Biochemistry of Soil Organic Matter in Relation to Crop Production

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Content

Lecture 1.

Formation of Humic Substances through Transformation of Plant Residues

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1. Introduction
2. Degradation of plant constituents during humification.
3. Lignin as an initial material for formation of humic substances.
   - 3.1 Isolation of lignin fractions and their elemental composition.
   - 3.2 Differences in the degradation of building blocks of lignins during humification.
   - 3.3 Function of the oxygen.
   - 3.4 Function of the nitrogen.
   - 3.5 Spectroscopic investigations.
   - 3.6 Degradation to low molecular weight components.
4. Introduction to biochemical degradation of lignins.

1. Introduction

The processes of humification occur mainly under aerobic conditions. Soil animals may first reduce the size of the fresh organic residues. Further transformations are promoted by the activity of the enzymes of bacteria and fungi living in the soil. Cellulose, proteins and fats are readily available carbon sources for the microorganisms, while compounds such as lignin and other phenolic plant constituents are decomposed more slowly. These as well as some of the new substances which are formed through oxidation of phenolic units have toxic properties to different degrees. They can therefore only serve as a carbon source for special species of microorganisms. Besides the organic residues derived from higher animals and plants, many substances synthesized by microorganisms can serve as carbon sources.

Certain species of microorganisms also synthesize phenolic or quinonoid metabolic products which decompose slowly by reason of their more or less markedly toxic properties or their sorption on inorganic soil constituents.

The transformation of nitrogen containing substances plays an important role during humification. The microorganisms use as a nitrogen source the proteins and their decomposition products derived from dead animals and plants as well as from the microorganisms themselves.

The nitrogen compounds of the humus are the natural reservoir for the nitrogen nutrition of plants, because this element is not supplied in significant quantities by the weathering of the rocks and the minerals of the soil. Furthermore the amount of nitrogen which reaches the soil in the rainwater and which is fixed by nitrogen fixing organisms is not sufficient for the annual plant growth. The nitrogen containing organic compounds of the soil humus are, therefore, very important for the

productivity of the soil under natural conditions.

The humification process does not only involve the decomposition of high and low molecular weight plant, animal and microbial cell constituents and transformation products but also the synthesis of low and high molecular weight compounds, which are not formed within living cells, but must be considered as typical organic soil constituents formed by humification processes. These compounds are dark coloured and are called humic substances. They can be separated in different fractions from the other substances of the humus by their characteristic solubilities or dispersabilities.

Examples of the distribution of the soil organic carbon in the various fractions of humic substances are presented in the following summary of SCHREINER and SHOREY S.a.S. (1910), BERTHELOT and ANDRÉ (B) (1892) and SHMUK (S) (1930), (tab. 1).

The composition of the different fractions from a single soil sample depends to a considerable degree on the methods used. The composition of fractions of different origin obtained by isolation with a standardized procedure is also variable. The names "Fulvic acids", "Hymatomelanic acids", "Humic acids", "Humins" are therefore only designations or symbols for fractions of substances, which are isolated and separated with conventional methods.

Tab. 1: Organic carbon of the soil = 100

Extraction with sodium hydroxyde 2 %

insoluble	alkaline solution
24 (S.a.S.)	76 (S.a.S.)
32 (B)	68 (B)
20 (S)	80 (S)

Humins	acidified and filtered
precipitate	acidic filtrate
37 (S.a.S.)	39 (S.a.S.)
28 (B)	40 (B)
60 (S)	20 (S)

extraction with boiling alcohol

insoluble	alcoholic solution
16 (S.a.S.)	21 (S.a.S.)
40 (S)	15 (S)

Humic acids — Hymatomelanic acids

Fulvic acids

contain substances of different molecular weights, compounds with partly known constitution

As an example the investigations of KONONOVA (1961) are as follows. The amounts of fulvic and humic acids of the soils of the UdSSR from North to South were investigated with a standardized procedure and their elemental composition determined.

Tab. 2: Elemental composition of humic acids (I) and fulvic acids (II) of the main soils of the UdSSR (as percentage of absolute weight of ash-free material according to KONONOVA, 1961).

Soils		C	H	O	N	C:H
Northern podzol under forest; humus illuvial horizon 16-24 cm; Arkhangel region	I	58.11	5.37	32.00	4.52	10.82
	II	52.37	3.53	42.89	1.21	14.84
Sod-podzolic soil, arable; 0-20 cm; Moscow region	I	57.63	5.23	35.33	4.81	11.02
	II	42.63	5.05	44.60	4.12	9.15
Dark-gray forest soil under oak; 12-19 cm; Shipov forest Voronezh region	I	61.20	3.60	31.32	3.88	17.00
	II	47.46	3.64	45.87	3.03	13.04
Ordinary chernozem, arable; 0-20 cm; Kamennaya Steppe, Voronezh region	I	62.13	2.91	31.38	3.58	21.35
	II	44.84	3.45	49.36	2.35	13.00
Chestnut soil; virgin land; 0-20 cm; Valuisk Exp. Sta. Stalingrad region	I	61.74	3.72	30.62	3.92	16.60
	II	43.19	3.61	51.43	1.77	11.96
Light serozem, arable; 0-20 cm; Pakhta-Aral, Kazakhsk SSR	I	61.94	3.93	29.46	4.67	15.76
	II	45.80	4.30	46.00	3.90	10.65
Krasnozem under farn; 0-20 cm; Anaseuli, Georgian SSR	I	59.65	4.37	31.54	4.44	13.65
	II	49.82	3.35	44.33	2.50	14.87

The percentage of the elements depends upon the conditions of formation of the humic substances. Humic acids have a higher C and N content but a smaller oxygen content than the fulvic acids.

In the following scheme nine soils of UdSSR from the North to the South are arranged. In the same direction the average temperature of the year increases from 2° to 11°C and the yearly rainfall decreases from about 600 mm to 100 mm. The values were collected from the book of KONONOVA (1966).

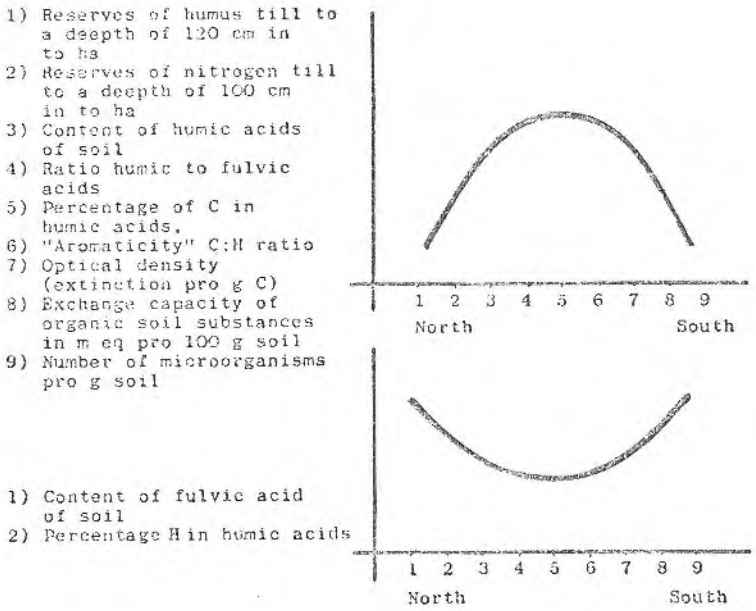


Fig. 1: Measurements of properties of soil organic matter of different soil types of UdSSR (according to KONONOVA 1966).

The course of the curves of the different properties of soil organic matter shall only indicate, that a maximum or a minimum exists for the data in the case of chernozem.

The different environmental factors and the inorganic initial materials lead in each case by the different ecological conditions to various biological processes, which finally influence the quantity and the properties of humic substances. These differences have again an influence on soil productivity by the interaction with the inorganic soil constituents.

It is clearly evident from these investigations, that the amount as well as the physical properties and the chemical composition of the fractions named fulvic or humic acids differ dependent on the inorganic

constituents of the soils.

2. Degradation of plant constituents during humification.

Studies on the decomposition of plant constituents in a straw mulch in the field (SAUERLANDT and GRAFF 1959) showed that the cellulose decomposes much faster than lignin.

The percentage of cellulose and lignin, lost from the beginning of September to the end of November in the humid climate of the middle of Europe were:

Tab. 3: Decrease of plant constituents during a 3 months' period.

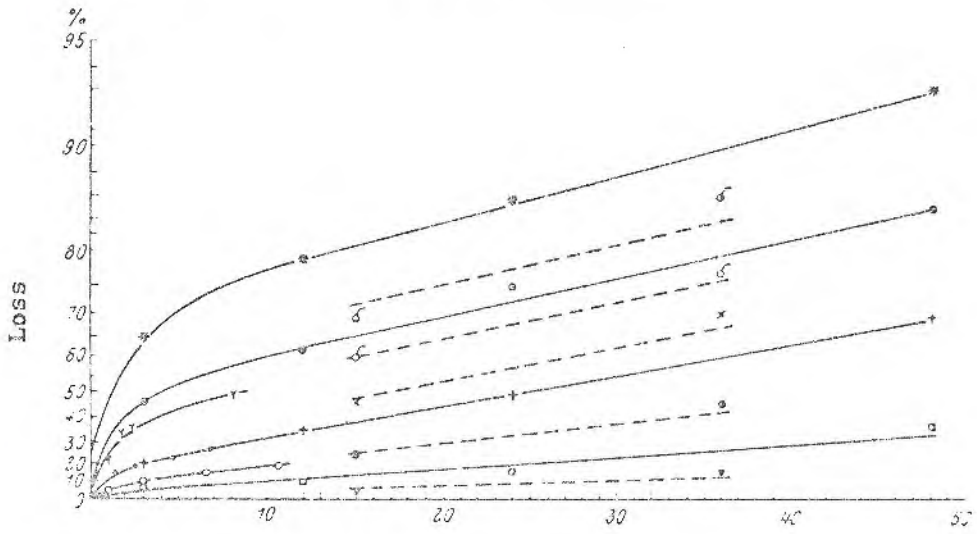
	Loss
Ether soluble fraction	52,1 %
Water soluble fraction	48,6 %
Cellulose	43,6 %
Lignin	4,7 %

	no additional water	sprinkled with water
Organic material	36,5 %	42,3 %
Lignin	21,7 %	7,3 %

The decomposition of the total organic matter and that of lignin was influenced in opposite directions under two moisture regimes.

The humification of plant material of different composition has been investigated primarily in the laboratory (KOLENBRANDER 1955, SPRINGER 1944, 1945, 1955, SPRINGER and LEHNER 1952 a,b , SPRINGER and SEISCHAB 1961). WAKSMAN and TENNEY (1927 a,b) call attention to the fact that young plants with a low methoxyl lignin content decompose easier than

older ones with a higher methoxyl content.



Rottingtime in months

Decomposition in soil (SIEGEL)
straw
manure (fresh)
" (fermented)
peat
Tornesch-lignin

Composts (SPRINGER and LEHNER)
green mass
straw
beach leaves
peat

Stable manure (decomposition)
GERRETSEN
SIEGEL
IVERSEN

Fig. 2: The losses of organic fertilizers on organic substances and drymatter during decomposition in soil, in composts and stable manures (KOLENBRANDER 1955).

Similar investigations were made with over-all labelled plant material by SAUERBECK (1968 (a,b,c)), JENKINSON (1965, 1966 b , 1968), OBERLÄNDER and ROTH (1968), SAUERBECK and FÜHR (1968, 1970), JANSSON and PERSON (1968). In principle the curves are the same, but it could be shown, that after 2 years about 30 % of labelled plant carbon remains in the soil and up to 4 % carbon are found in humic acids. More about this subject will be reported in the lecture "Use of isotopes in soil organic matter studies" (lecture 10).

Studies with carbon-14 labelled plant material have shown, that glucose decomposes faster than hemicelluloses and hemicelluloses faster than cellulose. The degradation of holocellulose occurs much faster than that of lignin. The degradation of lignin proceeds very slowly. The investigations showed further, that the radioactivity of added carbohydrate is found mainly in the hydrolysable parts of the humic acids, namely the amino acids, which are formed from the glucose through the metabolism of the microorganisms. Lignin or its degradation products, such as p-hydrohybenzaldehyde, vanillin and syringaldehyde is chiefly concentrated in the nonhydrolysable fraction of the humic acids. (SIMONART and MAYAUDON 1958 (a,b), SIMONART, MAYAUDON and BATISTIC 1959, MAYAUDON and SIMONART 1958, 1959 a,b , SØRENSEN 1963 a,b , FÜHR 1962, FÜHR and SAUERBECK 1966).

The most intensive studies on the processes of humification have been made with straw, a plant material, which is relatively rich in cellulose and lignin and poor in protein (BARTLETT and NORMAN 1938, BARTLETT, SMITH, BROWN 1937, BROADBENT 1954, FLAIG, SCHOBINGER and DEUEL 1959, KAILA 1952, MAEDER 1960, MOHTADI 1962, PHILLIPS 1934, SMITH, STEVENSON, BROWN 1930, SCHOBINGER 1958, SPRINGER and LEHNER 1952 a,b , WAKSMAN, TENNEY and DIEHM 1929).

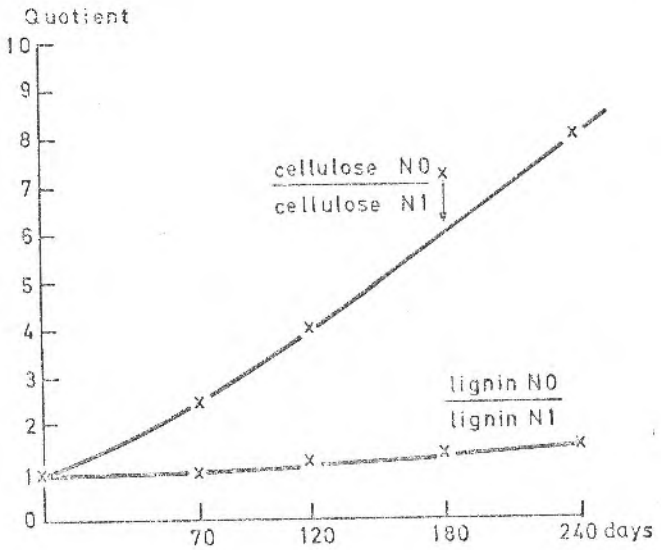
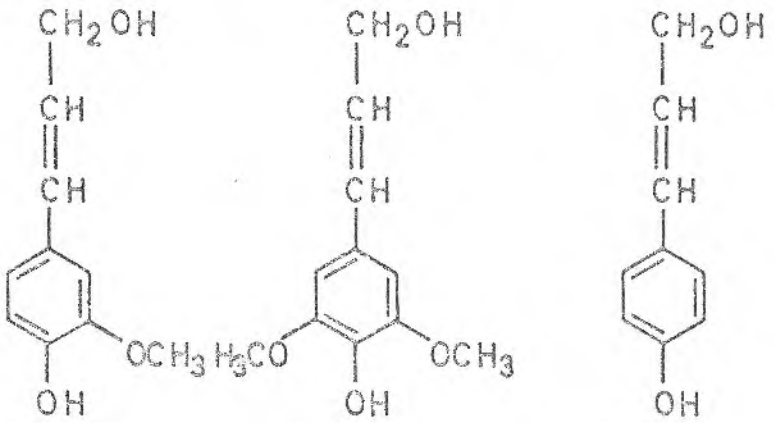


Fig. 3: Acceleration of the degradation of cellulose and lignin of rye straw by addition of nitrogen during 240 days. N 0 = no nitrogen added; N 1 = 1 % N as NH_4NO_3 per dry weight of straw (according to MAEDER 1960).

Since the content of available nitrogen may be a limiting factor for the activity of the microorganisms and therefore also for the rate of humification, the addition of nitrogen to low nitrogen residues accelerates decomposition. The quotient of the amount of the cellulose remaining after a given time without addition of nitrogen divided by the amount of the cellulose remaining with addition of nitrogen increases more rapidly than that of lignin (Fig. 3). This means, that the degradation of the cellulose is accelerated much more than that of lignin by added nitrogen (FLAIG 1962).

3. Lignin as an initial material for formation of humic substances.

Monomers of different Lignins.



Coniferous trees	+		
Deciduous trees	+	+	
Gramineees	+	+	+

Structure Scheme of Spruce Lignin

(FREUDENBERG et al. 1964, 1968)

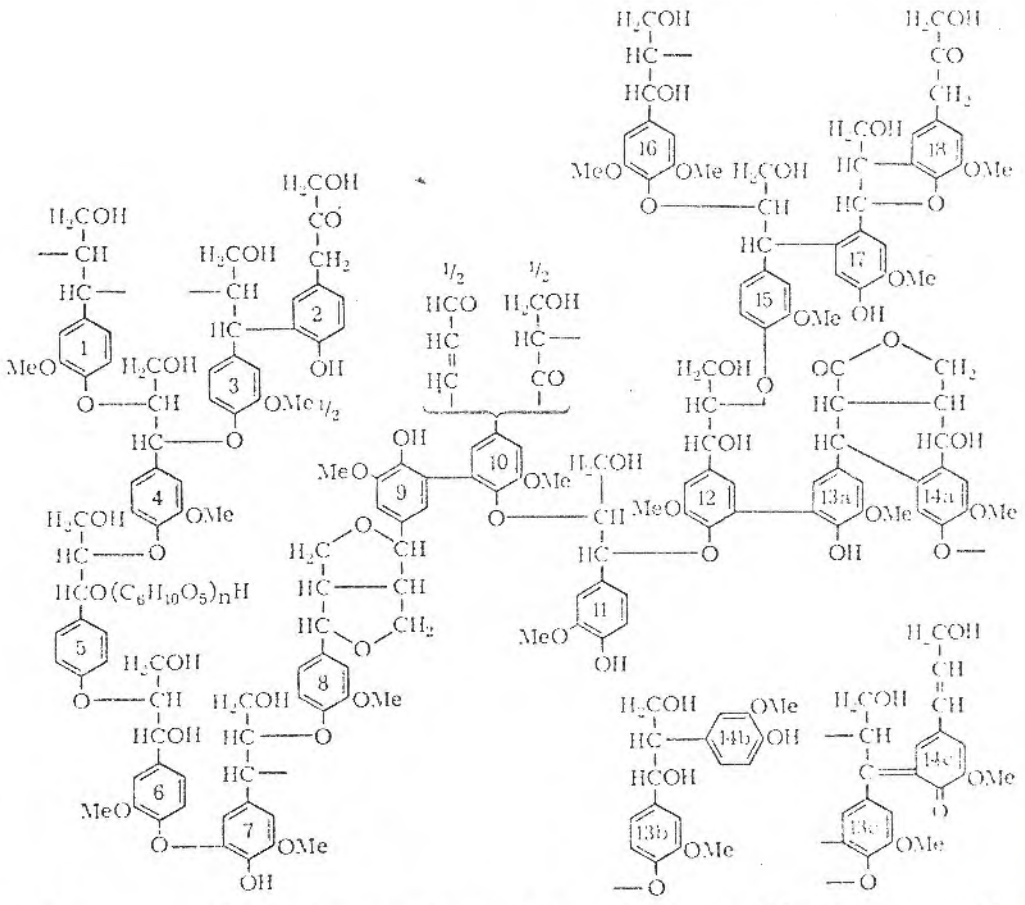


Fig. 4: Structure scheme of coniferous lignin according to FREUDENBERG (1964, et al. 1968).

The lignins of different species of plants are polymers or copolymers of different phenylpropenylalcohols, which are substituted in the benzene ring with one hydroxyl group. The ring may have no, one or two methoxyl groups. The lignin of conifers consists mainly of coniferyl alcohol, that of deciduous trees of a mixture of coniferyl and sinapyl alcohol and in the case of graminees, p-coumaryl alcohol copolymerises as a third component.

The structure scheme of spruce lignin of FREUDENBERG and coworkers (FREUDENBERG 1962, 1964, FREUDENBERG and HARKIN 1964, FREUDENBERG and NEISH 1968) will be used to illustrate the transformations of lignin during the formation of humic substances (see Fig. 4). Coniferyl alcohol as the building block is connected through different C=C-linkages of the side chains and the rings and through ether linkages to form a three dimensional polymer. The different linkages and their frequencies are described by several authors (ADLER 1961, FREUDENBERG 1962, 1964, FREUDENBERG et al. 1964, 1968).

The relatively slow decomposition of the lignin and other phenolic plant constituents leads to the conception, that these are important initial materials for the formation of humic substances. Other findings support this conclusion, for example the chemical degradation of humic acids to phenolic compounds, which may be derived from lignin and will be discussed later. For this reason the changes in the properties of lignins during humification have been intensively studied by various investigators.

3.1 Isolation of lignin fractions and their elemental composition.

Different investigations have been made to determine the sources of error during the isolation of lignin with sulfuric acid. One error,

coprecipitation of pentoses, (NORMAN and JENKINS 1934 a) is reduced by pretreatment with dilute acids. The coprecipitation of proteins (NORMAN and JENKINS 1934 b) which causes errors in the nitrogen content of isolated fractions has also been investigated. The conditions for the isolation of different lignins from different plant species and the necessary precautions for good yields with the sulphuric acid procedure, are described by PLOETZ (1940). Different methods for the isolation of lignin from rotted straw have been checked in extensive investigations (FLAIG, SCHOBINGER and DEUEL 1959).

The most useful values were obtained with the 72 % sulfuric acid method by careful treatment of the rotted straw (MAEDER 1960). "Sulfuric acid" lignins can be obtained with a sulfur content of 0,6 to 0,8 % and an ash content of 8 to 11 %.

The "lignin fractions", which can be isolated from straw during its humification, differ in their elemental composition from the original lignin. Therefore it is incorrect to call them lignin;it is better to speak about lignin fractions. The alterations in carbon and oxygen content are not as pronounced as the value for nitrogen and methoxyl content, even when the lignin fractions are isolated with dioxane according to the method of BJÖRKMAN (1954, 1956), (compare also: BROADBENT 1954, BARTLETT and NORMAN 1938, BARTLETT 1939, FLAIG, SCHOBINGER and DEUEL 1959, FLAIG 1960, WAKSMAN and SMITH 1934, STÖCKLI 1952, NEHRING and SCHIEMANN 1952 a,b).

Tab. 4: Elementary analysis of the ligain fractions of rye straw from experiments with and without added nitrogen calculated for ash-free substances (MAEDER 1960).

Days nitrogen	C %	H %	O % (Diff.)	N %	S %	OCH_3 %	ash %
0	62.73	5.48	30.55	0.53	0.55	17.08	6.15
70 ON*)	62.73	5.48	31.20	0.54	0.49	15.53	7.65
70 1N**)	61.42	5.25	30.20	1.44	0.69	12.76	9.00
120 ON	62.13	5.42	31.41	0.56	0.48	14.99	8.62
120 1N	60.93	5.41	31.20	1.68	0.78	11.33	10.02
180 ON	62.20	5.41	31.30	0.56	0.53	14.37	9.31
180 1N	60.94	5.38	31.15	1.74	0.79	10.95	11.24
240 ON	62.14	5.27	31.03	0.56	0.97	13.46	9.36
240 1N	59.61	5.13	32.77	1.88	0.61	13.46	11.69

*) ON = no nitrogen added,
**) 1N = 1 % N as NH_4NO_3 per dryweight of straw

Tab. 5: Elementary analysis of isolated "sulfuric acid" and "Björkman" lignin fractions of wheat straw. (Addition of 0,5 % N as $NaNO_3$ per dryweight of straw) (SCHOBINGER 1958).

Days of humification		C %	H %	O % (Diff)	N %	S %	OCH_3 %
H_2SO_4-Lignin	0	58,59	5,60	31,37	0,54	3,9	15,33
	70	58,78	5,93	29,48	2,01	3,8	11,14
	180	58,67	5,91	29,15	2,37	3,9	9,06
	340	54,97	5,96	32,09	3,08	3,9	8,57
Björkman-Lignin	0	60,68	5,79	33,11	0,42		16,76
	70	59,75	7,35	30,93	1,97		10,84
	180	58,81	6,56	31,27	3,36		8,19
	340	57,37	6,95	31,14	4,54		7,50

Tables 4 and 5 show, that the conditions during humification and the composition of the initial material (rye and wheat straw) influence the transformations of the lignin. But in all cases a correlation exists between the decrease of the methoxyl content and the increase of the nitrogen content (FLAIG 1960 a), which will be mentioned later.

3.2 Differences in the degradation of building blocks of lignins during humification.

It was also investigated, if the different building blocks of different lignin types are decomposed with the same rate during humification.

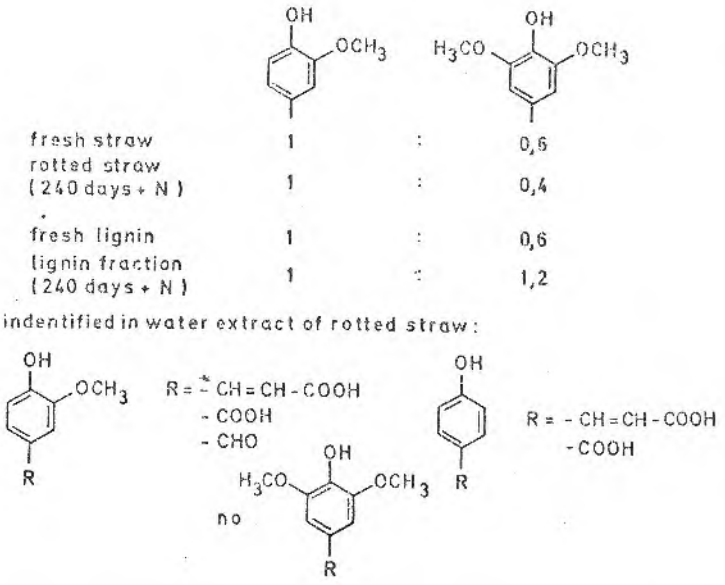


Fig. 5: Alterations of the content of the guaiacyl- or syringyl-component of rye straw during humification (according to KRATZL and CLAUS 1962).

KRATZL and CLAUS (1962) found by ethanolysis of rotted rye straw that the ratio of guaiacyl to syringyl component is shifted from 1 : 0,6 to 1 : 0,4 after 240 days (1 % N per dry weight of straw was added as

NH_4NO_3). This means, that the guaiacyl component is enriched in the rotted straw, this may be caused by a favoured degradation of the syringyl component. Syringyl components seem to be more utilized by the microorganisms than the guaiacyl components.

In water extracts of rotted straw only guaiacyl components such as ferulic acid, vanillic acid or vanillin but never syringyl compounds could be identified. Furthermore p-hydroxybenzoic acid and its aldehyde were found (MAEDER 1960). Lignin degradation products were also isolated by investigations of other humified materials (JACQUIN 1963, BRUCKERT, JACQUIN and METCHE 1967).

The ratio of guaiacyl to syringyl component changed from 1 : 0,6 to 1 : 1,2 in the lignin fraction of rye straw after humification. The guaiacyl component seems to be split off more than the syringyl component or, if the guaiacyl component remains in the lignin molecule, it is demethylated to a larger extent.

The differential degradation of various lignins seems to be connected with the linkages of the monomers in the lignin molecule. It is suggested, that the linkages occur mainly through the carbon atom 2 of the side chains. The type of linkages may be prevalent in lignins containing sinapyl alcohol units, because both o-positions of the hydroxyl group in the ring are substituted with methoxyl groups and therefore the linkages between the rings and the side chains or between two rings might be rare (comp. scheme of lignin structure p. 10).

Tab. 6: Elemental composition of lignin, humified lignin, humic and fulvic acids.
(Accord.to FREUDENBERG and HARKIN 1964, MAEDER 1960[1], KONONOVA 1966[2], DRAGUNOV 1948[3])

		% C	% H	% O	%OCH_3	% N
Lignin						
1) Beech (Fagus silvaticus)	$C_9H_{6,5}O_2(H_2O)_{0,64}(OCH_3)_{1,41}$	61,87	6,03	32,10	21,65	
2) Spruce (Picea exelsa)	$C_9H_{7,12}O_2(H_2O)_{0,40}(OCH_3)_{0,92}$	65,08	5,88	29,04	12,87	
3) Peat-moss (Sphagnum)	$C_9H_{7,96}O_2(H_2O)_{0,90}(OCH_3)_{0,25}$	61,67	5,89	32,44	4,36	
4) Rye straw (Secale cereale)	$C_9H_{6,51}O_2(H_2O)_{1,05}(OCH_3)_{1,13}N_{0,08}$	63,10	5,92	30,67	17,20	0,54
Humified lignin						
5) Rye straw[1] decomposed 180 days	$C_9H_{5,45}O_2(H_2O)_{1,42}(OCH_3)_{0,68}N_{0,24}$	61,15	5,42	32,42	11,05	1,75
Humic acids						
Fulvic acids						
6) Northern podsol under forest[2]		53,11 52,37	5,37 3,33	32,00 42,89	-	4,52 1,21
7) Podzolic soil[3]		57,94	5,79	31,41	1,54	4,86
8) Ordinary chernozem, arable[2]		62,13 44,84	2,91 3,45	31,38 49,36	-	3,58 2,35
9) Chernozem[3]		57,32	4,25	34,39	1,17	4,04

Tab. 7: Transformation of the lignin of oat straw at different stages of humification with (1N) and without (0N) addition of ammoniumphosphate (1N=225 ml ammoniumphosphate with 100 ppm per 75 g fresh straw = 3% N calc. per fresh straw; room temperature). According to BROADBENT (1954). Determination of lignin according to NORMAN and JENKINS (1934 (1,2)).

	loss of weight of org.subst.		Some chemical properties											
	% C		% H		% OCH_3		% OH		COOH mg pro 100 g		CEC me pro 100 g	
days	0 N	1 N	0 N	1 N	0 N	1 N	0 N	1 N	0 N	1 N	0 N	1 N	0 N	1 N
0	0	0	61,5	63,0	6,67	6,25	11,40	11,43	6,82	7,84	91	81	29	44
14	27,4	22,7	61,9	63,0	6,30	5,83	10,32	11,42	7,53	7,24	98	85	42	47
40	38,8	37,7	61,6	63,9	6,21	6,14	9,52	11,23	7,77	6,63	105	101	62	74
88	44,6	47,6	61,2	63,1	6,35	6,04	10,39	10,37	5,05	5,32	112	107	82	81
135	58,0	56,4	59,7	61,7	6,30	9,24	9,24	8,66	4,13	6,77	122	117	101	110
180	60,1	58,0	60,2	60,7	6,34	5,65	8,33	8,96	4,01	6,70	117	127	100	109
244	67,2(?)	59,3	60,7	61,1	5,81	5,74	8,56	9,00	5,83	6,31	135	115	126	102
355	66,0	61,3	59,3	62,0	6,23	5,85	7,85	7,71	6,37	5,77	128	142	116	118
452	65,5	63,9	59,4	60,5	5,93	5,67	7,35	7,99	6,05	5,20	161	141	124	131

The elementary analysis of lignin and humic acids (Tab. 6) demonstrates that the carbon content of the lignin of different plants is higher than that of humic acids. The decrease of carbon content and the increase of oxygen content show, that oxidative processes play an important role during the transformation of lignin into humic acids. Furthermore the content of nitrogen is increased, whilst the content of methoxyl groups decreased remarkably during humification.

KRATZL et al. (1964, 1966) conclude by their investigations of sulphite liquors of cellulose production from coniferous wood, that demethylation occurs through semiquinone formation during oxidation in alkaline medium. Thereby the methylether group reacts like an ester and is saponified by alkali. Reactive groups are formed by demethylation, which is important for further reactions of lignin with other reactive compounds such as amino acids finally for the degradation which occurs in nature by enzymatic processes.

3.3 Function of the oxygen.

BARTLETT and NORMAN (1938) and BROADBENT (1954) (Tab. 7) have found, that the number of hydroxyl groups tends to decrease upon degradation.

The content of carboxylic groups and the cation exchange capacity progressively increases with humification (comp. tab. 7).

Also the titration of lignin fractions, isolated from wheat straw according to the method of BJÖRKMAN, in ethylendiamine with ethanolamine according to BROCKMANN and MEYER (1953) shows a decrease in equivalent weight with increasing time of humification.

Tab. 8: Transformation of lignin fractions of wheat straw at different periods of humification according to FLAIG, SCHOBINGER and DEUEL (1959).

	equivalent weight	acidic groups equiv./ 100 g	readily decarboxylated groups in mol CO_2/ 100 g	CO_2-formation in % of the acidic groups
fresh straw	560 ± 13	178	10.6	6
70 days rotted	677 ± 11	173	14.5	8
180 days rotted	429 ± 7	233	30.4	13
340 days rotted	412 ± 9	243	-	

The titration curves indicate, that an increase of acidic groups occurs, which is due primarily to carboxylic groups. A portion of these new acid groups can be split off with 12 % hydrochloric acid to form carbondioxide. This may also originate from the side chain of the oxidised lignin building blocks or from acids, which are formed by the cleavage of the ring. The lignin of the fresh straw is altered by treatment with strong acids, whereby ring condensations occur (BRAUNS and BRAUNS 1960, p. 516 - 518). The products formed are decomposed by oxidation to benzene polycarboxylic acids.

The formation of carbondioxide can be explained by these reactions as well as by the decomposition of pentosanes which might be included. According to the investigations of DEUEL and DUBACH (1958 a,b) and DEUEL, DUBACH and BACH 1958) cetocarboxylic acids, unsaturated heterocyclic and aromatic hydrocarboxylic acids are decarboxylated by treatment with 12 % HCl.

The appreciable increase in exchange capacity is, according to BARTLETT and NORMAN (1938), not associated with proteins, which might be coprecipitated during the isolation of the lignin fractions. An addition of egg albumin to lignin isolated from fresh wheat or oat straw,

in an amount equivalent to the nitrogen content of rotted straw lignin had little effect on the exchange capacity. Furthermore the authors believe that the increase in the exchange capacity of the lignin fractions isolated from the humified straw is not caused by the condensation of nitrogen compounds with the transformed lignin.

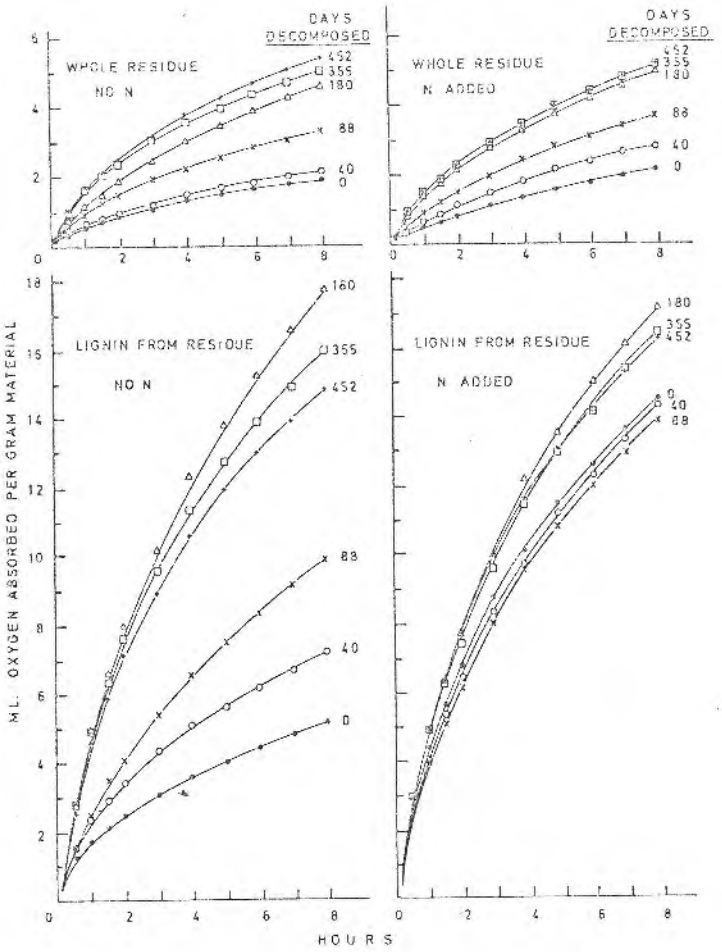


Fig. 6: Oxygen absorption by straw residues and by their lignin fraction in alkaline suspension (BROADBENT 1954).

The lignin fractions of the oat straw incubated for 180 days with the addition of ammonium phosphate were more readily oxidised in 20 % sodium hydroxide solution than similar fractions isolated from composted straw without supplemental nitrogen. The increased oxygen uptake can only be observed for 180 days, after which it decreases in both cases up to the 452 day period of humification. The activity of the microor-

ganisms is accelerated by the addition of nitrogen salts, whereby the transformations of the lignin occur faster. The greatest change occurs during the first 180 days, afterwards, there is little change. The alterations in many other properties of the lignin fractions were always greater during the first 180 days in all experiments (BROADBENT 1954, SCHOBINGER 1958, MAEDER 1960).

The conditions of humification with the addition of nitrogen were approximately comparable in all these studies. This observation is important with respect to the later discussion of the spectra of the lignin fractions.

Further investigations on functional oxygen in the lignin fractions isolated from wheat straw according to BJÖRKMAN showed an increase in carbonyl content from 0,3 % in the fresh straw to 0,47 % and 0,59 % after 70 and 410 days respectively. Carbonyl content was determined with 2,4-dinitrophenylhydrazone (TRAYNARD and EYMERY 1956). This increase may be due to an increase of the carbonyl groups in the side chains and perhaps also to an oxidation of phenolic hydroxyl groups to quinones during humification. STEELINK and TOLLIN (1962) have demonstrated, that free radicals increase in the lignin fractions during humification and that the free radicals were probably related to the presence of quinonoid groups.

Tab. 9: Methylation of lignin fractions of wheat straw isolated by the Björkman method (SCHOBINGER 1958).

		N-content
Lignin from fresh straw	16.76 % OCH_3	0.42 % N
Lignin from fresh straw, methylated	21.76 % OCH_3	
Lignin 70 days rotted	10.84 % OCH_3	1.97 % N
Lignin 70 days rotted, methylated	13.97 % OCH_3	

The decrease of the methoxyl content of the lignin fractions during humification could theoretically lead to an increase of phenolic hydroxyl groups by cleavage of the methyl ether. But as the ratio of the methoxyl content before and after methylation is in both cases about 3 : 4, no increase in the number of free phenolic hydroxyl groups in the lignin fractions occurred. The increase of nitrogen from 0,42 % to 1,97 % shows that the phenols have reacted with nitrogen compounds. Model investigations with 1-hydroxy-2-methoxybenzene compounds demonstrated, that methoxyl containing phenols do not condense with primary amino compounds such as amino acids (HAIDER, FREDERICK and FLAIG 1965).

3.4 Function of nitrogen.

Tab. 10: Distribution of the nitrogen of the lignin fractions of wheat straw in percent after different periods of humification (calc. for ash-free substances) (FLAIG, SCHOBINGER and DEUEL 1959).

Days of humification	Residue of hydrolysis	Total N in %	In % of total-N(=100) before hydrolysis				
			α-amino nitrogen in the Hydrolysate	In residue of hydrolysis		Sum of α-NH_2-N + NH_3-N + "residual"-N	Loss of weight by Hydrolysis
				as NH_3	as "residual"-N		
			Lignin fractions (isolated with sulfuric acid)				
0	44,0	0,55	58,1	40,0	0	98,1	17
70	44,6	2,09	39,2	27,8	18,7	85,5	20
180	55,7	2,46	21,1	25,2	18,7	65,0	24
260	42,4	3,26	20,8	17,2	25,1	63,1	24
340	52,1	3,20	20,3	25,6	26,5	72,4	32

It is noted in this table, that for fresh straw the sum of nitrogen determined as α-amino-nitrogen and that which remains in the hydrolysate as NH_3-N and in the residue after hydrolysis is more than 90 %, while the sum is always lower for the rotting straw. This result may be explained by the investigations of GALE (1946), who found that certain amino acids are decarboxylated to amines by the action of microorganisms and therefore, can not be determined by the titrimetric method with ninhydrin (van SLYKE, MC FADYEN and HAMILTON 1941). Thirteen amino acids could be identified in some cases with paper chromatography in the hydrolysates of fractions, in which α-amino-nitrogen was found.

An oxidative deamination of amino acids can occur in an oxidising medium by o-diphenols or quinones which are formed from the lignin degradation products by cleavage of the methylethers. The continuous increase in the nitrogen content of the residues after hydrolysis or of the NH_3-N determined in a fusion with potassium hydroxide and sodium acetate under reducing conditions (BREYHAN 1956) and of the residual-N indicates, that the nitrogen is bound in such a way, that it can be split off only under the drastic conditions of the alkali fusion (NH_3-N) or is no longer hydrolysable ("residual"-N). Indol compounds could also be detected (FLAIG and BREYHAN 1956).

A considerable loss of weight is observed upon recovery of the residues after hydrolysis which cannot be explained on the basis of hydrolysable amino acids. Therefore other reactions must occur during the hydrolysis with 6 N hydrochloric acid, which are unknown.

Tab. 11: Elemental composition of the residues after hydrolysis of lignin fractions of wheat straw (A. Isolated with sulfuric acid, B. according to Björkman; calc. for ash-free substance; without addition of nitrogen salts).

days of humification	C %		H %		O % (diff)		N %	
	A	B	A	B	A	B	A	B
0	63,39	69,35	5,41	5,88	30,98	24,59	0,22	0,18
70	60,15	68,45	5,68	7,45	33,20	22,97	0,97	1,13
180	60,40	67,36	5,66	6,37	32,86	24,90	1,08	1,37
260	58,86		5,61		34,15		1,38	
340	56,66		5,62		36,05		1,67	

The elementary analysis of the residues after hydrolysis shows increased carbon values (tab. 11) in comparison with those of the nonhydrolysed lignin fractions (tab. 5). The observed increase of carbon and the decrease of oxygen following hydrolysis of the lignin fractions isolated by the Björkman method cannot be entirely explained by the splitting off of the amino acids. Presumably alterations can occur by treatment with 6 N hydrochloric acid, which lead to the formation of polycyclic condensation products (BRAUNS and BRAUNS 1960).

The quotient of the gramatoms of methoxyl divided by the gramatoms of nitrogen of the lignin fractions isolated from decomposing rye straw decrease with time and amount of the added nitrogen (FLAIG 1962).

The value of the quotient can be used as a measure of the increasing alteration of the lignins during humification. Fractions giving the same quotient were comparable, as it was the case for the infrared spectra of the lignin fractions 70 days/2N and 120 days/1N or 120 days/2N and 240 days/1N (tab. 12). Further analytical data for the

different fractions isolated from humified rye straw are given later.

Tab. 12: $\frac{\text{g-atoms } OCH_3}{\text{g-atoms N}}$ in the lignin fractions

	0 N	1 N	2 N
70 days	13.2	6.3	4.0
120 days	12.3	4.6	2.8
180 days	11.7	3.4	2.8
240 days	10.8	3.1	2.5

0 N = no nitrogen; 1 N = 0,5 % N and 2 N = 1,0 % N as NH_4NO_3 per dry weight of straw.

3.5 Spectroscopic investigations.

The absorption spectra of the lignin fractions change with increasing periods of humification.

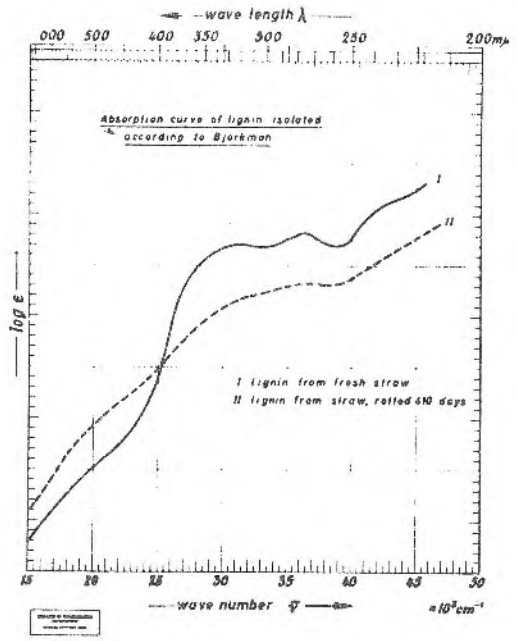


Fig. 7: UV-absorption spectra of lignin fractions
I lignin according to Björkman fresh
II lignin according to Björkman 410 days

The maximum in the region of 275 to 285 m/u, which is attributed to the benzene ring substitued with oxygen, and the maximum between 300 and 350 m/u, which is caused by the presence of chromophoric groups of the side chain (carbonyl group, olefinic double bounds) (JONES 1949), are reduced in the lignin fraction from rye straw decomposed for 410 days with added nitrogen (SCHOBINGER 1958). The absorption curves become less characteristic with increasing time of humification and tend to become more or less a straight line. The slope depends on the composition and gradually approaches the spectra of humic acids, which have been investigated more extensively at first by FRÖMEL (1938 a,b , 1941).

The transformation of the lignin fractions during humification has also been investigated by infrared spectroscopy (FLAIG, SCHOBINGER and DEUEL 1959, FLAIG 1958, 1964 a , FLAIG and BEUTELSPACHER 1968, FARMER and MORRISON 1960).

The lignin fractions of fresh wheat and rye straw show the same bands in the region between 5,8 - 7,75 /u. The method of isolation whether with 96 % alcohol according to BRAUNS (1939), with 90 % dioxane according to BJÖRKMAN (1954, 1957), with sulfuric acid according to a modified method of Klason (RITTER, SEBORG and MITCHELL 1932), or with thioglycolic acid according to HOLMBERG (1934), does not change the pattern. The C=O-valency vibrations of carboxyl groups at 5,8 /u are caused by the thioglycolic acid, if this acid is used for the isolation. Changes in the bands at 8 - 9 /u occur when sulfuric acid is used for isolation. These changes may be related to acid catalysed ring condensation similar to those which occur with coniferous lignin (BRAUNS and BRAUNS 1960).

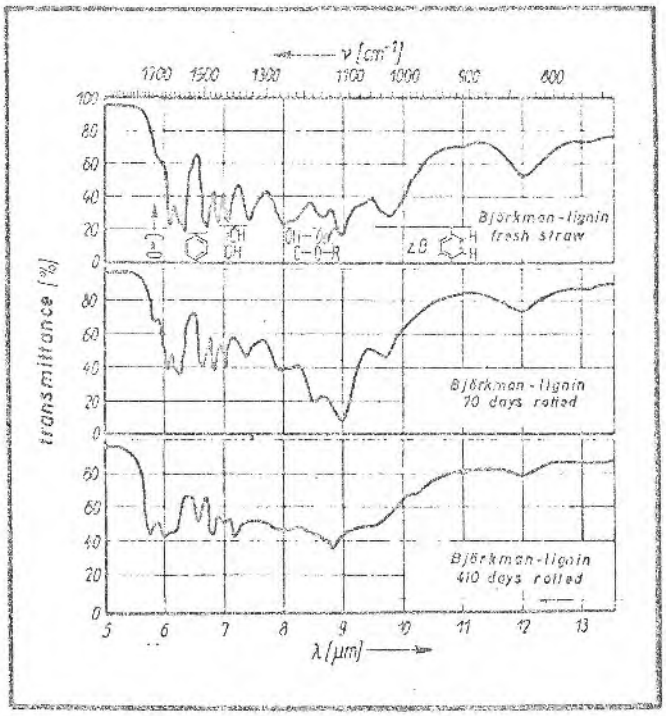


Fig. 8: Alterations of IR-spectra of lignin fractions during humification

An increase of the intensity of the C=O-band at 5,85 /u with increases of time of humification may be due to an increase of carboxyl groups because the consumption of alkali increases during titration (FLAIG, SCHOBINGER and DEUEL 1959, BROADBENT 1954). The number of carboxyl groups determined by chemical methods also increases (BROADBENT 1954).

The absorption of the C=C-valency vibrations at 6,25 and 6,65 /u may be caused chiefly by the aromatic parts of the lignin molecules and does not change very much with time.

The increasing background absorption may be explained by the assumption, that with time a greater variety of aromatic components is present although the total quantity may remain the same. The steady decrease of the methoxyl content of the lignin fractions, the increase of the syringyl component, and the increase of nonhydrolysable nitro-

gen supports this explanation.

A mixture of model substances such as p-hydroxybenzaldehyde, vanillin and syringaldehyde, which approximately simulate the composition of the corresponding building blocks of the lignin, gives a spectrum with approximatly the same arrangement of the bands as the lignin of the fresh straw isolated according to BRAUNS and BJÖRKMAN. The spectrum of this mixture also shows an increased background absorption in comparison with the spectra of the single aldehydes (FLAIG and BEUTELSPACHER in press). The spectrum of the mixture of aldehydes differs only by the bands of aldehyde goups in comparison with the spectrum of lignin from fresh straw.

The alterations of the C-H-deformation vibrations at 6,85 and 7 /u may be connected with alterations in the side chains. The strongly marked bands at 7,95 /u and 8,95 to 9,10 /u are due to arylalkyl and other ether linkages based on investigations with model substances. The strong absorption of the ether bands at 8,95 /u in the case of the lignin fractions of fresh or rotted straw, but which are weak for polymers of guaiacol may be caused by syringyl components (FLAIG 1964 (a)). Syringaldehyde as well as a mixture of the aldehydes, p-hydroxybenzaldehyde, vanillin, syringaldehyde in the ratio of 0,5 : 1 : 0,5, which is nearly the same ratio of these monomers in straw lignin, also show strong absorption at 9,05 or 9,00 /u.

The absorption at 6,1 - 6,20 /u increases with the increased nitrogen content of the lignin fractions during humification. In this region not only C=C bands but also the N-H-deformation and C=N-valency vibrations occur. The latter may be due to heterocyclic compounds.

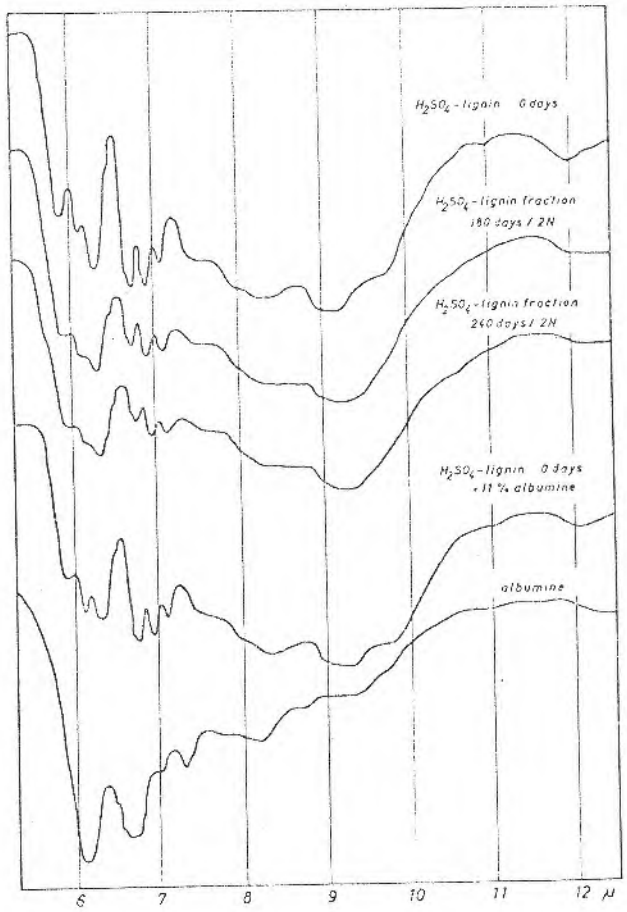


Fig. 9: Absorption spectra of 2 lignins of 2 differently rotted straw but the same nitrogen content and of a mixture with the same nitrogen content of unrotted lignin with albumin. All samples have a nitrogen content of 1,7 %.

The spectra of lignin fractions isolated with sulphuric acid from the same humified straw samples to which different amounts of nitrogen were added but which had the same nitrogen content, were identical in the region from 5,8 to 8,8 µ (FLAIG 1964 a) .

Polypeptides have a strong amide absorption band between 6,40 and 6,70 µ. Albumin from cow serum for example has a broad maximum at 6,60 - 6,70 µ. The intensity of the absorption at 6,65 µ is not changed during humification.

If a mixture of lignin and proteins was precipitated during the isolation of the lignin fractions, the absorption of this band should become stronger, because the nitrogen content of the lignin fractions increases with time. Only in the case of mixtures of lignin of fresh straw with those amounts of albumin which correspond to the nitrogen content of the lignin fractions of humified straw, was the band at 6,65 µ intensified.

A further proof, that the isolated lignin fractions are not mixtures of lignin and proteins, is evident from the treatment of mixtures of nitrogen containing lignin fractions with proteines such as albumin with 72 % sulphuric acid.

The nitrogen content of reprecipitated lignin fractions is not altered because the added albumin is hydrolysed by the 72 % sulphuric acid. Furthermore the hydrolysis of the lignin fractions with 6 N hydrochloric acid shows that the percentage of α-amino nitrogen decreases continually with time, while nonhydrolysable nitrogen increases. The latter is probably heterocyclic bound.

The α-mino nitrogen which is hydrolysable only with 6 N hydrochloric acid presumably consists of peptides which are difficult to hydrolyse and are linked to the lignin parts through the amino groups of the N-terminal amino acids. These problems require further elucidation and are discussed later (lecture 3).

3.6 Degradation of lignin to low molecular weight components.

Up to this point the transformations of lignin which may occur within or on the edges of the intact molecules have been described. Another type of transformation which definitely occurs , is the degradation into low molecular weight compounds. Various phenolic lignin degrada-

tion products are found even after a short treatment of lignin with acids or with alkali (BRAUNS and BRAUNS 1960, SAALBACH 1958). Several phenols which appear to be lignin derived have been isolated from decomposing plant materials and from microbial cultures - especially of lignin decomposing fungi living on Brauns lignin, needle trees, deciduous trees and grasses (BÖRNER, 1955, 1956, 1957; HENDERSON 1955; ISHIKAWA, SCHUBERT and NORD 1963 a ; SEIFERT 1962, and others).

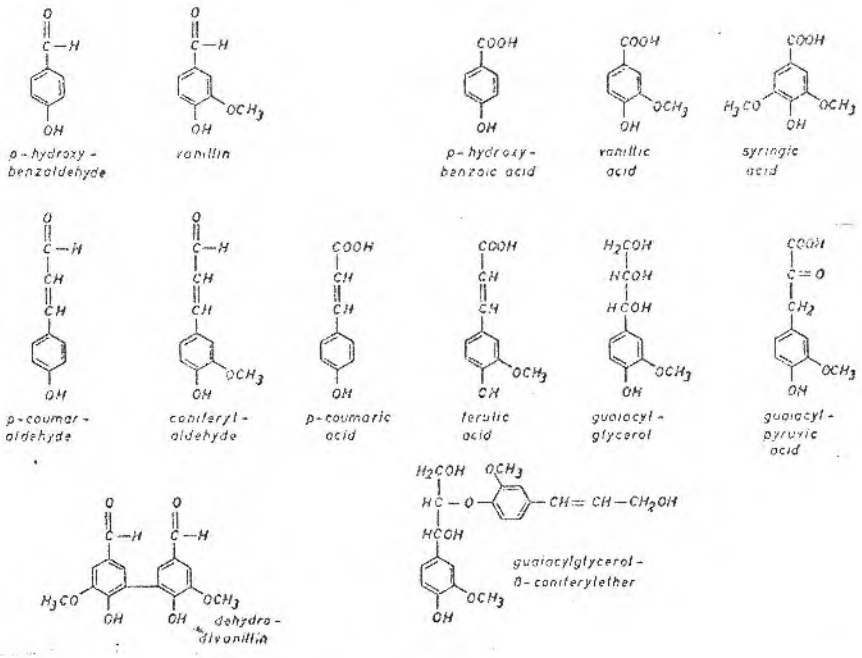


Fig. 10: Identified lignin degradation products in soil and cultures of microorganisms.

OGNER and SCHNITZER (1971) identified 21 phenolic and benzene polycarboxylic acids as methylethers and esters from fulvic acids isolated from a B_h-horizon of a podzol. Some of these compounds were directly isolated from different materials. So p-hydroxybenzaldehyde, vanillin, vanillic acid, p-hydroxycinnamic acid, and ferulic acid could be isolated during 240 days of humification of rye straw (MAEDER 1960). Obviously these compounds were continually released during the entire

incubation period, although their resistance to oxidation or biological decomposition varies (SÖCHTIG 1961 a,b).
Their formation can occur by oxidation and cleavage reactions on the side chains and by cleavage of the aromatic ring, the benzyl- and the arylmethyl-ether. These lignin degradation products are important for the formation of humic acids or their precursors;in that some of them condense to dark coloured polymers in the presence of nitrogen containing compounds derived from proteins. The condensation occurs in the presence of phenoloxidases in an oxidising environment. The properties of the dark coloured polymers are similar to those of humic acids (FLAIG and HAIDER 1961 a). Further attention will be given to these reactions in a later section. Some of the lignin degradation products have been identified in soils. WHITEHEAD (1964) identified p-hydroxybenzoic acid, vanillic acid, p-hydroxycinnamic acid and ferulic acid in concentrations of ca. 10^{-5} mol in soil solutions obtained by pretreatment of four different soils with calcium oxide in aqueous solution followed by filtration and acidification. The phenols were recovered by extraction of the filtrates with ether. Some decades ago only p-hydroxybenzoic acid (WALTERS 1917) and vanillin (SHOREY 1913) have been isolated.

4. Introduction to biochemical degradation of lignins.

Tab. 13: Methoxyl- and nitrogen content of different lignins in percent (BONDY and MEYER 1948).

	% OCH_3	% N
Hardwood groups	20.0	0
Softwood groups	15.0	0.2 - 0.3
Graminees	10.0	1.2 - 1.6
Leguminoses	5.0	2.9 - 3.4

Lignin is the phenolic compound which occurs in a larger amount in plants. The methoxyl and nitrogen content of lignin differs according to plant groups and varies from 5 to 20 %.

As previously indicated, during decomposition the methoxyl content of lignin fractions decreases while the nitrogen and the oxygen contents increase. The products formed are dark coloured and have physico-chemical properties (spectra, solubility, cation exchange capacity) which are comparable to those of humic acids (FLAIG, SCHOBINGER and DEUEL 1959; FLAIG 1963). The products formed from lignin decomposition have a methoxyl content, which is higher than that of humic acids from manures or composts (NEHRING and SCHIEMANN 1952 a,b).

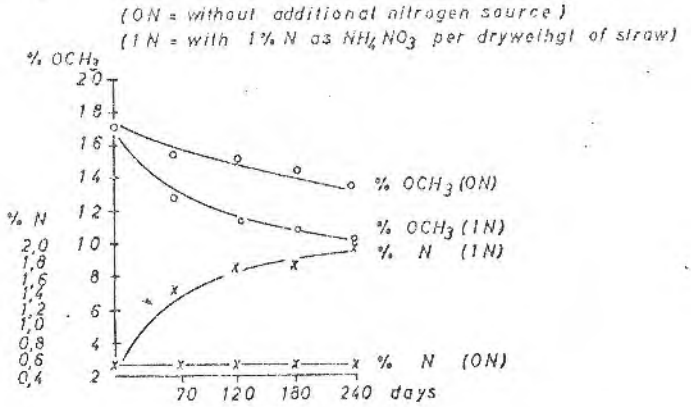


Fig. 11: Alterations of the content of nitrogen and methoxyl of the lignin fractions of straw during humification.

If one isolates the lignin fractions from rotted plant material for instance straw, with sulphuric acid, the content of methoxyl groups decreases and the nitrogen content increases concurrently with the time of rotting (BROADBENT 1954, BARTLETT and NORMAN 1938, BARTLETT 1939, FLAIG, SCHOBINGER and DEUEL 1959, RITTER , SEBORG and MITCHELL 1932, FLAIG 1960 b , WAKSMAN and SMITH 1934, STÖCKLI 1952, NEHRING

and SCHIEMANN 1952 a,b). This suggests that the cleavage of the methoxyl group preceeds the introduction of nitrogenous groups (FLAIG 1960 b).

The degradation of lignin is caused by enzymes of special species of microorganisms (comp. SCHANEL 1962, TROJANOWSKI et al. 1966, 1967). Addition of nitrogenous salts (1 N against 0 N) accelerates degradation.

The fixation of nitrogen compounds after alteration of several groups in the lignin preserves its high molecular structure and renders the nitrogen less accessible to microorganisms.

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