

# Reaction mechanisms for pyrolysis of benzaldehydes

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## Summary

Benzaldehydes are major products of biomass pyrolysis that undergo further pyrolysis reactions, including elimination of pendant groups on the benzene ring, and condensation to form polycyclic aromatic hydrocarbons. To elucidate these secondary reactions that occur during the pyrolysis of biomass, the analytical pyrolysis of 4-hydroxybenzaldehyde (HBA), vanillin (VL), syringaldehyde (SA) and veratrumaldehyde (VA) was performed via pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), and the mechanisms for formation of secondary products were evaluated. Four pyrolysis products from SA and eleven pyrolysis products from VA were identified, while only two pyrolysates were detected from HBA and VL. On the basis of these results, several major pyrolysis mechanisms were proposed. The most common pyrolysis reactions involved the homolytic elimination, and addition of ·H, ·OH, ·CHO, and ·OCH<sub>3</sub>, while the homolytic elimination of methyl group from methoxy group, and rearrangement of the methoxy group occurred infrequently. Furthermore, benzaldehydes with a phenolic hydroxyl group were stabilized by conjugation of the aromatic ring with the phenolic-OH, and fewer pyrolysis products were produced than were obtained from compounds with non-phenolic benzyl alcohol groups, such as VA.

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**Key words** : analytical pyrolysis, reaction mechanism, lignin, benzaldehydes,

## 1. Introduction

Bio-oil produced from the fast pyrolysis of biomass is considered to be a substitute for fuel oil or diesel in many static applications, such as boilers, furnaces, engines, and turbines for electricity generation or chemical production (Bridgwater, 2003). Many types of biomass have been examined for bio-oil production, and pilot plants have been established worldwide (Bridgwater and Peacocke, 2000; Zhang *et al.*, 2007). Several studies on the pyrolytic conversion of crops other than wood materials, such as wheat straw (Fidalgo *et al.*, 1993), rice husks (Gai *et al.*, 2013), tobacco residues (Cardoso and Ataide, 2013), orange waste (Lopez-Velazquez *et al.*, 2013), giant canes (Temiz *et al.*, 2013), and microalgae (Wang *et al.*, 2013), have also been reported. These plants consist of cellulose, hemicelluloses, and lignin. Therefore, bio-oil consists of a mixture of pyrolysates from these components. Lignin is the second most abundant natural biopolymer found in lignocellulosic plants, and is a heterogeneous and complex polymer primarily synthesized mainly from three p-hydroxycinnamyl alcohols differing in their degree of methoxylation: p-coumaryl, coniferyl, and sinapyl alcohols. Each of these monolignols gives rise to a different type of lignin unit called (p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively), generating a variety of structures and linkages within the polymer (Higuchi, 1997; Boerjan *et al.*, 2003; Ralph *et al.*, 2004). The distribution of the phenols in lignin may significantly affect the physical and chemical properties of the bio-oil obtained

from the pyrolysis of biomass. The distribution of pyrolysates and the process of bio-oil formation vary as a function of the pyrolysis conditions and the original lignin structure of the feedstock. A better understanding of the chemical reactions that occur during the fast pyrolysis of lignin should therefore provide useful information for controlling the pyrolysis process for suitable bio-oil production.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was previously developed as a convenient tool for the rapid and sensitive analysis of lignin structures (Río *et al.*, 2004; Meier *et al.*, 2005; Ralph *et al.*, 1991).

Ren *et al.* investigated the product distribution from moso bamboo during pyrolysis and detected benzaldehydes, such as vanillin and syringaldehyde, in the pyrolysate (Ren *et al.*, 2013). Hassan *et al.* also found vanillin in the pyrolysis products of pretreated pine wood (Hassan *et al.*, 2010). Furthermore, the same benzaldehydes were detected in pyrolysates from non-wood biomass (Lira *et al.*, 2013; Zheng, 2007) and enzymatic acidolysis lignin (Lou *et al.*, 2010), hydrolysis lignin (Huang *et al.*, 2012; Río *et al.*, 2012), and kraft lignin (Tumbalam, *et al.*, 2014). These findings suggest that benzaldehydes are major pyrolysis products that undergo further pyrolysis reactions, such as elimination of pendant groups on the benzene ring and condensation to form polycyclic aromatic hydrocarbons.

The goal of this investigation was to evaluate the effect of methoxy groups on the secondary pyrolytic reactions of lignin pyrolysates via the Py-GC/MS analysis of benzaldehyde models.

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## 2. MATERIALS AND METHODS

Three phenols and one non-phenolic compound were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan as guaranteed grades. The model compounds used in this study are listed in Fig.1. Three benzaldehydes were selected as hydroxyl-, guaiacyl-, and syringyl-type models. Veratrumaldehyde was also used as a model of a non-phenolic benzaldehyde for the estimation of the effect of the phenolic hydroxide group on the pyrolytic reaction mechanism.

The pyrolysis of the samples was performed using a Frontier Lab PY-2020iD pyrolyzer. The dried sample cup was inserted into the pyrolyzer chamber, which was purged with helium prior to performing the pyrolysis. The furnace in the pyrolyzer was then preheated at 600 °C. Next, the sample was placed in the middle of the furnace for 0.2 min and then moved to the top of the furnace. The pyrolysates produced at these positions were separated and analyzed using a GC/MS coupled directly with the pyrolyzer.

An Agilent GC/MS system composed of an Agilent 6890

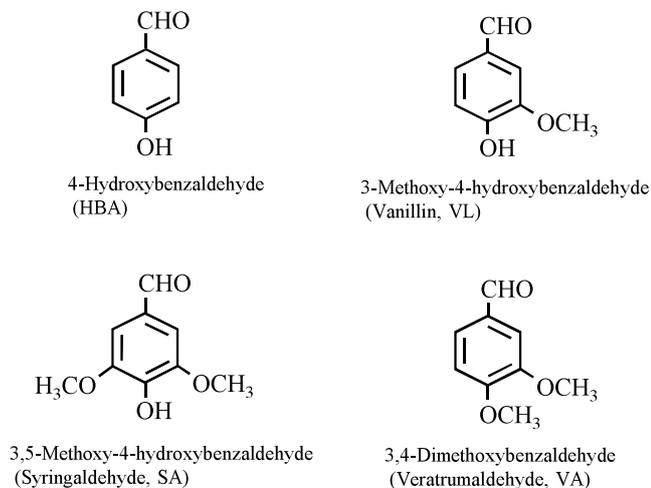


Fig.1 Model compounds of lignin used in this study

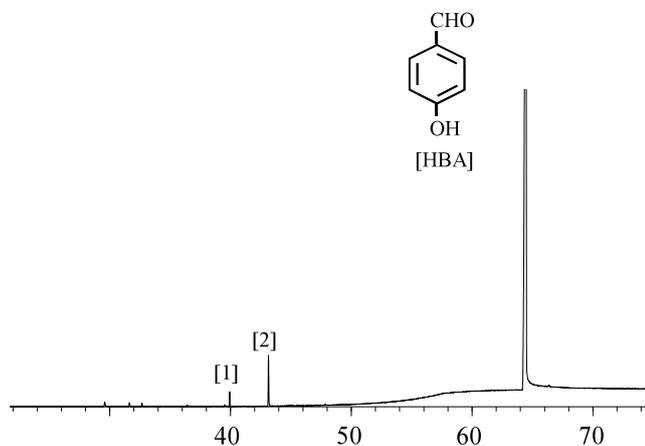


Fig.2 Py-GC/MS chromatogram of HBA

gas chromatograph and an Agilent 5975 inert mass selective detector was used to separate and obtain the mass spectra of the compounds derived from each sample. The samples were injected in split mode (100:1 ratio). Helium at a flow rate of 0.9 mL/min was used as the carrier gas. The oven was initially held at 40°C for 5 min, then increased at a rate of 4°C per minute up to 250 °C, and finally held at this temperature for 60 min. An Rtx-Wax cross-linked polyethylene glycol fused-silica capillary column (RESTEK, 60 m × 0.25 mm i.d., 0.25 μm film thickness) was used to separate the samples. The column was interfaced directly to the electron impact (EI) ion source of the mass spectrometer. The ion source was operated at 70 eV. The injection port was set at 250 °C. The separated peaks were identified using the NIST05 MS Library.

## 3. RESULTS AND DISCUSSION

### 3.1 Pyrolysis of 4-hydroxybenzaldehyde (HBA)

A profile of the total ion chromatogram (TIC) obtained for the Py-GC/MS of HBA is shown in Fig.2. In this TIC, only two pyrolysis products and unreacted starting material were detected. Generally, compounds with simple structures (with a low leaving group content) are considered to be more stable to thermal treatment than complex compounds (with large numbers of leaving groups) (Hosoya *et al.*, 2008). On the basis of their mass spectra, products [1] and [2] were identified as phenol and benzyl alcohol, respectively. The mass spectrum of product [2] is illustrated in Fig.3.

The formation of products [1] and [2] is thought to

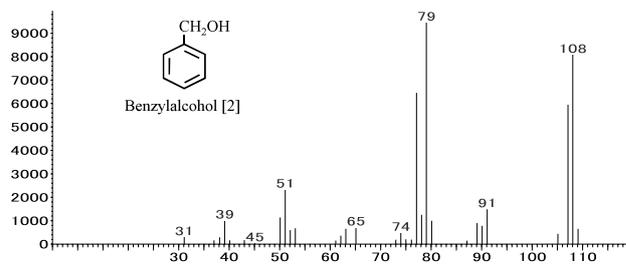


Fig.3 Mass spectrum and chemical structure of a product [2]

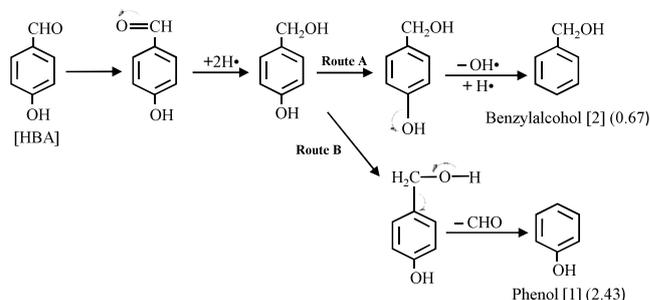


Fig.4 Proposed formation mechanisms of product [1] and [2] from HBA

proceed via the same intermediate 4-hydroxybenzylalcohol. In this route, the  $-C=O$  bond of the aldehyde group is subjected to homolysis and forms the biradical structure  $\cdot C-O\cdot$ , which then reacts with two protons to generate 4-hydroxybenzylalcohol. Subsequently, this intermediate is subjected to two different homolytic cleavage reactions: phenolic hydroxy elimination (route A) and benzyl alcohol elimination (route B). The former reaction affords product [2], while the latter reaction yields product [1]. The proposed mechanisms for the formation of products [1] and [2] are shown in Fig.4. The numbers in parentheses indicate the percentages of the corresponding TIC peak areas.

### 3.2 Pyrolysis of vanillin (VL)

The TIC profile obtained for the Py-GC/MS of VL is shown in Fig.5. As was observed for HBA, two pyrolysis products and unreacted starting material were detected in this TIC. The mass spectra of products [3] and [4] indicate that these compounds were guaiacol and 5-formylsalicylaldehyde, respectively. The mass spectrum of product [4] is illustrated in Fig.6.

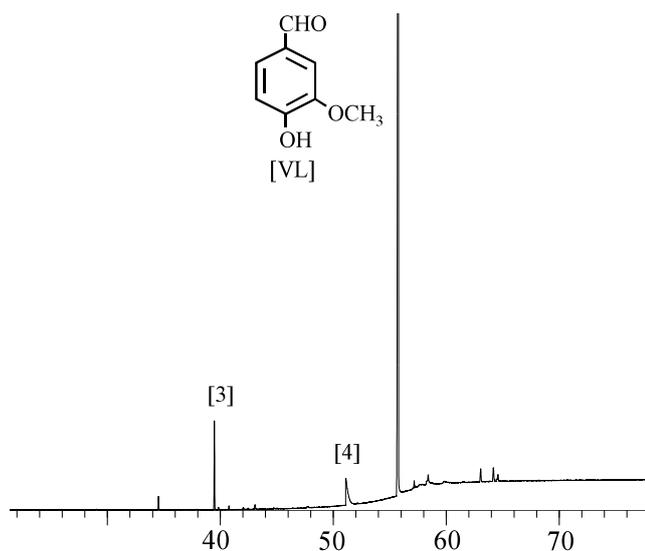


Fig.5 Py-GC/MS chromatogram of VL

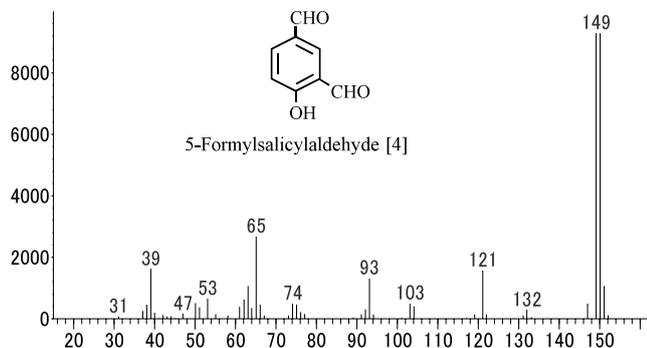


Fig.6 Mass spectrum and chemical structures of a product [4]

Product [3] is thought to form via the elimination of benzaldehyde, as in the case of route B above. However, product [4] is thought to form via the rearrangement of the methoxy group (route C), as shown in Fig.7. This reaction pathway was proposed by Asmadi *et al.* for syringol (Asmadi *et al.*, 2011).

### 3.3 Pyrolysis of syringaldehyde (SA)

The pyrolysate from SA consisted of four main products and recovered starting material as shown in Fig.8. On the basis of the mass spectrums illustrated in Fig.9, products [5]-[8] were respectively identified as syringol, 3,5-dimethoxybenzaldehyde, vanillin, and 4-hydroxy-3-methylbenzaldehyde.

Product [5] is thought to form via route B (elimination of the benzaldehyde group), while product [6] is thought to form

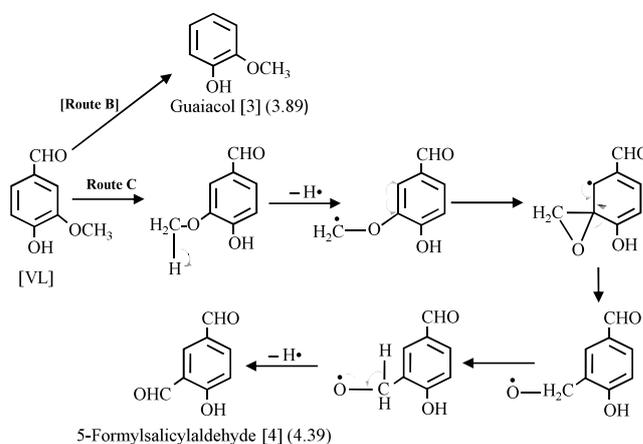


Fig.7 Proposed formation mechanism of product [3] and [4] from VL

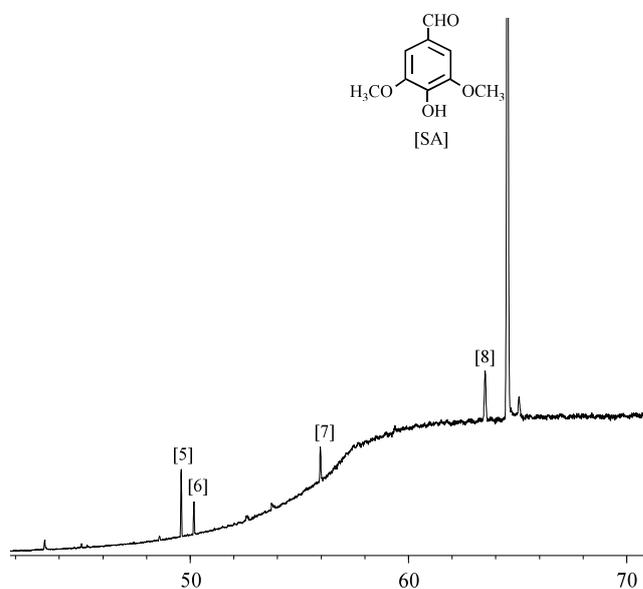


Fig.8 Py-GC/MS chromatogram of SA

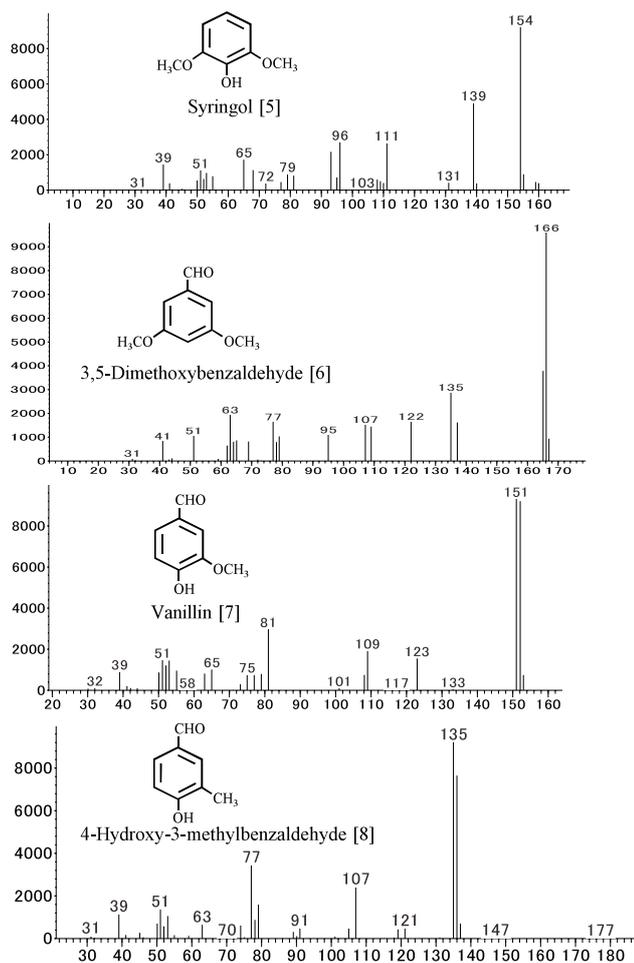


Fig.9 Mass spectra and chemical structures of products [5]-[8]

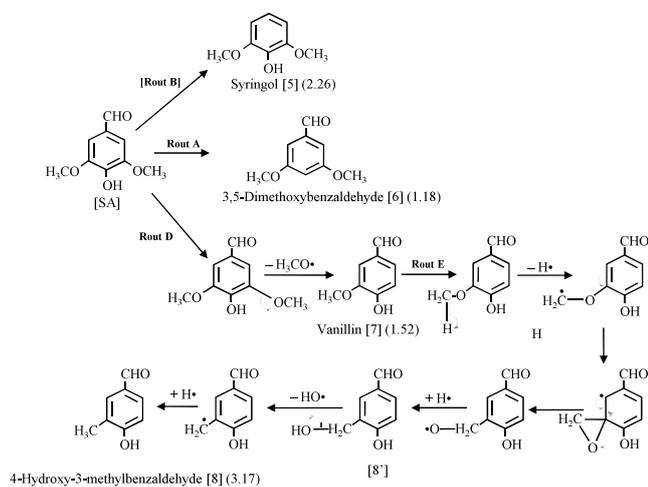


Fig.10 Proposed formation mechanisms of [5]-[8] from SA

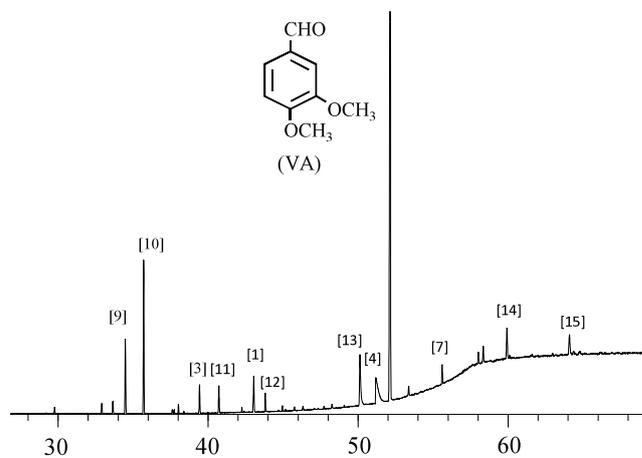


Fig.11 Py-GC/MS chromatogram of VA

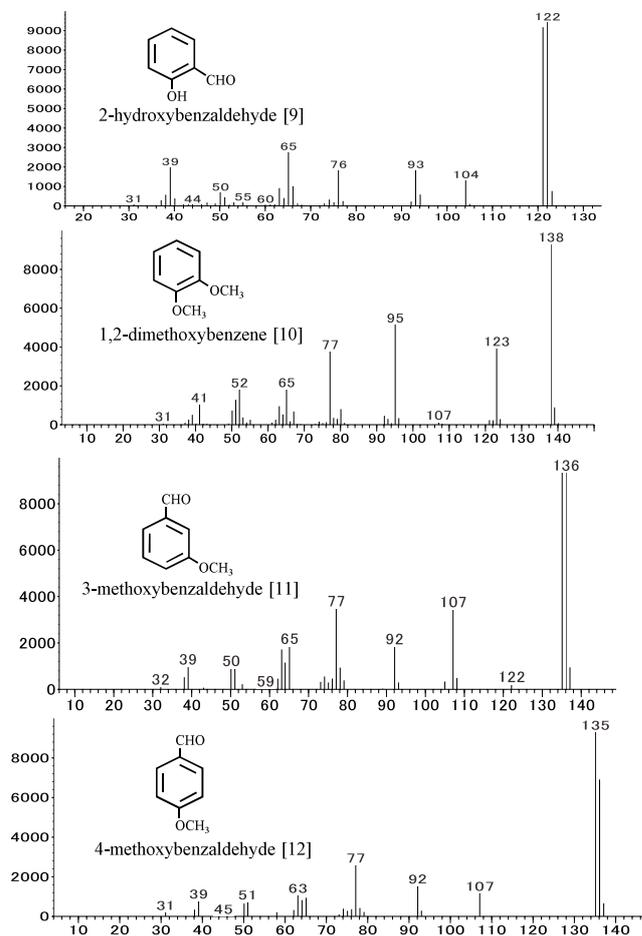
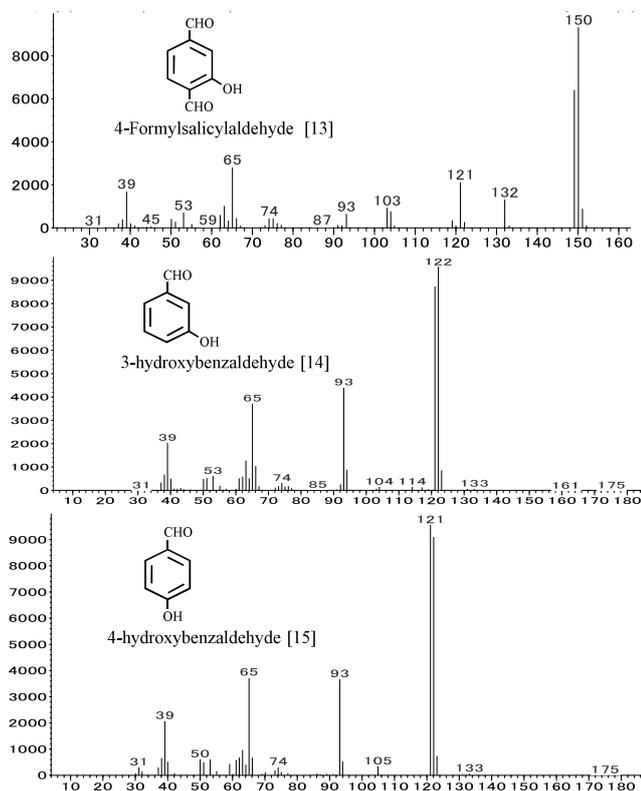


Fig.12 Mass spectra and chemical structures of products [9]-[12]



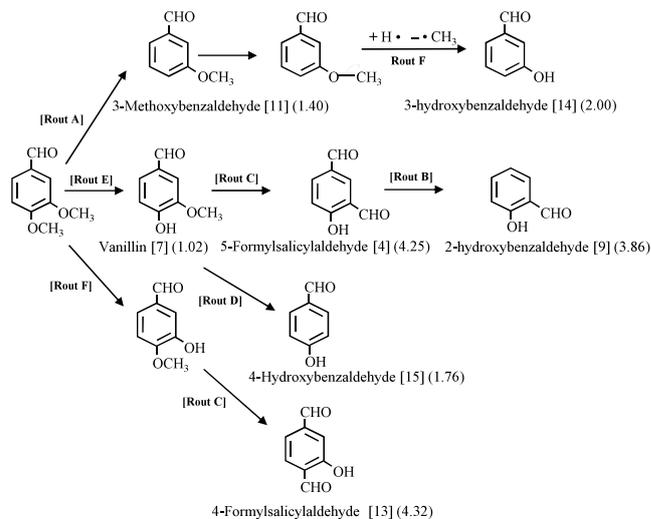
**Fig.13** Mass spectrums and chemical structures of products [13]-[15]

via route A (elimination of the phenolic hydroxy group). Product [7] is believed to form via elimination of a methoxy group from the aromatic ring (route D). Product [7] is then subjected to rearrangement of a methoxy group to form the hydroxymethyl intermediate [8]. The hydroxy group in [8] is subsequently eliminated via homolytic cleavage from the hydroxymethyl group, followed by the addition of a proton radical to the methyl radical (route E), generating product [8]. The proposed mechanisms for the formation of products [5][8] are shown in Fig.10.

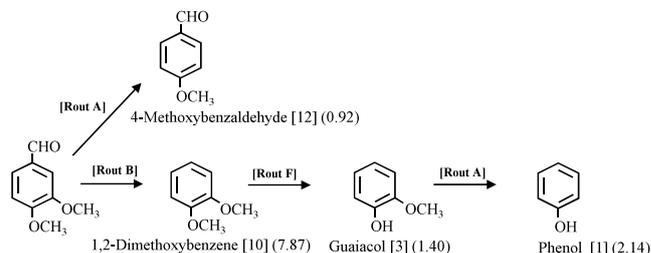
### 3.4 Pyrolysis of Veratrumaldehyde (VA)

Numerous peaks appeared in the TIC profile obtained for the Py-GC/MS of VA, as shown in Fig.11. This result suggested that substitution of a methoxy group for a hydroxy group on the aromatic ring induces high pyrolytic reactivity. In addition to unreacted starting material, 11 peaks were found as main products of VA pyrolysis. These products were identified on the basis of their mass spectrums as shown in Figs.12 and 13.

Most routes of formation for the pyrolysates were the same as those observed in the pyrolysis of HBA, VL, and SA. In addition to these pathways, product [14] is thought to form via the homolytic cleavage of the methyl ether of a methoxy group (route F) in the structure of product [11], which is



**Fig.14** Proposed formation mechanisms of [4], [7], [9], [11] and [13]-[15] from VA



**Fig.15** Proposed formation mechanisms of [1], [3], [10] and [13] from VA

thought to form via route A. Product [7] via route E, product [4] via route C, and product [9] via route B are thought to form successively. Product [15] is believed to form from product [7] via route E, while product [13] is thought to form via routes F and C. Product [13] is an isomer of product [4], which has a typical peak shape in the TIC. Product [12] is thought to form via route A. Routes B, F, and A are also thought to provide products [10], [3], and [1], respectively. These proposed formation pathways are shown in Figs.14 and 15.

## 4. Conclusion

Several reaction mechanisms were found for the pyrolysis of four benzaldehydes. All the pendant groups were pyrolyzed at 600 °C via Py-GC/MS. The elimination of pendant groups occurred via route A (-OH), route B (-CHO), and route D (-OCH<sub>3</sub>). Homolytic cleavage of a methyl ether group occurred via route F (-OCH<sub>3</sub> → -OH), while rearrangement of the methoxy group to form aldehyde and methyl groups proceeded via routes C and E, respectively. Phenolic benzyl alcohols were more stable to pyrolysis and

yielded fewer pyrolysis products than the etherified benzyl alcohol. All the model compounds used in this study have been detected in the pyrolysates of lignocellulosic materials; a portion of these materials are known to undergo further pyrolysis. This study thus revealed possible reaction pathways for these secondary pyrolysis reactions.

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## ベンズアルデヒド類の熱分解反応機構

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(平成26年7月25日受付)

### 要 約

ベンズアルデヒド類はバイオマスの熱分解における主要な反応生成物であり、それらはさらにベンゼン環の置換基の脱離反応や多環芳香族(炭や煤)を形成するような縮合反応へと反応が進行していく。これらの熱分解2次反応を明らかにするために、4-hydroxybenzaldehyde (HBA), vanillin (VL), syringaldehyde (SA), veratrumaldehyde (VA) をモデル化合物として熱分解-GC/MSを行い、2次熱分解反応機構を検討した。HBAやVLからの熱分解生成物は2種しか検出されず、その反応機構が単純であったが、SAからは4種、さらにVAからは11種の熱分解生成物が検出され、2次熱分解反応が多様であることが示された。これらの基本的な熱分解反応はH・、HO・、OHC・、H<sub>3</sub>CO・などのホモリテイクなラジカル開裂や付加反応、それにメトキシル基からのメチル基の脱離やメトキシル基の分子内転移によるメチル基の生成を含む。さらにベンジル位のアルデヒド基はフェノール性水酸基と共役して熱分解反応に対して安定化していることが、その熱分解生成物の少なさから推測された。

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キーワード: 分析熱分解、反応機構、リグニン、ベンズアルデヒド

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