JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Formation of Strecker Aldehydes from Polyphenol-Derived Quinones and α-Amino Acids in a Nonenzymic Model System

GEORGE P. RIZZI*

Procter & Gamble Company, Winton Hill Business Center, 6300 Center Hill Road, Cincinnati, Ohio 45224

Fruits and vegetables contain naturally occurring polyphenolic compounds that can undergo enzyme-catalyzed oxidation during food preparation. Many of these compounds contain catechol (1,2-dihydroxybenzene) moieties that may be transformed into *o*-quinone derivatives by polyphenoloxidases and molecular oxygen. Secondary reactions of the *o*-quinones include the Strecker degradation of ambient amino acids to form flavor-important volatile aldehydes. The purpose of this work was to investigate the mechanism of the polyphenol/*o*-quinone/Strecker degradation sequence in a nonenzymic model system. By using ferricyanide ion as the oxidant in pH 7.17 phosphate buffer at 22 °C, caffeic acid, chlorogenic acid, (+) catechin, and (−) epicatechin were caused to react with methionine and phenylalanine to produce Strecker aldehydes methional and phenylacetaldehyde in 0.032−0.42% molar yields (0.7−10 ppm in reaction mixtures). Also, by employing L-proline methyl ester in a reaction with 4-methylcatechol, a key reaction intermediate, 4-(2′-carbomethoxy-1′-pyrrolidinyl)-5-methyl-1,2-benzoquinone (**7**), was isolated and tentatively identified.

KEYWORDS: Strecker degradation; quinones; polyphenols; ferricyanide; aldehydes

INTRODUCTION

Polyphenolic compounds such as flavonoids occur widespread in foods, but their chemical reactions with amino acids, carbohydrates, and lipids to produce volatile flavor compounds have not received much attention. Structurally, many flavonoids are catechol derivatives that upon oxidation to *o*-quinones may function as progenitors of volatile flavor compounds via the Strecker degradation (*1*).

The Strecker degradation (SD) of amino acids leading to structurally related flavorful aldehydes is a widely known and well-investigated reaction (*2*). Most often, the SD is described as a corollary of the Maillard reaction typically occurring during food processing and involving the interaction of sugar-derived α-dicarbonyl compounds with free amino acids. In chemical terms, the reaction is a decarboxylation-induced reductive amination process in which an amino acid loses its carboxyl carbon atom (as CO_2) and is ultimately transformed into an aldehyde. The structural requirements of SD for aldehyde formation are summarized in **Figure 1**. Typically, α-dicarbonyls with $n = 0$, such as glyoxal, pyruvaldehyde, 2,3-butanedione, etc. are reported as SD reagents, but in principle, any dicarbonyl compound with extended conjugation ($n > 0$) is also a potential Strecker candidate. The latter structural category can be extended to include certain cyclic compounds (i.e., the *p*- and *o*-benzoquinones (see **Figure 1**, structures **1** and **2**)), which are especially relevant in this study.

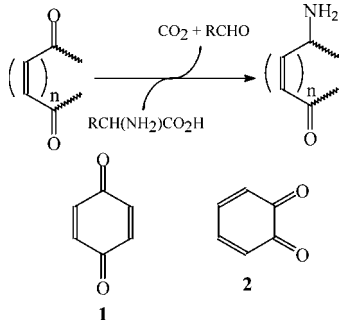


Figure 1. Generalized Strecker degradation showing quinone reactants.

Quinones per se have not received much attention as participants in the Strecker degradation especially with regard to food systems. On the other hand, quinones as a class have been widely invoked as intermediates in the enzymatic browning of foods (*1*). Many foods and beverages of vegetable origin contain polyphenolic compounds of which many are catechol derivatives (i.e., substances with 1,2-dihydroxybenzene moieties), which can undergo rapid oxidation by molecular oxygen in the presence of ambient phenolases (polyphenoloxidases) to form corresponding *o*-quinones. The transiently formed, highly reactive *o*-quinones quickly enter into secondary reactions with amino compounds, mercaptans, or proteins to form highly colored condensation products (*3*). Also, because of their high redox potential, these quinones can participate in coupled oxidations with easily oxidized substrates such as ascorbic acid.

In an early model study, James et al. investigated the chemical behavior of amino acids in phosphate buffer in the presence of

* To whom correspondence should be addressed. Tel. (513) 761-0816; e-mail: georgerizzi@prodigy.net.

10.1021/jf052781z CCC: $33.50
Published on Web 01/31/2006

catechol (1,2-dihydroxybenzene), oxygen, and a phenolase isolated from *Atropa belladonna L.* (*4*). To explain the fact that two atoms of oxygen were consumed per molecule of catechol, a two-step mechanism was postulated involving the initial formation of an *o*-quinone followed by conjugate addition of the amino acid and reoxidation to yield a highly colored 4-amino-1,2-benzoquinone intermediate. It was further suggested that this intermediate reacted with glycine and alanine to produce observed low yields of α-ketoacids, but neither decarboxylation nor aldehyde formation were observed indicative of SD. However, in more recent studies, Strecker aldehydes have been detected in reactions of amino acids and various catechol derivatives with polyphenolases isolated from a variety of sources including the microbe *Alternaria tenuis*, as well as extracts of tea leaves, cocoa beans, and coffee beans (*5*). In some instances, amino acids were proven to be aldehyde precursors by radiochemical tracer studies (*6*); however, the direct involvement of *o*-quinoid intermediates in food-related Strecker reactions has yet to be chemically established. Although many reports have associated the Strecker degradation with relatively high temperatures such as those used in roasting or cooking, the reaction will also take place near room temperature (ca. 25 °C) with enzymes (*5*) and in some nonenzymic model systems (*7*). Preliminary experiments in our lab demonstrated the formation of highly colored intermediates and Strecker aldehydes in model unbuffered reactions of α-amino acids with 1,4-benzoquinone in aqueous solution at 22 °C (*8*).

The objective of this study was to further characterize the nature of the low-temperature reactions of amino acids and catechol-derived oxidation products, viz., *o*-quinones. In particular, our plan was to investigate the oxidative chemistry of α-amino acids with catechol derivatives including natural flavonoids in a simplified nonenzymic model system in which potassium ferricyanide was used instead of polyphenoloxidases.

MATERIALS AND METHODS

Reagents. All chemical reagents and solvents were high quality commercially available materials. C-18 SepPak cartridges were obtained from Waters Inc. Analytical and preparative TLC was done on Analtech silica gel GF plates (0.25 mm layer thickness) using 4:1 hexane−ethyl acetate [A], 1:1 methanol-ethyl acetate [B], or 90:16:8 $CHCl_3$-MeOH-HOAc [C] v/v as eluting solvents. Phosphate buffer was prepared by combining 0.10 M aqueous solutions of Na_2HPO_4 and NaH_2PO_4. 2,4-Dinitrophenylhydrazine reagent was a saturated solution of 2,4-dinitrophenylhydrazine in 1:10 diluted hydrochloric acid. 2,4-Dinitrophenylhydrazone standards were prepared by adding pure aldehydes to excess 2,4-DNP reagent followed by purification by preparative TLC.

Instrumental Analyses. For GC/MS, an Agilent 6890 GC/5973 quadrupole MS combination was used. GC was performed on a 30M × 0.32 mm i.d. Restek Stabilwax column (film thickness 0.25 μM) temperature programmed from 40 to 200 °C at 7 °C/min followed by 200−240 °C at 25 °C/min. MS identification was by direct comparison with standard reference spectra. Electrospray ionization MS (ES/MS) employed a Micromass Platform LCZ instrument using direct injection infusion, with source and desolvation temperatures of 130 and 300 °C, respectively, or a Thermo LCQ ion trap mass spectrometer. With ES/MS, both positive (+) and negative (−) modes were used to optimize the detection of analyte ions. NMR spectra were obtained with a 500 MHz Varian Unity Inova spectrometer in CD_3OD using solvent signals for calibration, and multiplicity in analyte signals is indicated by s = singlet and m = multiplet. UV−vis data were obtained in MeOH solution using a computer interfaced Hitachi U-3010 spectrophotometer.

General Strecker Degradation Procedure. Reactions were performed in common screw-capped vials at ambient room temperature (ca. 22 °C) for periods of 1.0 h. At zero time, 1.00 mL of 0.1 M phosphate buffer (pH 7.17) containing 0.50 mmol of $K_3Fe(CN)_6$ was added to 4.00 mL of like buffer containing 0.30 mmol of amino acid plus 0.15 mmol of catechol derivative, and mixtures were shaken briefly to obtain complete mixing. Also, control reactions were run in which the catechol was omitted. After 1.0 h, the mixtures were optionally centrifuged to separate precipitated solids (15 min at 5000 rpm). Using syringe manipulation, the clear supernatant solutions were forced through C-18 SepPak cartridges, and cartridges were rinsed with 5.0 mL of distilled water followed by 5.0 mL of air. Strecker aldehydes were eluted from the water-free cartridges with 4.0 mL of methylene chloride, and final volumes were adjusted to 5.00 mL prior to analysis. For GC/MS analyses to determine relative and absolute aldehyde yields, methylene chloride solutions were spiked with an internal standard (d^4-pyrazine) and analyzed by direct injection. Yield data were calculated assuming 100% SepPak extraction efficiency and GC response factors of 1.00. For initial qualitative identification of aldehydes, 2,4-dinitrophenylhydrazone derivatives were prepared by shaking the 5 mL of methylene chloride solutions with 3 mL of 2,4-DNP reagent (see Materials and Methods) for 5 min. The separated methylene chloride phase was evaporated to dryness under a stream of N_2, and residues were fractionated by preparative TLC to obtain pure samples of 2,4-DNP derivatives for analysis by TLC, ES/MS, and UV−vis spectroscopy. Isolated derivatives were identified by comparing their data with those of standard reference compounds. Strecker aldehydes could not be detected in the control experiments either as free aldehydes or as 2,4-DNP derivatives.

Quantification of Methional 2,4-Dinitrophenylhydrazone. UV−vis spectroscopy was used to quantify the yield of methional produced in the reaction of $K_3Fe(CN)_6$/methionine/caffeic acid. The total crude 2,4-DNP product obtained under the General Procedure was dissolved in 5.00 mL of chloroform, and using quantitative techniques, a 0.500 mL aliquot was fractionated by preparative TLC, R_f 0.24 (solvent A). The isolated TLC band was eluted with MeOH (volume adjusted to 2.00 mL) and analyzed by UV−vis. Using the observed absorption (A = 0.483) at the absorption maximum (358 nm) and the molar extinction (ϵ) of pure methional 2,4-DNP (22, 400), the total yield of methional 2,4-DNP was 0.122 mg (0.29% molar yield) equivalent to 8.9 ppm of free aldehyde in the original reaction mixture (5.0 mL) based on the limiting reagent, caffeic acid.

Preparation of Caffeic Acid Quinone and Reaction with 1,2-Diaminobenzene (OPD). A solution containing 52.0 mg (0.29 mmol) of caffeic acid in 50 mL of MeOH was treated with 63.0 mg (0.27 mmol) of potassium periodate and stirred for 30 min at 22 °C. Following the addition of OPD (82.0 mg, 0.76 mmol), the mixture was stirred for 1 h. MeOH was evaporated under a stream of dry N_2, and the black residue was fractionated by prep TLC (solvent C) to afford 46.2 mg (78% molar yield) of 2,3-diimino-2,3,5,10-tetrahydrophenazine **5** as a deep reddish-black solid. Dilute solutions of the compound in MeOH were clear bright yellow. TLC: R_f 0.36 (solvent C); PMR: δ 7.057 (s, 2H, H-1 and H-4), 7.64−7.66 (m, 2H, H-7 and H-8), and 7.97−7.99 (m, 2H, H-6 and H-9) ppm. ^{13}C NMR: δ 103.0 (C-1 and C-4), 128.0 (C-6 and C-9), 128.5 (C-7 and C-8), 141.1 (C-5a and C-9a), 143.7 (C-4a and C-10a), and 146.4 (C-2 and C-3) ppm. UV: nm, (log ϵ): 426 (3.48), 259 (3.92), 217 (3.69). ES/MS (+) ion mode: m/z 211 amu (MH^+) indicative of MW 210 amu.

Ferricyanide Oxidation of 4-Methylcatechol in the Presence of L-pro(OMe). A solution containing 22.5 mg (0.18 mmol) of 4-methylcatechol and 50.0 mg (0.30 mmol) of l-pro(OMe) hydrochloride in 4.0 mL of 0.1 M pH 7.17 phosphate buffer was treated at room temperature (ca. 22 °C) with 1.0 mL of similar buffer containing 197 mg (0.60 mmol) of $K_3Fe(CN)_6$. The mixture, which instantly became deep blood red and later changed to purple, was extracted after 5 min with 5 mL of ethyl acetate. TLC analysis of the clear, deep purple extract indicated a single colored product at R_f 0.52 (solvent B). UV: 504.0 nm. ES/MS (+) ion mode: m/z 250 amu (MH^+) indicative of MW 249 amu.

RESULTS AND DISCUSSION

It is well-established that Strecker aldehydes are formed under mild conditions in reaction mixtures containing amino acids, catechols, molecular oxygen, and a polyphenoloxidase (PPO) catalyst. Since catechols are known to be oxidized to *o*-quinones

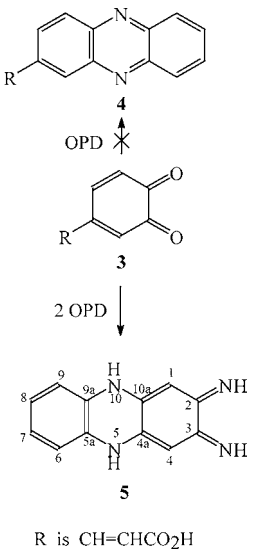


Figure 2. Reaction of caffeic acid quinone with *o*-phenylenediamine (OPD).

by PPO/O_2, it has been generally assumed that the Strecker aldehydes observed in the catechol reactions originated in a subsequent nonenzymic *o*-quinone/amino acid reaction. In fact, *o*-quinoid intermediates have never been isolated in PPO induced Strecker degradation, and evidence for their presence rests solely on one report citing UV spectroscopic data (*9*). Our work was designed to further extend the proposed mechanistic hypothesis (*4*) by seeking the formation of Strecker aldehydes from amino acids/catechols in a completely nonenzymic system that has been shown to generate *o*-quinones in situ.

Polyphenoloxidases (PPO) are copper-containing enzymes (*o*-diphenol oxidases) that function by transferring electrons from ene-diols such as catechols to molecular oxygen to produce *o*-quinones plus water. Presumably, copper ions in the enzyme operate in a redox fashion to assist the exchange of electrons. We envisioned an analogous nonenzymic system in which iron (III) in inorganic ferricyanide $Fe(CN)_6^{-3}$ ion could substitute for enzymic copper ions to act as a sink for electrons from catechol reactants. The use of ferricyanide salts for oxidation for phenols is well-known (*10*), and for monohydric phenols, electron transfer from phenolate (ArO^-) is known to form phenoxy radicals (ArO•). Reasoning by analogy, we predicted that the reaction of a catechol with 2 equiv of ferricyanide in a buffer suitable to provide catechol ionization would generate a diradical (•O−Ar−O•) that could then isomerize to a *o*-quinone.

To fulfill the development of our nonenzymic model, we first considered the problem involved with the production of *o*-quinones in aqueous systems. Because *o*-quinones are highly electrophilic and extremely reactive toward conjugate addition of nucleophiles (including water), we decided to begin by preparing a known catechol quinone for comparisons using more conventional nonaqueous conditions. Caffeic acid quinone, 3-(3′,4′-dioxo-1′,5′-cyclohexadienyl)propenoic acid (**3**), was prepared in methanol by periodate oxidation of caffeic acid (3′,4′-dihydroxycinnamic acid) according to Tazaki et al. (*11*). Rather than attempting to isolate the reportedly unstable quinone, we tried instead to obtain a more stable phenazine derivative, 2-(2-carboxyethen-1-yl)phenazine (**4**), by subsequent reaction with 1,2-diaminobenzene (*o*-phenylenediamine,OPD) (**Figure 2**). We failed to obtain the expected derivative and instead isolated in 78% molar yield a bright yellow compound (λ_{max} 426 nm), which proved to be 2,3-diimino-2,3,5,10-tetrahydrophenazine (**5**) by NMR and ES/MS analyses. Apparently, a redox reaction occurs in which OPD is oxidized by caffeic acid quinone to form a *o*-benzoquinone diimine that then reacts with a second mol of OPD to form the novel phenazine derivative. In any event, the formation of the yellow derivative served for us as an indicator for the preexistence of caffeic acid quinone.

Addition of potassium ferricyanide (2 mol equiv) to 0.05 M caffeic acid in aqueous 0.1 M phosphate buffer at pH 7.25 at 22 °C produced an instant color change to deep yellow−red, indicative of quinone formation. After subsequent reaction with OPD and workup, a yellow product was isolated in ca. 32% molar yield and shown to be compound **5** by comparison of its TLC and spectral properties with those of authentic material. From this, we concluded that *o*-quinones could be produced in situ by ferricyanide oxidation of catechols in nearly neutral aqueous solution.

Ferricyanide/Catechin Model System for Strecker Degradation. A model system for Strecker degradation was developed using stoichiometry similar to one suggested by James et al. for enzyme catalyed reactions (*4*) in which a molar ratio of oxidant/amino acid/catechol of 4:2:1 was considered. Our system consisted of 0.1 M phosphate buffer (pH 7.17) containing potassium ferricyanide, an amino acid, and a catechol at initial concentrations of 0.10, 0.060, and 0.030 M, respectively. Reactions were done at room temperature (ca. 22 °C) for 1.0 h and initiated by adding buffer solutions of ferricyanide to buffer solutions containing the other reactants. After 1 h reaction times, the mixtures were optionally centrifuged to remove any precipitated solids, and the clear aqueous phases were flowed through C-18 coated silica gel SepPak cartridges to extract Strecker aldehydes. Cartridges were water-washed and eluted with methylene chloride to provide aldehyde solutions for further analysis. Initially, our model was tested using 4-methylcatechol (4-methyl-1,2-dihydroxybenzene) and a series of common amino acids. In our preliminary experiments, Strecker aldehydes were detected and were identified qualitatively as their 2,4-dinitrophenylhydrazone derivatives (DNPs). Methylene chloride extracts from reaction solutions were treated with acidic 2,4-dinitrophenylhydrazine reagent, and DNPs isolated by preparative TLC were identified by comparing their UV−vis, ES/MS, and TLC retention data with those of authentic DNP standards. In this way, it was established that reactions of 4-methylcatechol with L-valine, L-leucine, and L-methionine led to the formation of Strecker aldehydes 2-methylpropanal, 3-methylbutanal, and 3-methylthiopropanal (methional), respectively. In a subsequent quantitative experiment involving a more typically food-related catechol derivative, the molar yield of methional 2,4-DNP was determined for ferricyanide/methionine/caffeic acid (0.29%) indicating that 8.9 ppm of methional had been formed in the initial caffeic acid reaction mixture.

The ferricyanide-based model system was then combined with GC/MS analysis to investigate Strecker aldehyde formation with the common naturally occurring flavonoids caffeic acid, chlorogenic acid, (+) catechin, and (−) epicatechin (**Table 1**). L-Methionine and L-phenylalanine were selected as substrates in these studies because their respective Strecker aldehydes (methional and phenylacetaldehyde) are well-kown contributors to flavors and off-flavors in foods. Among the flavonoids tested, the cinnamic acid derivatives caffeic acid and chlorogenic acid produced the highest amounts of Strecker aldehydes with molar yields ranging from 0.096 to 0.42%. Despite low chemical yields, the actual amounts of aldehydes formed in all cases (0.7−10 ppm) were still organoleptically significant when compared with reported flavor threshold values for methional (0.2 ppb) and phenylacetaldehyde (4 ppb) (*12*). The relatively lower aldehyde yields obtained with the catechins may have been

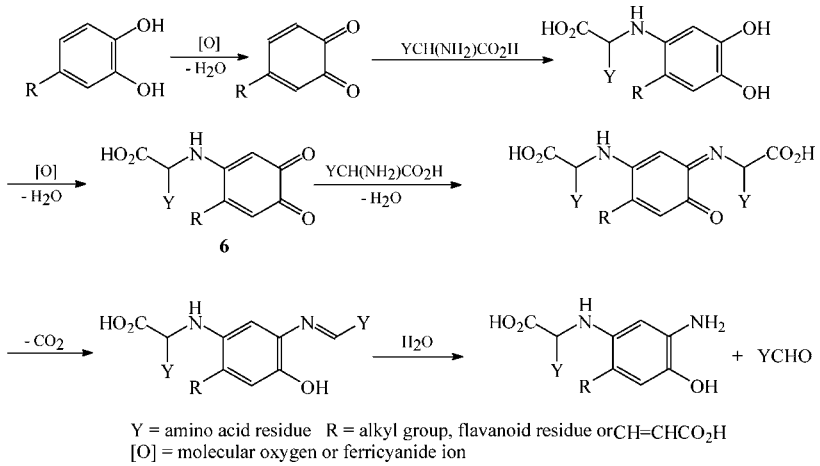


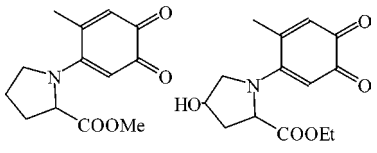
Figure 3. Putative scheme for Strecker degradation induced by catechol oxidation.

Table 1. Strecker Aldehydes Produced in Amino Acid/Polyphenol Reactions

amino acid polyphenol reactions	relative weight of aldehyde formed	GC determined molar yield(%)	ppm in reaction mixture
methionine reactions		methional	
caffeic acid	1.00	0.19	3.8
chlorogenic acid	0.50	0.096	1.9
(+) catechin	0.19	0.032	0.7
(–) epicatechin	0.29	0.059	1.1
Phenylalanine reactions		phenylacetaldehyde	
caffeic acid	1.00	0.42	10.0
chlorogenic acid	0.89	0.34	8.9
(+) catechin	0.46	0.21	4.6

related to the more extensive precipitate formation observed during their ferricyanide oxidation, possibly leading to insolubilization of key reaction intermediates. The molar yield of methional from caffeic acid determined by GC/MS (0.19%) was significantly lower than what we obtained via 2,4-DNP derivatization (0.29%). This discrepancy may have resulted from partial deterioration of methylene chloride aldehyde solutions during 1 week storage at − 20 °C prior to GC analysis.

Reaction Mechanism and 4-Amino-1,2-benzoquinone Intermediate. A generalized scheme for the formation of Strecker aldehydes from *o*-quinones resulting from polyphenol oxidation is shown in **Figure 3**. This putative scheme combines the suggested 4-amino-1,2-benzoquinone intermediate of James et al. (*4*) and its subsequent involvement in Strecker degradation first proposed by Bokuchava et al. (*13*).



7 **8**

In our study, several attempts were made to verify the presence of 4-amino-1,2-benzoquinone intermediates (see **Figure 3**, structure **6**). TLC analyses of ethyl acetate extracts of ferricyanide oxidation mixtures indicated low yields of reddish-yellow products that were difficult to isolate in pure form for identification. To facilitate the identification of an intermediate, we investigated the ferricyanide oxidation of 4-methylcatechol in the presence of L-proline methyl ester under our general reaction conditions. Ethyl acetate extraction of this reaction mixture followed by TLC separation led to a relatively stable purple compound, λ_{max} 504.0 nm, which we tentatively identified as 4-(2′-carbomethoxy-1′-pyrrolidinyl)-5-methyl-1,2-benzoquinone (**7**) based on its ES/MS data. A similar compound, 4-(4′-hydroxy-2′-carboethoxy-1′-pyrrolidinyl)-5-methyl-1,2-benzoquinone (**8**), λ_{max} 525 nm, had been isolated previously in a reaction in which silver oxide was added to a mixture of 4-methylcatechol and hydroxyproline ethyl ester in ethanol solvent (*14*). On the basis of these results, we are confident that 4-amino-1,2-benzoquinones are indeed intermediates in the formation of Strecker aldehydes from polyphenols under oxidative conditions. Final confirmation of this hypothesis will require further study of the interaction between isolated individual reaction components.

ACKNOWLEDGMENT

I thank the Procter & Gamble Company for allowing me to pursue independent research in their laboratories following my retirement. Also, I thank Mrs. Deborah Ewald and Dr. Robert Strife for ES/MS analyses, Mrs. Molly Armstrong for obtaining the NMR spectra, and Dr. David Zyzak for help with GC/MS.

LITERATURE CITED

(1) Mathew, A. G.; Parpia, H. A. B. Food browning as a polyphenol reaction. In *Advances in Food Research*; Chichester, C. O., Mrak, E. M., Stewart, G. F., Eds.; Academic Press: New York, 1971; Vol. 19, pp 75−135.

(2) Yaylayan, V. A. Recent advances in the chemistry of Strecker degradation and Amadori rearrangement: Implications to aroma and color formation. *Food Sci. Technol. Res.* **2003**, *9*, 1−6.

(3) Mason, H. S.; Peterson, E. W. Melanoproteins I. Reactions between enzyme-generated quinones and amino acids. *Biochim. Biophys. Acta* **1965**, *111*, 134−146.

(4) James, W. O.; Roberts, E. A. H.; Beevers, H.; De Kock, P. C. The secondary oxidation of amino acids by the catechol oxidase of belladonna. *Biochem. J.* **1948**, *43*, 626−636.

(5) Motoda, S. Formation of aldehydes from amino acids by polyphenol oxidase. *J. Ferment. Technol.* **1979**, *57*, 395−399.

(6) Saijo, R.; Takeo, T. The production of phenylacetaldehyde from L-phenylalanine in tea fermentation. *Agric. Biol. Chem.* **1970**, *34*, 222−226.

(7) Pripis-Nicolau, L.; de Revel, G.; Bertrand, A.; Maujean, A. Formation of flavor compounds by the reaction of amino acid and carbonyl compounds in mild conditions. *J. Agric. Food Chem.* **2000**, *48*, 3761−3766.

(8) Rizzi, G. P. Formation of flavor compounds in reactions of quinones and amino acids. In the proceedings of the 11th Weurman Flavour Research Symposium, Roskilde, Denmark, 2005, in press.

(9) Saijo, R.; Takeo, T. The formation of aldehydes from amino acids by tea leaves extracts. *Agric. Biol. Chem.* **1970**, *34*, 227−233.
(10) Mihailovic, M. L.; Cekovic, Z. Oxidation and reduction of phenols. In *The Chemistry of the Hydroxyl Group*; Patai, S., Ed.; Interscience Publishers: New York, 1971; part 1, pp 505−590.
(11) Tazaki, H.; Taguchi, D.; Hayashida, T.; Nabeta, K. Stable isotope-labeling studies on the oxidative coupling of caffeic acid via *o*-quinone. *Biosci. Biotechnol. Biochem.* **2001**, *65*, 2613−2621.
(12) Guadagni, D. G.; Buttery, R. G.; Turnbaugh, J. G. Odor thresholds and similarity ratings of some potato chip components. *J. Sci. Food Agric.* **1972**, *23*, 1435−1444.
(13) Bokuchava, M. A.; Skobeleva, N. I. The chemistry and biochemistry of tea and tea manufacture. In *Advances in Food Research*; Chichester, C. O., Mrak, E. M., Stewart, G. F., Eds.; Academic Press: New York, 1969; Vol. 17, pp 215−241.
(14) Jackson, H.; Kendal, L. P. The oxidation of catechol and homocatechol by tyrosinase in the presence of amino acids. *Biochem. J.* **1949**, *44*, 477−487.

Received for review November 9, 2005. Revised manuscript received December 27, 2005. Accepted January 1, 2006.

JF052781Z