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Contribution of Volatiles to Rice Aroma

Ron G. Buttery,* Jean G. Turnbaugh, and Louisa C. Ling

The odor thresholds in water solution of 64 known rice volatiles are listed and compared. Compounds with the lowest odor thresholds (T) include (E,E)-2,4-decadienal ($T = 0.07$ ppb), (E)-2-nonenal ($T = 0.08$ ppb), and 2-acetyl-1-pyrroline ($T = 0.1$ ppb). Data from quantitative analysis (using a Tenax trap isolation method) of the major volatiles in cooked California long-grain rice were used to determine the ratio of each compound's concentration in the cooked rice to its odor threshold (odor unit value). This indicated that the probable major contributors to the Californian long-grain cooked rice odor included 2-acetyl-1-pyrroline, (E,E)-2,4-decadienal, nonanal, hexanal, (E)-2-nonenal, octanal, decanal, 4-vinylguaiacol, and 4-vinylphenol.

More than 100 volatile aroma components have been identified in cooked rice. These have been covered in some recent reviews (Maga, 1984; Tsugita, 1985–1986) and publications (Tsugita et al., 1980; Yajima et al., 1978). However, there has been little scientific information reported on the relative importance of these compounds to total rice aroma. The present work was carried out in order to compare the odor potencies of various major rice components and to make some estimate of their probable relative contribution to the total rice aroma. A number of odor thresholds on rice components had been determined by some of the authors in previous studies of other foods (Buttery et al., 1971; Guadagni et al., 1966; Guadagni and Turnbaugh, 1980). Other odor thresholds were determined during the present work.

EXPERIMENTAL SECTION

Materials. California long-grain rice (variety L-202) was purchased from local retail markets and stored at room temperature in the dark. It was used within a few weeks. Chemical compounds were obtained from reliable commercial sources or synthesized by established methods. All compounds were purified by gas–liquid chromatography (GLC) separation before use and their identities verified by spectral (MS or IR) methods.

Quantitative Analysis of Volatiles in Cooked Rice. Rice (California long grain, variety L-202) was cooked in the normal way (500 g of rice was added to 1 L of water and the mixture brought to a boil and held at 100 °C for 20 min). The freshly cooked rice (300 g) was immediately placed in a 2-L round-bottom flask (containing an efficient magnetic stirrer) with 300 mL of odor-free (20 °C) water. A quantity (10.0 mL) of a standard solution of 50.0 ppm 2-octanone (internal standard) in water was then added. The volatiles were then isolated by a Tenax trap procedure similar to that previously described by Buttery et al.

Western Regional Research Center, U.S. Department of Agriculture—Agricultural Research Service, Albany, California 94710.

(1987). This was done as follows. A Tenax trap (a Pyrex tube containing a 14 cm × 2.2 cm column of 60–80-mesh Tenax) and air inlet head were attached to the neck of the flask. The mixture was vigorously stirred, and purified air (3 L/min) was passed over the cooked rice slurry and led out of the flask through the Tenax trap. The isolation was carried out for 60 min; the trap was then removed and eluted with freshly distilled diethyl ether (50 mL). The ether extract was concentrated to ca. 10 µL with a warm water bath and Vigreux distillation column. This concentrate was used for the quantitative GLC analysis.

GLC Analysis. A commercially obtained 60-m length × 0.32-mm i.d. DB-wax wall coated fused silica capillary column was used in a HP5880 gas chromatograph with electronic peak integration. The column was temperature programmed by holding the column at 30 °C for the first 5 min and then increasing the temperature at 4 °C/min until 170 °C where it was held for another 30 min. Injector temperature was 150 °C and He flow velocity 32 cm/s.

Odor Threshold Determinations. Odor thresholds of GLC-purified compounds were determined as described previously (Guadagni and Buttery, 1978) using an experienced panel of 16–20 members. Odor-free Teflon squeeze bottles and tubes were used to contain the solutions, and the judging room was supplied with a slight positive pressure of odor-free air (purified by passage through activated charcoal).

RESULTS AND DISCUSSION

The odor thresholds (T) found for a number of major volatile rice components are listed in Table I in parts (mL) of compound per billion (10^9) parts (mL) of water. Most of these had been determined in the authors' laboratory either in the present study or in other food volatile studies over the last 20 years (Buttery et al., 1971). A few figures were obtained from data published by other laboratories, and these are indicated by a footnote in Table I. Most of the compounds in Table I had been identified in rice by the authors listed in the reviews cited above.

Of the compounds listed in Table I the aldehydes (E)-2-nonenal ($T = 0.08$ ppb) and (E,E)-2,4-decadienal (T

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Table I. Odor Thresholds of Some Major Rice Volatiles Determined in Water Solution

compound	odor threshold,[a] ppb	compound	odor threshold,[a] ppb
Aliphatic Alcohols			
butanol	500	octanol	110
3-methylbutanol	300	nonanol	50
pentanol	4000	1-octen-3-ol	1
hexanol	2500		
Aliphatic Aldehydes			
acetaldehyde	15	decanal	2
propanal	10	(E)-2-hexenal	17
butanal	9	(E)-2-heptenal	13
pentanal	12	(E)-2-octenal	3
hexanal	5	(E)-2-nonenal	0.08
heptanal	3	(E)-2-decenal	0.4
octanal	0.7	(E,E)-2,4-decadienal	0.07
nonanal	1		
Aliphatic Ketones			
2-heptanone	140	3-penten-2-one	1.5
2-octanone	50	6-methyl-5-hepten-2-one	50
3-octanone	28	6-methyl-3,5-	380
2-nonanone	200	heptadien-2-one	
2-undecanone	7	geranylacetone	60
Esters			
ethyl benzoate	60	methyl palmitate	>2000
geranyl acetate	9	ethyl palmitate	>2000
Aliphatic Acids			
hexanoic	3000[b]	tridecanoic	10000[b]
octanoic	3000[b]	myristic	10000[b]
nonanoic	3000[b]	pentadecanoic	10000[b]
decanoic	10000[b]	stearic	20000[b]
Aromatics			
benzyl alcohol	10000	acetophenone	65
2-phenylethanol	1100	guaiacol	3
furfural	23000	p-cresol	55
benzaldehyde	350	4-vinylguaiacol	3
phenylacetaldehyde	4	4-vinylphenol	10
Nitrogen Compounds			
2-acetyl-1-pyrroline	0.1	2,6-dimethylpyrazine	1500
2-acetylpyrrole	170000	2,3-dimethylpyrazine	2500
pyridine	2000	quinoline	700[b]
2-methylpyrazine	60	benzothiazole	80
2,5-dimethylpyrazine	1700	indole	140
Others			
limonene	10		

[a] Parts (mL) of compound per billion (10^9) parts (mL) of water. [b] Data obtained from van Gemert and Nettenbreijer (1977).

= 0.07 ppb) have the lowest odor thresholds. These compounds also occur in average amounts and are likely therefore to contribute a reasonable amount to the total rice aroma. Other aldehydes such as (E)-2-decenal (T = 0.4 ppb), octanal (T = 0.7 ppb), nonanal (T = 1 ppb), and decanal (T = 2 ppb) also have relatively low thresholds and are likely also to contribute. All of these aldehydes, however, are very common components of other foods. It seems that, except for conveying the general odor of a food, this common combination of aldehydes must not be very characteristic of any one food. The exception to this might be in the cases where one or more of these aldehydes predominate much more than usual and then can provide the characteristic odor of that food.

The only other component found with a threshold lower than 1 ppb was 2-acetyl-1-pyrroline (T = 0.1), which has a very characteristic odor, described by panel methods as "popcorn-like" in previous work carried out by Buttery et al. (1983). It had also been shown in this previous work that 2-acetyl-1-pyrroline was largely responsible for the aroma of the highly aromatic basmati-type rice varieties (also called scented rice). It is interesting that a local name for some of the basmati-type rices (e.g., Texmati) in some parts of Southern United States is "popcorn rice".

Odor Units. Some idea of the relative significance of

Table II. Concentrations Found for Some Major Volatile Aroma Compounds in Cooked California Long-Grain Rice (Using Tenax Trapping) and Calculations of the Number of Odor Units Present for Each Compound

compound	concn in cooked rice,[a] ppb	no. of U_o[b]
hexanal	12	2
heptanal	0.7	0.2
2-pentylfuran	1	0.2
(E)-2-heptenal	0.4	0.03
2-acetyl-1-pyrroline	0.6	6
hexanol	0.4	0.0002
octanal	0.9	1
nonanal	3	3
benzaldehyde	0.7	0.002
(E)-2-nonenal	0.1	1
decanal	2	0.7
(E)-2-decenal	0.05	0.2
nonanol	0.2	0.004
(E,E)-2,4-decadienal	0.4	5.7
2-phenylethanol	90	0.09
4-vinylguaiacol	2	0.6
4-vinylphenol	2	0.6

[a] Parts of compound per billion (10^9) parts of cooked rice (wet weight). [b] The number of odor units is equal to the concentration of the compound (ppb) divided by its odor threshold in water (ppb).

any individual component to the total aroma can be obtained by the calculation of a quantity called odor units (U_o) for that compound (Guadagni et al., 1966). Most foods are 70–90% water. For such foods the odor unit value was obtained by dividing the concentration (C) of the compound in the food by its odor threshold in water (T); i.e., $U_o = C/T$. This value gives the number of threshold concentrations for a particular compound present in that food (for a largely aqueous food making the assumption that T is the same for the food). Each threshold concentration can give a detectable response. The probability of a compound's odor being detected (i.e. how obvious its odor is) should then be greater the larger the number of threshold concentrations (U_o) present. If the U_o value is much smaller than 1, the threshold for that compound would not be reached and it seems unlikely that its character could contribute significantly to the total odor. These figures can give us some idea of what compounds are likely to be most significant to the total odor and which are likely to be least significant.

Table II lists the concentrations of compounds found in cooked rice (discussed later) and U_o values calculated from these and the T values from Table I. From Table II the compounds expected to contribute most to the odor include 2-acetyl-1-pyrroline, (E,E)-2,4-decadienal, nonanal, hexanal, (E)-2-nonenal, and octanal. Decanal, 4-vinylguaiacol, and 4-vinylphenol are present in amounts close to their odor thresholds. All other compounds in Table I occur at concentrations considerably less than their odor threshold concentration. Of the other volatiles identified in rice and listed in Table I few seem potent enough to be able to contribute significantly to the total odor. Another possibility is that there are still some compounds that have not been identified. The GLC–MS methods that have been applied to rice are generally most suitable for a middle range of compounds from about C_4 to C_{15}. Very low boiling compounds and very high boiling compounds are frequently overlooked. One very low boiling compound that probably also contributes is hydrogen sulfide, identified previously in cooked rice by Obata and Tanaka (1965). The accuracy of the U_o values is dependent on the accuracies of both the measurements of the odor threshold and the quantitative analysis of the volatiles in the food.

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Both types of values are difficult to obtain accurately. The exact odor threshold is dependent somewhat on the different individuals used for the judging (who vary in sensitivity). The authors, in their own studies, have always tried to use a panel (ca. 16–24 people) consisting principally of individuals experienced at judging but with an average distribution of sensitivity. Odor threshold determinations with such panels have been reasonably reproducible (within ±50%) over a period of more than 20 years even though the composition of the panel has changed.

The samples used for the odor threshold determinations need to be of high purity. The authors have used gas chromatography separation to purify their samples.

As with any measurement, background noise (in this case background odors) should be kept to a minimum. In the authors' laboratory methods to minimize background odors have included (1) supplying a continual flow of purified air to the panel booths, (2) thoroughly cleaning the Teflon bottles used for the measurement, and (3) using odor-free water to make up the solutions.

Quantitative Analysis of Volatiles. Quantitative analysis of food volatiles presents many problems, particularly because foods commonly contain reactive and dynamic systems. Some compounds are continually being generated during the volatile isolation process. Other compounds can be involved in reactions with other molecules or undergo isomerization. Adsorption effects, on the surface of the equipment used, can cause problems with the quantitative analysis of trace amounts such as are present in rice. These adsorption effects are most noticeable with very polar compounds such as phenols and free acids.

Isolation of volatiles from cooked rice by vacuum steam distillation was used by Buttery et al. (1983) in previous studies, but they felt that some compounds (e.g., aliphatic aldehydes and vinylphenols) were being continually generated from the rice during the isolation process. A more suitable method is a particular type of Tenax trapping method recently applied by Buttery et al. (1987) to fresh tomato volatiles. This method was shown to give a reasonable quantitative recovery (>50%) for most volatiles. The method is described in the Experimental Section of this paper. The results of applying this method to cooked Californian long-grain rice are listed in Table II. From studies with recovery of known concentrations of standard compounds from model systems (Buttery et al., 1987, 1988), the quantitative data for the aliphatic aldehydes and alcohols in Table II are probably correct within ±20%. The recovery factor for phenols such as 4-vinylguaiacol and 4-vinylphenol, however, are considerably lower than those found for the average type of rice volatile. A 10% recovery was found for water solutions of 4-ethylphenol, and a similar recovery would be expected for 4-vinylphenol and 4-vinylguaiacol. The aromatic alcohol 2-phenylethanol has a relatively high solubility in water, and only 3% was recoverable under the isolation conditions used. A correction factor (10× for the vinylphenols and 33× for 2-phenylethanol) based on these recoveries was applied to the raw concentration data to prepare Table II. A considerably greater margin of error would be expected for compounds with such large correction factors. The recovery of trace amounts of the unstable 2-acetyl-1-pyrroline was not studied with the Tenax isolation technique (a quantitative recovery was assumed for Table I), and the actual amount in the rice may be higher than that shown.

Odor Threshold of Cooked Rice and the Sum of Odor Unit Values. An odor threshold was carried out on the cooked California long-grain rice itself. To do this,

weighed amounts of freshly cooked rice were added to 100 mL of water in the Teflon odor containers. The container was allowed to equilibrate for 20 min with occasional swirling of the container before judging started. The whole cooked rice was used rather than a blended form (which would have been more uniform) because it was felt that blending would cause extensive cell damage and could thus produce additonal volatiles not present in normal cooked rice. The determination gave a threshold of 2×10^4 parts of rice per million parts of water.

Guadagni et al. (1963) had found from experimental studies that the odor unit value for a mixture of volatiles was equal to the sum of the individual odor unit values of the constituents

$$U_o(\text{mix}) = U_{o1} + U_{o2} + U_{o3} + \ldots + U_{on}$$

where $U_o(\text{mix})$ is the odor unit value for the mixture and U_{o1}, U_{o2}, U_{on}, etc., are the odor unit values for the individual constituents. For California long-grain rice $U_o(\text{mix})$ = $10^6/(2 \times 10^4)$ = 50.

From Table II the addition of the odor unit values of the constituents is equal to 22. Considering the margin of error in the threshold and quantitative concentration measurements, these figures seem in reasonable agreement. Other compounds could contribute odor units of the same order as the compounds in Table II without altering the sum very much, but it seems unlikely that there could be any unsuspected compound that could contribute a significantly greater amount.

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Influence of Heat and Cure Preservatives on Residues of Sulfamethazine, Chloramphenicol, and Cyromazine in Muscle Tissue

Robert L. Epstein,* Victor Randecker, Paul Corrao, Jimmy T. Keeton, and H. Russell Cross

Animals were given medications to produce incurred residues of sulfamethazine or chloroamphenicol in swine and cyromazine and melamine metabolite residues in cattle. This muscle tissue was subjected to combinations of curing or noncuring and temperatures of 2–3, 68 (casing), and 122 °C (canning) with the analytes of interest quantitated before and after processing. Sulfamethazine survived in pork cured and thermally processed, although losses of up to 50% were observed. Half the chloramphenicol concentration in pork was lost in uncured processed tissue, with greater losses observed after curing and complete loss for canned product. Cyromazine losses of approximately 35% occurred in beef after processing and curing. Cyromazine levels increased when the beef was processed at 68 °C in casing, due to water loss. In canned product, melamine was present at 1 ppm for the dosed and nondosed tissue. The melamine contamination may be due to the melamine–formaldehyde resin in the can lining.

Various drugs or chemical agents have been used for controlling diseases and as growth promotants in livestock, but unacceptable concentrations of residues may remain if animals are not properly withdrawn prior to slaughter. Information is available from the manufacturers of various veterinary agents indicating appropriate withdrawal times of the compound in uncooked animal tissue. However, before meat products are consumed, they are cooked and/or cured. No information is currently available concerning the fate of residues in such products. The study objective was to evaluate the influence of cure, preservatives, and heating on chemical residues in processed meats. Chemical information for the three compounds chosen for this study, sulfamethazine, chloramphenicol, and cyromazine, is listed in Table I.

Sulfamethazine (110 mg/kg) in feed is widely used in the swine industry in combination with other antibiotics with growth-promotant properties. The U.S. Food and Drug Administration (FDA) established a tolerance of 0.1 ppm (Code of Federal Regulations, 1987) for sulfamethazine in edible swine tissue. However, sulfamethazine contamination of nonmedicated feed occurs when medicated feed is prepared at the feed mill, resulting in animals with sulfamethazine residues. In addition, a recycling of the sulfamethazine residues can occur through residues in the feces and urine.

Chloramphenicol, a potent antibiotic, is not approved for use in food-producing animals in the United States.

Residues of chloramphenicol, in edible tissue, is a public health concern because it can cause aplastic anemia in man (Meyer et al., 1974; Settepani, 1984).

Cyromazine is an insecticide approved for use by the U.S. Environmental Protection Agency (EPA) in chickens. Cyromazine is administered as a feed-through larvicide incorporated into feed at 0.50 mg/kg for laying hens to prevent flies from hatching in the manure (Federal Register, 1984). The tolerance of cyromazine and the melamine metabolite is 0.05 ppm each (Code of Federal Regulations, 1985) in edible poultry tissue. Cyromazine is used in other animals species by other meat-producing countries.

EXPERIMENTAL SECTION

Materials. In this study four market-weight hogs averaging 81.4 kg live weight were selected for dosing, one with chloramphenicol, two with sulfamethazine, and one animal served as a control. Similarly, three yearling cattle weighing 200–250 kg were used; two were fed cyromazine as a Larvadex premix to produce cyromazine-incurred tissues, and the third served as a control.

Two market-weight hogs were fed ASP-250 (American Cyanamid, Inc., Princeton, NJ). This antibiotic blend contains chlortetracycline, penicillin, and sulfamethazine. Sulfamethazine was fed to swine at 110 mg/kg in feed for a period of 7 days. One hog was slaughtered 48 h and the second hog 72 h after placement on nonmedicated feed to produce target sulfamethazine residue concentrations in muscle tissue of 0.5 and 0.2 ppm, respectively (Randecker et al., 1987).

Chloramphenicol was purchased from Sigma Chemical Co., St. Louis, MO, and prepared at 150 mg/mL in propylene glycol. One hog was dosed at 0.2 mg/kg intrave-

Science, Food Safety and Inspection Service, USDA, 300 12th Street, SW, Washington, DC, 20250 (R.L.E., V.R., P.C.), and Department of Animal Science, Texas A&M University, College Station, Texas 77843 (J.T.K., H.R.C.).