Application of New Methods for the Investigation of Lignin Structure

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The main cell wall phenolics, detrimental to forage digestibility (Jung, 1989), have been classified into core and “noncore” lignins, on the basis of their relative susceptibility towards hydrolysis. Noncore lignin consists of low-molecular weight phenolics, released from cell walls by mild hydrolyses, and is chiefly represented by ester-linked p-hydroxycinnamic acids (Hartley & Ford, 1989). As these noncore lignin components are discussed elsewhere (see chapter 9 by Ralph and Helm in this book), the focus here will be on core lignins. Core lignins are the highly condensed phenylpropanoid cell wall polymers that are largely resistant to mild degradation procedures. They are composed of p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) building units, in various proportions according to their origin. Gymnosperm lignins are chiefly constituted of G units. Angiosperm lignins are a mixture of G and S units. In addition, grass lignins are composed of H, G, and S units. These phenylpropane units are interconnected by a series of ether and carbon-carbon linkages (Adler, 1977; Tanahashi & Higuchi, 1989), in various bonding patterns (Fig. 6-1). The most frequent interunit \( \beta-O-4 \) bonds are the targets of lignin depolymerization processes. In contrast, the other \( \beta-\delta \), \( \beta-1 \), \( \beta-\beta \), 5-5, and 5-0-4 interunit bonds (Fig. 6-1), referred to as the condensed bonds, are more resistant towards degradation. Their relative amounts are not yet clearly established. A lignin-building unit may be involved in one, two, or more bonding patterns, such as those depicted in Fig. 6-1. Besides these main substructures, there are other minor ones.

The objective of this chapter is to present the structural information gained from three analytical strategies recently developed in the field of lignin research or which have significantly benefited from instrumental strides. Structural information discussed herein concerns the monomer composition of lignins, their key functionalities, and their main interunit linkages. These are relevant with regard to forage research as it has been frequently emphasized that not only the lignin amount, but also the lignin structure influences the forage nutritional value (Jung, 1989). These structural features should