Observation of Ether-Linked Phenolic Products during Thermal Degradation of Ferulic Acid in the Presence of Alcohols

George P. Rizzi* and Lois J. Boekley

Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio 45239-8707

Thermally induced decarboxylation of ferulic acid (4-hydroxy-3-methoxycinnamic acid) (**2b**) in the presence of benzyl alcohol produces 1-(4-hydroxy-3-methoxyphenyl)ethyl benzyl ether (**10**). A similar reaction with starch also produced an ether-linked product and suggested a mechanism for the incorporation of phenolic moieties into food macromolecules during cooking.

Cinnamic acid derivatives occur widely among foodstuffs both as free acids or as bound esters or glycosides (Herrmann, 1989). Certain cinnamic acids behave as flavor precursors since they break down during heat treatment to form new molecules with lower flavor thresholds. Heat treatment causes the cinnamic acids to undergo decarboxylation to form ring-substituted styrenes with well recognized aroma properties (Maga, 1978; Tressl et al., 1976). A notable example is ferulic acid (4-hydroxy-3-methoxycinnamic acid) (**2b**), which produces upon heating 4-hydroxy-3-methoxystyrene (**8b**) [4-vinylguaiacol], a potent clovelike flavor compound. In roasted coffee, for example, the level of **8b** is very low (0.012%) compared to much higher levels of available precursors, i.e., 0.4–2.1% (feruloylquinic acids) present in unroasted beans (Heinrich and Baltes, 1987a). Since most of the precursors are lost on roasting, styrenes like **8b** may actually have been formed in higher yield initially but later reacted to form other products.

Thermogravimetric analysis of ferulic acid decomposition suggested that the reaction proceeds in stages and that the first stage is the production of **8b** via decarboxylation (Fiddler et al., 1967). Later studies on copper-catalyzed decarboxylation of ferulic acid led to isolation of dimers and trimers in addition to monomeric **8b**, thereby corroborating the multistage nature of the overall reaction (Klaren-De Wit et al., 1971).

The known tendency of styrenes to polymerize suggested to us that monomers like **8b** could also react with other ambient food molecules during cooking. Conceivably, phenolic acid decomposition in the presence of food macromolecules can lead to graft polymerization of phenolic residues. The presence of covalently linked phenols in food melanoids has already been suggested by Curie point pyrolysis experiments (Heinrich and Baltes, 1987b).

The purpose of this work was to examine the formation of oligomers when cinnamic acids decompose under food roasting conditions and to determine if styrene monomers are capable of forming stable ether bonds with ambient alcohol groups.

EXPERIMENTAL PROCEDURES

Materials. Reagents were purchased as follows: cinnamic acids **1**, **2a–c**, **3**, **4**, and **5** and benzyl alcohol (Aldrich Chemical Co.); *p*-toluenesulfonic acid monohydrate (Sigma Chemical Co.); soluble starch, ACS reagent grade (Matheson Coleman and Bell); 4-vinylguaiacol (Oxford Chemicals Ltd.). Dialysis membrane was Spectra/POR 1 molecular porous membrane (Spectrum Medical Industries, Inc.). Common inorganic reagents and solvents were also commercial products of at least analytical grade purity. Silica gel coated TLC plates (silica gel 60, 0.25-mm thickness) and 70–230-mesh silica gel for chromatography were obtained from EM Scientific Co.

Methods of Analysis. HPLC was done on a Spectra Physics SP8800 system using a 15 cm × 0.46 cm Supelcosil LC-18 (ODS) column (3-μm film thickness) (Supelco Inc.) under isocratic conditions at room temperature. Solvent was 1:1 MeOH–water at a flow rate of 1.00 mL/min, and the UV detector was set at 280 nm. Samples were analyzed via 20-μL loop injection at an instrument sensitivity of 0.20 AUFS to provide an analytical precision of ca. 10%. Cinnamic acid peak areas were quantitated vs peak areas of standards with a Hewlett-Packard Model 3390A recording integrator.

Decarboxylation of cinnamic acids (Table I) was followed in a specially constructed all-glass flow-through chamber that was heated in the thermostated convection oven of a gas chromatograph maintained at 210 °C. The temperature was chosen somewhat arbitrarily to emulate typical food roasting conditions. The minimum temperature required for decarboxylation was not determined. Small beakers containing ca. 1 mmol of each compound were heated in the chamber, and evolved carbon dioxide was swept out with nitrogen into vessels containing 0.1 M barium hydroxide solution. The weights of precipitated barium carbonate were used to calculate the yields of carbon dioxide during 160-min heating periods.

TLC was done on commercially available 0.25-mm silica gel G plates using 100% ethyl ether (solvent A) or 80:20 (v/v) benzene–ethyl ether (solvent B). Spots were visualized with iodine vapor at room temperature.

GC/MS was done with a Finnegan Model 800 (ion trap detector) mass spectrometer interfaced to a Hewlett-Packard 5880 GC. A 30 m × 0.53 mm fused silica column containing DB-5 (1.5-μm film thickness) was programmed for zero hold time at 50 °C and 4 °C/min to 200 °C. Mass spectra were obtained in the electron ionization (EI) mode (70 eV) at a scan acquisition of 26–300 amu spectrum^{-1} s^{-1}. Mass spectra other than GC/MS were 70-eV data acquired on a Hewlett-Packard Model 5985B instrument using a source temperature of 200 °C and a probe temperature programmed to rise ballistically from ambient to 325 °C.

Proton NMR data were obtained on a Bruker Model AC-300 (300 MHz) spectrometer using $CDCl_3$ solvent except for **9c**, which was analyzed in d_4-MeOH. Spectrum calibration was by deuterium lock signals provided by the solvents.

UV spectra were obtained in MeOH or 50:50 (v/v) MeOH–water solutions on a Beckman DU-50 spectrophotometer.

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected.

Reaction Procedures. Cinnamic acid loss during pyrolysis (Table I) was determined by heating 0.1–0.2 mmol of each cinnamic acid in flame-sealed, 1-mL glass ampules in a thermostated oil bath at 205 °C for 45 min. Pyrolysis products were

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subsequently dissolved in 50:50 MeOH/water and analyzed for residual cinnamic acids by HPLC.

Dimer Formation during Pyrolysis of Cinnamic Acid Derivatives. A 15-mL flask arranged with a water-cooled reflux condenser and a bubbler to monitor gas evolution was charged with 1.07 g of ferulic acid (**2b**) and heated in a 205 °C oil bath. After gas evolution ceased (1 h), the cooled product was dissolved in benzene and column-chromatographed over 64 g of 70–230-mesh silica gel. The column was eluted with benzene and ether–benzene mixtures containing increasing amounts of ether. Benzene eluted 0.0032 g of material: TLC (system A), R_f 0.60. Major components were tentatively identified (GC/MS) as 4-vinylguaiacol (**8b**), 4-ethylguaiacol, and acetovanillone. Elution with 10% ether gave 0.344 g of the styrene dimer **9b** (Table II) as a colorless viscous oil, R_f 0.41 (42% yield). Proton NMR and MS data are given in Table II. UV_{max} in MeOH was 266 nm (log ϵ = 3.56); dibenzoate derivative had mp 142–143 °C [lit. mp 146–147 °C (Klaren-De Wit et al., 1971)]. Further elution with 20–60% ether gave 0.420 g of more polar products (R_f 0–0.35) which were not completely characterized. Similar experiments with cinnamic acids **2a** and **2c** led to isolation of styrene dimers **9a** and **9c**, respectively. Dimer **9a** was a colorless oil, R_f 0.48, isolated in 2.2% yield; UV_{max} in 50:50 MeOH/water was 260 nm (log ϵ = 4.33). In addition to **9a**, a trace product, R_f 0.60, was tentatively identified by GC/MS as 4-ethylphenol. Dimer **9c** was a pale yellow oil, R_f 0.33, isolated in 14% yield; UV_{max} in 50:50 MeOH/water was 285 nm. In addition to **9c**, traces of catechol and 4-ethylcatechol were tentatively identified in early column fractions by HPLC.

Reaction of 4-Vinylguaiacol with Benzyl Alcohol. A room temperature solution of *p*-toluenesulfonic acid monohydrate (0.028 g) in 5.0 mL of benzyl alcohol was stirred magnetically and treated dropwise with 0.20 mL of 4-vinylguaiacol during 5 min. After 23 h at room temperature, the reaction mixture was dissolved in ether (100 mL) and extracted with 3 × 20 mL of 1 N NaOH solution. The caustic extract was cooled, acidified with concentrated HCl, and extracted with ether (60 mL). The dried ether solution (Na_2SO_4) was evaporated to yield 0.225 g of crude product which was column chromatographed on 40 g of 70–230-mesh silica gel. Elution with benzene gave 0.008 g of 1-(4-hydroxy-3-methoxyphenyl)ethyl benzyl ether (**10**) as a colorless oil: TLC (solvent B) R_f 0.49; proton NMR 1.39 (d, J = 6.5 Hz, CH_3CH), 3.83 (s, CH_3O), 4.15–4.45 (unresolved peaks, CH_2O and CH–O), 5.52 (s, OH), 6.7–6.85 (aromatic ring, 3 H) and 7.15–7.25 (phenyl ring, 5 H) ppm; GC/MS R_t 6.67 min; m/z 258 [M^+] (2), 91 (100), 150 (44), 151 (43), 107 (41), 77 (36), 79 (34), 152 (31) and 135 (28); UV_{max} in 50:50 MeOH/water 277 nm (log ϵ = 3.50). Further elution with 2–5% ether in benzene afforded 0.071 g of 1,3-bis(4-hydroxy-3-methoxyphenyl)butyl benzyl ether (**11**) as a pale yellow oil: TLC (solvent B) R_f 0.34; proton NMR 1.07 (d, J = 6.9 Hz, CH_3-CH), 1.15 (d, J = 7.0 Hz, CH_3CH), 1.60–1.85, and 1.95–2.25 (unresolved groups of peaks, CH–CH_2–CH), 3.72, 3.75, 3.77, 3.78 (s, CH_3O groups), 3.99–4.2 (unresolved peaks, CH_2O), 4.22–4.4 (unresolved peaks, CH–O), 5.45, 5.46, 5.56, 5.59 (s, hydroxy groups), 6.4–6.85 (aromatic rings, 6 H), and 7.1–7.4 (phenyl ring, 5 H); MS m/z 408 [M^+] (2), 151 (100), 150 (97), 152 (79), 300 (74), 135 (38), 299 (28), and 149 (25); UV_{max} at 278 nm (log ϵ = 3.85).

Decarboxylation of Ferulic Acid in Benzyl Alcohol. A mixture of ferulic acid (**2b**) (0.384 g) and benzyl alcohol (5 mL) was heated at reflux in a nitrogen atmosphere for 20 min. The cooled reaction mixture was dissolved in ether and extracted with 1 N NaOH (see above) to isolate a total acidic fraction. Trituration of the solid product with benzene separated 0.307 g of unreacted starting material (80%) and 0.0323 g of oily product. GC/MS analysis of the crude product indicated 68% 4-vinylguaiacol (**8b**) (29% yield based on reacted **2b**) and 16% 1-(4-hydroxy-3-methoxyphenyl)ethyl benzyl ether (**10**) (3.9% yield based on reacted **2b**).

Reactions of Ferulic Acid with Starch. A mixture of reagent grade soluble starch (0.555 g) and ferulic acid (0.223 g) (**2b**) was finely pulverized in an agate mortar. The powder was transferred to a glass flask and heated under nitrogen for 1.0 h in an oil bath maintained at 205 °C. The product obtained after extensive washing with ether and acetone was a pale brown powder with a faint phenolic aroma. For UV analysis 0.0552 g of starch product was slurried in 2 mL of water and added dropwise to 100 mL of boiling water. A clear, pale brown solution was immediately obtained which was boiled for 5 min and allowed to cool to room temperature; UV_{max} was at 277 nm [A(1 cm path) = 0.865]. A control experiment was run with 0.55 g of pure starch. A water solution of the product, 0.0538 g/100 mL, exhibited a UV_{max} at 280 nm (A = 0.12).

In a similar experiment the reactants were heated for 1.25 h at 205 °C, and an aqueous solution containing 0.052 g of starch product/100 mL of water was analyzed: UV_{max} was at 277 nm (A = 0.635). Part of the solution was subjected to dialysis to isolate materials of molecular weight greater than 6000–8000. For dialysis 25.0 mL of starch product solution was placed in a 30-cm length of 2 cm i.d. cellulose dialysis tubing (>6000–8000 molecular weight cutoff), and dialysis was performed vs distilled water for 48 h at 22 °C. The UV spectrum of the tubing contents had a maximum at 277 nm (A = 0.331, corrected for volume increase).

Table I. Decarboxylation of Cinnamic Acids

compd	X—CH=CH—CO_2H X	% conversion[a]	CO_2 yield[b]
1	C_6H_5	48	
2a	4-HO–C_6H_4	>99	89
2b	4-HO-3-MeO–C_6H_3	>99	97
2c	3,4-di-HO–C_6H_3	>99	75
3	3-HO–C_6H_4	24	
4	4-MeO–C_6H_4	22	
5	3-HO-4-MeO–C_6H_3	0	

[a] Percent cinnamic acid lost at 205 °C after 45 min, determined by HPLC. [b] Percent of theoretical; isolated as $BaCO_3$ during 160 min of heating at 210 °C. Exception: **2b** heated for 100 min.

RESULTS AND DISCUSSION

Initial experiments were designed to investigate the mechanism of cinnamic acid decarboxylation. When cinnamic acids were heated at 205 °C, degradation took place to different degrees depending on the type and orientation of aryl ring substituents (Table I). Compounds containing a *p*-hydroxy substituent, i.e., *p*-coumaric acid (**2a**), ferulic acid (**2b**), and caffeic acid (**2c**), underwent nearly complete destruction vs partial destruction for the unsubstituted parent compound **1**. Also, less degradation took place if a hydroxyl group was meta-substituted on the ring, i.e., compound **3**, or if a *p*-hydroxy group was replaced by a methoxy group, i.e., compound **4**. On the basis of these observations we concluded that thermal degradation of cinnamic acid was uniquely accelerated by a *p*-hydroxy substituent. The mechanism of degradation was further evidenced by quantitative measurement of carbon dioxide formation (Table I). The amounts of carbon dioxide produced during thermal decomposition of **2a–c** (75–97%) indicated that the respective styrenes **8** (R = H, MeO, and HO) were at least initially formed in moderate to high yields. A mechanism for decarboxylation of *p*-hydroxycinnamic acids which is consistent with our observations is shown in Figure 1.

It is well-known that β,γ-unsaturated carboxylic acids undergo facile decarboxylation. In addition, α,β-unsaturated acids that are capable of isomerizing to β,γ systems via shift of a proton are also readily decarboxylated (March, 1985). It follows, therefore, that acids **2a–c** which can tautomerize to form β,γ-unsaturated trienones **6** are also predicted to lose carbon dioxide readily. Cinnamic acids not having a free *p*-hydroxy group, i.e., **1** and **3–5**, are unable to isomerize via proton transfer and therefore are decarboxylated with greater difficulty. Following decarboxylation, the newly formed trienones **7** can easily rearomatize to yield the observed styrenes **8**. Earlier investigators (Fiddler et al., 1967) suggested a free-radical chain reaction mechanism for ferulic acid decarboxylation

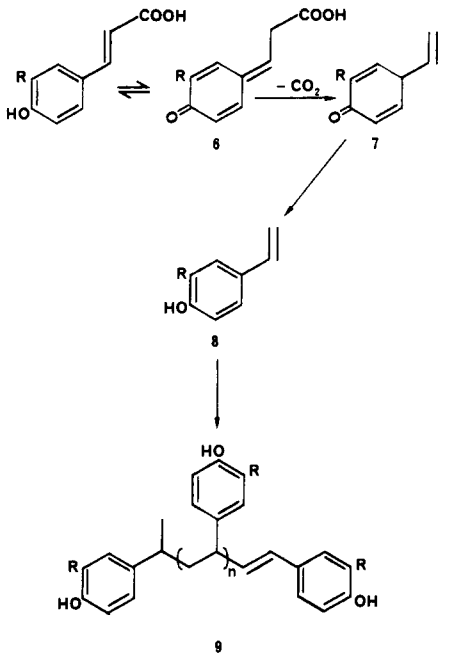


Figure 1. Decarboxylation of *p*-hydroxycinnamic acids.

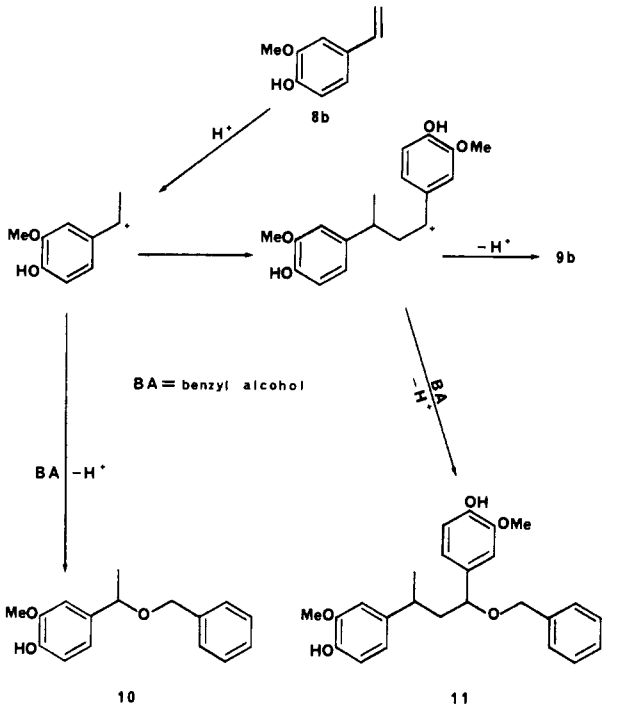


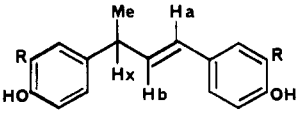
Figure 2. Acid-catalyzed ether formation.

based primarily on kinetic data indicative of a $^3/_2$ order reaction. We feel that a radical mechanism is unwarranted in view of the ionizable nature of a free carboxyl group and the ample literature precedent for polar decarboxylation (March, 1985). In addition, radical chain processes would be rapidly quenched by ambient phenols, which as a class are capable of fast hydrogen-transfer termination of chain propagating carbon or peroxy radicals (Sherwin, 1985; Uri, 1961). We believe that the $^3/_2$ order kinetics reported by previous workers was a consequence of TGA analysis which probably measures a complex group of reactions occurring simultaneously, not simply the decarboxylation reaction in question. Column chromatography was used to fractionate the major products formed by pyrolysis of **2a–c** at 205 °C, and fractions were analyzed by TLC. Monocyclic products, i.e., **8**, were observed in trace quantities only and were not completely characterized in this study. The major reaction product appeared on TLC as a complex series of spots ranging in polarity from R_f 0 to the R_f of **8**. In each case the compound nearest in R_f to **8** was isolated and shown by proton NMR and MS data (Table II) to be the styrene dimers **9a–c** [**9**; n = 0, R = H, OMe, OH]. Definitive structural data were not obtained for the more polar reaction products, but UV spectral data suggested they all were higher molecular weight oligomers of **8**, i.e., **9** with $n > 0$. Physical data of **9b** were identical with those reported for the styrene dimer isolated from a copper-catalyzed decarboxylation of ferulic acid (Klaren-De Wit et al., 1971). The trans geometry of the olefinic bond in **9a** and **9b** is established by inspection of proton NMR coupling constants (J) in clearly defined ABX systems (Table II); i.e., J_{ab} = 15.9 Hz and J_{ax} = 0 Hz. The value observed for J_{ab} lies within the diagnostic range (12–18 Hz) reported for trans olefinic protons, and J_{ax} = 0 is in the normal range (0–3 Hz) reported for long-range allylic coupling (Silverstein and Bassler, 1967).

A mechanism for oligomerization of styrenes, e.g., 4-vinylguaiacol (**8b**), is shown in Figure 2. In lieu of radical species we suggest an acid-catalyzed process leading eventually to the olefin, **9**. Acid was present, i.e., cinnamic acids, and the tendency of styrenes with electron-releasing ring substituents to undergo cationic polymerization is well-known (Matyjaszewski, 1989).

The trace quantities of styrenes, e.g., **8b**, found in roasted foods suggest that the bulk of the material originally formed must either have polymerized or reacted with other

Table II. Proton NMR and MS Data for Styrene Dimers



compd	R	NMR Data[a] Me d	MeO s	Ha d	Hb dd	Hx m	MS data, *m/z* (% of base peak)
9a	H	1.33 (7.0)		6.22 (15.9)	6.10 (6.4)	3.47	240 [M$^+$] (89), 225 (100), 131 (80), 121 (50), 107 (42), 103 (25)
9b	MeO	1.45 (7.0)	3.88 3.89	6.32 (15.9)	6.21 (6.3)	3.56	300 [M$^+$] (100), 285 (68), 253 (35), 161 (24), 299 (22), 151 (13)
9c	HO	1.23 (6.6)		*b*	*b*	3.43	272 [M$^+$] (100), 162 (90), 73 (89), 75 (62), 71 (62), 111 (54)

[a] Chemical shifts in ppm. Multiplicity: s, singlet; d, doublet; dd, doublet of doublets; m, complex multiplet. Coupling constants (J, in Hz), left to right: J(Me–Hx), J(Ha–Hb) and J(Hb–Hx). In all cases J(Ha–Hx) = 0.0 Hz. [b] Assignment not done because of extensive overlap with aromatic ring protons.

molecules present. Since the amount of styrene precursors, i.e., cinnamic acids, in foods is small, the resulting low concentration of styrene should limit the rate of polymerization relative to reaction with ambient molecules. Statistically, considering the availability of functional groups, styrenes should react most often with macromolecules like starch or proteins. Cationic intermediates postulated during oligomerization (Figure 2) may also be regarded as alkylating agents capable of reacting with ambient nucleophiles, i.e., HO, HS, or HN groups, to form ether, thioether, or amino linkages. In this way phenolic residues derived from cinnamic acids could, during roasting, become covalently attached to food macromolecules.

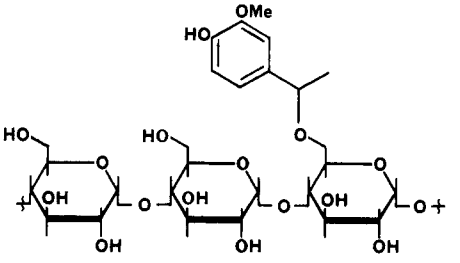
The alkylation potential of **8b** was demonstrated in a model system by treating a solution of the substance in benzyl alcohol with a catalytic quantity of *p*-toluenesulfonic acid at room temperature. Column chromatography of the reaction mixture separated two products of O-alkylation: 1-(4-hydroxy-3-methoxyphenyl)ethyl benzyl ether (**10**) and 1,3-bis(4-hydroxy-3-methoxyphenyl)butyl benzyl ether (**11**) in 2.5 and 29% yields, respectively. The formation of ethers **10** and **11** is explained by nucleophilic trapping of cationic intermediates generated by protonation of **8b** (Figure 2). Compound **10** is explained by nucleophilic attack of benzyl alcohol on protonated **8a** followed by loss of a proton. Protonated **8b** may also react with ordinary **8b** before encountering a molecule of benzyl alcohol, in which case the 2:1 adduct **11** is the expected product. Acid-catalyzed addition of water and alcohols to styrene has been reported previously (Baggett, 1979; Emerson, 1949); however, no mention was made of derivatives relevant to food systems.

The direct availability of alkylating species from cinnamic acid precursors was demonstrated by decarboxylating ferulic acid in boiling benzyl alcohol at ca. 205 °C. By stopping the decarboxylation at low conversion (20%), it was possible to isolate relatively low molecular weight reaction products. Under these conditions GC/MS confirmed the presence of **8a** and the derived ether **10** in 29 and 3.9% yields, respectively. Presumably **10** was formed by protonation of **7** or **8** (R = OMe) followed by reaction with benzyl alcohol. These results suggested that foods containing cinnamic acids could experience alkylation at ambient nucleophilic sites during cooking. The possibility of alkylation was further explored in a starch/ferulic acid model system.

Alkylation was observed in a food macromolecule by reacting ferulic acid with starch. Dry mixtures of ferulic acid and soluble starch containing 29% ferulic acid were heated for 0.25–5.0 h at 205 °C to induce decarboxylation. The heated products were washed with acetone and ether to remove unchanged ferulic acid and low molecular weight products. Finally, the modified starches were dissolved in boiling water and analyzed by UV spectroscopy. Samples which had been heated for >1 h developed a strong, well-defined absorption centered at 277 nm which was qualitatively identical with the UV absorption spectra of **10** and **11**, suggesting the presence of a guaiacol, i.e., a 3-methoxy-4-hydroxyphenyl moiety. In addition, these samples exhibited complete lack of ferulic acid (or ester) absorption at >300 nm and characteristic 4-vinylguaiacol absorption at 260 nm. Control samples of pure starch developed a relatively weak UV absorption at 280 nm upon heating apparently due to products not related to the starch/ferulic acid reaction. After 1 h at 205 °C, the absorption produced by pure starch at 280 nm was only 9.8% of the value obtained at 277 nm by an equivalent amount of starch heated in the presence of ferulic acid. A separate HPLC analysis proved that the absorption observed in the case of heated pure starch did not arise from 5-(hydroxymethyl)furfural (UV_{max} 282 nm). On the basis of these data we tentatively concluded that soluble starch was partially O-alkylated by cationic species derived from ferulic acid to produce an ether-linked phenolic derivative, e.g., **12**. Compound **12** represents the simplest possible alkylation product. In reality, multiple alkylation is likely and the alkylating species can contain more than one phenolic residue, i.e., like the precursor of **11**.

Dialysis of a 1.25-h-heated starch/ferulic acid mixture established that starch molecules with molecular weight >6000–8000 also contained the 277-nm chromophor. When the starch reaction product was boiled in water and subjected to dialysis through a 6000–8000 cutoff membrane, 52% of the absorption at 277 nm was retained by the membrane.

We conclude that molecules like **12** may be formed when foods containing starch and cinnamic acids (or their



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derivatives) are roasted. Further degradative studies are needed to prove the structures of starch/ferulic acid reaction products.

ACKNOWLEDGMENT

We thank A. R. Steimle for obtaining the GC/MS data and M. P. Lacey for the probe MS data.

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Received for review March 23, 1992. Accepted May 17, 1992.

Registry No. 2a, 7400-08-0; **2b**, 1135-24-6; **2c**, 331-39-5; **8b**, 7786-61-0; **9a**, 143122-86-5; **9b**, 33604-33-0; **9b** dibenzoate, 143122-87-6; **9c**, 143122-88-7; **10**, 143122-89-8; **11**, 143122-90-1; $PhCH{=}CHCO_2H$, 621-82-9; $3\text{-}OHC_6H_4CH{=}CHCO_2H$, 588-30-7; $4\text{-}OMeC_6H_4CH{=}CHCO_2H$, 830-09-1; $4\text{-}EtC_6H_4OH$, 123-07-9; $2\text{-}OHC_6H_4OH$, 120-80-9; $PhCH_2OH$, 100-51-6; 3-hydroxy-4-methoxycinnamic acid, 537-73-5; 4-ethylguaiacol, 2785-89-9; acetovanillone, 498-02-2; 4-ethylcatechol, 1124-39-6; starch, 9005-25-8.