# **Comparison of Volatile Compounds Isolated from the Skin and Flesh of Four Potato Cultivars after Baking**

Maria Jose Oruna-Concha, S. Craig Duckham, and Jennifer M. Ames\*

School of Food Biosciences, The University of Reading, Whiteknights, Reading RG6 6AP, United Kingdom

Four potato cultivars, Cara, Nadine, Fianna, and Marfona, were selected. Potatoes were baked in their skins prior to separating the skin and flesh and preparing extracts of the volatile flavor compounds using a modified Likens–Nickerson apparatus. The concentrated extracts were analyzed by gas chromatography–mass spectrometry. Volatiles were identified and classified according to their origin, that is, lipid, sugar degradation and/or Maillard reaction not involving sulfur amino acids, sulfur compounds, methoxypyrazines, and other compounds. Quantitative and qualitative differences were observed between isolates from flesh and skins and among cultivars grown at different sites. Strongest isolates from skin were obtained for Nadine. For flesh, Cara gave isolates  $\sim$ 10-fold more concentrated than the other three cultivars. For skin, sugar degradation and/or the Maillard reaction was by far the most important source in all cultivars except Nadine, for which 62% of the volatiles were accounted for by the sesquiterpene solavetivone. Lipid and sugar degradation and/or the Maillard reaction of the key potato volatiles identified reinforce the effects of cultivar and growing site on baked potato flavor.

**Keywords:** *Potato; flavor; aroma; solavetivone; potato skin; potato flesh; baked potato; cultivar effects* 

## INTRODUCTION

Potato (*Solanum tuberosum* L.) is cultivated throughout the world and is a staple dietary item in many cultures. It can be stored for prolonged periods, it is available all year round, and it is a source of many essential nutrients. Potatoes are always cooked before consumption, traditionally by boiling, baking, or frying. They are also processed into powder and granules by the food industry.

The aroma volatiles of cooked potato have been the subject of many studies. Over 250 compounds have been isolated from baked potatoes alone (1), and two major studies have been reported (2, 3). Compounds considered to be important in baked potato flavor include certain pyrazines (such as 2-ethyl-3,5-dimethylpyrazine), formed from sugar-amino acid interactions, methional (the Strecker aldehyde of methionine), and some lipid degradation products, for example, (*E*,*E*)-2,4-decadienal (1). Buttery et al. (2) compared the volatile compounds isolated from the skin and flesh of Russet Burbank potatoes and showed that the pyrazines/ aliphatic aldehydes ratio was higher in skins than in flesh, compared to isolates from whole baked potatoes.

As well as compounds formed from lipid and sugaramino acid interactions, the raw tuber contains a number of volatile compounds deriving from biosynthetic processes in the tuber or associated microorganisms. These include methoxypyrazines, which give potatoes an earthy aroma (3, 4), and certain sesquiterpenes, produced by the tuber in response to damage or microbial attack (5,  $\theta$ ). Surprisingly, there appear to be no studies in the literature comparing the volatile flavor components of different potato cultivars after baking. However, betweencultivar comparisons have been made of the flavor components of boiled potato (7, 8) and the sensory properties of steamed (9) and fried (10) potatoes. Such studies are of value because they provide information for the consumer about the use of specific cultivars for particular purposes and they guide plant breeders who aim to produce new cultivars with defined attributes.

This study reports the volatile compounds from the skin and flesh of baked potatoes and compares the levels of such compounds isolated from four potato cultivars.

#### EXPERIMENTAL PROCEDURES

**Materials.** Four potato (*Solanum tuberosum* L.) cultivars, that is, Cara, Marfona, Fianna, and Nadine, were supplied by the British Potato Council (Oxford, U.K.). They were grown at different sites in the United Kingdom and were all harvested in late September 1996. They were cured for 2 weeks at 12 °C and ambient relative humidity (RH) before the storage conditions were applied, which were a temperature of 4 °C and 95–98% RH. Tubers were kept at room temperature (18–20 °C) for 3–5 days immediately prior to analysis. Potatoes were used 3.5 months after harvest. Potatoes were freed from adhering soil particles by thorough washing and scrubbing. Care was taken not to bruise or damage the potatoes by overabrasion.

**Characterization of Raw Tubers.** Dry matter content was determined indirectly from the specific gravity of the tubers using the method of Tai et al. (*11*). For analysis of sugars, a random sample of 3–4 kg of washed tubers was cut to give 12 mm section strips. A random sample (200 g) was homogenized with water (200 mL), suspended material was precipitated with Carrez reagents, and the filtrate was clarified by centrifugation. A 1 mL sample was diluted to 10 mL with water and analyzed on a Dionex (Camberly, U.K.) system

<sup>\*</sup> Author to whom correspondence should be addressed (telephone +44 118 931 8730; fax +44 118 931 0080; e-mail j.m.ames@afnovell.reading.ac.uk).

using a Carbo-Pac PA1 ion-exchange column (Dionex), 150 mM sodium hydroxide solution as mobile phase, and pulsed amperometric detection. Quantitation was by comparison with external standards. Extracts of amino acids were prepared from lyophilized tissue (50 mg) with ethanol/water (50:50, v/v). Following clarification by centrifugation and addition of homoserine (internal standard), extracts were analyzed by high-performance liquid chromatography (HPLC) (*12*). All extracts were prepared in at least duplicate for analysis.

**Preparation of Concentrated Extracts of Volatile Compounds.** Individual tubers (~200 g) were not wrapped in foil. They were baked at 190 °C for 1 h in a fan-assisted oven. The skin of each baked potato was removed from the flesh. The skin and flesh from six tubers of one cultivar were separately diced and mixed well to give  ${\sim}1.5$  kg total of flesh and  $\sim$ 320 g total of skin. Flesh ( $\sim$ 250 g) or skin ( $\sim$ 75 g) was mixed with 2 L of distilled water in the sample flask of a modified Likens-Nickerson apparatus (13) fitted with a condenser cooled with circulating ethylene glycol at 4 °C. Antibumping granules and antifoam agent (0.5 mL) were added. Pentane (AnalaR grade, Fisons, Loughborough, U.K.)/ diethyl ether (AnalaR grade, Prolabo, Manchester, U.K.) (9:1 v/v, 30 mL) was the extraction solvent. Volatile components were extracted for 2 h. Four extracts were prepared from both the flesh and the skin of each cultivar. Extracts were cooled at -18 °C overnight to remove water. 1,2-Dichlorobenzene (99%, Aldrich, Gillingham, U.K.) (0.1% v/v, in diethyl ether, 0.1 mL), internal standard, was added to each solvent extract prior to concentration. Extracts were concentrated to 0.5 mL using a Kuderna-Danish apparatus with the water bath at 45 °C, prior to final reduction to 0.1 mL under a slow stream of nitrogen. Blank extracts were prepared using only water in the sample flask. All concentrated extracts were stored at -18°C for no longer than 1 week, prior to analysis. All four individual extracts prepared from each cultivar were analyzed once for skin. Due to the relatively low strength of extracts from flesh, extracts from each cultivar were pooled, and the combined concentrated extracts were analyzed four times.

**Gas Chromatography—Mass Spectrometry (GC-MS).** A Hewlett-Packard (Bracknell, U.K.) GC 5890 series II instrument connected to an HP 5972 mass spectrometer was used. The fused silica column (50 m × 0.32 mm i.d.), coated with BPX-5 (0.25  $\mu$ m film thickness), was obtained from SGE Ltd. (Milton Keynes, Bucks, U.K.). The flow rate was 1 mL/min. Spit/splitless injection was used, and the injection volume was 1  $\mu$ L. The injection temperature was 250 °C. Operation parameters for mass spectra registration were as follows: mass range, 29–400; EI mode (70 eV); carrier gas, helium; interface temperature, 280 °C; source temperature, 200 °C; temperature program, 35 °C for 3 min followed by a ramp rate of 4 °C/min to 250 °C, held for 10 min. Semiquantitative data were obtained from the mass spectral integration report and were based on the peak area of the internal standard.

Experimental linear retention indices (LRI) were calculated with reference to the retention times of a series of standard *n*-alkanes, run under the same GC-MS conditions. Identification of compounds was based on correlation of MS data with spectra in the NBS75K MS library and by comparison of experimental LRI values with LRI data published for authentic compounds (*14*, *15*) or run using the same GC stationary phase.

Where both MS and LRI data were consistent with those in the literature or obtained for authentic compounds, identifications were considered to be positive. When MS data agreed but no reference LRI data were available, identifications were considered to be tentative.

**Statistical Analysis.** Semiquantitative data for the volatile compounds of potato skins were analyzed using two-way analysis of variance (ANOVA). For compounds with significant *F* values (p < 0.05), Fisher's least significant difference (LSD) test was applied (two-tailed with p < 0.05) to indicate which cultivars contained significantly different levels of the compound.

## RESULTS AND DISCUSSION

Data were obtained for tubers grown at different sites from a single harvest. Tubers were stored under one set of conditions and baked using a standardized procedure. Variations in year-on-year agronomic conditions, as well as different storage and baking conditions, would be expected to affect the data and may influence the conclusions drawn.

Raw Tubers. Amounts of dry matter, sugars, and free amino acids in all four cultivars are given in Table 1. Levels of dry matter and total sugars are the same order of magnitude as those reported by Finglas and Faulks (16). Levels of amino acids were similar to those reported by Paul and Southgate (17). Dry matter varied from 16.5% in Nadine to 19.7% in Cara. Of the three sugars measured (glucose, fructose, and sucrose), glucose was the most abundant in all cultivars and sucrose occurred at the lowest levels. The highest level of total sugars was in Nadine (2.12% fresh weight) with Fianna having the lowest total level (0.91% fresh weight). Marfona contained the greatest concentration of total amino acids (6 mg g<sup>-1</sup>), and Nadine possessed the lowest amount (4.5 mg g<sup>-1</sup>). Asparagine was the most abun-dant amino acid (range = 31.6-47.2% of total amino acids), and glycine, threonine, and tryptophan were among those present in lower concentrations. Amounts of methionine (the precursor of methional) ranged from 40  $\mu$ g g<sup>-1</sup>, in Fianna, to 70  $\mu$ g g<sup>-1</sup>, in Marfona.

**Volatile Compounds.** The compounds identified in the skin and flesh from the four potato cultivars are listed in Tables 2 and 3, respectively. Statistical analysis of the levels of compounds identified in potato skin indicated that amounts of only five of them differed significantly (p < 0.05) among cultivars, and the data are shown in Table 4. Minor peaks, due to solvent impurities, have been omitted from the tables. The compounds are grouped according to their main source, that is, lipid, sugar and/or Maillard reaction not involving sulfur amino acids, sulfur compounds (requiring, for example, a sulfur amino acid or thiamin for their formation), methoxypyrazines, and others.

Skin. The strength (total amount of volatile compounds per gram of potato sample) of the concentrated isolates ranged from 1.46  $\mu$ g/g (Fianna) to 2.88  $\mu$ g/g (Nadine). Sugar degradation and/or the Maillard reaction was a major source of volatiles from potato skin (71-78% of the total amount) in all cultivars except Nadine (28%), with pyrazines contributing from 56% (Nadine) to 73% (Cara) of amounts in this group. 2,5and/or 2,6-dimethylpyrazine was the most abundant representative in every cultivar. The absolute amounts of compounds in this group do not appear to be related to the sugar concentration in the raw tuber (Nadine possessed the highest levels) but could be associated with levels of amino acids, Nadine having the lowest total amounts. Hwang et al. (23) prepared model systems comprising wheat starch, glucose, glycine, and one other amino acid, containing 12-14% water and heated at 180 °C for 1 h. They showed that asparagine had the highest contribution to pyrazine formation, whereas glutamine and glutamic acid had the lowest, and attributed this to the faster rate of deamidation for asparagine, compared to that for glutamine. Nadine possessed the lowest level of asparagine, and this may account, in part, for the low observed levels of pyrazines. Phenylacetaldehyde was another major contributor to the sugar degradation/Maillard category. Levels of both

Table 1. Dry Matter, Sugars, and Free Amino Acids in Raw Potato Tubers<sup>a</sup>

| component                      | Cara                 | Nadine               | Fianna               | Marfona              |
|--------------------------------|----------------------|----------------------|----------------------|----------------------|
| dry matter (% fresh wt)        | 19.7                 | 16.5                 | 19.5                 | 18.9                 |
| sugars (% fresh wt)            | Cara                 | Nadine               | Fianna               | Marfona              |
| glucose<br>fructose<br>sucrose | 0.84<br>0.74<br>0.20 | 1.34<br>0.72<br>0.06 | 0.33<br>0.33<br>0.25 | 0.60<br>0.53<br>0.05 |
| total sugars                   | 1.78                 | 2.12                 | 0.91                 | 1.18                 |

|                       | (                        | Cara       | Nadine                 |            | Fianna                 |            | Marfona                |            |
|-----------------------|--------------------------|------------|------------------------|------------|------------------------|------------|------------------------|------------|
| amino acid (fresh wt) | $\mu { m g}~{ m g}^{-1}$ | % of total | $\mu {f g} {f g}^{-1}$ | % of total | $\mu {f g} {f g}^{-1}$ | % of total | $\mu {f g} {f g}^{-1}$ | % of total |
| Ala                   | 48                       | 1.0        | 30                     | 0.7        | 40                     | 0.7        | 81                     | 1.3        |
| Arg                   | 230                      | 4.6        | 218                    | 4.9        | 208                    | 3.8        | 316                    | 5.2        |
| Asn                   | 2263                     | 45.4       | 1703                   | 38.2       | 2581                   | 47.2       | 1912                   | 31.6       |
| Asp                   | 375                      | 7.5        | 324                    | 7.3        | 516                    | 9.4        | 305                    | 5.0        |
| Gĺn                   | 863                      | 17.3       | 1321                   | 29.7       | 1041                   | 19.0       | 1771                   | 29.3       |
| Glu                   | 357                      | 7.2        | 234                    | 5.3        | 483                    | 8.8        | 351                    | 5.8        |
| Gly                   | 13                       | 0.3        | 11                     | 0.2        | 14                     | 0.3        | 17                     | 0.3        |
| His                   | 101                      | 2.0        | 48                     | 1.1        | 66                     | 1.2        | 115                    | 1.9        |
| Ile                   | 67                       | 1.3        | 56                     | 1.3        | 51                     | 0.9        | 117                    | 1.9        |
| Leu                   | 47                       | 0.9        | 44                     | 1.0        | 33                     | 0.6        | 60                     | 1.0        |
| Lys                   | 95                       | 1.9        | 81                     | 1.8        | 72                     | 1.3        | 189                    | 3.1        |
| Met                   | 51                       | 1.0        | 43                     | 1.0        | 40                     | 0.7        | 70                     | 1.2        |
| Phe                   | 84                       | 1.7        | 77                     | 1.7        | 73                     | 1.3        | 152                    | 2.5        |
| Ser                   | 92                       | 1.8        | 64                     | 1.4        | 91                     | 1.7        | 149                    | 2.5        |
| Thr                   | 6                        | 0.1        | 28                     | 0.6        | $\mathbf{nd}^{b}$      |            | 36                     | 0.6        |
| Try                   | 50                       | 1.0        | 12                     | 0.3        | 23                     | 0.4        | 61                     | 1.0        |
| Tyr                   | 77                       | 1.5        | 28                     | 0.6        | 29                     | 0.5        | 74                     | 1.2        |
| Val                   | 165                      | 3.3        | 129                    | 2.9        | 104                    | 1.9        | 266                    | 4.4        |
| total amino acids     | 4983                     |            | 4453                   |            | 5465                   |            | 6026                   |            |

<sup>a</sup> All values are the means obtained from single analyses of at least duplicate extracts. Coefficient of variation < 10%. <sup>b</sup> nd, not determined.

phenylalanine (the amino acid from which it derives) and phenylacetaldehyde were similar for Cara, Nadine, and Fianna, whereas higher levels of phenylalanine and significantly higher levels (p < 0.05) phenylacetaldehyde were observed in Marfona.

The second major source of volatiles was lipid degradation (5-9%) of the total amount). Fatty acids were not determined in the raw tubers, but levels of the relatively reactive linoleic and linolenic acids are reported to be 0.05 and 0.01 g/100 g of flesh, respectively (17).

Only four sulfur compounds are reported, and dimethyl trisulfide is the only one in all four cultivars. Methional, possessing a cooked potato aroma, could not be identified, probably due to masking by 2,5- and/or 2,6-dimethylpyrazine. Single ion monitoring of the ion at m/z 48, which is characteristic of methional, is likely to have confirmed its presence.

Certain methoxypyrazines have been associated with the characteristic musty, earthy note of potato (21, 24, 25), and the 2-isopropyl-3-methoxy derivative was present in Marfona. This compound has previously been identified in raw potato (24), baked potato (26), boiled potato (20, 21), and boiled potato peelings (27); it is of particular interest due to its very low odor threshold value of 2 ng/L (28). It has been identified from cultures of Pseudomonas taetrolens, and Buttery and Ling (24) have suggested that it may be formed in the soil or on the tuber surface, from where it could be absorbed into the tuber. The potato is related to the bell pepper, which can produce relatively large amounts of the related compound 2-isobutyl-3-methoxypyrazine (24), also identified in boiled potato by Petersen et al. (21). Because 2-isopropyl-3-methoxypyrazine was present in identifiable amounts only in Marfona, it would appear that there may be differences among the cultivars examined

in their ability to synthesize this compound. Also, differences in cultural conditions may affect its synthesis.

The sesquiterpene, solavetivone, was tentatively identified in all four cultivars. A relatively high level (1780 ng/g) is reported in Nadine, that is, twice the level of compounds derived from sugar degradation and/or the Maillard reaction and significantly higher (p < 0.05) than for the other three cultivars. Various sesquiterpenes, including solavetivone, are produced by tubers in response to fungal and bacterial infections, for example, by Erwinia carotovora ssp. atroseptica, the main cause of tuber soft rot and stem rotting of potato (5, 29). Such sesquiterpenes are associated with tuber resistance to rotting, and the accumulation of these compounds differs with cultivar (6). The observed level of solavetivone in Nadine is at the lower end of the ranges reported for tubers treated with the sesquiterpene elicitor, arachidonic acid ( $\boldsymbol{6}$ ), or inoculation with  $\boldsymbol{E}$ . carotovora ssp. atroseptica (5). This suggests that Nadine tubers were under some stress during storage, although they (and tubers of the three other cultivars) appeared to be in good condition. Nadine may have been biochemically less stable than the other cultivars under the chosen storage conditions.

Three methoxyphenols were identified, with total amounts varying from 121 ng/g (Nadine) to 426 ng/g (Marfona). None has previously been reported among the volatiles of raw or cooked potato. 2-Methoxy-4-vinylphenol and eugenol possess clove-like odors (*30*) and derive from the thermal degradation of phenolic acids or lignin.

*Flesh.* Fianna gave the weakest volatiles isolate (85 ng/g), whereas Cara gave the strongest (869 ng/g). Lipid degradation was the predominant source of volatiles in

## Table 2. Volatile Compounds<sup>a</sup> Identified in Potato Skin

|  |                   |                       | cultivar  |          |           |          |
|--|-------------------|-----------------------|-----------|----------|-----------|----------|
| source and compound  | $LRI_{exptl}^{b}$ | LRI <sub>lit.</sub> c | Cara      | Nadine   | Fianna    | Marfona  |
| lipid  | -                 |                       |           |          |           |          |
| hexanal <sup>d,e,f,g</sup>   | 810               | 809                   | 0         | 7        | 4         | 0        |
| etnylbenzene <sup>g</sup>  | 866<br>964        | 865<br>959            | 8         | 3        | 1         | 3        |
| benzaldehyde <sup>d,e,f,g</sup>  | 979               | 983                   | 79        | 54       | 53        | 89       |
| 2-pentylfuran <sup>d,e,f,g</sup>   | 992               | 993                   | 14        | 15       | 3         | 8        |
| nonanal <sup>e,t,g</sup>   | 1116              | 1118                  | 11        | 3        |           | 25       |
| (E)-2-nonenal <sup>d,e,f,g</sup>   | 1175              | 1173                  | 5         | 5        |           | 3        |
| decanal <sup>e,f,g</sup>   | 1218              | 1217                  | 5         |          | 3         | 7        |
| 1-hexadecanol <sup>t</sup>   | 1900              |                       | 10        | 07       | 48        | 21       |
| octadecyl acetate  | 2005              |                       | 10        | 37       | 2         |          |
| total  |                   |                       | 136       | 134      | 111       | 158      |
| sugar and/or Maillard reaction (not involv   | ving sulfur ar    | nino acids)           |           |          |           |          |
| pyridine <sup>e,f,g</sup>  | 756               | 756                   | 6         | 8        | 10        | 14       |
| 2-methyl-3(2 <i>H</i> )-furanone <sup>4,g</sup><br>methylpyrazine <sup>e,f,g</sup> | 819<br>836        | 819<br>837            | 16        | 15       | 6<br>12   | 14       |
| 2-furfural <sup>d,e,f</sup>  | 846               | 848                   | 34        | 62       | 21        | 29       |
| 2,5(6)-dimethylpyrazine <sup>d,e,f</sup>   | 922               | 925                   | 192       | 133      | 211       | 365      |
| ethylpyrazine <sup>f,g</sup>   | 925               | 930                   | 78        | 26       | 32        | 52       |
| 5-methylfurfural <sup><i>t,g</i></sup>   | 976               | 976                   | 2         | 25       | 40        | 6        |
| z-ethyl-o-methylpyrazine <sup>f</sup>  | 1006              | 1010                  | 55<br>46  | 20<br>31 | 40<br>50  | 59<br>70 |
| 2-ethyl-5-methylpyrazine <sup><i>e</i>,<i>f</i>,<i>g</i></sup>                     | 1010              | 1014                  | 48        | 40       | 76        | 109      |
| 2-ethyl-3-methylpyrazine <sup>f</sup>  | 1015              | 1016                  | 74        |          |           |          |
| 2-ethenyl-5-methylpyrazine <sup>g</sup>  | 1041              |                       | 5         | 8        | 7         | 2        |
| 2-ethenyl-6-methylpyrazine <sup>4,g</sup>  | 1047              | 1066                  | 270       | 240      | 255       | 12       |
| 2-ethyl-3.5(6)-dimethylpyrazine <sup>f,g</sup>                                     | 1084              | 1087, 1093            | 124       | 61       | 157       | 152      |
| 2-acetylpyrrole <sup><i>f,g</i></sup>  | 1086              | 1087                  |           | 9        | 101       | 4        |
| a diethylpyrazine  | 1091              |                       | 21        | 13       | 8         | 23       |
| a diethylpyrazine  | 1094              |                       | 27        | 13       | 11        | 26       |
| a methyl-(2-methylpropyl)pyrazine  | 1143              |                       | 21        | 9        | 5         | 34<br>13 |
| 2.3-diethyl-5-methylpyrazine <sup>f,g</sup>  | 1157              | 1161                  | 4         | 5        |           | 6        |
| 3,5-diethyl-2-methylpyrazine <sup>h,i</sup>  | 1161              | 1168                  | 21        | 7        | 18        | 39       |
| a diethylmethylpyrazine  | 1167              | 1100                  | 28        | 13       | 39        | 3        |
| 1-(2-furanylmethyl)-(1 <i>H</i> )-pyrrole  | 1199              | 1196                  | 3         | 11       | 8         | 4        |
| 2-methyl-5-propenylpyrazine  | 1221              |                       | 24        | 11       | 6         | 40<br>5  |
| 2,5-dimethyl-3-(2-methylpropyl)pyrazine <sup>f</sup>                               | 1227              |                       | 3         |          |           | 8        |
| 2,5-dimethyl-3-propenylpyrazine  | 1243              |                       |           | 6        | 5         | 2        |
| a C6 substituted pyrazine  | 1250              |                       | 13        | 4        | 1         | 14       |
| a C6 substituted pyrazine  | 1265              |                       | 12        | 6        | 23        | 19       |
| a C7 substituted pyrazine  | 1279              |                       | 3         | 1        | 0         | 4        |
| a C7 substituted pyrazine  | 1284              |                       | 7         | 1        | 1         | 7        |
| 2,6-dimethyl-3-(2-methylbutyl)pyrazine   | 1307              |                       | 13        | 8        | 6         | 32       |
| 2,3-dimethyl-3-(3-methylbutyl)pyrazine <sup><math>f</math></sup>                   | 1319              |                       | 22        | 16       | 30        | /8<br>9  |
| total  | 1000              |                       | 1919      | 825      | 1035      | 1036     |
| total  |                   |                       | 1616      | 020      | 1055      | 1950     |
| sulfur compounds   | 754               | 707                   |           | 0        |           | 0        |
| dimethyl disulfide <sup>e,g</sup>  | 754<br>085        | 121<br>081            | 14        | 2<br>11  | 6         | 0<br>25  |
| 5-methyl-2-thiophenecarboxaldehyde   | 1111              | 304                   | 14        | 11       | 0         | 20       |
| benzyl methyl sulfide  | 1185              |                       | 4         | 3        |           |          |
| total  |                   |                       | 18        | 28       | 6         | 31       |
| mothowymymozines   |                   |                       |           |          |           |          |
| 2-isopropyl-3-methoxypyrazine <sup>d,e,f</sup>                                     | 1103              | 1097                  |           |          |           | 21       |
| other compounds  |                   |                       |           |          |           |          |
| limonene <sup>e,t,g</sup>  | 1039              | 1040                  | 15        |          | 17        |          |
| 2-memoxyphenol<br>1-vinyl-2-methovyphenol  | 1101              | 1333                  | 45<br>109 | 111      | 1/<br>999 | 107      |
| eugenol  | 1376              | 1369                  | 5         | 1        | 202       | 13       |
| solavetivone   | 1838              |                       | 34        | 1780     | 9         | 8        |
| total  |                   |                       | 186       | 1892     | 308       | 428      |
| total of all volatiles   |                   |                       | 1552      | 2879     | 1460      | 2574     |
|  |                   |                       |           |          |           |          |

<sup>*a*</sup> Amounts of components in ng/g of potato sample. Means of at least four replicate analyses. Relative standard deviations < 25%. Means with a different superscript letter within a row are significantly different (p < 0.05) by Fisher's LSD test. <sup>*b*</sup> Calculated LRI values for identified components. <sup>*c*</sup> Linear retention indexes obtained for authentic compounds analyzed on the same GC column or from the literature (*14*, *15*). Values for authentic compounds are in italics. <sup>*d*</sup> Identified in raw potatoes (*18*). <sup>*e*</sup> Identified in boiled potatoes (*8*, *18–21*). <sup>*f*</sup> Identified in baked potatoes (*18*). <sup>*g*</sup> Identified in French-fried potatoes (*18*, *22*).

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# Table 3. Volatile Compounds Identified in Potato Flesh<sup>a</sup>

|   |                   |                           | cultivar |        |        |         |
|---|-------------------|---------------------------|----------|--------|--------|---------|
| source and compound   | $LRI_{exptl}^{b}$ | $LRI_{lit.}$ <sup>c</sup> | Cara     | Nadine | Fianna | Marfona |
| lipid   |                   |                           |          |        |        |         |
| hexanal <sup>d,e,f,g</sup>                                      | 813               | 809                       | 192      | 2      | 10     | 3       |
| ethylbenzene <sup>g</sup><br>hontanal <sup>d.e.f.g</sup>        | 866               | 865                       | 0        |        |        | 2       |
| (E)-2-heptenal <sup>d,e,f</sup>                                 | 910               | 954                       | 2        |        |        |         |
| 3-ethylcyclopentanone   | 975               | 976                       | 3        |        |        |         |
| benzaldehyde <sup>d,e,f,g</sup>                                 | 978               | 983                       | 7        | 5      | 3      | 7       |
| 1-octen-3-ol <sup><i>a,e,t</i></sup>                            | 987               | <i>980</i>                | 23       |        |        |         |
| 2,3-octanedione<br>2-nentvlfuran $d^{e,f,g}$                    | 991<br>991        | 980                       | ю<br>81  | 2      | 6      | 2       |
| (E,Z)-2,4-heptadienal <sup>d,e</sup>                            | 1011              | 1012                      | 18       | ~      | 3      | ~       |
| $(E, E)$ -2,4-heptadienal $^{d, e, f}$                          | 1030              | 1026                      | 50       |        | 9      |         |
| cycloheptane  | 1052              | 1000                      | ٣        | 1      |        |         |
| 3,3-octadien-2-one  | 1081              | 1083                      | о<br>З   |        |        |         |
| nonanal <sup>e,f,g</sup>  | 1108              | 1118                      | 8        | 1      | 1      | 2       |
| 3,5,5-trimethyl-2-cyclohexen-1-one                              | 1137              | 1138                      |          | 1      |        | 2       |
| (E)-2-nonenal <sup>d,e,f,g</sup>                                | 1172              | 1173                      | 9        |        |        |         |
| (E,Z)-2,4-nonadienal <sup><i>a,g</i></sup>                      | 1209              | 1917                      | 3        | 1      | 1      |         |
| (F F)-2 4-nonadienal <sup>d,e,f,g</sup>                         | 1214              | 1217                      | 10       | 1      | 1      |         |
| (E,Z)-2,4-decadienal <sup>d,e,g</sup>                           | 1310              | 1309                      | 43       |        | 5      |         |
| undecanal <sup>f</sup>  | 1316              | 1311                      | 6        |        |        |         |
| (E,E)-2,4-decadienal <sup>d,e,f,g</sup>                         | 1345              | 1336                      | 239      |        | 22     |         |
| 2-methylnaphthalene $a_g$                                       | 1360              | 1976                      | 95       |        |        |         |
| (E)-2-dodecenal   | 1378              | 1370                      | 29       |        |        |         |
| 2-pentadecanone <sup>g</sup>                                    | 1705              | 1700                      | 1        |        |        |         |
| methyl tetradecanoate   | 1738              | 1727                      |          | 1      | 2      |         |
| methyl hexadecanoate <sup>g</sup>                               | 1920              | 1929                      | 0        |        | 1      | 2       |
| octadecyl acetate   | 2009              | 2140                      | Z        |        | 1      |         |
| tatal   | 2141              | 2140                      | 910      | 14     | 64     | 91      |
| totai   |                   |                           | 810      | 14     | 04     | 21      |
| sugar and/or Maillard reaction (not invol                       | ving sulfur a     | amino acids)              |          |        |        |         |
| pyridine <sup>e,f,g</sup>                                       | 757               | 756                       | 4        | 2      | 2      |         |
| 3-methyl-1-butanol <sup><i>u,e,g</i></sup><br>2.5. dihydrofuran | 770               | /3/                       |          | 17     | 1      |         |
| 2-methyl-3(2 <i>H</i> )-furanone <sup><math>f,g</math></sup>    | 823               | 819                       |          | 1      | 1      |         |
| methylpyrazine <sup><i>e,f,g</i></sup>                          | 837               | 837                       | 1        | 1      |        | 2       |
| 2-furfural <sup>e,f,g</sup>                                     | 846               | 848                       | 5        | 4      | 2      | 8       |
| 2,5- and/or 2,6-dimethylpyrazine <sup><i>e,t,g</i></sup>        | 932               | 925                       |          | 3      |        |         |
| 5-methyl-2-furfural <sup>f,g</sup>                              | 930<br>987        | 930<br>976                |          | 1      |        |         |
| 2-ethyl-6-methylpyrazine $^{e,f}$                               | 1019              | 1010                      |          | 1      |        |         |
| trimethylpyrazine <sup>f,g</sup>                                | 1023              | 1014                      |          |        |        |         |
| 2-ethyl-5-methylpyrazine <sup>e,f</sup>                         | 1025              | 1014                      |          | 1      | ~      |         |
| phenylacetaldehyde <sup><math>a,e,r,g</math></sup>              | 1060              | 1066                      | 31       | 27     | 7      | 28      |
| 2.5-dimethyl-3-(2-methylpyrazine <sup>-/s</sup>                 | 1082              | 1087, 1093                |          |        | 1      | 2       |
| 1-butyl-1( <i>H</i> )-pyrrole                                   | 1432              |                           | 2        |        |        |         |
| total   |                   |                           | 43       | 58     | 14     | 41      |
|   |                   |                           |          |        |        |         |
| dimethyl digylfide#   | 759               | 797                       |          |        |        | 10      |
| 3-(methylthio)propanal (methional) <sup>e,f,g</sup>             | 921               | 909                       | 13       |        | 2      | 10      |
| methyl propyl disulfide $^{g}$                                  | 940               | 913                       | 10       |        | ~      | 2       |
| dimethyl trisulfide <sup>g</sup>                                | 984               | 984                       |          | 1      | 3      | 8       |
| 5-methyl-2-thiophenecarboxaldehyde                              | 1104              |                           |          | 1      |        | 3       |
| methyl /V-pentyl disulfide<br>othyl poptyl disulfido            | 1150              |                           | 4        |        | 1      | 2       |
| benzyl methyl sulfide   | 1184              |                           |          |        | 1      | 2       |
| benzyl methyl disulfide   | 1417              |                           |          |        |        | 6       |
| dipentyl disulfide  | 1456              |                           |          |        | 1      | 1       |
| total   |                   |                           | 17       | 3      | 8      | 50      |
| other compounds   |                   |                           |          |        |        |         |
| 2-methoxy-4-vinylphenol   | 1348              | 1333                      |          | 5      |        |         |
| solavetivone  | 1870              |                           |          | 11     |        |         |
| total   |                   |                           |          | 16     |        |         |
| total of all volatiles  |                   |                           | 860      | 91     | 85     | 111     |
|   |                   |                           | 003      | 31     | 00     | 111     |

 $^{a}$  For footnotes, see Table 2.

 
 Table 4. ANOVA and F Values for Compounds Identified in Significantly Different<sup>a</sup> Amounts in Potato Skin

|   | cultivar |        |                   |         |       |
|---|----------|--------|-------------------|---------|-------|
| compound                                    | Cara     | Nadine | Fianna            | Marfona | value |
| 2-pentylfuran                               | b        | b      | а                 | а       | 11.41 |
| 5-methylfurfural                            | а        | b      | $\mathbf{nd}^{b}$ | а       | 7.09  |
| phenylacetaldehyde                          | а        | а      | а                 | b       | 4.12  |
| 2,5-dimethyl-3-(3-methyl-<br>butyl)pyrazine | а        | а      | а                 | b       | 6.58  |
| solavetivone                                | а        | b      | а                 | а       | 6.55  |

 $^a$  Compounds with a different letter within a row possess means that are significantly (p < 0.05) different by Fisher's LSD test.  $^b$  Not detected.

Cara (93%), the main source in Fianna (75%), but accounted for only 15 and 19%, respectively, of the total volatiles in Nadine and Marfona. The strength of the isolate prepared from Cara was primarily due to high contributions from the 2,4-decadienals and hexanal. In contrast, the 2,4-decadienals were present at  $\sim^{1}/_{10}$  the levels in Fianna and were not identified in Nadine or Marfona. Isomers of 2,4-heptadienal were also identified at substantial levels in Cara, were present in Fianna, but were absent from both Nadine and Marfona.

Similar total amounts of sugar/Maillard-derived volatiles were isolated from Cara, Nadine, and Marfona (41-58 ng/g) and were at least 3-fold higher than for Fianna (14 ng/g). Far lower relative amounts from this category were isolated from flesh compared to skin, in agreement with a previous study (2). In particular, levels of pyrazines were much lower in the flesh, and those compounds that were identified may have migrated from the skin, where the higher temperature and lower water activity (compared to the interior of the tuber) encountered during baking would favor their formation (2). In contrast to results for skin, levels of sugar degradation/Maillard reaction volatiles from flesh increased with sugar concentration in the raw tuber, but there was no relationship with levels of amino acids.

Highest levels of sulfur volatiles were isolated from Marfona, with methional being the most abundant at 15.1  $\mu$ g/g. Methional occurred at 13 ng/g in Cara, at 2 ng/g in Fianna, and was absent from Nadine. Methionine, the amino acid from which it derives, was highest in Marfona and second highest in Cara, suggesting a relationship between levels of this amino acid and its Strecker aldehyde. Solavetivone was tentatively identified only in Nadine, in which it was present at much lower levels (10.6 ng/g) compared to the skin (from where it presumably migrated). Only one methoxyphenol, the 2-methoxy-4-vinyl derivative, was identified and only in Nadine. Again, it probably formed in the skin and migrated to the flesh.

*Key Compounds.* On the basis of their yields and odor threshold values, various compounds are considered to



**Figure 1.** Odor unit values (calculated by dividing the quantitative data in Table 2 by the odor threshold values in Table 5) of selected key potato aroma compounds identified in baked potato skin.

be important contributors to the flavor of baked, boiled, and/or chipped potatoes (1). These include methanethiol, methyl sulfide, dimethyl disulfide, methional, 1-octen-3-ol, (Z)-4-heptenal, (E)-2-nonenal, 3-methylbutanal, phenylacetaldehyde, (E,Z)-2,6-nonadienal, (E,E)-2,4decadienal, (E)-1,5-octadien-3-one, 2-ethyl-3,5-dimethylpyrazine, 2-ethyl-3,6-dimethylpyrazine, 2-ethyl-3methoxypyrazine, and 2-isopropyl-3-methoxypyrazine. Eight of these compounds were identified in this study from the skin and/or flesh of baked potatoes. They are listed in Table 5, together with their aroma descriptions and odor threshold values. Their odor unit values in potato skin and flesh of the cultivars studied are given in Figures 1 and 2. The data indicate those key compounds that contribute to aroma in the skin and flesh of the different cultivars together with their importance. For skin, 2-isopropyl-3-methoxypyrazine has the highest odor unit value and contributes importantly to aroma only in Marfona, clearly distinguishing this cultivar from the others. However, sensorily significant amounts are likely to be present below the MS detection threshold (~10 pg or ~13 pg/g of skin) in the other cultivars. GC-olfactometry would have helped to reveal their presence. Phenylacetaldehyde and 2-ethyl-3,5(or6)-dimethylpyrazine feature in all cultivars,

 Table 5. Aroma Descriptions and Odor Thresold Values of Selected Key Potato Aroma Compounds Identified in Skin and/or Flesh of Baked Potatoes

| compound                               | aroma description <sup>a</sup>            | odor threshold<br>value (ng/L) <sup>b</sup> |
|--|---|---|
| dimethyl disulfide                     | onion-like, cooked cabbage                | 200   |
| methional                              | cooked potato                             | 200   |
| 1-octen-3-ol                           | mushroom-like                             | 1400  |
| (E)-2-nonenal                          | cucumber, cardboard                       | 80  |
| ( <i>E</i> , <i>E</i> )-2,4-decadienal | oily, deep fried-like                     | 70  |
| phenylacetaldehyde                     | floral, roses                             | 4000  |
| 2-ethyl-3,5-dimethylpyrazine and/or    | nutty, roasted                            | <b>400</b> <sup>c</sup>                     |
| 2-ethyl-3,6- dimethylpyrazine          | nutty, roasted, earthy, baked potato-like |   |
| 2-isopropyl-3-methoxypyrazine          | earthy, raw potato, potato-like           | 2   |
|  |   |   |

<sup>a</sup> References 31 and 32. <sup>b</sup> References 1, 28, and 33. <sup>c</sup> Odor threshold value for 2-ethyl-3,6-dimethylpyrazine.



**Figure 2.** Odor unit values (calculated by dividing the quantitative data in Table 3 by the odor threshold values in Table 5) of selected key potato aroma compounds identified in baked potato flesh.

whereas dimethyl disulfide and (*E*)-2-nonenal play roles in all cultivars except Fianna.

In flesh, (E,E)-2,4-decadienal appears to be the most important contributor to aroma in Cara and Fianna. (E)-2-Nonenal also features prominently in Cara. Methional is important in Marfona and Cara and also contributes in Fianna, to which it will give a cooked potato note. Phenylacetaldehyde makes small contributions to all cultivars. Marfona is distinguished from the other cultivars by the contribution made by dimethyl disulfide.

In conclusion, the volatile composition of the skin and flesh of baked potatoes varies quantitatively and qualitatively among cultivars grown at different sites. Sugar degradation and/or the Maillard reaction is a major source of volatiles in skin, due largely to pyrazines. Solavetivone was the major volatile in Nadine skins, suggesting that tubers of this cultivar were under stress during storage. The strength of isolates from potato flesh varied by a factor of 10, according to cultivar/ growing conditions. Levels of lipid-derived volatiles ranged from 14 to 810 ng/g, whereas levels of volatiles from sugar degradation and/or the Maillard reaction were more similar (14-58 ng/g). When odor threshold values are taken into account for a selection of key potato aroma compounds identified, the impact of the observed differences among cultivars grown at different sites and their effects on potato flavor become even more apparent.

#### ABBREVIATIONS USED

GC-MS, gas chromatography-mass spectrometry; LRI, linear retention index; RA, relative abundance.

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