114*	877	875	0.4
17	2-octanone	39, 43, 58, 71, 113, *128*	979	978	0.3
21	3-octen-2-one	41, 43, 55, 97, 111, *126*	1026		12
24	3,5-octadien-2-one	39, 43, 53, 81, 95, 109, *124*	1048		0.8
26	3,5-octadien-2-one	39, 43, 53, 81, 95, 109, *124*	1072		0.9
27	2-nonanone	43, 58, 71, *142*	1079	1078	0.9
33	2-decanone	43, 58, 71, 85, *156*	1184	1184	0.1
37	3,5-undecadien-2-one	41, 43, 81, 95, 151, *166*	1342		0.6
38	3,5-undecadien-2-one	41, 43, 81, 95, 151, *166*	1386		0.3
		Aliphatic Alcohols			
2	1-butanol	31, 41, 43, 55, 56, *74*	655	652	0.3
3	1-penten-3-ol	29, 39, 43, 55, 57, *86*	672	669	0.01
6	1-pentanol	31, 41, 42, 55, 70, *88*	755	752	8
10	1-hexanol	31, 41, 43, 55, 56, 69, *102*	859	858	0.8
15	1-heptanol	31, 41, 55, 56, 70, 98, *116*	961	959	2
16	1-octen-3-ol	41, 43, 55, 57, 72, *128*	978	975	2
25	1-octanol	31, 41, 56, 70, 84, *130*	1063	1061	2
		Lactones			
35	γ-octalactone	29, 41, 43, 57, 85	1236	1236	0.5
36	γ-nonalactone	29, 41, 43, 57, 85	1336	1337	0.4
		Aromatics and Heteroaromatics			
11	*m,p*-xylene	51, 77, 91, 105, *106*	863	864	0.1
14	benzaldehyde	50, 51, 77, 105, *106*	947	949	0.5
18	2-(*n*-pentyl)furan	39, 53, 81, 95, 109, *138*	984	982	0.7
22	acetophenone	51, 65, 77, 105, *120*	1045	1045	0.1
28	2-(*n*-hexyl)furan	39, 53, 81, 123, *152*	1083		0.2
31	3-(*n*-butyl)pyridine	77, 78, 79, 92, 93, 106, *135*	1142		0.1
32	napthalene	51, 102, 127, *128*, 129	1175	1174	0.2
		Hydrocarbons			
20	*n*-decane	43, 57, 71, 85, *142*	1000	1000	0.1
30	*n*-undecane	43, 57, 71, 85, 99, 119, *156*	1102	1100	0.2
34	*n*-dodecane	43, 57, 71, 85, 99, *170*	1200	1199	0.3
39	*n*-tetradecane	43, 57, 71, 85, 99, *198*	1400	1399	0.2
40	*n*-pentadecane	43, 57, 71, 85, *212*	1500	1499	0.2
41	*n*-hexadecane	43, 57, 71, 85, *226*	1600	1599	0.1

[a] Mass spectrum (complete spectrum) and Kovats GLC index of all compounds listed are consistant with those of authentic samples. [b] Not necessarily the most intense ions, but five of those considered the most unique for that compound and molecular ion (if found) are shown in italic type. [c] Using the SE-30 coated Pyrex capillary column described under Experimental Section.

The main temperature programming conditions (those used for the chromatogram in Figure 1 with the SE-30 column) were to hold the capillary at 70 °C for 2 min after injection and then to program linearly from 70 to 170 °C at 5 °C/min and hold at the upper limit. The carrier gas (helium) had a linear velocity of 20 cm/s with a head pressure of 5.5 psi. The capillary inlet system was in the split mode with a split ratio of 1.5:1.

The glass capillary column effluent was split in half by a platinum–iridum splitter to a flame ionization detector and a 5982 Hewlett-Packard quadrupole mass spectrometer via a platinum–iridium transfer line. A mass spectrometer source temperature of 180 °C and an ionizing potential of 70 eV were used. Mass spectral identifications were confirmed by computer-assisted spectra matching of authentic standards of literature spectra. The calculation of Kovats retention indexes were compared to those of standards to further confirm mass spectral data.

RESULTS AND DISCUSSION

The volatile oil obtained from the PBPM by vacuum degassing amounted to 50–65 parts per million (ppm) of the poultry byproduct meal. The essence had an odor very similar to the intact PBPM which can be described as having green, fatty–soapy, hay, and cardboard-like notes.

The results of the analysis of the PBPM essence by capillary GLC–MS are presented in Table I. Compounds presented in this table had mass spectra and Kovats retention indexes consistent with those of authentic standards. Each compound in Table I is identified by a peak number pertaining to the indicated peak in Figure 1, the SE-30 gas chromatogram of the volatile oil. The relative

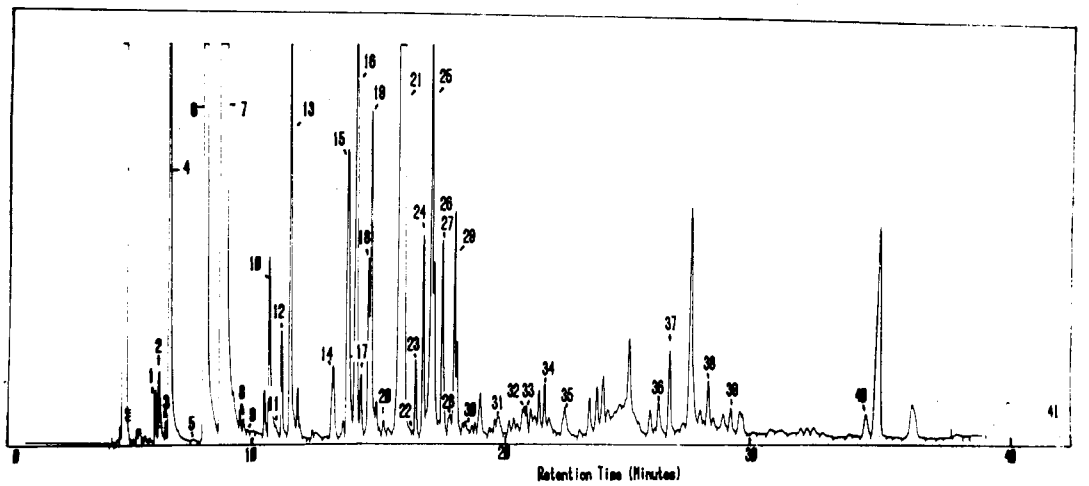

Figure 1. Capillary GLC analysis of the volatile oil of poultry byproduct meal (PBPM). For GLC conditions, see the text. The identity of the numbered peaks is shown in Table I.

concentration of the components in the volatile oil is presented in the last column of Table I. These are based on measurement of peak areas of a typical essence.

The major components identified include hexanal, 3-octen-2-one, 1-pentanol, pentanal, heptanal, octanal, 1-heptanol, 1-octanol, and 1-octen-3-ol. These compounds can arise through autoxidative degradation of arachidonic, linoleic, or linolenic acids as reviewed by Eriksson (1975), Grosch et al. (1974), and Ohloff (1973).

3,5-Octadien-2-one and 3,5-undecadien-2-one are each present in two isomers. These ketones may be derived from linolenic and arachidonic acids, respectively, via enzymatic oxidative reactions as demonstrated by Grosch and Laskawy (1975) in model tests.

The 2-(*n*-pentyl)furan has been identified by Smouse and Chang (1967) to be predominantly responsible for the reversion flavor of soybean oil. These authors postulated that 2-(*n*-pentyl)furan originates from linoleic acid.

The remaining compounds in Table I have all been found to be flavor compounds in lipid systems as reviewed by Forss (1972). The major exception appears to be 3-(*n*-butyl)pyridine which is not a direct lipid oxidation product. Buttery et al. (1977) have found 12 alkylpyridines including 3-(*n*-pentyl)pyridine in roasted lamb fat volatiles. The authors postulated that the pyridines may be formed from the reaction of aldehydes with ammonia or other amino compounds. They further suggested that the odors of pyridines are less pleasant than those of the corresponding pyrazines, and it is possible that the alkylpyridine content of lamb fat is the reason for its rejection by some consumers.

The majority of the volatiles isolated in PBPM are those commonly associated with rancid foodstuff. The aliphatic aldehydes produce green, fatty, fruity, and pungent odors. The green top note is the dominate odor desciptor in a freshly open container of PBPM. The aliphatic ketones and alcohols impart green, floral, fruity, fatty, and soapy notes. The unsaturated aldehydes and ketones help impart intense fatty, hay–straw notes which dominate the PBPM essence after the top green notes have dissipated. These odor descriptions are this author-s opinion reached as a result of GC-effluent sniffing.

Badings (1970) has described the odors of 3,5-octadien-2-one and 3,5-undecadien-2-one as being fruity–fatty and fatty–fried, respectively. These compounds also have thresholds (in paraffin oil) of under 1 ppm. *trans*-2-Octenal imparts a cardboard, woody note and has a threshold measured to be 0.2 ppm in paraffin oil. 1-Octen-3-ol imparts a mushroom- and tin-like odor to PBPM. The two furans, 2-(*n*-pentyl)- and 2-(*n*-hexyl)furan, impart beany-licorice-like notes. These odor descriptions are this author's opinion reached as a result of GC-effluent sniffing.

PBPM does not contain volatiles usually associated with pleasant cooked-meat odors. The high fat content of PBPM coupled with the severe cooking (rendering) conditions such as those described by Rao and Mahadevan (1976) may promote substantial autoxidation. Thomas et al. (1971) have shown that the action of heat on lipids during cooking can accelerate autoxidation and increase the amount of carbonyl compounds.

PBPM, unlike the prime meats which are cooked and consumed within a short (less than 1 week) time, can be stored without mold development due to its low moisture. Considerable oxidative changes in PBPM during storage have been reported by Rao and Mahadevan (1976). These authors reported the fatty acid levels in lipid extracts of fresh and stored PBPM. For example, linoleic acid content decreased from 17.2 to 8.1% of the fatty acid content in the lipid extracts of fresh and 3 month stored PBPM, respectively.

PBPM volatiles differ from those of cooked prime meats such as roast beef or pork liver in that PBPM lacks pyrazines, thiazoles, oxazoles, thiophenes, furanones, and other compounds that contribute to savory meat-like aromas in those foods. Major volatiles in prime cuts of cooked chicken have been reported by a number of investigators and appear to contain a number of components not found in PBPM. Wilson and Katz (1972) have identified 2,4-heptadienal, -nonadienal, and -decadienal from stewed chicken. These compounds impart desirable fatty, fried notes to cooked meat and are not present in PBPM.

The major volatiles isolated in cooked chicken meat volatiles by Nonaka et al. (1967) were substantially different from those of PBPM. These authors found 1-hexanal, phenylpropionaldehyde, 2-(*n*-heptyl)furan, 1-heptanal, and *n*-hexylbenzene as major flavor components.

SUMMARY

PBPM, an inexpensive protein source used in pet foods and animal foods, has been subjected to volatile flavor isolation via a vacuum distillation technique. The isolated volatiles were identified by gas chromatography–mass spectrometry and further verified in most cases by Kovats retention indexes. A number of aliphatic aldehydes, ketones, and alcohols were found which contribute to the top green, soapy, fatty notes. The major volatile contributing to the top notes was 1-hexanal (40% relative concentration). Volatiles contributing to the fatty, hay, and card-

board-like notes include 2-(*n*-pentyl)furan, 2-octenal, 3-octen-2-one, 3,5-octadien-2-one, and 3,5-undecadien-2-one. These compounds contribute to the flavor of PBPM and pet foods containing this ingredient.

Lipids appear to be the primary source of flavor in PBPM. This is supported by the fact that the majority of the compounds isolated in this study have been identified in literature reports to be products of lipid (specific fatty acid) oxidation reactions. This is further supported by the fact that PBPM has a high fat content (usually greater than 14%) which when rendered can accelerate autoxidation. A literature report has also demonstrated storage instability of fatty acids such as linoleic acid in PBPM.

This study identified 41 volatile compounds in PBPM. Future studies will center on identifying more of the volatiles, many of which need further concentration before assigning structures and organoleptic importance to them.

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Methyl 3,4-Dimethyl-5,6-dihydro-α-pyran-6-carboxylate in Roast Beef Volatiles: Identification and Synthesis

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Methyl 3,4-dimethyl-5,6-dihydro-α-pyran-6-carboxylate was identified as a compound in the volatiles isolated from roast beef. This compound was synthesized by Diels–Alder reaction between methyl glyoxylate and 2,3-dimethyl-1,3-butadiene. The structure of the synthesized compound was established by infrared, nuclear magnetic resonance, and mass spectroscopy. The identification of this compound in the volatiles of roast beef was confirmed by comparing the mass spectrum with that of the authentic sample.

The volatile flavor components of meats have been reviewed by Herz and Chang (1970) and by Dwivedi (1975). Up to now ~600 components are mentioned in the literature or have been identified in meat flavor (Flament et al., 1978).

The present paper reports the isolation, identification, and synthesis of a new heterocyclic compound, methyl 3,4-dimethyl-5,6-dihydro-α-pyran-6-carboxylate (MDDPC) in the volatiles of roast beef.

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EXPERIMENTAL SECTION

Isolation of Volatile Flavor Compounds (VFC). Good quality, "medium rare" roast beef of top round was purchased from a local delicatessen. The meat was trimmed of excess fat and cut into $^1/_2$-in. chunks. The VFC were isolated by using a specially designed apparatus employing headspace gas flushing with an inert carrier gas (Chang et al., 1977). This apparatus could be used to isolate VFC from 22 lb of roast beef in each batch. The roast beef was maintained at 86 °C by circulating water in the jacket of the cylinder which held the roast beef on a perforated bottom. The VFC were condensed in a series of cold traps cooled with a dry ice–acetone slurry. The VFC from 160 lb of roast beef were isolated.

The flavor isolated was extracted with ethyl ether and the extract dried over anhydrous sodium sulfate. Approximately 4000 mL of ether solution was obtained. The roast beef flavor solution was then preconcentrated to 150 mL by using a 30-plate Oldershaw distillation column and

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