E:N (essential amino acids to nonessential amino acids), E:P (essential amino acids to protein), and E:T (essential amino acids to total amino acids) ratios, chemical score, EAAI, and BV in rye, triticale, and wheat are presented in Table V. The results show that E:N and E:T ratios are highest in triticale, followed by wheat, Kalyan Sona, and rye. The results obtained for chemical score, EAAI, and BV in the cases of wheat and rye agree very closely with those of Sharbati Sonora and rye reported by Eggum (1970) and Duggal and Eggum (1977). As observed from Table V, PER is well correlated with chemical score in the case of rye and wheat, but this is not true in the case of triticale. Superiority in terms of PER, NPR, and growth of triticale over wheat in this study could not be due to essential amino acids, but it could be due to some other unknown factors, such as digestibility.

ACKNOWLEDGMENT

The authors are thankful to M. S. Naik for providing facilities to conduct research work. They are also grateful to B. O. Eggum for help in amino acid analysis.

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Received for review March 24, 1977. Accepted February 3, 1978.

Volatile Aroma Components of Cooked Artichoke

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The volatile oil of artichokes (*Cynara scolymus*), obtained by atmospheric steam distillation continuous extraction, was analyzed by the direct combination of capillary gas chromatography and mass spectrometry. A total of 32 compounds were characterized. The major components were β-selinene and caryophyllene. Odor threshold determinations indicated that the components most important to the aroma included oct-1-en-3-one, hex-1-en-3-one, decanal, non-*trans*-2-enal, phenylacetaldehyde, and eugenol.

California is the main growing area for artichokes (*Cynara scolymus*) in the United States. An improved knowledge of the aroma constituents of artichokes could give a better basis for breeding for improved flavor in the production of artichokes. There have been a number of studies on the nonvolatile constituents of artichokes particularly in regard to bitter off-flavor components such as the sequiterpene lactones (Samek et al., 1971; Schneider and Thiele, 1974). However, there does not seem to have been any previous reports on the volatile aroma constituents of artichoke. The present work was begun with the purpose of characterizing the major important volatile aroma constituents.

EXPERIMENTAL SECTION

Materials. Whole fresh California artichokes (*Cynara scolymus*) were obtained from local retail markets.

Authentic samples of organic compounds were obtained from reliable commercial sources or synthesized by established methods. They were purified by gas–liquid chromatography (GLC) separation before use.

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Isolation of Volatile Oil. Fresh artichokes (3 kg) were cut into quarters and placed in a 12-L round-bottom flask. They were covered with odor-free water (6 L) and a Likens-Nickerson steam distillation continuous extraction head attached to the top of the flask. Freshly distilled diethyl ether (150 mL) containing a trace of Ionox 330 antioxidant was placed in a flask attached to the solvent arm of the head. The extraction was carried out at atmospheric pressure for 3 h. After drying over anhydrous sodium sulfate, the ether was removed by distillation through low hold-up Vigreux distillation columns to give the artichoke volatile oil.

For separation into hydrocarbon and oxygenated fractions, the artichoke volatile oil (50 μL) was placed on a column (12 × 100 mm) of silica gel (Mallinckrodt SilicAR CC-7). The hydrocarbon fraction was eluted with pentane (200 mL). The oxygenated fraction was then eluted with freshly distilled diethyl ether (200 mL). Solvent from both fractions was removed by distillation using low hold-up distillation columns.

Capillary GLC–Mass Spectral Analysis. This was carried out in a similar way to that previously described by the authors (Buttery et al., 1975). In the present work, two major types of capillary columns were used: a 150 m long × 0.75 mm i.d. Pyrex glass capillary column coated

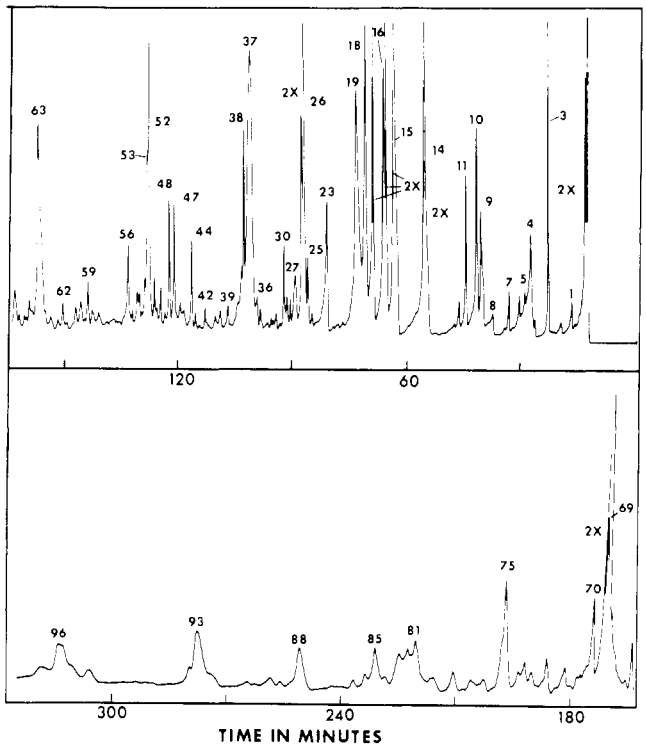

Figure 1. Capillary GLC analysis of the oxygenated fraction of the atmospheric steam volatile oil of artichokes. GLC column was a 150 m long × 0.75 mm i.d. Pyrex glass capillary coated with Tween 20 containing 5% Igepal CO-880. The column was held at 50 °C for 12 min after injection and then temperature programmed from 50–170 °C at 1 °C min.

with Tween 20 containing 5% Igepal CO-880 and a 300 m long × 0.75 mm i.d. stainless steel capillary coated with Silicone SF96(50) containing 5% Igepal CO-880. With these columns several different GLC–mass spectral runs were made using different GLC conditions. The main one was, however, that using the Pyrex glass capillary, holding at 50 °C for the first 12 min after injection and then temperature programming from 50–170 °C at 1 °C/min. A silicone rubber membrane molecular separator was used to couple the end of the capillary GLC column to the mass spectrometer (a modified Consolidated 21-620 cycloidal type). Electron ionization voltage was 70 V.

Packed Column GLC–Infrared Spectral Analysis. Samples were separated from both the hydrocarbon and oxygenated fractions using a 3 m long × 0.64 cm o.d. stainless steel column packed with 80–100 mesh Chromosorb G-DMCS coated with 2% silicone SF96(50). The column was temperature programmed nonlinearly from 50–170 °C. The infrared (IR) absorption spectra were measured as films between ultramicro salt plates or as solutions in CCl_4 in ultramicrocavity cells using a reflecting beam condensor with a Perkin-Elmer Model 237 instrument.

Odor Thresholds. These were measured in water solution (on the GLC purified compounds) as previously described (Guadagni et al., 1963) using Teflon bottles and tubing for the odor solutions.

RESULTS AND DISCUSSION

The raw artichoke has little aroma and flavor, and artichokes are usually eaten cooked. For this reason, it was felt that steam distillation continuous extraction at atmospheric pressure would be a satisfactory method of isolating the volatile oil. Using this method, a volatile oil amounting to 10 parts per million (ppm) of the artichoke was obtained. This oil was judged by four experienced

Table I. Identities of Constituents of the Steam Volatile Oil of Artichokes

Compound	Approx. relative percent in whole oil
Aliphatic alcohols[a,b]	
(9) 2-Methylbutanol MS, RT	0.9
(9) 3-Methylbutanol MS, RT	
(14) 3-Methylbut-2-en-1-ol MS, RT	2.2
(16) Hex-*cis*-3-enol MS, RT	3.5
(17) Hex-*trans*-2-enol MS, RT	1.3
(18) Hexanol MS, RT	2.7
Aliphatic aldehydes	
Pentanal MS, RT	0.2
(5) Hexanal MS, RT	0.5
Heptanal MS, RT	0.2
Octanal MS, RT	0.2
(19) Nonanal MS, RT	0.6
Decanal MS, RT	0.4
(10) Hex-*trans*-2-enal MS, RT	1.6
Non-*trans*-2-enal MS, RT	0.2
Aliphatic ketones	
Pentan-2-one MS, RT	0.1
Butan-2,3-dione MS, RT	0.1
(4) Hex-1-en-3-one MS, RT	0.8
Oct-1-en-3-one, MS, RT	0.6
Aromatic and heterocyclic compounds	
Pyridine MS, IR, RT	0.2
2-Pentylfuran MS, RT	0.9
(18) Furfural MS, IR, RT	2
2-Acetylthiazole MS, RT	0.1
(23) Benzaldehyde MS, IR, RT	0.8
(37) Phenylacetaldehyde MS, RT	7
(52) Benzyl alcohol MS, RT	1
(69) Eugenol MS, IR, RT	2–5
Terpene alcohols	
(30) Linalool MS, RT	0.4
α-Terpineol MS, RT	0.2
(44) Linalool oxide C (5-hydroxy-2,6,6-trimethyl-2-vinyltetrahydropyran) MS, RT	0.5
Sesquiterpene hydrocarbons	
Caryophyllene MS, IR, RT	19
Humulene MS, RT	1
β-Selinene MS, IR, RT	40
Tentatively identified compounds	
(26) Methylheptanol	2.5

[a] Peak numbers corresponding to peaks in Figure 1 are shown in parentheses immediately before the compounds name. [b] MS, IR, RT = mass spectral, infrared absorption spectral, and GLC retention evidence, respectively. Evidence cited is consistent with that of an authentic sample.

odor judges to have an odor very similar to that of cooked artichokes. The whole volatile artichoke oil was first examined by the direct combination of capillary GLC and mass spectrometry (GLC–MS) and major components characterized. For a more detailed study, the whole oil was separated into a hydrocarbon fraction and an oxygenated fraction by selective liquid chromatography separation on a silica gel column. These fractions were found to be roughly 60% (hydrocarbon) and 40% (oxygenated) of the whole oil. Each fraction was then separately analyzed by GLC–MS and also by packed column GLC isolation of selected peaks for infrared spectral characterization.

Figure 1 shows a capillary GLC analysis of the oxygenated fraction. Components characterized in this and the hydrocarbon fraction are listed in Table I. Peak numbers corresponding to the peaks in Figure 1 are shown in parentheses immediately before the compounds name in Table I. Compounds not assigned a peak number are either hydrocarbons (hence not in oxygenated fraction) or

Table II. Odor Thresholds and Calculations of Relative Odor Units of Some Artichoke Components

Component	Threshold (T_c) in parts of compound per 10^9 parts of water	Rel % of whole oil	Odor units, $U_o \times 10^{-6}$	% odor units
Whole artichoke oil	0.6	100	1690	100
Oct-1-en-3-one	0.005	0.6	1200	71
Hex-1-en-3-one	0.024	0.8	330	20
Non-*trans*-2-enal	0.08	0.2	25	1.5
Decanal	0.1	0.4	40	2
Octanal	0.7	0.2	3	0.2
Nonanal	1	0.6	6	0.4
Heptanal	3	0.2	0.7	0.04
Phenylacetaldehyde	4	7	20	1.1
Hexanal	4.5	0.5	1	0.06
Eugenol	6	5	8	0.5
Linalool	6	0.4	0.7	0.04
2-Pentylfuran	6	0.9	2	0.1
Pentanal	12	0.2	0.2	0.01
Hex-*trans*-2-enal	17	1.6	0.9	0.05
Caryophyllene	64	19	3	0.2
Hex-*cis*-3-enol	70	3.5	0.5	0.03
3-Methylbutanol	250	0.9	0.04	0.002
Benzaldehyde	350	0.8	0.02	0.001
α-Terpineol	350	0.2	0.006	0.0004
Hexanol	500	2.7	0.05	0.003
Furfural	3000	2	0.007	0.0004

are covered by other peaks in this particular GLC analysis. Different GLC conditions favored some compounds over others. Some idea of the approximate relative percentages of the components in the whole oil (calculated from peak areas) is also listed in Table I.

The major components of the volatile oil are the sesquiterpene hydrocarbons β-selinene and caryophyllene forming 40 and 19%, respectively, of the whole oil. These compounds do not seem to be closely related to the nonvolatile sesquiterpene lactones previously characterized in artichokes (Samek et al., 1971). More than ten volatile oxygenated sesquiterpenoids (mostly alcohols), occurring in relatively small concentration, were detected but none could be characterized from their mass spectra. There are a number of aliphatic alcohols occurring in reasonable concentration such as hex-*cis*-3-enol (3.5%) and hexanol (2.7%) which are common in many vegetables and fruits. An unusual aliphatic alcohol occurring in reasonable concentration (2.5%) is peak 26. This compound has a mass spectrum very similar to that of 6-methylheptanol, but its GLC retention is slightly shorter. The mass spectrum is different from that of 2-methylheptanol and the branch may possibly be in the 3 or 4 or 5 position. No authentic samples of these isomers were available, however.

As far as the authors can determine, hex-1-en-3-one has not been found in foods before. Oct-1-en-3-one had been found previously in dairy products (Forss et al., 1962), mushrooms (Cronin and Ward, 1971), and potatoes (Buttery et al., 1970) but is not widely occurring although the corresponding alcohol oct-1-en-3-ol has been found in a large number of foods. Both of these ketones are potent odorants.

Most of the other components characterized such as the aliphatic aldehydes, terpene alcohols, and aromatic and heterocyclic compounds commonly occur in vegetables.

The mass spectra of most of the components are well enough known. The mass spectrum of hex-1-en-3-one (two most intense ions every 14 mass units above m/e 34, intensities in parentheses, molecular ion in boldface type) showed 41 (45), 43 (59); 55 (100), 56 (13); 70 (42), 71 (12), 83 (12), 84 (0.5); 97 (6), **98** (10).

Importance of Components to Aroma. During the capillary GLC analysis of the whole artichoke volatile oil, the odor of the effluent was informally evaluated to determine the odor quality of the components. The only individual GLC peak that was felt to have a characteristic artichoke aroma was that corresponding to hex-1-en-3-one. The peak corresponding to oct-1-en-3-one had a mushroom-like odor.

Odor thresholds (T_c) in water of most components had been determined previously by the authors during studies on other foods (e.g., Buttery et al., 1970; Guadagni et al., 1966). These are listed in Table II together with thresholds determined for the present study. The percentage of the component in the oil is also shown, and these data were used to calculate odor units (U_o) for each compound (cf. Guadagni et al., 1966). If we consider the concentration of each component in the oil in parts per billion (ppb) expressed as F_c, then odor units have been defined by Guadagni et al. (1966) as $U_o = F_c/T_c$. The percent odor units is also shown. This gives some idea of the relative importance of the components to the total odor. The most important odorants seem to include oct-1-en-3-one, hex-1-en-3-one, decanal, non-*trans*-2-enal, phenylacetaldehyde, and eugenol. Mixtures of dilute solutions of some of these components in informal evaluations gave aromas reminiscent of cooked artichokes.

ACKNOWLEDGMENT

The authors thank Robert A. Flath and Thomas R. Mon for the use of the Pyrex glass capillary GLC column.

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Received for review November 14, 1977. Accepted March 27, 1978.