reported to be one of the nutrients that is deficient in the diets of low-income people, particularly infants, preschool children, and pregnant and lactating women. Therefore, the loss of calcium in the form of seed coat will have greater nutritional implications. Consumers should therefore be encouraged to eat whole chickpea and attempts should be made to study the bioavailability of calcium from the seed coat.

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Gas Chromatography–Mass Spectroscopy Identification of Volatiles from Rancid Oat Groats

A systematic GC–MS study of the volatiles present in oxidatively rancid oat groats is presented. Autooxidation compounds expected from the fatty acid composition of oats (high linoleic content) were observed. The most abundant volatiles found were hexanal, pentanal, 1-pentanol, and 3,5-octadien-2-one. A total of 45 compounds were identified, including 24 aldehydes, ketones, and alcohols probably arising from lipid autooxidation.

The oxidative stability of oatmeal is good and well-known. In contrast, some other processed oat products develop rancidity quite quickly (Martin, 1958). The highly unsaturated fat content (4–11%) of oats is usually cited as the cause for these problems. To our knowledge there has not been a systematic study of the volatiles present in rancid oat products to fully document these conclusions.

Fritsch and Gale (1977) showed that rancid odors occurred in ready-to-eat oat cereals when the hexanal concentration reached 5–10 ppm. The appearance of rancidity in oat products or ready-to-eat cereals is suspected to be primarily due to autooxidation rather than enzymatic activity because of the very low moisture content of the cereal systems. Heimann et al. (1975) showed volatile aldehydes including (*E*)-2-nonenal were produced by incubation of linoleic acid with oat lipoxygenase. Heydanek and McGorrin (1980) reported carbonyls including hexanal, pentanal, 2,4-decadienal, and benzaldehyde were present in the volatiles of cooked oatmeal. The present study was undertaken to define the volatile components present in a noticeably rancid oat groat system in order to help define the cause and possible mechanism of the rancidity.

EXPERIMENTAL SECTION

Materials. Dried oat groats (A grade) were obtained from commercial production streams at 7.5% moisture and had a typical flavor. The groats were boiled for 30 min in distilled water, drained, freeze-dried overnight, and stored in polyethylene bags at ambient temperatures. Within 1 week noticeable rancidity odors were observed, and when analyzed at 3 weeks of age, the oats had a pronounced rancid, "old chicken fat" aroma.

All standard flavor chemicals were purchased from commercial sources (e.g., Aldrich Chemical Co.) and verified by GC–MS analysis.

Volatile Isolation. Rancid oat groats (2 kg) were mixed with 6 L of distilled water in a 12-L flask. The flask was immersed in a 55 °C water bath and vacuum distillation at 30 torr carried out for 2 h. Condensation was accomplished in a series of traps immersed in dry ice–2-propanol. The resulting 1 L of distillate water was made 20% (w/v) with NaCl and extracted 5 × 100 cm^3 with CH_2Cl_2. The organic extract was dried with Na_2SO_4 and reduced to a 5-cm^3 volume in a Kudurna-Danish concentrator. The extract was held at 0 °C until analyzed.

GC–MS Analysis. The volatiles obtained were analyzed by GC–MS using the following system. Separation with an H-P 5840GC was done on a 50 m × 0.5 mm i.d. Pyrex WCOT column coated with SE-30. Temperature was programmed from 40 °C, after a 3-min initial hold, to 170 °C at 3 °C/min. The GC effluent was split to an H-P 5980A mass spectrometer via a Pt-Ir open split. The data were acquired on an H-P 5933 disc drive data system. Electron ionization was at 70 eV.

Kovats retention index values were obtained by spiking a series of *n*-alkanes into a portion of the oat groat volatiles. Comparison of standard compound retention times were also obtained by coinjection with the *n*-alkane series.

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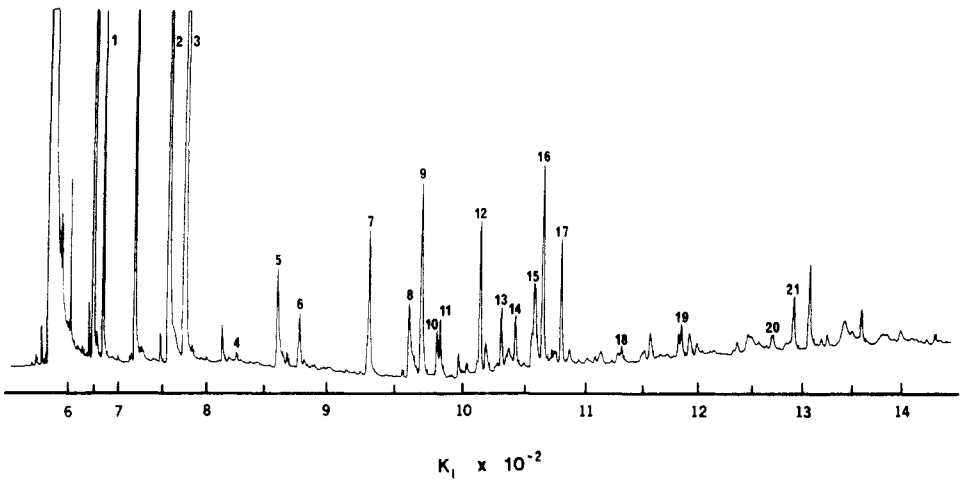

Figure 1. SE-30 capillary GC FID response of rancid oat groat volatiles as a function of Kovats retention indexes. Peak numbers correspond to those listed in Table I.

Table I. GC-MS Identifications of Volatiles Obtained from Vacuum Steam Distillation of Rancid Oat Groats

peak[a]	K_I[b]	compound[c]	autooxidation source[d]
	631	2-methylbutanal	
	642	benzene	
1	669	pentanal	L, A
	710	pyrazine	
	718	pyridine	
	748	toluene	
2	756	1-pentanol	L
3	776	hexanal	L, Ln, A
	813	furfural	
4	825	(*E*)-2-hexen-1-al	Ln
5	859	1-hexanol	L
	867	2-heptanone	
6	876	2,4-hexadien-1-al	unknown
6	877	heptanal	O, L
	886	2,5-dimethylpyrazine	
	889	2-heptanol	
7	929	(*E*)-2-hepten-1-al	L, A
7	931	benzaldehyde	
8	960	1-heptanol	L, O
9	970	1-octen-3-ol	L
9	972	2-octanone	
10	974	(*Z,E*)-2,4-heptadien-1-al	Ln
11	981	octanal	O, L
11	983	(*E,E*)-2,4-heptadien-1-al	Ln
12	1015	3-octen-2-one	A
13	1033	(*E*)-2-octen-1-al	L, A
	1038	*o*-tolualdehyde	
	1039	acetophenone	
	1040	*m*-tolualdehyde	
14	1045	(*Z,E*)-3,5-octadien-2-one	Ln
	1058	*o*-cresol	
15	1061	1-octanol	O
16	1068	(*E,E*)-3,5-octadien-2-one	Ln
17	1083	1-nonanal	O
	1094	isophorone	
18	1135	(*E*)-2-nonen-1-al	L
	1160	1-nonanol	
	1162	(*Z,E*)-2,4-nonadien-1-al	unknown
	1163	naphthalene	
	1185	decanal	
19	1188	(*E,E*)-2,4-nonadien-1-al	L
20	1270	(*Z,E*)-2,4-decadien-1-al	L, A
	1288	2-methylnaphthalene	
21	1291	(*E,E*)-2,4-decadien-1-al	L, A
	1324	γ-nonalactone	

[a] See corresponding number in Figure 1. [b] K_I for the SE-30 capillary system is described under Experimental Section. [c] All compounds listed have K_I values and mass spectra identical with those of authentic standards. [d] According to Murray et al. (1976) or Forss (1972). O = oleic; L = linoleic; Ln = linolenic; A = arachidonic.

Solvent blanks showed no peaks with a K_I greater than 700.

Sensory Analysis. The odor of the stored oat groats was typical of a highly rancid oil system and was unmistakably rancid. The distillate water and extracted volatiles had an identical but stronger character. The odor descriptions obtained by a five-member trained laboratory panel included "old oil", "rancid", and "old chicken fat".

RESULTS AND DISCUSSION

The volatiles obtained from vacuum steam distillates of rancid oat groats should contain a collection of known carbonyls. The GC separation obtained on a 50-m SE-30 capillary column is illustrated in Figure 1. Table I details the compounds identified by GC–MS analysis, and indeed most of them are carbonyls. All of the major components have been reported to occur in some form of oxidized lipid system (Forss, 1972). In agreement with the observation of Fritsch and Gale (1977), hexanal is the most abundant volatile produced. Its concentration in the rancid groat sample was estimated at 10–15 ppm. However, the sensory characterization of the rancid odor as "old chicken fat" would suggest that the fatty, deep-fried odors of the 2,4-dienals are also important.

The fatty acid composition of oat lipids has been reported to be highly unsaturated (Sahasrabudhe, 1979). The unsaturated acid contribution to the total fatty acids was 41% oleic, 36% linoleic, 2.1% linolenic, and 2.2% C_{20}/C_{22} with up to four double bonds. These fatty acids can account for all the observed autooxidation products (Murray et al., 1976). It appears that a random oxidation of all the major fatty acids occurred. After 30 min of boiling no residual enzyme activity would be expected. Rancidity only appeared after several days of storage.

Hexanal, pentanal, and 2,4-decadien-1-al would seem to be good indicators for the development of oxidative rancidity from oat oil fatty acids. Heydanek and McGorrin (1980) reported these components, as well as pyrazines, to be present in cooked oatmeal of acceptable flavor character. Therefore, rancidity in oat-containing foods would be a function of alteration of the concentrations of these oxidative components rather than their absolute presence. Investigations into the correlation of oxidative rancidity components and storage off-flavors are currently under way in this laboratory.

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A Rapid, Inexpensive, Quantitative Procedure for the Extraction and Analyses of Penncap-M (Methyl Parathion) from Honeybees (*Apis mellifera* L.), Beeswax, and Pollen

A rapid, inexpensive, quantitative procedure for the acetone–*o*-xylene (19:1) extraction of Penncap-M (methyl parathion) from honeybees (*Apis mellifera* L.), beeswax, and pollen is reported. Mean recoveries for six concentrations of methyl parathion were 98.0, 97.8, and 94.2% from honeybees, beeswax, and pollen, respectively. Mean recovery of methyl parathion from honey seeded at five concentrations of Penncap-M was 87.3%.

Penncap-M insecticide is a water-based slurry of microcapsules (30–50-μm cross-linked nylon polymer) containing methyl parathion [*O,O*-dimethyl *O*-(*p*-nitrophenyl) phosphorothioate)]. Because methyl parathion is sparingly soluble in water, the moist microcapsules provide slow, controlled release of methyl parathion by diffusion through capsule walls, maintaining pesticide levels on crops for much longer than nonencapsulated formulations (Ivy, 1972).

Because Penncap-M microcapsules mimic pollen grains in size, honeybees (*Apis mellifera* L.) are unable to discriminate the microcapsules and pollen and transport contaminated pollen back to the hive (Stoner et al., 1978). Thus, Penncap-M contaminates foraging honeybees in the field, but it also is introduced into the food chain of the colony (Stoner et al., 1979; Burgett and Fisher, 1977). Methyl parathion residues have been found in honeybee combs stored for 14.5 months; introduction of these combs into small colonies resulted in death of adult honeybees (Rhodes et al., 1979).

Currently, there is no quantitative method for analysis of microencapsulated methyl parathion in honeybees, beeswax, or pollen. Rhodes et al. (1979) utilized warm acetonitrile–hexane for extraction of Penncap-M from honey, pollen, and beeswax. Their method involved an extrapolation based on a 30% recovery of methyl parathion. Pennwalt Corp. (Carlson, 1980) utilized the Association of Official Analytical Chemists (1975) method of analysis for nonmicroencapsulated methyl parathion with modifications for analysis of honeybees, pollen, and beeswax. They reported an 80% recovery of methyl parathion. We found Pennwalt's modified AOAC method of analysis time consuming and expensive, and we recovered only 65% methyl parathion. Therefore, we developed a rapid, less expensive method for the quantitative analysis of microencapsulated methyl parathion in honeybees, beeswax, and pollen.

MATERIALS AND METHODS

Solvents and Reagents. Penncap-M, technical grade (907.2 g of methyl parathion/3.8 L), was supplied by Pennwalt Corp., AgChem Division, Fresno, CA. A methyl parathion standard of 99.0% purity was obtained from Chem Service, West Chester, PA. Acetone and hexane, spectrograde, were distilled in glass obtained from Burdick and Jackson, Muskegon, MI; *o*-xylene was purchased from Eastman Organic Chemicals.

Sample Preparation and Extraction. Triplicate samples (2.5 g) of honey bees, beeswax, and pollen were spiked individually with 0.1, 1.0, 5.0, 10.0, or 25.0 ppm of Penncap-M and placed in 250-mL Erlenmeyer flasks. One-hundred milliliters of acetone–*o*-xylene (19:1) was added, and samples were placed in a hot-water bath (100 °C) for 3 min. Fifty milliliters of hexane was added, and the sample was blended with a Polytron equipped with a PT 20ST probe generator (Brinkmann Instruments, Westbury, NY) for 30 s at high speed. The samples were then transferred with two 5-mL acetone washes to 250-mL round-bottom flasks and concentrated to 40 mL on a rotary evaporator at 40 °C. The samples were transferred to 50-mL centrifuge tubes with two 2.5-mL acetone washes, placed in an ice bath (0 °C), and shaken for 10 min (Grussendorf et al., 1970; McLeod and Wales, 1972). The samples were then centrifuged in an International Model NH tabletop centrifuge (International Equipment Co., Neeham Heights, MS) at 10000*g* for 15 min.

The supernatants were decanted into 250-mL round-bottom flasks, concentrated to less than 10 mL on a rotary evaporator at 40 °C, transferred to 10-mL volumetric flasks, and diluted to volume with *o*-xylene.

Gas–Liquid Chromatography. A Hewlett-Packard 5730A chromatograph equipped with a flame photometric detector in the phosphorus mode was used for analysis. Five microliters of sample extract was injected on a 91.44 cm long glass column (6.35-mm i.d.) packed with 10% (w/w) OV-1 on Chromosorb (80–100 mesh) WHP. Analyses were carried out at the following temperatures: column oven, 200 °C; injection port, 250 °C; detector, 200 °C. Flow rates of the gases were as follows: nitrogen carrier, 60 mL/min; hydrogen, 200 mL/min; air, 50 mL/min; oxygen, 20 mL/min. Samples were quantitated