Condensation Degree of Softwood Protolignin*

Masamitsu Funaoka and Isao Abe**

Summary

The condensation degrees of protolignins in 12 species of softwoods, and its variation within the trunk of 30-year-old Hinoki (*Chamaecyparis obtusa* Endl.) were discussed, using the phenyl nucleus-exchange method. The phenyl nucleus-exchange method is a novel degradation method for lignin allowing the C-C linkages between side chains and phenyl nuclei to be cleaved selectively and almost quantitatively. The procedures in this method are simple, and based on the products, information on the condensation degree of protolignin is rapidly obtained without isolating lignin.

The variation of condensation degree of protolignin in horizontal sequence within the trunk of 30-year-old Hinoki was approximately similar at each height, in which it increased slightly once from bark side to pith, then exhibited a minimum value at the sapwood/heartwood boundary section, and increased again in heartwood. On the other hand, the variation of condensation degree in oblique sequence, which is the succession from the top downwards of the sections formed in the same years, was less on the whole, compared with that in horizontal sequence. The condensation degrees in 12 species of softwoods were close one another.

Introduction

The phenyl nuclei of lignin are divided into two types. One is a condensed type with some substituent in addition to the alkyl side chain (C_1), the methoxyl group (C_3, or C_3 and C_5), and the phenolic hydroxyl group or its ether (C_4). The other is a non-condensed type. The condensed type structures strongly influence the physical properties and reactivity of lignin. Therefore, information on condensation degree of lignin is of importance in chemical and physical processing of wood as well as its biosynthesis. In this connection, various attempts have been made to estimate the condensation degree of lignin.

Freudenberg et al.[1], by deuterium exchange, showed that about 45% of the coniferyl units in DHP were substituted at the C_5 position. Adler et al.[2] determined the condensation degree at the C_5 position to be about 50% for phenolic units in spruce milled wood lignin by means of an oxidation with potassium nitrosodisulphonate (Fremy's salt), and Tomimura et al.[3] found it to be about 50% for quaiacyl units in pine protolignin by a tracer method.

Using permanganate oxidation, Larsson et al.[4] determined the condensation degree at C_2 or C_6 positions to be 1.5–2.5% for birch milled wood lignin, and Erickson et al.[5] reported 2.5–3.0% for spruce milled wood lignin. Further, Tomimura et al.[3] estimated less than 4% in the quaiacyl nucleus of some softwood and hardwood protolignins, using the tracer method.

Through NMR spectroscopy by which the total condensation degree at C_2, C_5 and C_6 positions was examined, Lenz[6] estimated it at 43% for spruce milled wood lignin, Ludwig et al.[7] at 40–50% for spruce milled wood lignin, Morohoshi et al.[8] at 48% for Japanese fir milled wood lignin, and Bland et al.[9] at 42% for radiata pine methanol lignin.

However, most of the conventional methods for the determination of condensation degree of lignin as mentioned above were restricted to isolated lignin preparations or protolignins in limited wood sections around

the cambium.   Thus, the question has been raised whether the results obtained by such methods represent those of whole protolignins in the species.

The phenyl nucleus-exchange method is a novel degradation method for lignin allowing the C-C linkages between side chains and phenyl nuclei to be cleaved selectively and almost quantitatively[10–22].   The procedures in this method are simple, and based on the products, information on the condensation degree of protolignin is rapidly obtained without isolating lignin.   In the present work, the condensation degrees of protolignins in various softwoods and its variation within the trunk were discussed, using the phenyl nucleus-exchange method.

Methods

Phenyl nucleus-exchange method

The phenyl nucleus-exchange method was developed in order to allow the C-C linkages between side chains and phenyl nuclei to be cleaved selectively, and the phenyl nuclei to be liberated finally as polyhydric phenols. The important characteristic of this method is to take advantage of the dealkylation in diphenylmethane type structures in the presence of boron trifluoride and excess phenol, for the degradation of lignin.   By phenolation at the α-positions of side chains, diphenylmethane type structures containing the phenyl nuclei of lignin are formed.   This results in decreasing cleavage energies of C-C linkages between phenyl nuclei and side chains. Subsequently, phenyl nuclei of lignin are dealkylated, and cations formed are rapidly stabilized by phenol. Released phenyl nuclei of lignin are further demethylated to give polyhydric phenols.   That is, this method consists of the following three reaction steps; the formation of diphenylmethane type structures by the phenolation of side chains to be followed by the exchange of the phenyl nuclei of lignin for phenol, and finally the demethylation of methoxyl groups (Fig. 1).   The lignin building units which give phenol monomers (NEP) almost quantitatively, quaiacol and/or catechol in softwood lignin, are non-condensed types and diphenylmethane types, and each of these units has any of the following: benzyl alcohol, benzyl ether, conjugated double bond, α-carbonyl group, and Cα-aryl bond, in the side chain (Fig. 2).

The condensed type linkages in lignin are mainly of β-5, 5-5, β-6 (or β-2), and 4-0-5 types. The β-5 and 5-5 type linkages have been considered to be present in about $0.14/C_9$ as phenylcoumaran structures and in about $0.25/C_9$ as biphenyl structures, respectively[23].   The amounts of β-6 (or β-2) and 4-0-5 type linkages are much less, about 0.025-$0.03/C_9$ and 0.035-$0.04/C_9$ for spruce milled wood lignin, respectively[5].   The phenyl
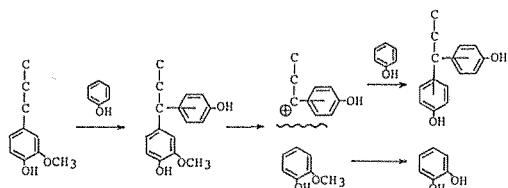

Fig. 1.   Formation of catechol from softwood lignin by the phenyl nucleus-exchange method.
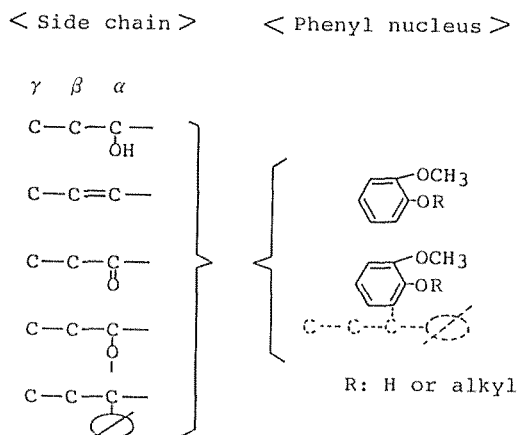

Fig. 2.   Lignin building units giving guaiacol and/or catechol almost quantitatively by the phenyl nucleus-exchange method.

nuclei carrying such condensed type linkages do not give NEP (Fig. 2). On the other hand, each unit of protolignin can be regarded as containing any of the side chain structures shown in Fig. 2. Therefore, NEP yield in protolignin directly reflects the number of units without β-5, 5-5, β-6 (or β-2), and 4-0-5 type linkages, non-condensed units. The condensation degree of protolignin is calculated by the following equation:

$$\text{Condensation degree} = 1 - \text{NEP Yield (mol/OCH}_3)$$

During the aging phase in the plant over a long period of time, it is probable that diphenylmethane type structures would be secondarily formed in protolignin[24]. However, such linkages are not determined as condensed types in the phenyl nucleus-exchange method, because diphenylmethane type linkages are easily cleaved. Namely, information on the condensation degree of protolignin formed during the initial lignin biosynthesis is obtained by the phenyl nucleus-exchange method.

Samples

In order to determine the variation of condensation degree of protolignin within the trunk, 30-year-old Hinoki (*Chamaecyparis obtusa* Endl.) was used. Five cm-thick discs were taken at 0.2, 1.2, 3.2, 5.2, 7.2, 9.2, and 10.2 m height from the ground. All discs were divided every five annual rings from the bark side. These samples were termed as shown in Table 1.

Table 1. Abbreviation of each section within the trunk of 30-year-old Hinoki
(*Chamaecyparis obtusa* Endl.).

Height from the ground (m)	Year of ring formation				
	1982–1978 (I)	1977–1973 (II)	1972–1968 (III)	1967–1963 (IV)	1962–1958 (V)
0.2	0.2-I	0.2-II	0.2-III*	0.2-IV	0.2-V
1.2	1.2-I	1.2-II	1.2-III*	1.2-IV	1.2-V**
3.2	3.2-I	3.2-II	3.2-III*	3.2-IV	—
5.2	5.2-I	5.2-II*	5.2-III	—	—
7.2	7.2-I	7.2-II*	—	—	—
9.2	9.2-I	—	—	—	—
10.2	10.2-I	—	—	—	—

* The section including the sapwood/heartwood boundary.
** 1962–1959

For the comparison of condensation degrees between species, the following 12 species of softwoods were used: Spruce (*Picea abies* Karst.), Yezo spruce (*Picea jezoensis* Carr.), Glehn's spruce (*Picea glehnii* Mast.), Slash pine (*Pinus elliottii* Engelm.), Japanese red pine (*Pinus densiflora* Sieb. et Zucc.), Japanese black pine (*Pinus thunbergii* Parl.), Japanese larch (*Larix leptolepis* Gord.), Japanese fir (*Abies firma* Sieb. et Zucc.), Japanese hemlock (*Tsuga sieboldii* Carr.), Sugi (*Cryptomeria japonica* D. Don), Hinoki (*Chamaecyparis obtusa* Endl.), and Japanese torreya (*Torreya nucifera* Sieb. et Zucc.). These wood samples were obtained in the shape of blocks and the positions where they originated from within the trunks were unknown.

These samples were ground roughly by a Wiley mill and then ground finely enough by a vibrational mill (Heiko Seisakusho, Model TI–500) to pass an 80 mesh screen[22]. The wood meals were extracted with ethanol-benzene (20:80, V/V) and then with ethanol, for 48 hrs, respectively. Extractive-free wood meals were freed of solvent and dried over phosphorus pentoxide *in vacuo*.

Reagent

Ten parts of xylene, 19 parts of phenol and 4 parts of boron trifluoride-phenol complex ($BF_3 \cdot 2C_6H_5OH$) were homogeneously mixed (phenol : BF_3 : xylene, mol ratio; 1:0.08:0.32)[22] and the solution was stored in an automatic buret intercepting moisture.

Procedures

Wood meal (400 mg) and 14 ml of the reagent were placed in a stainless steel bomb, and sealed. The reaction mixture was heated by means of an oil bath at 180°C for 4 hrs[22]. The mixture was cooled to room temperature, and was vigorously stirred with excess ethyl ether. The ether insoluble substances were filtered and washed with ethyl ether. The filtrate and washings were combined and vigorously stirred with excess water saturated with sodium chloride. The ether layer was separated and dried over anhydrous sodium sulfate. The reaction products in ether solution were converted to their trimethylsilyl derivatives by treating with N,O-bis (trimethylsilyl) acetamide at room temperature for 1 hr and were analyzed by gas chromatography. s-Diphenylethane was used as an internal standard for the determination of products. Apparatus: YANAGIMOTO G 3800 instrument, Column: 5% Silicone GE SE-30 on Chromosorb WAW 60/80 mesh, stainless steel $3 \text{mm}\phi \times 3 \text{m}$, Column temperature: 155°C, Injection temperature: 230°C, Carrier gas: Helium, Detector: FID.

Results and Discussion

Variation of condensation degree of protolignin within the trunk

Wood properties are very different between species, trees of the same species, and within a tree. For example, in horizontal sequence, the ring width increases rapidly from the fifth to tenth ring from the pith, and then decreases gradually outwards[25]; the fiber length in the ring nearest the pith is very short, increases rapidly in the next few rings, and then increases more slowly until a maximum length is reached[26]. Such heterogeneity of wood has been observed also in the chemical structures of the constituents. Chemical structures of lignins are different between xylem and bark[27], between reaction wood and normal wood[28], and microscopically, between compound middle lamella and secondary wall sections[29]. However, most previous works on the heterogeneity of lignin structures within the tree are in regard to reaction woods or cell walls as mentioned above. There seems to be little quantitative information on the variation of lignin structures within the trunk. However, wood samples for an investigation are not generally obtained as timber, but as lumber or blocks. Therefore, in order to estimate chemical structures of whole protolignins in the wood from analytical data of samples which represent a part of the wood, the structural variation of protolignins within the trunk should be elucidated. Such information is also of importance from the point of view of lignin biosynthesis as data indicating the relation between lignin chemical structures and age of meristem or environment etc.

NEP Yields within the trunk of Hinoki are shown in Table 2. The NEP yield of protolignin in each wood section was in the range of about 25 to 30%, which is more than about two or three times that of technical lignins[20].

The variation of condensation degree in horizontal sequence at each height was approximately similar, in which it increased slightly once from bark side to pith, then exhibited a minimum value at the sapwood/ heartwood boundary section, and increased again in heartwood. The factors causing the variation of condensation degree in horizontal sequence include the difference of lignin chemical structures by the age of meristem or the environment at initial lignin biosynthesis and the secondary changes within a tree. However, protolignin having lowest condensation degree is in the sapwood/heartwood boundary section at every height. This fact strongly suggests that the change of lignin chemical structure within a tree was caused during heartwood formation. Lignification of the secondary xylem of a tree occurs within the zone of developing cells. However, besides this process, it has also been found that lignification takes place much later in certain cells. For example, lignification in cell walls of radial ray parenchyma occurs during heartwood formation in some trees[30]. Therefore, the structural change of lignin at the sapwood/heartwood boundary section may be partly due to this secondary lignification. Also, it may be due to the combination with some extractives or to enzymatical oxidation. Those are under investigation at present.

Table 2. Condensation degree of protolignin within the trunk of 30-year-old Hinoki (*Chamaecyparis obtusa* Endl.).

Sample	Sap or Heart	Ethanol-benzene extract (%)	Klason lignin		NEP Yield*		Condensation degree**
			% of wood	OCH₃, %	% of Klason lignin	mol/OCH₃	
0.2-I	Sap	0.9	32.9	14.95	28.72	0.542	0.46
0.2-II	Sap	2.0	33.0	15.24	26.85	0.496	0.50
0.2-III	Sap and Heart	3.9	33.1	15.12	30.79	0.574	0.43
0.2-IV	Heart	7.8	32.4	14.45	26.88	0.524	0.48
0.2-V	Heart	8.5	31.7	14.57	27.86	0.539	0.46
1.2-I	Sap	0.5	30.9	15.33	27.84	0.512	0.49
1.2-II	Sap	0.9	32.3	14.65	26.43	0.508	0.49
1.2-III	Sap and Heart	3.1	33.0	14.88	28.52	0.540	0.46
1.2-IV	Heart	5.1	33.3	14.31	25.97	0.512	0.49
1.2-V	Heart	4.0	32.5	14.57	27.30	0.528	0.47
3.2-I	Sap	1.0	32.0	14.63	26.21	0.505	0.50
3.2-II	Sap	1.1	31.6	14.91	25.99	0.491	0.51
3.2-III	Sap and Heart	2.5	31.0	14.71	27.75	0.532	0.47
3.2-IV	Heart	2.6	33.0	14.34	25.76	0.506	0.49
5.2-I	Sap	0.6	31.0	14.88	25.46	0.482	0.52
5.2-II	Sap and Heart	0.8	31.5	14.29	25.98	0.512	0.49
5.2-III	Heart	2.3	33.4	14.40	23.05	0.451	0.55
7.2-I	Sap	0.7	30.8	14.77	24.67	0.471	0.53
7.2-II	Sap and Heart	1.3	32.1	14.70	26.42	0.507	0.49
9.2-I	Sap	1.2	32.6	14.11	25.68	0.513	0.49
10.2-I	Sap	1.7	31.7	13.87	27.49	0.559	0.44

* The sum of guaiacol and catechol yields by the phenyl nucleus-exchange method.

** Condensation degree $= 1 - $ NEP Yield (mol/OCH₃)

The oblique sequence, which is the succession from the top downwards of the sections formed in the same years, indicates the variation due to the age of the meristem, because it is the succession of the sections in which the environment at biosynthesis and the aging years within the tree are the same. The variation in oblique sequence was less on the whole, compared with that of horizontal sequence. In sequence I (1982–1978), the condensation degree increased gradually from the bottom to the top, exhibited a maximum value just under the crown, and then decreased. The analogous variation patterns within a trunk have been observed in the ring width[25] or the fiber length[26]. This suggests that there is a relation between the age of meristem and the wood formation.

The average condensation degree at each height increased gradually from the bottom to the top, exhibited a maximum value at middle height or under the crown, and then decreased (Table 3). This trend is similar to that of oblique sequence I. On the other hand, the variation of average condensation degree in each oblique sequence was less (Table 3).

Condensation degree of softwood protolignin

The condensation degrees in 12 species of softwoods are shown in Table 4. Although it is higher in Japanese larch and Japanese torreya, and is slightly lower in Japanese red pine, it is approximately in the range of 0.45 to 0.50 in other species. The wood samples were obtained in the shape of blocks and the positions where they originated from within the trunks were unknown. However, interspecies variation does not

Table 3. Average condensation degree in horizontal- and oblique sequences.

Horizontal sequence		Oblique sequence	
Height (m)	Average condensation degree	No.	Average condensation degree
0.2	0.47	I (1982-1978)	0.49
1.2	0.48	II (1977-1973)	0.50
3.2	0.49	III (1972-1968)	0.48
5.2	0.52	IV (1967-1963)	0.49
7.2	0.51	V (1962-1958)	0.47
9.2	0.49		
10.2	0.44		

Table 4. Condensation degree of softwood protolignin.

Species		Klason lignin		NEP Yield*		Condensation degree**
		% of extr. free wood	OCH$_3$, %	% of Klason lignin	mol/OCH$_3$	
Spruce	*Picea abies* Karst.	27.0	15.05	28.10	0.515	0.49
Yezo spruce	*Picea jezoensis* Carr.	27.5	15.12	28.52	0.532	0.47
Glehn's spruce	*Picea glehnii* Mast.	27.4	15.26	29.84	0.551	0.45
Slash pine	*Pinus elliottii* Engelm.	27.9	14.34	25.96	0.499	0.50
Japanese red pine	*Pinus densiflora* Sieb. et Zucc.	26.0	14.74	30.42	0.570	0.43
Japanese black pine	*Pinus thunbergii* Parl.	27.1	15.58	29.30	0.519	0.48
Japanese larch	*Larix leptolepis* Gord.	29.3	15.31	24.27	0.446	0.55
Japanese fir	*Abies firma* Sieb. et Zucc.	30.5	15.30	28.04	0.507	0.49
Japanese hemlock	*Tsuga sieboldii* Carr.	32.1	14.65	27.64	0.522	0.48
Sugi	*Cryptomeria japonica* D. Don	32.8	14.49	28.76	0.549	0.45
Hinoki	*Chamaecyparis obtusa* Endl.	31.8	14.58	28.63	0.554	0.45
Japanese torreya	*Torreya nucifera* Sieb. et Zucc.	34.8	15.12	25.39	0.465	0.54

* The sum of guaiacol and catechol yields by the phenyl nucleus-exchange method.
** Condensation degree $= 1 - $ NEP Yield (mol/OCH$_3$)

exceed that observed within the trunk of Hinoki.   Therefore, the condensation degrees of softwood protolignins can be regarded to be close one another, independent of the species.

Softwood lignin is a polymer formed by random coupling mainly of coniferyl alcohol radicals.   However, its chemical structures have been found to be very heterogeneous within cell walls[29].   This heterogeneity has been considered to be due mainly to the concentration of monomer radicals at biosynthesis[31].   Present results indicating little differences in the condensation degrees of protolignins between species suggest strongly that biosynthesis mechanisms of softwood lignin, namely formation and transport mechanisms of monomer radicals, are very analogous among the species.

Acknowledgement

References

1) FREUDENBERG, K., V. JOVANOVIC and F. TOPFMEIER: Versuche mit deuteriertem Coniferylalkohol zur Bestimmung der Substitution am C-Atom 5 der Coniferyleinheit des Lignins. Chem. Ber., 4, 3227, 1961.

2) ADLER, E. and K. LUNDQUIST: Estimation of "Uncondensed" Phenolic Units in Spruce Lignin. Acta Chem. Scand., 15, 223, 1961.

3) TOMIMURA, Y., T. YOKOI and N. TERASHIMA: Heterogeneity in Formation of Lignin. V. Degree of condensation in guaiacyl nucleus. Mokuzai Gakkaishi, 26, 37, 1980.

4) LARSSON, S. and G. E. MIKSCHE: Gaschromatographische Analyse von Ligninoxydationsprodukten. IV. Zur Struktur des Lignins der Birke. Acta Chem. Scand., 25, 647, 1971.

5) ERICKSON, M., S. LARSSON and G. E. MIKSCHE: Gaschromatographische Analyse von Ligninoxydationsprodukten. VIII. Zur Struktur des Lignins der Fichte. Acta Chem. Scand., 27, 903, 1973.

6) LENZ. B. L.: Application of Nuclear Magnetic Resonance Spectroscopy to Characterization of Lignin. Tappi, 51, 511, 1968.

7) LUDWIG, C. H., B. J. NIST and J. L. McCARTHY: Lignin. XIII. The high resolution nuclear magnetic resonance spectroscopy of protons in acetylated lignins. J. Amer. Chem. Soc., 86, 1196, 1964.

8) MOROHOSHI, N. and A. SAKAKIBARA: The Chemical Composition of Reaction Wood. I. Mokuzai Gakkaishi, 17, 393, 1971.

9) BLAND, D, E. and S. STERNHELL: Estimation of Aromatic Protons in Methanol Lignins of Pinus Radiata and Eucalyptus Regnans from Proton Magnetic Resonance Spectra. Aust. J. Chem., 18, 401, 1965.

10) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride I. On the formation of catechol from MWL, dioxane lignin and kraft lignin. Mokuzai Gakkaishi, 24, 256, 1978.

11) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride II. The effect of methoxyl group and ethylenic double bond on the formation of catechol. Mokuzai Gakkaishi, 24, 892, 1978.

12) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride III. The chemical structure of lignin required for the liberation of phenyl nucleus. Mokuzai Gakkaishi, 26, 334, 1980.

13) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride IV. The structure formed by the nuclear exchange for phenol. Mokuzai Gakkaishi, 26, 342, 1980.

14) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride V. The role of boron trifluoride and phenol on the formation of catechol. Mokuzai Gakkaishi, 28, 522, 1982.

15) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride VI. The behavior of lignin building units unable to form the diphenylmethane structure. Mokuzai Gakkaishi, 28, 529, 1982.

16) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride VII. The cleavage of C-C linkage by disproportionation. Mokuzai Gakkaishi, 28, 563, 1982.

17) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride VIII. The decomposition of softwood lignin. Mokuzai Gakkaishi, 28, 627, 1982.

18) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride IX. The decomposition of hardwood lignin. Mokuzai Gakkaishi, 28, 635, 1982.

19) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride X. The properties of residual lignin and the degradation mechanism of lignin. Mokuzai Gakkaishi, 28, 705, 1982.

20) FUNAOKA, M. and I. ABE: The Reaction of Lignin under the Presence of Phenol and Boron Trifluoride XI. The decomposition of industrial lignins. Mokuzai Gakkaishi, 28, 718, 1982.

21) FUNAOKA, M.: Studies on the Reaction of Lignin in the Presence of Phenol and Boron Trifluoride. Bull. Mie Univ. Forest, No. 13, 1, 1984.

22) FUNAOKA, M. and I. ABE: Degradation of Protolignin by the Nuclear Exchange Method. Mokuzai Gakkaishi, 31, 671, 1985.

23) LAI, Y. Z. and K. V. SARKANEN: Lignins, K. V. SARKANEN and C. H. LUDWIG (ed.), New York, Wiley-Interscience, p. 195, 1971.

24) LEARY, G. J.: Quinone Methides and the Structure of Lignin. Wood Sci. Technol., **14**, 21, 1980.

25) TAJIMA, T.: Tree Growth and Wood Properties. Memoirs of the Faculty of Agriculture, Tokyo University of Education, No. 13, 65, 1967.

26) TAJIMA, T.: Tree Growth and Variation of Wood Properties. Mokuzai Gakkaishi, **17**, 423, 1971.

27) SARKANEN, K. V. and H. L. HERGERT: Lignins, K. V. SARKANEN and C. H. LUDWIG (ed.), New York, Wiley-Interscience, p. 81, 1971.

28) YASUDA, S. and A. SAKAKIBARA: The Chemical Composition of Lignin from Compression Wood. Mokuzai Gakkaishi, **21**, 363, 1975.

29) WHITING, P. and D. A. I. GORING: Chemical Characterization of Tissue Fractions from the Middle Lamella and Secondary Wall of Black Spruce Tracheids. Wood Sci. Technol., **16**, 261, 1982.

30) BAUCH, J., W. SCHWEERS and H. BERNDT: Lignification during Heartwood Formation. Comparative study of rays and bordered pit membranes in coniferous woods. Holzforschung, **28**, 86, 1974.

31) SARKANEN, K. V.: Lignins, K. V. SARKANEN and C. H. LUDWIG (ed.), New York, Wiley-Interscience, p. 116, 1971.

摘　　　要

針葉樹プロトリグニンの芳香核縮合度

船岡　正光・阿部　　勲

　針葉樹12種のプロトリグニンの縮合度および30年生ヒノキ (*Chamaecyparis obtusa* Endl.) 樹幹内におけるその変動に検討を加えた。

　ヒノキ樹幹内において，各樹高での半径方向における変動パターンは互いに類似しており，いずれも心辺材境界部を含む区分で最小値を示した。一方，形成年度を同じくする区分の樹高方向の変動は，半径方向と比較して全般に小さかった。

　プロトリグニンの縮合度は，針葉樹12種で互いに近似していた。