SUPPLEMENTAL INFORMATION

Calculation of 5-5' etherified moieties according to (9).

The amount of 5-5' etherified moieties was estimated using a modified procedure of a previously reported method (8, 9, 38). Accordingly, the resonance at 157-151 ppm embodies the signals of C-3 in 5-5' etherified structures, C-3/C-5 in etherified 4-O-5' structures, C-3/C-5 in syringyl units, as well as C-4 in etherified conjugated carbonyl structures and C-α in coniferaldehyde. The amount of etherified conjugated carbonyl moieties was estimated as the sum of vanillin and α-CO/β-O-4, ~0.07/Ar (9, 10, 38). We have made the following corrections: etherified coniferaldehyde moieties (0.04/Ar) contribute to the integral at 157-151 ppm not only with C-α, but also with C-4 (20). The amount of conjugated carbonyl groups has been estimated from the resonance at 200-190 ppm to be ~0.14/Ar. 2 conjugated COOR moieties also should be included. However it was not possible to distinguish between etherified/non-etherified conjugated structures because there is very little difference between the chemical shifts for the carbonyl carbon in etherified/phenolic and condensed/non-condensed carbonyl moieties of these types (20). Moreover, C-3 and C-6 of spirodienone moieties also resonate in the area of 157-151 ppm (31). Taking all conjugated CO and COOR moieties as etherified and assuming that the amount of etherified syringyl units in spruce MWL is negligible, the minimal amount of etherified 5-5' and 4-O-5' moieties comes as:

\[ T_{et} + 2S_{et} = 0.37 - (0.14 + 0.02 + 0.04 + 2 \times 0.02) = 0.13/Ar. \]

Assuming the amount of 4-O-5' units in spruce MWL to be ~0.02/Ar (2, 9), the value for the 5-5' is:

\[ T_{et} = 0.13 - 2 \times 0.02 = 0.09/Ar. \]
This value is much lower that obtained earlier (9), because of the corrections made and apparently it is too low considering the amount of 5-5' atoms only in dibenzodioxocin as \(2 \times 0.07 = 0.14/\text{Ar}\). Therefore, this approach for calculation of 5-5' \(_e\) structures is not precise.

**The nature of signals at 145-140 ppm.**

The resonance in the region of 145-140 ppm was assumed to embody C-4 of both etherified and non-etherified 5-5' moieties together with C-3 of phenylcoumaran structures (9, 10, 38). However, examination of chemical shifts for the corresponding model compounds in different databases shows that the signals of C-4 of 5-5' etherified units vary between 144-146 ppm (20, 26-28, 31, 38, 39) and can be partially overlapped with intensive signals at 148-146 ppm. Therefore, we were trying to estimate the amount of only phenolic 5-5' moieties from the peak at 142-144 ppm. The integral value is 0.18/Ar, which also includes the C-3 in phenylcoumaran moieties (0.09/Ar). It is very tempting to assign the remaining, about 0.18 - 0.09 = 0.09/Ar, to C-4 in 5-5' \(n_e\) (and C-5 in 4-O-5'\(n_e\)). However, this integral is the same in the spectrum of the MWL-Ac preparation (Table 3), implying that the moieties giving resonance in this area are non-phenolic. C-4 of conjugated 4-O-5' etherified moieties can contribute to the signal at 144-142 ppm (20), but their amount is not supposed to be as big as 0.09/Ar. Therefore, additional studies are needed to clarify the nature of this signal.

**Etherified conjugated carbonyl/carboxyl moieties** were approximately estimated from the integral at 162-148 ppm in the spectrum of MWL-Ac lignin (Table 3, 4):
\[(I_{162-148})_{ac} = \text{All } C_3 - E_3 - h_3 + h_4 + S_5 + I_{12a} + I_6 + \text{Conj.-et} - 4 =
= 1 - E - S + L + I + \text{Conj.-et} - 4
\]

\[\text{Conj.-et} = (I_{162-148})_{ac} - 1 + E - S - L - I\]

An approximate amount of 4'-O-5' structures is 0.04/Ar (2), therefore, the amount of conjugated CO/COOH etherified moieties is:

\[\text{Conj.-et} = 1.07 - 1.00 + 0.09 - 0.04 - 0.04 - 0.02 = 0.06/\text{Ar}\]

**Phenolic conjugated carbonyl/carboxyl moieties and 5-5' structures.**

The sum of moieties \(L, M\) and \(R\) is about 0.11/Ar (Table 4). Therefore, even if all conjugated CO/COOH etherified moieties are of the \(L, M\) and \(R\) types, at least 0.11 - 0.06 = 0.05/Ar of these moieties are phenolic and correspondingly must be condensed to be bonded to lignin (type \(T_L\)). This number reflects an order of the magnitude rather than a precise value taking in account the way it was obtained. However, it correlates well with the nature of phenolic 5-5' moieties discussed in the text and another method to estimate the amount of these moieties by comparison of the integral at 125-103 ppm in the spectra of MWL and MWL-Ac. There is a difference of 0.10/Ar in the integral at 125–103 ppm between the acetylated and non-acetylated lignins (Tables 2, 3). This can be explained by a shift of the resonance of C-β in coniferyl alcohol moieties from 127 to 121 ppm, C-6 in non-etherified vanillin structures from 126 to 123 ppm (20) and probably a similar shift for coniferaldehyde 5-5' non-etherified moieties. The amount of coniferyl alcohol is about 0.02/Ar, therefore the amount of the non-etherified 5-5' moieties with a conjugated carbonyl group is about 0.10 - 0.02 = 0.08/Ar. Thus, the
majority of phenolic condensed (5-5' and 4-O-5') lignin moieties have conjugated carbonyl/carboxyl group and their amount is ~0.05–0.08/Ar.