

NOTE

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Mechanism of formaldehyde adsorption of (+)-catechin

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Abstract The reaction of (+)-catechin with formaldehyde vapor was investigated as a model reaction of formaldehyde adsorption of (+)-catechin. It was found by ^1H nuclear magnetic resonance spectroscopy, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, and gel permeation chromatography of the product that the vapor reaction of (+)-catechin with formaldehyde without a solvent or a catalyst proceeds via methylation, condensation, and polymerization. This is the same as the reaction in a solvent in the presence of an acid or a base. The formation of polyoxymethylenes such as paraformaldehyde was not confirmed.

Key words Adsorption · (+)-Catechin · Bark tannin · Formaldehyde · Vapor reaction

Recently, (+)-catechin has been noted as a HCHO scavenger to solve the problem of indoor air pollution caused by volatile organic compounds (VOCs).^{10–12} It has been reported that any HCHO adsorbed by (+)-catechin was hardly released again. Therefore, the HCHO adsorption mechanism of (+)-catechin should be mainly due to chemical adsorption, that is, the reaction of (+)-catechin with HCHO vapor. However, the vapor reaction has been described briefly in only one report, in which the detailed analyses of the vapor reaction products were not published.¹⁰ In the present study, the reaction of (+)-catechin with HCHO vapor without a solvent and a catalyst was investigated as a model reaction of HCHO adsorption of (+)-catechin.

Introduction

Many studies have been made to investigate the utilization of condensed tannin from bark as wood adhesive by replacement of the phenol component in phenol–formaldehyde (HCHO) resins.^{1–4} From this point of view, much attention has focused on the reaction of (+)-catechin, which is a tannin model compound, with HCHO.^{5–8} (+)-Catechin–HCHO reaction products under strong acid conditions in water are known as Stiasny precipitates, which are used to estimate the amount of reactive polyflavonoids.⁹ The reaction mechanism of (+)-catechin with HCHO in the presence of an acid or a base in an aqueous solution has been proposed as in Fig. 1, on the basis of ^1H nuclear magnetic resonance (NMR) and ^{13}C NMR data of the products.^{5,6} It is widely accepted that the reaction is an aldol condensation-type reaction and comprises methylation, condensation, and polymerization (by repeated methylation and condensation).

Materials and methods

Materials

(+)-Catechin and formalin (HCHO content 37%, special grade) were purchased from Nacalai Tesque (Kyoto, Japan). The former was ground in a mortar with a pestle and dried in vacuo at room temperature overnight before use, and the latter was used without further purification.

Vapor reaction

(+)-Catechin (40 mg) was added to a 10-ml round-bottom flask, which was equipped with a 10-ml Dean-Stark trap in which formalin (1 ml) was added (Fig. 2). The flask was kept at 20°C for 48 h. The HCHO adsorbed (+)-catechin was dried in vacuo at room temperature for 3 days to give a HCHO-(+)-catechin product.

Measurements

^1H NMR spectra were collected with a Varian INOVA300 FT-NMR (300 MHz) spectrometer in methanol- d_4 with

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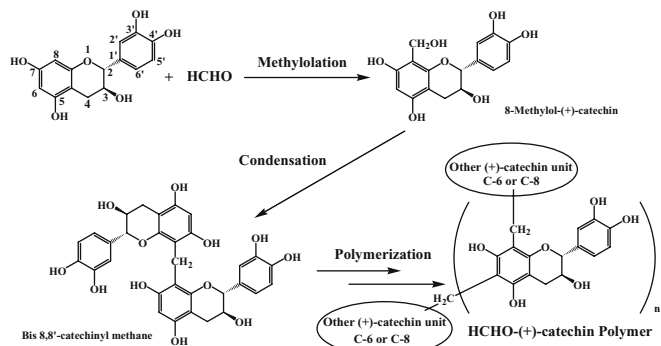


Fig. 1. Proposed reaction mechanism in the reaction of (+)-catechin with HCHO in the presence of an acid or a base in aqueous solution

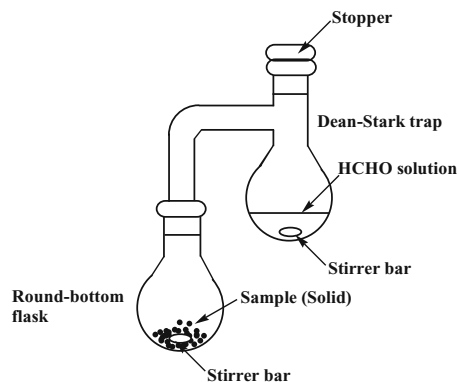


Fig. 2. Reaction apparatus for HCHO vapor reaction

tetramethylsilane (TMS) as an internal standard. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a REFLEX III MALDI-TOF (Bruker) with an LSI VSL 337-nm nitrogen laser. 2,5-Dihydroxy-benzoic acid (DHB) and angiotensin II were used as matrix and standard sample, respectively.

The HCHO-(+)-catechin product and (+)-catechin were acetylated with acetic anhydride/pyridine at room temperature overnight before gel permeation chromatography (GPC) measurements. GPC analyses of the acetylated products were performed on a Shimadzu LC-10 system equipped with a Shimadzu UV-VIS detector (SPD-10Avp) under the following conditions: columns, Shodex-K802, -802.5, and -805 columns connected in series; column temperature, 40°C; eluent, chloroform; flow rate, 1.0 ml min⁻¹; detection wavelength, 250 nm. Calibration curves were obtained by using standard polystyrenes (Shodex).

Results and discussion

The reaction of (+)-catechin with HCHO vapor without a solvent and catalyst was carried out at 20°C for 48 h. The reaction product and its acetate were subjected to ¹H NMR and MALDI-TOF MS analyses and to GPC measurements, respectively.

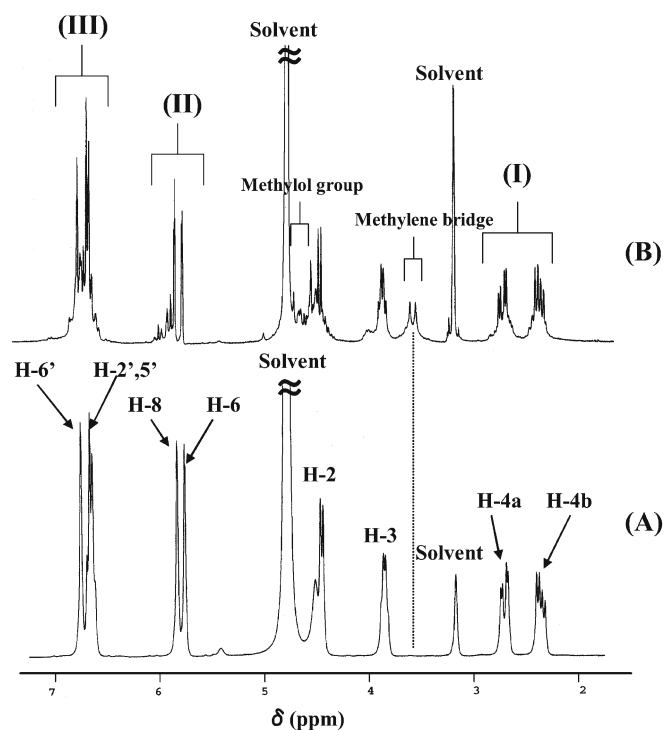


Fig. 3A, B. ¹H Nuclear magnetic resonance spectra of **A** (+)-catechin and **B** HCHO-(+)-catechin product

¹H NMR spectra of the HCHO-(+)-catechin product and (+)-catechin are shown in Fig. 3. In the spectrum of the product, the signals at 5.75 and 5.83 ppm, which were assigned to H-6 and H-8 in A-ring, respectively, decreased, and the signals around 3.50–3.70 ppm, which were due to a methylene bridge,^{6,13} and 4.50–4.80 ppm, which were thought to be a methylol group,^{14,15} newly appeared. The ratio of peak area (II) for the signals at 5.75 and 5.83 ppm from A-ring protons to peak area (I) for the signals at 2.39 and 2.74 ppm, which were assignable to H-4 protons in C-ring, was approximately 0.5, suggesting that half the total protons in A-rings of (+)-catechin used were substituted by HCHO. On the other hand, the ratio of peak area (III) of the signals around 6.60–6.80 ppm, which were assigned to B-ring protons, to peak area (I) for the above signals from the C-ring protons was almost 1.50, indicating that the B-ring did not participate in the methylation or condensation under the above conditions. However, further investigation is required to elucidate the ratio of 6-6, 6-8, and 8-8 methylene bridges.

Figure 4 shows the MALDI-TOF mass spectrum of the product. The signals of main ions were observed at *m/z* 615.5 (*n* = 2), 917.3 (*n* = 3), 1219.2 (*n* = 4), 1520.9 (*n* = 5), 1822.5 (*n* = 6), 2123.7 (*n* = 7), and 2425.8 (*n* = 8) as sodium adducts, and 631.4 (*n* = 2), 933.3 (*n* = 3), 1235.2 (*n* = 4), 1536.9 (*n* = 5), 1839.2 (*n* = 6), 2140.4 (*n* = 7), and 2442.7 (*n* = 8) as potassium adducts. The difference in molecular weight between consecutive main ions was 302, corresponding to the molecular weight of the repeating unit of HCHO-(+)-catechin polymer shown in Fig. 1.

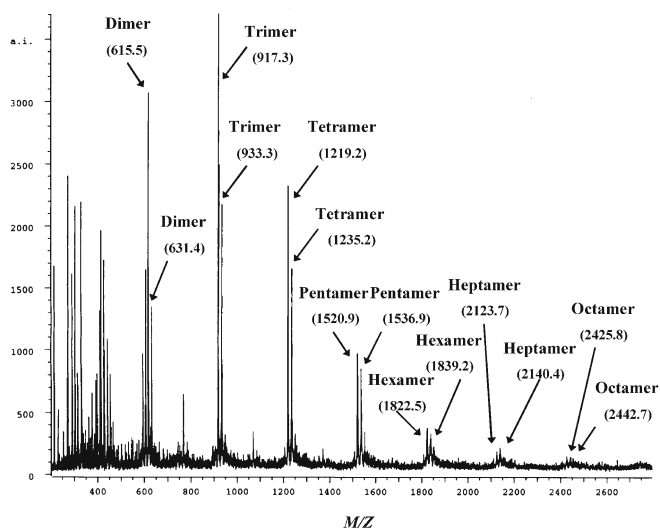


Fig. 4. Matrix-assisted laser desorption/ionization time-of-flight mass spectrum of HCHO-(+)-catechin product

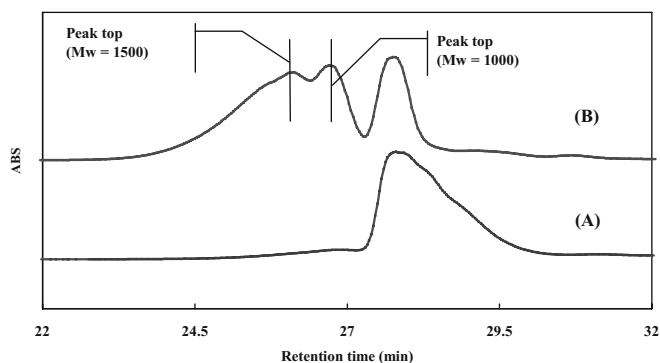


Fig. 5. Gel permeation chromatography elution curves of (+)-catechin acetate (A) and acetylated HCHO-(+)-catechin product (B)

GPC elution curves of the acetylated HCHO-(+)-catechin product and (+)-catechin acetate are shown in Fig. 5. In the elution curves of the acetylated product, the peak corresponding to (+)-catechin acetate ($M_w = 500$) decreased, and peaks at higher molecular weight appeared. The molecular weights for the latter peaks were 1500 and 1000, corresponding to that of trimer or dimer.

These findings indicate that methylation, condensation, and oligomerization, as shown in Fig. 1, proceeded gradually, even in the reaction of (+)-catechin with HCHO vapor without a solvent or catalyst, as well as the reaction in the presence of an acid or a base in aqueous solution. The possibility that (+)-catechin itself might act as a weak acid catalyst in the vapor reaction can be considered, because it has been reported that a noncatalyzed

resorcinol-HCHO reaction proceeded as a Novolak-type reaction.¹⁶ On the other hand, it is well known that HCHO forms polyoxymethylenes such as paraformaldehyde under acidic conditions in the vapor phase,¹⁷ but the formation of such compounds was not confirmed by the data of the present experiments. Consequently, our results indicate clearly that the aldol condensation-type reaction, shown as Fig. 1, is one of the HCHO adsorption mechanisms of (+)-catechin.

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