

Chemistry and Biochemistry of Aromatic Compounds with β (8)-O-4' Linkages in Forest Biomass

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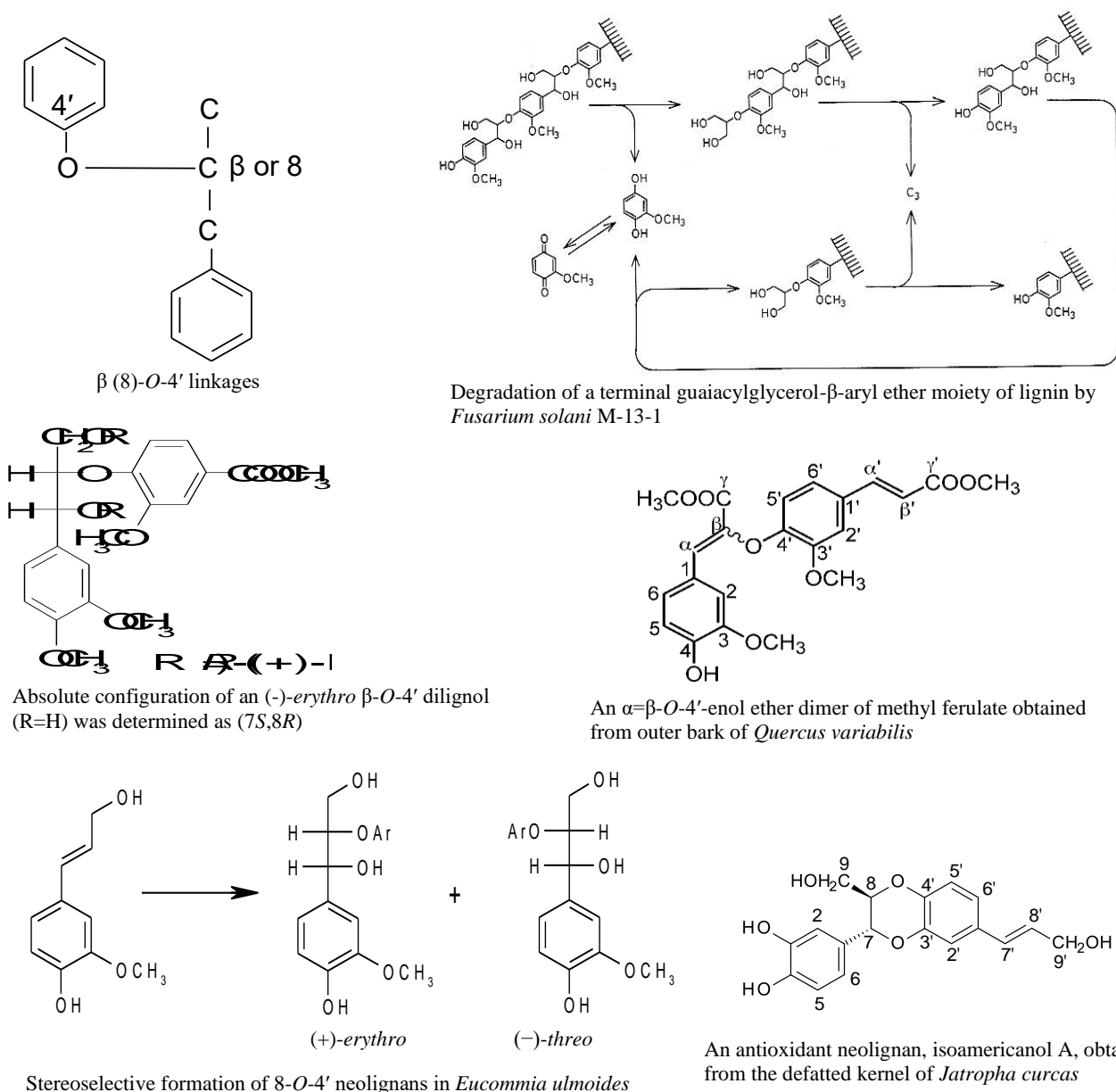
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Graphical Abstract



Abstract

Arylglycerol- β -aryl ether (β -O-4') bonds or arylglycerol-8-O-4'-aryl ether (8-O-4') bonds are predominant ones in lignin, and also present in neolignans and suberin aromatic domains. Therefore, their linkages are most major between the monomeric units of natural polymers and dimeric or higher low-molecular weight compounds, except for the glycosidic bonds of polysaccharides. Research results by the authors since 1977 on the chemistry and biochemistry of aromatic compounds with β (8)-O-4' linkages in forest biomass are as follows.

1. Arylglycerol- β -aryl ether (β -O-4') dimers with a C3 or C1 side chain on the β -aryl groups were prepared in high yields by convergent synthesis [1].
2. The degradation of lignin by a fungus, *Fusarium solani* M-13-1 was studied using lignin substructure model compounds [2]. And the chemical mechanism of degradation of the β -O-4' dimers, arylglycerol- α,β -diaryl ether trimers with a non-cyclic benzyl aryl ether (α -O-4') bond, and α -ketone compounds of the β -O-4' dimers which was a degradation intermediate of the trimer was elucidated.
3. The above α -ketone compound is racemic (β RS). This ketone was found to be stereoselectively reduced by the fungus to give a β -O-4' dimer. Its *erythro*/*threo* ratio was 9:1 and each was enantiomerically pure. The absolute configuration of the *erythro* and *threo* forms was determined as (α S, β R) and (α S, β S), respectively. This reduction was found to occur from the *re* face of the α -ketone [3].
4. In order to elucidate the structure of the aromatic domain of suberin, methanolysis of the outer bark of *Quercus variabilis* and *Q. suber* was performed. As a result, an $\alpha=\beta$ -O-4'-enol ether dimer of methyl ferulate was isolated and identified, suggesting the presence of a polymer structure of ferulic acid ester in suberin [4].
5. Biosynthesis and stereochemistry of 8-O-4' neolignans in *Eucommia ulmoides* were studied [5]. A cell-free extract of the stems was found to catalyze the stereoselective conversion of coniferyl alcohol (CA) to (+)-*erythro*- and (-)-*threo*-guaiacylglycerol-8-O-4'-coniferyl alcohol ethers in the presence of hydrogen peroxide. In addition, the diastereomer of guaiacylglycerol-8-O-4'-sinapyl alcohol ether present in the stems was identified as the *erythro* form. Feeding experiments showed that it was produced by stereoselective cross-coupling of CA with sinapyl alcohol.
6. One lignan (3,3'-bisdemethylpinoresinol) and seven neolignans (five dimers and two trimers) with catechol nuclei were isolated and identified from the defatted kernel of *Jatropha curcas* L., which has been cultivated in the tropics, Thailand for biodiesel fuel production [6]. All of them were found to be optically active and to have high antioxidant activity. All of the neolignans had a 1,4-benzodioxane ring. Among them isoamericanol A with 8-O-4' and 7-O-3' linkages and americanol A with 8-O-3' and 7-O-4' linkages were the main.

Keywords: Lignin; neolignan; suberin; biodegradation; biosynthesis.

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Nationality: Japanese. Born in Kanagawa Prefecture in 1954 (Age 68).
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Academic background:

1973-77: Kyoto University, Faculty of Agriculture, Dept. of Wood Science and Technology.

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1989: Doctor of Agriculture, Kyoto University. Thesis title: Degradation of lignin substructure model compounds by *Fusarium solani* M-13-1

Career history:

1982-2020: Research Associate (82-89), Associate Professor (89-97), Professor (97-2020), Faculty of Agriculture, Kagawa University.

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