

Research article

# Reaction mechanisms of pyrolysis of four different phenylpropanoids

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## Abstract

Phenylpropanoids are known as typical intermediates in biomass pyrolysis, and part of them are converted through further complex pyrolysis reactions into low-molecular weight pyrolysates. The latter reaction is categorised as a secondary pyrolysis pathway to yield several pyrolysis products. In this study, four propanoids with different C<sub>γ</sub>-groups in the side chain, (*E*)-isoeugenol, (*E*)-coniferyl alcohol, (*E*)-coniferylaldehyde and (*E*)-ferulic acid were subjected to analytical pyrolysis with Py-GC/MS to elucidate the effect of C<sub>γ</sub>-group on pyrolysate composition, and their formation pathways were proposed. The basic reaction is homolytic cleavage, which occurred around bonds, including oxygen (C–O- and H–O-). Therefore, several products were formed by the elimination and/or addition of proton and hydroxyl radicals, the demethylation and demethoxylation of the methoxyl group adjacent to the aromatic ring, the displacement of C<sub>γ</sub>-hydroxyl radical and the isomerisation from the (*E*) to (*Z*) form on the unsaturated bond in the side chain. Some of their formation routes were initiated via the formation of quinone methide intermediates.

**Keywords:** Pyrolysis, secondary reaction, Reaction mechanism, Lignin model, Phenylpropanoids,

## Introduction

Bio-oil produced from the fast pyrolysis of biomass is considered as a new resource and substitute for fuel oil or diesel in many static applications such as boilers, furnaces, engines and turbines used in electricity generation and chemical production (1). Lignin is the second most abundant natural biopolymer found in lignocellulosic plants and is considered to be one of potential biomass source. The distribution of phenols from lignin pyrolysis significantly affects the physical and chemical properties of the bio-oil. Notably, the formation of different phenols and the consequent phenol distribution are determined by the pyrolysis conditions and the original lignin structure. Therefore, a better understanding of the chemical reactions that occur during the fast pyrolysis of lignin could provide useful information to control the pyrolysis process for suitable bio-oil production.

Lignin model compounds such as lignin monomers and lignin dimers have been pyrolyzed in order to investigate the mechanisms of phenol formation. The pyrolysis of simple phenols was reported to produce various polycyclic aromatic hydrocarbons (PAHs) and heterocyclic compounds (2). The same group has also reported the effect of methoxyl and phenolic hydroxyl groups on the pyrolysis reaction mechanisms using lignin monomer models (3). Hage et al. developed the Curie-point LC/MS analytic method for the detection of oligomeric and polar compounds present in bio-oil prepared from lignin dimer models (4). Using pyrolysis and GC/MS, Kuroda et al. determined that the major product of the pyrolysis of a  $\beta$ -5 structure model (dehydro-diconiferylalcohol) and its methylated compound was methyl guaiacol (5), which was produced from the aryl ether of the ring-opened dimer formed via hydrogenation of the  $C_{\alpha}$ - $C_{\beta}$  bond of the dimer model. Kawamoto et al. evaluated the relative reactivity of depolymerisation and condensation/carbonisation (primary pyrolysis) reactions on the basis of the formation of major pyrolysis products using four lignin dimer models ( $\alpha$ -O-4,  $\beta$ -O-4, biphenyl and  $\beta$ -1) (6). They concluded that the order of reactivity for depolymerisation was  $\alpha$ -O-4,  $\beta$ -O-4 >  $\beta$ -1 > biphenyl and that both phenolic and non-phenolic forms of these compounds influenced the reactivity. They also studied the influence of side chain hydroxyl groups at the  $C_{\alpha}$  and  $C_{\gamma}$  positions on the pyrolytic  $\beta$ -ether cleavage of aryl ether-type dimer models and proposed that cleavage of the  $\beta$ -ether bond proceeds via a quinone methide intermediate with intermolecular hydrogen bond formation between the  $C_{\alpha}$ - and  $C_{\gamma}$ -hydroxyl groups as the first step (7). Klein et al. studied lignin pyrolysis using phenethyl phenyl ether as a lignin model for  $\beta$ -aryl ethers and detected phenol and vinyl phenol as major products (8). The bond dissociation enthalpies for the homolytic cleavage of  $\beta$ -aryl ethers have also been reported in a computational study using a  $\beta$ -O-4 dimer model (9).

The present study evaluates the effect of  $C_{\gamma}$  groups on the mechanisms of side chain reactions via Py-GC/MS analysis of five phenylpropanoids with different  $C_{\gamma}$  groups: eugenol, isoeugenol, coniferylalcohol, coniferylaldehyde and ferulic acid.

## Materials and Method

Isoeugenol, coniferylalcohol, coniferylaldehyde, and ferulic acid (*E*-isomers, guaranteed grade) were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. The chemical structures of the model compounds are illustrated in Figure 1. These samples were pyrolyzed with a Frontier Lab PY-2020iD pyrolyzer. Each dried sample cup was inserted into the pyrolyzer chamber, which was previously purged with helium. After pre-heating the pyrolyzer furnace (400–600 °C), each 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 temperatures were separated and analyzed using a GC/MS system coupled directly to the pyrolyzer. The GC/MS conditions are described below. An Agilent GC/MS system consisting of an Agilent 6890 gas chromatograph and an Agilent 5975 inert Mass Selective Detector was used to separate and obtain the mass spectra of the compounds in each sample. The samples were injected in split mode (100:1 ratio). The carrier gas was helium with a flow rate of 0.93 mL/min. The oven was initially

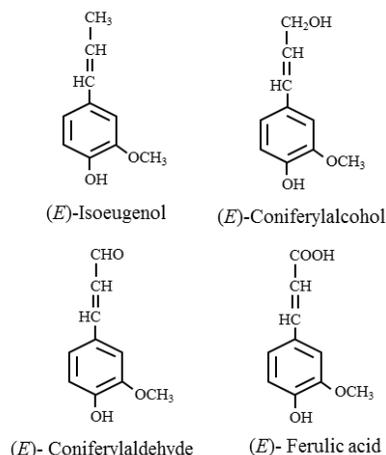


Fig.1. Four model phenylpropanoids used in this study

maintained at 40 °C for 5 min, increased at a rate of 4 °C per min up to 250 °C, and then maintained 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 ion source of the mass spectrometer. The ion source was operated at 70 eV, and the temperature of the injection port was set at 250 °C. The separated peaks were identified using the NIST05 MS Library.

## Results and Discussion

### 1) Identification and formation of pyrolysates from (*E*)-isoeugenol

Rather than the absolute area, the area percentage served as the dependent variable in order to eliminate any inconsistencies due to the variations in sample size and product carryover. It was confirmed that the contribution of the area for a given peak was statistically similar between experiments. As is common for pyrolysis-GC/MS, most of the pyrolysis products were identified by comparing their mass data and the data in a widely used MS database. However, some of the pyrolysis products were not registered in this MS database. Therefore, the compounds were identified using the mass fragmentation method and their GC retention times in addition to the MS database. The total ion chromatograph (TIC) obtained for the Py-GC/MS of (*E*)-isoeugenol at 600 °C is shown in Figure 2. In the major pyrolysate, 11 products and the unreacted starting material were identified, and their formation mechanisms were proposed. The proposed formation mechanisms of products [1], [6], [10] and [11] are shown in Figure 3. (*Z*)-Isoeugenol [6] is formed via the isomerisation of (*E*)-isoeugenol, which is known to occur at elevated temperatures (10). This reaction is initiated

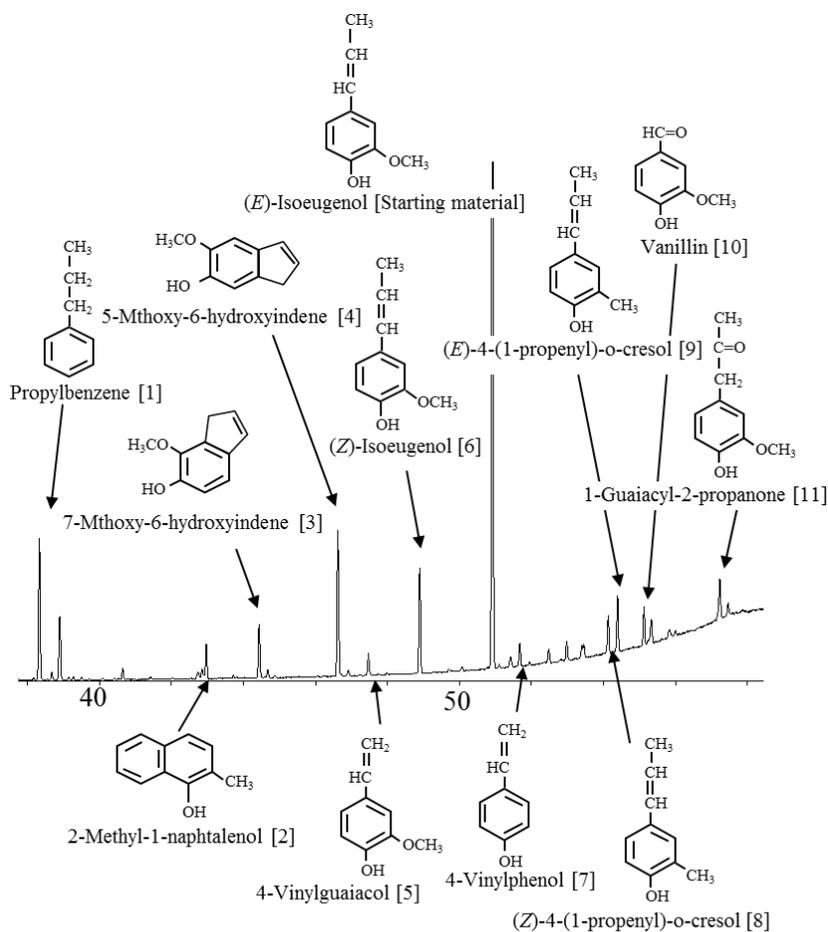


Fig.2. Total ion chromatograph for the Py-GC/MS of (*E*)-isoeugenol at 600 °C

through the  $C_{\alpha}$  radical of quinone methide (**route D**). Proton radicals add to the  $C_{\alpha}$  radical and then form the (*Z*)-isomer (**route G**). This reaction route is supported by the experimental result that the pyrolytic isomerization of (*E*)-cinnamyl alcohol to (*Z*)-cinnamyl alcohol hardly occurred, while other phenyl propanols with phenolic hydroxyl groups formed isomers in higher yields. Therefore, the phenolic hydroxyl group is considered to promote the isomerisation reaction via the quinone methide intermediate (3). Propylbenzene [1] is formed by the homolytic

displacement of a methoxyl group (**route B**) and phenolic hydroxyl group (**route C**) from propylguaiacol, which is derived from the addition of two proton radicals to the  $C_\alpha$ - $C_\beta$  unsaturated bond of (*E*)-isoeugenol (**route A**). The production of vanillin [10] is also initiated by the  $C_\alpha$  radical of quinone methide, which is followed by the addition of a hydroxyl radical to the  $C_\alpha$ -radical to form 1-guaiacyl-propanol (**route E**). The proton radical from the  $C_\alpha$ -hydroxyl group of 1-guaiacyl-1-propanol is then subjected to homolytic displacement, which leads to the cleavage of the  $C_\alpha$ - $C_\beta$  bond (**route E1**) to produce vanillin [10]. In the same manner, guaiacol may be produced as an intermediate by another electron transfer, resulting in the cleavage of the  $C_\alpha$ - $C_1$  bond (**route E2**) of 1-guaiacyl-propanol. This intermediate may be subjected to further pyrolytic reaction. In contrast, the addition of a hydroxyl radical to the  $C_\beta$  radical (**route F**) forms a guaiacyl-2-propanol intermediate. Then, a proton radical displacement from the  $C_\beta$ -hydroxyl group of the intermediate produces the  $C_\beta$ -carbonyl structure (**route F1**) and produces 1-guaiacyl-2-propanone [11]. The proposed formation pathways of products [5], [7], [8] and [9] are shown in Figure 4. The formation of (*E*)-4-(1-propenyl)-*o*-cresol [8] occurs via methoxyl group rearrangement in multiple reaction steps. First, the starting material undergoes rearrangement from the methoxyl group to epoxide, which is initiated by the proton radical donation from the methoxyl group, followed by intermolecular radical coupling. The epoxide is then opened by the cleavage of the O-C (aromatic) bond to form the hydroxymethyl group, and a hydroxyl radical is eliminated to form (*E*)-4-(1-propenyl)-*o*-cresol [8] (**route I**). These reaction mechanisms have been proposed by Asmadi et al. (11). (*Z*)-4-(1-Propenyl)-*o*-cresol [9] is formed by the isomerisation reaction (**routes D and G**) of the product [8]. (*E*)-Isoeugenol is also undergoes homolytic cleavage at the saturated  $C_\beta$ - $C_\gamma$  bond (**route H**) to produce 4-vinylguaiacol [5], and the subsequent homolytic

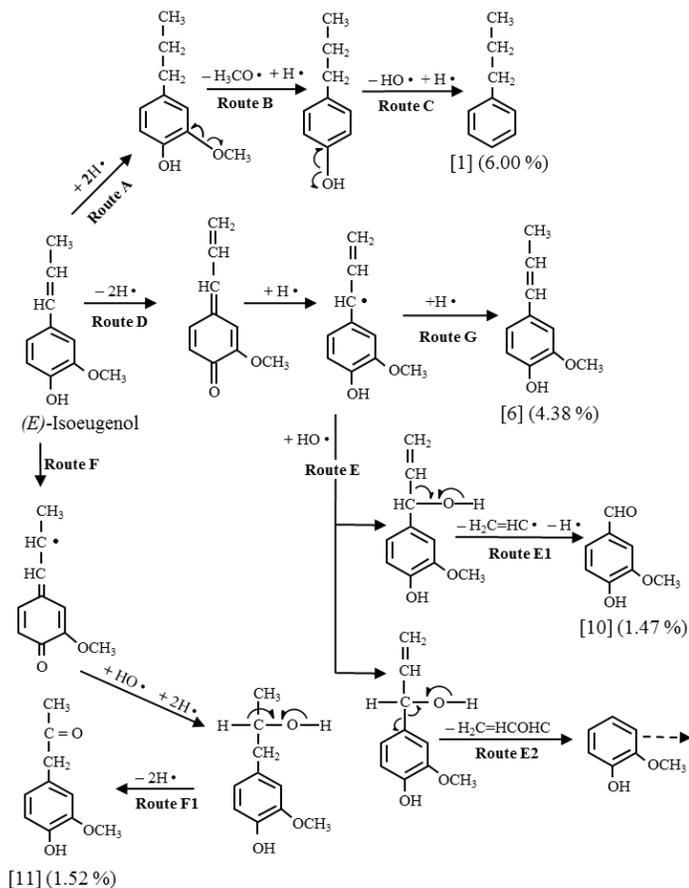


Fig.3. Proposed pathways for the formation of products [1], [6], [10] and [11]

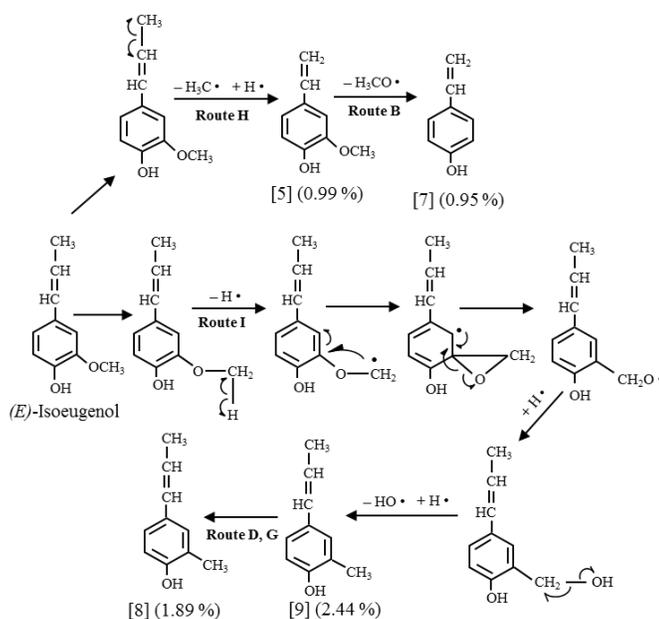


Fig.4. Proposed pathways for the formation of products [5], [7], [8] and [9]

displacement of a methoxyl group yields 4-vinylphenol [7] (**route B**). Generally, 4-vinylphenols are known as typical pyrolysates from softwood and herbaceous species (12). 4-Vinylphenol is produced via demethoxylation of 4-vinylguaiacol from softwood pyrolysis, and produced via C<sub>β</sub>-C<sub>γ</sub> scission of *p*-coumaryl ester from herbaceous plants pyrolysis (13).

The proposed formation pathway of product [2] is illustrated in Figure 5. The cyclohexadiene-1-one structure is derived from the guaiacol intermediate (**route J**) produced from (*E*)-isoeugenol by route D, E and E2. Carbon monoxide is then abstracted from cyclohexadiene to yield the corresponding pentadienyl biradical followed by intermolecular coupling to form the cyclopentadiene structure. The unsaturated bond in this intermediate structure is subjected to homolytic electron transfer to form different two cyclopentenyl biradicals. These biradicals couple with each other to form a polycyclic compound. Naphthalene structures are produced by the intermolecular arrangement associated with the release of four proton radicals, a methyl radical displacement from the methoxyl group and an arrangement of the methoxyl group to the methyl group (**route J, I**). In this reaction route, cyclopentadiene is an important intermediate for the formation of naphthalene. This pathway has been proposed by Egsgaard et al. (14). An alternate formation mechanism was proposed by Evans et al. (15) and Melius et al. (16), who reported that the naphthalene structure is produced by the combination and rearrangement of two

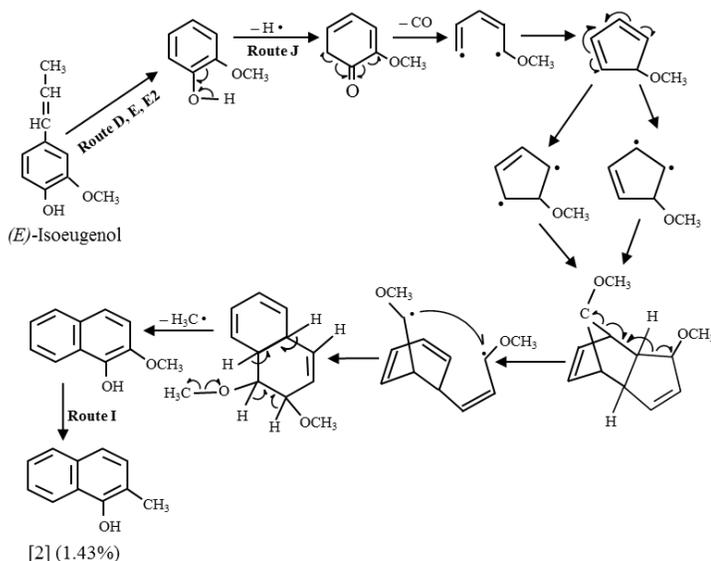


Fig. 5. Proposed pathway for the formation of product [2]

cyclopentadienyl radicals (Figure 6). The pathway reported by Egsgaard includes the two-point coupling of biradical structures, while the pathway proposed by Evans includes the one-point coupling of two radical structures. In both pathways, pentadienyl radical is a key intermediate, as shown by Khachatryan et al. (17).

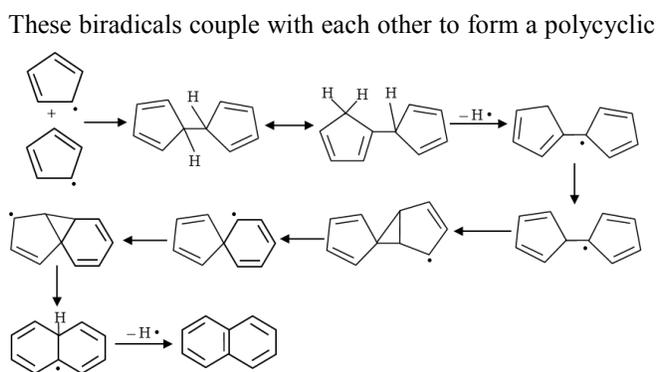


Fig. 6. Formation pathway of naphthalene proposed by Evans et al.

The proposed formation mechanisms of products [3] and [4] are shown in Figure 7. (*E*)-isoeugenol undergoes electron transfer to form eugenol quinone methide (**route K**), which is converted to two cyclohexadiene biradicals by the homolysis of the C<sub>β</sub>-C<sub>γ</sub> unsaturated bond. Intermolecular radical coupling between C<sub>γ</sub> and C<sub>2</sub> followed by electron transfer (**route L**) yields the 7-Methoxy-6-hydroxyindene [3]. Alternatively, intermolecular radical coupling between C<sub>γ</sub> and C<sub>6</sub> followed by electron transfer (**route M**) yields the 5-methoxy-6-hydroxyindene [4].

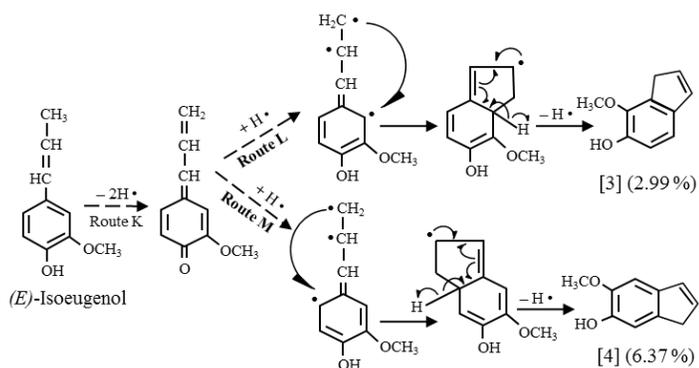


Fig. 7. Proposed pathways for the formation of products [3] and [4]

## 2) Identification and formation of pyrolysates from (*E*)-coniferylalcohol

The TIC obtained for the Py-GC/MS of (*E*)-coniferylalcohol at 600 °C is shown in Figure 8. In the major pyrolysate, 12 products and unreacted starting material were detected and identified, and mechanisms for product formation were proposed. The proposed formation pathways of products [6], [13], [15], [16] and [19] are shown in Figure 9. Product [19] is formed by isomerization via the reaction described in Figure 3 (**route D**). The formation of (*E*)-isoeugenol [16] is initiated by the elimination of the C<sub>γ</sub>-hydroxyl group on the side chain of (*E*)-coniferylalcohol followed by the addition of a proton to the resulting methylene radical (**route N**). Two pathways are proposed for the formation of (*Z*)-isoeugenol [6]: one from product [16] via isomerization (**route D**) and a second from product [19] via reduction (**route O**). Both pathways should occur during the pyrolysis of (*E*)-coniferylalcohol. The formation of (*E*)-eugenol [15] is initiated by the homolytic displacement of a C<sub>γ</sub>-hydroxyl group followed by the transfer of an electron (**route O**). Product [15] is then subjected to further pyrolysis to form a quinone methide intermediate in association with C<sub>α</sub>-C<sub>β</sub> cleavage (**route P**); electron transfer then occurs in the quinone methide structure to form product [13]. The proposed formation pathways of products [10], [12] and [20] are illustrated in Figure 10. (*E*)-Coniferylaldehyde [20] is formed by the elimination of two proton radicals from the C<sub>γ</sub>-hydroxymethyl group of the side chain (**route Q**). This reaction is initiated by the homolytic elimination of proton radical from a C<sub>γ</sub>-hydroxyl group. Guaiacol [12] and vanillin [10] are produced from the C<sub>α</sub> radical of (*E*)-isoeugenol, as shown in Figure 3. The proposed formation pathways of products [5],

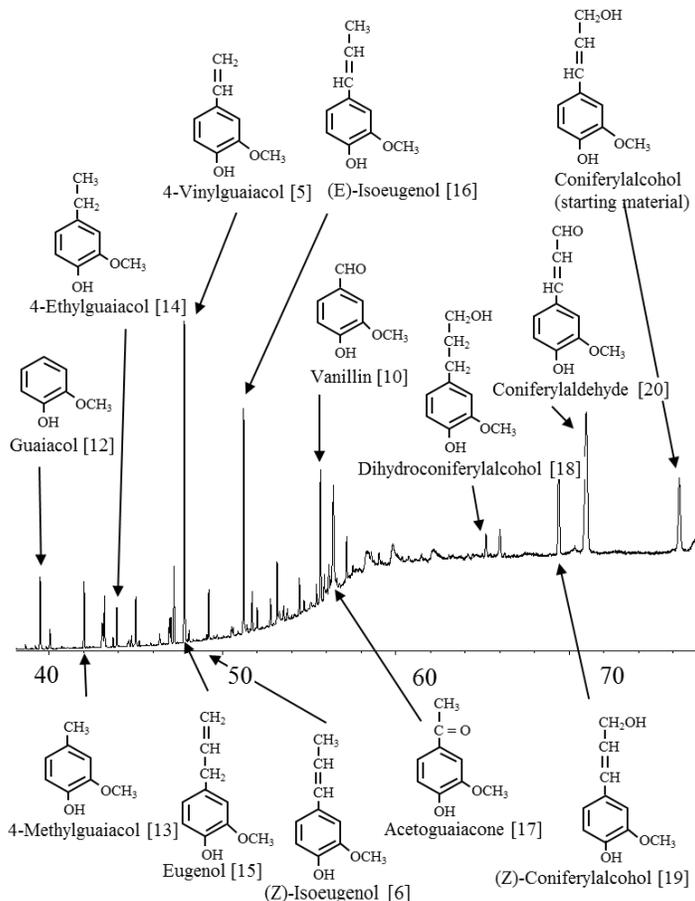


Fig.8. Total ion chromatogram for the Py-GC/MS of (*E*)-coniferyl alcohol at 600 °C

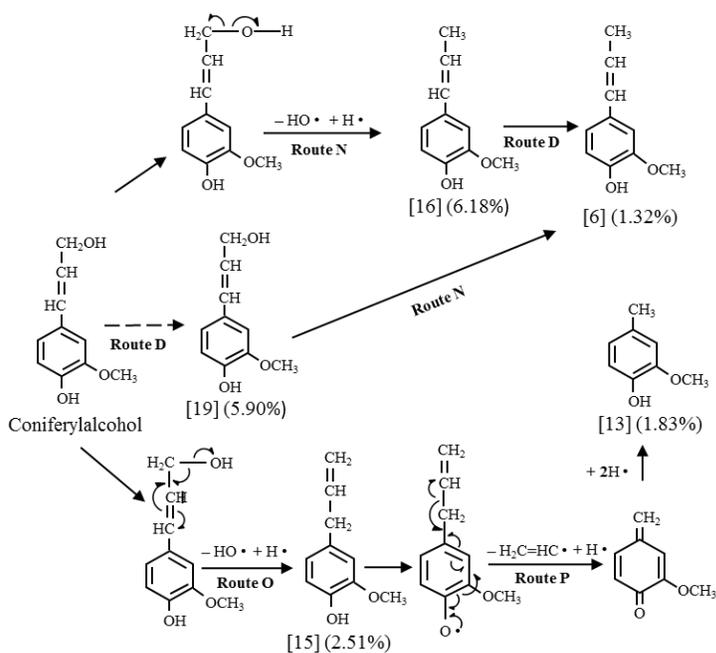


Fig.9. Proposed pathways for the formation of products [6], [13], [15], [16] and [19]

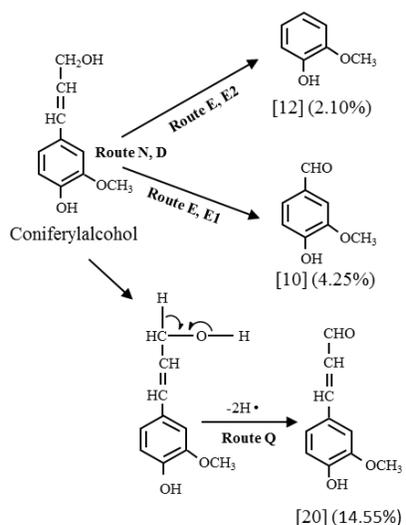


Fig.10. Proposed pathways for the formation of products [10], [12] and [20]

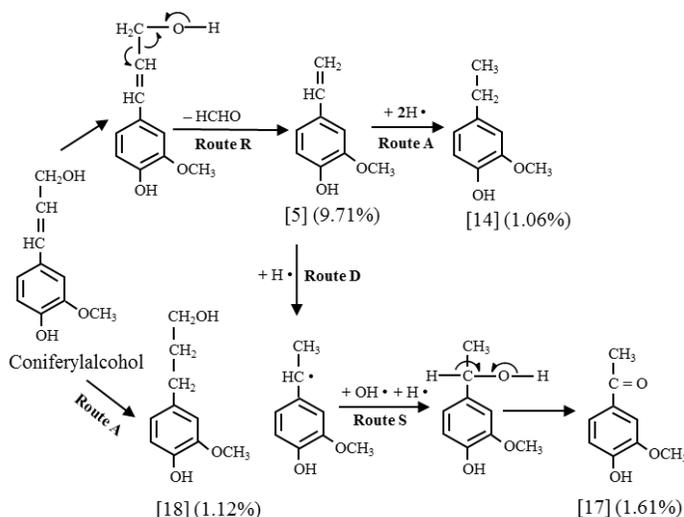


Fig.11. Proposed pathways for the formation of products [5], [14], [17] and [18]

[14], [17] and [18] are illustrated in Figure 11. 4-Vinylguaiacol [5] is formed from (*E*)-coniferylalcohol via the elimination of a proton radical from the C<sub>7</sub>-hydroxyl group followed by the displacement of formaldehyde

to generate a C<sub>β</sub>-methine radical followed by the addition of a proton radical (**route R**). Ethylguaiacol [14] is then obtained via the addition of two proton radicals to the C<sub>α</sub>-C<sub>β</sub> unsaturated bond on the side chain of product [5] (**route A**). Product [5] is subjected to another pyrolysis and forms a C<sub>α</sub>-radical structure via quinone methide (**route D**). A hydroxyl radical then adds to a C<sub>α</sub>-radical to form apocynol followed by the release of a proton radical from the C<sub>α</sub>-hydroxyl group to produce acetoguaiacone [17] (**route S**). The most abundant compounds produced from the pyrolysis of coniferylalcohol at 650 °C have been reported to be 3-(4-hydroxy-3-methoxyphenyl)-2-propenal, trans-isoeugenol, vanillin, 2-methoxy-4-propyl-phenol and homovanillic acid (Harman et al. 2013). 4-Vinylguaiacol could not be detected as a major product in that investigation, although 4-vinylguaiacol is the highest yield product in the pyrolysate from (*E*)-coniferylalcohol. This discrepancy is primarily explained by the difference in pyrolysis temperature; Harman et al. performed at the pyrolysis at high temperature. This subject is discussed in more detail in Section 3.5.

### 3) Identification and formation of pyrolysates from (*E*)-coniferylaldehyde

The TIC) obtained for the Py-GC/MS of (*E*)-coniferylaldehyde at 600 °C is shown in Figure 12. In the major pyrolysate, 12

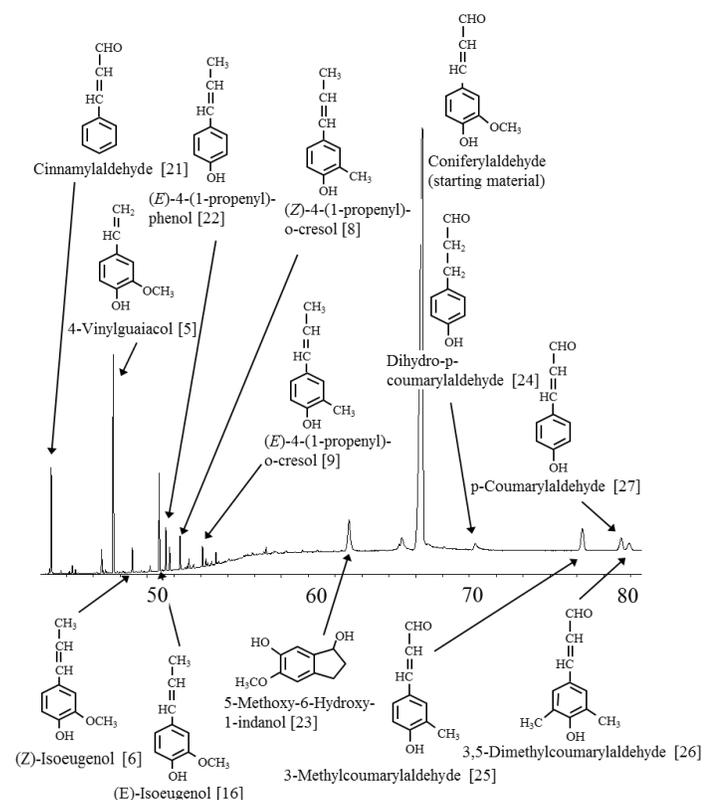


Fig.12. Total ion chromatogram for the Py-GC/MS of (*E*)-coniferylaldehyde at 600 °C

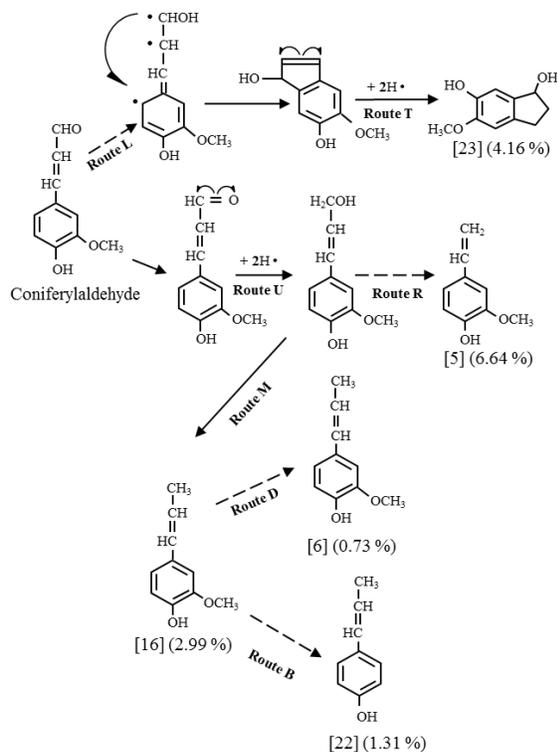


Fig.13. Proposed pathways for the formation of products [5], [6], [16], [22] and [23]

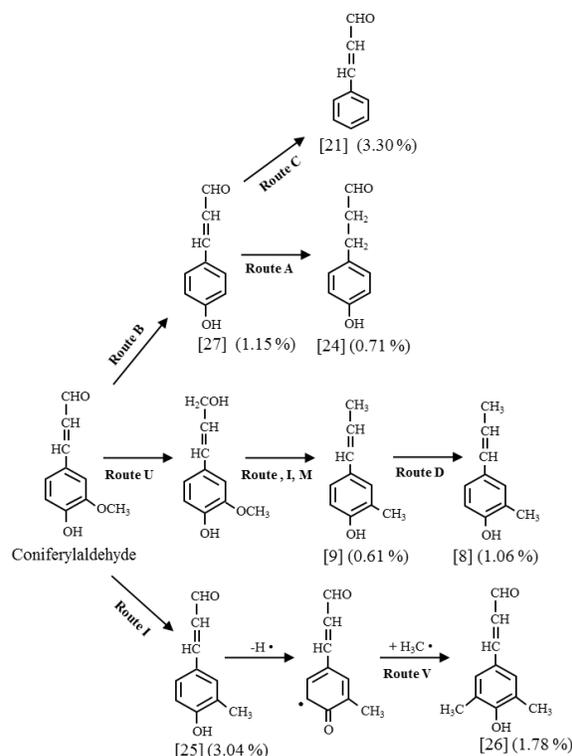


Fig.14. Proposed pathways for the formation of products [8], [9], [21] and [24]-[27]

products and unreacted starting material were identified, and mechanisms for product formation were proposed. The proposed formation pathways of products [5], [6], [16] and [22], [23] are illustrated in Figure 13. 5-Methoxy-6-hydroxy-1-indanol [23] is formed in the same manner as product [4], except for the final addition of two proton radicals (route T). Therefore, product [23] has an indanol structure, whereas product [4] has an indene structure. 4-vinylguaiacol [5] is formed via an (*E*)-coniferylalcohol intermediate. A C<sub>γ</sub>-aldehyde group of (*E*)-coniferylaldehyde is reduced to an alcohol group by the addition of two proton radicals (route U), and the (*E*)-coniferylalcohol intermediate is further pyrolyzed to produce 4-vinylguaiacol [5] (route R), as shown in Figure 11. The coniferylalcohol intermediate is also reduced to (*E*)-isoeugenol [16] (route N). (*E*)-Isoeugenol is isomerization (route D) and demethoxylated (route B) to produce (*Z*)-isoeugenol [6] and 4-(1-propenyl)-phenol [22], respectively. The proposed formation pathways of products [8], [9], [21] and [24-27] are illustrated in Figure 14. (*E*)-*p*-Coumarylaldehyde [27] is formed by the homolytic elimination of a methoxyl group from (*E*)-coniferylaldehyde (route B). Under further pyrolysis, product [27] forms (*E*)-cinnamaldehyde [21] via the displacement of the phenolic hydroxyl group (route C). The saturation of the C<sub>α</sub>-C<sub>β</sub> unsaturated bond by two proton radical additions (route A) then forms dihydro-*p*-coumarylaldehyde [24]. (*E*)-4-(1-Propenyl)-cresol [9] is produced by the reduction of (*E*)-coniferylaldehyde via a (*E*)-coniferylalcohol intermediate (routes U, I and N), and the product [9] is isomerized (route D) to form (*Z*)-4-(1-propenyl)-cresol [8]. (*E*)-3-Methylcoumarylaldehyde [25] is produced from (*E*)-coniferylaldehyde via the rearrangement of the methoxy group to a methyl group (route I). The addition of a methyl radical to the C<sub>6</sub> position of the product [25] via a quinone methide intermediate then yields 3,5-dimethylcoumarylaldehyde [26].

#### 4) Identification and formation of pyrolysates from ferulic acid

The TIC obtained for the Py-GC/MS of ferulic acid at 600 °C is shown in Figure 15. Six products were identified in the major pyrolysate, and mechanisms for their formation were proposed. The proposed formation pathways of

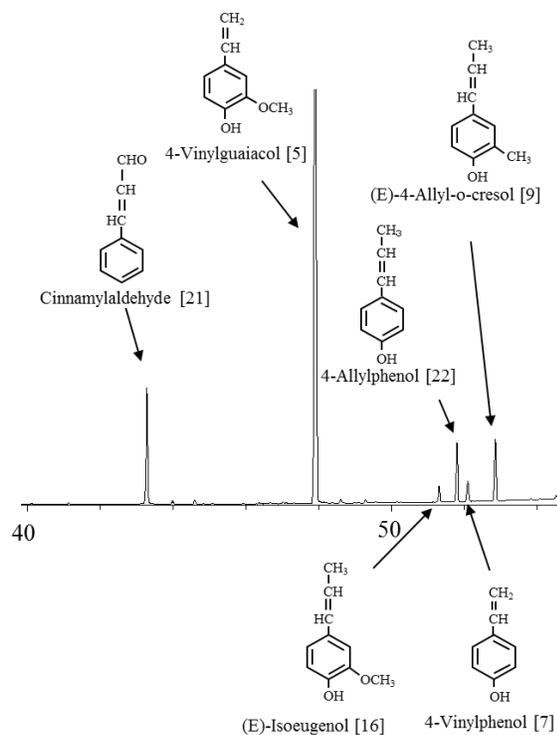


Fig.15. Total ion chromatograph for the Py-GC/MS of ferulic acid at 600 ° C

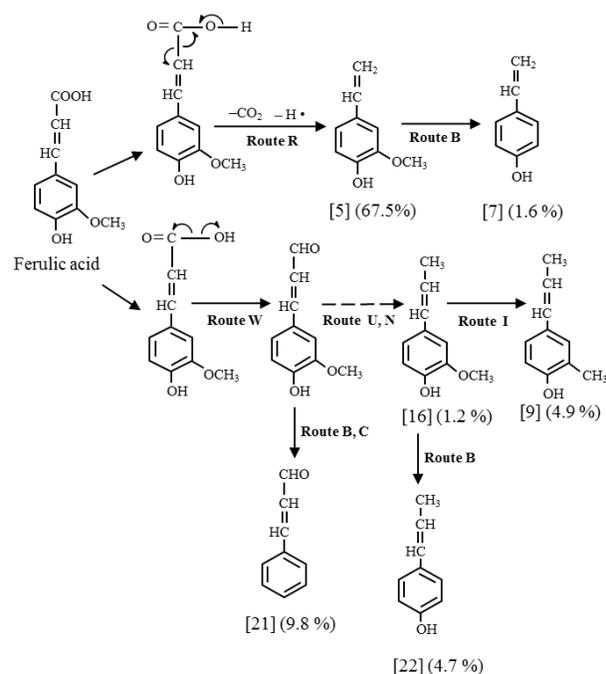


Fig.16. Proposed pathways for the formation of products [5], [7], [16], [21] and [22]

products [5], [7], [9], [16], [21] and [22] are illustrated in Figure 16. The  $C_{\beta}$ - $C_{\gamma}$  cleavage of ferulic acid and the following release of carbon dioxide is induced by the  $C_{\gamma}$ -proton radical elimination to produce 4-vinylguaiacol [5] (**route Q**) as the major product (67.5%). A part of the product [5] is further pyrolyzed (**route B**) to produce 4-vinylphenol [7]. Alternatively, the elimination of  $C_{\gamma}$ -hydroxyl radical produces (*E*)-isoeugenol [16] via coniferylaldehyde intermediate (**routes W, S and N**). 4-(1-Propenyl)-*o*-cresol [9] is provided from product [16] via

methyl group rearrangement (**route I**). 4-(1-Propenyl)-phenol [22] is also provided from product [16] via the homolytic displacement of a methoxyl group (**route B**). Cinnamaldehyde [21] is formed from the (*E*)-coniferylaldehyde intermediate by the homolytic eliminations of methoxyl and hydroxyl groups (**routes B and C**).

### 5) Effects of pyrolysis temperature on the pyrolysate composition and the yields of major products

The effects of pyrolysis temperature on the pyrolysate compositions from four phenyl propanoids were estimated from the TIC peak areas of Py-GC/MS. The recovery yields of the starting materials reflected the reactivity under experimental pyrolytic conditions. The recovery yields of the starting materials, (*E*)-isoeugenol, (*E*)-coniferylalcohol, and (*E*)-coniferylaldehyde at different pyrolysis temperature are illustrated in Figure 17. (*E*)-Ferulic acid is not shown in the figure because the compound could not be detected in Py-GC/MS. Increasing the pyrolysis temperature from 400 to 500 °C generated no differences in the recovery yields, whereas the recovery yields decreased when the pyrolysis temperature was further increased to 600 °C. A comparison of the starting materials shows that for all experimental temperatures, the highest recovery yield was obtained for (*E*)-isoeugenol and (*E*)-coniferylaldehyde, while the lowest yield was obtained for (*E*)-coniferylalcohol. The high stability of (*E*)-coniferylaldehyde may be caused by the strong conjugate system in the molecular structure.

For (*E*)-isoeugenol, (*Z*)-isoeugenol [6] and 1-guaiacyl-2-propanone [11] were formed in high yield at 400 °C, and vanillin [10] was formed in the same yield at each temperature, as shown in Figure 18. These results indicate that the  $C_{\alpha}$  radical of quinone methide is easily derived at low temperature; therefore, the isomerization (**route D**)

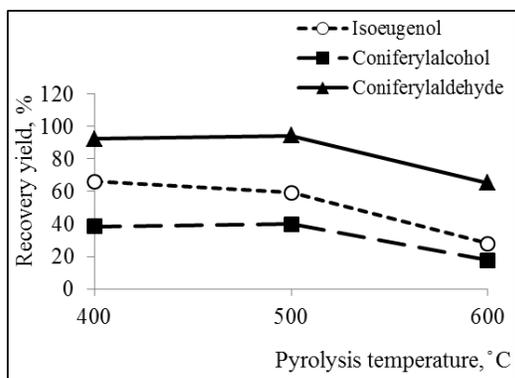


Fig.17. Recovery yields of starting materials at various pyrolysis temperatures

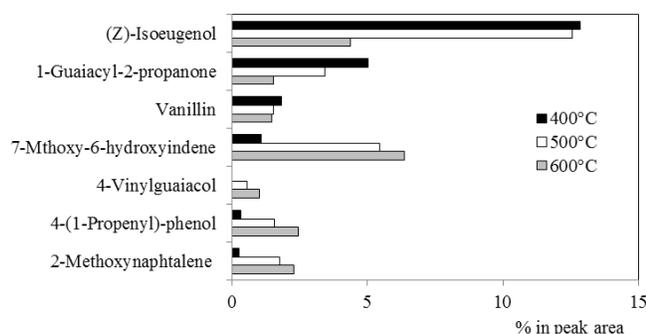


Fig.18. Effect of pyrolysis temperature on the yields of major products from (E)-isoeugenol

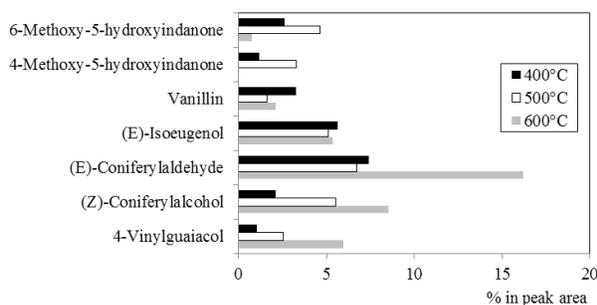


Fig.19. Effect of pyrolysis temperature on the yields of major products from (E)-coniferylalcohol

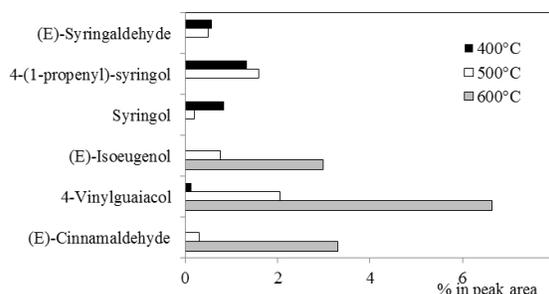


Fig.20. Effect of pyrolysis temperature on the yields of major products from (E)-coniferylaldehyde

isoeugenol [6], 1-guaiacyl-2-propanone [11] and vanillin [10]. 4-Vinylguaiacol [5] was a minor product and was not detected at low pyrolysis temperature (400 °C). The yields of 4-(1-propenyl)-phenol [22] and bicyclic compounds such as 7-methoxy-6-hydroxyindene [3] and 2-methoxy-1-naphthalene [2] increased with the pyrolysis temperature. Therefore, demethoxylation and intermolecular coupling were accelerated by a high pyrolysis temperature.

In the case of (E)-coniferylalcohol, pyrolysis temperature had no effect on the product yields of vanillin [10] and (E)-isoeugenol [16], as shown in Figure 19. These results indicate that the homolytic displacement of the aliphatic C<sub>γ</sub> hydroxyl group followed by the addition of a proton radical to the C<sub>γ</sub> position (route M) occurred at low temperature and were not accelerated by increasing pyrolysis temperature. Isomerization of (E)-coniferylalcohol to the (Z) form [19] was facilitated by increasing temperature. The formations of (E)-Coniferylaldehyde as a major product and 4-vinylguaiacol [5] were accelerated by increasing temperature. Bicyclic compounds such as 4-methoxy-5-hydroxyindanone and 6-methoxy-5-hydroxyindanone are formed at low temperatures in very low yields. The results indicate that heterocyclic products are unstable under high-temperature pyrolysis conditions.

For (E)-coniferylaldehyde, the typical reaction pathways observed under low- and high-temperature pyrolysis conditions are shown in Figure 20. Syringyl-type products such as syringaldehyde, 5-methoxy-isoeugenol and syringol were formed by low-temperature pyrolysis but were hardly detected in the pyrolysates from pyrolysis at 600°C. On the other hand, 4-vinylguaiacol was a major product, and its formation reaction was accelerated by increasing the pyrolysis temperature. This suggests that the presence of a C<sub>γ</sub>-aldehyde group greatly influences the formation of 4-vinylguaiacol. Isoeugenol and cinnamylaldehyde, which were not detected in the pyrolysates from pyrolysis at 400 °C, were formed in high yield during pyrolysis at 600 °C.

## Conclusion

Four propanoids with different side-chain C<sub>γ</sub> groups were subjected to analytical pyrolysis with Py-GC/MS to elucidate the effects of these groups on pyrolysis composition, and the formation pathways of the pyrolysis products were proposed. The basic reaction pathways occurred around the oxygen C–O and H–O bonds and involved homolytic cleavage. Therefore, many of the products were formed by the elimination and addition of

proton and hydroxyl radicals, the demethylation and demethoxylation of the methoxyl group adjacent to the aromatic ring, the displacement of C<sub>γ</sub> hydroxyl radical and the (E) to (Z) form isomerisation on the unsaturated side-chain bond. The formation routes of some products were initiated by the formation of a quinone methide intermediate.

In the case of (*E*)-isoeugenol, the major product, 5-methoxy-6-hydroxyindene [4], formed via intermolecular radical coupling, and the formation reaction was accelerated by increasing the pyrolysis temperature. The second major product, (*Z*)-isoeugenol [6], was produced by isomerisation, and it was dominantly formed by low-temperature pyrolysis. In the case of (*E*)-coniferylalcohol, many of the pyrolysates were obtained at high temperatures. However, bicyclic compounds such as 4-methoxy-5-hydroxyindanone and 6-methoxy-5-hydroxyindanone were predominantly produced by intermolecular radical coupling between C<sub>5</sub>-radical and C<sub>γ</sub>-radical position under low-temperature conditions. The major reaction pathways are the displacement of two protons on the C<sub>γ</sub>-hydroxyl radical to form (*E*)-coniferylaldehyde and the isomerisation of the (*E*) form to the (*Z*) form. In the case of (*E*)-coniferylaldehyde, 4-vinylguaiacol [5] and (*E*)-cinnamaldehyde [21] were formed predominantly by high-temperature pyrolysis. On the other hand, syringyl-type products were produced by the addition of methoxyl radicals to the C<sub>5</sub>-positions of aromatic rings, and these products were formed in undetectable or hardly detectable yields at 600 °C.

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