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LIGNIN IN THE RESTORATION OF THE CULTURAL HERITAGE

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ABSTRACT

The restoration and recovery of the cultural heritage is a challenging field for the application of the basic sciences, the engineering and the definition and maintenance of a nation identity mostly in Latin America home of unique artists. The colonial artists were forced to adapt to the new world and found that American woods, like the common cedar ("Cederalla Odorata") provides excellent properties of durability, malleability and resistance to the fungus and insects; these properties are bound to the nature of lignin and its precursors, the alcohols p-Coumaryl, coniferyl, and sinapyl, molecules responsible in the terrestrial plants of these characteristics; in this work we will study some of their structural, electronic and optical properties of these molecules, using the MNDO, AM1, PM3 and ZINDO/S semiempirical methods of the computational chemistry, also we will outline some general strategies for the materials design based on the specialty polymers from lignin.

Keywords: Lignin, Semiempirical Methods, Restoration

RESUMEN

La restauración y recuperación de los bienes culturales es un campo desafiante para la aplicación de las ciencias básicas, la ingeniería, la definición y el mantenimiento de la identidad nacional especialmente para América Latina hogar de artistas únicos. Los artistas coloniales, privados de sus materias primas se vieron forzados a adaptarse al nuevo mundo y encontraron en las maderas americanas, especialmente en el cedro común ("Cederalla Odorata") excelentes propiedades de durabilidad, maleabilidad y resistencia a los hongos e insectos; estas propiedades están íntimamente ligadas a la naturaleza de la lignina y sus precursores, los alcoholes p-cumaril, coníferil, y sinapil, moléculas responsables en las plantas terrestres de estas características; en este trabajo estudiaremos algunas de las propiedades estructurales, electrónicas y ópticas de estos precursores, utilizando los métodos semiempíricos de la química computacional MNDO, AM1, PM3, y ZINDO/S.

Palabras Clave: Lignina, Métodos Semiempíricos, Restauración.

The lignin is a highly complex biopolymer, second biggest source of carbon in the planet after the hydrocarbons, it undergoes vital functions for the terrestrial plants as molecule in charge of the structural strength, conduction of water and defense against pathogen agents; despite this roles, its study has been limited by the nature of this molecule, the fact that the structural pattern can vary from species to species has make almost impossible to generate a detailed macromolecular model of it. The main studies of the structural, electronic and optic properties have been carried out on samples obtained form the processes of wood pulp extraction in the production of paper, where the conditions of the material don't reflect the true nature of lignin due to the highly destructive procedures required to separate the cellulose fibers that lignin binds together. For these and others reason studies of the lignin properties are more easily carried out from the study of its precursors, which have already been identified and can be synthesized throughout

the reactive dehydrogenization methods. Figure 1 shows the three units attached in determined patterns outline lignin; in softwoods like cedar, witch was the mainly favored wood by the colonial artists, the most abundant lignin precursor in is the coniferyl alcohol, (90 - 95% of the total units) [1].

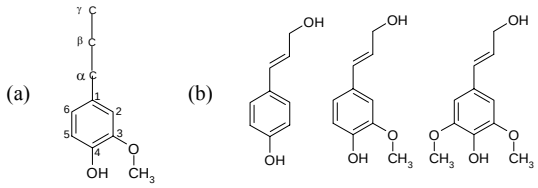

Figure 1. Schematic representation of the structures. (a) Basic unit of phenylpropane C9 (numbers and letters aid the identification of the bond type). (b) The three precursors of lignin in their basic form, in their order: p-Coumaryl Alcohol; Coniferyl Alcohol and Sinapyl Alcohol.

During the last two decades, great efforts have been dedicated to the study of the lignin chemistry and reactions; in many cases to alter it genetically so the lignin content in plants as the forages for cattle and trees for paper production diminishes to increase the efficiency of industrial processes.

Figure 2 shows the generally accepted reaction outlines that lead to the formation of the most abundant dimmeric products of the coniferyl alcohol; each one of these products is formed through an initial radical - radical joining followed by a rearrangement or a nucleophilic addition of water. The nomenclature of the products is derived of the places where the initial radical - radical joining takes place; for example, the β-β dimmer is formed by the joining between the β carbons of both molecules [1].

The chemical and technological aspects of lignin modification products are huge, beginning with the great amounts of raw material available from the paper production industries that are usually disposed or burn as a secondary energy source, these products have great energy content due to the presence of the aromatic ring, its carbon skeleton presents a wide range of reaction sites for substitution and addition reactions, great compatibility with basic chemicals like Sulfur, Sodium and Nitrogen, good absorbent, adhesion and ion exchange properties, and also are a direct source of various kinds of phenolic and aromatic compounds [6]. In this work, we will investigate some of the structural, electronic and optical properties of the of the lignin precursors, by means comparison of the results obtained from the application of the semiempirical methods (MNDO[2], AM1[3], PM3[4], and ZINDO/S[5]).

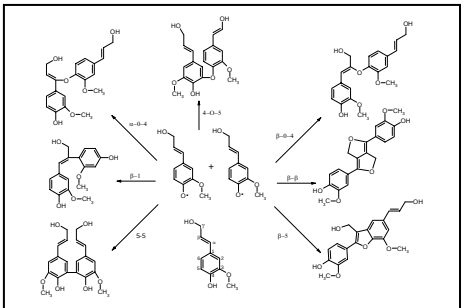

Figure 2. Reactions that lead to the formation of some of the most abundant dimmeric products of the lignin precursors

Methodology

We will obtain theoretically the geometries of the three precursors using the semiempirical methods of the NDO[7] (Neglect of Differential Overlap) family, which are design to work properly with organic molecules with elements of the first two rows of the periodic table We will use the methods PM3, AM1, and MNDO for the precursors geometry studies, due to the fact

that the MNDO method presents lower energy values this one has been elected for the dimmers geometry optimization. For the simulation of the optical spectrum, the ZINDO/S method has been used in the interaction configuration mode; this methodology is broadly in the study of organic molecules. [11,13].

Results and Discussion

Figure 3. Heat of Formation of the lignin precursors optimized with the methods PM3, AM1 y MNDO, in kcal/mol.

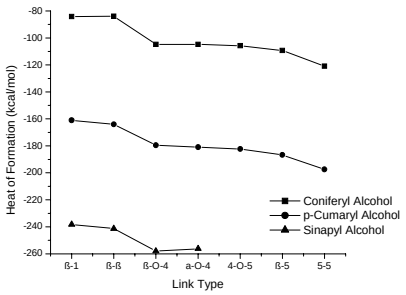

Figure 4. Heat of formation of the most abundant dimmeric products of lignin, optimized with MNDO method in kcal/mol

Figure 3 shows the behavior of the precursors heat of formation from the geometry optimization in the three methods used, it is observed that the MNDO gives us the best results, for that reason we choose it for the observations of the remaining structures, it is important to notice that although the methods AM1 and PM3 are generally considered an improvement of the original MNDO method, the results in this case don't support such statement, this is due to the fact that these experiments have been carried out every time a new method of the NDO family is designed (MNDO is the first one) and so the inherent systematic errors to for the parameters had been minimized.

Figure 4 shows the heat of formation values obtained for the linkages present in lignin [2] and although the 5-5 linkage offers lower values than β-O-4 it has been confirmed that β-O-4 is this the one that should be more frequently found the structure just as it is reported in literature [3]; this because the 5-5 linkage as the β-β β-1, all of the type C-C don't allow a polymerization beyond two units, they close the structure preventing that a third unit links to any of the carbons in the reaction sites. This is justified the because the carbon ($1s^2$ $2s^2$ $2p^2$) can unite to four more carbons, but, in a polymerization by means of the C-C linkage mechanism a third will find complete the octet in both units; in contrast the β-O-4, α-O-4 and 4-O-5 are of the type C-O-C where the presence of the oxygen bridge allows the addition of any amount of units, therefore we confirm the theoretical data that shows the β-O-4 linkage as the most abundant and stable [10]; for the Sinapyl alcohol something similar happens but at the dimerization level, in connections that involve additions in the position 5 of the benzene ring, the second unit will always find the octet complete; and so the addition of more units is impossible; the behavior of the heat of formation values is almost regular, with about 40 kcal/mol of difference between the higher and lower values for the p - Coumaryl and Coniferyl alcohols, and 20 kcal/mol for Sina

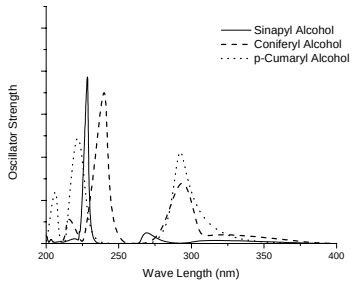

Figure 5. UV spectra of lignin precursors, wave length in nm and oscillator intensity in arbitrary units.

pyl alcohol, this suggests a determined behavior in the quantity of necessary energy to create a structure in a specific direction. From the observations of the precursors structural characteristics we can affirm that; inside the aromatic ring, the values on the average bond lengths and angles are respectively 1.417 Å and 119.998°, and for the main chain the values are respectively 1.446 Å and 123.888°; the torsion angle for the connections of chain is, on the average, 179.583 [11]. Figure 5 shows the ultraviolet spectra simulation of the lignin precursors obtained with the ZINDO/S [5] method, the are located in the overall range from 200 to 260 nm which concords with the experimental values found in literature also the difference observed with the absorption range can be easily explained based on the fact that the experimental values were obtained with analytical samples that contain an undetermined number of fragmented units contaminated with various metals (Na and S typically) which alter the absorption ranges. [12]

In this work the best results were obtained through the MNDO method optimizations, confirming that the linkages with more possibilities of prevailing in the macromolecular structure o softwood lignin is the β-O-4 due the nature of the Carbon - Oxygen - Carbon bridges that favors the structures growth, the resulting angle between planes that contain the benzene rings it is of approximately 120° being compatible with the reported results.

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