PMR SPECTRA OF THE DIOXANE LIGNINS OF SOME PLANTS OF THE FAMILY MALVACEAE

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Analysis of PMR spectra of the dioxane lignins of three species of *Athea*, of kenaf, and of the cotton plant has shown that the number of free aromatic protons does not correlate with the number of OCH_3 groups, which indicates different degrees of condensation of the dioxane lignins studied. In all the preparations a very small amount of coumarane structures were found. The aliphatic OH groups have been distinguished as primary (γ-OH) and secondary (α-OH) and their quantitative estimation has been carried out from the PMR spectra.

Continuing PMR spectroscopic investigations [1, 2] of dioxane lignins (DLAs), we have studied preparations from the ripe stems of *Althea rhuticarpa, A. nudiflora,* and *A. rosea* and of kenaf of the variety Uzbekskii 15-74 in comparison with the DNA of the ripe stems of the cotton plant of variety 108-F. The isolation and characterization of the DLAs has been described previously [3-5]. Below we give the developed formulas of the preparations:

DLA of *Althea rhuticarpa*

$$C_9H_{7.61}O_{1.0}(OCH_3)_{1.07}(OH_{ph})_{0.43}(OH_{\text{ал}})_{0,93}(O_{CO})_{0.52}(O_{ar-al})_{0.57};$$

DLA of *Althea nudiflora*

$$C_9H_{6.84}O_{1,21}(OCH_3)_{1.2}(OH_{ph})_{0.35}(OH_{\text{ал}})_{0.77}(O_{CO})_{0.41}(O_{ar-al})_{0.62};$$

DLA of *Althea rosea*

$$C_9H_{6,35}O_{0,82}(OCH_3)_{1.25}(OH_{ph})_{0.2}(OH_{\text{ал}})_{0,97}(O_{CO})_{0,3}(O_{ar-al})_{0.8}(OOH_{COOH})_{0,056};$$

DLA of kenaf

$$C_9H_{6.6}O_{0,9}(OCH_3)_{1.34}(OH_{ph})_{0,25}(OH_{\text{ал}})_{1.01}(O_{CO})_{0,17}(O_{ar-al})_{0.75}(OOH_{COOH})_{0.02};$$

DLA of the cotton plant

$$C_9H_{8.02}O_{0.58}(OCH_3)_{1.23}(OH_{ph})_{0.44}(OH_{\text{ал}})_{0.96}(O_{CO})_{0,22}(O_{ar-al})_{0.56}(OOH_{COOH})_{0,085}.$$

The PMR spectra of the DLA preparations investigated in the present work and those studied previously [1, 2] were similar but on calculation a substantial difference in the number of protons in them was found. The signals were identified in accordance with the literature [6-8]. For this purpose all the spectra were divided into seven regions corresponding to definite types of protons. In the quantitative determination of the protons, as a basis we took the number of methoxyls on C9 found by the analysis of functional groups (see the empirical formulas) as was done previously [1, 2]. The distribution of the protons in the phenylpropane units of the DLAs is given in Table 1.

As follows from Table 1, the number of aromatic protons (zone I) in all the DNA preparations excluding those of the cotton plant is less than two, which shows a high degree of substitution in the benzene rings. If we base ourselves on the number of aromatic protons calculated from the PMR spectra by the method proposed previously [8] it is impossible to calculate the percentage content of condensed aromatic nuclei in the preparations since, according to alkaline nitrobenzene oxidation, they contain a considerable proportion of p-coumaryl structures to every guaiacyl structural unit: for the DLA of *A. rhuticarpa,* 0.2; for *A. nudiflora,* 0.4; for *A. rosea*, 0.5; and for henaf, 0.3 [3, 9]. Thus, these structures are not considered in the determination of the degree of condensation.

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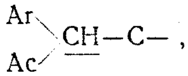
TABLE 1.

Zone	Boundaries of the zone, ppm	Althea rhuticarpa		Althea nudiflora		Althea rosea		Kenaf		Cotton plant	
		A	B	A	B	A	B	A	B	A	B
I	2,0—3,7	12,04	1,74	11,96	1,50	11,40	1,45	12,50	1,61	17,27	2,34
II	3,7—4,2	4,01	0,46	3,08	0,39	3,80	0,48	5,20	0,67	4,24	0,58
III	4.2—4,8	2,40	0,28	1,93	0,24	2,85	0,36	2,00	0,26	2,36	0,32
IV	4,8—7,5	45,78	5,30	45,94	5,79	48,57	6,17	46,87	6,03	45,05	6,12
IVa	6,0—6,8 (OCH_3)	27,71	3,60*	28,57	3,60*	29,52	3,75*	31,25	4,02*	27,16	3,69*
Other protons		18,67	2,09	17,37	2,19	19,05	2,42	15,62	2,02	17,89	2,43
V	7,5—7,9	5,22	0,61	7,72	0,97	4,75	0,60	5,20	0,67	7,06	0,95
VI	7,9—8,4	24 89	2,88	23,25	2,93	21,90	2,78	20,30	2,61	21,35	2,90
VII	8.4—9,5	7,22	0,84	6,17	0,78	6,66	0,85	7,80	1,00	2,67	0,36
	Total	100	17,41	100	18,39	100	18,86	100	18,88	100	13,58

A) Percentage content of the signal; B) number of protons at C_9. The values marked by asterisks are taken from the empirical formulas.

A calculation of the protons of benzyl acetate groups  $\overset{Ar}{\underset{Ac}{}}\!\!>\underline{CH}-C-$, corresponding to cydroxyls present in the α-positions to benzene rings (zone II) showed that in the preparations studied their amounts differed fewest in the DLA of *A. nudiflora* (0.31/C_9) and most in the kenaf DLA (0.67/C_9).

The protons of coumarane structures are found in region III. In all the preparations studied the number of such structures was small, ranging from 0.12/C_9 in the DLA of *A. nudiflora* to 0.18/C_9 (in the DLA of *A. rosea*).

The signals of the protons of methoxy groups and of the C_3 side chains appear in zone IV. The number of the latter in the different preparations ranges from 2 to 2.4/C_9. These protons are difficult to differentiate from the PMR spectra, since they appear in the form of a broadened signal.

A large amount of information on the hydroxy groups is given by regions V and VI, where the protons of the acetyl groups appear: in the zone V the aromatic and in zone VI the aliphatic acetyl groups. Below we give the numbers of OH groups calculated from the results of functional group analysis (column I) and from the PMR spectra (II):

DLA	OH_{phen}		OH_{aliph}		OH_{tot}		*α-OH*	*γ-OH*
	I	*II*	*I*	*II*	*I*	*II*		
Althea rhuticarpa	0,43	0,30	0,93	0,96	1,36	1.26	0,46	0.50
Althea nudiflora	0,38	0,32	0,77	0,97	1,15	1,29	0,39	0.58
Althea rosea	0,20	0,20	0,97	0,93	1,17	1,13	0,48	0,45
Kenaf	0,25	0,23	1,01	0,87	1,26	1,10	0,67	0,20
Cotton plant	0,44	0,32	0,96	0,97	1,40	1,29	0,58	0,39

Knowing the total number of aliphatic hydroxyls and γ-hydroxyls (II) it is possible to calculate the β-hydroxy groups, bearing in mind the fact that in lignins β-OH groups are either not found or are present in very small amounts. The sum of the aliphatic hydroxyls in all the preparations was close to 1. Consequently, in each of the DLAs studied there must be one hydroxyl in the side chain. In the DLA of *A. rhuticarpa* and *A. rosea* α- and γ-hydroxyls are present in approximately equal amounts, in the DLA of kenaf and the cotton plant α-OH groups predominate, and in the DLA of *A. nudiflora* γ-OH groups.

Furthermore, in all the lignins a very small amount of highly screened protons (zone VII) was found. These are possibly aliphatic methyl and methylene protons [6, 8]. With the exception of the kenaf DLA, their amount is everywhere less than 1.

On summing the numbers of protons of zones I, II, III, IV (without OCH_3), and VII, we obtain the total number of protons in the lignin preparations without functional groups. For the DLA of *A. rhuticarpa* it is 5.41, for *A. nudiflora* 5.10, for *A. rosea* 5.56, for kenaf 5.55, and for the cotton plant 6.01. Thus, this number ranges within fairly narrow limits but it is always 1-2 units lower than that calculated from the empirical formulas.

The preparations of dioxane lignins were acetylated with a mixture of acetic anhydride and pyridine at room temperature for a day. After the end of the reaction, the aceylated preparations were precipitated in water. After drying, they were purified by reprecipitation from dioxane solutions in ether. The precipitated preparations were carefully dried in a vacuum desiccator over P_2O_5.

The PMR spectra were recorded on a JNM-4H-100/100 MHz instrument at 22-24°C, C 10-12% by weight, internal standard MHDS, τ scale, solvent deuterochloroform.

K. L. Seitanidi took part in the recording and interpretation of the spectra.

SUMMARY

Analysis of the PMR spectra of the dioxane lignins of three types of the *Althea*, of kenaf, and of the cotton plant has shown that the number of free aromatic protons does not correspond with the number of OCH_3 groups, which indicates different degrees of condensation of the dioxane lignins studied. In all the preparations there is a considerable amount of coumarane structures. The aliphatic hydroxy groups have been differentiated into primary (γ-OH) and secondary (α-OH) from the PMR spectra, and they have been calculated quantitatively.

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