Compounds Contributing to the Characteristic Aroma of Malted Barley

Andrew D. Beal† and Donald S. Mottram*

Department of Food Science and Technology, University of Reading, Whiteknights, Reading RG6 2AP, United Kingdom

The volatiles from malt, sampled at stages during roasting, were examined by GC odor-port evaluation and by GC–MS. The technique of odor dilution was applied to volatile extracts from samples exhibiting strong malt-like characteristics. Seven odors from the GC column persisted through several dilutions. 3- and 2-methylbutanal were responsible for the odors with the highest dilution factors which had malty characteristics. The other five odors were malty or cereal-like; ethylmethylpyrazines and maltol may contribute to these odors, but other compounds responsible were present at very low concentrations and have not yet been identified. The levels of 2- and 3-methylbutanal increased dramatically in malt during roasting.

Keywords: *Aroma; malted barley; roasting; methylbutanal*

INTRODUCTION

Malting involves the controlled germination and subsequent drying of cereal grains, usually barley. The many different types of malt are produced by manipulating the conditions of these two operations (Bevan, 1988; Briggs et al., 1981).

Malt is used as an ingredient in a number of products but is seldom used as a food in its own right. It is principally used by the brewing and distilling industries as a source of fermentable carbohydrate and diastatic enzymes. Speciality malts are used by brewers to impart color to the beer. Advances in malting technology have improved these properties, but less attention has been paid to the development of flavor in malt. The use of malt as a food ingredient has, until recently, been limited to bakery and confectionery products and a number of milk-based drinks.

Adverse consumer attitudes are behind a move away from artificial flavors and colors. Malt, the product of a traditional industry, has an inherently natural image and has been viewed as a potential source of color and flavor for a range of products such as snacks, ice cream, soft drinks, and coatings (Hall, 1988). Suitable manipulation of malting conditions could optimize the malty character of malt, yielding a more flavorful product for use as an ingredient.

A number of studies have examined the volatile components of the various types of malt, including green malt and barley, but these have been concerned mainly with the role of malt in the flavor of beer and the fate of volatiles during fermentation (Jackson and Hudson, 1978; Lukes et al., 1988; Tressl et al., 1974; Zuercher et al., 1981). Two studies have attempted to correlate volatile components with sensory characteristics. Przybylski and Kaminski (1983) described the effect of pH and temperature on the odor of malt and its volatile components, and Kaminski et al. (1981) used fractionation combined with GC eluate sniffing to assign odor characteristics to several chromatographic peaks in extracts prepared from samples of rye grain, malt, and whole-meal bread.

In a recent paper, we described the sensory properties of a range of malts, sampled during the production of a crystal malt (Beal and Mottram, 1993). It was found that those samples taken from the later stages of roasting were described by the panel as "malty", "caramel-like", and "chocolate-like".

The aim of the work described in this paper was to identify potential contributors to malt aroma in samples selected during the roasting of malted barley. Volatiles were analyzed by GC–MC, and components of odor significance were detected using GC odor-port evaluation of a series of diluted volatile extracts.

EXPERIMENTAL PROCEDURES

Preparation of Malt. Malted barley (var. Scottish Tyne), from a normal production run of crystal malt, was supplied by H. W. Baird and Sons, Witham, Essex, England. The grain was loaded into steep tanks and subjected to a steeping cycle involving one 6 h and two 8 h soaks punctuated by two 10 h air rests. Gibberellic acid at 0.3% was applied after steeping, and the grain was transferred to a saladin box for a further 4 days at 17 °C. The green malt was then transferred by truck from the company's Lothian Maltings to Essex (approximately 8 h), where the grain was roasted in a cylindrical rotating coffee roaster (capacity 2 tonne). A stewing phase was unnecessary as sufficient saccharification occurred during transport. Roasting was continued in a dry current of air until the malt had attained the characteristic color of crystal malt. Samples of malt were collected at approximately 5 min intervals during the final 30 min of roasting. Samples were then freeze-dried to a moisture content of between 3% and 7% and stored in sealed polythene containers at −20 °C.

Isolation of Volatiles by Simultaneous Distillation Extraction. A volatile extract was prepared from one of the malt samples which sensory profiling had judged to have the strongest malt-like aroma (Beal and Mottram, 1993). The malt (100 g) was milled in a domestic coffee mill for 15 s and dispersed in 1 L of distilled water in a modified Likens–Nickerson simultaneous distillation extraction apparatus (Mottram and Puckey, 1978). The steam distillate was continuously extracted for 2 h with 45 mL of redistilled diethyl ether containing 100 μg of *n*-octadecane as an internal standard. The extract was concentrated using a Kuderna–Danish apparatus, over a water bath at 45 °C. A series of dilutions (40%, 4%, 0.4%, 0.2%, 0.025%, 0.015%) was prepared from the concentrated extract using redistilled diethyl ether.

* Author to whom correspondence should be addressed.

† Present address: SmithKline Beecham Consumer Brands, Stoke Poges Lane, Slough, Berkshire SL1 3NW, U.K.

0021-8561/94/1442-2880$04.50/0

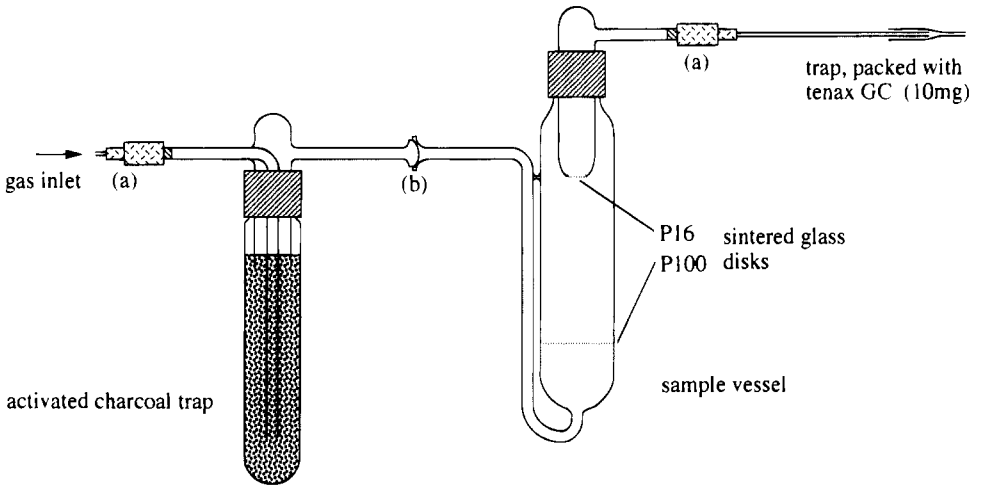

Figure 1. Apparatus for collection of headspace volatiles from malted barley.

Gas Chromatography. A split/splitless injection was used to introduce 1 μL aliquots of each dilution onto a fused silica capillary column installed in a Hewlett-Packard HP5890 gas chromatograph. The column effluent was split equally between a flame ionization detector and an odor port, where the aromas of the eluting components could be evaluated.

Each extract was analyzed on a 30 m × 0.32 mm (i.d.) capillary column coated with DB-5 at 1 μm film thickness (J&W Scientific). Helium was used as a carrier gas, with a flow set at 2 mL/min. The oven was held at 5 °C for 30 s during injection; the temperature was then raised to 60 °C in 1 min, held for 5 min, and then programmed at 4 °C/min to 250 °C. The 40% dilution of the concentrate was also analyzed on a 50 m × 0.32 mm (i.d.) column, coated with BP-20 at 0.5 μm film thickness (SGE Ltd.), under similar conditions except the final temperature was 200 °C.

GC Odor-Port Evaluation and Odor Dilution. The odors of the eluting components were evaluated for the series of diluted extracts, by a total of six assessors evaluating the extracts separately. Each was asked to describe the odors perceived, which were recorded with the retention times of the odors. The diluted extracts were assessed in order of increasing dilution until aromas could no longer be detected.

Gas Chromatography–Mass Spectrometry (GC–MS). The extract (40% dilution) was also analyzed by GC–MS using a Hewlett-Packard HP5988A mass spectrometer fitted with an HP 5980 GC and an HP Chemstation data system. Both the DB-5 and the BP-20 columns were used. The GC conditions used were the same as those described above. The following conditions were used for the mass spectrometer: source temperature, 200 °C; ionizing voltage, 70 eV; scan range from *m/z* 29 to 290, with 1 scan/s.

Identification of mass spectra was made by comparison with known spectra from compounds analyzed in this laboratory or from spectra in reference collections (NIST/EPA/MSDC, 1992; ten Noever de Brauw et al., 1980). Whenever possible, identification was confirmed by comparing the linear retention indices (LRI) of sample peaks with those of authentic standards, run under similar conditions.

Isolation of Volatiles by Headspace Concentration. Malt from each of the 11 samples obtained during the roasting was analyzed by headspace concentration and GC–MS. Samples (15 g) were milled for 15 s in a domestic coffee mill. Each sample was placed on a glass frit in a special sampling tube (Figure 1). Oxygen-free nitrogen was passed through the sample for 1 h at a rate of 40 mL/min, and the volatiles were swept onto a trap packed with Tenax GC (SGE Ltd.) (Whitfield et al., 1988). The sample was maintained at 35 °C throughout collection.

After collection, the volatiles were thermally desorbed, using a modified injector port, directly onto the front of the DB-5 column in the oven of the GC–MS. The GC oven was held at 0 °C for 5 min while the volatiles were desorbed from the Tenax trap (held at 250 °C in the modified injector) onto the front of the column. The oven temperature was raised to 60 °C over 1 min, held for 5 min at 60 °C, and then programmed to 250 °C at a rate of 4 °C/min. Other GC and MS conditions were as described above.

Table 1. Odors Detected in GC Effluent

no.	odor description	LRI (DB-5)	dilution factor[a]
a	chocolate, almond, malty, cheesy	641–648	8000
b	estery apple, almond, malty	651–659	4000
c	almond, husk-like, malt biscuit	765–777	1000
d	brothy, malty, cereal, yeast, sweet	911–932	4000
e	brothy, malty	949–960	1000
f	brothy, bready, biscuit, cake	999–1009	1000
g	butter, biscuit, malty	1116–1123	1000

[a] Dilution factor for extract at which odor could be detected. Only those odors with dilution factors >1000 are reported.

RESULTS AND DISCUSSION

The previous sensory work had indicated that the maximum malt-like character was obtained in the malted barley which was sampled during the last 15 min of the roasting treatment for crystal malt (Beal and Mottram, 1993). Over 200 compounds have now been isolated from malted barley roasted under these conditions. These include aliphatic alcohols, aldehydes and ketones, pyrroles, furans, and pyrazines. To establish those components which contributed to the characteristic aroma of the malted barley, odor-port evaluation of the eluting components was carried out and the method of odor dilution was used to estimate the relative contributions of the different components. In this technique (Ullrich and Grosch, 1987) a series of increasingly dilute solutions of the aroma extract were analyzed by GC odor-port evaluation, and those components persisting through the maximum number of dilutions were considered to be the major contributors to the overall aroma of the extract.

The assessors varied in sensitivity by approximately 2 orders of magnitude, and there was not a full consensus of descriptive terms. However, individuals were consistent within their own vocabularies and, most importantly, there was agreement on the retention times of those odors which persisted in the series of dilutions. Of the principal odors, four were easily resolved by the assessors and fell into tight linear retention index (LRI) bands. The remaining three came from a region of intense odor activity between LRI 900 and 1000 (Table 1). In the undiluted extract a large number of odors elute in this region of the chromato-

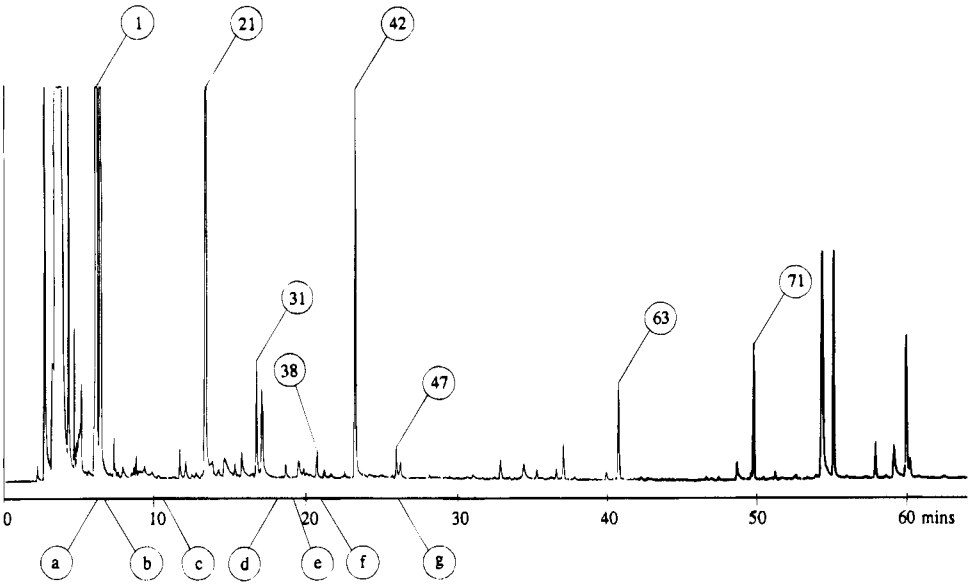

Figure 2. Chromatogram of volatiles from extract of malted barley, showing areas where main odors were detected in GC effluent (a–g). Major peaks are numbered.

gram, and it was the persistence of some of these odors that gave rise to "tailing" of the odor descriptions and relatively wide LRI bands for the odors.

From the chromatogram (Figure 2) and Table 1, it can be seen that the odor with the highest dilution factor (labeled a) coincided with the largest peak on the chromatogram. This compound was identified as 3-methylbutanal (Table 2). Of the two odors with the second highest dilution factors, the one at LRI 651–657 (b) coincided with the second largest peak on the chromatogram and was identified as 2-methylbutanal. The odor of 3-methylbutanal has been previously reported as malty in aqueous solution (Amoore et al., 1976), in wheat and rye bread crusts (Schieberle and Grosch, 1987), and in milk (Badings, 1991). It has also been given descriptions such as fruity, chocolate-like, sweet, bready, toasted, and burnt cheese (Fors, 1983). Similar descriptions have been used for 2-methylbutanal, and it has also been described as malty in milk (Badings, 1991), although at high concentration both methylbutanals were described as pungent, overpowering, and irritating (Arctander, 1969). The descriptions used by the panel for the methylbutanals were consistent with those reported in the literature.

The odor eluting at LRI 911–932 (d) could not be attributed to any of the dozen or so peaks from this part of the chromatogram. Ethyl- and dimethylpyrazines elute in this region on the DB-5 column and in an equivalent odor active region on the BP-20 phase. These compounds have odors that have been described as nutty, green, and roasted (Fors, 1983). Although these descriptions are not dissimilar to those reported in this work (sweet, cereal-like, and malty), the relatively high odor thresholds (Van Gemert and Nettenbreijer, 1977) of these compounds made it unlikely that the pyrazines were responsible for the odors with these high dilution factors. This was confirmed by GC odorport evaluation of solutions of ethyl and dimethylpyrazines at concentrations of 100, 10, and 1 mg/L; none of the compounds could be detected at these low concentrations. The compounds responsible for these and the later odor active regions are present at much lower concentrations than the 2- and 3-methylbutanals and must have low odor threshold values, making them potentially important malt character-impact compounds.

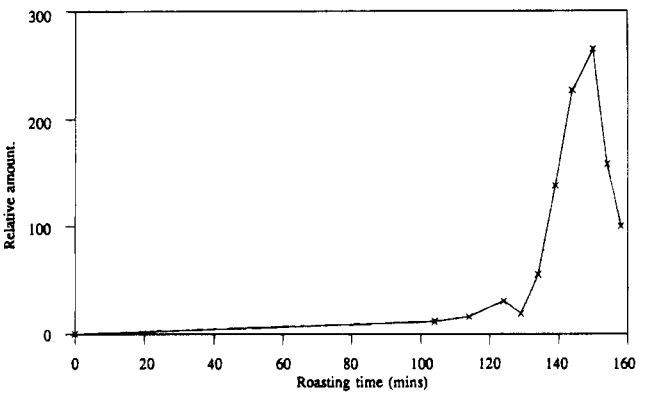

Figure 3. Changes in the relative amount of 3-methylbutanal in the headspace volatiles of malted barley sampled during roasting.

Identifications of some components present in the four other odor active regions (c, e, f, g), which share the third highest dilution factors, are also given the Table 2. The ethylmethyl- and trimethylpyrazines (LRI 994–1001) have been described as roast, nutty, and toffee-like (Fors, 1983; Maga, 1992). They have much lower odor threshold values than the dimethylpyrazines and are probably responsible for the odor eluting at LRI 999–1009 (f). Maltol (3-hydroxy-2-methyl-4-pyranone, LRI 1110), which has a caramel-like, malty, fruity odor (Fors, 1983), may be responsible for the aroma in the region described as malty biscuit-like and buttery (g), although it has a relatively high odor threshold value (7–35 mg/L) suggesting that another compound may be involved. The adjacent compounds, 2-isopropyl-5-methyl-2-hexenal (LRI 1106) and 2-phenylethanol (LRI 1116), have been described as floral (Bauer et al., 1990). No compounds responsible for the other odor-active regions (c and e) have been identified.

An examination of the changes in methylbutanal content of malt, during roasting, has been made on samples from three separate malt roastings, using headspace concentration on Tenax and GC–MS analysis. All showed similar trends, of which Figure 3 is typical. The level of 2-methylbutanal and 3-methylbutanal rose, from undetected in the "green" malt before roasting, to a maximum during the last 10–15 min of

Table 2. Compounds Identified in Areas of Aroma Interest in the Gas Chromatogram of the Volatiles from Malted Barley

peak no.[a]	identity[b]	LRI DB-5	LRI BP-20	method of identification[c]
1	3-methylbutanal	642	923	MS + LRI
2	2-methylbutanal	652	944	MS + LRI
3	2,3-pentanedione	658	1071	MS + LRI
4	*3-hydroxy-2-butanone*	*705*	*1317*	*MS + LRI*
10	methylbenzene	761		MS + LRI
	2-ethenylfuran	761	1192	ms
	1-pentanol	761		MS + LRI
13	2-ethyl-5-methylfuran	771		MS + LRI
14	2-methyl-2-butenal	777		ms
16	*hexanal*	*795*	*1099*	*MS + LRI*
21	*2-furfural*	*832*	*1495*	*MS + LRI*
24	*2-furylmethanol*	*853*	*1692*	*MS + LRI*
28	*5-methylene-2(5H)-furanone*	*878*	*1623*	*ms*
31	*3-methylthiopropanal*	*901*	*1484*	*ms*
32	2-acetylfuran	907	1536	MS + LRI
	2,5-dimethylpyrazine	908	1306	MS + LRI
	2,6-dimethylpyrazine	909	1325	MS + LRI
33	unknown MW 112	911	1281	
	2-ethylpyrazine	913	1361	MS + LRI
	an aldehyde	913		ms
	2,3-dimethylpyrazine	915	1367	MS + LRI
	3-methyl-2-butenoic acid	921		ms
	3(2*H*)-furanone	924		ms
	2-ethenylpyrazine	926		ms
	unknown MW 142	945	1294	
	4-methylpentanoic acid	949		ms
	5-methyl-2-furanmethanol	953	1753	ms
	benzaldehyde	957	1557	MS + LRI
34	5-methylfurfural	959	1605	MS + LRI
35	dimethyl trisulfide	968	1410	ms
38	*2-pentylfuran*	*989*	*1248*	*MS + LRI*
39	2-ethyl-6-methylpyrazine	994	1411	MS + LRI
	2-ethyl-5-methylpyrazine	997	1406	MS + LRI
	trimethylpyrazine	999	1423	MS + LRI
	2-ethyl-3-methylpyrazine	1001	1424	MS + LRI
	2-propionylfuran	1005		MS + LRI
	2-ethenyl-6-methylpyrazine	1012		ms
	2-acetylthiazole	1015		MS + LRI
42	*2-phenylethanal*	*1043*	*1679*	*ms*
47	2-isopropyl-5-methyl-2-hexenal	1106	1378	ms
48	3-hydroxy-2-methyl-4-pyranone (maltol)	1110		ms
50	2-phenylethanol	1116	1953	ms
	a terpene MW 136	1116		ms
53	*2-phenyl-2-butenal*	*1273*	*1972*	*ms*
63	*5-methyl-2-phenyl-2-hexenal*	*1495*	*>2000*	*ms*
71	*n-octadecane*	*1800*	*1800*	*MS + LRI*

[a] Numbers correspond with chromatogram peaks shown in Figure 2. [b] Major volatile components outside areas of odor significance are shown in italices. [c] MS + LRI, identification from comparison with mass spectrum and LRI of authentic compounds; ms, tentative identification from comparison of spectra with those in mass spectral libraries.

roasting. However, the concentration fell markedly in the finished crystal malt. Color forming reactions associated with the Maillard reaction may have been responsible for the loss of these aldehydes, since the crystal malt was visibly darker than the other samples.

The present work clearly demonstrates that the methylbutanals are major contributors to the malt-like aromas of malted barley and that these compounds could be used to follow the development of malt flavor. The results show that their importance diminishes in highly roasted malts, such as crystal malt, while they have not achieved prominence in lightly roasted malts. These findings concur with those of several workers who have shown that the concentration of carbonyl compounds is more prominent in darker malts than in pilsner malts (Arkima and Ronkainen, 1971; Baerwald et al., 1969). The malting process can produce a wide range of products with very different aroma characteristics. This work, together with the recent sensory studies (Beal and Mottram, 1993), demonstrates that malt-like aromas are associated with the roasting stage of the malting process.

ACKNOWLEDGMENT

We are grateful to Dr. S. Elmore for advice and assistance with the GC–MS analyses. The work was supported by the Agricultural and Food Research Council and SmithKline Beecham Consumer Brands Ltd.

LITERATURE CITED

Amoore, J. E.; Forrester, L. J.; Pelosi, P. Specific anosmia to isobutyraldehyde: the malty primary odor. *Chem. Senses Flavour* **1976**, *2*, 17–25.

Arctander, S. *Perfume and Flavor Chemicals*; published by the author: Monclair, NJ, 1969.

Arkima, V.; Ronkainen, P. Gas chromatographic determination of the volatile carbonyl compounds in barley and malt. *Monatsschr. Brau.* **1971**, *24*, 161–163.

Badings, H. T. Milk. In *Volatile Compounds in Foods and Beverages*; Maarse, H., Ed.; Dekker: New York, 1991; pp 91–106.

Baerwald, G.; Niefind, H. J.; Hompel, U. Investigation of volatile constituents in barley and malt. *Monatsschr. Brau.* **1969**, *22*, 114–117.

Bauer, K.; Garbe, D.; Surburg, H. *Common Fragrance and Flavor Materials: Preparation, Properties and Uses*, 2nd ed.; VCH Verlsgeselschaft: Weinheim, Germany, 1990.

Beal, A. D.; Mottram, D. S. An evaluation of the aroma characteristics of malted barley by free choice profiling. *J. Sci. Food Agric.* **1993**, *61*, 17–22.

Bevan, D. Malting and malt products. *Food Trade Rev.* **1988**, *58*, 397–398.

Briggs, D. E.; Hough, J. S.; Stevens, R.; Young, T. W. *Malting and Brewing Science: Malt and Sweet Wort*, 2nd ed.; Chapman and Hall: London, 1981; Vol. 1, p 387.

Fors, S. Sensory properties of volatile Maillard reaction products and related compounds. In *The Maillard Reaction in Foods and Nutrition*; Waller, G. R., Feather, M. S., Eds.; American Chemical Society: Washington, DC, 1983; pp 185–286.

Hall, J. A. D. Malt derived products. New horizons? What does the future hold? *Food Trade Rev.* **1988**, *58*, 26–33.

Jackson, S. W.; Hudson, J. R. Flavour from crystal malt. *J. Inst. Brew.* **1978**, *84*, 34–40.

Kaminski, E.; Wasowicz, E.; Przybylski, R. Volatile compounds in cereals: separation and condensation for chromatographic analyses and description of their aroma characteristics. *Acta Aliment. Pol.* **1981**, *7*, 59–72.

Lukes, B. K.; McDaniel, M. R.; Deinzer, M. L. Isolation of aroma components from beer and malt by combined sensory and analytical-instrumental techniques. *Proc. Conf. Inst. Brew. 20th Conv.* **1988**, 105–108.

Maga, J. A. Pyrazine update. *Food Rev. Int.* **1992**, *8*, 479–578.

Mottram, D. S.; Puckey, D. J. Artefact formation during the extraction of bacon volatiles in a Likens-Nickerson apparatus. *Chem. Ind.* **1978**, 385–386.

NIST/EPA/MSDC. *Mass Spectral Database*; Office of Standard Reference Data of the National Institute of Standards and Technology: Gaithersburg, MD, 1992.

Przybylski, R.; Kaminski, E. Thermal degradation of precursors and formation of flavour compounds during heating of cereal products. II. The formation and changes of volatile flavour compounds in thermally treated malt extracts at different temperature and pH. *Nahrung* **1983**, *27*, 487–496.

Schieberle, P.; Grosch, W. Evaluation of the flavour of wheat and rye bread crust by aroma extract dilution analysis. *Z. Lebensm. Unters. Forsch.* **1987**, *185*, 111–113.

ten Noever de Brauw, M. C.; Bouwman, J.; Tas, A. C.; La Vas, G. F. *Compilation of Mass Spectra of Volatile Compounds in Food*; Institute for Nutrition and Food Research TNO: Zeist, The Netherlands, 1980.

Tressl, R.; Kossa, T.; Renner, R. Formation of aroma compounds in malt, wort and beer. *Monatsschr. Brauwiss.* **1974**, *27*, 98–102.

Ullrich, F.; Grosch, W. Identification of the most intense volatile flavour compounds formed during autoxidation of linoleic acid. *Z. Lebensm. Unters. Forsch.* **1987**, *184*, 277–282.

Van Gemert, L. J.; Nettenbreijer, A. H. *Compilation of Odour Threshold Values in Air and Water*; Central Institute for Nutrition and Food Research TNO: Zeist, Netherlands, 1977.

Whitfield, F. B.; Mottram, D. S.; Brock, S.; Puckey, D. J.; Salter, L. J. The effect of phospholipid on the formation of volatile heterocyclic compounds in heated aqueous solutions of amino acids and ribose. *J. Sci. Food Agric.* **1988**, *42*, 261–272.

Zuercher, C.; Gruss, R.; Alex, H.; Kleber, K. Malt analysis and beer flavour. *Proc. Congr. Eur. Brew. Conv.* **1981**, 260–270.

Received for review July 6, 1994. Accepted September 13, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.