

Identification of Fruity/Fermented Odorants in High-Temperature-Cured Roasted Peanuts

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Gas chromatography/olfactometry on a concentrate of volatiles obtained by solvent-assisted flavor evaporation (SAFE) from roasted peanuts containing a fruity/fermented off-note was used to identify the odorants responsible for the flavor defect. Freshly dug peanuts were divided into two classes, mature and immature, using pod mesocarp color, and subjected to normal (27 °C) and high (40 °C) temperature curing. Sensory evaluation of the roasted peanuts found that immature peanuts cured at high temperature contained the fruity/fermented off-note. Mature peanuts cured at high temperature and both immature and mature peanuts cured at low temperature were free of the off-note. Peanuts with the off-flavor were found to contain fruit-like esters (ethyl 2-methylpropanoate, ethyl 2-methylbutanoate, and ethyl 3-methylbutanoate) along with increased levels of short chain organic acids (butanoic, 3-methylbutanoic, and hexanoic). These findings were confirmed by sensory evaluation of models, where the addition of these compounds produced the fruity/fermented flavor defect in a control peanut paste. This is the first time that the odorants responsible for this off-note in roasted peanuts have been identified.

KEYWORDS: Peanut; gas chromatography/olfactometry; ethyl 2-methylbutanoate; ethyl 3-methylbutanoate; fruity/fermented; off-flavor

INTRODUCTION

Peanut (*Arachis hypogaea*) is a herbaceous legume whose seed is of significant economic importance around the world. A large percentage of peanut seed is used for oil production, whereas in the United States approximately 60% of production is consumed as food. In the US, peanuts are grown in nine states, roughly divided into two geographic regions, the Southeast (Georgia, Alabama, Florida, Virginia, North Carolina, South Carolina) and the Southwest (Texas, Oklahoma, New Mexico). Most commercial varieties of peanut are indeterminate plants, producing fruit over the entire growing period. This means that at harvest pods are in all stages of maturity. Within this maturity distribution, immature peanuts are more prone to the development of off-flavors (1).

During postharvest curing, the moisture level of peanuts must be reduced from 30% in fresh dug peanuts to approximately 10%, to allow for safe storage. This is achieved by allowing peanuts to dry in the field, mechanical drying, or a combination of both. The effect of drying on off-flavor formation has been the focus of much research since the development of artificial drying techniques in the early 1950s. The fruity/fermented flavor defect was originally described as a high-temperature curing off-flavor. Over 40 years ago, Bailey and co-workers (2) and Beasley and Dickens (3) showed that off-flavors were produced in immature peanuts subjected to drying temperatures in excess

of 35 °C. It was also reported that high-temperature curing induced anaerobic respiration in peanuts, which in turn produced these off notes (3–5). Formaldehyde, acetaldehyde, acetone, 3-methylpropanal, butanal, 3-methylbutanal, 2-methylpentanal, hexanal, ethanol, and ethyl acetate were detected in high-temperature-cured peanuts and were believed to be indicators of flavor deterioration (6, 7). It was also shown that improper curing was more detrimental to immature peanuts than mature peanuts. Both qualitative and quantitative differences in volatiles of mature and immature peanuts were observed (8).

More recent work by Sanders and co-workers (9) also found that immature peanut cured at higher temperatures (above 35 °C), subjected to sensory analysis, had higher fruity/fermented scores and lower roasted peanut and sweet aromatic scores. Pattee and co-workers (10) showed that roasted peanut paste from Virginia-type peanuts with high levels of headspace volatiles, as measured by an organic volatile meter, contained higher levels of fruity/fermented off-flavor. They also observed that the fruity/fermented character not only produced the perceivable off-note, but also reduced the roasted peanut character. Similar results were observed in runner-type peanuts, where the fruity fermented intensity was shown to be inversely proportional to the roasted peanut attribute in immature peanut (11). Osborn and co-workers (12) measured the levels of acetaldehyde, ethanol, and ethyl acetate in peanuts during curing. The highest concentration of these volatiles were observed in immature peanuts dried at 40 °C. Very little increase in these volatiles was detected in mature peanuts dried at 40 °C.

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From the literature, one can clearly see that a relationship exists between immaturity, high-temperature curing, and the formation of fruity/fermented notes. Immature peanuts subjected to high-temperature curing generate the fruity/fermented off-notes, whereas mature peanuts do not. There also appears to be a correlation between the concentration of marker compounds, such as acetaldehyde, ethanol, and ethyl acetate, and the off-note. Nevertheless, the actual odorants responsible for the fruity/fermented off-notes had yet to be identified.

The purpose of the present study was to determine the impact of high-temperature curing on the formation of the fruity/fermented off-note in immature peanuts and use GC/olfactometry to identify the odorants responsible for the note.

MATERIALS AND METHODS

Peanuts. A high oleic acid indeterminate variety of peanuts (FlavorRunner 458) was freshly dug in West Texas in October of 2002. The peanuts were sorted by maturity, using pod mesocarp color as an indicator of maturity, and shipped overnight to New Jersey. The raw peanuts were divided into two groups, mature (black and brown mesocarp color) and immature (yellow and orange mesocarp color). The sorted samples were dried in air ovens (Barnstead/ThermoLyne 9000 Mechanical Convection Oven, Cole Parmer Instrument Co., IL), using a standard curing temperature of 27 °C and an elevated temperature, 40 °C, to a target moisture level of 10%. The moisture content was determined using a Karl Fischer technique (Orion Turbo2 Karl Fischer, Thermo Electron Corp., Beverly, MA).

The cured peanuts were roasted using the following procedure: blanched for 13 min at 94 °C and air roasted at 160 °C for 12.5 min, typical conditions for peanut roasting. The peanuts were roasted to a final color value of $L^* = 55$ on the L^*A^*B scale (Minolta Spectrophotometer CM-3500d, Ramsey, NJ). Since for a given roast time, immature peanuts roast darker than mature peanuts (1), the roasting times were slightly adjusted to obtain similar roast colors. The roasted peanuts were sealed in airtight bags and stored at -40 °C until analyzed.

Chemicals. The reference compounds ethyl 2-methylpropanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, propyl 3-methylbutanoate, butanoic acid, 3-methylbutanoic acid, and hexanoic acid were obtained from Sigma-Aldrich (Milwaukee, WI). D₁₁-Hexanoic acid was obtained from Cambridge Isotope Laboratories (Andover, MA).

Preparation of Aroma Extracts. Roasted peanut (100 g) was ground to a paste in a coffee mill. Saturated sodium chloride solution (100 mL) was added, and the slurry was extracted twice with 100 mL of redistilled diethyl ether (Burdick & Jackson, Muskegon, MI). The slurry was centrifuged to separate the ether layer. The ether layers were combined. The volatile fraction was obtained using the solvent-assisted flavor evaporation technique (SAFE) (13). The volatiles were distilled for 1.5 h under vacuum (9×10^{-5} mbar) with the sample temperature held at 30 °C. The ether distillate was dried using sodium sulfate, concentrated to 5 mL using a Vigreux column (60 × 1 cm i.d.) at 45 °C, and further concentrated to 200 μ L using a micro Vigreux apparatus (Wilmad/Labglass, Buena, NJ).

High-Resolution GC/Olfactometry (HRGC/O) and High-Resolution GC/Mass Spectrometry (GC/MS). HRGC/olfactometry was performed using an Agilent 5890 GC, equipped with a FFAP (free fatty acid phase; 30 m × 0.32 mm id × 0.25 μ m, Agilent J&W, Palo Alto, CA) fused silica capillary column. The samples were injected using an on-column injection technique at 35 °C. The oven temperature was held constant for 1 min and raised at 60 °C/min to 60 °C and then raised at 6 °C/min to a final temperature of 230 °C. The flow rate of helium (1.8 mL/min) was split 1:1 using a fused silica y-connector between the FID detector and the sniffport, both held at 230 °C. Linear retention indices were calculated using alkanes (C₇–C₂₄). Mass spectrometry was done using an Agilent 6890GC/5973 MSD (Palo Alto, CA) equipped with a FFAP (free fatty acid phase; 30 m × 0.25 mm id × 0.25 μ m, Agilent J&W, Palo Alto, CA) fused silica capillary column. The samples were injected using the split injection technique (10:1) at 250 °C. The oven temperature was held constant for 1 min at 35 °C, raised at 60 °C/min to 60 °C, and then raised at 6 °C/min to a final

temperature of 230 °C. The flow rate of helium was held constant at 1 mL/min. The electron impact spectra was generated at 70 eV. All of the odorants were identified using retention indices, mass spectra, and authentic standards.

Quantification of Compounds. For the determination of ethyl 2-methylbutanoate, ethyl 3-methyl butanoate, and ethyl 3-methylpropanoate, propyl 3-methylbutanoate was used as the internal standard. Since the esters coeluted with other peanut flavor compounds, selected ion monitoring (SIM) was used for quantification. For ethyl 2-methylbutanoate (m/z 102), ethyl 3-methylbutanoate (m/z 88), and ethyl 2-methylpropanoate (m/z 116), the ions in parentheses were monitored. Response factors were calculated using authentic standards and propyl 3-methylbutanoate (m/z 103). For the quantification of the organic acids in the peanut paste, D₁₁-hexanoic acid was used as the internal standard (m/z 63). Response factors were calculated for butanoic acid, 3-methylbutanoic acid, and hexanoic acid using m/z 60.

Sensory Evaluation. The roasted peanuts were ground to a paste and then evaluated by trained panelists using the flavor descriptive spectrum analysis technique (14). Both the qualitative and quantitative aspects of the peanut flavor were assessed. The panelists evaluated the following attributes: roasted peanut, dark roast, wood/hulls/skins, raw beany, fruity, and fermented, using the universal intensity scale 0–15.

For the recombination experiments, stock solutions of ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl 2-methylpropanoate, hexanoic acid, butanoic acid, and 3-methylbutanoic acid in peanut oil were prepared.

The individual compounds were added to a peanut paste free of off-notes, at levels detected in peanuts containing the fruity/fermented off-note. Ethyl 2-methylpropanoate and hexanoic acid were omitted from additional recombination work, since their overall contribution to the fruity/fermented flavor was minor as compared to the other esters and acids. This was due to the relatively low concentrations detected and higher odor thresholds of these compounds.

The control paste was produced from freshly roasted peanuts that were free of any off-notes. This paste had a strong roasted peanut aroma and no fruity or fermented notes.

The models selected for further testing were the control paste with the addition of two esters, ethyl 2-methylbutanoate and ethyl 3-methylbutanoate; the control with the addition of two acids, butanoic acid and 3-methylbutanoic acid; and the control with the addition of ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, butanoic acid, and 3-methylbutanoic acid.

The model paste samples were evaluated by the panel using the technique described above.

RESULTS AND DISCUSSION

Upon arrival, the wet peanuts were placed in air ovens to dry. The peanuts dried at 27 °C took 5 days to achieve a moisture level of 10%. The moisture content was measured daily until the target moisture content was achieved. The peanuts held at 40 °C took 3 days to achieve a moisture content of 6%. The peanuts cured at 40 °C were slightly lower in moisture, since they were dried over a weekend. In appearance, the immature and mature peanuts were identical in both size and shape.

Several hundred compounds (15, 16) have been identified in roasted peanut, most of which are not odor-active. This makes the chromatogram extremely complex. Some of the more potent odorants detected by GC/O in both the immature and mature high-temperature-cured roasted peanuts are summarized in **Table 1**. The identities of the odorants were confirmed using the retention index, odor quality, mass spectra, and, when available, the use of authentic standards. In the aroma isolate of the immature peanuts, three fruit-like odorants were detected. The odorants ethyl 2-methylpropanoate (**1**), ethyl 2-methylbutanoate (**4**), and ethyl 3-methylbutanoate (**5**) had fruity, apple-like aromas. In addition to the fruity esters, organic acids butanoic (**17**), 3-methylbutanoic (**19**), and hexanoic acid (**20**) were also detected. These odorants were not detected by GC/O

Table 1. Odorants Identified in Immature and Mature High-Temperature-Cured Roasted Peanuts Using GC/O

no.	compound	RI ^a	odor quality	immature ^b	mature	method of ID ^c	ref ^d
1	ethyl 2-methylpropanoate	969	fruity	+	–	MS	15
2	2,3-butanedione	984	buttery	+	–	MS + RI	15
3	2,3-pentanedione	1062	buttery	+	+	MS	16
4	ethyl 2-methylbutanoate	1055	green, fruity	+	–	MS + RI	15
5	ethyl 3-methylbutanoate	1072	fruity, apple-like	+	–	MS + RI	
6	hexanal	1087	grassy	+	+	MS + RI	15
7	octanal	1294	citrus-like	+	+	MS + RI	15
8	2,6-dimethylpyrazine	1334	nutty	+	+	MS	16
9	2-ethylpyrazine	1341	nutty	+	+	MS	16
10	2,3-dimethylpyrazine	1353	nutty	+	+	MS + RI	16
11	2-ethyl-5-methylpyrazine	1395	sweet, nutty	+	+	MS	15
12	trimethylpyrazine	1407	nutty	+	+	MS + RI	16
13	2-ethyl-3,6-dimethylpyrazine	1449	roasty	+	+	MS + RI	15
14	2-furanmethanethiol	1456	coffee-like	+	+	MS + RI	15
15	2-ethyl-3,5-dimethylpyrazine	1459	roasty	+	+	MS + RI	15
16	methional	1465	potato-like	+	+	MS + RI	16
17	butanoic acid	1633	sharp, sour	+	–	MS + RI	
18	phenylacetaldehyde	1658	honey-like	+	–	MS + RI	16
19	3-methylbutanoic acid	1673	rancid, cheesy	+	–	MS + RI	15
20	hexanoic acid	1848	cheesy, fatty	+	–	MS + RI	15
21	2-methoxyphenol	1870	sweet, smoky	+	+	MS	15
22	4-hydroxy-2,5-dimethyl-3(2H)-furanone	2039	strawberry-like	+	+	MS + RI	

^a RI on a FFAP capillary column. ^b +, detected by GC/O; –, not detected by GC/O. ^c Method of identification: MS, identified by comparison of mass spectrum to NIST mass spectral database, retention index, and odor quality; MS + RI, identified by comparison of mass spectrum, odor quality, and retention index to authentic compound.

^d Reference number where identified earlier.

Table 2. Concentration of Odorants in Immature and Mature Roasted Peanuts Cured at 40 and 27 °C

odorant	concentration, $\mu\text{g/g}$			
	cured at 40 °C		cured at 27 °C	
	immature	mature	immature	mature
ethyl 2-methylpropanoate	0.09	– ^a	– ^a	– ^a
ethyl 2-methylbutanoate	0.13	– ^b	– ^b	– ^b
ethyl 3-methylbutanoate	0.11	– ^b	– ^b	– ^b
butanoic acid	0.55	0.21	0.13	0.13
3-methylbutanoic acid	3.04	0.59	0.28	0.07
hexanoic acid	0.17	0.05	0.04	0.03

^{a,b} Limit of detection: $a = 0.010 \mu\text{g/g}$, $b = 0.002 \mu\text{g/g}$.

in the immature peanuts cured at low temperature and mature peanuts cured at either low or high temperatures. Besides these odorants, 16 additional potent peanut odorants detected in both the immature and mature high-temperature-cured peanut isolates are also shown in **Table 1**.

The roasty, nutty note in the isolates was due to a series of alkyl pyrazines, 2,6-dimethylpyrazine (**8**), 2-ethylpyrazine (**9**), 2,3-dimethylpyrazine (**10**), 2-ethyl-5-methylpyrazine (**11**), trimethylpyrazine (**12**), 2-ethyl-3,6-dimethylpyrazine (**13**), and 2-ethyl-3,5-dimethylpyrazine (**15**). 2,3-Butanedione (**2**) and 2,3-pentanedione (**3**) produced butter-like aromas. Hexanal (**6**) and octanal (**7**) had green, fatty aromas. 2-Furanmethanethiol (**14**), 2-methoxyphenol (**21**), and methional (**16**) contributed sulfury coffee, sweet smoky, and potato-like notes. Phenylacetaldehyde (**18**) provided a sweet honey-like note. The remaining odorants, with the exception of 4-hydroxy-2,5-dimethyl-3(2H)-furanone (**22**), have all been reported in roasted peanuts or peanut oil. (15, 17). Matsui and co-workers (15), using aroma extract dilution analysis (AEDA), detected ethyl 2-methylbutanoate (**4**) and ethyl 2-methylpropanoate (**1**) in roasted peanut oil. This would seem to indicate that the peanuts used for oil extraction contained to some degree the fruity/fermented off-note.

Table 2 shows the quantitative results for the esters and acids in the immature and mature peanut samples cured at high and low temperature. Ethyl 2-methylpropanoate, ethyl 2-methyl-

butanoate, and ethyl 3-methylbutanoate were only detected in the high-temperature-cured immature peanuts. The levels of butanoic, 3-methylbutanoic, and hexanoic acids were higher in the immature high-temperature-cured samples.

Sensory analysis of the immature peanuts cured at high-temperature found a high intensity of fruity, fermented, and sour notes (**Figure 1**). Both the mature and immature peanuts cured at 27 °C had no fruity, fermented, or sour attributes and also had higher roasted peanut notes than those cured at high temperature. When comparing immature and mature peanuts cured at low temperature, the immature peanuts also had lower roasted peanut and higher dark roast notes than the mature peanut. The sensory results agreed well with published data that found lower sweet aromatic and roasted peanut ratings and higher ratings for fruity/fermented, painty, sour, and bitter for immature peanuts cured at higher temperatures (9).

The three esters detected in fruity/fermented peanuts but absent in the peanuts free of the defect are common to many fruits (18). Ethyl 2-methylpropanoate and ethyl 2-methylbutanoate have been found in melon (19), grapefruit juice (20), oranges (21), durian fruit (22), and hop cones (23). Ethyl 2-methylbutanoate has been identified as the aroma impact compound in apple (24), pineapple (25), and Asian pear (26). Ethyl 2-methylbutanoate and ethyl 3-methylbutanoate have been detected in fresh strawberry juice (27). All three esters have been found in white wines Gewürztraminer and Scheurebe (28) and red wines Cabernet Sauvignon and Merlot (29). They also have been shown to contribute to the aroma of virgin olive oil, where their odor thresholds (orthonasal in oil) were also reported: ethyl 2-methylpropanoate (1.24 $\mu\text{g/L}$), ethyl 2-methylbutanoate (0.26 $\mu\text{g/L}$), and ethyl 3-methylbutanoate (0.62 $\mu\text{g/L}$) (30).

The organic acids detected are usually associated with cheese and dairy flavors (31) but have also been found in a wide variety of other foods. 3-Methylbutanoic acid has been detected in cooked rice (32), fermented apple (33), milk chocolate (34), honey (35), wine vinegar (36), and strawberry juice (27). It has also been identified as a contributor to the characteristic off-odor of sugar beet (37). Due to the relatively high odor

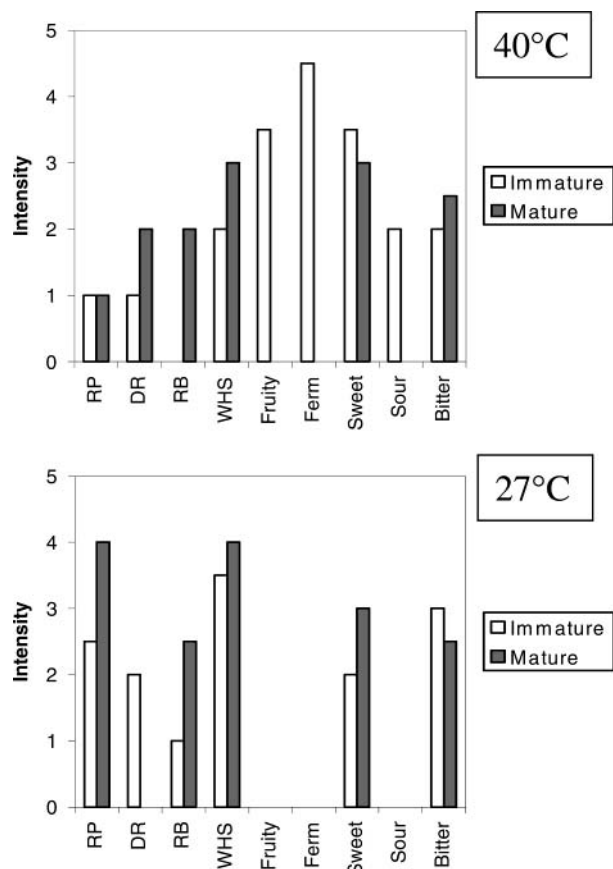


Figure 1. Flavor profile analysis for immature and mature roasted peanuts cured at 40 and 27 °C. RP = roasted peanut, DR = dark roast, RB = raw beany, WHS = wood/hulls/skins, Fruity = fruity, Ferm = fermented. Intensity range = 0–15.

Table 3. Concentration of Odorants in Immature Unroasted Peanuts Cured at 40 °C and 27 °C

odorant	concentration, $\mu\text{g/g}$	
	40 °C	27 °C
ethyl 2-methylpropanoate	0.08	— ^a
ethyl 2-methylbutanoate	0.29	— ^b
ethyl 3-methylbutanoate	0.28	— ^b
butanoic acid	0.06	— ^b
3-methylbutanoic acid	0.07	— ^b
hexanoic acid	0.02	— ^b

^{a,b} Limit of detection: $a = 0.05 \mu\text{g/g}$, $b = 0.01 \mu\text{g/g}$. Raw peanut paste in solvent forms an emulsion that affects the recovery of odorants. This explains the higher detection limit in raw peanuts when compared to roasted peanuts.

thresholds (orthonasal in oil) of 3-methylbutanoic acid (22 $\mu\text{g/L}$) (30), butanoic acid (135 $\mu\text{g/L}$) (38), and hexanoic acid (5400 $\mu\text{g/L}$) (38), the contribution of these organic acids to the odor of a given food can range from relatively little impact to important key odorants. In the case of the fruity/fermented off-note for peanuts, the contribution of 3-methylbutanoic acid to the fermented aroma was significant.

The presence of the fruity, fermented odorants was also examined in unroasted immature peanuts cured at high and low temperatures (see **Table 3**). The esters and organic acids were detected in the high-temperature-cured (40 °C) unroasted immature peanuts. Neither the esters nor acids were detected in the low-temperature-cured (27 °C) unroasted immature peanuts.

Table 4. Retronasal Flavor Profiles of Peanut Paste from High-Temperature-Cured Immature Peanuts and Fruity/Fermented Peanut Paste Models^a

model	concentration, $\mu\text{g/g}$				sensory results ^b		
	E2MB	E3MB	BA	3MB	RP	fruity	fermented
control	—	—	—	—	5.5	0.0	0.0
1	0.10	0.10	—	—	4.0	3.0	0.0
2	—	—	0.45	2.16	5.0	0.0	1.0
3	0.10	0.10	0.45	2.16	3.0	3.0	4.0
immature	0.13	0.11	0.55	3.04	1.0	2.0	4.5

^a E2MB = ethyl 2-methylbutanoate, E3MB = ethyl 3-methylbutanoate, BA = butanoic acid, 3MB = 3-methyl butanoic acid, RP = roasted peanut. ^b The intensity of the attributes was evaluated using the universal intensity scale 0–15.

When comparing roasted and unroasted immature high temperature cured samples, the level of ethyl 2-methylpropanoate was comparable in both the roasted and unroasted samples. The levels of ethyl 2-methylbutanoate and ethyl 3-methylbutanoate were slightly higher in the unroasted peanuts. The reduction in odorants in roasted peanut may be due to a loss of volatiles during roasting. Roasting had the opposite effect on the organic acid levels, where an increase ranging from 10- to 40-fold in the organic acids levels was observed in the roasted peanut samples. An increase after roasting was also seen in the low-temperature-cured immature peanuts. The high temperature, along with the rapid moisture loss during roasting, may generate free fatty acids. The esters and organic acids were not detected in the unroasted low-temperature-cured peanut. Sensory analysis of the raw samples found no difference between mature and immature peanut due to the intense raw beany flavor of raw peanut, which masked any perception of the fruity/fermented flavor.

A series of recombination studies was performed to determine the effect of the fruity esters and organic acids on the perception of the fruity/fermented off-note. The concentrations of the odorants added to the peanut paste and the sensory scores for the attributes roasted peanut, fruity, and fermented are shown in **Table 4**. The level of odorants detected in the immature high-temperature-cured peanuts and the sensory score is also shown. The addition of ethyl 2-methylbutanoate and ethyl 3-methylbutanoate in model 1, as expected, increased the fruity note and slightly reduced the perception of roasted peanut. The addition of organic acids butanoic and 3-methylbutanoic (model 2) produced a slight increase in the fermented note with no significant effect on the roasted peanut perception. The addition of both the esters and acids (model 3) yielded a similar level of the fruity note as esters alone and an increase in the perception of the fermented note. There was also a significant reduction in perception of the roasted peanut note. The sensory results are shown in **Figure 2**.

The fruity esters themselves had a pleasant fruit-like aroma. When tasted in a peanut matrix in the presence of the organic acids, the esters were no longer perceived as positive flavors. The presence of these odorants also suppressed the perception of the roasted peanut note. This effect enhanced the off-note, since in addition to perceiving the off-flavor, there was also a reduction in the positive peanut aroma.

These results are in agreement with those of Pattee and co-workers (39), who found that the fruity/fermented attribute in some roasted peanut samples associated with immaturity and exposure to extreme environmental conditions consistently related to a reduction in the roasted peanut attribute response.

The exact chemical pathway leading to the formation of the fruity/fermented compounds is not clear. Temperature stress in

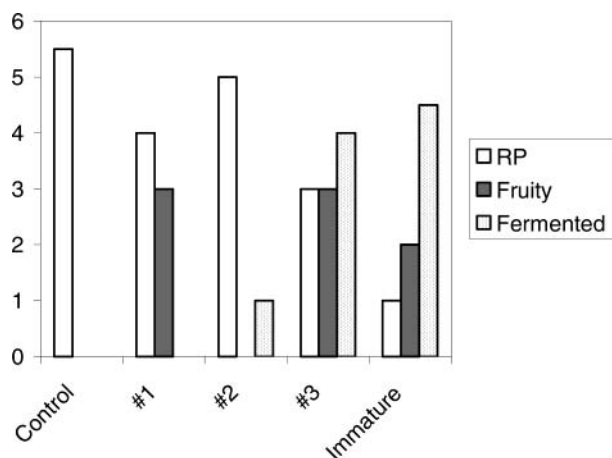


Figure 2. Flavor profiles of control peanut paste, fruity/fermented models, and paste from high-temperature-cured immature peanuts.

peanuts has been shown to produce cell damage, which allows for mixing of cellular components (40). In immature peanuts, the biosynthesis of protein, fat, and carbohydrate is incomplete (41, 42). This mixing of cellular components may explain why immature peanuts are more susceptible to off-note formation.

Whitaker and co-workers (4, 5) had proposed that during high-temperature curing of immature peanuts there was a limited diffusion rate of oxygen. This in turn, converted respiration from an aerobic to an anaerobic process, resulting in the high levels of acetaldehyde, ethyl acetate, and ethanol seen in immature peanuts. It has been proposed that this process generates the off-note compounds.

In summary, these results have confirmed that the fruity/fermented note can be generated in immature peanuts cured at high temperature, 40 °C. The note is due to fruity esters, ethyl 2-methylpropanoate, ethyl 2-methylbutanoate, and ethyl 3-methylbutanoate. The elevated level of organic acids, butanoic acid and 3-methylbutanoic acid, enhanced the perception of this off note. The combination of both the esters and acids also reduced the perception of the roasted peanut note of the freshly roasted sample.

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LITERATURE CITED

- Sanders, T. H.; Vercellotti, J. R.; Crippen, K. L.; Civille, G. V. Effect of maturity on roast color and descriptive flavor of peanuts. *J. Food Sci.* **1989**, *54*, 1989.
- Bailey, W. K.; Pickett, T. A.; Futral, J. G. Rapid curing adversely affects quality of peanuts. *Peanut J. Nut. World* **1954**, *33*, 17.
- Beasley, E. O.; Dickens, J. W. Engineering research in peanut curing. *North Carolina Exp. Sta. Technol. Bull.* **1963**, No. 155.
- Whitaker, T. B.; Dickens, J. W. The effects of curing on respiration and off-flavor in peanuts. *Proceedings of the Third National Peanut Research Conference*; Auburn University, Auburn, AL, 1964; p 71.
- Whitaker, T. B.; Dickens, J. W.; Bowen, H. D. Effects of curing on the internal oxygen concentration of peanuts. *Trans. ASAE* **1974**, *17*, 567.
- Pattee, H. E.; Beasley, E. O.; Singleton, J. A. Isolation and identification of volatile components from high-temperature-cured off-flavor peanuts. *J. Food Sci.* **1965**, *30*, 388.
- Singleton, J. A.; Pattee, H. E.; Johns, E. B. Influence of curing temperature on the volatile components of peanuts. *J. Agric. Food Chem.* **1971**, *19*, 130–133.
- Pattee, H. E.; Singleton, J. A. Peanut quality: Its relationship to volatile compounds—A review. In *Quality of Fruits and Vegetables in North America*; ACS Symposium Series 170; Teranishi, R., Ed.; American Chemical Society: Washington, DC, 1981; pp 147–161.
- Sanders, T. H.; Vercellotti, J. R.; Blankenship, P. D.; Crippen, K. L.; Civille, G. V. Interaction of maturity and curing temperature on descriptive flavor of peanuts. *J. Food Sci.* **1989**, *54*, 1066–1069.
- Pattee, H. E.; Rogister, E. W.; Giesbrecht, F. G. Interrelationship between headspace volatile concentration, selected seed size categories and flavor in large-seeded Virginia-type peanuts. *Peanut Sci.* **1989**, *16*, 38–42.
- Pattee, H. E.; Yokoyama, W. H.; Collins, M. F.; Giesbrecht, F. G. Interrelationship between headspace volatile concentration, marketing grades, and flavor in runner type peanuts. *J. Agric. Food Chem.* **1990**, *38*, 1055–1060.
- Osborn, G. S.; Young, J. H.; Singleton, J. A. Measuring the kinetics of acetaldehyde, ethanol, and ethyl acetate within peanut kernels during high-temperature drying. *Trans. ASAE* **1996**, *39*, 1039–1045.
- Engel, W.; Bahr, W.; Schieberle, P. Solvent Assisted Flavour Evaporation (SAFE)—A new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrices. *Eur. Food Res. Technol.* **1999**, *209*, 237–241.
- Muñoz, A. M.; Civille, G. V. *The Spectrum Descriptive Analysis Methodology Manual on Descriptive Analysis Testing for Sensory Evaluation*; ASTM:MNL13; ASTM: Philadelphia, PA, 1992; pp 22–34.
- Walradt, J. P.; Pittet, A. O.; Kinlin, T. E.; Muralidhara, R.; Sanderson, A. Volatile components of roasted peanuts. *J. Agric. Food Chem.* **1971**, *19*, 972–979.
- Sanders, T. H.; Pattee, H. E.; Vercellotti, J. R.; Bett, K. L. Advances in Peanut Flavor Quality. In *Advances in Peanut Science*; Pattee, H. E., Stalker, H. T., Eds.; APRES: Stillwater, OK, 1995; pp 528–553.
- Matsui, T.; Guth, H.; Grosch, W. A comparative study of potent odorants in peanut, hazelnut, and pumpkin seed oils on the basis of aroma extract dilution analysis (AEDA) and gas chromatography—olfactometry of headspace samples (GCOH). *Fett/Lipid* **1998**, *100*, 51–56.
- Paillard, N. M. M. The flavor of apples, pears and quinces. In *Foods Flavours Part C. The Flavour of Fruit*; Marton, I. D., MacLeod, A. J., Eds.; Elsevier: Amsterdam, 1990; pp 1–41.
- Bauchot, A. D.; Mottram, D. S.; Dodson, A. T.; John, P. Effect of aminocyclopropane-1-carboxylic acid oxidase antisense gene on the formation of volatile esters in cantaloupe charantais melon (*Cv. Vedrandais*). *J. Agric. Food Chem.* **1998**, *46*, 4787–4792.
- Buettner, A.; Schieberle, P. Evaluation of key aroma compounds in hand-squeezed grapefruit juice (*Citrus paradisi* Macfayden) by quantitation and flavor reconstitution experiments. *J. Agric. Food Chem.* **2001**, *49*, 1358–1363.
- Buettner, A.; Schieberle, P. Evaluation of aroma differences between hand-squeezed juices from valencia late and navel oranges by quantification of key odorants and flavor reconstitution experiments. *J. Agric. Food Chem.* **2001**, *49*, 2387–2394.
- Weenen, H.; Koolhaas, W. E.; Apriyantono, A. Sulfur-containing volatiles of durian fruits (*Durio zibethinus* Murr.) *J. Agric. Food Chem.* **1996**, *44*, 3291–3293.
- Steinhaus, M.; Schieberle, P. Comparison of the most odor-active compounds in fresh and dried hop cones (*Humulus lupulus* L. Variety Spalter select) based on GC—olfactometry and odor dilution techniques. *J. Agric. Food Chem.* **2000**, *48*, 1776–1783.
- Flath, R. A.; Black, D. R.; Forrey, R. R.; McDonald, G. M.; Mon, T. R.; Teranishi, R. Volatiles in Gravenstein apple essence identified by GC mass spectrometry. *J. Chromatogr. Sci.* **1969**, *7*, 508–512.
- Rettinger, K.; Karl, V.; Schmarr, H. G.; Detter, F.; Hener, U.; Mosandl, A. Chiroselective analysis of 2-alkyl-branched alcohols, acids and esters: Chirality evaluation of 2-methylbutanoates from apples and pineapples. *Phytochem. Anal.* **1991**, *2*, 184–188.

- (26) Takeoka, G. R.; Buttery, R. G.; Flath, R. A. Volatile constituents of Asian pear (*Pyrus serotina*). *J. Agric. Food Chem.* **1992**, *40*, 1925–1929.
- (27) Schieberle, P.; Hofmann, T. Evaluation of the character impact odorants in fresh strawberry juice quantitative measurements and sensory studies on model mixtures. *J. Agric. Food Chem.* **1997**, *45*, 227–232.
- (28) Guth, H. Identification of character impact odorants of different white wine varieties. *J. Agric. Food Chem.* **1997**, *45*, 3022–3026.
- (29) Kotseridis, Y.; Baumes, R. Identification of impact odorants in Bordeaux red grape juice, in the commercial yeast used for its fermentation, and in the produced wine. *J. Agric. Food Chem.* **2000**, *48*, 400–406.
- (30) Reiners, J.; Grosch, W. Odorants of virgin olive oil with different flavor profiles. *J. Agric. Food Chem.* **1998**, *46*, 2754–2763.
- (31) Sable, S.; Cotteceau, G. Current knowledge of soft cheeses flavor and related compounds. *J. Agric. Food Chem.* **1999**, *47*, 4825–4236.
- (32) Jezussek, M.; Juliano, B. O.; Schieberle, P. Comparison of key aroma compounds in cooked brown rice varieties based on aroma extract dilution analyses. *J. Agric. Food Chem.* **2002**, *50*, 1101–1105.
- (33) Schumacher, K.; Asche, S.; Heil, M.; Mittelstadt, F.; Dietrich, H.; Mosandl, A. Methyl-branched flavor compounds in fresh and processed apples. *J. Agric. Food Chem.* **1998**, *46*, 4496–4500.
- (34) Schnermann, P.; Schieberle, P. Evaluation of key odorants in milk chocolate and cocoa mass by aroma extract dilution analyses. *J. Agric. Food Chem.* **1997**, *45*, 867–872.
- (35) Himoda, M.; Wu, Y.; Osajima, Y. Aroma compounds from aqueous solution of haze (*Rhus succedanea*) honey determined by adsorptive column chromatography. *J. Agric. Food Chem.* **1996**, *44*, 3913–3918.
- (36) Charles, M.; Martin, B.; Ginies, C.; Etievant, P.; Coste, G.; Guichard, E. Potent aroma compounds of two red wine vinegars. *J. Agric. Food Chem.* **2000**, *48*, 70–77.
- (37) Marsili, R. T.; Miller, N.; Kilmer, G. J.; Simmons, R. E. Identification and quantitation of the primary chemicals responsible for the characteristic malodor of beet sugar by purge and trap GC-MS–OD techniques. *J. Chromatogr. Sci.* **1994**, *32*, 165–171.
- (38) Schieberle, P.; Gassenmeier, K.; Guth, H.; Sen, A.; Grosch, W. Character impact odour compounds of different kinds of butter. *Lebensm. Wiss. Technol.* **1993**, *26*, 347–356.
- (39) Pattee, H. E.; Giesbrecht, F. G. Adjusting roasted peanut attribute scores for fruity attribute and nonoptimum CIELAB L* values. *J. Sensory Stud.* **1994**, *9*, 353–363.
- (40) Singleton, J. A.; Pattee, H. E. The effects of cold and heat stress on the chemistry and cell structure of peanut seeds. *Peanut Sci.* **1997**, *24*, 32–37.
- (41) Pattee, H. E.; Purcell, A. E.; Johns, E. B. Changes in carotenoid and oil content during maturation of peanut seeds. *J. Am. Oil Chem. Soc.* **1969**, *46*, 629–631.
- (42) Pattee, H. E.; Johns, E. B.; Singleton, J. A., Sanders, T. H. Composition changes of peanut fruit parts during maturation. *Peanut Sci.* **1974**, *1*, 57–62.

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