Chemistry of Natural Compounds, Vol. 32, No. 2, 1996

SCHEMATIC STRUCTURE OF A FRAGMENT OF THE COTTONPLANT LIGNIN MACROMOLECULE

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UDC 543.422.5:547.992.3

A schematic structure has been proposed for an average fragment of the macromolecule of cottonplant dioxane lignin on the basis of the results of a chemical study and quantitative ^1H and ^{13}C NMR spectroscopy.

The results of a study of the structure of the dioxane lignin (DLA) of mature cottonplant stems from the variety 108-F by chemical methods and an analysis of its quantitative ^1H and ^{13}C NMR spectra has permitted us to calculate the average structure of the DLA macromolecule and to show it as a schematic formula.

The numbers of phenylpropane structural units (PPSUs) contained in schematic structures proposed previously for average fragments of lignin macromolecules were 18 [1] and 28 [2] for spruce lignin, 14 for reed lignin [3], and 15 for beech lignin [4].

The DLA from mature cottonplant stems of the variety 108-F was obtained by Pepper's method and had $\bar{M}_w$ = 12,000. Its developed empirical formula was calculated from the results of chemical methods of analysis as $C_9H_{8.02}O_{0.74}\cdot(OCH_3)_{1.33}(OH_{ph})_{0.42}(OH_{al})_{0.85}(O_{CO})_{0.22}(OOH_{COOH})_{0.06}(O_{ar\text{-}al})_{0.58}$ [5], from which it followed that the molecular mass of one PPSU was 205 c.u. Quantitative ^1H and ^{13}C NMR spectroscopy showed that the mean formula of a unit of the DLA was very close to the composition of the PPSU: $C_{9.49}H_{11.89}O_{3.20}(OCH_3)_{1.39}$ [7], and its molecular mass was also close to the molecular mass of the PPSU calculated on the basis of chemical methods of analysis, which was 220 c.u. Consequently, it will be justified to use the results of calculations from the NMR spectra of the number of structrual parameters of the cottonplant DLA per 1 (or 100) aromatic ring(s) (AR(s)) in the DLA macromolecule for the deduction of an average schematic structure of the lignin macromolecule from PPSUs. From the value of $\bar{M}_w$ it is possible to calculate the number of PPSUs in the DLA macromolecule: it will consist of 58 PPUs.

For comparing formulas we selected a fragment of 18 PPUs, i.e. 1/3 of the DLA macromolecule. This number describes a fairly representative part of the lignin macromolecule, and since it is necessary to include fragments I and II in the formula, 18 is the smallest number at which fragment II is reflected in the formula. The numbers of structural fragments and bonds per 18 PPSUs (or 18 ARs) were calculated from the results of PMR spectroscopy and are given in Table 1, which, for comparison, also gives the numbers of fragments and bonds in the average structural formulas of spruce, beech, and reed lignins.

It has been established from the results of alkaline nitrobenzene oxidation, cleavage with metallic sodium in liquid ammonia, and ^{13}C NMR spectra that the main PPSUs of DLA are guaiacyl and syringyl structures [6, 7]. There are very few *p*-coumaryl structures in them.

The main types of bonds in the DLA, as in all lignins, were $C_{ar}-O-C_{al}$ and $C_{ar}-C$ bonds.

A distinguishing feature of the cottonplant DLA is the presence of structures I and II, of carboxy groups, and of a large number of ester bonds. The possibility of the substitution of aromatic rings in both structures I and II followed from the qualitative and quantitative analysis of ^{13}C NMR spectra [7]. The pinoresinol ring was included in the formula on the basis

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0009-3130/96/3202-0205$15.00

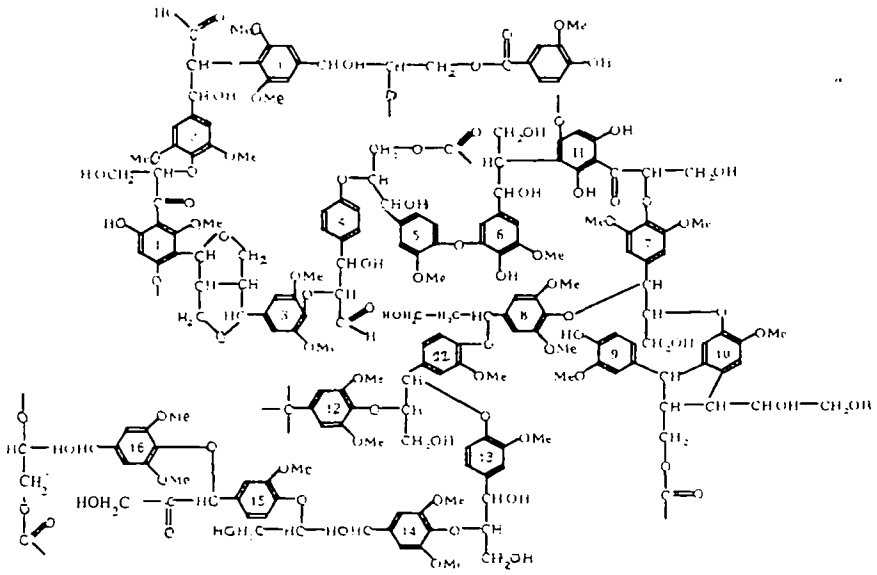

Fig. 1. Schematic structure of a fragment of the cottonplant lignin macromolecule.

TABLE 1. Amounts of Fragments and Groups in Lignin Formulas

Fragments and groups	Lignin			
	reed [3]	spruce [1]	beech [4]	cottonplant
Sum of the PPSUs	14	18	15	18
p-Coumaryl	2	2	–	0.35
Guaiacyl	4	16	7	7.3
Syringyl	8	–	8	7.9
Structure I	–	–	–	1.5
Structure II	–	–	–	1.0
Pinoresinol	3	1	1	1
Furocoumarin	1	1	1	–
OH_{phen}	6	6	5	6.6
OH_{aliph}	10	18	13	25
CO_{ketone}	2	3	3	1.9
$CO_{aldehyde}$	1	1	–	1.4
Sum of CH_{arom}	31	46	30	19.5
$C_{al}-O-C_{al}$	7	3	4	2.2
$C_{ar}-O-C_{ar}$	–	–	–	0.72
$C_{ar}-O-C_{al}$	7	10	9	13.4
COOH	–	–	–	0.93
COOR	–	–	–	6.6
$CH_{\beta-\beta}$	6	4	4	2.25

of NMR results: two $C_{al}-O-C_{al}$ bonds and two $CH_{\beta-\beta}$ bonds. The presence of carboxy groups was confirmed by two independent methods: chemical and ^1H and ^{13}C NMR. The diisoeugenol structure was included in the formula because it has been detected in the products of the cleavage of cottonplant stems with metallic sodium in liquid ammonia [8].

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