

## RESULTS AND DISCUSSION

Thirty-one pyrazines and three thiazoles are being reported as identified in the volatile flavor isolated from 540 lb of baked potatoes. Many of the pyrazines and thiazoles identified have never been reported before as volatile flavor components of baked potato or potato products (Table I).

Baked potato flavor is a very mild flavor but it is extremely complex. The total flavor yielded 420 fractions. In our opinion, the pyrazines and thiazoles were the most important compounds to the characteristic baked potato flavor. The results of this research indicate that a natural baked potato flavor is not due to a single compound, but is the result of the mixture of a number of components. The pyrazines and thiazoles thought to be important to the flavor of baked potato are listed in Table I. The compounds which are considered important contribute earthy, nutty, baked, sweet earthy, potato, and baked potato-like aromas. 2-Ethyl-6-vinylpyrazine was described as buttery, baked, and potato-like. 2-Ethyl-3-methylpyrazine contributes a pleasant earthy and nutty note to the total flavor. 2-Ethyl-3,6-dimethylpyrazine (Buttery et al., 1973) possessed an earthy, baked potato-like aroma and is very important to the flavor. The alkylated five- and six-membered bicyclic pyrazines, namely, 5-methyl-6,7-dihydro-5*H*-cyclopentapyrazine, 5,7-dimethyl-1,2,3,4,7,8-hexahydroquinoxaline, 2-methyl-6,7-dihydro-5*H*-cyclopentapyrazine, and 3,5-dimethyl-6,7-dihydro-5*H*-cyclopentapyrazine, contribute very pleasant earthy, baked, and potato-like aromas. 2,3-Dimethyl-5-butylpyrazine and 2,5-dimethyl-4-butylthiazole were characterized as having sweet earthy odors.

The results of this work indicate a similarity in odor for pyrazines and thiazoles with similar alkyl substituents. The dimethylbutyl trisubstituted thiazole and the dimethylbutyl trisubstituted pyrazines (with the butyl group adjacent to the nitrogen atom) have a sweet earthy aroma. Also, 2,5-diethyl-4-methylthiazole and 2,5-dimethyl-4-ethylthiazole were found to have odors very similar to the diethylmethyl and the dimethylethyl trisubstituted pyrazines.

The mechanisms by which pyrazines form in food have been reviewed previously (Maga and Sizer, 1973a; Walradt et al., 1971). The high content of amino acids and sugars in potato provide a reservoir of precursor compounds for the formation of pyrazines. The results of this research show the presence of a large number of pyrazines in baked potato flavor (31 identified in this work). There are more pyrazines in baked potato flavor than in other forms of cooked potato because of the presence of baked potato skins. Koehler et al. (1969) reports that temperatures

greater than 100 °C are needed for an appreciable rate of pyrazine formation. Because of the high water content of the potato, the temperature of the inside will remain too low for pyrazine formation. Most of the pyrazines form in the baked potato skins which dry out and reach temperatures high enough for the formation of pyrazine compounds.

## ACKNOWLEDGMENT

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A Convenient Synthesis of (*E,E,Z*)-2,4,7-Decatrienal

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A convenient synthesis of (*E,E,Z*)-2,4,7-decatrienal in 42% yield from (*Z*)-hex-3-enol has been developed. The IR, MS, <sup>1</sup>H NMR spectra, odor threshold, and description of this compound are reported.

It is well known that oxidized lipids can produce off-aromas in food. Meijboom and Stroink (1972) reviewed

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the literature dealing with fishy off-aromas in food and reported the presence of (*E,E,Z*)-2,4,7-decatrienal in oxidized linolenic acid. They synthesized the dinitrophenylhydrazine (DNPH) derivatives of two isomers (*E,Z,Z* and *E,E,Z*) of 2,4,7-decatrienal using a seven-step synthesis. The present authors needed samples of (*E,E,Z*)-2,4,7-decatrienal to confirm the identity of a sus-

pected decatrienal in potato chips. A shorter, more convenient synthesis than the Meijboom and Stroink (1972) method was devised from readily available starting material.

#### EXPERIMENTAL SECTION

**Materials.** (*Z*)-Hex-3-enol (Aldrich Chemical Co.), methylene chloride (99.9%; J. T. Baker Chemical Co.), and silica gel cc-7, 100–200 mesh (Mallinckrodt Chemical Works), were used as received. Chromium trioxide (Mallinckrodt) was dried over P<sub>2</sub>O<sub>5</sub>. Methoxy-1-buten-3-yne 50% in aq. methanol (Aldrich Chemical Co.) was distilled at 43 °C/ca. 15 mm, Ionox 330 added, and dried with MgSO<sub>4</sub> (anhydrous) just prior to use. Tetrahydrofuran (THF) from Eastman Kodak was purified by setting over LiAlH<sub>4</sub>, refluxing 0.5 h, and distilling just prior to use.

**Gas-Liquid Chromatography (GLC).** A 0.45 cm i.d. × 150 cm long stainless steel column packed with Chromosorb G 80/100 mesh (DMCS treated and acid washed) was coated with 2% Carbowax 20M containing a trace of the antioxidant Ionox 330. The column was used isothermally at 150 °C with a helium flow of 30 mL/min. The injector was at 185 °C and the thermal conductivity detector at 180 °C.

**Spectral Information.** Purified GLC samples were collected in Pyrex tubes for spectral analysis. Infrared absorption (IR) spectra were run neat on salt plates using a Perkin Elmer 237 instrument. The mass spectrum (MS) was determined on a modified Consolidated 21-620 cycloidal-type mass spectrometer at 70-eV ionization voltage. The nuclear magnetic resonance (<sup>1</sup>H NMR) spectra (sample in CDCl<sub>3</sub>) was determined on a Varian A100 instrument using Me<sub>4</sub>Si as reference standard.

**Synthesis of (*Z*)-Hex-3-enal.** (*Z*)-Hex-3-enol was oxidized to (*Z*)-hex-3-enal by the method of Kajiwara et al. (1975). (*Z*)-Hex-3-enol (10 g) in methylene chloride (50 mL) was added in one portion to a previously prepared solution of dry chromium trioxide (60 g), pyridine (95 mL), and methylene chloride (1500 mL), stirred 0.25 h, and decanted. The solid chromium complex was washed with ether (500 mL). The combined methylene chloride and ether wash, with a trace of Ionox 330 added as antioxidant, was passed through a silica gel column (7 × 25 cm; ca. 0.7 kg) to remove the dissolved chromium complex. The eluted solvent was washed with the following solutions: 2 × 1000 mL of 1 N HCl (to remove pyridine), 1 × 500 mL of saturated aqueous NaHCO<sub>3</sub>, 1 × 500 mL of water. It was then dried over anhydrous MgSO<sub>4</sub>. The solution was concentrated in vacuo to 200 mL. The yield of (*Z*)-hex-3-enal by GLC analysis was 6.2 g (66% yield), although only 7% unreacted (*Z*)-hex-3-enol was found.

**Synthesis of (*E,E,Z*)-2,4,7-Decatrienal.** Ethyl bromide (13.9 g) in THF (20 mL) was added to magnesium turnings (2.9 g) in THF (50 mL). After completion of the reaction, methoxy-1-buten-3-yne (10.7 g) in THF (70 mL) was added dropwise while maintaining the temperature at 40 °C. (*Z*)-Hex-3-enal (6.2 g) in methylene chloride (200 mL) was concentrated in vacuo to 30 mL, THF (30 mL) was added, and the concentration continued to 30 mL. The (*Z*)-hex-3-enal solution was added dropwise to the cooled (10 °C) Grignard solution (from above) and stirred 1.5 h at 25 °C. The solution was cooled again to 10 °C, ethanol (4.6 g) was then added, and the mixture was stirred for 0.25 h, followed by an addition of solid LiAlH<sub>4</sub> (3.8 g) in portions over 0.5 h and stirring an additional 0.5 h before storing in the freezer overnight. The solution was then stirred for 1.5 h at 25 °C, cooled to 15 °C, and treated sequentially with ethyl acetate (4.8 mL), water (23 mL), and cold 4 N H<sub>2</sub>SO<sub>4</sub> (112 mL). The organic layer was

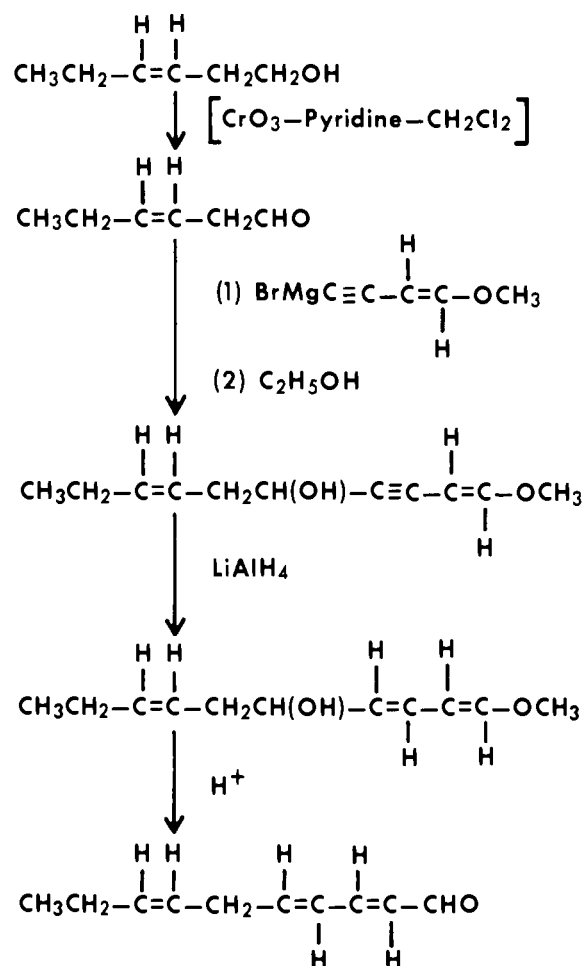


Figure 1. Synthesis of (*E,E,Z*)-2,4,7-decatrienal.

separated and the aqueous phase extracted with ether (3 × 75 mL). A trace of Ionox 330 was added to the combined organic phases which were then washed with 10% aqueous Na<sub>2</sub>CO<sub>3</sub> (1 × 100 mL) and water (2 × 50 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The sample was concentrated in vacuo. The calculated yield by GLC analysis was 6.5 g (66% yield from (*Z*)-hex-3-enal).

#### RESULTS AND DISCUSSION

(*E,E,Z*)-2,4,7-Decatrienal was obtained in 42.5% overall yield using the recently published method of Kajiwara et al. (1975) for oxidation of (*Z*)-hex-3-enol to (*Z*)-hex-3-enal, combined with the diene reaction sequence of Pippin and Nonaka (1958). Figure 1 shows the reaction sequence starting with (*Z*)-hex-3-enol. The high yield from the chromium-pyridine complex oxidation (Kajiwara et al., 1975) depends upon maintaining anhydrous conditions in a dilute methylene chloride solution. The series of reactions from (*Z*)-hex-3-enal to (*E,E,Z*)-2,4,7-decatrienal are conveniently effected in one vessel by reacting the (*Z*)-hex-3-enal with the prepared methoxy-1-buten-3-yne Grignard, decomposing the complex with ethanol, followed by LiAlH<sub>4</sub> reduction of the acetylenic bond. Subsequent treatment with acid results in a spontaneous dehydration of the OH group and rearrangement of the double bond. Undesirable oxidation was reduced by using dilute solutions with Ionox 330 antioxidant added, keeping samples cold, and assaying solutions directly by GLC rather than distilling the samples.

The GLC assay of crude (*E,E,Z*)-2,4,7-decatrienal showed a peak (peak A) just before the desired product (peak B) and one just after it (peak C). The IR spectrum

of A (representing 4% of the trio) was consistent with the structure (*E,E,Z*)-2,4,7-decatrienal when compared to a reference spectra of (*E,Z*)-2,4-decadienal and the spectral information published by Meijboom and Stroink (1972) for (*E,E,Z*)-2,4,7-decatrienal. The absorptions at 963, 988, and 1005  $\text{cm}^{-1}$  with approximately equal intensities were a particular characteristic for this isomer. The IR spectrum of peak C (representing 6% of the trio) was similar to that of the (*E,E,Z*)-2,4,7-decatrienal except for a strong absorption at 1610  $\text{cm}^{-1}$ . This compound was not identified.

The IR spectrum from 2000 to 800  $\text{cm}^{-1}$  obtained for the GLC-purified sample of (*E,E,Z*)-2,4,7-decatrienal is as follows where S means strong, M moderate, W weak, and VW very weak absorption: S, 1685, 1645; M, 1162, 1120, 1012, 990; W, 1620, 1462, 1262, 1070, 905, 855, 795, 725; VW, 1603, 1595, 1428, 1400, 1375, 1335, 1310, 1295, 1220, 1180, 950. This IR spectrum was similar to that of (*E,E*)-2,4-decadienal as might be expected. It was also reasonably consistent with the IR data reported by Meijboom and Stroink (1972) for (*E,E,Z*)-2,4,7-decatrienal.

The  $^1\text{H}$  NMR spectrum was consistent with that expected for (*E,E,Z*)-2,4,7-decatrienal and identical with the proton shifts on carbons 1–5 obtained from a reference spectra of (*E,E*)-2,4-decadienal obtained under the same conditions as the decatrienal, i.e.,  $\delta$  6.05 (dd), complex multiplet center  $\delta$  6.4, multiplet center  $\delta$  7.08 and  $\delta$  9.52 (d), characteristic of (*E,E*)-2,4-dienals. The decoupled spectrum of the decatrienal also confirmed the assignments given. The spectra obtained for the decatrienal with carbon position designated  $\text{C}_1\text{C}_2$ , etc. followed by the number of protons with multiplet (mult) positions given at the center is  $\text{C}_1$  (1 H) d  $\delta$  9.52;  $\text{C}_3$  (1 H) mult  $\delta$  7.08;  $\text{C}_2$  (1 H) dd  $\delta$  6.05;  $\text{C}_{4,5}$  (2 H) mult  $\delta$  6.4;  $\text{C}_{7,8}$  (2 H) ABqt t  $\delta$  5.26;  $\text{C}_6$  (2 H) t  $\delta$  2.94;  $\text{C}_9$  (2 H) q  $\delta$  2.03;  $\text{C}_{10}$  (3 H) t  $\delta$  0.95. Spectral differences between this data, particularly in the region from  $\delta$  5.3–6.9, and that reported by Meijboom and Stroink (1972) may be due to interpretation rather than actual spectral differences. It is difficult to compare data since Meijboom and Stroink did not publish their actual spectrum.

The mass spectra obtained for (*E,E,Z*)-2,4,7-decatrienal was consistent with its structure and with spectra obtained from Meijboom (Meijboom, 1973). The spectra are listed below (two most intense ions every 14 mass units above  $m/e$  34, intensities in parentheses, molecular ion in boldface): 39 (81), 41 (76); 53 (48), 55 (57); 67 (50), 68 (69); 79 (82), 81 (100); 91 (44), 93 (26); 103 (14), 107 (15); 117 (5), 121 (34); 132 (1), 135 (2); **150 (6)**.

The presence of decatrienal in products containing linolenic acid has been reported in cooked chicken (Harkes and Begemann, 1974) and in mackerel oil (Ke et al., 1975). A suspected decatrienal was reported in potato chips

(Buttery and Ling, 1972) and in cooked asparagus (Tressl et al., 1977). The compound found in asparagus and potato chips had identical mass spectra but differed from the spectrum of the authentic (*E,E,Z*)-2,4,7-decatrienal the authors has synthesized. The compound in potato chips and asparagus must therefore have a different structure.

The odor characteristics of the decatrienal had not been previously determined by panel methods. The personal descriptions given by Meijboom and Stroink (1972) were "fishy" for the (*E,Z,Z*)-2,4,7-decatrienal and less "fishy" and "sweet, greeny, cucumber, and melon-like flavor" for the (*E,E,Z*)-2,4,7 isomer. Badings (1973) characterized the odor as "sliced beans" for both isomers. He also concluded that other compounds along with the deca-2,4,7-trienals were responsible for the "fishy" odor associated with oxidized linolenic acid.

The authors have determined the odor threshold of (*E,E,Z*)-2,4,7-decatrienal in water using the method of Guadagni et al. (1963) except that Teflon bottles and tubing were used to contain the solutions submitted to the panel. The odor threshold and 95% confidence intervals were 0.93 ppb (0.80–1.08 ppb). The panel ( $n = 41$ ) described the odor at the 1 ppm level in water as cucumber, green-grassy, and oily with no statistical significance between these descriptions, although the majority preferred the word cucumber.

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