

Targeted precursor addition to increase baked flavour in a low acrylamide potato-based matrix

Article

Accepted Version

Creative Commons: Attribution-Noncommercial-No Derivative Works 4.0

Kocadagli, T., Methven, L., Kant, A. and Parker, J. K. ORCID: <https://orcid.org/0000-0003-4121-5481> (2021) Targeted precursor addition to increase baked flavour in a low acrylamide potato-based matrix. *Food Chemistry*, 339. 128024. ISSN 0308-8146 doi: <https://doi.org/10.1016/j.foodchem.2020.128024> Available at <https://centaur.reading.ac.uk/92872/>

It is advisable to refer to the publisher's version if you intend to cite from the work. See [Guidance on citing](#).

To link to this article DOI: <http://dx.doi.org/10.1016/j.foodchem.2020.128024>

Publisher: Elsevier

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the [End User Agreement](#).

www.reading.ac.uk/centaur

CentAUR

Central Archive at the University of Reading

Reading's research outputs online

1 **Targeted precursor addition to increase baked flavour in a low acrylamide**
2 **potato-based matrix**

3
4 Tolgahan Kocadağlı^{a,#}, Lisa Methven^a, Avinash Kant^b, Jane K. Parker^{a,*}

5 ^aDepartment of Food and Nutritional Sciences, University of Reading, Whiteknights, Reading RG6
6 6AP, UK

7
8 ^bPepsiCo International UK, Beaumont Park, Leycroft Road, Beaumont Leys, Leicester, LE4 1ET,
9 United Kingdom

10

11

12

13

14

15

16

17

18

19

20 *Corresponding author: Jane K. Parker

21 E-mail: j.k.parker@reading.ac.uk

22 Phone: +44 118 378 7455

23 [#]Current address: Department of Food Engineering, Hacettepe University, Ankara, Turkey

24

25 **Abstract**

26 The aim of this study was to increase the baked flavour of low acrylamide potato products. Strecker
27 aldehydes and pyrazines make an important contribution to the flavour of potato products and are
28 formed alongside acrylamide in the Maillard reaction. However, the Maillard reaction can be
29 directed in favour of aroma formation by selecting appropriate precursors and intermediates based
30 on the fundamental chemistry involved.

31 Selected precursors were added to potato dough prior to baking. Addition of glycine and alanine
32 together doubled high impact pyrazines and addition of 2,3-pentanedione or 3,4-hexanedione also
33 promoted the formation of key trisubstituted pyrazines. Quantitative descriptive profiling of
34 sensory attributes indicated that baked flavour was increased most when both Strecker aldehydes
35 and pyrazines were increased together. This work shows that it is possible to enhance baked flavour
36 in low acrylamide products by adding a specifically targeted combination of amino acids and key
37 intermediates, without increasing acrylamide concentration.

38

39 **Keywords: potato, complex matrix, acrylamide mitigation, flavour, Maillard, pyrazines**

40

41 **1. Introduction**

42 Fundamental research on exploring mitigation approaches for process contaminants, such as
43 acrylamide, is an important area for the food & beverage industries. Specifically, greater
44 understanding is required on maintaining the flavour quality of products as mitigation may alter
45 flavour profiles. Model systems are useful approaches to study specific pathways, however this
46 approach should also be supplemented with work on complex food systems to allow better
47 translation into real food products. The use of simplified real food matrices is seen as a bridge
48 between simple model systems and complex real food systems, and more studies using this
49 approach can help in uncovering interaction and synergistic effects which may not occur in simple
50 model systems.

51 High temperature thermal processing of asparagine rich foods results in the formation of acrylamide
52 during the Maillard reaction (Mottram, Wedzicha, & Dodson, 2002; Stadler, Blank, Varga, Robert,
53 Hau, Guy, et al., 2002) and it is classified as a Class 2a probable carcinogen in humans (International
54 Agency for Research on Cancer, 1994). As flavour and browning also develop during this process, it
55 is often a challenge to mitigate acrylamide formation from the viewpoint of food quality. Several
56 strategies have been developed for this purpose however only a few of them mitigate acrylamide
57 formation whilst allowing the cooked flavour and colour to develop. Selection of low sugar potato
58 varieties and the use of asparaginase in bakery products have been proposed as the best mitigation
59 strategies (Palermo, Gökmen, De Meulenaer, Ciesarová, Zhang, Pedreschi, et al., 2016).

60 Lowering thermal input is a convenient approach for baked foods for the mitigation of acrylamide
61 formation (Gokmen, Acar, Koksel, & Acar, 2007; Taeymans, Wood, Ashby, Blank, Studer, Stadler, et
62 al., 2004), but as this strategy depends on limiting the overall Maillard reaction, the final food
63 product lacks baked flavour.

64 A pool of reactive intermediates is formed from the reaction between sugars and amino acids in the
65 intermediate stage of the Maillard reaction (Yaylayan, 1997). The composition of this pool
66 determines the flavour and browning characteristics of the final product (Yaylayan, 2003) and also
67 influences acrylamide formation. The baked flavour is largely obtained by Strecker aldehydes and
68 trisubstituted alkylpyrazines which are formed from the intermediates found in the pool. Addition
69 of amino acids and other precursors can be used to alter the composition of the pool to manipulate
70 flavour formation.

71 Strecker aldehydes are formed from free amino acids during the Maillard reaction via a number of
72 different pathways (Yaylayan, 2003). In particular, α -dicarbonyl compounds transform amino acids
73 to their Strecker aldehydes via decarboxylation. Strecker aldehydes which are important for aroma
74 are 2-methylpropanal (malty), 2-methylbutanal (malty, cacao like), 3-methylbutanal (malty, cacao
75 like), methional (boiled potato) and phenylacetaldehyde (floral, honey like) and they are formed
76 from valine, isoleucine, leucine, methionine and phenylalanine, respectively (Martin & Ames, 2001).
77 In addition, the Strecker aldehydes formaldehyde and acetaldehyde, formed from glycine and
78 alanine respectively, contribute to the pool of intermediates and can be precursors of methyl and
79 ethyl substituted pyrazines, respectively (Amrani-Hemaimi, Cerny, & Fay, 1995; Low, Koutsidis,
80 Parker, Elmore, Dodson, & Mottram, 2006).

81 α -Dicarbonyl compounds are converted into α -amino carbonyl compounds during the Strecker
82 degradation of amino acids, whereas the reaction of α -hydroxycarbonyl compounds and ammonia
83 may produce α -aminocarbonyl compounds via Amadori rearrangement (Yaylayan, 2003). N-
84 terminal amino acids in peptides have also been shown to transform α -dicarbonyl compounds into
85 their α -amino carbonyl derivatives with a different reaction mechanism to Strecker degradation
86 (Van Lancker, Adams, & De Kimpe, 2010, 2012). Condensation of two α -amino carbonyl compounds
87 produces a dihydropyrazine and subsequent oxidation yields a pyrazine (Shibamoto & Bernhard,

88 1977). Methyl substitution in pyrazines may originate from methylglyoxal (via 2-aminopropanal or
89 1-amino-2-propanone), 1-hydroxy-2-propanone (via 2-aminopropanal), 2,3-butanedione and 3-
90 hydroxy-2-butanone (via 3-amino-2-butanone) followed by oxidation of the corresponding
91 dihydropyrazines (Chu & Yaylayan, 2009). Ethyl substitution may come from 2-oxobutanal, 2,3-
92 pentanedione and 3,4-hexanedione via this oxidative pathway (Chu & Yaylayan, 2009). In addition
93 to this oxidative pathway, nucleophilic attack by a dihydropyrazine at the carbonyl centre of
94 formaldehyde or acetaldehyde, followed by the elimination of a water molecule, also yields alkyl
95 substituted pyrazines in a non-oxidative way (Amrani-Hemaimi, Cerny, & Fay, 1995; Cerny & Grosch,
96 1994).

97 The pyrazines which we are targeting in this work are the trisubstituted alkylpyrazines with relatively
98 low odour thresholds and baked aroma (2-ethyl-3,5-dimethylpyrazine, 2-ethyl-3,6-
99 dimethylpyrazine and 2,3-diethyl-5-methylpyrazine) since they are known to contribute to the
100 baked flavour in potato products (Buttery, Seifert, Guadagni, & Ling, 1971; R. Wagner, Czerny,
101 Bielohradsky, & Grosch, 1999; R. K. Wagner & Grosch, 1998). On the basis of the chemistry
102 underpinning the formation of these baked flavour compounds, we propose that with addition of a
103 carefully targeted selection of precursors to a potato-based matrix, we will be able to increase the
104 formation of key aroma compounds whilst maintaining low levels of acrylamide. Glycine and alanine
105 were selected to increase overall Maillard reaction and also as alkylpyrazine precursors. Leucine,
106 isoleucine, valine, phenylalanine, and methionine were selected as Strecker aldehyde precursors.
107 2,3-Pentanedione (PD) and 3,4-hexanedione (HD) were used as intermediates in alkylpyrazine
108 formation. Moreover, the addition of whey protein hydrolysate was assessed, also together with
109 2,3-pentanedione and 3,4-hexanedione, as oligopeptides have previously been shown to be very
110 effective in alkylpyrazine formation (Scalone, Lamichhane, Cucu, De Kimpe, De Meulenaer, 2019).

111 **2. Materials and Methods**

112 **2.1 Chemicals and Consumables**

113 ¹³C₃-Acrylamide was purchased from Cambridge Isotope Laboratories (QMx, Thaxted, UK).
114 Acetonitrile (LC-MS grade), NaCl (reagent grade) and formic acid (LC-MS grade) were purchased
115 from Fisher Scientific (Loughborough, UK). Deionised water was supplied from a MilliQ system at
116 18.2 MΩ.cm resistivity. Food grade amino acids were supplied from S.A. Ajinomoto OmniChem N.V.
117 (Wetteren, Belgium). Amino acids reference mix solution (2.5 mM each), 2,3-pentanedione (food
118 grade) and 3,4-hexanedione (food grade) were purchased from Sigma-Aldrich (Poole, UK).

119 **2.2 Preparation of Potato-Based Matrix**

120 A potato-based dough was prepared by mixing 342 g potato flake, 90 g waxy maize starch, 4.5 g
121 lecithin, 4.5 g NaCl, 9 g sucrose and 300 g tap water at room temperature. Sucrose and NaCl were
122 dissolved in water for the control formula. Amino acids, 2,3-pentanedione and 3,4-hexanedione
123 were also dissolved in water to incorporate them homogeneously into the dough. The amount of
124 added amino acids was four times that of the naturally occurring levels in the potato flake (Table
125 S1, see supplementary material) for all amino acids except Gly. Gly was added at 20- or 100-fold the
126 naturally occurring level in the potato flake. Additionally, the 'all amino acids' recipe contained twice
127 that of the naturally occurring concentrations of each amino acid except asparagine and γ -
128 aminobutyric acid which were omitted from the mix. 2,3-Pentanedione and 3,4-hexanedione were
129 added at 100 mg/kg on a dry basis. Whey protein hydrolysate was added at 5% on a dry basis. Dry
130 ingredients were mixed on setting 1 (Kenwood Mixer) for 30 s and then the aqueous mixture was
131 gradually added during mixing for 1 min. The dough was sheeted by using a pastry sheeter (Rondo,
132 Burgdorf, Switzerland) to a thickness of 1.2 ± 0.06 mm. The dough was cut into disks of 5 cm and
133 the pieces were pinned. Twenty-four pieces were transferred onto an open mesh baking mat and
134 were baked at 160 °C for 6 min followed by drying at 130 °C for 10 min under full convection mode.

135 They were cooled down for 5 min on an aluminium foil at room temperature and immediately
136 packed in foil pouches by heat sealing and kept at -20 °C until chemical or sensory analysis.

137 **2.3 Amino Acids Analysis**

138 Ground potato flake (1.0 ± 0.05 g) was extracted with water in three stages using 10, 5 and 5 mL
139 respectively. At each stage, the tube was vortexed for 5 min followed by centrifugation at $6654 \times g$
140 for 5 min. Supernatants were combined in a tube, and 0.2 mL of combined extract was mixed with
141 0.8 mL acetonitrile. The mixture was centrifuged and a part of the supernatant was filtered through
142 0.2 μm PTFE filter (Fisher Scientific, UK) into an autosampler vial. External calibration curves of
143 amino acids were built between 1-50 μM in water:acetonitrile mixture (2:8, v:v).

144 Amino acids were analysed using an Agilent 1200 high-performance liquid chromatography (HPLC)
145 system coupled to a 6410 triple quadrupole mass spectrometer with electrospray ion source (ESI)
146 in positive mode. Chromatographic separation was carried out on a Synchronis HILIC column (150 \times
147 4.6 mm i.d., 3 μm) with a Synchronis HILIC precolumn (10 \times 4.6 mm i.d., 3 μm , ThermoFisher
148 Scientific, Waltham, MA, USA). The mobile phase A was 5 mM ammonium formate with 0.5% formic
149 acid in water, and B was 5 mM ammonium formate with 0.5% formic acid in acetonitrile:water (9:1,
150 v:v) at a flow rate of 1 mL/min at 20 °C with gradient elution. Mobile phase A was increased from
151 10% to 40% for 8 min and then decreased to 10% in 1 min and kept at 10% for 4 min. The total run
152 time was 13 min. The injection volume was 5 μL . ESI source had the following settings: gas
153 temperature 330 °C, gas flow 13 L/min, nebuliser pressure 40 psi, capillary 4000 V. Amino acids
154 were identified by multiple reaction monitoring (MRM) using the ion transitions and parameters
155 previously reported (Kocadađlı, Özdemir and Gökmen, 2013).

156 **2.4 Acrylamide Analysis**

157 The ground sample (1 ± 0.05 g) was put into 50 mL centrifuge tube and 2 mL 1 mg/L $^{13}\text{C}_3$ -acrylamide
158 was added followed by 38 mL water. After vortexing for 20 min, the tubes were centrifuged at
159 $8422\times g$ for 15 min at 15 °C. An aliquot of the supernatant was filtered through a 0.2 μm nylon
160 syringe filter (Fisher Scientific, Loughborough, UK) into an autosampler vial. An external calibration
161 curve of acrylamide was built between 0.5-20 $\mu\text{g/L}$, each containing 50 $\mu\text{g/L}$ $^{13}\text{C}_3$ -acrylamide.

162 Samples were analysed using an Agilent 1200 high-performance liquid chromatography (HPLC)
163 system coupled to a 6410 triple quadrupole mass spectrometer with electrospray ion source (ESI)
164 in positive mode. Chromatographic separation was carried out using a Hypercarb column (100×3.0
165 mm i.d., 5 μm) with a Hypercarb precolumn (10×3.0 mm i.d., 5 μm , ThermoFisher Scientific,
166 Waltham, MA, USA). The mobile phase was 0.1% aqueous formic acid at a flow rate of 0.3 mL/min
167 at 30 °C. The injection volume was 5 μL . ESI source had the following settings: gas temperature 350
168 °C, gas flow 10 L/min, nebuliser pressure 35 psi, capillary 3000 V and fragmentor voltage 40 V. The
169 MRM transitions of m/z 72 \rightarrow 55 (N_2 collision energy (CE), 8 eV) and 72 \rightarrow 27 (CE, 16 eV) were
170 measured for acrylamide, and the MRM transition of m/z 75 \rightarrow 58 (CE, 8 eV) was measured for $^{13}\text{C}_3$ -
171 acrylamide. A dwell time of 100 ms was set for all three MRM transitions.

172 **2.5 Aroma Analysis**

173 Volatile compounds were collected onto Tenax TA using dynamic headspace extraction. The cooked
174 potato-based matrix was ground and 10 g was transferred into a 250 mL conical flask with a screw-
175 thread neck and 15 mL saturated NaCl solution (35 g/100 mL) was added. The flask was kept at 50
176 °C in a water bath during the extraction. Oxygen-free nitrogen was passed over the sample for 1 h
177 at a rate of 40 mL/min, carrying volatiles onto a preconditioned glass trap (105 mm \times 3 mm i.d.)
178 containing Tenax TA (85 mg) (SupelCo, Poole, UK). At the end of the collection, 130.6 ng of 1,2-
179 dichlorobenzene in 1 μL methanol was injected onto the trap as an internal standard. Then, the trap

180 was flushed with nitrogen at a flow rate of 100 mL/min for 10 min to remove water. Volatiles
181 collected on the trap were desorbed using a Turbomatrix ATD system (Perkin Elmer, Beaconsfield,
182 UK) coupled to an Agilent GC-MS system (7890A-5975C). The Tenax traps were desorbed at 300 °C
183 (heating rate 40 °C/s) and cryofocused in a cold trap at -30 °C. Chromatographic separation was
184 achieved on a Phenomenex ZB-Wax column (30 m × 250 µm i.d. × 1 µm). The time-temperature
185 program employed was 10 min at 30 °C, a ramp of 4 °C/min to 250 °C, and hold at 250 °C for 10 min.
186 The carrier gas was He at 1 mL/min. The mass spectrometer was operated in electron ionization
187 mode with an ionizing voltage of 70 eV and source temperature of 200 °C. A scan range of m/z 29-
188 450 was employed with a scan time of 0.7 s. The data were controlled and stored using ChemStation.

189 A series of *n*-alkane standards (C₅-C₂₅) in diethyl ether was run to obtain linear retention index (LRI)
190 values. The identity of the compounds was confirmed by comparing their mass spectra with NIST
191 Mass Spectral Database, authentic compounds and LRI values (Table S2 & S3, see supplementary
192 material). The compounds were semi-quantified by comparing the peak areas of extracted ion
193 chromatograms with that of the internal standard 1,2-dichlorobenzene, using a response factor of
194 1.

195 **2.6 Sensory Analysis**

196 A trained in-house panel of 11 assessors (10 female, 1 male) were used to estimate sensory changes
197 quantitatively. Samples were presented to assessors with random codes to discuss as a group, with
198 the help of a panel leader, and to develop a consensus vocabulary on the sensory attributes of the
199 cooked potato-based products. References (real food or aroma compounds) were available for the
200 panel to help define the product attributes during four sessions of 1 h (Table S4, see supplementary
201 material). During development of the sensory attributes, panellists were first asked to sniff and then
202 bite into the sample to define aroma, taste, flavour and aftertaste attributes. The day before the

203 quantitative sensory assessment took place, the panellists were exposed again to the references
204 and samples to standardise the vocabulary associated with defined attributes (30 min). Panellists
205 were asked to score the attributes of the control sample during the training session to obtain
206 average scores. The quantitative sensory assessments were carried out in well-ventilated individual
207 sensory booths controlled at 21 ± 1 °C, in duplicate (replicates were presented on consecutive days).
208 The panellists were given the average scores together with the control sample (introduced with a
209 code 'reference') during the quantitative sensory assessments. Panellists were asked to score each
210 attribute in reference to the control sample on an unstructured 15 cm line, scaled 0-100, with an
211 anchor defining the average score for the reference product, using Compusense @Hand
212 (Compusense Inc., Guelph, Ontario, Canada). The samples, with three-digit random codes, were
213 introduced in a randomised and balanced order, always with a blind control sample in each session.
214 Between samples, panellists were asked to cleanse their palate with warm water.

215 ***2.7 Statistical Analysis***

216 One-way analysis of variance was performed on the instrumental data to indicate statistical
217 differences between recipes using the Duncan test. ANOVA and Fisher's LSD multiple comparison
218 test at $p = 0.05$ were carried out using the statistical programme Senpaq 5.01 (Qi Statistics Ltd.,
219 Reading, UK).

220 **3. Results and Discussion**

221 ***3.1 Concentration of amino acids and reducing sugars in the potato flake***

222 The potato flake contained relatively low amounts of reducing sugars (6.7 ± 0.24 g/kg glucose and
223 3.7 ± 0.04 g/kg fructose). The concentration of Asn was 2552 mg/kg, similar to previously reported
224 data (Elmore, Koutsidis, Dodson, Mottram, & Wedzicha, 2005). Concentrations of free amino acids

225 in the potato flake were determined (Table S1, see supplementary material) and these values were
226 used to increase their initial concentrations 2 to 100-fold by adding amino acids to the recipe. The
227 amount of added Ala, Leu, Ile, Val and Met was 4 times the naturally occurring amount to make
228 their concentrations 5 times that of the control recipe. However, glycine was one of the lowest
229 amino acids in the potato flake and therefore its concentration was further increased to 100-fold to
230 maintain a level similar to alanine. This corresponded to Gly addition of 0.18% and Ala addition of
231 0.21% (4 times the naturally found level) on potato flake basis. An additional recipe was formed by
232 adding all amino acids (except Asn and γ -aminobutyric acid) at twice the naturally occurring levels.

233 ***3.2 Determination of low thermal input conditions to limit acrylamide formation and monitor*** 234 ***alkylpyrazine formation***

235 Apart from the time-temperature conditions used in the main body of this paper (baking at 160 °C
236 for 6 min followed by drying at 130 °C for 10 min), two other conditions, one lower and one higher,
237 were also performed during preliminary trials. At lower temperature conditions (baking at 140 °C
238 for 8 min followed by drying at 110 °C for 15 min), either adding amino acids individually or as binary
239 mixtures did not have a significant effect on alkylpyrazine formation (Figure S1, see supplementary
240 material). Only trimethylpyrazine, 2-ethyl-6-methylpyrazine, 2-ethyl-3-methylpyrazine and 2-ethyl-
241 3,6-dimethylpyrazine were found to be slightly higher when Gly and Ala were added together.
242 Overall, these conditions generated fewer pyrazines than the more severe time-temperature
243 conditions and 2-ethyl-3,5-dimethylpyrazine, one of the key odour-active aroma compounds of
244 interest, was not detected under these conditions at all. The concentration of acrylamide was also
245 very low (10 to 15 ng/g, data not shown). Under these low temperature conditions, the formation
246 of the dicarbonyl/hydroxycarbonyl precursors required for pyrazine formation and acrylamide
247 formation is slow and there were insufficient intermediates formed to significantly increase the
248 concentration of alkylpyrazines. However, the 4-fold addition of Val, Ile, Leu and Met significantly

249 increased the corresponding Strecker aldehydes, by about 4-fold (Figure S1, see supplementary
250 material). It has been previously shown that Strecker aldehydes are kinetically formed earlier than
251 alkylpyrazines in a potato matrix (Low, Mottram, & Elmore, 2006). This may partly explain increases
252 in Strecker aldehydes but no significant changes in alkylpyrazines.

253 At a higher temperature (baking at 160 °C for 6 min followed by drying at 140 °C for 8 min) the
254 concentration of acrylamide in the product was 233±43 ng/g (data not shown), compared to 91±8.2
255 ng/g using the baking conditions discussed in the main body of this article (baking at 160 °C for 6
256 min followed by drying at 130 °C for 10 min). It was possible to observe the effect of amino acid
257 additions on alkylpyrazine formation under both sets of conditions, but only the results (chemical
258 and sensory) for the moderate thermal input conditions are presented below as the focus of the
259 work was on a low acrylamide products.

260 ***3.3 Strecker aldehyde formation and effect of the addition of corresponding amino acids***

261 By adding a targeted mixture of corresponding amino acids (recipe: 4 × Met+Ile+Leu+Val), Strecker
262 aldehydes methional, 2-methylbutanal, 3-methylbutanal, and 2-methylpropanal all increased in
263 similar proportions to the added amounts, namely 499%, 440%, 419% and 437%, respectively
264 (Figure 1). Similarly, addition of Phe at twice the natural level (recipe: all amino acids ×2) increased
265 phenylacetaldehyde to 204%. When the targeted Strecker aldehyde precursor amino acids (×4)
266 were added together with Gly (×100) and Ala (×4), the increases were only 370%, 343%, 318% and
267 326% for methional, 2-methylbutanal, 3-methylbutanal, and 2-methylpropanal , respectively. In
268 accordance with this smaller increase, phenylacetaldehyde decreased 31% in
269 ‘Gly(×100)+Ala+Met+Ile+Leu+Val’ recipe however it was statistically insignificant ($p>0.05$). Similar
270 decreases were also observed in Gly and Ala added samples with respect to control however they
271 were also not significant. This smaller increase in the presence of Gly and Ala is likely to be due to

272 the fact that amino acids compete with each other for the available dicarbonyls, increasing the
273 Strecker aldehydes derived from Gly and Ala (formaldehyde and acetaldehyde) whilst decreasing
274 the others. This observation was also evident in a previous study in which 1.3% Gly on dry basis was
275 added to a potato model system cooked at 180 °C (Low et al, 2006).

276 In addition to changes in Strecker aldehydes, dimethyl disulfide and dimethyl trisulfide, the
277 degradation products of methionine and methional, increased 98% and 41% in the
278 'Met+Ile+Leu+Val' recipe, 139% and 148% in 'Gly(×100)+Ala+Met+Ile+Leu+Val' recipe and 45% and
279 43% in 'all amino acids' recipe, respectively (Table S2, see supplementary material). These sulfide
280 compounds have very low odour thresholds and they also contribute to the cooked flavour in
281 potato-based matrices (Martin & Ames, 2001).

282 ***3.4 Effect of amino acid addition on alkylpyrazine formation***

283 Addition of individual amino acids Gly, Ala, Gln and also Ser+Thr was performed at the higher
284 thermal input condition mentioned above, and there were no changes in alkylpyrazines (Figure S2,
285 see supplementary material). A binary mixture of Ser and Thr without carbonyls has been shown to
286 produce certain alkylpyrazines under pyrolytic conditions (Shu, 1999), and Gln, Ser and Thr have
287 been shown to produce various alkylpyrazines in the presence of reducing sugar at pH 8 and 160 °C
288 (Chen & Ho, 1999). However, these conditions do not correspond to the low thermal input
289 conditions used here. On the other hand, when Gly and Ala were added together significant
290 increases in certain alkylpyrazines were observed at both thermal input conditions (Figure 1; and
291 Figure S2, see supplementary material).

292 Pyrazine, methylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, ethylpyrazine, 2,3-
293 dimethylpyrazine and 2-ethyl-5-methylpyrazine did not change considerably with amino acid
294 addition with respect to control (Table S2, see supplementary material). As shown in Figure 1,

295 trimethylpyrazine increased by 81% and 134% when Gly was increased 100 fold in the recipes
296 Gly($\times 100$)+Ala and Gly($\times 100$)+Ala+Met+Ile+Leu+Val, respectively ($p < 0.05$). In Gly($\times 20$)+Ala recipe,
297 the increase in trimethylpyrazine was 44% without statistical significance ($p > 0.05$). This is consistent
298 with the non-oxidative route for formation of pyrazines, where one of the methyl substituents
299 comes from Gly, probably via formaldehyde.

300 Remarkable increases were observed for 2-ethyl-6-methylpyrazine, 2-ethyl-3-methylpyrazine, 2,6-
301 diethylpyrazine, 2,3-diethylpyrazine, and more importantly for the lowest odour threshold
302 trisubstituted pyrazines 2-ethyl-3,6-dimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine, when Gly
303 and Ala were added together. The amounts were more than twice or three times that of the control
304 recipe in most cases with statistical significance. The increase in 2-ethyl-3,6-dimethylpyrazine was
305 261%, 210% and 348% in 'Gly($\times 20$)+Ala', 'Gly($\times 100$)+Ala' and 'Gly($\times 100$)+Ala+Met+Ile+Leu+Val'
306 recipes, respectively ($p < 0.05$). 2-Ethyl-3,5-dimethylpyrazine increased 98% ($p > 0.05$), 142% and
307 155% ($p < 0.05$) in 'Gly($\times 20$)+Ala', 'Gly($\times 100$)+Ala' and 'Gly($\times 100$)+Ala+Met+Ile+Leu+Val' recipes,
308 respectively. These trisubstituted pyrazine isomers 2-ethyl-3,6-dimethylpyrazine and 2-ethyl-3,5-
309 dimethylpyrazine have odour thresholds (3.6 ng/L air and 0.011 ng/L air respectively), particularly
310 compared to other pyrazines (Table S2) and have been shown to contribute to the baked flavour in
311 a potato matrix (Wagner & Grosch, 1998).

312 Addition of all free amino acids (except Asn and GABA) at twice that of the natural level did not have
313 a significant effect on the alkylpyrazine formation, neither did addition of Gly and Ala separately
314 (see above). However, Figure 1 shows that addition of Gly and Ala together increased the formation
315 of key alkylpyrazines with low odour thresholds in low acrylamide cooked potato-based matrices,
316 whereas the addition of Gly alone did not have this effect, at least in the high temperature baked
317 products. However, Low et al (2006) showed an increase ($> 100\%$) in a wider range of pyrazines
318 (particularly 2,3-dimethylpyrazine, trimethylpyrazine, 2-ethyl-3,5-dimethylpyrazine, and

319 tetramethylpyrazine) when Gly (1.3% on dry basis) was added to mitigate the formation of
320 acrylamide in potato cakes baked at 180 °C. The reason for not observing the effect of individual
321 addition of Gly on alkylpyrazine formation in this study might be due to the low thermal input
322 condition used to prepare low acrylamide potato products, and also the added Gly was 7.2-fold
323 lower.

324 Both Gly and Ala have many possible roles in the Maillard reaction. They participate in the first step
325 of the Maillard reaction and facilitate the formation of α -dicarbonyl compounds from reducing
326 sugars which are important precursors of pyrazines. However, they can also compete with the other
327 amino acids for Strecker degradation of the available carbonyls. Additionally, Strecker degradation
328 of Gly and Ala yield their Strecker aldehydes (formaldehyde and acetaldehyde respectively) and α -
329 amino carbonyl compounds, both of which are intermediates in alkylpyrazine formation.
330 Formaldehyde and acetaldehyde formed from Gly and Ala also participate in the chain elongation
331 process of sugar-derived α -dicarbonyl compounds and these α -dicarbonyl compounds with ethyl
332 and/or methyl substituents from amino acids may be involved in alkylpyrazine formation through
333 oxidative or non-oxidative pathways. In the oxidative pathway, the dihydroalkylpyrazine
334 intermediates readily oxidise to form the corresponding alkylpyrazines and this has been shown to
335 be a major pathway (Chu & Yaylayan, 2009). Formaldehyde and acetaldehyde formed from Gly and
336 Ala participate in the non-oxidative pathway of pyrazine formation and yield ethyl or methyl
337 substituted alkylpyrazines upon dehydration of the alkylated site of dihydropyrazines.

338 It is interesting that the 2-ethyl-3,6-dimethylpyrazine is influenced more than 2-ethyl-3,5-
339 dimethylpyrazine by the addition of alanine, suggesting greater incorporation of the alanine
340 backbone into the molecule via the non-oxidative mechanism. The 2-ethyl-3,6-dimethylpyrazine is
341 also formed in greater quantities than the 2-ethyl-3,5-dimethylpyrazine, which was not detected at
342 all under the lower temperature conditions. The 2-ethyl-3,6-dimethylpyrazine can be formed by the

343 condensation of two molecules of 1-amino-2-propanone (from methylglyoxal, and sterically
344 favoured over 2-aminopropanal) and incorporation of acetaldehyde (from alanine) (Figure S3). The
345 former is readily formed and more reactive than higher molecular weight dicarbonyls (Hofmann,
346 1999) such as 2,3-pentanedione which is required for the oxidative pathway. This may explain both
347 the greater quantity formed and the greater response to alanine addition. Although it is hard to
348 clarify the mechanism, it is clear that Gly and Ala are effective together in increasing certain
349 pyrazines, especially the lower threshold trisubstituted isomers, in low acrylamide cooked potato
350 model systems.

351 ***3.5 Targeted addition of carbonyl compounds as carbon backbones for alkylpyrazine formation***

352 The carbonyl pool formed in the intermediate stage of Maillard reaction can also be manipulated
353 by adding 2,3-pentanedione (PD) and 3,4-hexanedione (HD) to provide the required carbon
354 backbone for alkylpyrazine formation. They can be converted into their corresponding α -
355 aminocarbonyl derivatives which may then participate in the alkylpyrazine formation in the
356 presence of amino compounds. Addition of 100 mg/kg 2,3-pentanedione on a dry basis increased
357 its headspace concentration 15 and 10 times in cooked 2,3-PD and 2,3-PD-Leu-Ile-Met-Val+Phe
358 recipes, respectively. There was no 3,4-hexanedione in the headspace of the control sample and its
359 addition level was 100 mg/kg dry basis as well.

360 Addition of 2,3-pentanedione alone increased 2-ethyl-3-methylpyrazine and 2-ethyl-3,5-
361 dimethylpyrazine 155% and 121% with respect to control recipe (Figure 2) ($p < 0.05$). On the other
362 hand, 2-ethyl-3,6-dimethylpyrazine did not change when 2,3-pentanedione added alone. We
363 speculate that this is because the methyl-substituted second carbon in 2,3-pentanedione is less
364 sterically hindered than the ethyl substituted third carbon and it is preferably transformed into 2-
365 amino-3-pentanone during Strecker degradation. 2-Amino-3-pentanone condenses with 1-amino-

366 2-propanone, which for the same reason is preferably formed from methylglyoxal instead of 2-
367 aminopropanal, and produces 2-ethyl-3,5-dimethylpyrazine (See supplementary material for the
368 proposed mechanism, Figure S3). Therefore, the addition of 2,3-pentanedione targets the formation
369 of lower odour threshold trisubstituted isomer 2-ethyl-3,5-dimethylpyrazine in the potato matrix.
370 Adding Leu, Ile, Met, Val and Phe together with 2,3-pentanedione increased 2-ethyl-3-
371 methylpyrazine, 2-ethyl-3,6-dimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine even more (272%,
372 146% and 390%, respectively), as more amino acids aided the transformation of α -dicarbonyls into
373 their α -aminocarbonyl derivatives during the Strecker degradation ($p < 0.05$). Scalone et al (2019)
374 also suggested this pathway of 2-ethyl-3,5-dimethylpyrazine formation from 2,3-pentanedione in
375 whey protein hydrolysate-glucose model systems (pH 7.8 phosphate buffer) heated at 180 C for 90
376 min.

377 Addition of 3,4-hexanedione alone increased 2,3-diethylpyrazine by 84% however, it was not
378 statistically different to the control recipe (Figure 2). A further increase in 2,3-diethylpyrazine
379 (338%) was achieved when Leu, Ile, Met, Val and Phe were also added ($p < 0.05$). 2,3-Diethyl-5-
380 methylpyrazine was not detected in the control sample in this set of baking. By the addition of 3,4-
381 hexanedione alone and together with Leu, Ile, Met, Val and Phe, 2,3-diethyl-5-methylpyrazine was
382 detected at levels comparable to 2-ethyl-3,5-dimethylpyrazine. This pyrazine has a roast, potato
383 aroma and a low threshold, and is known to be important in baked potato aroma.

384 ***3.6 Effect of whey protein hydrolysate addition on alkylpyrazine formation***

385 Addition of whey protein hydrolysate to enhance the Maillard reaction and also as an amine source
386 when it is added together with 2,3-pentanedione and 3,4-hexanedione was assessed for its effect
387 on alkylpyrazine formation. The total concentration of free amino acids in whey protein hydrolysate
388 was 75 mg/kg and they did not contribute to the free amino acid pool in potato flake, which was

389 1600-fold higher. Therefore, there were no changes for Strecker aldehydes (Table S3, see
390 supplementary material). On the other hand, all alkylpyrazines increased considerably by the
391 addition of 5% whey protein hydrolysate on dry basis (Figure 3). The differences for some
392 alkylpyrazines were statistically insignificant due to the higher baking variance between replicates
393 in this set of baking although the concentrations were more than doubled with respect to control.
394 Interestingly, a minor increase (30%) was observed only for unsubstituted pyrazine while others
395 increased at least one-fold or two (Table S2, see supplementary material). Pyrazine is formed from
396 two molecules of glyoxal, and vinylic pyrazines were also increased by the addition of whey protein
397 hydrolysate. These changes indicated that whey protein hydrolysate increases overall Maillard
398 reaction and thus aiding alkylpyrazine formation by enhancing the carbonyl pool at the intermediate
399 stage. The pH of the dough was 5.92 ± 0.01 and it did not change by the addition of 5% whey protein
400 hydrolysate (5.92 ± 0.01). It has been shown that the N-terminal amino groups found in peptides are
401 also effective for the formation of pyrazines with a different mechanism that is observed in the
402 Strecker degradation of free amino acids (Van Lancker et al, 2010, 2012). Scaleno et al (2015)
403 showed that whey protein hydrolysate contributes to the formation of pyrazines significantly more
404 than free amino acids during heating whey protein hydrolysate and glucose mixture with phosphate
405 buffer at pH 7.8. Moreover, by addition of 2,3-pentanedione and 3,4-hexanedione together with
406 whey protein hydrolysate, considerably higher amounts of corresponding alkylpyrazines were
407 observed (Figure 3).

408 ***3.7 Changes in acrylamide formation by recipe modifications***

409 The concentration of acrylamide in the control recipe was 91 ± 8.2 ng/g and it did not change by the
410 addition of mixtures of amino acids except 'all amino acids $\times 2$ ' recipe (Figure 4A) ($p > 0.05$). Adding
411 all amino acids at twice the level of those naturally present, except asparagine and γ -aminobutyric
412 acid, decreased acrylamide formation by 42% ($p < 0.05$). The initial ratio of asparagine to total amino

413 acids was 34% and decreased to 16% when all amino acids (except asparagine and γ -aminobutyric
414 acid) were 3 times their initial level.

415 In a different set of baking, the acrylamide concentration of the control sample was 78 ± 2.2 ng/g
416 (Figure 4B). Addition of 100 mg/kg 2,3-pentanedione and 5% whey protein hydrolysate (both on dry
417 basis) did not change the formation of acrylamide with respect to control ($p > 0.05$). On the other
418 hand, a 33% increase in acrylamide was observed when 3,4-hexanedione (100 mg/kg on dry basis)
419 was added alone ($p < 0.05$) and this effect was not apparent when it was added together with amino
420 acids. The increase in acrylamide formation by addition of 3,4-hexanedione could stem from the
421 presence of 4-hydroxy-3-hexanone in the aroma as an impurity which was identified in GC-MS
422 chromatogram. It has been shown that α -hydroxy functionality in carbonyl compounds favours
423 acrylamide formation (Stadler, Robert, Riediker, Varga, Davidek, Devaud, et al., 2004).

424 **3.8 Colour**

425 The addition of free amino acids or α -dicarbonyl compounds did not change surface browning. On
426 the other hand, in samples where whey protein hydrolysate had been added there was more surface
427 browning and sensory analysis was performed under red light.

428 **3.9 Sensory Analysis of Selected Recipes**

429 Quantitative descriptive sensory evaluation of selected amino acid added samples showed that
430 increasing alkylpyrazines (Gly($\times 100$)+Ala) and Strecker aldehydes (Leu+Ile+Val+Met) separately did
431 not have any effect on baked aroma and flavour (Table 1) ($p > 0.05$). Increasing alkylpyrazines and
432 Strecker aldehydes together, as in Gly($\times 100$)+Ala+Leu+Ile+Val+Met, was found to be necessary for
433 an increase in the perception of baked aroma and flavour. This was the case for overall aroma
434 intensity and overall flavour intensity as well. There were no changes for other attributes.

435 Interestingly, no significant increase in boiled potato aroma and flavour was observed even though
436 methional was increased considerably. On the other hand, a significant increase for boiled potato
437 aroma was determined in the samples with methionine baked at lower temperature conditions
438 when there was no difference for baked aroma and flavour according to the quantitative descriptive
439 sensory evaluation (data not shown).

440 As mentioned above, the addition of 2,3-pentanedione alone increased the lowest threshold
441 alkylpyrazine 2-ethyl-3,5-dimethylpyrazine by 121% with respect to the control recipe, however, it
442 had no effect on baked aroma and flavour (Table 2). Baked flavour, baked aroma and baked
443 aftertaste increased when 2,3-pentanedione and the Strecker aldehyde precursor amino acids were
444 added together. 3,4-Hexanedione addition together with Leu+Ile+Val+Met+Phe increased baked
445 aroma but not baked flavour. It should be noted that in this set of baking phenylalanine was also
446 added in Strecker mix of amino acids different from the samples given in the previous sensory
447 analysis. As phenylacetaldehyde has a floral and honey like flavour, it changed the flavour profile
448 and panellist were agreed on the presence of a cheesy attribute in certain samples during the
449 training session of this set of samples and it was added to the vocabulary list. Quantitative
450 descriptive sensory evaluation indicated that cheesy attribute appeared when there is
451 phenylalanine in the recipe. Only the control and the sample containing just 2,3-pentanedione had
452 a score of zero for cheesy. It should be mentioned that no buttery aroma and flavour was described
453 by the panellists in 2,3-pentanedione added samples during training sessions and this was later
454 assessed by introducing butter and also food grade 2,3-pentanedione aroma solution to the
455 panellists. Similarly, panellist did not describe 3,4-hexanedione aroma and flavour (caramel, nutty,
456 buttery) in these samples as confirmed also by introducing its food grade solution to the panellist.

457 In all whey protein hydrolysate added samples, overall aroma intensity was found to be higher but
458 there were no differences for baked aroma and flavour even though there were considerable

459 increases in alkylpyrazines (sensory data not shown). As mentioned above, there were no increases
460 in Strecker aldehydes in these samples. Therefore, increasing only alkylpyrazines did not contribute
461 to the perception of baked aroma and flavour when there were no increments of Strecker
462 aldehydes.

463 **4. Conclusion**

464 This work shows that it is possible to enhance baked flavour in low acrylamide potato-based
465 products (~80 ng/g acrylamide), by adding a specifically targeted combination of amino acids and
466 key intermediates, without increasing acrylamide concentration. Adding the full complement of free
467 amino acids (excluding asparagine) did not have the same effect, nor did addition of hydrolysed
468 whey protein. The best combination was glycine, alanine, valine, leucine, isoleucine and methionine,
469 a combination which was required to boost both Strecker aldehydes and pyrazines. The data add to
470 our understanding of the role of precursor mixtures and highlights merit for a targeted approach
471 over a single source of protein. Appropriate selection of food ingredients to reflect the desired
472 amino acid profile would be required. Similar chemistry has been demonstrated in binary or tertiary
473 aqueous model systems, but one of the achievements of this paper is to show how this can be
474 applied in a complex food matrix where up to 6 amino acids were used to achieve the desired effect.

475

476 **Declaration**

477 This study was funded by PepsiCo. Co-author, Avinash Kant, is employed by PepsiCo. The views
478 expressed in this article are those of the authors and do not necessarily reflect the position or policy
479 of PepsiCo, Inc.

480 **References**

481 Amrani-Hemaimi, M., Cerny, C., & Fay, L. B. (1995). Mechanisms of formation of alkylpyrazines in
482 the Maillard reaction. *J. Agric. Food Chem.*, 43(11), 2818-2822.

483 <https://doi.org/10.1021/jf00059a009>

484 Buttery, R. G., Seifert, R. M., Guadagni, D. G., & Ling, L. C., (1971). Characterization of volatile
485 pyrazine and pyridine components of potato chips. *J. Agric. Food Chem.*, 19(5), 969-71.

486 Cerny, C., & Grosch, W. (1994). Precursors of ethyldimethylpyrazine isomers and 2,3-diethyl-5-
487 methylpyrazine formed in roasted beef. *Z. Lebensm. Unters. Forsch.*, 198(3), 210-214.

488 <https://doi.org/10.1007/BF01192597>

489 Chen, J. H., & Ho, C. T. (1999). Comparison of volatile generation in serine/threonine/glutamine-
490 ribose/glucose/fructose model systems. *J. Agric. Food Chem.*, 47(2), 643-647.

491 <https://doi.org/10.1021/jf980771a>

492 Chu, F. L., & Yaylayan, V. A. (2009). Isotope labeling studies on the origin of 3,4-hexanedione and
493 1,2-butanedione in an alanine/glucose model system. *J. Agric. Food Chem.*, 57(20), 9740-9746.

494 <https://doi.org/10.1021/jf902117v>

495 Elmore, J. S., Koutsidis, G., Dodson, A. T., Mottram, D. S., & Wedzicha, B. L. (2005). Measurement of
496 acrylamide and its precursors in potato, wheat, and rye model systems. *J. Agric. Food Chem.*, 53(4),

497 1286-1293. <https://doi.org/10.1021/jf048557b>

498 Gokmen, V., Acar, O. C., Koksel, H., & Acar, J. (2007). Effects of dough formula and baking conditions
499 on acrylamide and hydroxymethylfurfural formation in cookies. *Food Chem.*, 104(3), 1136-1142.

500 <https://doi.org/10.1016/j.foodchem.2007.01.008>

501 Hofmann, T. (1999) Quantitative studies on the role of browning precursors in the Maillard reaction
502 of pentoses and hexoses with L-alanine. *Eur. Food Res. Technol.*, (1999) 209, 113–121.
503 <https://doi.org/10.1007/s002170050468>

504 International Agency for Research on Cancer. (1994). *IARC Monographs on the Evaluation of*
505 *Carcinogenic Risks to Humans 60*. Lyon, France: International Agency for Research on Cancer (IARC).

506 Kocadağlı, T. Özdemir, K.S., Gökmen, V. (2013). Effects of infusion conditions and decaffeination on
507 free amino acid profiles of green and black tea. *Food Res. Int.* 53(2), 720-725.

508 Low, M. Y., Koutsidis, G., Parker, J. K., Elmore, J. S., Dodson, A. T., & Mottram, D. S. (2006). Effect of
509 citric acid and glycine addition on acrylamide and flavor in a potato model system. *J. Agric. Food*
510 *Chem.*, 54(16), 5976-5983. <https://doi.org/10.1021/jf060328x>

511 Low, M. Y., Mottram, D. S., & Elmore, S. J. (2006). Relationship between acrylamide formation and
512 the generation of flavour in heated foods. In W. L. P. Bredie & M. A. Petersen (Eds.), *Developments*
513 *in Food Science*, vol. 43 (pp. 363-366): Elsevier.

514 Martin, F. L., & Ames, J. M. (2001). Formation of Strecker aldehydes and pyrazines in a fried potato
515 model system. *J. Agric. Food Chem.*, 49(8), 3885-3892. <https://doi.org/10.1021/jf010310g>

516 Mottram, D. S., Wedzicha, B. L., & Dodson, A. T. (2002). Acrylamide is formed in the Maillard
517 reaction. *Nature*, 419(6906), 448-449. <https://doi.org/10.1038/419448a>

518 Palermo, M., Gökmen, V., De Meulenaer, B., Ciesarová, Z., Zhang, Y., Pedreschi, F., & Fogliano, V.
519 (2016). Acrylamide mitigation strategies: critical appraisal of the FoodDrinkEurope toolbox. *Food*
520 *and Funct.*, 7(6), 2516-2525. <https://doi.org/10.1039/c5fo00655d>

521 Roberts, A. (2016). The Safety and Regulatory Process for Amino Acids in Europe and the United
522 States. *J. Nutr.* 146(12), 2635S-2642S. <https://doi.org/10.3945/jn.116.234591>

523 Scalone, G.L.L., Cucu, T., De Kimpe, N., De Meulenaer, B., (2015). Influence of Free Amino Acids,
524 Oligopeptides, and Polypeptides on the Formation of Pyrazines in Maillard Model Systems. *J. Agric.*
525 *Food Chem.*, 63, 5364-5372. <https://doi.org/10.1021/acs.jafc.5b01129>

526 Scalone, G.L.L., Lamichhane, P., Cucu, T., De Kimpe, N., De Meulenaer, B., (2019). Impact of different
527 enzymatic hydrolysates of whey protein on the formation of pyrazines in Maillard model systems.
528 *Food Chem.*, 278, 533-544. <https://doi.org/10.1016/j.foodchem.2018.11.088>

529 Shibamoto, T., & Bernhard, R. A. (1977). Investigation of pyrazine formation pathways in glucose-
530 ammonia model systems. *Agric. Biol. Chem.*, 41(1), 143-153.
531 <https://doi.org/10.1080/00021369.1977.10862443>

532 Shu, C. K. (1999). Pyrazine formation from serine and threonine *J. Agric. Food Chem.*, 47(10), 4332-
533 4335. <https://doi.org/10.1021/jf9813687>

534 Stadler, R. H., Blank, I., Varga, N., Robert, F., Hau, J., Guy, P. A., Robert, M. C., & Riediker, S. (2002).
535 Acrylamide from Maillard reaction products. *Nature*, 419(6906), 449-450.
536 <https://doi.org/10.1038/419449a>

537 Stadler, R. H., Robert, F., Riediker, S., Varga, N., Davidek, T., Devaud, S., Goldmann, T., Hau, J., &
538 Blank, I. (2004). In-depth mechanistic study on the formation of acrylamide and other vinylogous
539 compounds by the Maillard reaction. *J. Agric. Food Chem.*, 52(17), 5550-5558.
540 <https://doi.org/10.1021/jf0495486>

541 Taeymans, D., Wood, J., Ashby, P., Blank, I., Studer, A., Stadler, R. H., Gonde, P., Van Eijck, P., Lalljie,
542 S., Lingnert, H., Lindblom, M., Matissek, R., Muller, D., Tallmadge, D., O'Brien, J., Thompson, S.,
543 Silvani, D., & Whitmore, T. (2004). A review of acrylamide: an industry perspective on research,
544 analysis, formation and control. *Crit. Rev. Food Sci.*, 44(5), 323-347.

545 Van Lancker, F., Adams, A., & De Kimpe, N. (2010). Formation of pyrazines in Maillard model systems
546 of lysine-containing dipeptides. *J. Agric. Food Chem.*, *58*(4), 2470-2478.
547 <https://doi.org/10.1021/jf903898t>

548 Van Lancker, F., Adams, A., & De Kimpe, N. (2012). Impact of the N-terminal amino acid on the
549 formation of pyrazines from peptides in Maillard model systems. *J. Agric. Food Chem.*, *60*(18), 4697-
550 4708. <https://doi.org/10.1021/jf301315b>

551 Wagner, R., Czerny, M., Bielohradsky, J., & Grosch, W. (1999). Structure odour-activity relationships
552 of alkylpyrazines. *Z. Lebensm. Unters. Forsch.*, *208*(5-6), 308-316.
553 <https://doi.org/10.1007/s002170050422>

554 Wagner, R. K., & Grosch, W. (1998). Key odorants of French fries. *J. Am. Oil Chem. Soc.*, *75*(10), 1385-
555 1392. <https://doi.org/10.1007/s11746-998-0187-4>

556 Yaylayan, V. A. (1997). Classification of the Maillard reaction: a conceptual approach. *Trends Food*
557 *Sci. Technol.*, *8*(1), 13-18. [https://doi.org/10.1016/S0924-2244\(96\)20013-5](https://doi.org/10.1016/S0924-2244(96)20013-5)

558 Yaylayan, V. A. (2003). Recent advances in the chemistry of Strecker degradation and Amadori
559 rearrangement: Implications to aroma and color formation. *Food Sci. Technol. Res.*, *9*(1), 1-6.
560 <https://doi.org/10.3136/fstr.9.1>

561 **Figure Captions**

562 **Figure 1.** Relative amounts of Strecker aldehydes and selected alkylpyrazines formed in a potato-
563 based matrix with or without the addition of amino acids. Bars with the same lowercase letters
564 above the bars indicate no statistically significant difference between them ($p>0.05$).

565 **Figure 2.** Effect of 2,3-pentanedione (2,3-PD) and 3,4-hexanedione (3,4-HD) addition on the
566 corresponding alkylpyrazines. Bars with the same lowercase letters above the bars indicate no
567 statistically significant difference between them ($p>0.05$).

568 **Figure 3.** Effect of whey protein hydrolysate (WPH) addition on alkylpyrazine formation also
569 together with 2,3-pentanedione (2,3-PD) and 3,4-hexanedione (3,4-HD). Bars with the same
570 lowercase letters above the bars indicate no statistically significant difference between them
571 ($p>0.05$).

572 **Figure 4.** The concentration of acrylamide formed in different recipes. Samples in A and B graphs
573 are different sets of baking and they have their own control sample. * indicates a statistically
574 significant difference within a group ($p\leq 0.05$).

Table 1. Quantitative descriptive sensory evaluation of selected amino acid added samples

| | Control | Gly(×100)+Ala | Leu+Ile+ Val+Met | Gly(×100)+Ala+ Leu+Ile+Val+Met | ANOVA p- value |
|---------------------------|-----------------|-----------------|---------------------|-----------------------------------|-------------------|
| <i>Aroma</i> | | | | | |
| Overall aroma intensity | 38 ^c | 38 ^c | 39 ^{bc} | 44 ^a | 0.01 |
| Baked | 38 ^b | 36 ^b | 40 ^{ab} | 43 ^a | 0.02 |
| Boiled potato | 5 | 5 | 6 | 5 | 0.74 |
| Fatty | 24 | 23 | 22 | 24 | 0.19 |
| Sweet | 13 | 13 | 15 | 16 | 0.13 |
| <i>Taste</i> | | | | | |
| Sweet | 17 | 16 | 13 | 16 | 0.07 |
| Salty | 14 | 16 | 15 | 16 | 0.26 |
| Bitter | 3 | 1 | 4 | 3 | 0.22 |
| Umami | 18 | 19 | 17 | 21 | 0.24 |
| <i>Flavour</i> | | | | | |
| Overall flavour intensity | 38 ^c | 39 ^c | 40 ^{bc} | 45 ^{ab} | 0.02 |
| Baked | 39 ^b | 38 ^b | 39 ^b | 44 ^a | 0.01 |
| Boiled potato | 6 | 7 | 7 | 7 | 0.85 |
| Fatty | 24 | 21 | 20 | 20 | 0.08 |
| <i>Aftertaste</i> | | | | | |
| Baked | 34 | 34 | 34 | 38 | 0.07 |
| Boiled potato | 4 | 5 | 6 | 5 | 0.50 |
| Sweet | 17 | 16 | 15 | 18 | 0.15 |
| Salty | 15 | 15 | 15 | 16 | 0.04 |
| Umami | 17 | 17 | 16 | 19 | 0.08 |
| Fatty | 18 | 15 | 15 | 16 | 0.13 |

Mean scores (n=12) Within a row, scores with the same lowercase letters are not statistically different ($p>0.05$).

Table 2. Quantitative descriptive sensory evaluation of 2,3-pentanedione and 3,4-hexanedione added samples

| | Control | 2,3-PD | 2,3-PD+Leu+Ile +Val+Met+Phe | 3,4-HD+Leu+Ile +Val+Met+Phe | Leu+Ile+Val +Met+Phe | ANOVA | p-value |
|---------------------------|--------------------|-------------------|-----------------------------|-----------------------------|----------------------|-------|---------|
| <i>Aroma</i> | | | | | | | |
| Overall aroma intensity | 33.5 ^b | 29.4 ^c | 40.3 ^a | 36.1 ^b | 36.6 ^{ab} | | 0.0001 |
| Baked | 35.0 ^b | 33.2 ^b | 42.0 ^a | 39.6 ^a | 40.4 ^a | | 0.0015 |
| Boiled potato | 5.5 | 4.7 | 4.3 | 4.4 | 4.3 | | 0.8745 |
| Fatty | 17.1 ^{bc} | 15.3 ^c | 21.1 ^a | 21.3 ^a | 19.5 ^{ab} | | 0.0011 |
| Sweet | 12.1 | 11.8 | 12.7 | 12.4 | 12.0 | | 0.9731 |
| Cheesy | 0.0 ^b | 0.0 ^b | 5.9 ^a | 1.6 ^b | 3.6 ^{ab} | | 0.0293 |
| <i>Taste</i> | | | | | | | |
| Sweet | 13.2 | 12.0 | 12.7 | 11.8 | 11.3 | | 0.6764 |
| Salty | 13.6 | 12.5 | 13.5 | 13.4 | 12.8 | | 0.8655 |
| Bitter | 2.5 ^b | 2.6 ^b | 6.8 ^a | 6.2 ^a | 2.0 ^b | | 0.0011 |
| Umami | 12.4 ^{bc} | 11.1 ^c | 15.8 ^a | 13.9 ^{abc} | 14.8 ^{ab} | | 0.0366 |
| <i>Flavour</i> | | | | | | | |
| Overall flavour intensity | 32.3 ^b | 26.7 ^c | 43.4 ^a | 32.9 ^b | 35.2 ^b | | <.0001 |
| Baked | 32.3 ^b | 24.3 ^c | 39.7 ^a | 33.3 ^b | 35.5 ^{ab} | | <.0001 |
| Boiled potato | 6.0 | 7.3 | 5.1 | 4.4 | 3.1 | | 0.2763 |
| Fatty | 11.2 ^{bc} | 10.9 ^c | 15.9 ^a | 14.0 ^{ab} | 14.1 ^a | | 0.0064 |
| Cheesy | 0.0 ^b | 0.0 ^b | 10.6 ^a | 0.8 ^b | 4.0 ^b | | 0.0001 |
| <i>Aftertaste</i> | | | | | | | |
| Baked | 31.0 ^b | 23.1 ^c | 38.4 ^a | 31.7 ^b | 33.8 ^{ab} | | 0.0003 |
| Boiled potato | 5.1 ^{ab} | 5.8 ^a | 3.2 ^b | 3.9 ^{ab} | 3.1 ^b | | 0.1390 |
| Sweet | 8.6 | 7.7 | 9.1 | 8.0 | 8.6 | | 0.6608 |
| Salty | 11.3 | 9.3 | 12.2 | 10.9 | 11.5 | | 0.0705 |
| Umami | 10.9 ^{bc} | 9.0 ^c | 13.9 ^a | 11.9 ^{ab} | 12.7 ^{ab} | | 0.0127 |
| Fatty | 10.4 ^{bc} | 9.2 ^c | 13.7 ^a | 12.8 ^{ab} | 13.1 ^{ab} | | 0.0177 |
| Cheesy | 0.0 ^b | 0.0 ^b | 6.3 ^a | 0.5 ^b | 2.6 ^{ab} | | 0.0261 |

Mean scores (n=12) Within a row, scores with the same lowercase letters are not statistically different (p>0.05).

Figure 1

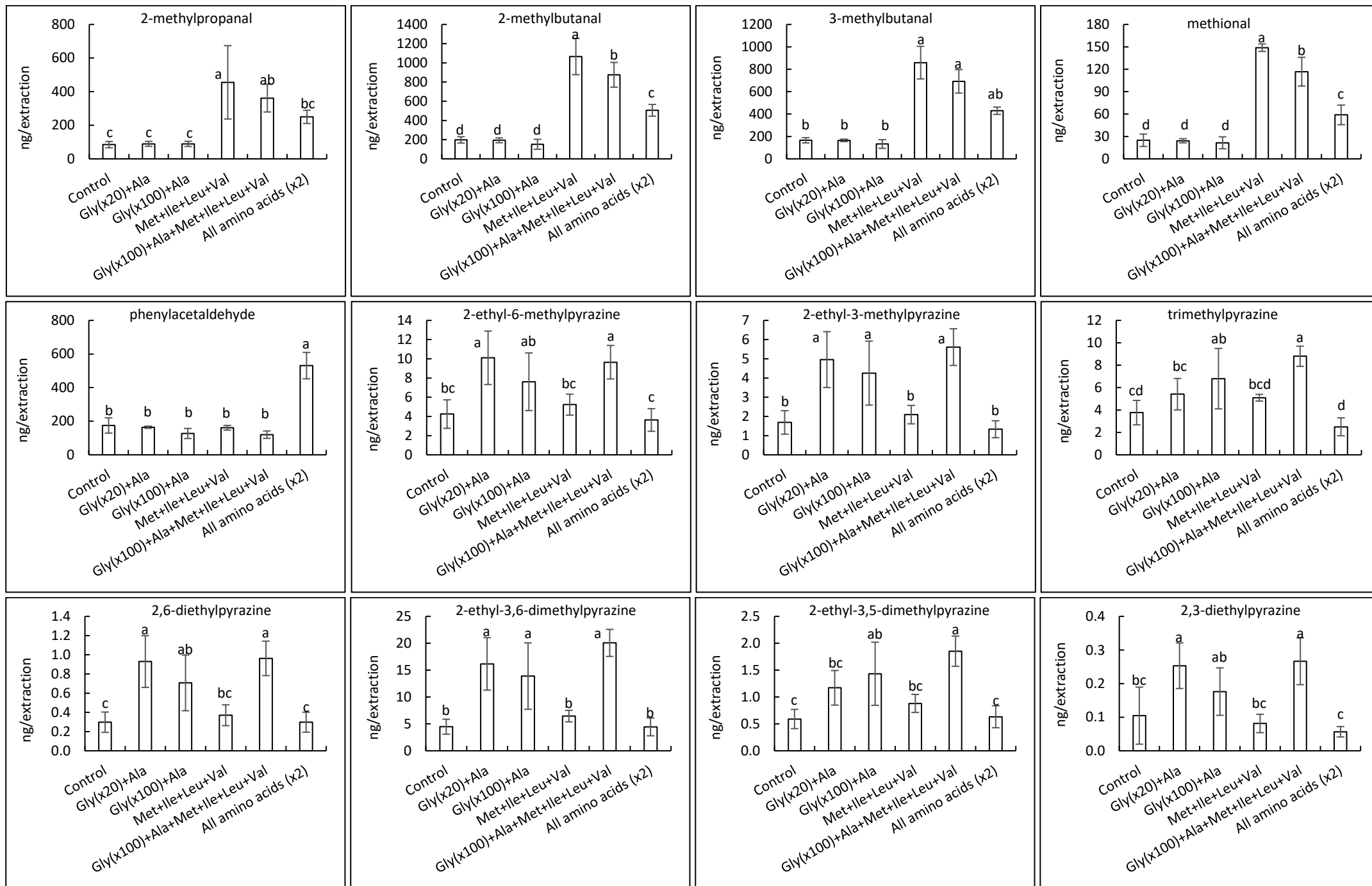


Figure 2

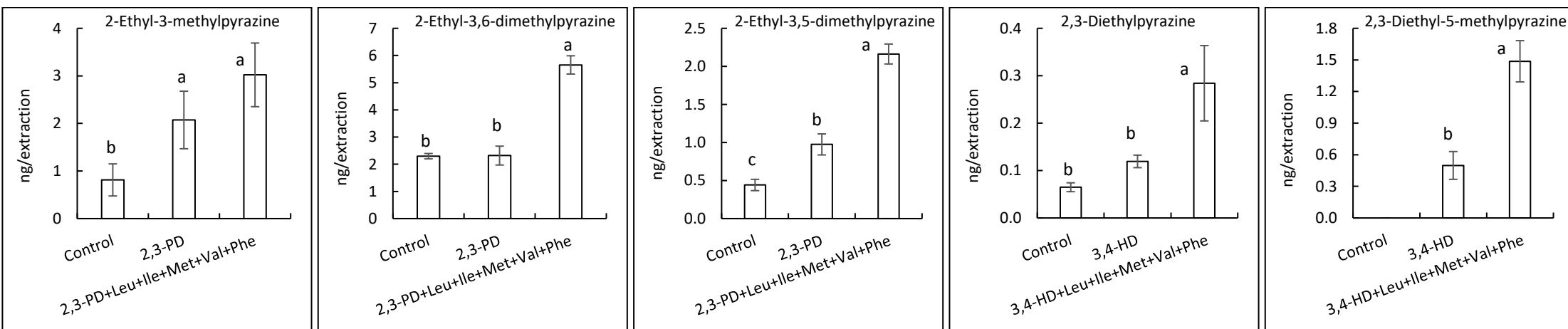


Figure 3

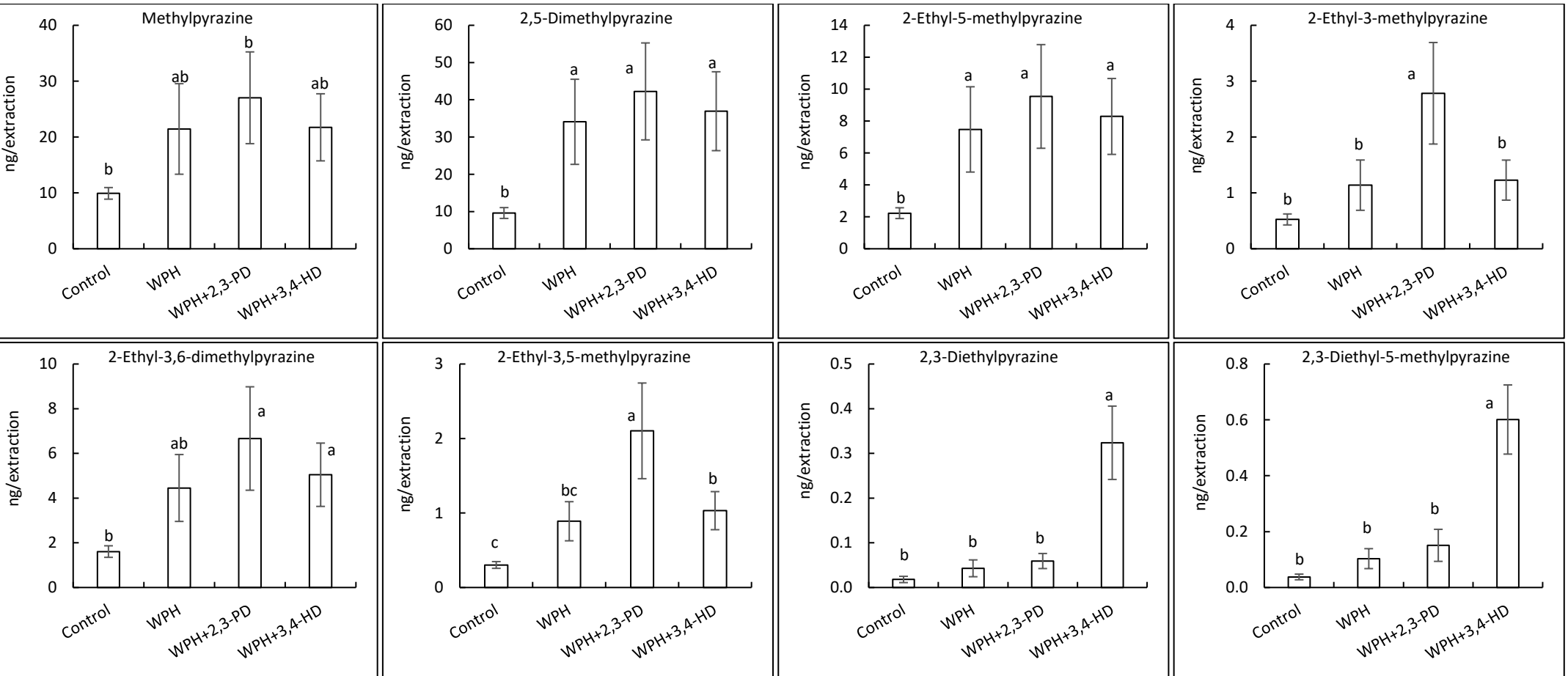


Figure 4

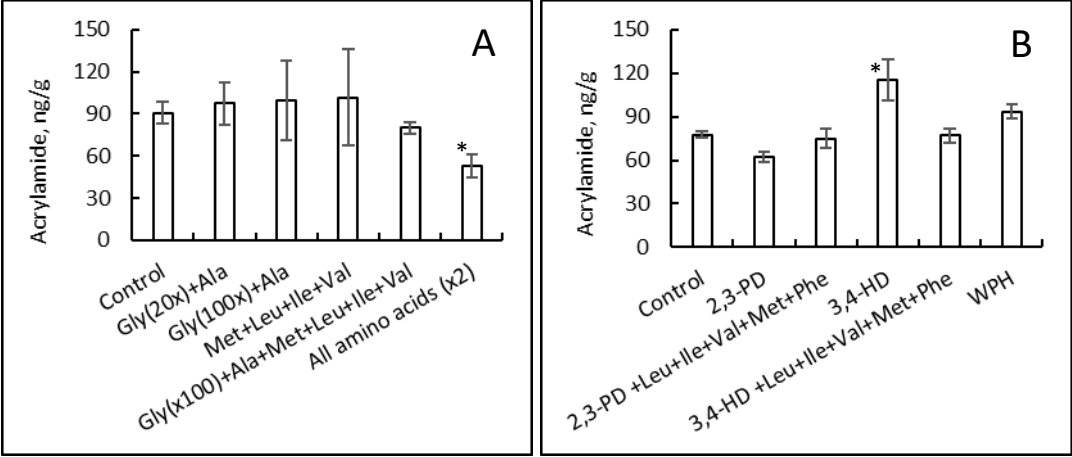


Figure S1. Formation of Strecker aldehydes and selected alkylpyrazines by addition of individual amino acids and also binary mixtures of amino acids during baking at 140 °C for 8 min followed by drying at 110 °C for 15 min (unless indicated amounts of added amino acids are 4-times the naturally occurring levels)

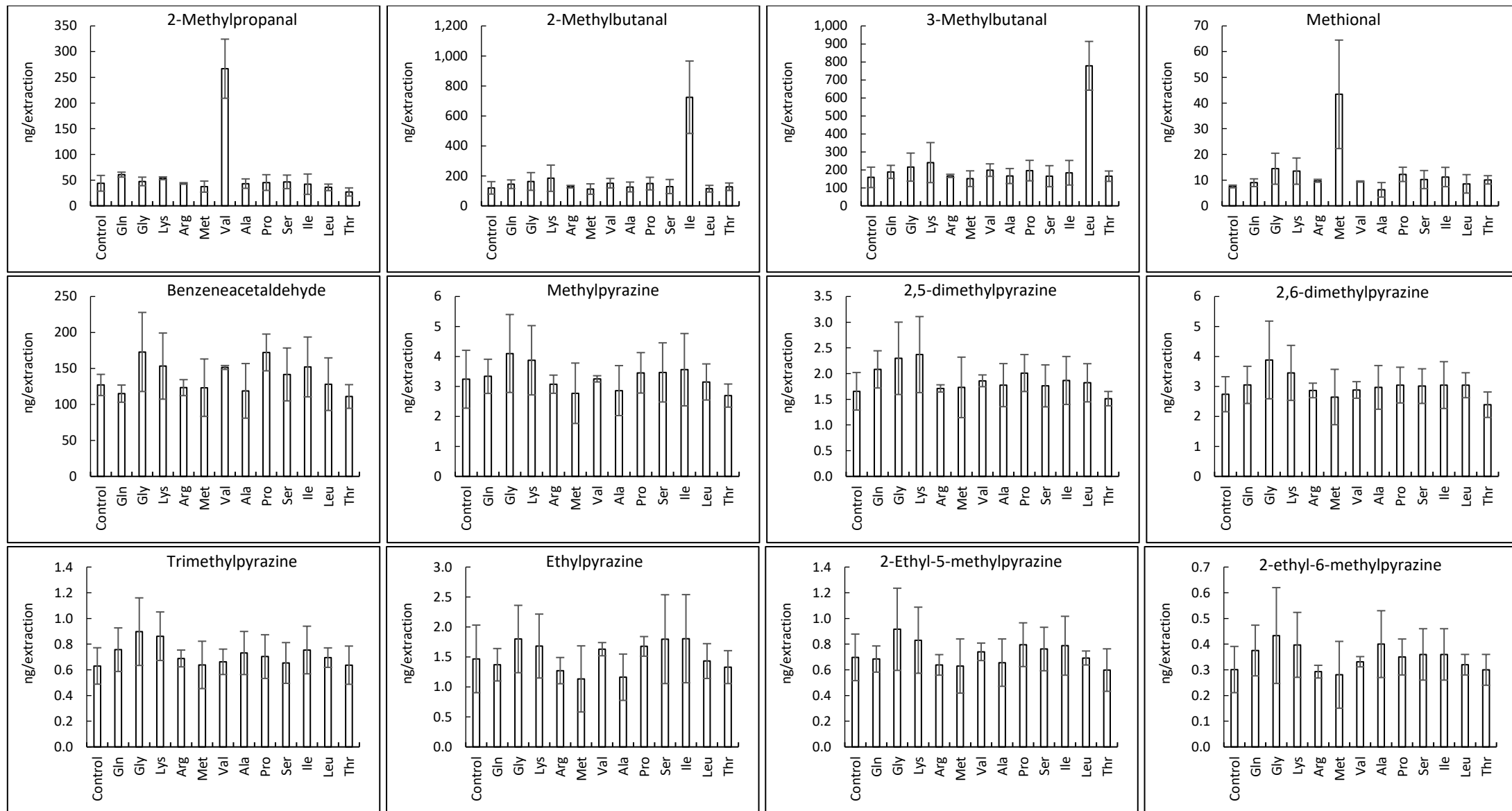


Figure S1 (continued)

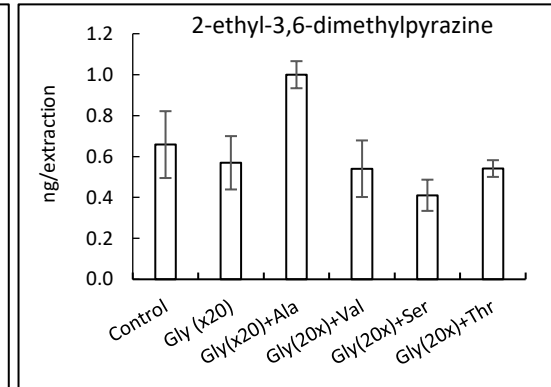
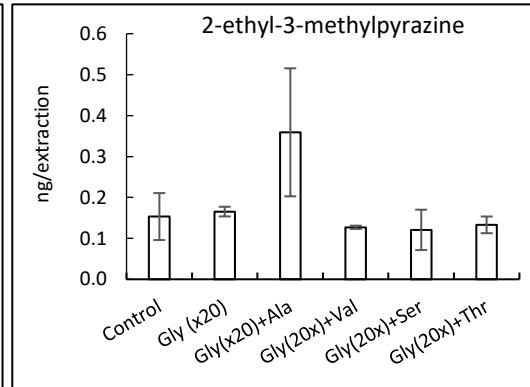
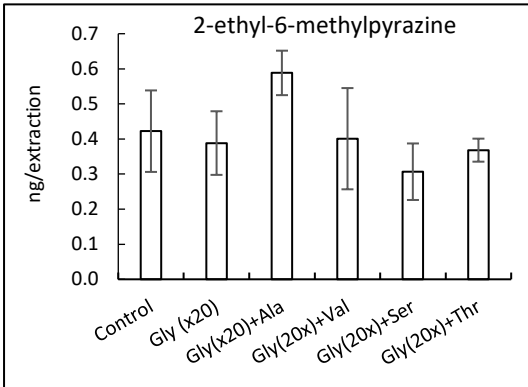
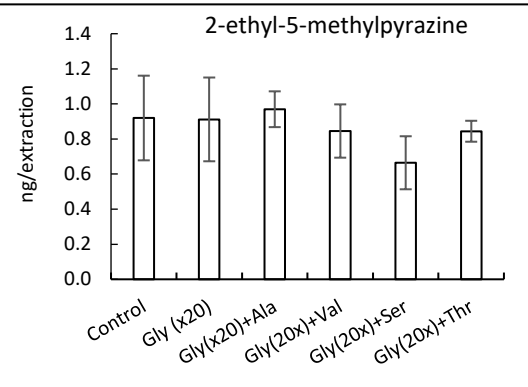
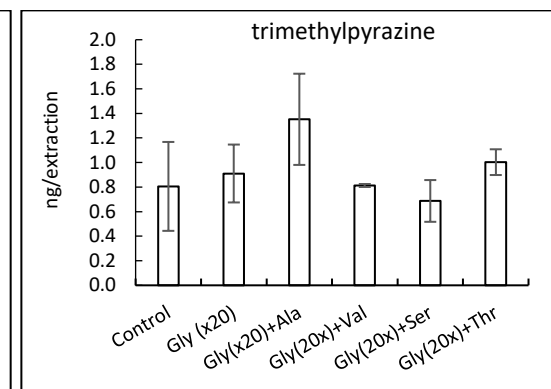
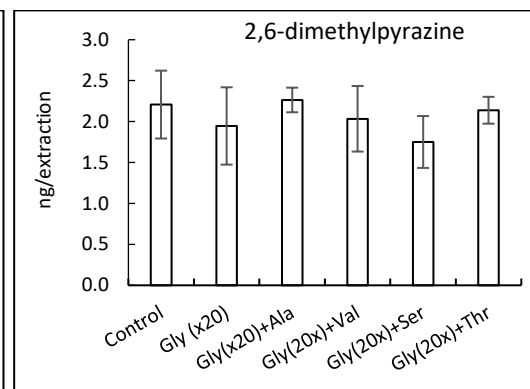
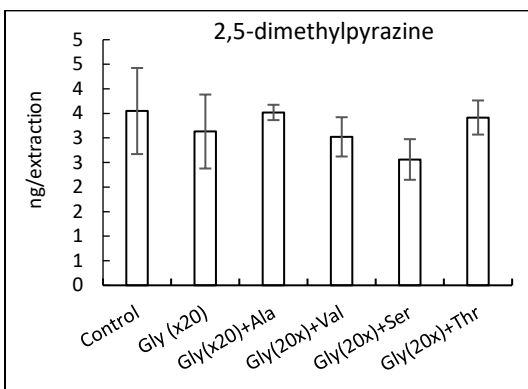
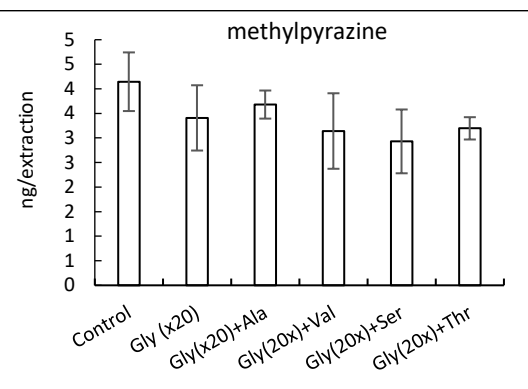


Figure S2. Formation of selected alkylpyrazines by addition of individual amino acids and also binary mixtures of amino acids during baking at 160 °C for 6 min followed by drying at 140 °C for 8 min (Unless indicated amounts of added amino acids are 4-times the naturally occurring levels)

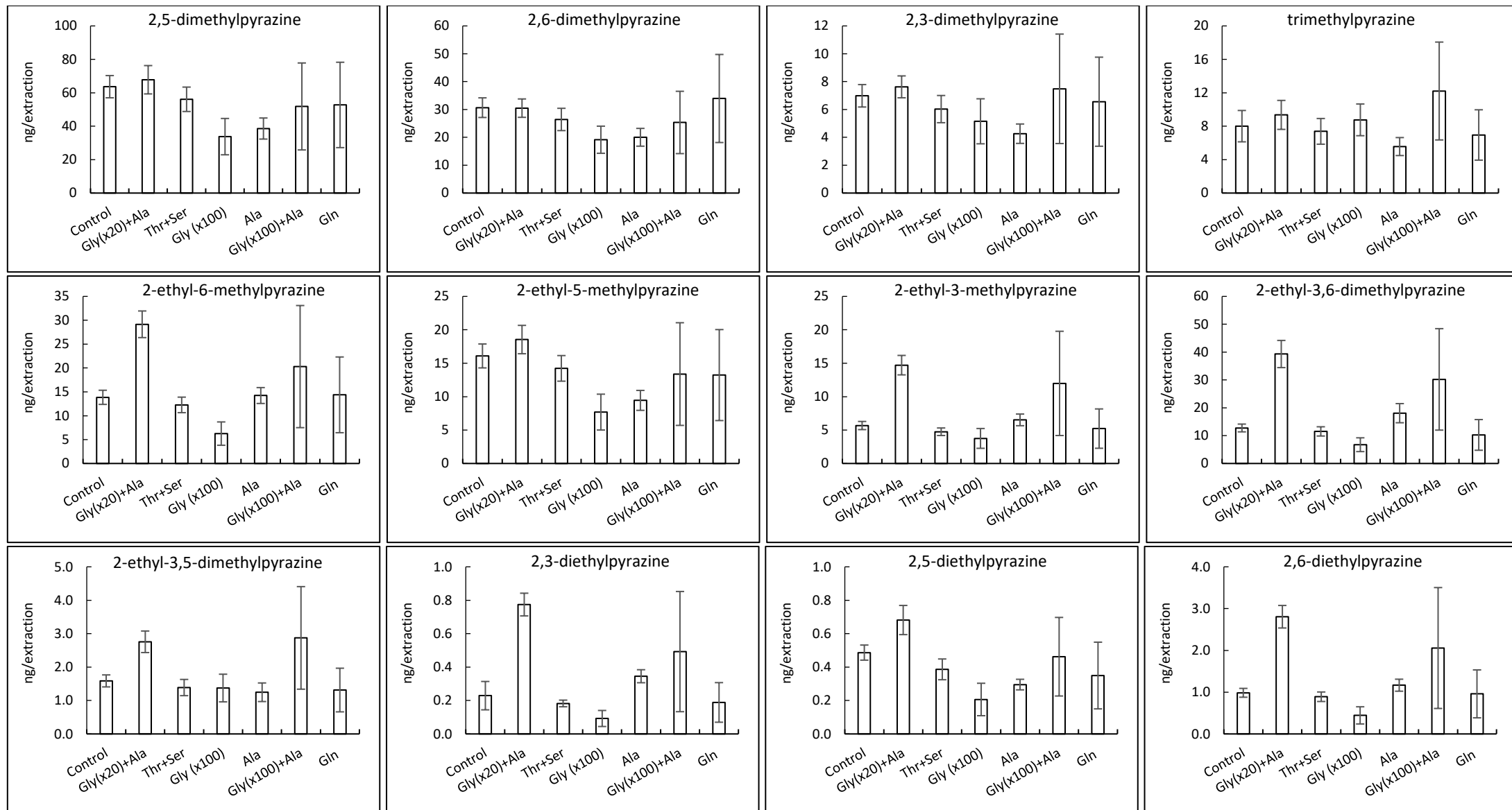


Figure S3. Formation of 2-ethyl-3,6-dimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine

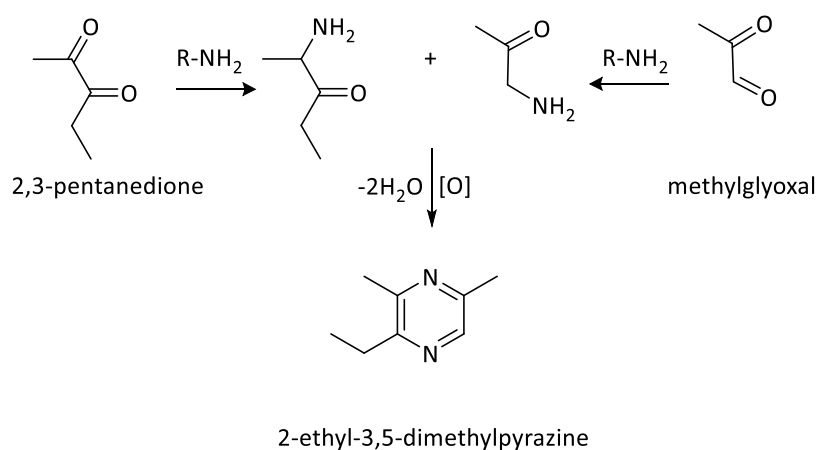
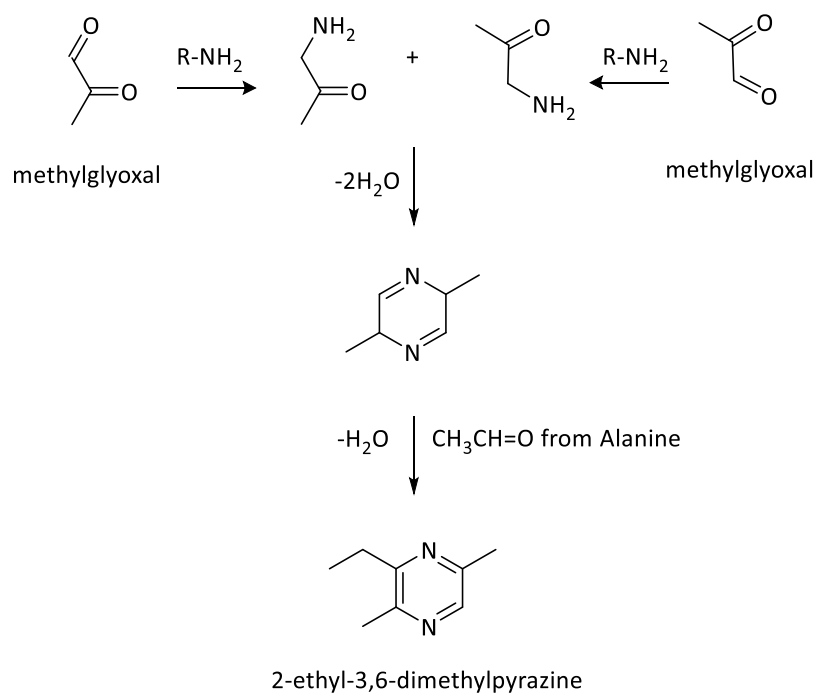


Table S1. Concentrations of free amino acids (mg/kg) and reducing sugars (g/kg) in potato flake and the final concentration (mg/kg) of added amino acids in the recipes on potato flake basis

| Potao flake | | Recipes in Figure 1 | | | | | Recipes in Figure 2 | | Recipes in Figure S1 and S2 | | | | | | | | | | | | | | | | | | | |
|-------------|-----------------------|---------------------|-------------------|-----------------------------|---|------------|---------------------|--|-----------------------------|-----|-----|-----|------|-----|------|-----|-----|-----|-----|-----|--------------|----------------------|----------------------|----------------------|-------------|---------------|-----------------------|------|
| Amino acid | Concentration (mg/kg) | Gly(x20) +Ala | Gly(x100) +Ala | Met +Ile +Leu +Val | Gly(x100) +Ala+Met +Ile+Leu +Val | AA (x2) | 2,3-PD | 2,3-PD +Met+Ile +Leu+Val +Phe | Gln | Gly | Lys | Arg | Met | Val | Ala | Pro | Ser | Ile | Leu | Thr | Gly (x20) | Gly (x20) +Ala | Gly (x20) +Val | Gly (x20) +Thr | Thr +Ser | Gly (x100) | Gly (x100) +Ala | |
| Ala | 531±1.3 | 2655 | 2655 | | 2655 | 1593 | | | | | | | | | 2655 | | | | | | | 2655 | | | | | | 2655 |
| Arg | 66±18.2 | | | | | 198 | | | | | | 330 | | | | | | | | | | | | | | | | |
| Asn | 2552±36.4 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Asp | 585±27.5 | | | | | 1755 | | | | | | | | | | | | | | | | | | | | | | |
| Cys | nd* | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| GABA | 580±4.3 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Gln | 401±2.8 | | | | | 2005 | | | 2005 | | | | | | | | | | | | | | | | | | | |
| Glu | 952±31.9 | | | | | 2856 | | | | | | | | | | | | | | | | | | | | | | |
| Gly | 18±0.6 | 378 | 1818 | | 1818 | 54 | | | | 90 | | | | | | | | | | | 378 | 378 | 378 | 378 | | 1818 | 1818 | |
| His | 90±0.4 | | | | | 270 | | | | | | | | | | | | | | | | | | | | | | |
| Ile | 157±3.3 | | | 785 | 785 | 471 | | 785 | | | | | | | | | | 785 | | | | | | | | | | |
| Leu | 168±5.9 | | | 840 | 840 | 504 | | 840 | | | | | | | | | | | 840 | | | | | | | | | |
| Lys | 35±5.3 | | | | | 105 | | | | 175 | | | | | | | | | | | | | | | | | | |
| Met | 107±0.2 | | | 535 | 535 | 321 | | 535 | | | | 535 | | | | | | | | | | | | | | | | |
| Phe | 223±3.1 | | | | | 669 | | 1115 | | | | | | | | | | | | | | | | | | | | |
| Pro | 97±1.1 | | | | | 291 | | | | | | | | | | 485 | | | | | | | | | | | | |
| Ser | 68±0.6 | | | | | 204 | | | | | | | | | | | 340 | | | | | | | | | 340 | | |
| Thr | 98±0.2 | | | | | 294 | | | | | | | | | | | | | | 490 | | | | 490 | 490 | | | |
| Trp | 67±2.1 | | | | | 201 | | | | | | | | | | | | | | | | | | | | | | |
| Tyr | 250±2.0 | | | | | 750 | | | | | | | | | | | | | | | | | | | | | | |
| Val | 235±1.6 | | | 1175 | 1175 | 705 | | 1175 | | | | | 1175 | | | | | | | | | | 1175 | | | | | |
| Sugar | Concentration (g/kg) | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Glucose | 6.7±0.24 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Fructose | 3.7±0.04 | | | | | | | | | | | | | | | | | | | | | | | | | | | |

*nd: not detected

Table S2. Effect of amino acid addition on the formation of volatile Maillard reaction products (ng/extraction) during baking at 160 °C for 6 min followed by drying at 130 °C for 10 min (unless indicated amounts of added amino acids are 4-times the naturally occurring levels) (Within a row, values with the same lowercase letters are not statistically different at p=0.05).

| | r threshold in μ/L) ^φ | ol | (!0)+Ala | (!00)+Ala | le+Leu+Val | (!00)+Ala+ Met+Ile+Leu+Val | mino acids (×2) except Asn | |
|--|-------------------------------------|------|-------------------------|-------------------------|--------------------------|----------------------------|----------------------------|------------------------|
| 2-Methylpropanal ^A | | 902 | 85±19 ^c | 89±15 ^c | 89±15 ^c | 456±218 ^a | 362±83 ^{ab} | 250±39 ^{bc} |
| 2-Methylbutanal ^A | | 1003 | 197±33 ^d | 193±25 ^d | 152±52 ^d | 1066±189 ^a | 875±129 ^b | 506±61 ^c |
| 3-Methylbutanal ^A | | 1008 | 166±24 ^b | 165±11 ^b | 133±39 ^b | 859±146 ^a | 692±105 ^a | 429±33 ^{ab} |
| Methional ^A | | 1465 | 25±8 ^d | 24±3 ^d | 22±8 ^d | 149±5 ^a | 117±19 ^b | 59±13 ^c |
| Phenylacetaldehyde ^A | | 1634 | 175±46 ^b | 164±6 ^b | 127±30 ^b | 161±14 ^b | 120±22 ^b | 531±79 ^a |
| 2,3-Butanedione ^A | | 1057 | 37±4.5 ^{abc} | 39±2.2 ^{ab} | 45±10 ^a | 34±5.4 ^{bc} | 37±5.9 ^{abc} | 28±2.3 ^c |
| 2,3-Pentanedione ^A | | 1130 | 26±4.4 ^{ab} | 31±2.8 ^a | 28±8.9 ^a | 23±2.9 ^{ab} | 24±4.4 ^{ab} | 17±1.6 ^b |
| Dimethyl disulfide ^A | | 1136 | 44±6.3 ^{cd} | 39±4.2 ^{cd} | 32±7.0 ^d | 88±19 ^{ab} | 106±26 ^a | 64±9.2 ^{bc} |
| Dimethyl trisulfide ^A | | 1387 | 5.2±2.4 ^b | 4.5±1.1 ^b | 6.2±2.5 ^b | 7.3±0.3 ^b | 13±2.9 ^a | 7.4±1.6 ^b |
| Pyrazine ^A | | 1258 | 3.1±1.1 ^a | 3.1±0.70 ^a | 2.3±0.59 ^a | 3.5±0.76 ^a | 2.7±0.33 ^a | 2.4±0.52 ^a |
| Methylpyrazine ^A | >2000 | 1296 | 24±8.0 ^{ab} | 27±6.3 ^a | 20±7.1 ^{ab} | 29±6.1 ^a | 23±3.5 ^{ab} | 14±3.9 ^b |
| 2,5-Dimethylpyrazine ^A | 1820 | 1343 | 21±6.7 ^{ab} | 30±8.5 ^a | 25±11 ^{ab} | 30±3.6 ^a | 33±3.7 ^a | 13±4.7 ^b |
| 2,6-Dimethylpyrazine ^A | 1720 | 1348 | 12±3.5 ^{ab} | 15±3.3 ^a | 13±5.2 ^{ab} | 14±0.66 ^{ab} | 15±2.4 ^a | 7.9±2.1 ^b |
| Ethylpyrazine ^A | >2000 | 1351 | 13±4.6 ^{ab} | 14±3.0 ^{ab} | 9±3.1 ^{ab} | 16±4.2 ^a | 11±2.3 ^{ab} | 8.9±2.3 ^b |
| 2,3-Dimethylpyrazine ^A | 880 | 1363 | 2.5±0.81 ^{bc} | 3.3±0.79 ^{ab} | 3.4±1.3 ^{ab} | 3.2±0.40 ^{ab} | 4.0±0.58 ^a | 1.6±0.48 ^c |
| 2-Ethyl-6-methylpyrazine ^A | | 1393 | 4.2±1.5 ^{bc} | 10±2.8 ^a | 7.6±3.0 ^{ab} | 5.2±1.1 ^{bc} | 9.6±1.7 ^a | 3.6±1.2 ^c |
| 2-Ethyl-5-methylpyrazine ^A | | 1398 | 5.6±1.8 ^{ab} | 7.8±2.1 ^a | 6.2±2.6 ^{ab} | 7.9±1.5 ^a | 8.6±1.1 ^a | 4.1±1.4 ^b |
| 2-Ethyl-3-methylpyrazine ^A | 35 | 1411 | 1.7±0.61 ^b | 5.0±1.5 ^a | 4.3±1.7 ^a | 2.1±0.48 ^b | 5.6±1.0 ^a | 1.3±0.44 ^b |
| Trimethylpyrazine ^A | 50 | 1412 | 3.8±1.1 ^{cd} | 5.4±1.4 ^{bc} | 6.8±2.7 ^{ab} | 5.1±0.30 ^{bcd} | 8.8±0.90 ^a | 2.5±0.80 ^d |
| 2,6-Diethylpyrazine ^A | 1.7 | 1437 | 0.30±0.11 ^c | 0.93±0.27 ^a | 0.71±0.29 ^{ab} | 0.37±0.11 ^{bc} | 0.96±0.18 ^a | 0.30±0.10 ^c |
| 2-Ethenylpyrazine ^B | >2000 | 1444 | 2.0±0.66 ^{ab} | 2.0±0.34 ^{ab} | 1.3±0.44 ^b | 2.3±0.55 ^a | 1.6±0.32 ^{ab} | 1.2±0.32 ^b |
| 2-Ethyl-3,6-dimethylpyrazine ^A | 3.6 | 1448 | 4.5±1.4 ^b | 16±4.9 ^a | 14±6.2 ^a | 6.5±1.1 ^b | 20±2.5 ^a | 4.4±1.7 ^b |
| 2-Ethyl-3,5-dimethylpyrazine ^A | 0.011 | 1464 | 0.59±0.18 ^c | 1.2±0.32 ^{bc} | 1.4±0.59 ^{ab} | 0.88±0.17 ^{bc} | 1.9±0.28 ^a | 0.63±0.20 ^c |
| 2,3-Diethylpyrazine ^A | 6.6 | 1456 | 0.10±0.08 ^{bc} | 0.25±0.07 ^a | 0.18±0.07 ^{ab} | 0.08±0.03 ^{bc} | 0.27±0.07 ^a | 0.06±0.02 ^c |
| 2,5-Diethylpyrazine ^A | 74 | 1462 | 0.17±0.05 ^{bc} | 0.28±0.09 ^{ab} | 0.18±0.08 ^{abc} | 0.24±0.06 ^{abc} | 0.30±0.07 ^a | 0.13±0.04 ^c |
| 2-Ethenyl-6-methylpyrazine ^B | | 1492 | 7.0±2.1 ^{ab} | 9.2±1.6 ^a | 7.6±2.8 ^{ab} | 8.3±0.9 ^{ab} | 8.3±1.2 ^{ab} | 5.3±1.5 ^b |
| 2-Ethenyl-5-methylpyrazine ^B | | 1499 | 1.6±0.47 ^{ab} | 1.9±0.42 ^a | 1.5±0.58 ^{ab} | 2.1±0.41 ^a | 1.9±0.26 ^a | 1.0±0.27 ^b |
| 2-Ethenyl-3,5(6)-dimethylpyrazine ^B | 0.012(870) | 1532 | 1.4±0.39 ^{bc} | 2.0±0.44 ^{ab} | 1.6±0.70 ^{abc} | 1.9±0.34 ^{ab} | 2.4±0.41 ^a | 0.94±0.23 ^c |
| Isopropenylpyrazine ^B | | 1604 | 0.21±0.06 ^a | 0.21±0.04 ^a | 0.21±0.04 ^a | 0.21±0.02 ^a | 0.24±0.02 ^a | 0.22±0.02 ^a |
| 2-furfural ^A | | 1472 | 39±8.5 ^a | 45±3.9 ^a | 42±10.6 ^a | 42±1.7 ^a | 43±5.1 ^a | 40±8.4 ^a |

* LRI: Linear retention indices on Phenomenex ZB-Wax column (30 m × 250 μm i.d. × 1 μm), ^φ Values were taken from Wagner, R., Czerny, M., Bielohradsky, J., & Grosch, W. (1999). Structure odour-activity relationships of alkylpyrazines. Z. Lebensm. Unters. Forsch., 208(5-6), 308-316.

A : Identification was confirmed by LRI (authentic compounds) and mass spectra (NIST library)

B : Identification was confirmed by LRI (literature) and mass spectra (NIST library)

Table S3. Effect of whey protein hydrolysate (WPH), also together with 2,3-pentanedione and 3,4-hexanedione, on the formation of volatile Maillard reaction products (ng/extraction)

| | LRI* | Control | WPH | WPH+2,3-PD | WPH+3,4-HD |
|-----------------------------------|------|------------------------|-------------------------|------------------------|-------------------------|
| 2-Methylpropanal | 902 | 77±11 ^a | 87±6.2 ^a | 108±17 ^a | 81±36 ^a |
| 2-Methylbutanal | 1003 | 145±3.51 ^a | 161±35.3 ^a | 176±17 ^a | 167±24 ^a |
| 3-Methylbutanal | 1008 | 144±3.84 ^a | 137±28.6 ^a | 145±12 ^a | 138±18 ^a |
| Methional | 1465 | 11±2.0 ^a | 11±2.8 ^a | 13±2.4 ^a | 12±1.5 ^a |
| Phenylacetaldehyde | 1634 | 88±2.0 ^a | 77±14 ^a | 90±12 ^a | 88±10 ^a |
| 2,3-Butanedione | 1057 | 32±3.1 ^a | 35±4.6 ^a | 41±1.8 ^a | 37±7.8 ^a |
| 2,3-Pentanedione | 1130 | 13±0.34 ^b | 21±6.9 ^b | 260±32 ^a | 26±5 ^b |
| Dimethyl disulfide | 1136 | 17±1.29 ^b | 57±2.82 ^a | 66±11 ^a | 57±12 ^a |
| Dimethyl trisulfide | 1387 | 1.9±0.39 ^b | 4.2±0.47 ^{ab} | 5.8±2.4 ^a | 5±0.37 ^a |
| Pyrazine | 1258 | 1.8±0.16 ^a | 2.3±0.53 ^a | 2.6±0.41 ^a | 2±0.45 ^a |
| Methylpyrazine | 1296 | 10±1.0 ^b | 21±8.1 ^{ab} | 27±8.2 ^b | 22±6.0 ^{ab} |
| 2,5-Dimethylpyrazine | 1343 | 10±1.5 ^b | 34±11 ^a | 42±13 ^a | 37±11 ^a |
| 2,6-Dimethylpyrazine | 1348 | 6.5±1.1 ^b | 10±3.1 ^{ab} | 12±2.9 ^a | 11±2.6 ^{ab} |
| Ethylpyrazine | 1351 | 4.3±0.72 ^b | 7.7±3.3 ^{ab} | 10±3.4 ^a | 8±2.4 ^{ab} |
| 2,3-Dimethylpyrazine | 1363 | 1.1±0.13 ^b | 1.8±0.60 ^{ab} | 2.3±0.69 ^a | 1.9±0.52 ^{ab} |
| 2-Ethyl-6-methylpyrazine | 1393 | 1.5±0.24 ^b | 3.0±1.1 ^{ab} | 4.0±1.4 ^a | 3.2±0.94 ^{ab} |
| 2-Ethyl-5-methylpyrazine | 1398 | 2.2±0.34 ^b | 7.5±2.7 ^a | 9.5±3.2 ^a | 8.3±2.4 ^a |
| 2-Ethyl-3-methylpyrazine | 1411 | 0.53±0.10 ^b | 1.1±0.45 ^b | 2.8±0.91 ^a | 1.2±0.36 ^b |
| Trimethylpyrazine | 1412 | 1.9±0.32 ^b | 4.9±1.3 ^a | 5.8±1.6 ^a | 5.6±1.3 ^a |
| 2,6-Diethylpyrazine | 1437 | 0.10±0.02 ^b | 0.19±0.07 ^{ab} | 0.28±0.10 ^a | 0.22±0.05 ^{ab} |
| 2-Ethenylpyrazine | 1444 | 0.70±0.09 ^a | 1.1±0.41 ^a | 1.4±0.42 ^a | 1.1±0.32 ^a |
| 2-Ethyl-3,6-dimethylpyrazine | 1448 | 1.6±0.26 ^b | 4.5±1.5 ^{ab} | 6.7±2.3 ^a | 5.0±1.4 ^a |
| 2-Ethyl-3,5-dimethylpyrazine | 1464 | 0.30±0.05 ^c | 0.89±0.26 ^{bc} | 2.1±0.64 ^a | 1.0±0.26 ^b |
| 2,3-Diethylpyrazine | 1456 | 0.02±0.01 ^b | 0.04±0.02 ^b | 0.06±0.02 ^b | 0.32±0.08 ^a |
| 2,5-Diethylpyrazine | 1462 | 0.06±0.00 ^b | 0.19±0.07 ^{ab} | 0.31±0.11 ^a | 0.21±0.06 ^a |
| 2,3-Diethyl-5-methylpyrazine | 1485 | 0.04±0.01 ^b | 0.10±0.04 ^b | 0.15±0.06 ^b | 0.60±0.12 ^a |
| 2-Ethenyl-6-methylpyrazine | 1492 | 3.4±0.54 ^b | 6.2±1.7 ^{ab} | 7.4±1.7 ^a | 6.7±1.7 ^a |
| 2-Ethenyl-5-methylpyrazine | 1499 | 0.60±0.09 ^b | 1.5±0.57 ^a | 1.9±0.64 ^a | 1.6±0.45 ^a |
| 2-Ethenyl-3,5(6)-dimethylpyrazine | 1532 | 0.60±0.06 ^b | 1.8±0.56 ^a | 2.2±0.69 ^a | 1.9±0.46 ^a |
| 2-furfural | 1472 | 30±5.0 ^a | 28±4.0 ^a | 29±1.7 ^a | 29±4.3 ^a |

Within a row, values with the same lowercase letters are not statistically different at p=0.05.

* LRI: Linear retention indices on Phenomenex ZB-Wax column (30 m × 250 µm i.d. × 1 µm)

Table S4. Sensory characteristics of the samples defined by panellist and their reference materials

| Attribute | Reference Material |
|---------------------------|-------------------------------------|
| <i>Aroma</i> | |
| Overall aroma intensity | |
| Baked | Crust under skin of jacketed potato |
| Boiled potato | Boiled potato |
| Fatty | Cooked oil |
| Sweet | |
| Cheesy | Mild cheddar |
| <i>Taste</i> | |
| Sweet | |
| Salty | |
| Bitter | |
| Umami | |
| <i>Flavour</i> | |
| Overall flavour intensity | |
| Baked | Crust under skin of jacketed potato |
| Boiled potato | Boiled potato |
| Fatty | Cooked oil |
| Cheesy | Mild cheddar |
| <i>Aftertaste</i> | |
| Baked | Crust under skin of jacketed potato |
| Boiled potato | Boiled potato |
| Sweet | |
| Salty | |
| Umami | |
| Fatty | Cooked oil |
| Cheesy | Mild cheddar |