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LIGNINS OF HERBACEOUS PLANTS

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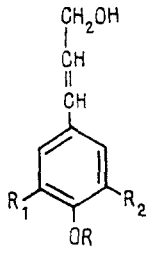
Literature information on the formation, chemical composition, and structural features of lignins of herbaceous plants for 1980-1992 is generalized and analyzed.

In terms of their distribution in Nature, lignins occupy the second position after cellulose. They can be subdivided into three broad groups: the lignins of the wood of coniferous species (Gymnospermae), the lignins of the wood of deciduous species (Angiospermae), and the lignins of herbaceous plants. The structures and properties of the lignins of the wood of coniferous and deciduous species have now been investigated the most fully [1-3] and schemes of the structure of fragments of spruce and beech lignins have been proposed [4, 5]. The lignins of woody plants form a fairly homogeneous group of substances and differ little from one another in structure and properties. The lignins of herbaceous plants have been little studied, and this is probably why greater variability according to the species of plant is shown.

The literataure material on the lignins of herbacaeous plants is scattered over various sources. In the present review an attempt has been made to generalize and analyze this information in order to reveal certain regularities in the formation, properties, and structure of the lignins of herbaceousa plants.

Formation of the Lignin of Herbaceous Plants

The mechanism of the formation of lignin in the plant has interested chemists from the moment of discovery of this substance. The essence of the process of lignification is a transformation taking place in plants in which an aromatic polymer — lignin — is synthesized, in the final account, from CO_2 through the formation of compounds of the carbohydrate type, such as *p*-glucocoumaryl alcohol, coniferin, and syringin (**1-3**).



R-carbohydrate residue

1. $R_1=R_2=H$
2. $R_1=OCH_3$; $R_2=H$
3. $R_1=R_2=OCH_3$

The presence of phenylpropanoid glycosides (**4-7**) in plant tissue permits the assumption that such compounds may be intermediates in the formation of lignin. Reports on the isolation and identification of similar compounds are frequently found in the literature [6-9].

The elucidation of the formation and structure of the lignin macromolecule in the cell is becoming an ever more urgent problem. Hitherto it has been considered that the lignin macromolecule has an irregular structure. However, an investigation of the formation of lignin at the cell level with the aid of a radioactive indicator has shown that lignin is never formed in the

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TABLE 1. Lignins of Herbaceous Plants

Plant	Part of the plant	Preparation studied	Literature
Gramineae family			
1. Rice (Oryza sativa)	Stems	DLA	22
2. Rice	Husks	DLA	23
3. Maize (Zea mays)	Stumps	DLA	24
4. Maize	Stumps	DLA	25
5. Rye (Secale)	Straw	DLA	26
6. Reed (Phragmites communis)	Stems	MWL	27
7. Reed	Stems	Alkali lignin	28
8. Wheat (Triticum aestivum)	Straw	MWL	29
9. Wheat	Straw	Alkali-soluble lignins 1-3	29
10. Wheat	Straw	Residual lignins	30
11. Wheat	Straw fibers	Residual lignin	31
12. Bamboo (Phyllostachys makinoy Hay)	Stems	Fractions 1 and 2	32
13. Bamboo	Stems	Isolated lignin	33
Leguminosae family			
14. Pea bush (Sesbania sesban)	Epigeal part	Organosoluble lignin	34
15. Pea bush (Sesbania asculeata)	Epigeal part	Organosoluble lignin	34
16. Liquorice (Glycyrryza glabra)	Root	DLA	35
17. Peanut (Arachis hypogeae)	Hulls	Organosoluble lignin	36
18. Peanut	Leaves	"	36
19. Peanut	Stems	"	36
20. Straw	Root	"	36
Linaceae family			36
21. Flax (Linum olgae)	Tow	DLA	37
22. Flax	Stems	DLA	37
23. Flax	Tow	DLA	26
Malvaceae family			
24. Medium-fiber (upland) cotton plant (Gossypium hirsutum)	Stems	MWL	38
25. Medium-fiber (upland) cotton plant	Bolls	MWL	38
26. Medium-fiber (upland) cotton plant	Seed husks	MWL	38
27. Cotton plant, variety Tashkent-1	Stems	MWL	39
28. Cotton plant, variety Tashkent-6	"	MWL	40
29. Cotton plant, variety S-6030	"	MWL	41
30. Thin-fiber (sea island) cotton plant (Gossypium barbadense)	"	DLA	41
31. Althaea nudiflora	"	DLA	42
32. Althaea rhyticarpa	"	DLA	42
33. Althaea rosea	"	DLA	42
34. Kenaf (Hibiscus cannabinus)	"	DLA	43
35. Kenaf	Phloem	DLA	43
36. Kenaf	Tow	DLA	43
Tiliaceae family			
37. Jute (Corhorius olitorius)	Stems	MWL 1,2	44
Euphorbiaceae family			
38. Castor oil plant (Ricinus communis)	Stems	DLA	43
Andropogonae			
39. Amur silvergrass (Miscanthus sachariflorus)	Epigeal part	Acid-soluble lignin	90

TABLE 2. Chemical Composistions of Herbaceous Plants, %

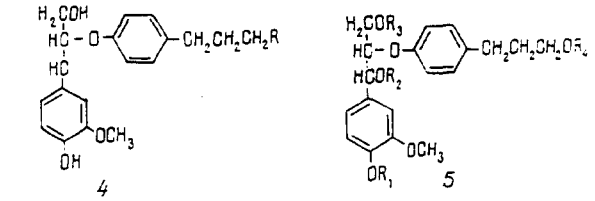
Plant	Lignin	Cellulose	Pentosans	Literature
Gramineae family				
1. Rice husks	17.8	21.0	21.0	46
2. Rice husks	20.0			47
3. Maize stumps	16.8			24
4. Maize stumps	20.3			25
5. Reed stems	20.1			27
6. Reed stems	22.1			48
7. Wheat straw	18.6			49
8. Maize cobs	20.3			25
Leguminosae family				
9. Peanut stems	8.9			36
10. Peanut leaves	13.0			36
11. Peanut root	19.8			36
12. Liquorice root	28.0			35
Malvaceae family				
13. Cottonplant stems	24.5			38
14. Cottonplant bolls	25.8			38
15. Cottonplant seed husks	23.8			38
16. Cottonplant stems. Tashkent-1	22.9	38.1		39
17. Cottonplant stems. Tashkent-6	25.5	35.7		40
18. Mexican cottonplant stems	28.2	27.9		40
19. Kenaf stems	15.0	52.9		43
20. Kenaf phloem	10.4	45.0		43
21. Kenaf tow	20.3	38.2		43
22. Kenaf tow	27.0	47.0	18.2	51
23. Kenaf phloem	10.2	88.5		52
24. Kenaf stems	18.5	44,3	16.4	53
25. Kenaf stems	16.0	48.3	19.2	53
26. Kenaf (*Hibiscus vulgaris*)	10.7	5.8	8.7	54
27. Kenaf (*Hibiscus viridix*)	11.4	5.8	9.4	54
28. *Althaea rhyticarpa* stems	15.1	27.5	27.4	42
29. *Althaea nudiflora* stems	13.3	30.6	23.7	42
30. Hollyhock	14.2	27.0	27.4	42
Linaceae family				
31. Flax phloem	2.2—6.3			37
32. Flax tow	20.3			37
Tiliaceae family				
33. Jute stems	19.3	50.0		55
34. Jute stems	23.6	39.7	22.1	44
35. Jute stems	23.8	42.2	22.3	44

TABLE 2 (continued)

Plant	Lignin	Cellulose	Pentosans	Literature
Compositeae family				
36. Sunflowerseed husks	26.5			25
37. Sunflower stems	11.0	76.0+		91
Euphoriaceae family				
38. Castor-oil plant stems	19.6	33.0		45
Andropogoneae family				
39. Chinese silvergrass	21.2			48

+Holocellulose content.

absence of carbohydrates, and the type of carbohydrates substantially influences its synthesis [10]. The protolignin of cell walls of wood xylem is, according to the results of this work, a heterogeneous polymer with a highly regular structure which is greatly affected by the biogenesis and architecture of the cell wall



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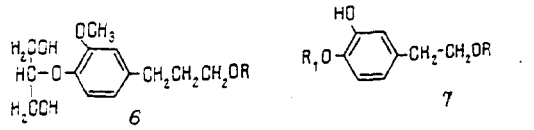

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R_1, R_2, R_3, R_4 - carbohydrate residues

Of what does the "regularity" of the lignin macromolecule consist?

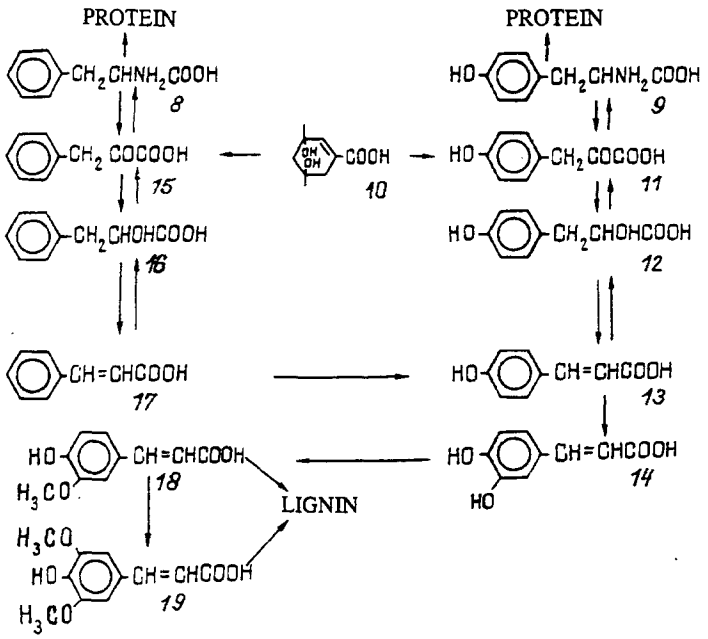
The formation of lignin is regulated in the plant by biochemical factors, and this explains its heterogeneity. In the opinion of some workers [11] lignin consists of phenylpropane structures that have different degrees of methoxylation of the aromatic ring but are linked into the macromolecule regularly. Thus, it has been shown by the microautoradiography of individual sections of the tissue of pine wood that lignin enriched with *p*-hydroxyphenyl structures is formed mainly in the middle lamella and the corners of the cells in an early stage of cell differentiation.

At this stage, in the middle lamella and the secondary wall of pine wood, "guaiacyl" lignin (i.e., lignin consisting of residues with guaicylpropane structures) is synthesized. Lignin consisting of residues of syringylpropane structural units, "syringyl" lignin, is formed mainly in the interior layers of the secondary cell wall in a later stage of lignification as a minor component.

The results of an investigation of lignification in plants of the Gramineae family [16, 19] have shown a selective distribution of labeled lignin precursors (*p*-glucocoumaryl alcohol, coniferin, syringin — (**1**)-(**3**), respectively, and phenylalanine and tyrosine — (**8**) and(**9**), respectively — over the structural elements of the plant tissue. As also in a study of lignification in pine wood [11], the authors drew the conclusion of a regular nature of the lignin-forming processes, having established that the lignin of the vessels included mainly *p*-hydroxyphenyl- and guaiacylpropane units while the lignin of the parenchyma — the basic tissue — included guaiacyl- and syringylpropane units.

The specificity of the formation of lignin in phylogenetically different groups is connected with features of the transformation of shikimic acid (**10**) [12]. In contrast to woody plants, herbaceous plants possess a unique capacity for converting *p*-hydroxyphenyllactic acid (**12**) into *p*-hydroxycinnamic acid (**13**) [13]. Scheme 1 shows the transformations of lignin precursors — phenylalanine and tyrosine (**8** and **9**) — during lignification [13].

All higher plants perform the deamination of phenylalanine with the aid of the enzyme phenylalanine ammonia lyase (PAL). It has been established that plants of the Gramineae family contain not only PAL but also tyrosine ammonia lyase, which catalyzes the direct conversion of tyrosine into *p*-hydroxycinnamic acid [38, 14, 15] (Scheme 1). In a study of the



Scheme 1. **8**) Phenylalanine; **9**) tyrosine; **10**) shikimic acid; **11**) *p*-hydroxyphenylpyruvic acid; **12**) *p*-hydroxyphenyllactic acid; **13**) *p*-coumaric (*p*-hydroxycinnamic) acid; **14**) caffeic acid; **15** phenylpyruvic acid; **16**) phenyllactic acid; **17**) cinnamic acid; **18**) ferulic acid; **19**) sinapic acid.

formation of lignin with the aid of microautoradiography it has been established that in rice stems tyrosine is a more effective precursor than phenylalanine [16]. However, a report has recently appeared in the literature of the detection of tyrosine ammonia lyase in a purified fraction of the PAL of kidney bean (Leguminosae family) [17]. In plants of the Leguminosae family the synthesis of lignin is catalyzed by the same enzymes as the biogenesis of the phenylpropanoid phytoalexins of these plants [18], which creates additional difficulties in the investigation of the lignin-forming process.

Not only phenylalanine and tyrosine ammonia lyases but also other enzymes participate in the formation of the lignin of herbaceous plants. Thus, a form of peroxidase ionically bound with the cell walls participates in the formation of lignin in woody tissues of flax [20, 50].

Chemical Compositions of Some Herbaceous Plants and Characterization of Their Lignins

The facts given in the literature on the chemical composition of herbaceous plants the lignins of which have been studied are extremely incomplete and in some cases incapable of being compared. This is due to morphological variability as a function of the species of plant, its growth site, the vegetaion period, and the environmental conditions.

Table 1 gives a list of the herbaceous plants the lignins of which have been isolated and investigated. As we see, the majority of lignins investigated are preparations of dioxane lignins (DLAs). Mechanically ground lignins ("milled wood lignins," MWLs), and alkali-soluble and organosoluble lignins, and others have also been investigated.

The lignins of plants of the Gramininеae and Malvaceae families have been studied to a greater degree. The lignins were isolated mainly from the lignocellulose wastes of technical plants (rice, wheat, maize, cotton, kenaf, etc.) with the aim of studying the properties and structure of lignin itself, although a not unimportant role in this was played by search for methods of using the lignocellulose wastes.

The chemical compositions of herbaceous plants have been widely studied (Table 2). During the development of a cotton plant of variety 108F, as an example, increases in the levels of lignin, cellulose, pentosans, and OCH_3 were shown. By the end of the vegetation period, the lignin of the stems of this cotton plant had changed not only quantitatively but also qualitatively, having become more highly methoxylated [21].

TABLE 3. Semiempirical Formulas of the Lignins of Some Herbaceous Plants

Sample	Semiempirical formula	Literature
Gramineae family		
1. Rice husk DLA	$C_9H_{7.57}O_{1.13}(OCH_3)_{0.93}(OH_{ph})_{0.33}$ $\times(OH_{al})_{0.89}(O_{CO})_{0.31}(O_{ar\text{-}al})_{0.67}$	23
2. Rice stem DLA	$C_9H_{8.03}O_{1.53}(OCH_3)_{0.97}(OH_{ph})_{0.39}$ $\times(OH_{al})_{0.84}(O_{CO})_{0.32}(O_{ar\text{-}al})_{0.61}$	22
3. Reed stem DLA	$C_9H_{7.82}O_{1.52}(OCH_3)_{1.11}(OH)_{1.21}(O_{CO})_{0.21}$	27
4. Reed stem DLA	$C_9H_{6.46}(OCH_3)_{1.19}(OH_{ph})_{0.64}(OH_{al})_{0.32}$ $\times(O_{CO})_{0.25}(OOH_{COOH})_{0.14}(O_{ar\text{-}al})_{0.52}$	25
5. Wheat straw MGL	$C_9H_{6.99}O_{2.76}(OCH_3)_{1.11}$	29
6. Rye straw DLA	$C_9H_{11.15}O_{1.76}(OCH_3)_{0.99}(OH_{ph})_{0.16}$ $\times(OH_{al})_{1.12}(CO)_{0.20}$	26
Malvaceae family		
7. DLA of Tashkent-1 cottonplant stems, early period	$C_9H_{7.67}O_{2.01}(OCH_3)_{0.53}(OH_{ph})_{0.66}$ $\times(OH_{al})_{0.33}(OCO)_{0.44}(OOH_{COOH})_{0.03}$ $\times(O_{ar\text{-}al})_{0.34}$	39
8. " , early period	$C_9H_{6.24}O_{1.59}(OCH_3)_{0.78}(OH_{ph})_{0.73}$ $\times(OH_{al})_{0.7}(O_{CO})_{0.18}(OOH_{COOH})_{0.08}$ $\times(O_{ar\text{-}al})_{0.37}$	39
9. " , ripe stems	$C_9H_{6.22}O_{1.21}(OCH_3)_{0.82}(OH_{ph})_{0.63}$ $\times(OH_{al})_{0.88}(O_{CO})_{0.46}(OOH_{COOH})_{0.17}$ $\times(O_{ar\text{-}al})_{0.37}$	39
10. DLA of Tashkent-60 cotton plant	$C_9H_{7.96}O_{0.62}(OCH_3)_{0.99}(OH_{ph})_{0.28}$ $\times(OH_{al})_{1.33}(O_{CO})_{0.31}(OOH_{COOH})_{0.06}$ $\times(O_{ar\text{-}al})_{0.72}$	40
11. DLA of C-6030	$C_9H_{8.7}O_{0.59}(OCH_3)_{1.18}(OH_{ph})_{0.29}$ $\times(OH_{al})_{1.19}(O_{CO})_{0.32}(OOH_{COOH})_{0.24}$ $\times(O_{ar\text{-}al})_{0.71}$	41
12. *Althea rhyticarpa* DLA	$C_9H_{7.6}O_{1.0}(OCH_3)_{1.07}(OH_{ph})_{0.43}$ $\times(OH_{al})_{0.93}(O_{ar\text{-}al})_{0.57}(O_{CO})_{0.52}$	42
13. Hollyhock DLA	$C_9H_{6.55}O_{0.99}(OCH_3)_{1.15}(OH_{ph})_{0.31}$ $\times(OH_{al})_{0.85}(O_{CO})_{0.3}(OOH_{COOH})_{0.03}$ $\times(O_{ar\text{-}al})_{0.69}$	42
14. *Althea nudiflora*	$C_9H_{6.84}O_{1.21}(OCH_3)_{1.2}(OH_{ph})_{0.38}$ $\times(OH_{al})_{0.93}(O_{CO})_{0.41}(OOH_{COOH})_{0.08}$ $\times(O_{ar\text{-}al})_{0.62}$	42
15. Kenaf stem DLA	$C_9H_{6.9}O_{0.9}(OCH_3)_{1.34}(OH_{ph})_{0.25}(OH_{al})_{1.01}$ $\times(O_{CO})_{0.17}(OOH_{COOH})_{0.02}(O_{ar\text{-}al})_{0.75}$	43
16. Kenaf phloem DNA	$C_9H_{6.97}O_{0.73}(OCH_3)_{1.37}(OH_{ph})_{0.34}$ $\times(OH_{al})_{0.88}(O_{CO})_{0.18}(OOH_{COOH})_{0.026}$ $\times(O_{ar\text{-}al})_{0.66}$	43

TABLE 3 (continued)

Sample	Semiempirical formula	Literature
17. Kenaf tow DLA	$C_9H_{7.14}O_{0.67}(OCH_3)_{1.39}(OH_{ph})_{0.27}$ $\times(OH_{al})_{0.92}(O_{CO})_{0.18}(OOH_{COOH})_{0.02}$ $\times(O_{ar\text{-}al})_{0.73}$	43
Linaceae family		
18. Flax tow DLA	$C_9H_{10.74}O_{1.29}(OCH_3)_{0.87}(OH_{ph})_{0.14}$ $\times(OH_{al})_{1.09}(CO)_{0.19}$	26
Tiliaceae family		
19. Jute stem DLA	$C_9H_{7.78}O_{2.96}(OCH_3)_{1.27}$	44
20. Jute stem DLA	$C_9H_{8.33}O_{3.52}(OCH_3)_{1.26}$	44
Euphorbiaceae family		
21. Castor-oil plant stem DLA	$C_9H_{7.8}O_{0.68}(OCH_3)_{1.18}(OH_{ph})_{0.19}$ $\times(OH_{al})_{1.05}(O_{CO})_{0.53}(OOH_{COOH})_{0.03}$ $\times(O_{ar\text{-}al})_{0.81}$	45

The considerable amount of cellulose and carbohydrates in cottonplant stems permits their use as a raw material in the hydrolysis industry, for obtaining alcohol, fodder yeast, and xylitol [56].

Information on the chemical composition of the stems of kenaf and related plants is sparse. Thus, kenaf stems contain (%): lignin, 16.4; cellulose, 49.0; pectin substances, 14.5 [57]. The amounts of the main components of kenaf stems grown in two regions of Pakistan were, respectively, (%): lignin, 18.5 and 16.0; α-cellulose, 44.3 and 48.3; pentosans, 16.4 and 19.2 [53]. The amount of lignin in the stems (phloem part and tow of three species of kenaf ranged within the limits 10.7-18.5, 10.2-10.4, and 20.3-28.0, respectively.

The amount of lignin in rice husks depends on the variety of rice and the conditions of its growth, and ranges between 19 and 25% [58]. An opinion exists that when the hemicellulose impurities are eliminated more carefully, the amount of cellulose in rice husks rarely exceeds 30%. This is considerably lower than in wood, and rice husks are therefore unsuitable for the production of paper.

The most important difference between rice husks and other wastes and wood is the anomalously high silicon content of their ash. The ash content of rice husks amounts to 16-20%. The ash is practically pure silica, and therefore rice husks have recently been considered as a source of very cheap and pure silicon-containing raw material.

It can be seen from Tables 1 and 2 that the lignin of technical crops has been isolated and studied; however, semiempirical formulas, which are the main characteristic and reflect the structure of the phenylpropane unit of the lignin macromolecule, have not been calculated for all specimens (Table 3).

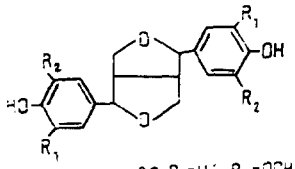
A comparison of the semiempirical formulas shows that the dioxane lignins of the cotton plant of three vegetation periods differ qualitatively [39]. As the plant develops, the lignin becomes more highly methoxylated, which shows a decrease in its degree of condensation. The degree of condensation of the lignins of wheat stems also falls during the growth of the plant [88]. Thus, in the early vegetation period a less highly methoxylated lignin is formed, and this in small amount. Kenaf lignins are more highly methoxylated than those of *Althea* and the cotton plant, which indicates their low degree of condensation in the series of lignins from plants of the Malvaceae family.

With respect to their methoxy group content, the lignins of herbaceous plants differ from the lignins of woody and lower plants. Thus, in their OCH_3/C_9 ratio the lignins of the Gramineae family are closer to the lignins of conifers, while the lignins of the Malvaceae, Tiliaceae, and Euphorbiaceae families are closer to the lignins of deciduous plants (Table 4).

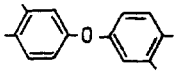
The low content of methoxy groups in the lignins of lower plants indicates their greater degree of condensation.

For lignins of algae and other hydrophytes a low content of OCH_3 groups is characteristic, but with evolutionary development from algae to higher plants the lignins become more highly methoxylated [59].

A comparison of the semiempirical formulas of the lignins of herbaceous plants shows that the amounts of "free" oxygen, not included in OCH_3, OH, and CO groups, are different. This oxygen probably belongs to all the other ether bonds in the lignin: they may be alkyl-alkyl ether bonds of pinoresinol (**20**) and syringaresinol (**21**), and diaryl ether bonds (**22**):



20. R_1=H; R_2=OCH_3
21. R_1=R_2=OCH_3



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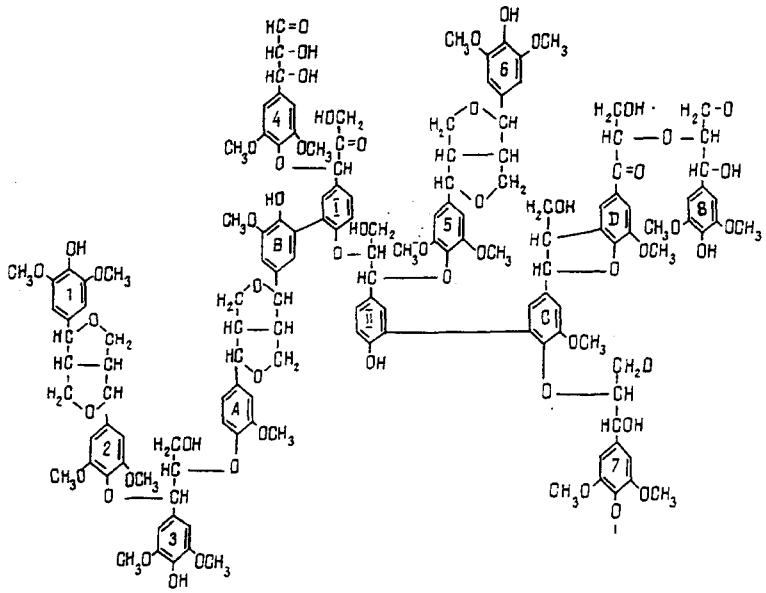
From the levels of aliphatic hydroxy groups it is possible to assume differences in the side chains of the lignins given in the Table. The different amounts of phenolic hydroxyls and the number of alkyl–aryl ether bonds calculated from them should explain the different reactivities of the lignins of herbaceous plants.

Features of the Structure of the Lignins of Herbaceous Plants

A number of investigations has been devoted to the structures of lignins, and they have been described in reviews [1-3], where the complex nature of the polymerization processes in the formation of lignin in wood is noted and the reactivity of its macromolecule is considered.

Attempts to establish the structure of lignins are limited to the proposal of possible schemes of fragments consisting of different numbers of propane structural units (PPSUs) — C_6C_3 monomers. Simonescu and Anton [60] have given a scheme of the structure of a fragment of the Brauns lignin of reeds consisting of 14 PPSUs (Scheme 2). It is difficult to cover the structure of lignin by a single scheme, and the authors therefore suggest the possibility of its modification when additional experimental results are obtained. Nevertheless, the proposed scheme is a statistical representation of a lignin model.



Scheme 2. Structure of a fragment macromolecule of reed stem lignin.

The main type of bond between the PPSUs of lignin consists of alkyl–aryl ether (α-O-4 and, to a smaller degree, β-O-4) bonds. In addition, the scheme illustrates C–C bonds between aliphatic hydrocarbons of the propane side chain and aryl–aryl C–C bonds of lignin. A predominance of methoxy-containing structures is shown. It can be seen that the fragment of the reed lignin macromolecule contains weakly condensed structures. On the whole, the formula takes into account the characteristic features of the structure of reed lignin, but certain generalizations — for example, the predominance of α-O-4 bonds over β-O-4 bonds — require additional consideration.

TABLE 4. OCH_3/C_9 Ratios in the Lignins of Herbaceous Plants

Sample	OCH_3/C_9
Gramineae family	
1. Rice DLA	0.93 — 0.97
2. Reed DLA	1.11 — 1.19
3. Rye DLA	0.999
4. Wheat MWL	1.11
Malvaceae family	
5. Cotton-plant DLA	0.47 — 1.38
6. *Althea* DLA	1.07 — 1.20
7. Kenaf DLA	1.34 — 1.39
Tiliaceae family	
8. Jute DLA	1.26 — 1.27
Euphorbiaceae family	
9. Castor-oil plant DLA	1.18
10. Spruce DLA (coniferous)	0.92 [1]
11. Beech DLA (deciduous)	1.41 [1]
12. DLA of the brown alga *Cystoseira* (lower plants)	0.007 — 0.45 [60]

Ester Bonds between Lignin and Other Components in Herbaceous Plants

Investigations devoted to establishing the type of bond between lignin and other components of plants have appeared in the literature. The presence of chemical bonds in plant tissues between lignin and carbohydrates, and between lignin and phenolic acids has been shown.

In rice straw, the lignin is bound with readily hydrolyzable xylan through the β-ketone group of the macromolecule [63]. Lignin–xylan ether bonds have been found in jute and kenaf fibers [64, 52]. A lignocarbohydrate complex having an ester bond with *p*-coumaric acid has been isolated from the cell wall of the tropical herb *Digiteria decumbens* [65]. It must be mentioned that many herbaceous plants are used as xylan-containing raw material. Thus, the preparation of D-xylose from rye straw, maize cobs, oat husks, and wheat bran has been described [66].

Higuchi considers the presence of 5-10% of phenolic acids bound by an ester bond to be a characteristic feature of the lignins of herbaceous plants [62].

There is voluminous material on the presence, the bonds, and the isolation of phenolic acids from herbaceous plants. The reason for the high content of phenolic acids is apparently the fact that, being precursors of lignin, these compounds are components of the cell walls of various monocotyledonous plants [67-70].

In plant tissue, the phenolic acids exist in the form of esters covalently bound with carbohydrates and lignin and are readily isolated on "cold" alkaline hydrolysis. Being components of the cell walls, the phenolic acids undergo unusual transformations. Thus, it has recently been reported that cyclobutane dimers of *p*-coumaric and ferulic acids are also components of the cell walls of herbaceous plants and, possibly, are formed photochemically [71-73]. The formation of a cyclobutane dimer of *p*-coumaric acid — 4,4′-dihydroxytruxillic acid — in the cell walls of bamboo (Gramineae family) under the action of light has been shown in [73]:

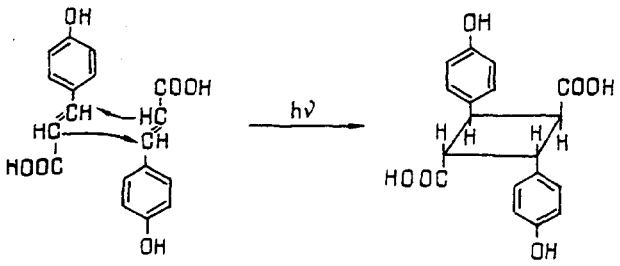


TABLE 5. Ratios of the Structural Units in the Lignins of Herbaceous Plants

Sample	Ratio* p:g:s p : g : s	Literature
Gramineae family		
1. Natural lignin of wheat straw	0.10 : 1.0 : 0.93	84
2. Natural lignin of rice straw	0.33 : 1.0 : 0.89	84
3. Residual lignin 1 of wheat straw	0.17 : 1.0 : 1.3	30
4. Residual lignin 2 of wheat straw	0.20 : 1.0 : 0.70	30
5. Natural lignin of wheat straw	0.21 : 1.0 : 0.72	30
6. Natural lignin of reed stems	0.23 : 1.0 : 0.27	48
Malvaceae family		
7. Natural lignin of Mexican cotton-plant stems	0.31 : 1.0 : 0.56	40
8. Natural lignin of Tashkent-6 cottonplant stems	0.20 : 1.0 : 0.62	40
9. DLA of Mexican cottonplant stems	0.08 : 1.0 : 0.72	40
10. DLA of Tashkent-6 cottonplant stems	0.07 : 1.0 : 0.61	40
11. Natural lignin of Tashkent-1 cottonplant stems	0.10 : 1.0 : 0.80	39
12. DLA of Tashkent-1 cottonplant stems	0.10 : 1.0 : 0.50	39
13. Natural lignin of kenaf stems	0.14 : 1.0 : 2.02	43
14. Natural lignin of kenaf phloem	0.21 : 1.0 : 1.50	43
15. Natural lignin of kenaf chaff	0.22 : 1.0 : 1.30	43
16. DLA of kenaf stems	0.26 : 1.0 : 1.50	43
17. DLA of kenaf phloem	0.26 : 1.0 : 2.02	43
18. DLA of kenaf chaff	0.15 : 1.0 : 2.40	43
19. Natural lignin of *Althea rhyticarpa* stems	0.08 : 1.0 : 0.40	42
20. Natural lignin of *Althea rhyticarpa* stems	0.10 : 1.0 : 1.10	42
21. Natural lignin of hollyhock stems	0.065 : 1.0 : 0.37	42
22. DLA of *Althea rhyticarpa* stems	0.01 : 1.0 : 1.20	42
23. DLA of *Althea nudiflora* stems	0.18 : 1.0 : 1.70	42
24. DLA of hollyhock stems	0.30 : 1.0 : 1.40	42
Leguminosae stems		
25. Organosoluble lignin of the pea tree (*Sesbania aegyptica*)	1.05 : 1.0 : 1.10	34
26. Organosoluble lignin of the pea tree (*Sesbania*)	1.01 : 1.0 : 0.53	34
27. Organosoluble lignin of the pigeon pea (*Cajanus*)	1.04 : 1.0 : 1.03	34
28. Natural lignin of liquorice root	0.20 : 1.0 : 0.60	35
Andropogoneae family		
29. Natural lignin of Chinese silvergrass	0.41 : 1.0 : 0.30	48

p:g:s — *p*-coumaryl:guaiacyl:syringyl.

It must be mentioned that 4,4′-dihydroxytruxillic acid has been identified in all sections of bamboo. On the grinding of the plant material, its amount increased by 20-30%, which shows a dimerization of *p*-coumaric acid under the action of mechanochemical energy. The methyl ether of coniferyl alcohol undergoes dimerization on grinding, forming a compound of the truxillic acid type [74].

The presence of phenolic acids in herbaceous plants affects the properties of the lignin. Thus, one of the reasons for the ready solubility of part of the lignin of wheat straw in alkalis is the increased level in these fractions of acid groups and structures unstable in an alkaline medium [29]. In the same investigation [29] it was established that wheat straw contains ~48% of *p*-coumaric acid and ferulic acid bound with the lignin by ether bonds, while the ferulic acid was bound both with the lignin and with the hemicelluloses.

The type of treatment of the plant material also affects the liberation of the phenolic acid bound with the lignin. As a results of two treatments with alkali and one with acid of wheat straw lignin it was shown that 93% of the *p*-coumaric acid was bound with the lignin by an ester bond [75].

Thus, *p*-coumaric acid is mainly bound with the lignin, while ferulic is bound not only with the lignin but with hemicelluloses and has been identified in many nonlignin tissues [76-80].

Literature exists that is devoted to the determination of ester groups in the lignins of herbaceous plants. The units attached by ester bonds to the lignin matrix were determined qualitatively and quantitatively in an ethereal extract of the saponified Björkman lignin of wheat straw by differential UV spectrometry. It was established that, on saponification, 1-2 structural units per 100 PPSUs are liberated and the main component (~70%) is *p*-coumaric acid [8].

The presence of an ester bond between phenolic acids and the lignin macromolecule in kenaf dioxane lignin was established by "mild" alkaline hydrolysis [43].

In addition to carbohydrates and phenolic acids, the lignins of herbaceous plants may be linked by covalent bonds with compounds of the cell wall — cellulose, pectin substances, and structural proteins [82] — and by ether bonds with dicarboxylic and hydroxy acids as components of suberin [83].

Ratios of the Structural Units in the Lignins of Herbaceous Plants

The oxidation of lignin by nitrobenzene in an alkaline medium is used for the taxonomic classification of plant materials [1]. The ratio of aldehydes obtained as the result of nitrobenzene oxidation (NBO) is considered in many investigations as a sufficient criterion of the relative amounts of the three different phenylpropane components of lignin (Table 5). Both natural and isolated lignins of herbaceous plants have been subjected to oxidation.

In the lignins of plants of the Gramineae family, guaiacyl units predominate (with the exception of sample No. 3, Table 5). In the lignins of plants of the Malvaceae family the picture is different: guaiacyl units predominate in the natural and isolated lignins of the cotton plant, and syringyl units in the lignins of kenaf and some *Althea* samples. In the lignins of plants of the Leguminosae family, in contrast to the Gramineae and Malvaceae families, attention is attracted by the high content of *p*-coumaryl structural units. Thus, the ratio of the structural units in the pea bush (*Sesbania aegyptica*) and in the pigeon pea (*Cajanus*) is close to 1:1:1, while in the lignin of another *Sesbania* species (*Sesbania asculeata*) the amount of *p*-coumaryl structures is almost twice as great as that of syringyl structures. This indicates a peculiar structure and a high degree of condensation of the lignins of these plants.

The ratio of structural units in lignin is estimated by different researchers differently. Erickson considered that the lignins of herbaceous plants contain fewer syringyl units than wood lignins [85]. In woody plants the proportion of syringyl components ranges between 20 and 60% while herbaceous species form a greater diversity, and among them extreme results of 65 and 15% have been found in a sundew (Droseraceae family) and spurrey (Caryophyllaceae family).

To characterize the lignins of herbaceous plants, some workers make use of the ratio of the amounts of syringaldehyde to vanillin (S/V).

Derivatives of ferulic acid predominate in the lignins of gymnosperms, and ferulic and sinapic acid derivatives in those of angiosperms, i.e., lignin of the "guaiacyl-syringyl" type is present [86]. From the ratio of syringaldehyde to vanillin, Sato has detected a closeness of the lignin of peanuts (Leguminoseae family) to the lignins of gymnosperms. This ratio has values of 0.31, 0.32, and 0.39 for the lignins of the stems, leaves, and roots of the peanut, respectively [36]. The ratio of syringaldehyde and *p*-benzaldehyde to vanillin in the MGL of sugar cane amounted to 1.6 and 1.5 [87] which shows a predominance of syringyl structures.

The ratio of syringaldehyde to vanillin varies according to the age of the plants. This phenomenon has been observed in a study of the products of the oxidation of the lignin of vegetating wheat [88], cotton [17], and reed [89], plants.

The ratio of structural units is determined not only with the aid of NBO. As a result of the acithioacidolysis of wheat and rice straws ratios of the structural units were found that showed a predominance of guaiacyl and syringyl structures [84].

Analysis of literature information shows that out of the enormous number of herbaceous plants the lignins of only a few, mainly technical crops, have been studied.

Results confirming the highly regular stucture of the lignin formed in the tissues of various plant organs contradicts the basic postulate of lignin chemistry according to which the structure of this polymer is irregular. Consequently, it is necessary to pass to the investigation of lignins isolated not from the whole plant but from the individual structural elements of the plant tissue.

A comparison of the results on the ratio of structural units permits the assumption that the lignins of herbaceous plants may have different degrees of condensation, depending on their species.

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