Lectures on
Soil Organic Matter

by

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Foreword

To my friends and the friends of the subject.

In this manuscript are some unpublished results and therefore only for friends and not to use for publication.

I would enjoy having any comments on this material.

W. Flaig

Acknowledgments

This manuscript came about as a result of the kind invitation of Prof. Dr. W. H. Pierre, Head, Department of Agronomy, to give lectures about soil biochemistry. I am very thankful for this opportunity.

I would like to express my best thanks also to my colleague, Prof. Dr. Lloyd Frederick, who stood by me helpfully at all times during the writing of these lectures in the English language and I appreciate his suggestions during our many discussions.

Without the help of his co-workers, Messrs. McIntosh Sims, Horton, Brown, and of the secretaries, Mrs. McLaughlin, Misses Sansgaard and Zart, it would not have been possible to mimeograph the lectures. Also to these, many thanks.

June, 1959

W. Flaig

SOIL ORGANIC MATTER

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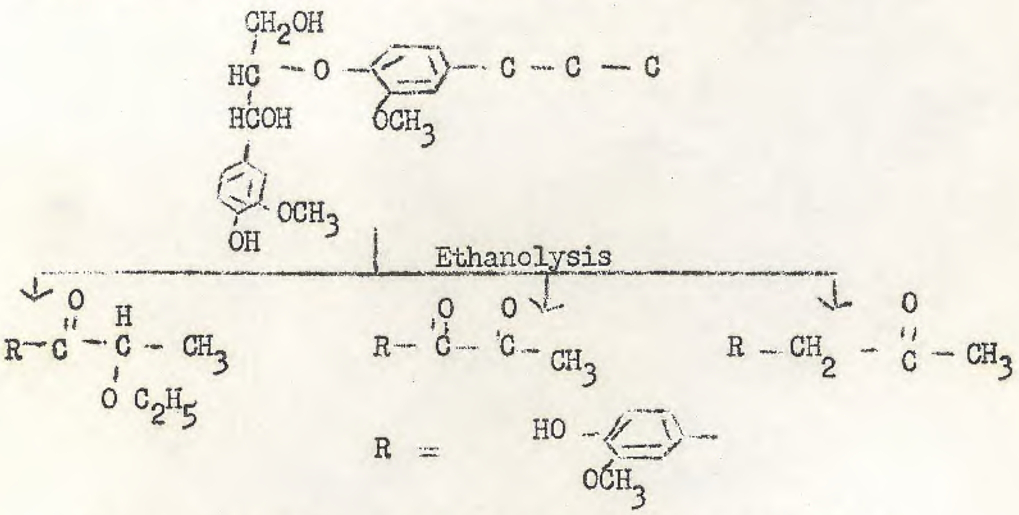
Chemistry of Quinones in so far as They Concern Chemistry of Humic Substances

(Outline numbers 14 and 15)

In the next section, we must study the possibilities of the decomposition of lignin. At first, we are interested in the decomposition products which occur during rotting of organic material in soils.

Now it is the question, which chemical compounds are formed by the decomposition of lignin or its building stones. There can be distinguished two possibilities:

1) The catabolism of the side-chains. The decomposition of this part of lignin is similar to that of carbohydrates, sugars glycerol, or aliphatic acids. All these compounds can serve as carbon sources for the growth of microorganisms. Some evidence can be given by the so-called "Hibbert Ketones". By boiling lignin with ethanol and dilute hydrochloric acid, there can be isolated usually three main products.



By this operation, the ether linkages are split up.

2) Formation of aromatic compounds.

a. Lignin building stones.

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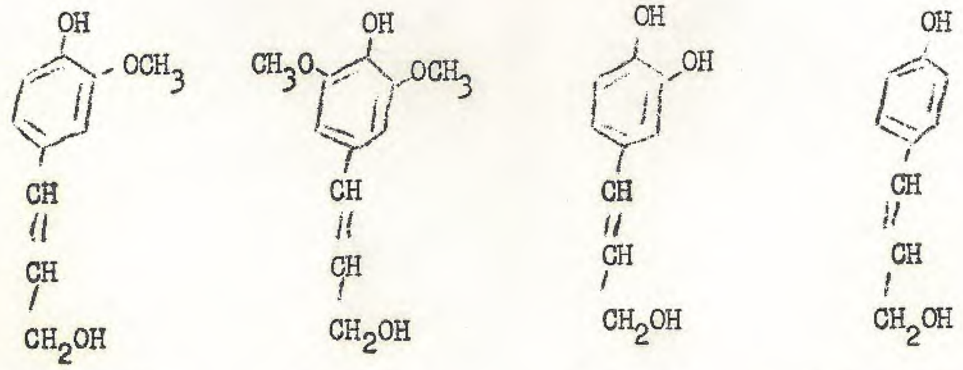
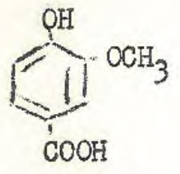


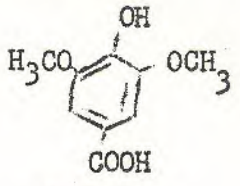
Coniferyl- Cinnapin Caeffic p-Hydroxycinnamic

Alcohols

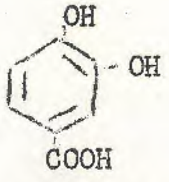
The first oxidation products of coniferyl-, cinnapin-, caeffic- and p-hydroxy-cinnamic alcohols are acids which are formed by breaking the side chains by oxidation on the double-bound.



Vanillinic acid



Syringic acid



Protocatechuic acid

p-hydroxy-benzoic acid

The formation of these acids can be derived from the structure scheme of lignin.

b. Dimerization products of lignin building stones.

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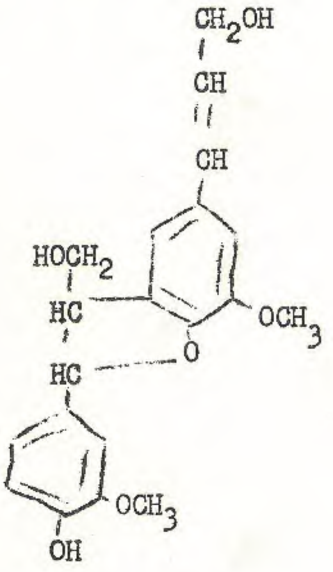
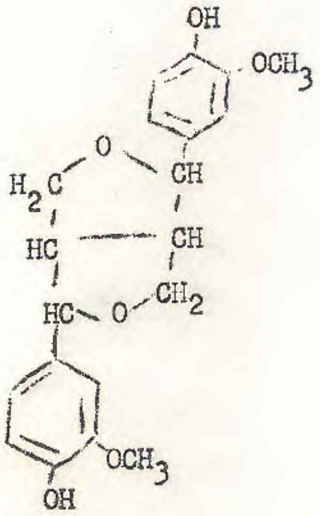
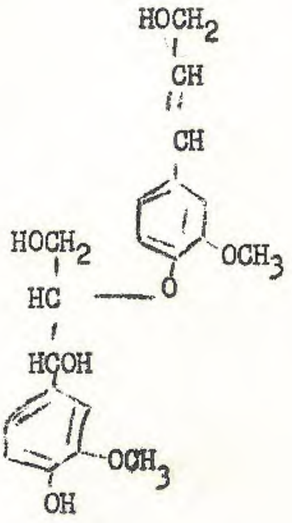


Dehydro-diconiferyl alcohol



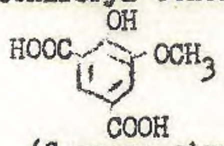
d,l-Pinoresinol



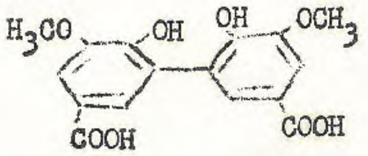
Guajacylglycerol-coniferyl ether

From the dimerization products dehydrodiconiferyl alcohol, D,L-Pinoresinol and guaiacylglycerol- β -coniferyl ether can be derived another new decomposition product.

Isohemipinic acid.



c. Lignin itself. (Compare structural scheme of lignin).



2,2' Dihydroxy-3,3'dimethoxy-diphenyl-5,5'dicarbonic acid

If we break up the side chains in this scheme, the same oxidation products as in the case of lignin building stones are formed. Furthermore, also isohemipinic acid occurs. But in this case we get also a fragment of the dimerization product, that is 2,2'-Di-hydroxy-3,3'-di-methoxy-di-phenyl-5,5'-di-carbonic acid.

Remember that it could be possible to isolate out of straw ferulic acid, p-hydroxy,-cinnamic acid, p-hydroxy benzoic acid, vanillinic acid by Börner, (Börner, H.: Die Abgabe organischer Verbindungen aus den Karyopsen, Wurzeln und Ernteruckstanden von Rohgen, Weizen und Gerste und ihre Bedeutung bei der gegenseittigen Beeinflussung der hohoren Pflanzen. - Beitr. Biol. Pfl. 33 (1956) S. 33). Also Smith (Smith, D. C. C.: Ester groups in lignin, Nature 176 (1955) Nr. 4475, S. 267-268) succeeded in isolation of the same acids from native lignin of sugarcane by treatment with sodium hydroxide. We had also been able to isolate this acid by careful treatment of native lignin of wheat straw. (E. Saalbach, Beitrag der Grundlagenforschung zum problem der Strohdungen - Landbauforschung, 18, 83-84 (1958)).

Some time before I told you that Schreiner and Shorey could isolate p-hydroxy benzoic acid and protocatechuic acid. Working with organic solvents we could also extract these two acids and some other phenolic compounds. The constitution of these is not yet sure. (Flaig, and Wahschaffe, Flaig and Scholl, unpublished).

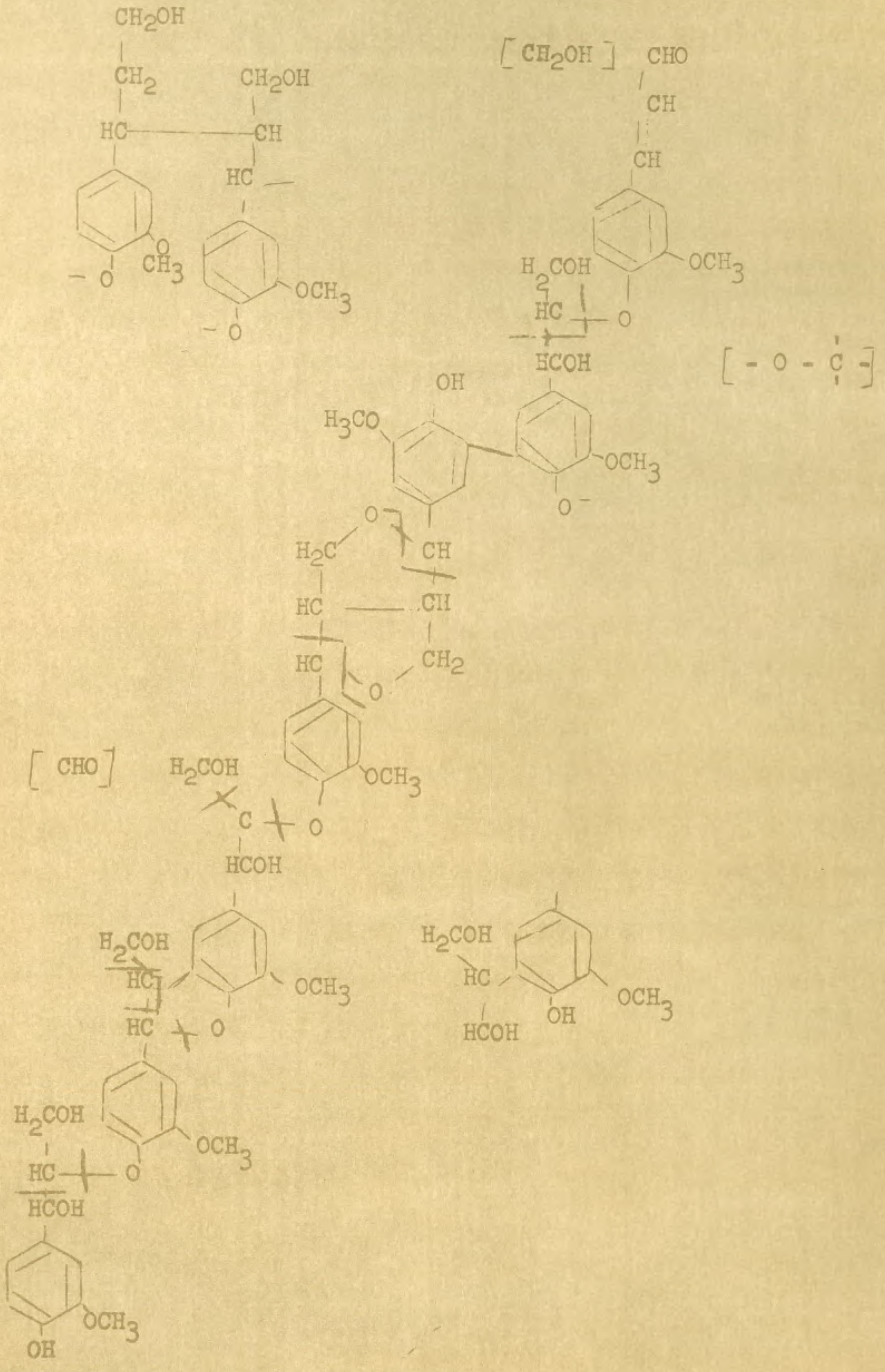
Even with these compounds de-hydrogenation reactions or oxidation reactions of quinones can occur, for instance, caeffeic alcohol or protocatechuic alcohol. The reactions are more numerous if the phenol-methyl-ether linkage can be broken. By demethylation polyphenols are formed. At first, we must discuss the observations about the splitting up of the phenol-methyl-ethers.

Waksman and Smith have been the first which made investigations about the decreased content of methyoxyl groups in rotted plant materials in comparison with the initial material. (Waksman, S. A. and Smith, H. W.: Transformations of the methoxyl group in lignin in the process of decomposition of organic residues by microorganisms. Jour. Amer. Chem. Soc. 56:1225-1229. 1934). Bartlett and Norman, (Journal paper No. J-589 of the Iowa Agricultural Experiment Station, Ames, Iowa) showed in some cases that the decrease of methoxyl groups of lignin can have some relationships with the increase of the nitrogen content during the decomposition of plant materials. Furthermore, Broadbent, F. E. (Modification in Chemical Properties of Straw During Decomposition, Soil Sci. Proc. 18:165-169. 1954) showed that the methoxyl groups in lignin are diminished during rotting. The same effect is also observed if nitrogen has been given to the rotting straw. He also determined that the content of hydroxyl groups is not remarkably changed during rotting.

Methoxyl and Hydroxyl in the Decomposed Lignin Fraction

	No Nitrogen		Nitrogen Added	
Days Incubated	Methoxyl in lignin %	Hydroxyl in lignin %	Methoxyl in lignin %	Hydroxyl in lignin %
0	11.40	6.82	11.48	7.84
14	10.38	7.53	11.42	7.24
40	9.52	7.77	11.28	6.53
88	10.39	5.05	10.37	5.32
135	9.24	4.13	8.66	6.77
180	8.33	4.01	8.96	6.70
244	8.56	5.83	9.00	6.31
355	7.85	6.37	7.71	5.77
452	7.85	6.05	7.99	5.20

STRUCTURE SCHEME OF LIGNIN



This table shows that the methoxyl content decreases. But the content of hydroxyl groups during the whole time is nearly the same in the lignin fraction. The hydroxyl groups were determined by acetylation of samples with acetic anhydride in pyridine for 45 minutes, after which the excess reagent was hydrolyzed with water and the acetate acid titrated with alcoholic alkali according to the method of Ogg, Porter and Willits. (Ogg, C. L., Porter, W. L. and Willits, C. O. Determining the hydroxyl groups of certain organic compounds. Ind. Eng. Chem. Anal. Ed. 17:394 (1945)). In the case of the hydroxyl groups there was a tendency toward decreasing.

The decrease of methoxyl groups by the demethylation of lignin would expose new hydroxyl groups. But it seems that hydroxyl groups disappear during the decomposition. The author discussed this fact and together with other investigations, for instance, the measurement of cation exchange capacity, he believes that indeed an increase in phenolic hydroxyl groups appears. By us (Flaig, Schobinger and Deuel, Umwandlung von Lignin in Huminsauren bei der Verrottung von Weizenstroh, in press) the decrease of methoxyl groups in addition had been brought in relation not only to the content of hydroxyl groups but also to the content of nitrogen in the lignin fraction.

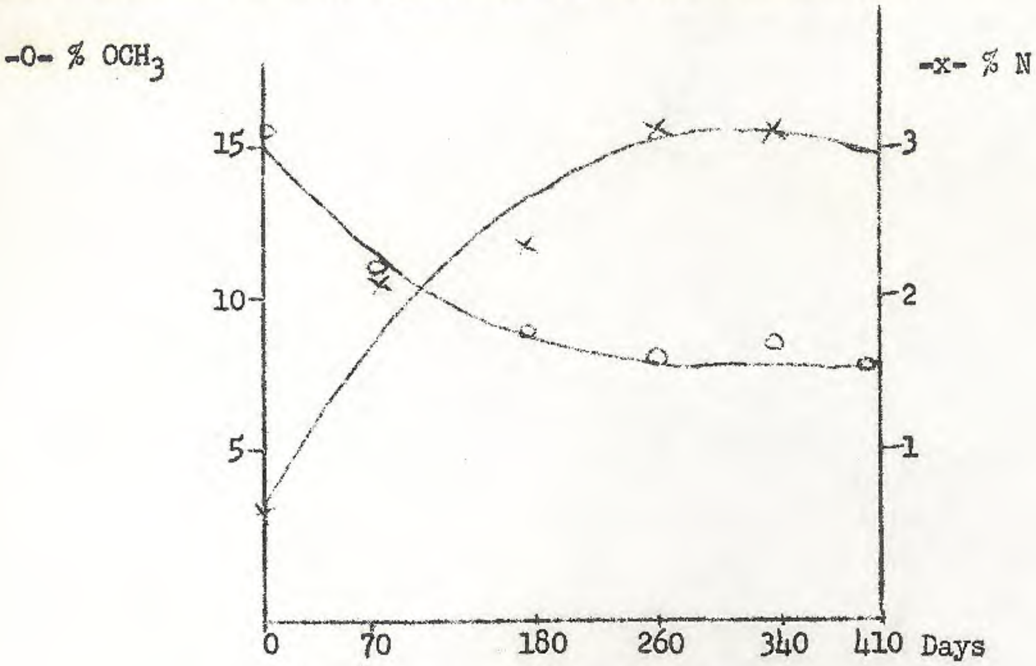
S 3 14

Elementarzusammensetzung der zu verschiedenen Zeitpunkten isolierten
Schwefelsaure -u. Bjorkman - Lignine.

	Rottezeit in Tagen	C%	H%	O%	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
	260	58.00	5.83	29.93	3.14	3.9	7.84
	340	54.97	5.96	32.09	3.08	3.9	8.57
	410	54.29	5.86	32.88	2.97	4.0	7.32
Björkman - Lig.	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

During the time of rotting different samples of straw have been analyzed to study the decomposition. With decrease of the methoxyl content the content of nitrogen increased. We isolated the lignin fraction not only with sulfuric acid but also with organic solvents according to Björkman.

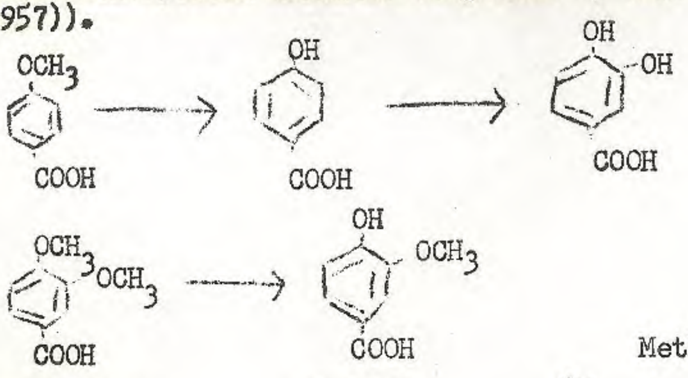
Before it has never been proved that the treatment with the relatively concentrated sulfuric acid of 72% doesn't give condensation reactions between the lignin components and proteins, amino acids or other amino compounds, respectively. By the extraction with organic solvents no condensation reactions are probable. In both cases we have the same tendency. In the case of extraction following Björkman lignins are isolated which have more or less a lower molecular weight, therefore, the amount of methoxyl groups and the content of nitrogen is relatively higher determined than in lignin isolated with sulfuric acid.



Decrease of OCH_3-content and increase of N-content in sulfuric acid-lignin fraction during rotting

The diagram shows in the case of sulfuric acid lignin, that there must be a chemical relationship between the demethylation and the reaction with amino compounds. Phenol ether does not react under these conditions. By demethylation phenols are formed. The decomposition process has been under aerobic conditions and as intermediary products quinones could be formed. These react very rapidly with amines as is known.

Another investigation belonging to the demethylation of lignin or its building blocks is done by Henderson with model substances. (Henderson, M. E. K.: Metabolism of methoxylated aromatic compounds by soil fungi. J. Gen. Microbiol. 16, 686 (1957)).



Hormodendrum species

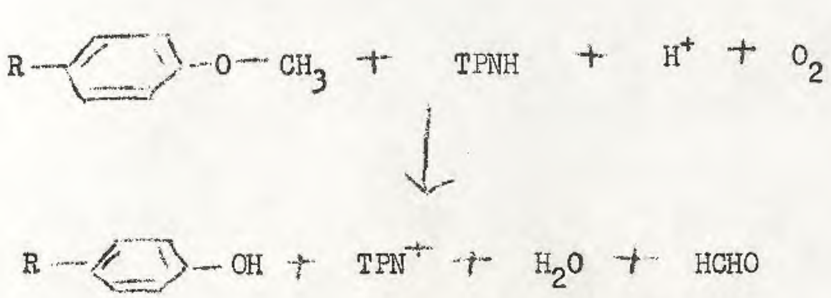
Control	Methoxy benzoic Acid		
	o-	m-	p-
40	52	148	213

Cleavage of Phenylmethylether by Soil Microorganisms

She could show that the methyoxybenzoic acids are split up by soil microorganisms such as Hormodendrum to hydroxy-benzoic acids. With the Warburg technique, it could be determined that the p- compound is split up more rapidly than the m- , and those more rapidly than the o- compounds. In this case another reaction interesting for our further considerations occurs. The formed p-hydroxybenzoic acid is oxidized in addition to protocatechuic acid. One of her other works is also shown. Thus, veratric acid is changed into vanillic acid. Only the ether group in p-position has been split up.

In connection with the chemistry of humic acids it has been of interest to us to find the effective enzyme systems which split up the phenol ethers. According to the experiments of Axelrod (Axelrod, J.: The enzymic cleavage of aromatic ethers. Biochem. J. 63, 634 (1956)), with preparations of liver, we investigated homogenates of cultures of fungi and mushroom dehydrogenases with acetanisidine. The cleavage could be identified by the indo-phenol reactions.

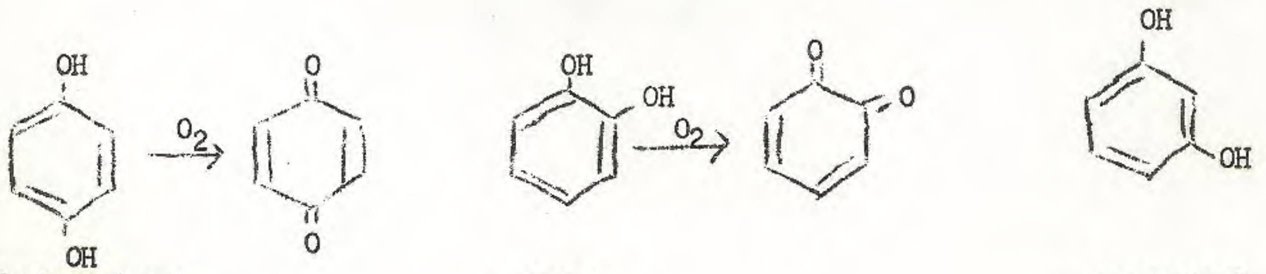
S 4 21



This work (Flaig, W. and Schmidt, G. not published) is not yet finished, but we can propose a scheme which explains the observed effects. We found that the cleavage is only possible in the presence of hydrated triphosphopuridinenucleotide. The methyloxyl is split off in this case as formaldehyde and could be identified.

After this reflection, we must consider which compounds must be investigated in addition. First we will remark that the reactions of polyphenols and their ethers will be some of the most important for the decomposition of lignin on the one hand and the formation of humic acids on the other.

In most cases, phenols can be oxidized very easily. The scheme for the oxidation of dihydroxy-benzenes, diphenols, is as follows:



hydroquinone

pyrocatechnol

resorcinol

1,2-and 1,4-dihydroxy benzenes can be easily oxidized to quinones. 1,3-dihydroxy benzene, resorcinol, cannot be oxidized to a quinone.

In which way can quinones be formed in the soils either as intermediates or only in small amounts? We must also discuss that quinones may have an effect on the physiological process even if they are present in very small amounts. I remember, for instance, that indole-3-acetic acid has its greatest effect on cell stretching in a concentration of 10^{-7} g/ml. That is a concentration of 0.6×10^{-6} mole/liter. If one would give this concentration on the surface of the soil in a depth of 20 cm. this would be approximately one kilogram/hectare. For this consideration, it must be mentioned that such calculations are only a hypothesis because the stability of the substances against the chemical compounds in the soil, the oxidation effect of microorganisms, and the absorption of soil minerals must be born in mind.

Our next considerations must be to study the possibilities of the formation of quinones. There are several.

1. Oxidation of lignin building blocks and fragments of lignin; the oxidation of phenolic substances which are found in plants; and the oxidation of tannins.

2. Metabolism products of plants and microorganisms.

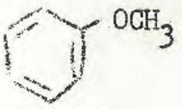
Some other possibilities will only be mentioned.

3. Oxidation products of aromatic amino acids.

4. Oxidation products of inositol.

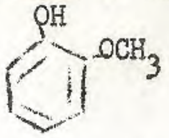
For each of these four points, I will give you some examples.

In plants occur different phenols or their ethers.



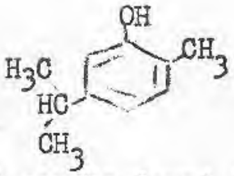
Anisole

This phenol ether is in different plants and possesses an aromatic oder.



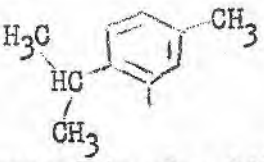
Guaiacol

Guaiacol is the mono methyl-ether of catechol. It can be isolated by distillation of guaiac resins.



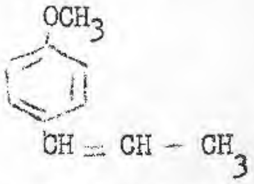
Carvacrol

Carvacrol can be found in different volatile oils in plants and are probably alteration products of terpene bodies.



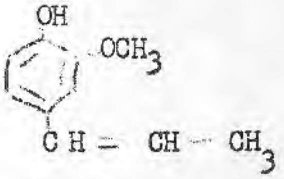
Thymol

This compound is also like carvacrol in ethereal oils of different plants and perhaps alteration product of terpene bodies.



Anethole

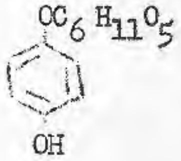
This is a compound of the oil of anis and similar kinds of oil. This compound is relatively reactive by the double bond in the side chain.



Eugenol

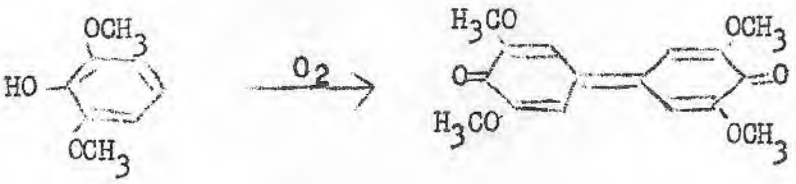
This is a widespread colorless liquid in plants and is prepared from the oil of cloves; about the condensation reactions of eugenol we had spoken before.

Some of the phenols occur in the plants as glucosides. One example for this is arbutin.



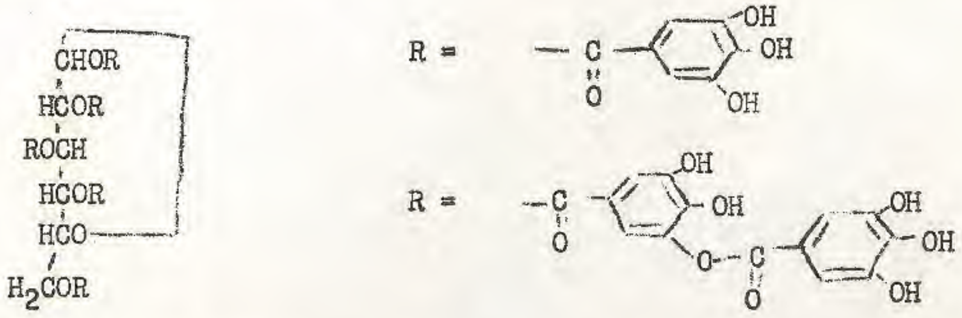
In the needles of pine and in the bark of willow there are other glycosides, piceïn and salicin. These glucosides are widespread in different plants.

By dry distillation of wood of beech pyrogallol-1,3-dimethylether is found.



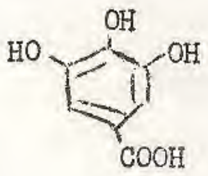
By oxidation a dimerization product can be isolated. Cörulignon is a dimeric quinone with a blue color. Dimerization reactions occur in many cases during formation of natural products and not only in this case but also for the formation humic substances is very interesting.

Other compounds such as gallic acid are not found free in the plants mostly as glycosides.

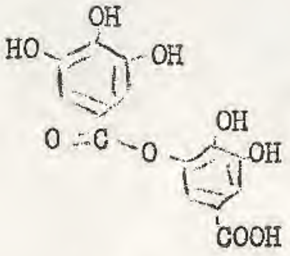


The next compounds we must speak of are the natural tannins. There are two kinds which are well known.

Since the work of Emil Fischer about the tannins of the gallnuts the building principle of these substances are known. An average of 10 molecules of gallic acid are combined with one molecule of glucose. Mostly in the form of m-digallic acid.



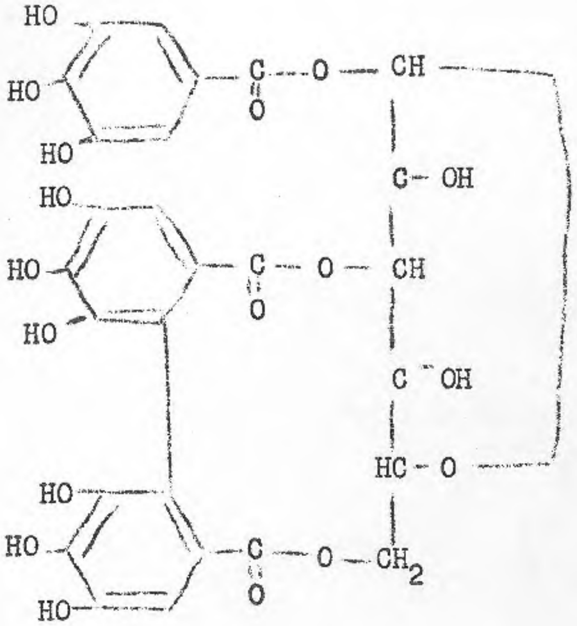
gallic acid



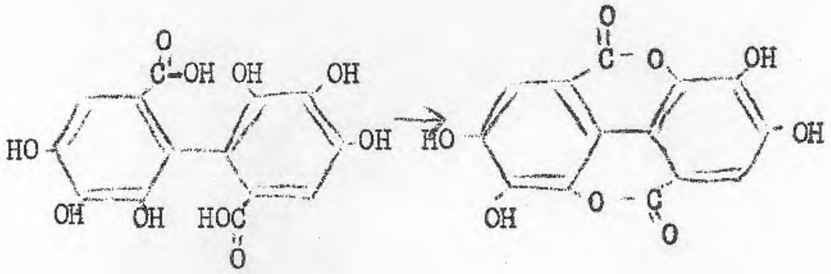
m-digallic acid

Nobody succeeded till now to isolate from the mixture of the many very similar compounds of gallo tannins definite compound of which exact constitution is given. Even the modern methods of counter current distribution or partition chromatogtaphy does not help. In the last years the ellagic tannins have been studied most intensively. By acid hydrolysis, the extracts of the tannins split up the ellagic acid. Now some crystallized ellagic tannins are known, the chebulag acid $C_{41}H_{30}O_{27}$. (Schmidt, O. Th., u. Nierswandt, W.: Naturwissenschaften 35, 191 (1948); Liebigs Ann. Chem. 568, 165 (1950); Schmidt, O. Th., u. Kademann, R.: Liebigs. Ann. Chem. 569, 149 (1950) and corilagin $C_{27}H_{22}O_{18}$ (Schmidt, O. Th. u. Lademann, R. Liebigs Ann. Chem. 571, 232 (1951); Schmidt, O. Th., u. Schmidt, D. M.: Liebigs Ann. Chem. 578, 31 (1952)).

The constitution of the corilagin (compare table) is 1 mole glucopyranose which has in 1 position combined -glucosidic 1 mole gallic acid, in the 3 and 6 position is 1 mole of hexahydroxy-diphenic acid. The hexahydroxy-diphenic acid can be split up with dilute acids. It is not stable and under loss of 2 molecules of water ellagic acid is found.



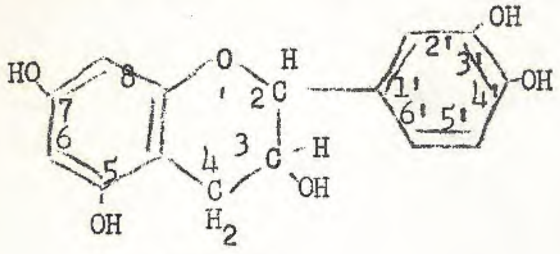
Coriligin



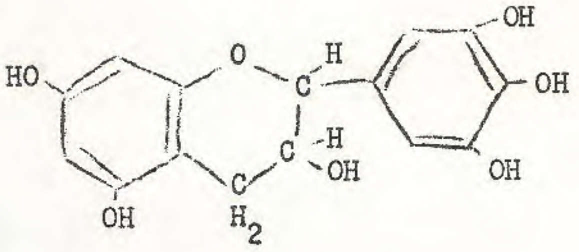
Hexahydroxy-
diphenic acid

Ellagic
acid

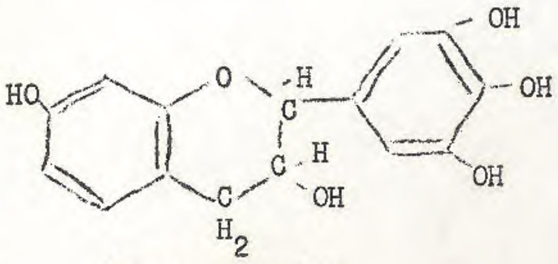
The second group are the catechins from which the constitution is known from the work of Freudenburg.



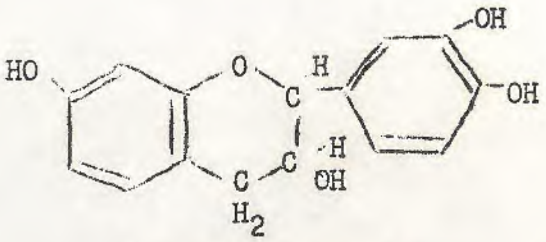
Catechin



Gallocatechin



Mimose-catechin

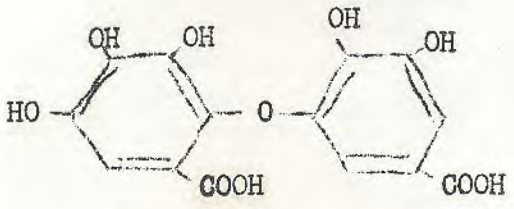


Quebracho-catechin

As building blocks for this class of tannins there must be named the catechin, then the gallocatachin which had been isolated from green leaves of tea; furthermore the 3, 7, 3', 4', 5'-pentohydroxy-flavan or mimosa-catechin and finally the quebracho-catechin which is the building block of the quebracho tannins.

The catechins are not yet tannins. But they are easily condensed by the treatment with enzyme or mineral acids, but also by boiling of their aqueous solution to amorphous tannins. The upper text are colorless and water soluble. The higher, water insoluble and more or less colored. It can be believed that the condensation from step to step follows a uniform principle. This is under natural conditions combined with dehydrogenation reactions.

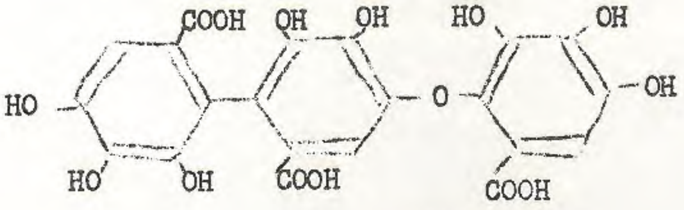
In more recent time some interesting new building blocks of tannins had been found by W. Mayer. (Mayer, W.: Liebigs Ann. Chem. 578, 34 (1952)). He found in young sprouts of chestnut (cartanea vesca) dihydro-digallic acid.



Dehydro-digallic acid

In this case also 2 molecules of gallic are combined by dehydrogenation as in hexahydroxy-dephenic acid but with linkage of a diphenyl ether.

Furthermore in the receptacles of oats there have been found another acid, valonea acid.

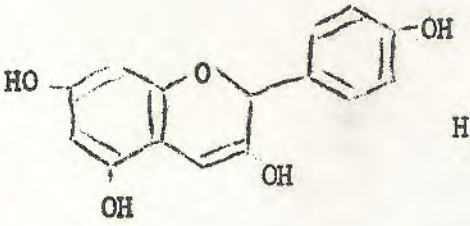


Valonea acid

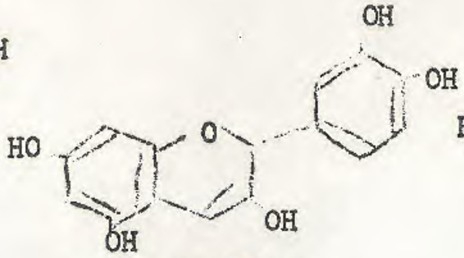
In this case we have both kinds of dehydrogenations, the dehydrogenation of the nucleus of two gallic acids to hexahydroxy-diphenic acid and the dehydrogenation of a phenol group of a third gallic acid. (Schmidt, O. Th., u. Komarek, E.: Liebigs Ann. Chem. 591, 156 (1955)).

This is the only case I know where in one compound two types of dehydrogenation reactions take place. It is very probable that in the plants these reactions have been carried out by dehydrogenesis of phenol oxidation. During our work we had not succeeded in isolation of diphenyl ether compounds oxidizing phenols such as gallic acid with phenol oxidases.

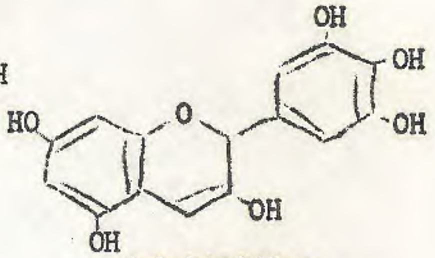
Another group of phenolic compounds in the plants are the anthocyanins. This type of phenol can be deduced from three compounds, pelargonidine, cyanidine, and delphinidine.



pelargonidine

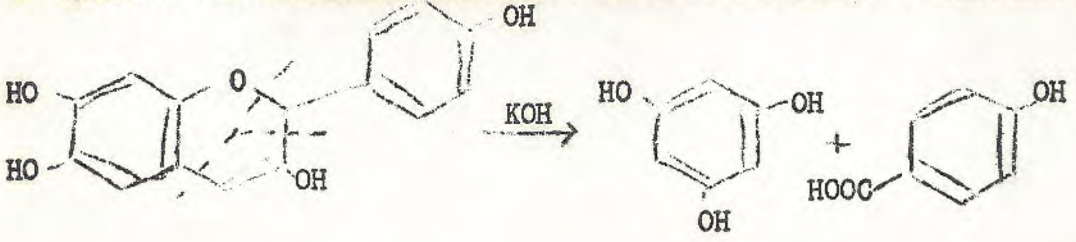


cyanidine



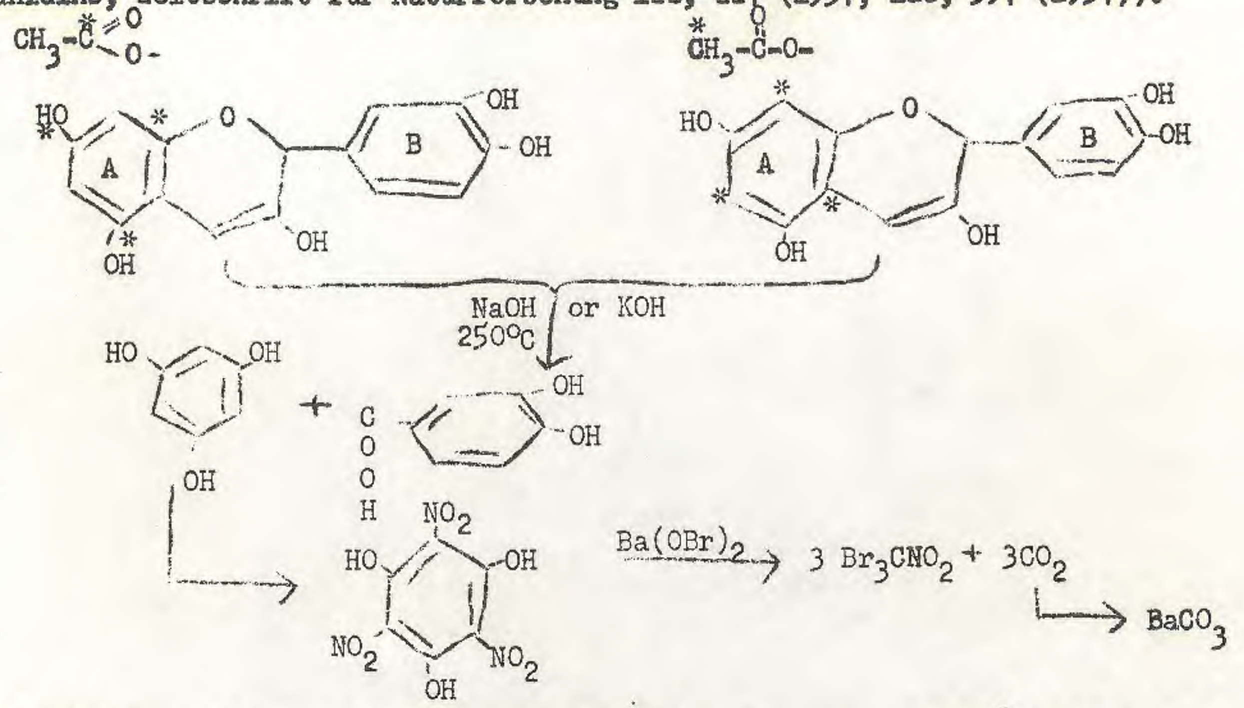
delphinidine

This type of phenolic compound is combined with sugars which can be in 3- or 5-position or both positions. Mostly they are the dyestuff of different flowers, such as cornflowers, carnations, dahlia, strawberry, rose, poppy, primrose, and others. They contain in every case in 3-, 5- and 7-position a hydroxyl group. They differ only by the number of the hydroxyl groups in the 2-phenyl ring. By oxidation they can be split off in different phenolic compounds and phenolic carbonate acid.



By this type of reaction, we get two different kinds of phenolic compounds. One is resorcinol, the other can be also triphenol but the hydroxyl groups are in 1, 2, 3-position.

In connection with this type of compounds, I must mention another synthesis of aromatic substances which can occur in plants. (Griesebach, H., Zur Biogenese des Cyanidins, Zeitschrift für Naturforschung 12b, 227 (1957; 12b, 597 (1957)).

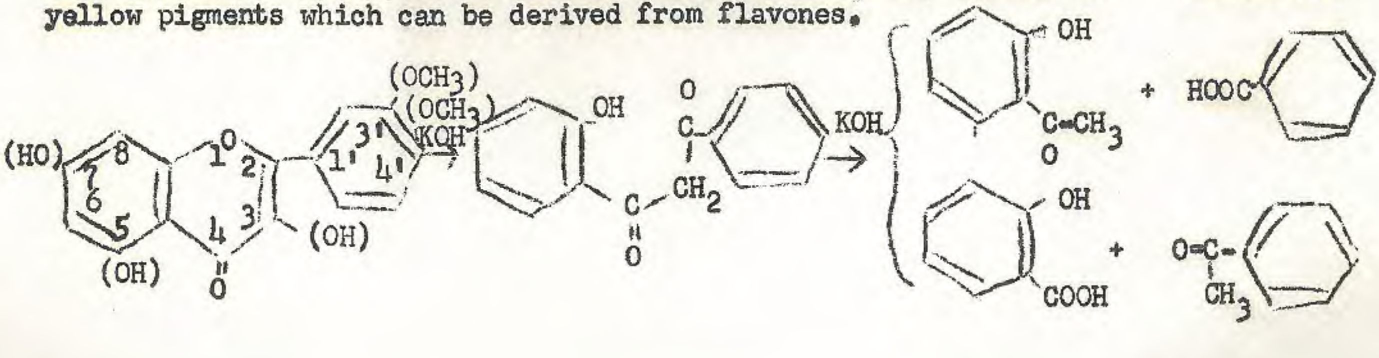


This author could show with different labeled acetate-groups that the ring A is formed by these groups. The ring B which is also aromatic will not be formed by acetate groups.

In the ring A the hydroxyl groups are symmetric, in m-position, in the ring B vicinal or in o-position.

It has been very interesting that with acetate labeled in carbon-atom 1 all the carbon atoms, which have hydroxyl group are labeled. In the case of labeled acetate in carbon atoms 2, the carbon atoms without hydroxyl groups are labeled. This fact could be shown by decomposition of these different labeled compounds as it is shown in the reaction scheme. The experiments had been made with seedlings of red cabbage. According to the hypothesis of Birch (A. I. Birch, Perspectives in Organic Chemistry, p. 134-154, Interscience Publishers, Inc., New York, 1956) there takes place a head-tail-addition. Presumably the ring B will be formed from substances of the carbohydrate cycle which I mentioned before.

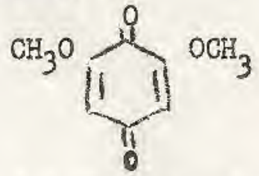
Another kind of phenolic substances which is widely spread in nature are yellow pigments which can be derived from flavones.



They possess two up to six hydroxyl- or alkoxyl substituents. In the plants they are also found as glycosides or esters of tannic acid. As an example acacetin is a 5,7-dihydroxy-4'-methoxyl flavone and quercetin is 3,5,7,3'-4'-hydroxy flavone.

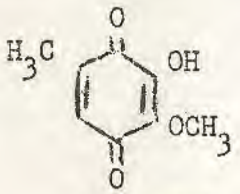
To 2) The number of isolated quinones out of plants and microorganisms are very numerous. Basic and summary work has been done by Raistrick and Quillico (Anslow, W. K., und Raistrick, H.: Studies in the biochemistry of microorganisms. LIX. Spinulosin (3,6-dihydroxy-4-methoxy-2,5-toluquinone) a metabolic product of a strain of aspergillus fumigatus fresenius. Biochem. J. 32, 228 (1938). - Anslow, W. K., und Raistrick, H.: CVIII. Studies in the biochemistry of microorganisms. LVIII. Synthesis of spinulosin (3,6-dihydroxy-4-methoxy-2,5-toluquinone) a metabolic product of penicillium spinulosum Thom. Biochem. J. 32, 803 (1938) - Anslow, W. K. und Raistrick, H.: Studies on the Biochemistry. LVII. Fumigatin (3-hydroxy-4-methoxy-2,5-toluquinone) and spinulosin (3,6-dihydroxy-4-methoxy-2,5-toluquinone) and spinulosin (3,6-dihydroxy-4-methoxy-2,5-toluquinone), metabolic products, respectively, of aspergillus fumigatus fresenius and penicillium spinulosum Thom. Biochem. J. 32, 687 (1938) - Raistrick, H., Anslow, W. K., und Breen, J.: Studies on the biochemistry of microorganisms. 64. Emodic acid (4,5,7-trihydroxyanthraquinone-2-carboxylic acid) and W-Hydroxyemodin (4,5,7-trihydroxy-2-(hydroxymethyl-anthraquinone), metabolic products of a strain of penicillium cyclypium Westling. Biochem. J. I 34, 159 (1940) - Quillico, A.: Recent developments de la chimie des produits naturals: la chimie des moisissures et des bacteries. Chimie et Industrie 66, 205 (1951)).

I will mention only some examples, which are characteristic and help us for our considerations of humus chemistry.



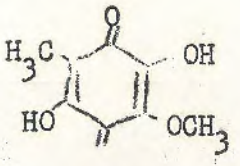
2,6-Dimethoxy benzochinon

2,6-dimethoxy quinone. This can be isolated from Adonis vernalis L. It can be synthesized by oxidation of hyrogalloltrimethyl ether. It prevents the growth of Staphyloccoccus aureus in vitro. The monomethyl derivative, 2,6-dimethoxy-3-methyl-1,4-benzoquinone has a similar effect.



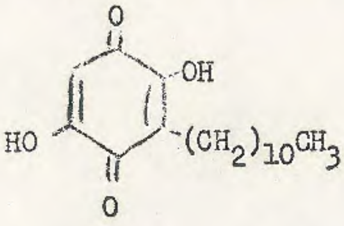
Fumigatin
(Brown, Fp. 116° C)

Fumigatin. This can be isolated from cultures of aspergillus fumagatus Fresenius.



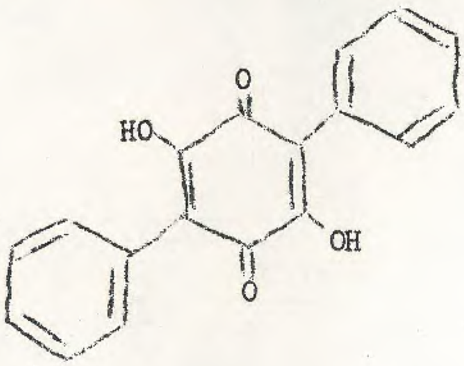
Spinulosin

Spinulosin isolated from Penicillium spinulosum Thom. This quinone has a similar construction as fumigatin but it's reactions are different from the former quinone because it is a 2,5-dihydroxy-1,4-benzoquinone. I call your attention to this fact because later on we will see that the more or less stable 2,5-dihydroxy-1,4-benzoquinones are only able to react in a small amount during formation reactions of humic substances.



Embelin

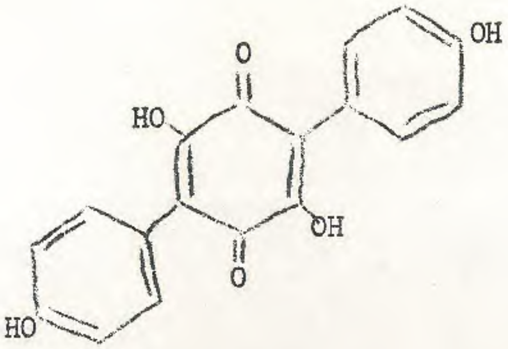
Embelin, a 2,5-dihydroxy-3-undecyl-1,4-benzoquinone is in the berries of an Indian shrub.



Polyporic acid

Polyporic acid. To this kind of compounds belong all the other phenyl derivatives. Most of them are isolated from fungi. The dyestuffs of fungi are different from those of assimilating plants. The different metabolism of the parasitic fungi may be the reason.

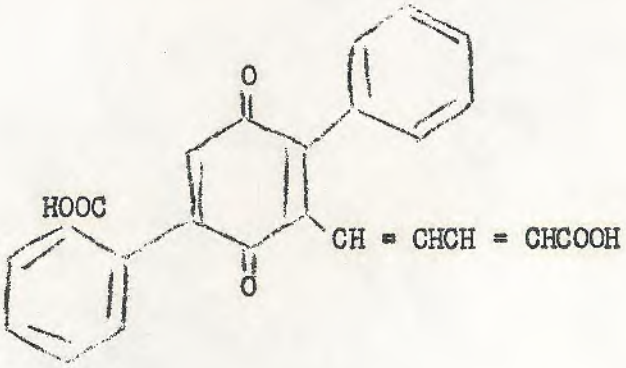
Polyporic acid could be isolated up to 18% of the dry weight of the fungi Polyporus nidulans Pers. This fungus grows on diseased oaks.



Atromentin

Atromentin. This dyestuff could be isolated from Paxillus atromentosus Batsch from a fungus growing on old oaks. The yield of atromentin is better if the fungi are harvested in fall. In this time the fungi is colored more intensively. The amount of this dyestuff in the fungi is 2%.

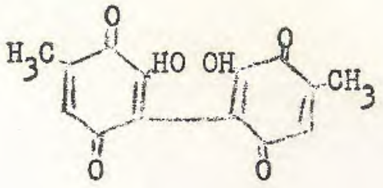
Atromentin has hydroxyl groups in p-position of the two phenyl groups. Therefore it adsorbs light more in the visible part of the light. Polyporic acid is brown-violet and atromentin bronze colored.



Muscarufin

Muscarufin is also a dyestuff of a fungus which is probably combined with sugars. It is a constituent of the red skin of the common poisonous fly, agarica-amanita muscaria L. The yield is relatively small during preparation. There could be isolated 850 mg out of 500 kg of fresh fungi.

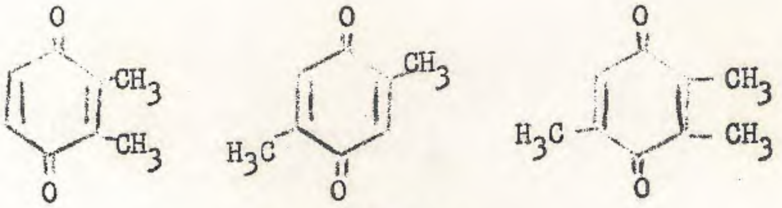
In this case the second hydroxyl group of atromentin is replaced by an acid side-chain. I will also mention here some facts, about which we will speak later on more intensively. If we compare the color of the mentioned hydroxy quinones, we can see that the depth of the color increases by introducing hydroxyl groups. In the case of atromentin and muscarufin the latter compound has a brighter color namely orange-red, than atromentin.



Phoenicin

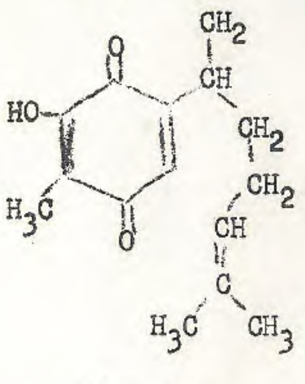
Phoenicin isolated from Penicillium phoeniceum van Beyma. It has a constitution of a demerized 2-hydroxy-6-methyl-1,4-benzoquinone. About demerization reactions of quinones which occur as natural products, we must speak later on, also in connection with the formation of humic substances.

It could be shown that this quinone increases, in very low concentration, the respiration of washed and colorless cells of Bacillus pyocyaneus more than 200 to 300%. It is not sure in which way this quinone takes part in the metabolism, presumably as a catalyst according to its reversible redox-system.

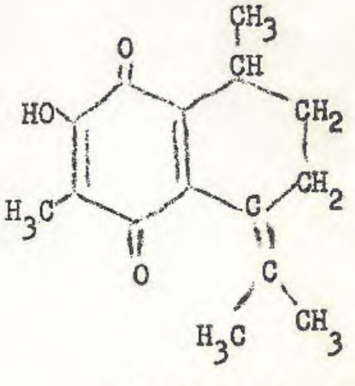


Gonyleptidine

In more recent time, a mixture of quinones could be isolated also from animals, for instance, from the secretion of a South American spider (Fieser, L. F. and Ardoa, M. J. J. Amer. Chem. Soc. 78, 778-781 (1956)). It is a mixture of 2,3-dimethyl-,2,5-dimethyl- and 2,3,5-trimethyl-1,4-benzoquinone. This mixture has bactericide and fungicide effects. The effects of the components alone are not so high as those of the mixture.

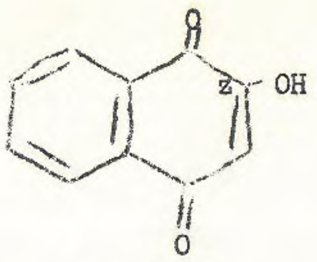


Perezon



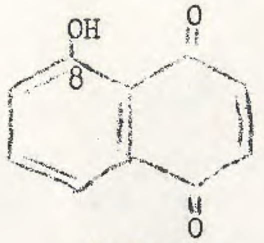
Perezinon

Perezon is a natural dyestuff which can be isolated from roots of different Mexican kinds of Perezonia with a yield . to 3.6%. It is a monohydroxy benzoquinone with 2 aliphatic residues, from which one is a branched unsaturated side-chain with 8 C-atoms. This side-chain can condense by further oxidation to a naphthyl-quinone, to the perezinon.



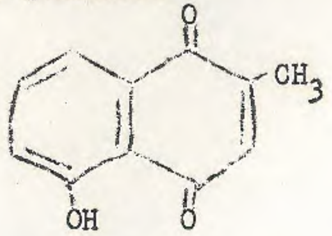
Lawson

Lawson can be extracted from leaves of a Henna-bush Lawsonis inermis growing in Egypt. With this 2-hydroxy-1,4-naphtho quinone, wool and silk can be colored with orange color. A mixture of dry henna leaves and catechu serves for coloring the hair red.



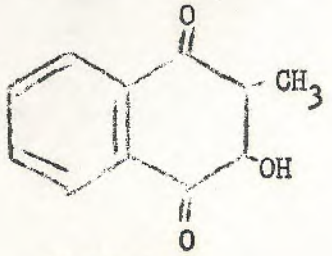
Juglon

Joglon is isomeric to Lawson and can be isolated from the unripe shells of walnuts, where it is in the form of its hydroquinone. In presence of air, the hydroquinone will be oxidized very rapidly. The formed quinone gives the skin dark brown spots. This is produced probably by addition reactions between the active groups of proteins and the quinones.



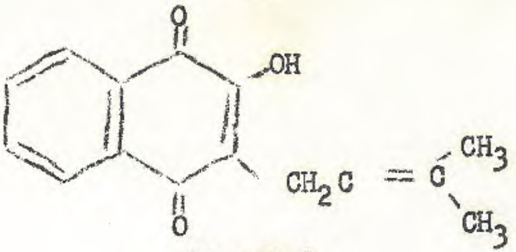
Plumbagin

Plumbagin could be isolated from an Indian shrub of different kinds of Plumbago. It is the active principle of chita, (medikament) medicine.



Phthiokol

Phthiokol. This quinone could be isolated from human bacilli of tuberculosis. It may be that it is formed during the isolation by decomposition of vitamin K, by treatment with alcoholic potassium hydroxide.



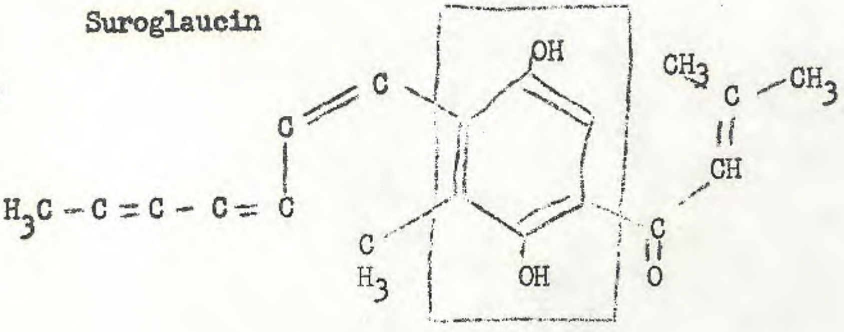
Lapachol

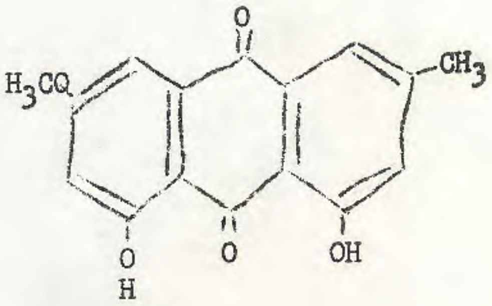
Lapachol is a crystallized yellow dyestuff isolated from special roots. The sodium salt is red. I mention this fact because later on we will see that it is possible to use the color of the salts of hydroxy quinones to divide them.

I will also mention some anthraquinones which are metabolism products of plants or microorganisms. It may be that some of them are formed by benzoquinones with suitable (adequate) side-chains.

S 5 248

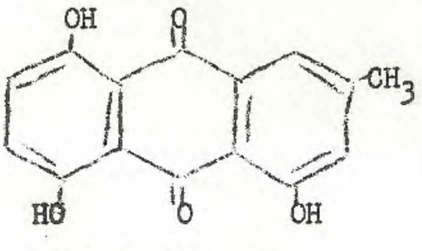
Suroglaucin



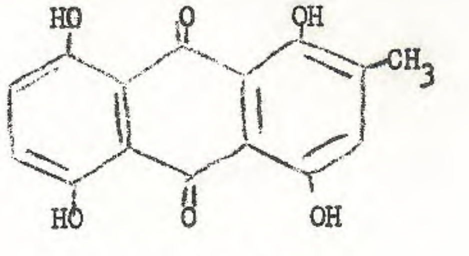


Physcion

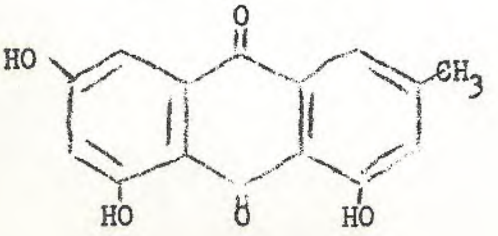
It can be possible that,for instance, auroglaucine is formed to physcion by condensation reactions. The anthraquinone derivatives are more stable than those of naphthoquinone and especially with a p-benzoquinone. The anthraquinones have a chemical relationship to ketones. The anthraquinones which occur in different fungi can mostly be derived from better methyl anthraquinones. Some of them are helminthosporin, cynodontin, catenarin.



Helminthosporin



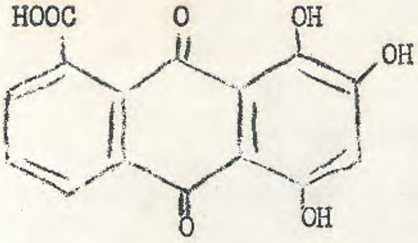
Cynodontin



Catenarin

Most of these anthraquinones have a bacteriostatic effect.

Another anthraquinone which has been isolated in boletol.

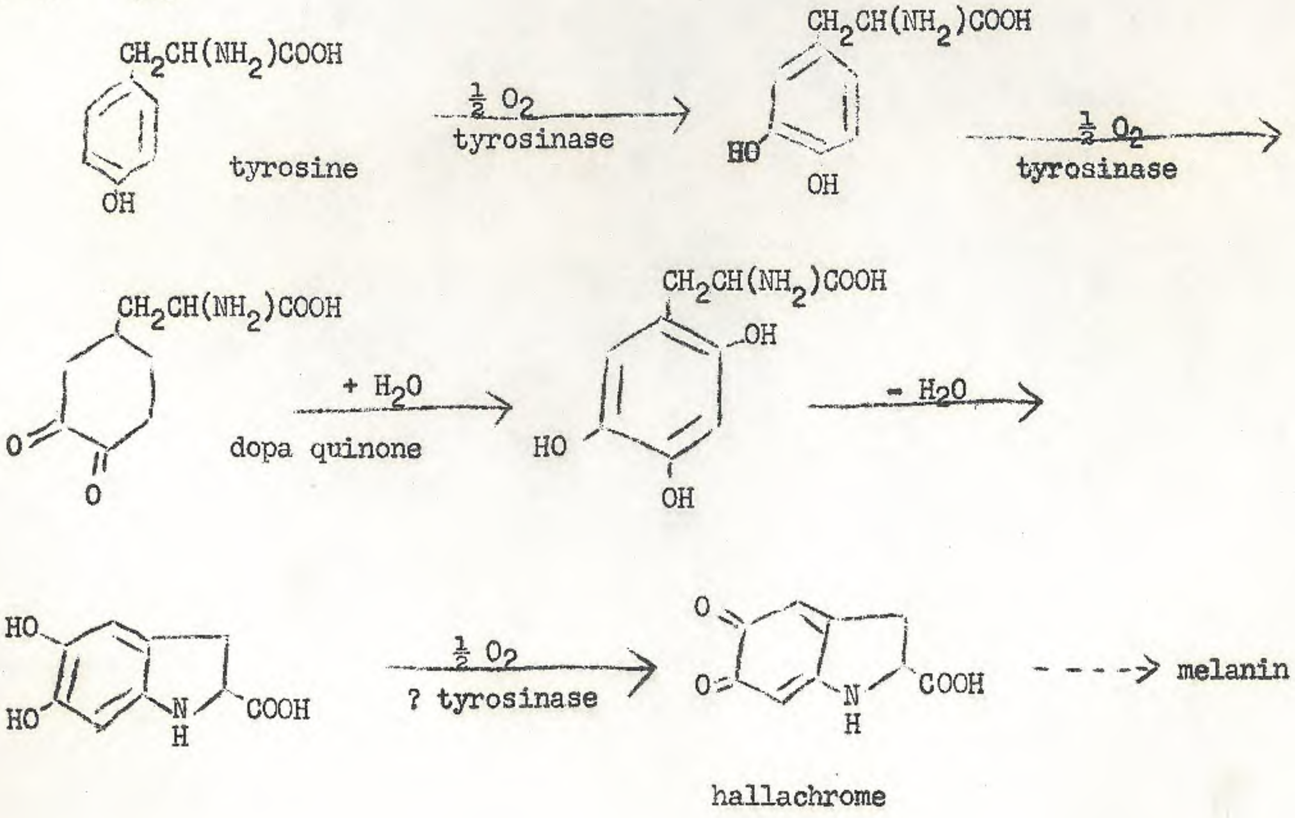


Boletol

Boletol. I will remark that the anthraquinone derivates are the only ones in which carboxyl groups are combined with the ring-system. Especially benzoquinone derivatives have mostly no carboxyl groups combined with a ring because this kind of carboxyl group is not very stable and can be split off very easily as CO_2. If benzoquinone systems possess carboxyl groups, they are mostly in the side-chain, compare muscarufin.

To 3) As an example of the oxidation of an aromatic amino acid, I will show you the oxidation of tyrosine. (Raper, H. S., Die Einwirkung von Tyrosinase auf Tyrosinase auf Tyrosin. Fermentforschung 9, 206 (1927)).

S 6 325



Formation of Melamin from Tyrosine

In the presence of tyrosinase at first a second hydroxyl group is introduced in o-position to 3,4-dihydroxy-phenyl alanine. By further oxidation the diphenol is oxidized to an o-quinone derivative; by addition of water in 6 position a hydroxyl group is introduced by 1,4-addition. Hydroxy hydroquinone derivate is formed. Water is split off and an indole carbonic acid is formed. By further oxidation the o-quinone hallachrome is formed which polymerizes to melanin. The higher melanin is polymerized the darker is its color. This kind of compounds has a comparable structure with humic substances.

To 4) Some lectures before, I told you that it is not possible to form aromatic systems out of inositol by dehydration in plants. It has been possible to prove it with meso-inositol-^{14}C. (Weygand, F., Brucker, W., Grisebach, H. and Schulze, E. Stoffwechseluntersuchungen mit meso-inosit-^{14}C. Zeitschr. fur Naturforsch. 12b, 222 (1957)).

With the aid of the labeled inositol, it could be shown that this compound is no precursor.

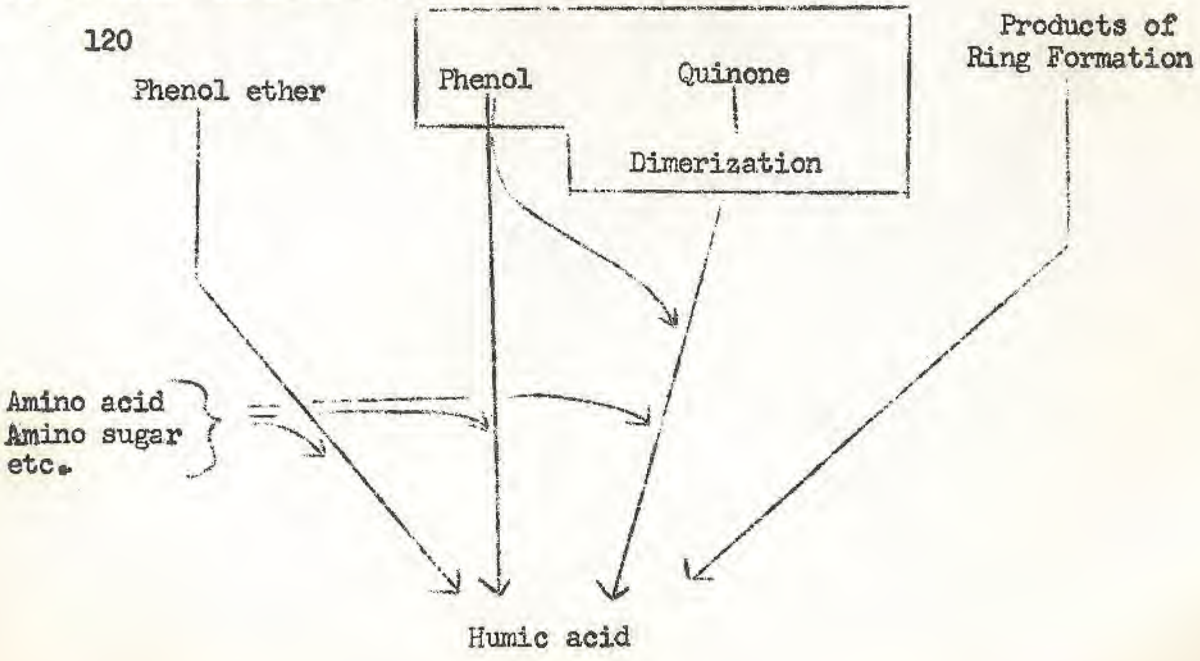
a. For the formation of catechins in leaves of tea.
b. For the biosynthesis of cyanidines in little plants of red cabbage.
c. In <u>Phycomyces blakesleeanus</u>, which forms 5% of its dry weight as phenol carbonic acids. It had not been possible to identify labeled gallic or protocatehuic acid after addition of labeled inositol to the nutrient solution.

But it had been possible to isolate tetrahydroxy-1,4-benzoquinone which has been radioactive from nutrient solutions of <u>Pseudomonas beijerinckii</u> Hof. By enzymatic oxidation a ketose, inosose is formed which can be transformed by treatment with sodium acetate to 1,2,4,5-tetrahydroxybenzene.

In the last cases, I mentioned some reactions which can be carried out by enzymes. About the enzymatic oxidation of phenols, we will speak later on, especially if we discuss the participation of microorganisms in the formation of humic substances.

For further considerations, I will give a scheme.

S 7 120



About the demethylation of phenol ethers, we have spoken. First of all, we must speak about the reactions of phenols and quinones. For this purpose, we will discuss the chemistry of quinones which have some relationship to the lignin precursors, the lignin fragments, the phenols in the plants, and the phenolic or quinonic metabolism products of microorganisms. These kinds of substances are model substances of the mentioned natural products.

To this consideration belongs also the dimerization reactions of quinones which have not been noticed enough in the chemistry of humus in my opinion. Among them are on the one hand products which can also be isolated from plants and on the other, products which have a relatively high physiological activity. By the oxidation of phenols the quinones are formed. Under natural conditions the oxidation does not stop, further reaction can occur as dimerization and the breaking of the ring. One of our next objects will be to study the possibilities of the cleavage of the ring and the products which are formed by this process. All these products, the phenol ethers, the phenols, the quinones, and their dimerization products, and the products formed by ring cleavage are more or less able to react with amino compounds such as amino acids, and amino sugars. Most rapidly react quinones and their dimerization products, then the products of ring cleavage, more slowly phenols and phenol ether. By this condensation reaction, humic substances can be formed.

In the following lectures, it is mostly spoken of the viewpoint of the formation of humic substances from lignin as raw materials. In this consideration, the formation of the humic substances from phenols or quinones as metabolism products of plants and microorganisms are included. About the formation of humic acids in nutrient solutions of microorganisms in absence of lignin or phenols and quinones will be mentioned later on.

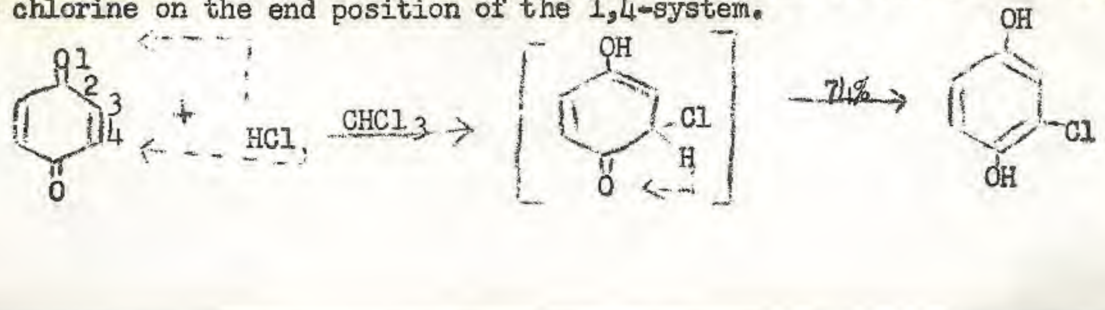
We spoke about the compounds which can be formed by decomposition of lignin. We have become acquainted with the chemical constitution of the phenolic and quinonic metabolism products of plant and microorganisms. To find the reactions which can occur with these products, we must study special types of quinones.

The lignin fragments which we discussed were phenols. We heard that phenols react only slowly with other substances. Under the aerobic conditions in the soil these phenols will be oxidized to quinones.

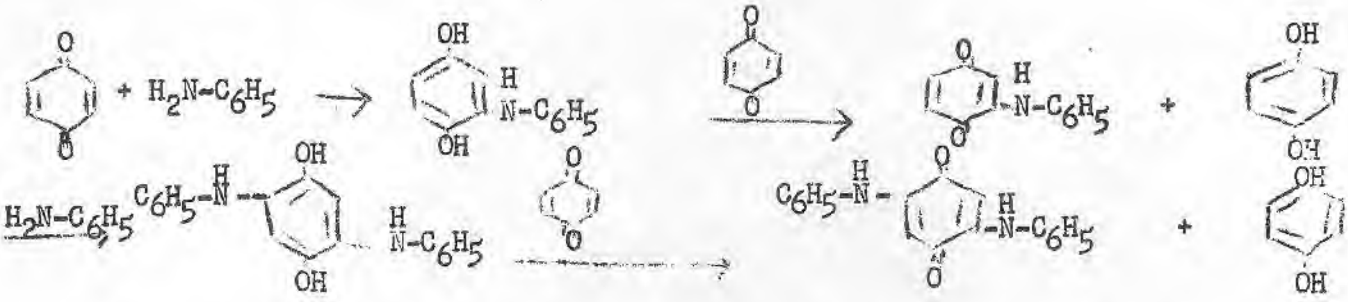
To study the possible changes of the natural products it is necessary to study quinones which are substituted with methyl-, hydroxy- and methoxyl groups. At first we must speak about some common reactions of quinones. For our considerations three types of reactions are more or less interesting.

p-quinones are yellow;	o-quinones are red
have higher melting points	have lower melting points

<u>1,4-addition</u> Quinones are more reactive than open-chained α, β unsaturated ketones and show larger variety of reaction. Especially characteristic is the 1,4-addition on the α β unsaturated keto groups, for instance the addition of dry hydrochloric acid. The hydrogen atom is added on one of the quinoid oxygen atoms, the chlorine on the end position of the 1,4-system.

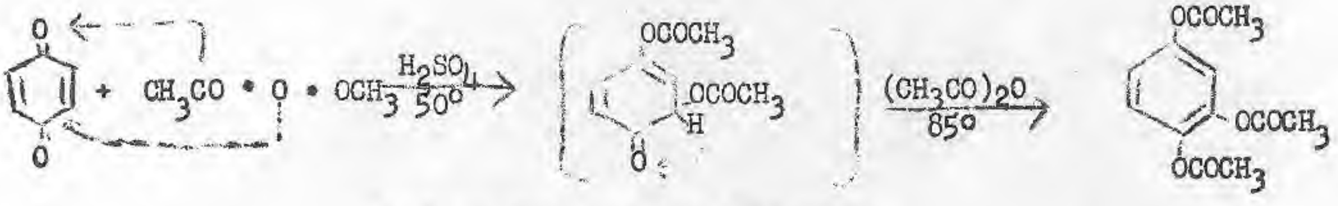


The primary reaction product possesses the unstable structure of a dihydrobenzene and enolizes to the aromatic chlorohydroquinone. Also the 1,4-addition of primary and secondary amines leads to substituted quinones.



2-anilino-quinone and 2,4-di-anilino-quinone will be formed. This reaction is interesting in connection with the formation of precursors of humic acids and humic acids themselves. This reaction can also take place with amino-acid and the corresponding derivatives are formed.

Another reaction which is interesting in the course of elucidation of the chemical constitution is addition of acetic anhydride.



hydroxy-hydroquinone-triacetate

At first, addition of the acetoxy group occurs. The second part of acetic anhydride, the acetyl group, is added on the OH-group which is formed by the reaction. A second acetic anhydride acetylates the second hydroxyl group, after isomerization to a phenol. The first reaction is catalyzed in the most cases by sulphuric acids or borontrifluoride. To have some ideas about the rate of the Thiele-reaction we (unpublished) investigated the methyl-substituted quinones. These investigations have been of interest in the case of reactions of model substances and in some cases also with the natural phenols, + quinones, respectively.

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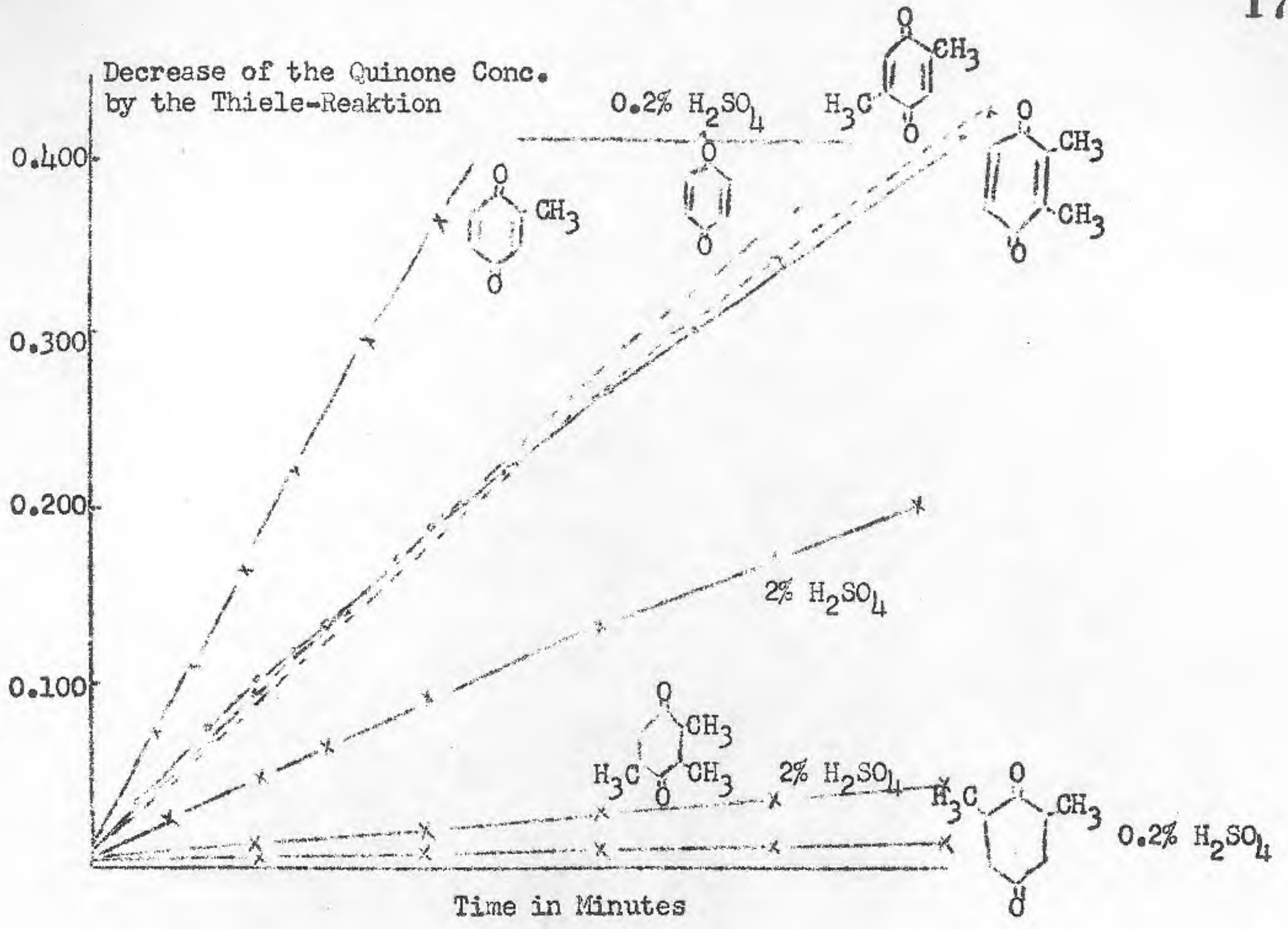
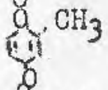
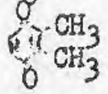
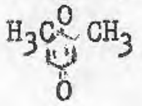
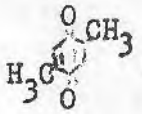
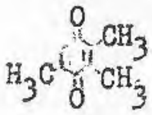
It seemed to us to be the simplest way for quantitative differences to determine the decrease of quinone concentration in the UV-range spectroscopically. In the presence of 0.2% concentrated sulfuric acid in acidic acid anhydride the transformation at 20° C of toluquinone has been the highest, this of benzoquinone as well as o- and p-xyloquinone is nearly the same, that of m-xyloquinone tenfold lower. No transformation with pseudoumico quinone could be observed in 0.2% sulfuric acid. Therefore, 2% sulfuric acid has been used and m-xyloquinone again as a comparable substance. Later on we will discuss if there are connections with other physical-chemical data.

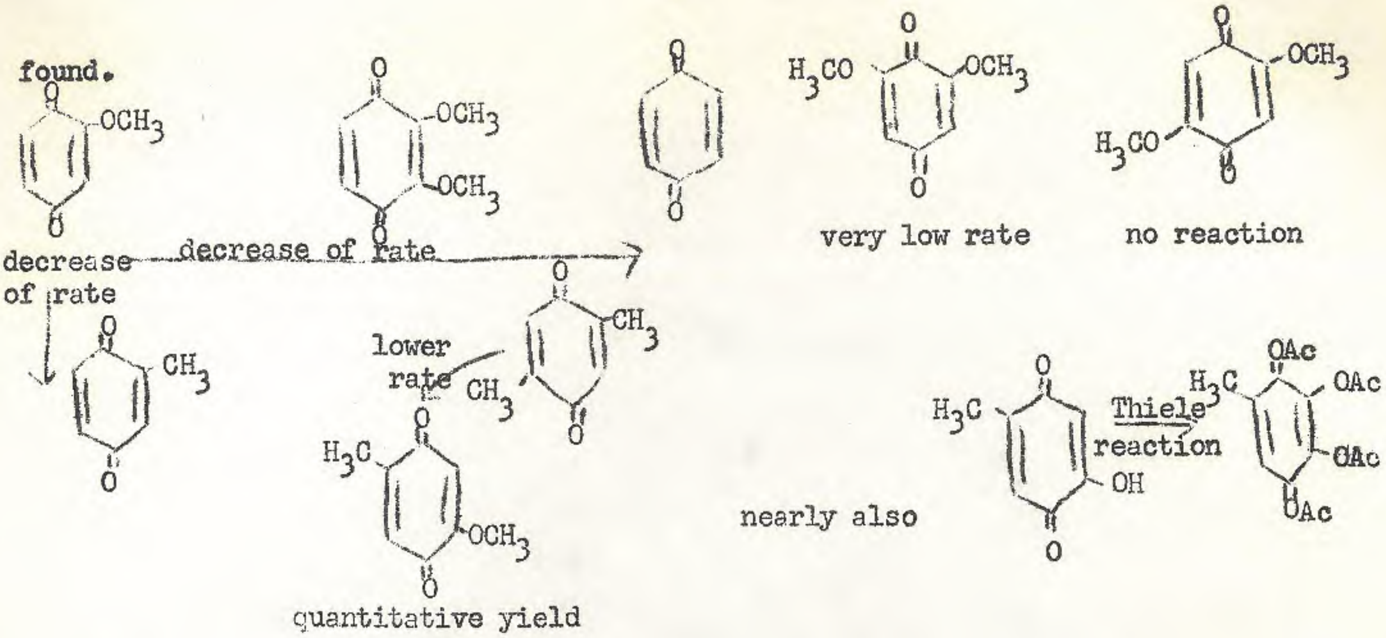
Erdtman (H. G. M. Erdtman. Proc. Roy. Soc. London Terre A. 143, 178 (1934)) investigated the Thiele-reaction quantitatively with different methoxy-quinones and



$$k = \frac{1}{t} \cdot \ln \frac{C_o}{C_o - C}$$

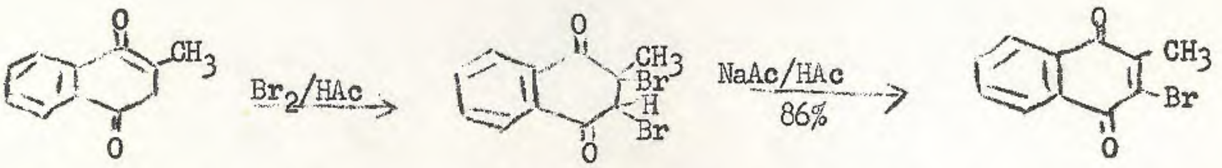
	0.2% H_2SO_4	2% H_2SO_4
	$3.7 \cdot 10^{-4}$	
	$7.2 \cdot 10^{-4}$	
	$3.9 \cdot 10^{-4}$	
	$0.1 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$
	$3.5 \cdot 10^{-4}$	
		$0.4 \cdot 10^{-4}$

found.

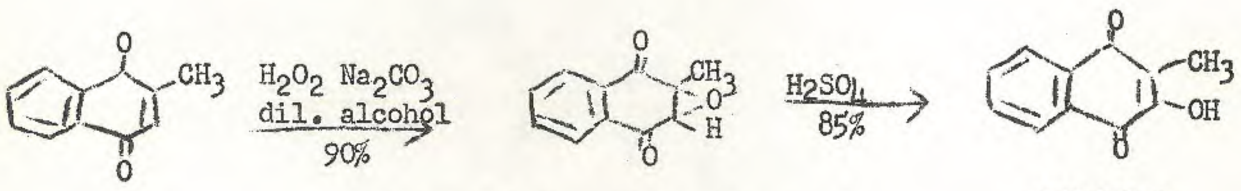


The position of -$OCOCH_3$ in the ring after reaction depends upon "the neutralization of the conjugated system".

Ethylene-addition. Different other compounds add easily to the two ethylene-bonds, for instance bromine. Dibromide is formed. In the case of α-naptha-quinone hydrobromic acid is split off and the mono-bromide is formed.



Another typical addition reaction is the formation of ethylene oxide derivatives to a solution of quinone in alcohol or dioxane, first diluted hydrogen peroxide is given and then a small amount of sodium carbonate. The yellow color disappears at once and the oxide crystallizes with the dilution of the colorless solution.

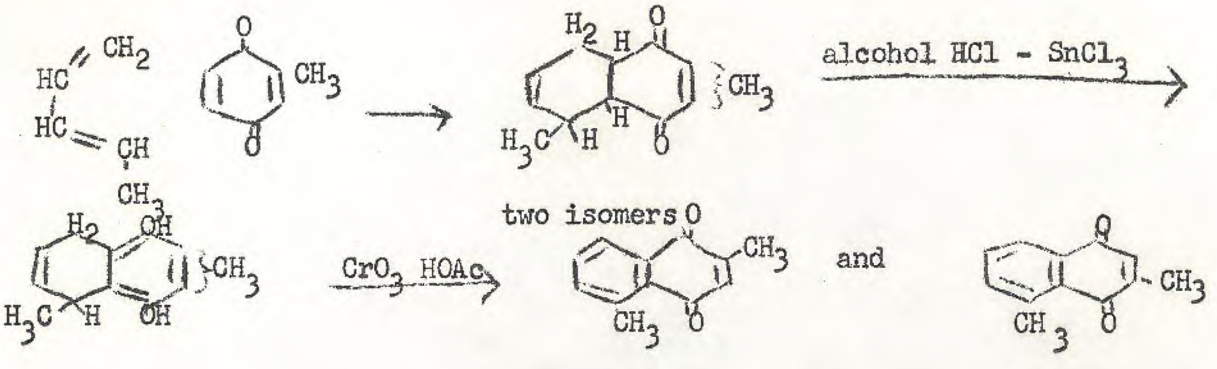


2-methyl-1,4-naphthoquinonoxyde

phthiokol

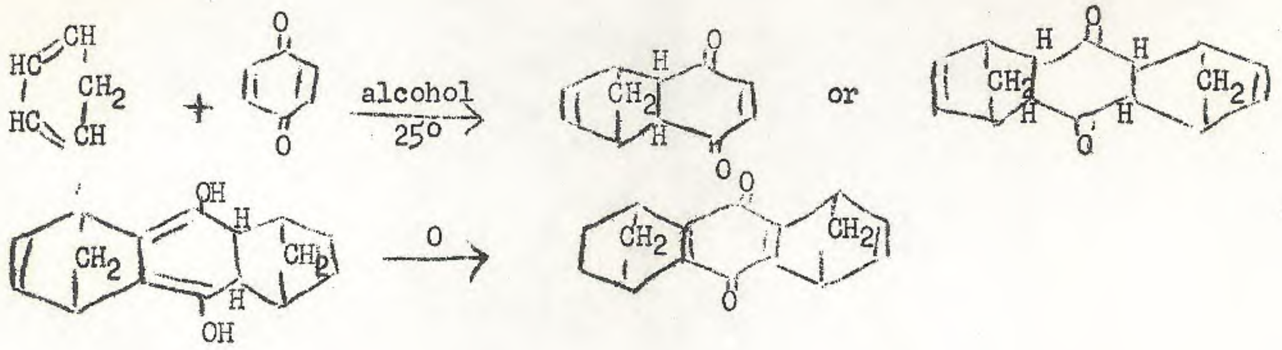
The oxygen ring can be easily opened by concentrated sulphuric acid, and oxy-quinones are formed.

Another reaction is the Diels-Alder-addition of a diene on a quinone. For instance, the reaction of methyl-butadiene and toluquinone which leads to dimethyl-naphthoquinone.



2-8-dimethyl-3-4-naphthoquinone

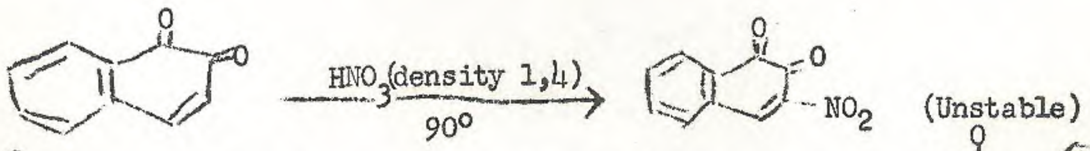
Another case of the diene reaction is the addition of cyclo-pentadiene with p-benzo-quinone.

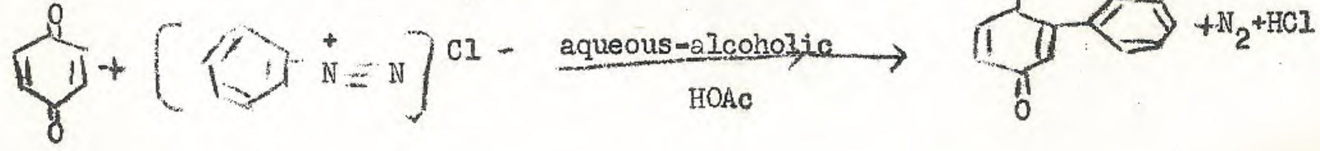


By this reaction rings with six carbon atoms, and in this case with methylene bridges are formed.

Substitution

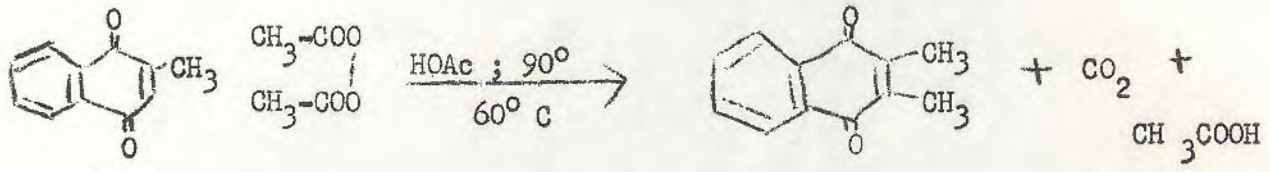
The quinones are very reactive and therefore it is not surprising that aromatic substitutions can really be done.   -naphthoquinone can be nitrated.





Quinones can be especially substituted with reactions in which free radicals take part. The conversion (reaction) with benzene diazonium salts is for instance one of these kind of reactions. The aryl group of the diazonium salt is introduced by the development of nitrogen in the ring of the quinones. If one uses the benzene diazonium salt in excess so it is possible to isolate in a small yield 2,5-diphenol quinone.

Another reaction which presumably follows a radical mechanism is the alkylation of the ring of the quinone by diacetyl peroxide or lead tetra acetate. In the case of diacetyl peroxide the following reaction can be observed.

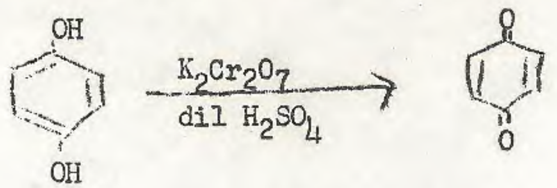


The same reactions in nearly all cases can be carried out with 1,2-benzoquinone. The o-quinones are mostly not so stable as the p-quinones. About this fact we will hear more later on.

Reactions of polyphenols with oxygen to form quinones

In most cases, the polyphenols can be oxidized with a usual oxidation reaction to the corresponding quinones. The oxidation must mostly be done in acid solution because quinones are not very stable in alkaline solutions.

For instance p-benzoquinone is prepared by oxidation of hydroquinone with potassium dichromate in dilute sulfuric acid.



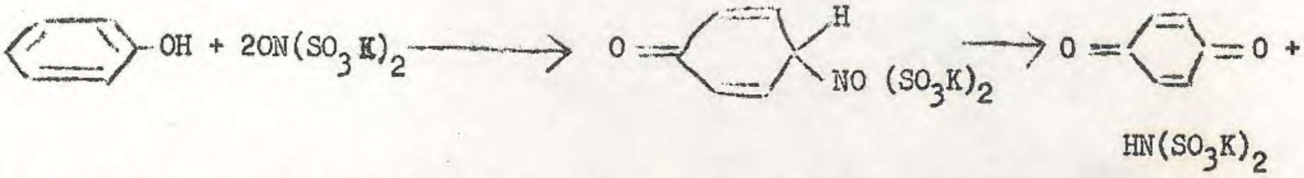
In the case of the preparation of o-benzoquinone, this method cannot be used. o-Benzoquinones are prepared by oxidation in ether with silver oxide or lead dioxide. From hydroxyhydroquinone, only hydroxy-p-quinone is formed.

Recently Teuber and co-workers have given a good method to prepare different types of quinones. (Teuber, H. J. u. Mitarb. Ber. 85, 95 (1952); 86, 1036 (1953); 87 to 1251 (1954); 88, 802 (1955); 89, 489 (1956); 89, 2654 (1956)). The authors use as an oxidation reagent potassium-nitroso-disulfonate, or the salt according to Fremy.

$$ON\,(SO_3K)_2$$

Hydroquinone can be oxidized by potassium-nitrosodisulfonate to benzoquinone; the oxidation reagent reacts with one oxidation equivalent

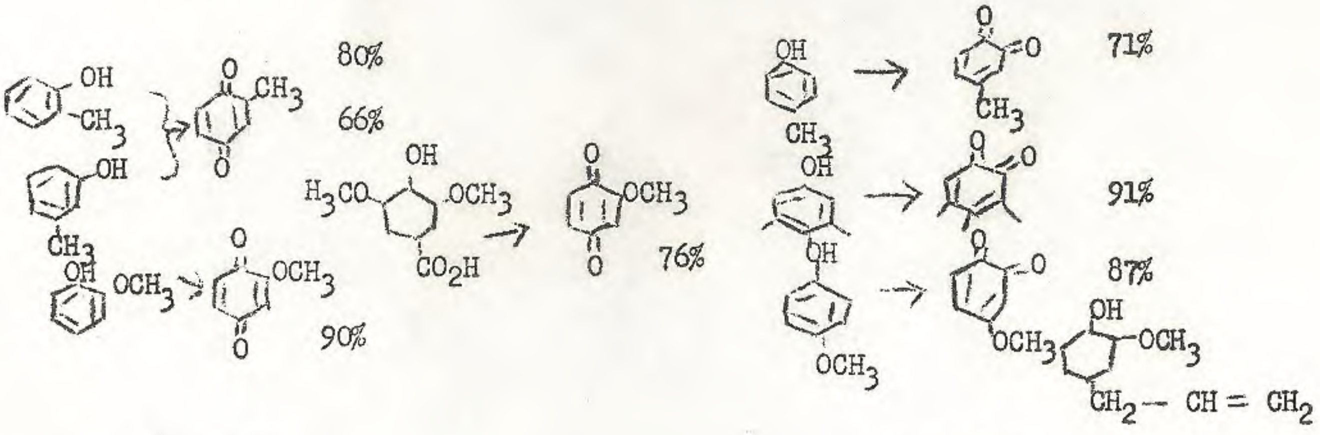
In the case of phenol also two mols of potassium nitrose-disulfonate react with three oxidation equivalents also to benzoquinone.



The reaction is mostly carried out in aqueous or alcoholic solution. More or less complicated quinones can be formed with high yields. This method is especially suitable for o-quinones.

Formation of p-quinones

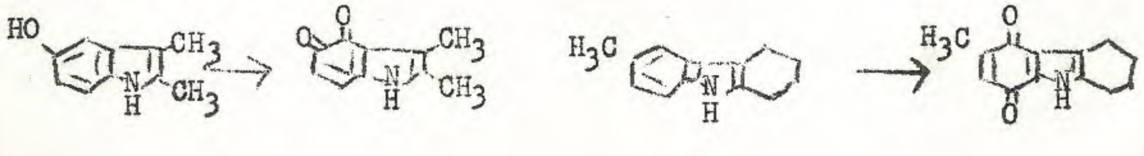
Formation of o-quinones



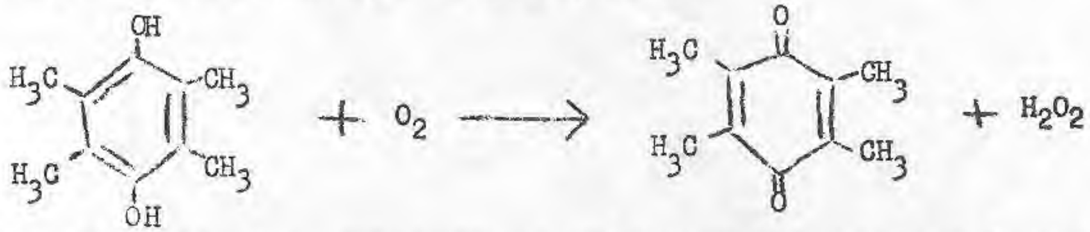
Guaiaeol

Eugenol

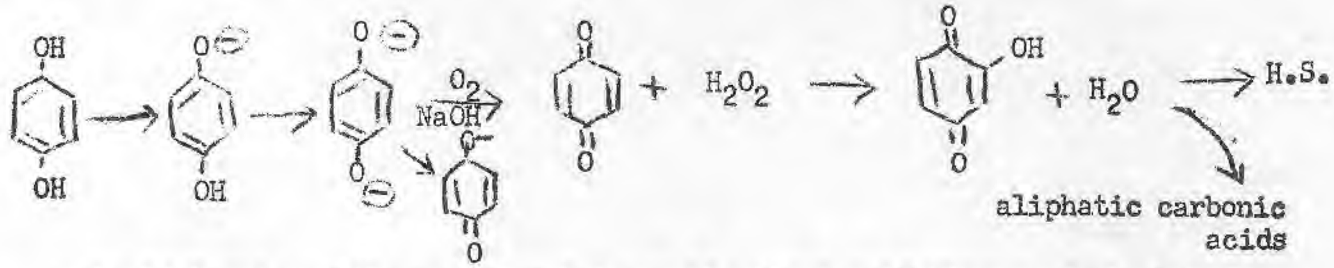
Furthermore we will remark that p-hydroxy-benzoic acid is oxidized to benzoquinone while meta-hydroxy-benzoic acid does not react. In the case of ferulic acid a product presumably with 18-C-atoms is formed; the constitution is not known. Formation of indole-quinones, possible building blocks of humic substances are indole derivatives,



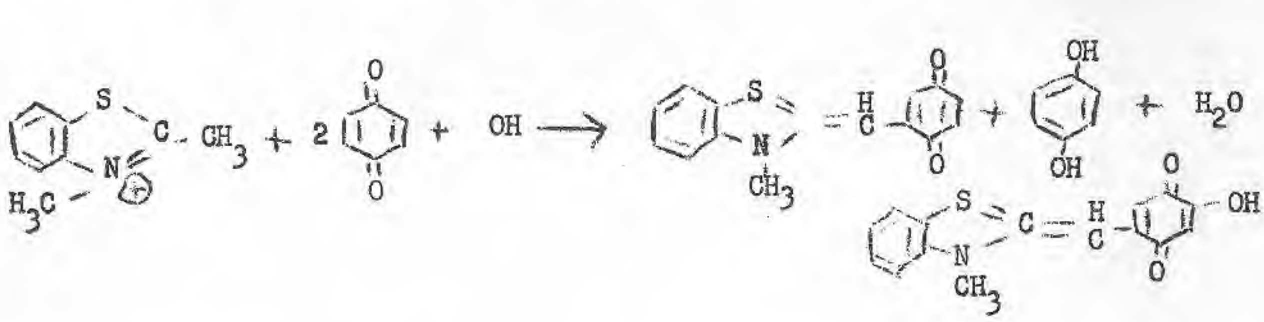
The reactions with molecular oxygen are different from those with other oxidation reagents. In acid solution the oxidation is very slow, in alkaline solution the rate of oxidation increases with the concentration of hydroxyl ions. The kinetics of the autoxydation of hydroquinone has been investigated in numerous works. A summary of all these papers has been given by James and Weissberger (T. H. James, J. M. Snell and A. Weissberger, Amer. Chem. Soc. Vol. 60, p. 98, Oxidation Processes. XI. The Autoxidation of Durohydroquinone; T. H. James, J. M. Snell, and A. Weissberger, Amer. Chem. Soc. 60, 2084. Oxidation Processes. XII. The Autoxidation of Hydroquinone and of the Mono-, Di-, and Trimethylhydroquinones, (1938)). They investigated the kinetics of the autoxidation, not only of hydroquinones, but also of mono-, di-, and trimethylhydroquinone and tetramethylhydroquinone. Summarizing, the following date are important.



During the autoxidation of durohydroquinone (tetramethylhydroquinone) with molecular oxygen in alkaline solution, pH from 7.2 to 8.2, duroquinone and hydrogen peroxide is formed. These results translate the authors also on the autoxidation of the hydroquinone. In this case, hydrogen peroxide reacts with the quinone to hydroxy-1,4-benzoquinone.



The high rate of the reaction between the first oxidation product of hydroquinone and the following oxidation product made it necessary for the identification of benzoquinone and hydrogen peroxide to use an acceptor (2-methylbenzothiazolemetho-p-toluenesulfonate) for the quinone to protect the hydrogen peroxide and to make it available for analysis. The reaction is the following:



2-methylbenzothiazole-
metho-p-toluenesulfonate

In the same way also the hydroxy benzoquinone could be identified. A spectroscopic method has been used. The substituted quinones were in general identified after isolation. The autoxidation rate of hydroquinones and its homologs is very closely dependent upon the square of the hydro-oxyl ion concentration in the pH range 7.2 to 8.2. This fact shows that the oxidation involved mainly the double charged hydroquinone ion.

A slight deviation from the second power may be due to a comparatively slow oxidation of the monovalent ion. This is suggested by the autoxidation of monomethyl ether of hydroquinone and of durohydroquinone.

In the case of durohydroquinone the first step of the oxidation is also the formation of the double charged durohydroquinone anion. In the case of hydroquinone, monomethyl hydroquinone and the dimethylhydroquinones, there is the same reaction. An exception is pseudo-cumohydroquinone.

In the case of cumohydroquinone, therefore, the reaction splits up in two processes:

a. the ion can interact with the oxygen without kinetically detected complication. The rate of oxidation is proportional to the concentration of oxygen and to that of durohydroquinone.

b. Duroquinone catalyzes the autoxidation in small amounts. The presence of duroquinone effects further reactions. The rate of this reaction is proportional to the concentration of the duroquinone and the durohydroquinone, but is independent of the oxygen pressure for the tested range from 0.2 to 1 atmosphere.

It is assumed that the rate controlling phase of the reaction catalyzed by the duroquinone is the formation of a highly oxidizable, charged radical in the interaction of the doubly charged durohydroquinone and duroquinone. These experiments with durohydroquinone have given much information about the autoxidation of hydroquinone and its mono- and di-methyl homologs. The rates of oxidation of hydroquinone, toluhydroquinone, and the xylohydroquinones vary directly with the concentration of oxygen and of the hydroquinones. During the autoxidation of these derivatives, no quinone catalysis has been detected. The authors discuss also in the case of hydroquinone, toluquinone and the xyloquinones, a radical as an intermediary step of the autoxidation.

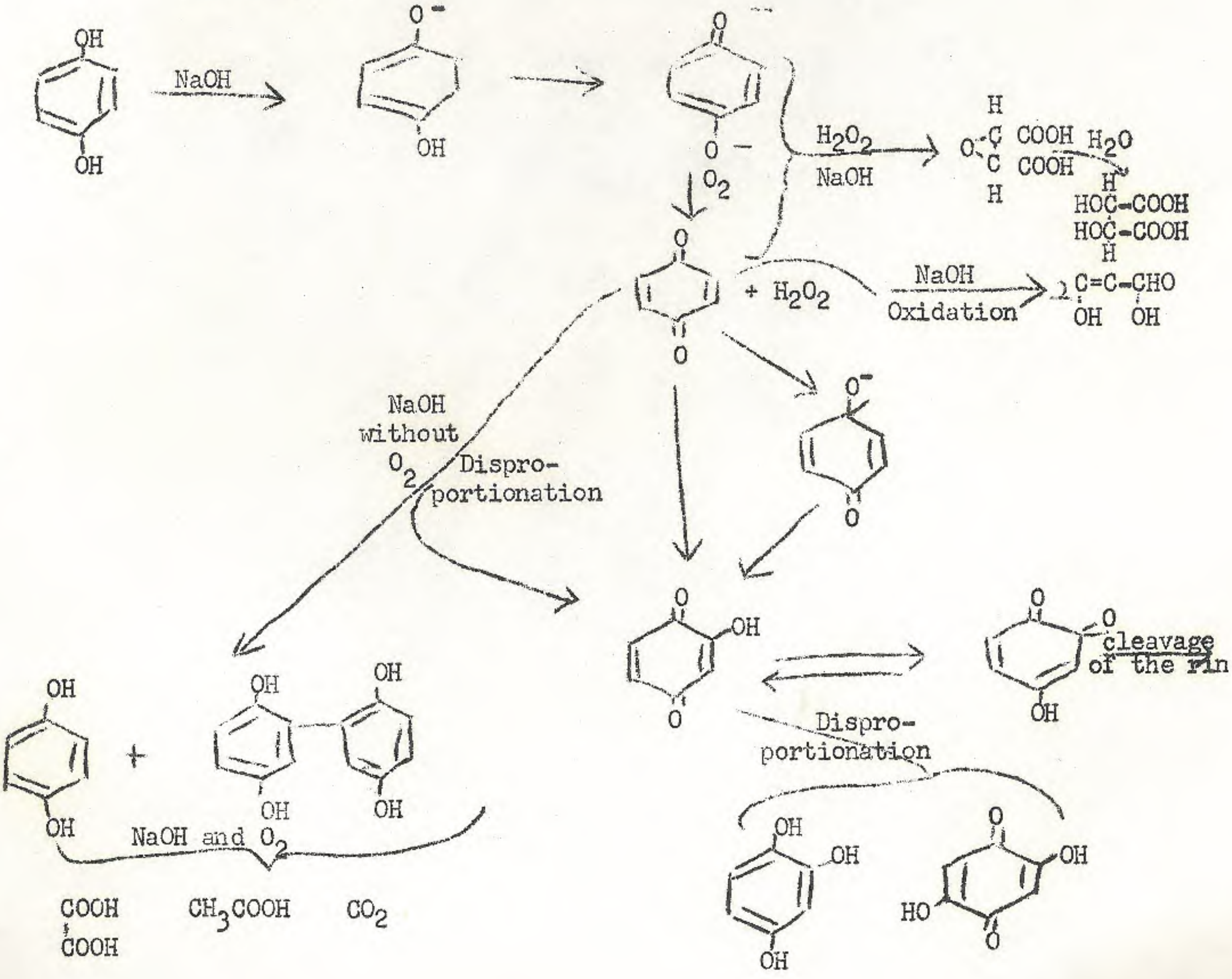
The oxidation of pseudo-cumohydroquinone is strongly catalyzed by small amounts of quinones. The catalytic action approaches a maximum. In the maximum, the autoxidation rate is proportional to the concentration of the pseudo-cumohydroquinone.

The rate of the reaction of pseudo-cumohydroquinone is independent of the oxygen concentration with low amounts of quinone as a catalyst. The reaction rate becomes proportional to the oxygen concentration as a quinone catalyzes, and reaches its maximum. The kinetics of the autoxidation of cumohydroquinone in the presence of small amounts of quinone are nearly those of the quinone catalyzed durohydroquinone reaction. The kinetics pass over into those of the autoxidation of the lower members of the hydroquinone series as the quinone concentration increases.

The authors believe also in the case of hydroquinone, toluhydroquinone and the xyloquinones the autoxidation is also catalyzed by small amounts of quinones but the maximum value is reached at quinone concentrations which are so low that they could not have been detected.

The relative oxidation rates are:

Hydroquinone	1.0
Toluhydroquinone	3.9
o-Xylohydroquinone	10.5
m-Xylohydroquinone	18.2
p-Xylohydroquinone	17.0
Pseudo-cumohydroquinone max. value 20% ethanol	31.0
Durohydroquinone (uncatalyzed)	1.0

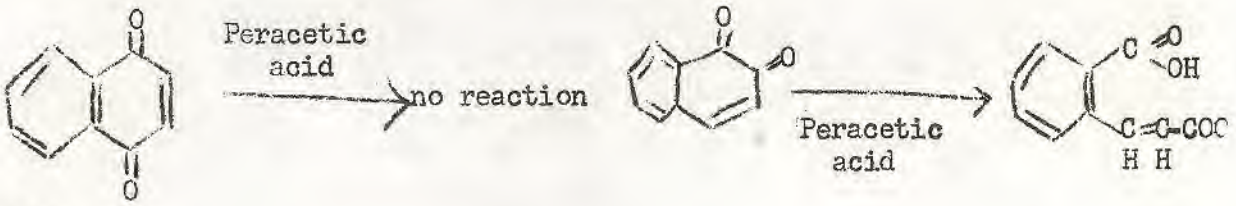


There are further reactions concerning the oxidation of hydroquinones. In a relatively high concentration of alkali hydroquinone is relatively stable and can only be oxidized by oxidation reagents such as hydrogen peroxide. (Reuben, J. G. und Shonle, H. A.; Journal American Chemical Society 67, 1034 (1945)). 2,5-dihydroxy-1,4-benzoquinone is formed. We found the same result with pyrocatechol (Flaig, W., Th. Ploetz u. H. Biergans: Zur Kenntnis der Huminsäuren. XIV. Bildung und Reaktionen einiger Hydroxy-chinone. Liebigs Ann. Chem. 597, 196-213 (1955)). This fact will be interesting for the course of the oxidation.

In absence of oxygen benzoquinone disproportionates into hydroquinone and hydroxyquinone. (Leubner, A.: Dissertation Dresden 1911). The latter is properly able to form hydroxy-hydroquinone and dihydroxyquinone. Staude proved this disproportionation by color reactions of the different quinonate ions (Staude, H.: Z. f. wissenschaftl. Photographie 38, 65 (1939)). Erdtman found dihydroquinone as a further reaction product of the disproportionation. (Erdtman, H. G. H.: Svensk Kemisk Tidskrift 63, 43 (1951)).

According to Weitz and co-workers tartaric acid is formed by the treatment of hydroquinone as well as quinone with alkaline solution in excess. As an intermediate ethylene-oxide-dicarbonic acid occurs. (Weitz, E., Schobert, H. und Seibert, H.: Ber. dtsch. chem. Ges. 68, 1163 (1935)). V. Euler and co-workers oxidized benzoquinone in alkaline solution and found two mols of reduction, dihydroxy-allyl-aldehyde. (Euler, H. V.: Chimia, Zürich 3, 209 (1949)).

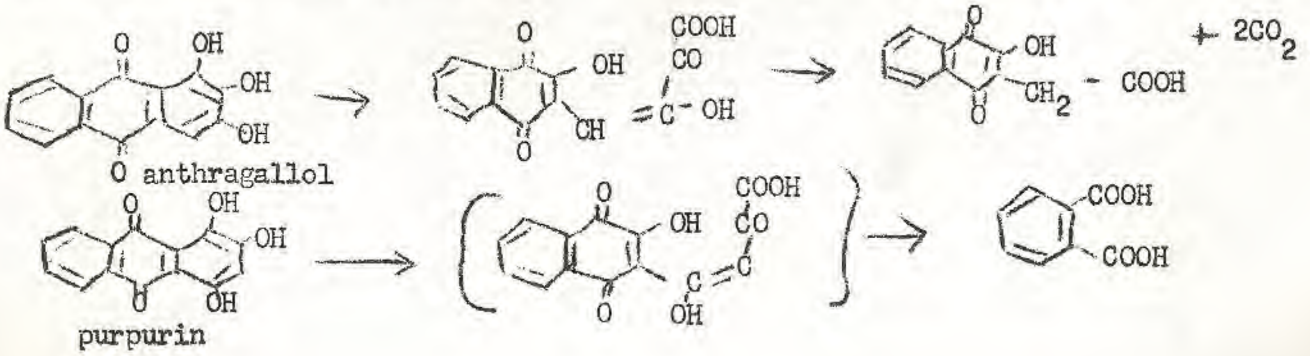
In connection with these investigations we must speak about the reaction of naphthoquinone with oxidation reagent as peracetic acid.



S 9 167

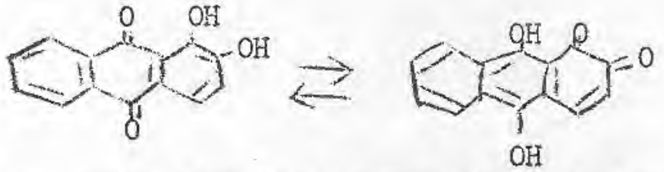
The effect of this oxidation reagent on 1,4-naphthoquinones and 1,2-naphthoquinones is different. (Boseken, J. und G. Sloff: Rec. des Trav. Chim. des Pays-Bas 49 (1939) 100. Karrer, P. und L. Schneider: Helv. chim. Acta 30 (1947) 859). In the case of 1,4-naphtho-quinone there is no reaction but in that of 1,2-naphthoquinone the ring is cleavaged to allo-cinnamic-o-carbonic acid.

Furthermore polyphenols such as naphthoquinones and anthroquinones can be split up in different ways, so for instance, anthragallol and purpurin are split up in alkaline solution. (O. Dimroth and E. Schultze, A. 411, 339 (1916)).



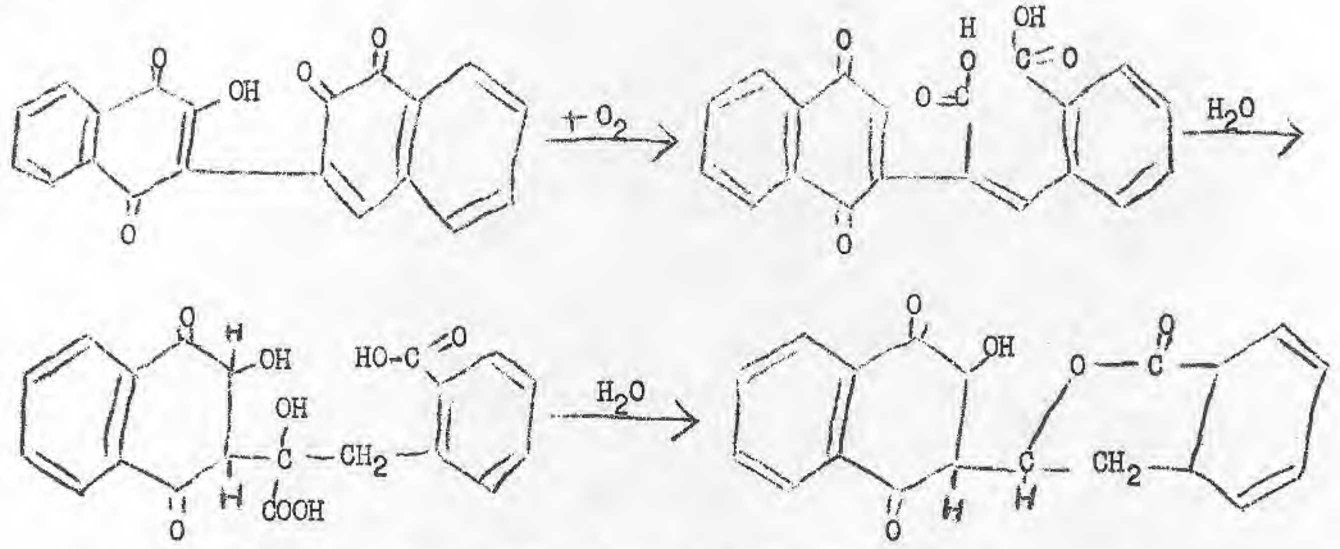
To this point can be said that there is a tautorism between the ketoform with the ketogroups in 9 and 10 position and the ketogroups in 1 and 2 position.

S 10 458



Hooker and Fieser could show, for instance, that 2-hydroxy-3,3'-dinaphthyl-1,4,1',2'-diquinone splits off in alkaline solution by oxidation under cleavage of the ring with the o-quinone group.

S 11 173



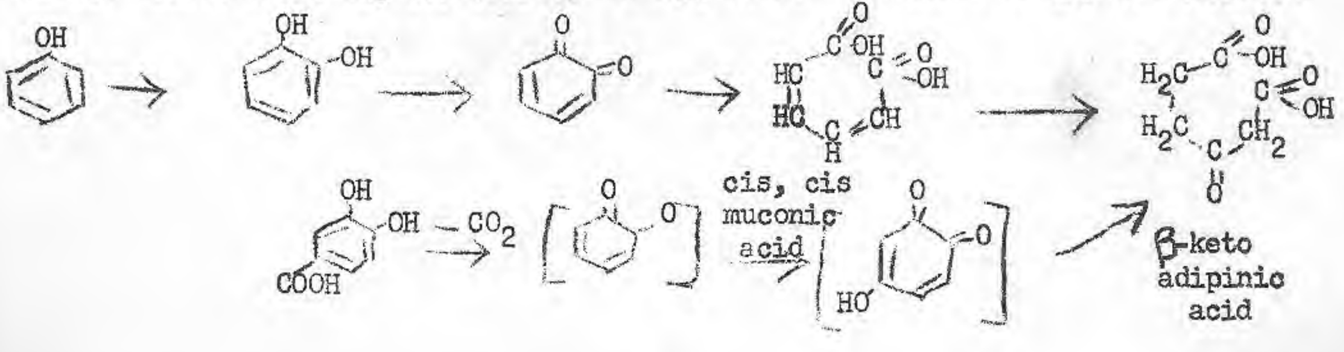
Cleavage of 2 Oxy-3,3'-dinaphthyl 1,4,1',2',-diquinone Fieser

Later on we will speak more about the cleavage of the ring and the different rate of this when o-quinones, p-quinones, or hydroxy p-quinones are used.

Our next consideration is the cleavage of the ring by microorganisms. A number of authors found that, for instance, phenol is oxidized to pyrocatechol in the presence of oxygen by the effect of microorganisms.

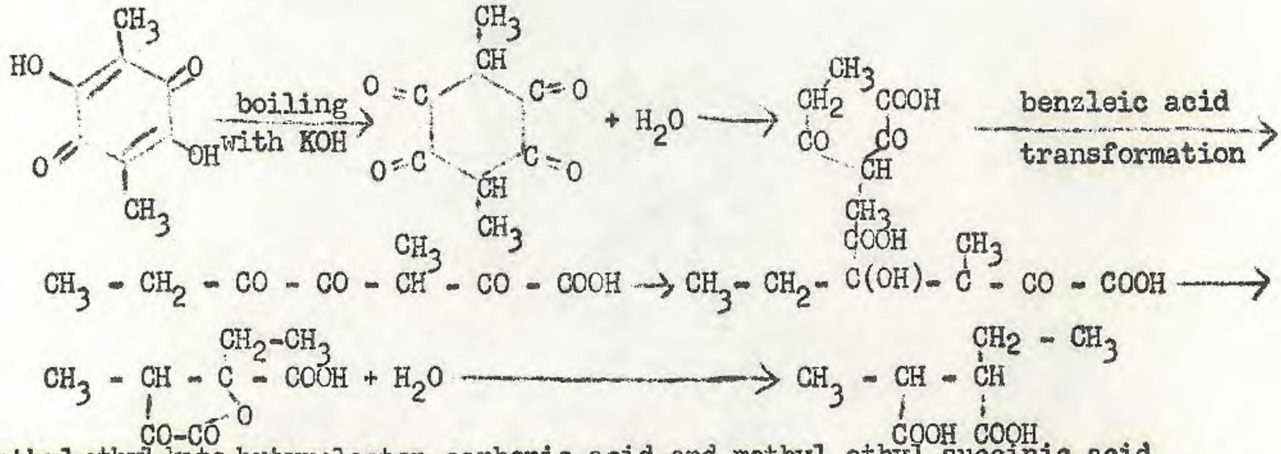
S 12 188 (253)

(Evans, W. C.: Biochem. J. 41, 373 (1947); Nature 168, 772 (1951), Stanier, R. Y.: Bact. Revs. 14, 179 (1950), Kilby, B. A.: Biochem. J. 49, 671 (1951)).



The pyrocatechol is presumably oxidized to o-benzoquinone and this is split off to cis-cis-muconic acid. By addition of water and biological hydration in the same time β-keto adipinic acid is formed. This acid decomposes to succinic acid and acetic acid. A similar way is possible in the case of protocatechuic acid. o-benzoquinone is formed and carbon dioxide is split off. Presumably β-keto adipinic acid will be originated from hydroxy-o-benzoquinone as an intermediary step.

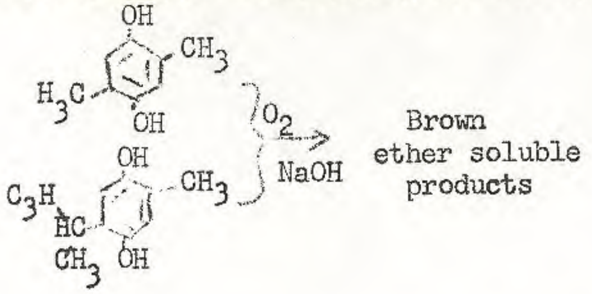
Now we must speak about the cleavage of the ring if polyphenols such as 1,2- and 1,4-dihydroxy benzene are oxidized. By the results which are reported before, we know that the first step of oxidation are quinone, p-benzoquinones or o-benzoquinones, respectively. In the case of p-benzoquinones the next step of oxidation is hydroxy-1,4-benzoquinone. The further reactions are unknown. Some substances like humic acids, some carbon dioxide and some low molecular aliphatic acids are formed. In one case, that of 2,5-dihydroxy-1,4-benzoquinone by the work of Fichter, some decomposition products can be mentioned. (Fichter, F. R.: Liebigs Ann. Chem. 361, 363 (1908)).

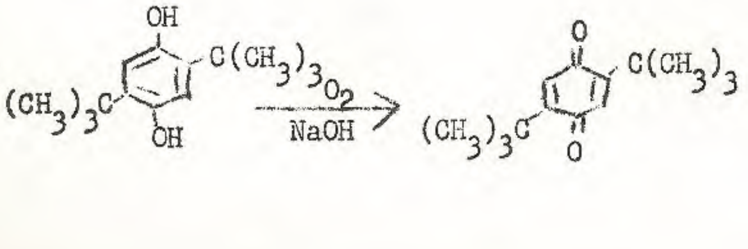


methyl-ethyl-keto-butyrolacton carbonic acid and methyl ethyl succinic acid

He found that p-alkylated dihydroxy-p-benzoquinones are split up to dialkalyted succinic acids. He suggest that in the case of 2,5-dihydroxy-1,4-benzoquinone pyruvic acid is formed, which decomposes in the presence of oxygen in acetic acid and carbon dioxide.

To isolate oxidation products, we substituted some of the reactive hydrogen atoms in hydroquinone derivatives with aliphatic groups. (Flaig, W., H. Schulze, E., Kuster, u. H. Biergans: - Zur Chemie der Huminsauren. Landbouwkund. Tijdschr. 66, 392-407 (1954)). Summarizing we have the following results.





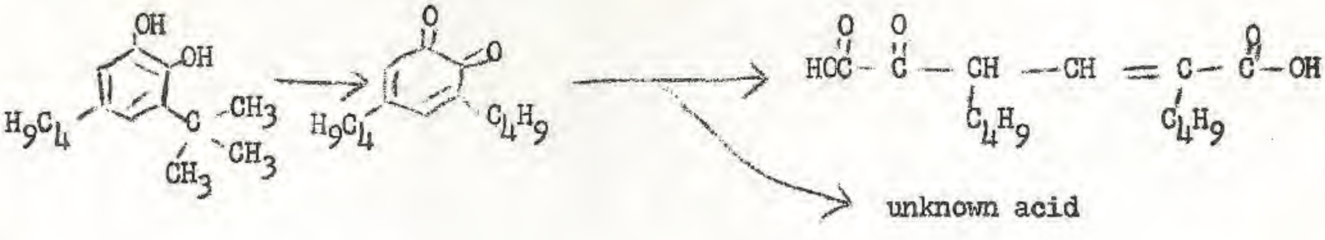
By substitution with two methyl groups in p-position or one methyl group and one isopropyl group also in p-position, brown products are formed with oxygen in alkaline solution. These products are ether soluble in contract to the brown products which are formed in the same way with unsubstituted hydroquinone. In the case of substitution with tertiary butyl groups in p-position, it could be observed that oxidation under the s ame conditions led to 2,5-di-tert.-butyl-p-benzoquinone after the uptake of two atoms of oxygen.

Remembering the fact that hydroquinone and pyrocatechol are oxidized in 50% solution of sodium hydroxide to 2,5-dihydroxy-1,4-benzoquinone, I will mention that under the same conditions, 2,5-di-tert.-butyl -hydroquinone is oxidized nearly quantitatively to the correspondent p-quinone and 3,5-di-tert.-butyl-pyrocatechol to the corresponding o-quinone in lower yield. It must be especially remarked that these two diphenols substituted with tert.-butyl groups are oxidized to the corresponding quinones without an introduction of hydroxyl groups.

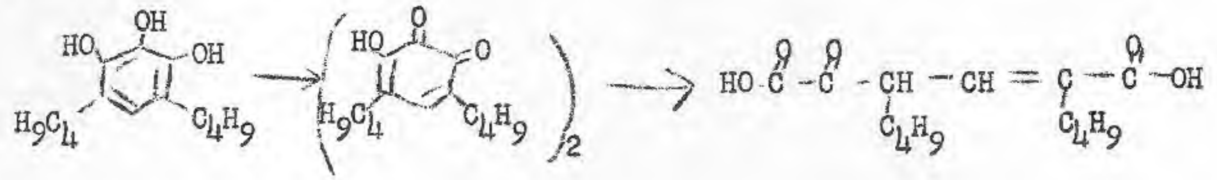
We will emphasize that not only the rate of the oxidation to a quinone but also the formation of condensation products and the cleavage of the ring depends upon the substitution. In the case of tert.-butyl groups we had the greatest possibility of isolating the oxidation products. ((Schulze, H. u. W. Flaig: - Zur Kenntnis der Huminsauren. IV. Uber die Ringsprengung mehrwertiger Phenole mit Sauerstoff in alkalischem Medium. Liebigs Ann. Chem. 575, 231-241 (1952)) (Flaig, W., Th. Ploetz u. H. Biergans: - Zur Kenntnis der Huminsauren. XIV. Bildung und Reaktionen einiger Hydroxy-chinone. Liebigs. Ann. Chem. 597, 196-213 (1955)).)

Cook and Somers called attention to the fact that the oxidative cleavage of the ring of alkylated naphtho-quinones occurs especially well, if the substituents are tert.-butyl groups (Cook and Somers, Nature 165, 314 (1950)).

If we look for the demethylated building blocks or the decomposition products of lignin, we must state that these are mono-, di-, and tri-hydroxy-phenolic compounds. By the investigation of M. Henderson, it has been shown that the mono-hydroxy-phenolic compounds are transformed to di-hydroxy. To investigate the way of transformation of lignin components, it is necessary to study di- and tri-hydroxy-phenols; in this case 3,5-di-tert.-butyl-pyrocatechol and 4,6-di-tert.-butyl-pyrogallol.

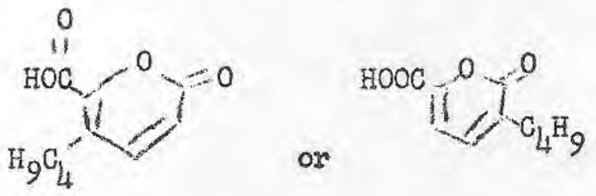


The oxidation of 3,5-di-tert.-butyl-pyrocatechol to the corresponding o-quinone can be done with oxygen in alkaline solution, with p-benzo-quinone in petroleum ether with powdered but not activated lead dioxide (R. Kuhn und J. Hammer, Chem. Ber. 83, 413 (1950)), or with silver oxide in ether. By further oxidation of this o-benzoquinone derivative in alkaline solution, two acids are found nearly in the same amount. Both have the same composition and the same equivalent weight. One of these is 2,4-di-tert.-butyl-4-oxalo-crotonic acid. This means that a cleavage of the ring took place.

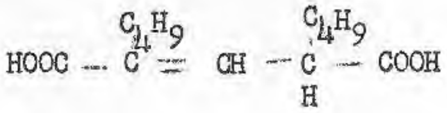


By the oxidation of 2,4-di-tert.-butyl-pyrogallol, it has been possible to isolate by careful oxidation a dimerized 3-hydroxy-4,6-di-tert.-butyl-o-benzoquinone and as a further reaction product also 2,4-di-tert.-butyl-4-oxalo-crotonic acid. Therefore, the pyrocatechol- and pyrogallol-derivative gave finally the same oxidation product. In one step of the oxidation reactions the same oxidation product must occur; this is 3-hydroxy-4,6-di-tert.-butyl-o-benzoquinone.

For the elucidation and chemical behavior of 2,4-di-tert.butyl-4-oxalo-crotonic acid some reactions are mentioned which can also occur with the unsubstituted acid (compare also: T. W. Campbell, Am. Soc. 73, 4190 (1951)).

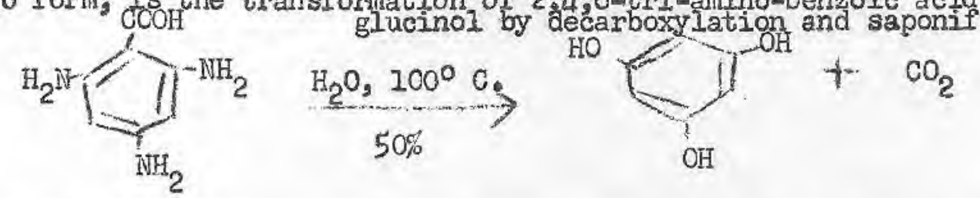


With sulfuric acid in water a tert.-butyl group is split off. The corresponding coumalic acid is formed, according to Lapworth, which describes the condensation of unsubstituted oxalo-crotonic acid to coumalic acid. (Lapworth, Soc. 79, 1280 (1901)). The splitting off of a tert.-butyl group is not unusual. (H. Meyer und K. Bernhauer, Monatshefte d. Chem. No. 54, 721 (1924)). To prove the constitution, this acid is treated with sodium hydroxide and hydrogen peroxide which gives, according to the behavior of pyruvic acid, a good yield of dicarbonic acid with one C-atom less, 1,3-di-tert.-butyl-glutaconic acid.

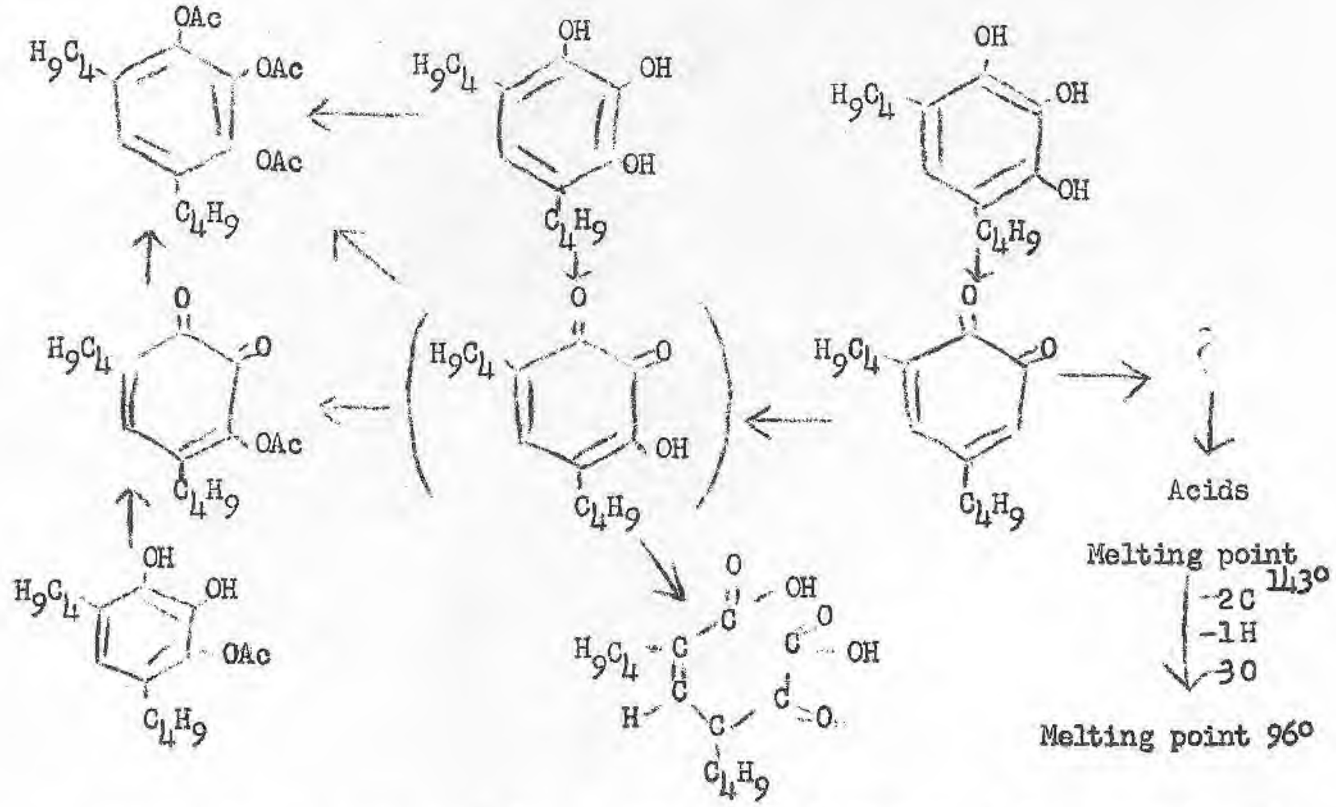


$$HOOC-\overset{C_4H_9}{C}=CH-\underset{H}{\overset{C_4H_9}{C}}-COOH$$

At this point we must mention some oxidation reactions of poly-phenols with hydroxyl-groups in m-position. Resorcinol does not react neither in 10% sodium-hydroxide solution with oxygen nor in 50% sodium hydroxide solution with hydrogen peroxide. However, 4,6-di-tert.-butyl-resorcinol reacts in 10% sodium hydroxide solution with oxygen mostly to resinous products and in a small amount to a quinone derivative. Phloroglucinol is known to react in its tri-keto form and can therefore be oxidized. It forms with hydroxyl-amine the tri-oxime of cyclo-hexane-1,3,5-trione. Another reaction from which it can be suggested that phloroglucinol reacts in its tri-keto form, is the transformation of 2,4,6-tri-amino-benzoic acid to phloroglucinol by decarboxylation and saponification.



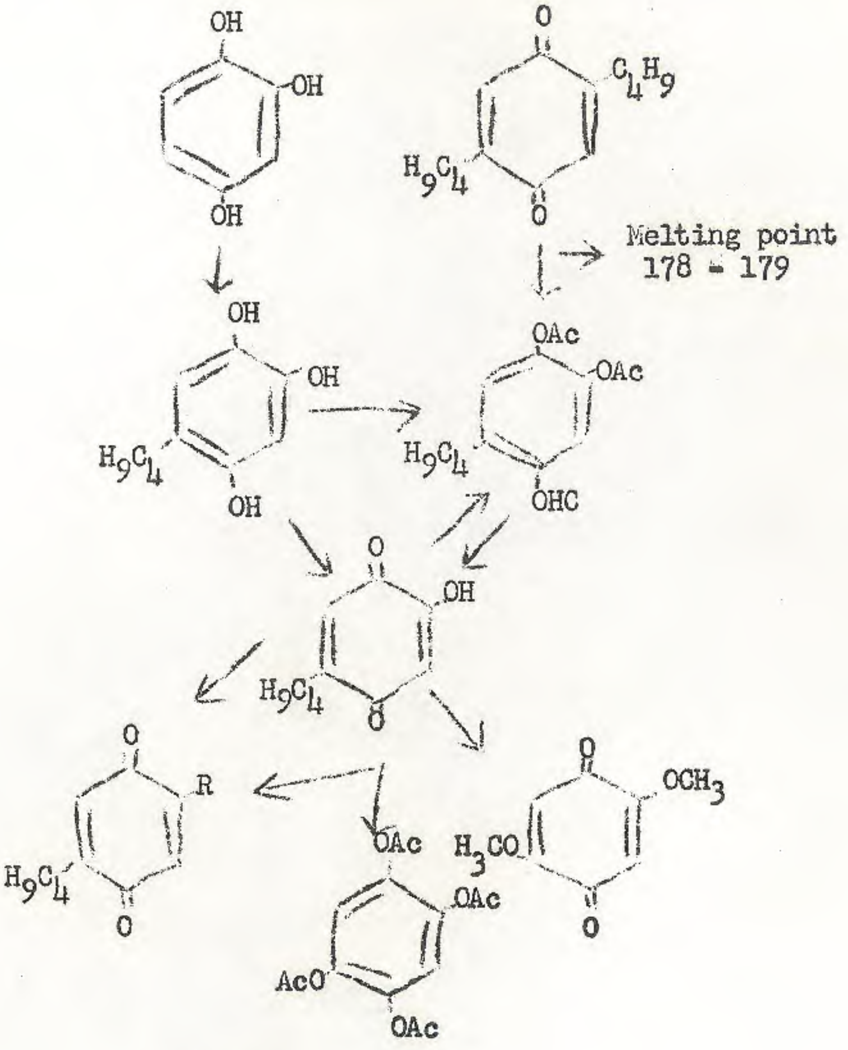
To get a better survey of the different reactions of the model substances, I will show you some reactions. These can be of interest for the knowledge of the reactivity of the model substances as well as natural products.



There is given a summary of the reactions of 3,5-di-tert.-butyl-pyrocatechol and 4,6-di-tert.-butyl-pyrogallol.

The pyrocatechol derivative can be oxidized to the corresponding quinone. Further oxidation results in different acids. Only one of these is known in its chemical constitution, 2,4-di-tert.-butyl-4-oxalo-crotonic acid. This must be formed from 3-hydroxy-4,6-di-tert.-butyl-1,2-benzoquinone. This hydroxy o-benzoquinone can be found after oxidation in alkaline solution with oxygen or in organic solvent with benzoquinone in a dimerized form.

4,6-di-tert.-butyl-pyrogallol can be easily acetylated. By oxidation, 3-hydroxy-2,4-di-tert.-butyl-1,2-benzo-quinone is also formed as a dimer product. By careful oxidation of 3-acetoxy-4,6-di-tert.-butyl-pyrocatechol, the corresponding 1,2-benzo-quinone can be isolated. By reduction and acetylation the corresponding tri-acetate is formed.



$R = OCOH_3$

$= OCOC_6H_5$

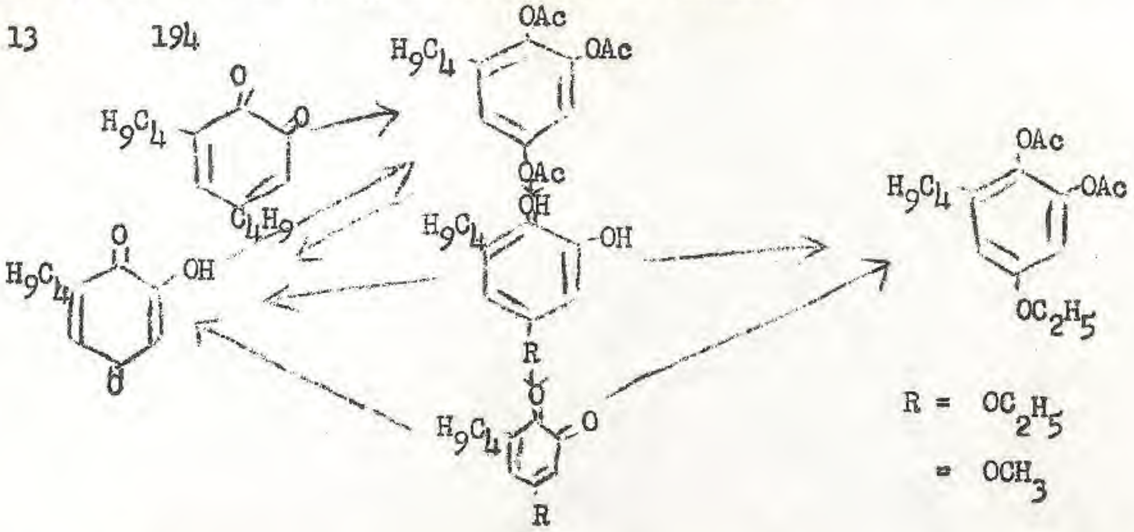
$= OCH_3$

Something must be said about the Thiele-reaction with tert.-butyl substituted quinones, such as, at first, 2,5-di-tert.-butyl-1,4-benzoquinone. In most cases with quinones, an acetyl group is introduced also if the 2,5-position is substituted. In the case of 2,5-di-tert.-butyl-1,4-benzoquinone a tert.-butyl is split off, 1,2,4-tri-acetoxy-5-tert.-butyl-benzene in low yield and another substance is formed with boiling point 178-179° C. A relatively high concentration of sulfuric acids is necessary. By hydrolysis and oxidation, the 2-hydroxy-5-tert.-butyl-1,4-benzoquinone is formed. This quinone can also be prepared by the reaction of hydroxyquinone with tert.-butyl alcohol in the presence of sulfuric acids and further oxidation.

From this quinone, 2,5-dihydroxy-hydroquinone tetraacetate is formed by treatment with acetic acid anhydride. The second tert.-butyl group is split off. This reaction proceeds under the same conditions as the Thiele-reaction, but is not comparable with it in other ways.

By acetylation or etherification of 2-hydroxy-5-tert.-butyl-1,4-benzoquinone, the corresponding derivatives are formed. By treatment with hydrochloric acid in methanol, 2,5-di-methoxy-1,4-benzoquinone is formed.

S 13 194



Also in the case of 2,4-di-tert.-butyl-1,2-benzoquinone some special reactions shall be mentioned. In nearly quantitative yield 1,2,4-tri-hydroxy-6-tert.-butyl-benzene is formed by Thiele-reaction by splitting of a tert.-butyl group. It could be shown that per mole quinone 1 mole sulfuric acid is reduced. By alkaline hydrolysis the latter triacetate is saponified; by oxidation 2-hydroxy-6-tert.-butyl-1,4-benzoquinone is formed.

By acid saponification of the 1,2,4-triacetoxy-6-tert.-butyl-benzene 4-ethoxy-(or methoxy)-6-tert.-butyl pyrocatechol is formed. This can be alkylated and oxidized to an o-benzoquinone, 4-ethoxy-(or methoxy)-6-tert.-butyl-1,2-benzoquinone.

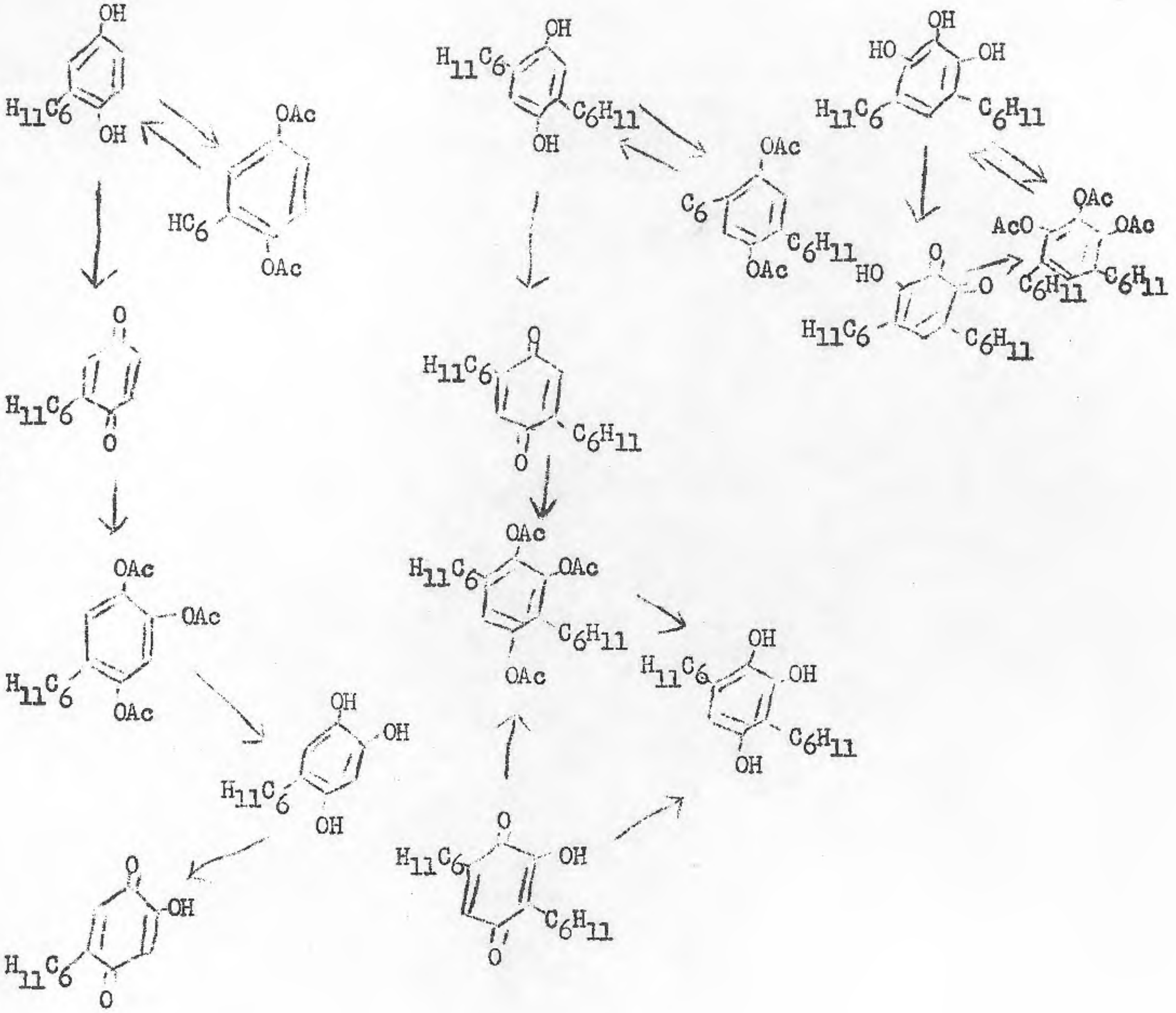
We will especially remark that by alkaline saponification the methyl group or ethyl group is split off and from 4-ethoxy-(or methoxy)-6-o-benzoquinone not the hydroxy derivative or the o-quinone but the 2-hydroxy-6-tert.butyl-p-benzoquinone is formed. Why this happened, we will explain later.

S 14 193 (page 37a)

In this table you see different reactions with cyclohexyl-substituted phenols. In the case of mono-cyclohexyl hydroquinone oxidation to the corresponding quinone, the Thiele-reaction, the saponification of the triacetate derivative and the oxidation to the corresponding hydroxy-p-quinone are normal reactions.

Also 2,5-di-cyclohexyl-hydroquinone can be oxidized with good yields to the corresponding quinone. In contrast to the di-tert.-butyl substituted quinone, this compound with 2-cyclohexyl groups in 2,5 position can be isolated in relatively good yields without splitting off a cyclohexyl group as in the case of the di-tert.-butyl substituted p-quinone. After saponification, the triacetate derivative can be oxidized to the corresponding 2-hydroxy-3,5-di-cyclohexyl-1,4-benzoquinone.

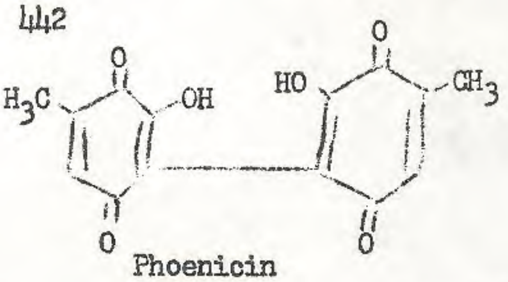
S 14 193


OH
$H_{11}C_6$
OH
OAc
HC_6
OAc
O
$H_{11}C_6$
O
OAc
OAc
$H_{11}C_6$
OAc
OH
OH
$H_{11}C_6$
OH
O
OH
$H_{11}C_6$
O
OH
$H_{11}C_6$
C_6H_{11}
OH
OAc
C_6
C_6H_{11}
OAc
HO
OH
OH
$H_{11}C_6$
C_6H_{11}
HO
O
O
$H_{11}C_6$
C_6H_{11}
OAc
AcO
OAc
C_6H_{11}
C_6H_{11}
O
$H_{11}C_6$
C_6H_{11}
O
OAc
$H_{11}C_6$
OAc
C_6H_{11}
OAc
O
$H_{11}C_6$
OH
C_6H_{11}
O
OH
$H_{11}C_6$
OH
C_6H_{11}
OH

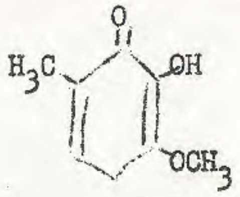
In the case of 4,6-di-cyclohexyl pyrogallol also the corresponding hydroxy-o-benzoquinone can be formed. It is not sure if it is monomer or dimer.

If one compares, for instance, the different possibilities of the Thiele-reaction with methyl groups, tert.-butyl groups, cyclohexyl groups, or methoxyl groups different results are obtained. Among the other reactions with the mentioned model substances there are also substances with different behavior in the case of the same reaction. You can estimate from which value some of these reactions are to determine, for instance, the content of phenolic groups in humic acids or the content of carboxylic groups. In the case of lignin precursors but also especially in the case of lignin fragments we have phenols methylated in different amounts, and with different numbers of side-chains which can possess a different length.

S 15 442



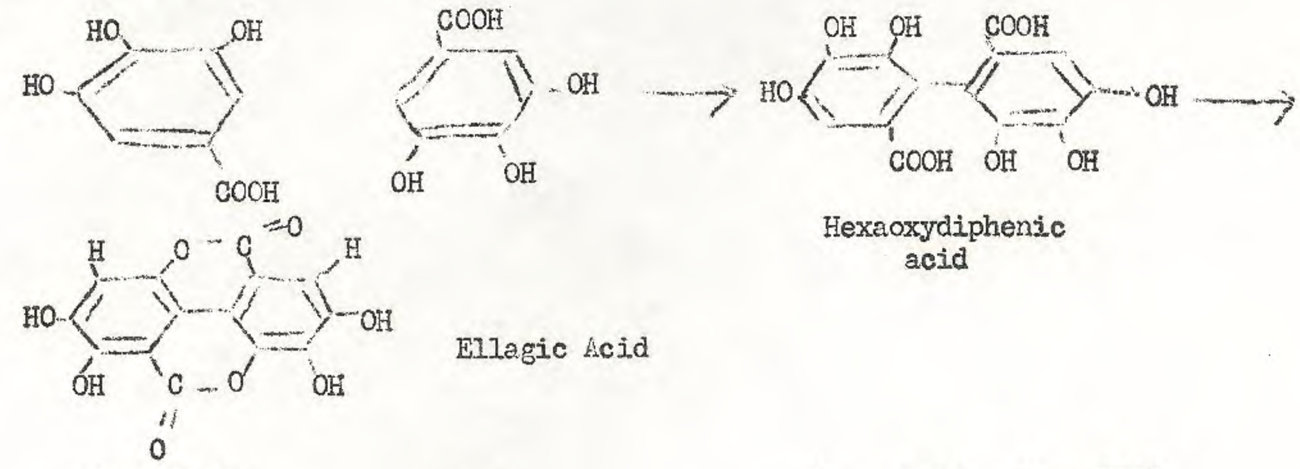
Phoenicin



Fumigatin

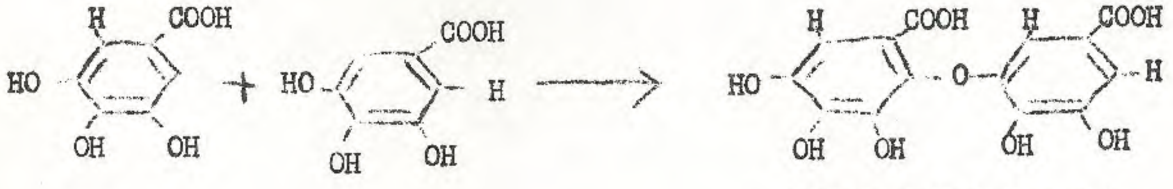
Before we speak about dimerization, I will remind you that among the metabolism products of microorganisms, there are dimerized quinones such as phoenicin or quinones which can dimerize for instance fumigatin.

S 16 724

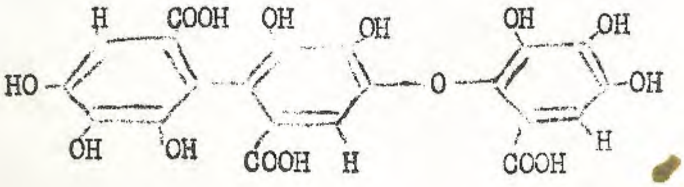


Hexaoxydiphenic acid

Ellagic Acid



Dehydrodigallic Acid



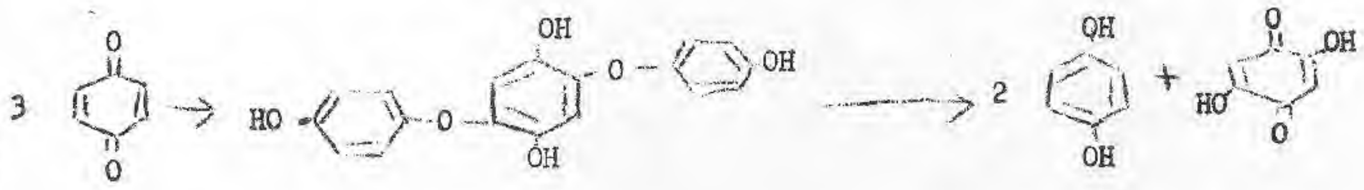
Valonia Acid

Another kind of dimerized phenols are the tannins. There are two different ways of connecting two rings, by dehydrogenation, for instance the formation of hexahydroxy-diphenic acid, which is unstable and forms ellagic acid, or dehydrodigallic acid in this case the rings are connected by an oxygen bridge.

In the valonea acid, the two principles of connection are combined.

Remember that we have also in the molecule of lignin and its precursors direct connection between the ring or through side-chains.

Some lectures before, I mentioned that it has not been possible to connect two phenols over an oxygen bridge by oxidation reactions, though this kind of linkage is found in nature. By the catalytic effect of pyridine, p-benzo-quinone can be trimerized. (Diels O. u. Kassebart; Liebigs Ann. 530, 51-67 (1937)).



This compound can be hydrolyzed to 2 molecules hydroquinone and 1 molecule 2,5-dihydroxy-p-benzoquinone.

One of the reasons that poly-phenyl-ethers cannot be found may be that they are easily oxidized, also by dioxidation reagent. 4,4'-dihydroxy-di-phenyl-ether can be oxidized by potassium-ferri-cyanide to 2 molecules of p-benzoquinone.

S 17 121 (page 39a)

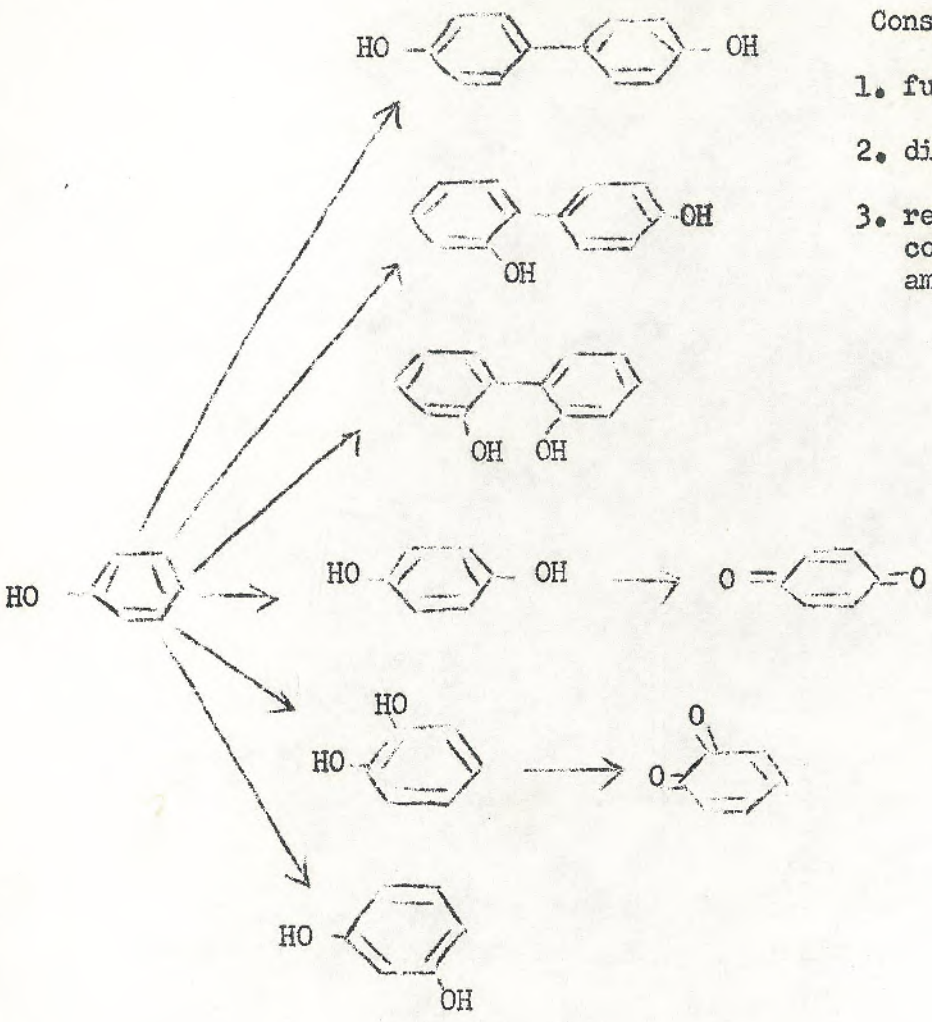
In this scheme the different possible ways of phenol oxidation are summarized. Either two molecules of phenol are oxidized to a di-dihydroxy-diphenyl derivative, or a second OH-group is introduced in the phenol molecule. The latter case results in further oxidation very easily, if hydroxyl groups are in p- or o-position. The succeeding reactions of the primary oxidation products can be subdivided:

1) A further oxidation.

2) Dimerization.

3) Addition of further compounds, from which in our case the amino compounds are of special interest.

Primary Oxidation Products

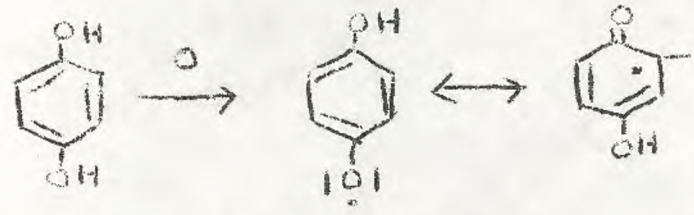


Consecutive reactions

1. further oxidation
2. dimerization
3. reaction with other compounds, especially amino compounds

Among the primary oxidation products the quinones are of special reactivity. The di-hydroxy-di-phenyl can also be oxidized to quinones. Later on we will see that they have a relatively high redox normal potential. Therefore, their formation under natural conditions is connected with some difficulties.

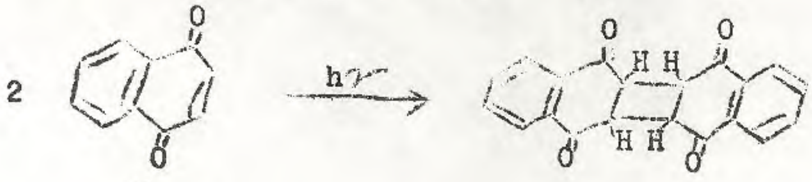
Concerning the dimerization, the o-quinones are more reactive than the p-quinones. Usually by the oxidation of p-quinones, hydroxy-quinones are formed, while the o-quinones split off the ring to dicarbonic acid, insofar as other reactions are not faster. We must discuss this point later on. At first we will speak about dimerization of p-quinones. The first step of the oxidation is the formation of a semi-quinone which can have a more ionic or more radical character.



The first form can lead to di-phenyl-ether, the second more to dimerization products. In the literature, there are very few examples for the dimerization reaction. These occur mostly by the treatment with light, alkali or acids.

S 18 122 Dimerization of p-Benzoquinone

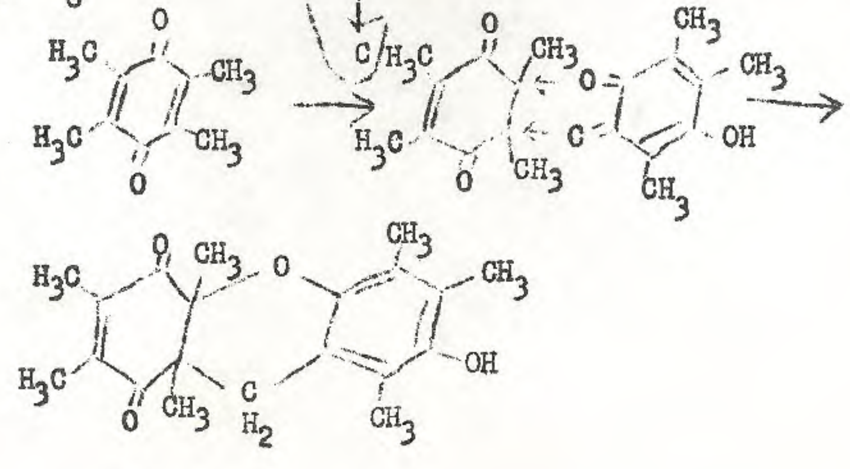
Light



Structure unknown

Structure of A, B and C unknown

Alkali

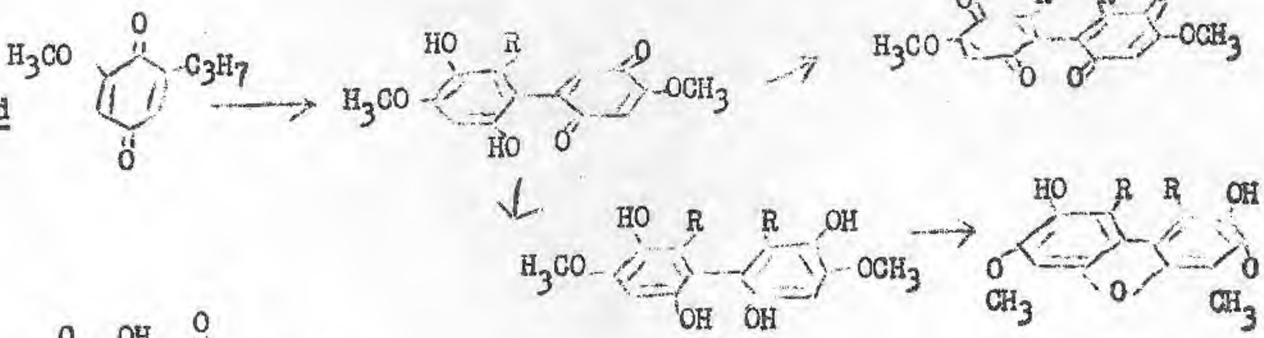


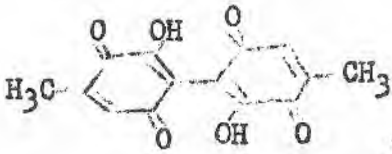
This scheme shows different possibilities. α-naphtho-quinone dimerized under the influence of light with formation of a cyclo-butane-ring. Thymo-quinone dimerizes to a compound of which constitution is not yet known. (Liebermann, G., Ber. dtsch. chem. Ges. 10, 613, 2177 (1877); 18, 3193 (1885); Lagodzinski, K. u. M. Mateesen, Ber. dtsch. chem. Ges. 27, 958 (1894); Smith, Lee I. u. Roy W. H. Tess, J. Am. Chem. Soc. 66, 1323 (1944)). Compare: W. Flaig u. J. C. Salfeld "Zur Photodimerisierung von 2,3-Dimethyl-p-benzochinon" in press.

Fieser and Ardao (Fieser, L. u. M. Ardao; J. Am. Chem. Soc. 78, 774 (1956)) have reported in more recent time about photodimerization of 2,3-dimethyl-p-benzoquinone. In connection with other works, we have also been interested in this reaction and found a lable intermediary product A which turns over to product B, described by Fieser. Product A leads to a stable product C by heating (W. Flaig, u. J. C. Salfeld, loc. cit.). Duroquinone dimerizes by treatment with alkali presumably over an o-quinonic intermediary step according to a scheme of a diene synthesis.

S 19 123 Oxidative dimerization of p-benzoquinone

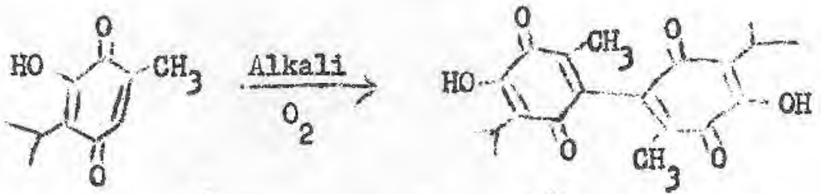
(a) Acid

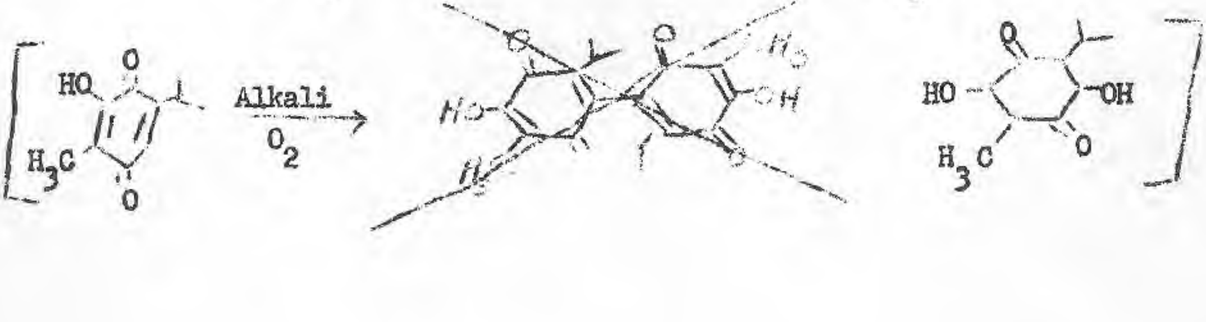




Phoenicin

(b) Alkali





The dimerization of 3-propyl-6-methoxy-p-benzoquinone catalyzed by hydrochloric acid has been investigated extensively by A. Robertson and co-workers. The dimerization occurs in p-position to the methoxyl-group by 1,4-addition. The primary form, hydroquinone-quinone, disproportionates to the diquinone and di-hydroquinone. The latter splits off water and a furan derivative is formed. The formation of phoenicin by dimerization of 2-hydroxy-6-methyl-p-benzoquinone follows another mechanism because the two quinones are connected in o-position. It may be that there are two kinds of mechanisms of dimerization, perhaps depending upon whether it occurs in acid, alkaline, or neutral medium.

We have found in recent time an oxidative dimerization in alkaline solution. 6-hydroxy-thymoquinone is altered to a di-quinone by alkaline oxidation with air. The constitution is elucidated. (Flaig, W. u. J. C. Salfeld, Liebigs Ann. 618, 117-139, (1958)). It could be ascertained that it is a steric hindered di-quinone, the two rings are not in one plane.

It will be remarked that under the same condition the 3-hydroxy-thymoquinone forms no di-quinone. 3,6-dihydroxy-thymoquinone is formed in a low yield. It may be that the formation of di-quinone does not occur due to a steric hinderance. Also in connection with the formation of model substances of humic acids, Erdtman investigated the dimerization of quinones. (Proc. Roy. Soc., London. Sci. A. 143, 177-241 (1933)).

An alkaline solution of vanillin is oxidized with hydrogen peroxide; the brown solution acidified and oxidized with ferric chloride. A blue violet product is separated. Erdtman discusses the two formulas A or D. In case A, a partially oxidized 4,4'-di-methoxy-dihydro-quinone, the vivid color of the substance can be explained on the basis of the "indigoid" formula. By further oxidation, 4,4'-dimethoxy-di-quinone is formed. By reducing with zinc and acetic acid, 4,4'-dimethoxy-dihydroquinone is formed. This can be acetylated in the usual manner; in alkaline solution it absorbs oxygen very rapidly and is converted into a brown amorphous humic acid. 2,4,5,2',4',5'-hexahydroxy-diphenyl can be obtained by short boiling of 4,4'-di-methoxy-dihydroquinone with concentrated hydro-bromic acid. This substance is more unstable than the dimethoxy-derivative and therefore, by hydrolysis with hydrobromic acid, 2,3,6,7-tetra-hydroxy-diphenylene oxide is formed as a second product.

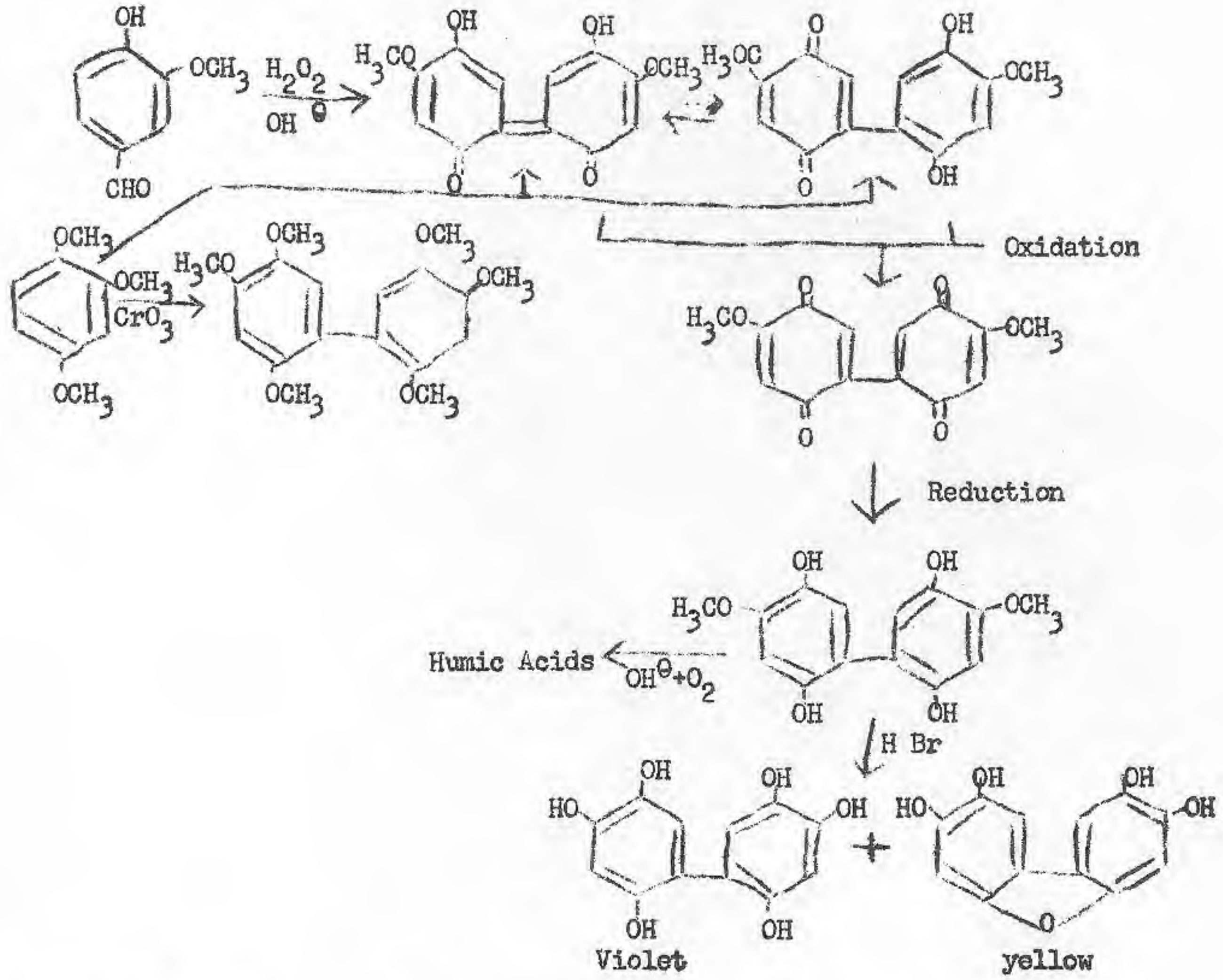
Another example is the oxidative coupling of hydroxy-hydroquinone-tri-methyl-ether.

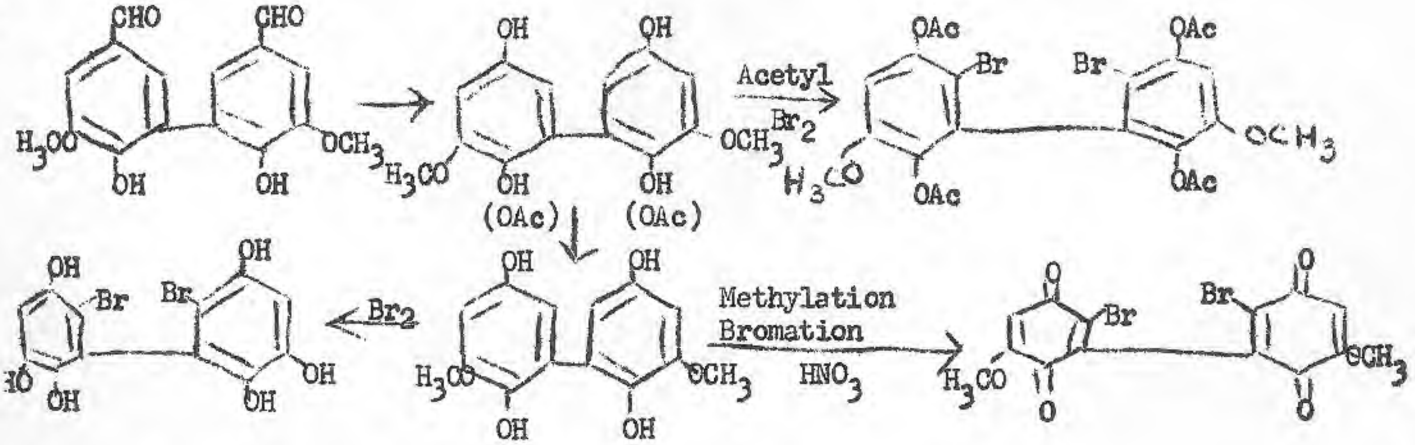
Under weak conditions, hydroxy-hydroquinone-tri-methyl-ether is oxidized by chromic acid and also by other oxidizing agents (anodic oxidation, ferric chloride, etc.) to 2,4,5,2',4',5'-hexamethoxy-diphenyl. In the presence of high amounts of chromic acid and higher temperature, the violet product is formed which has the constitution A or B.

By oxidation of dehydro-di-vanillin with hydrogen peroxide in alkaline solution, 3,3'-dimethoxy-dihydroquinone is formed. This can react with bromine in form of its tetra-acetate in acetic acid to the corresponding 6,6'-dibromide. 2,3,5,2',3',5'-Hexamethoxy-diphenyl is formed by hydrolysis of 3,3'-dimethoxy-dihydroquinone with diluted methyl-alcoholic sulfuric acid. This compound can also react with bromine to the 6,6'-dibromo-2,3,5,2',3',5'-hexamethoxy-diphenyl. After methylation to the hexamethoxy-diphenyl and after bromation to the corresponding 6,6'-dibromo-2,3,5,2',3',5'-hexamethoxy-diphenyl, it has been possible to oxidize the latter compound to the 6,6'-dibromo-3,3'-dimethoxy-diquinone. All these reactions occur only in acid solution. In alkaline solution, brown decomposition products are formed.

Dimerization of Polyphenols and their Esters.
Furthermore Dibenzoquinones

(Experiments of H. G. H. Erdtman)



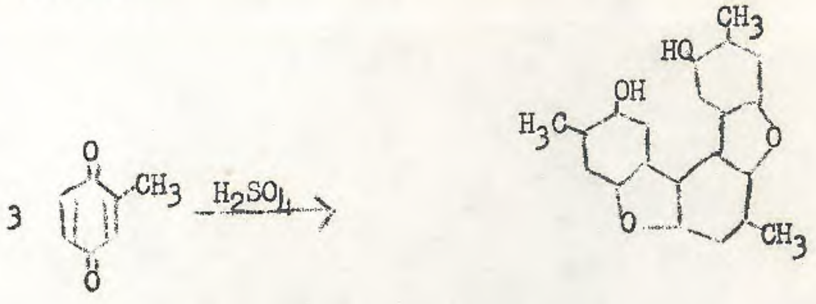


Proc. Roy. Soc. (London) Serie A, <u>143</u>, 177 (1934).

Under these acid conditions, it has not been possible to dimerize p-benzoquinone to diquinone.

Erdtman succeeded also to polymerize toluquinone to a trimolecular product from which the constitution is known. By splitting off water, furan rings are formed. (Dibenzofuran).

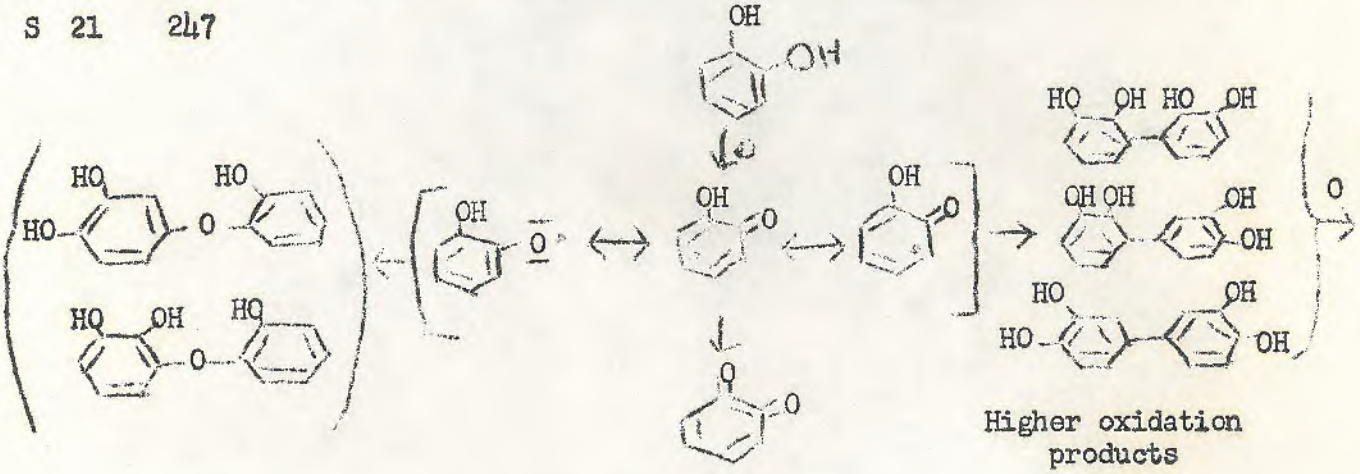
S 20 172



Trimerization of Toluquinone

Till now we have only spoken about the dimerization of 1,4-phenols. Now we will discuss the possibilities in the case of 1,2-diphenols.

S 21 247



The first step is also the formation of mesomeric forms. In one case, the active center is on the oxygen, in two other cases on the carbon atoms of the ring. In the latter cases, a semi-p or a semi-o quinone is formed.

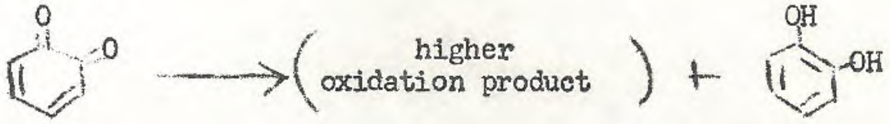
In the first case there is a possibility of the formation of two kinds of 3-hydroxy-diphenol ether. This could not be found in vitro, although in vivo, similar compounds exist.

By the reaction of 2 semi-p-quinones, 2 semi-o-quinones, and one semi-p-quinone with one semi-o-quinone, three different tetra-hydroxy diphenols can be formed. All these substances are known. By further oxidation, products with higher molecular weight are formed.

(V. W. F. C. Forsyth and V. C. Quesnel)

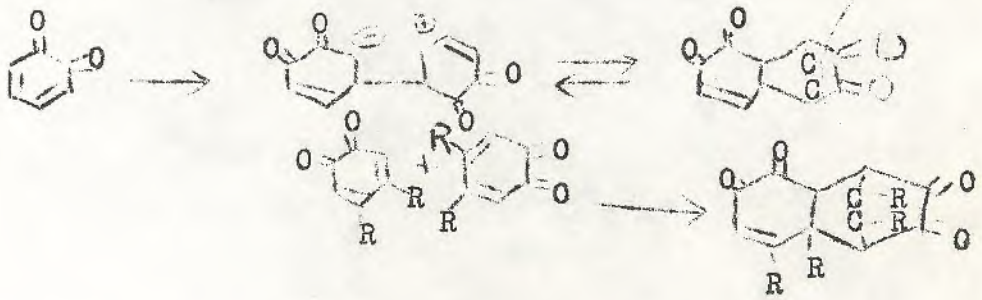
Further oxidation of the intermediary steps with radical character leads to o-quinones. o-Quinone reacts with oxygen to a peroxide which splits off by further reaction to a dicarbonic acid; in the case of o-benzoquinone, to muconic acid.

By disproportionation and simultaneous dimerization, different reactions can occur.

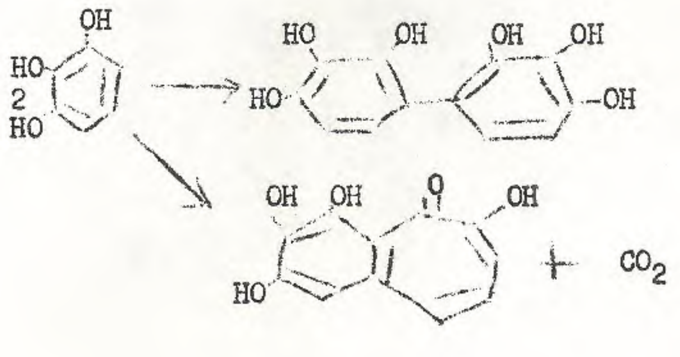


The formed 1,2-diphenols for instance dimerization products go partially back in the reaction or are oxidized to oxidation products with higher molecular weight.

The intermediary dimerization products can form dien-synthesis as in the case of 4,5-dimethyl-o-benzophenol. (Horner, L. u. K. Sturm: - Liebigs Ann. Chem. 597, 1 (1955)).



In the next section we will speak about the dimerization of 1,2,3-triphenols. In Baryth-solution 2,3,4,2',3',4'-hexahydroxy diphenol is formed. In neutral solution with different oxidation agents as potassium, ferric cyanide, nitrous acid, oxygen in presence of sodium phosphate, peroxydase, or dehydrogenation with palladium, purpurogallin is formed.



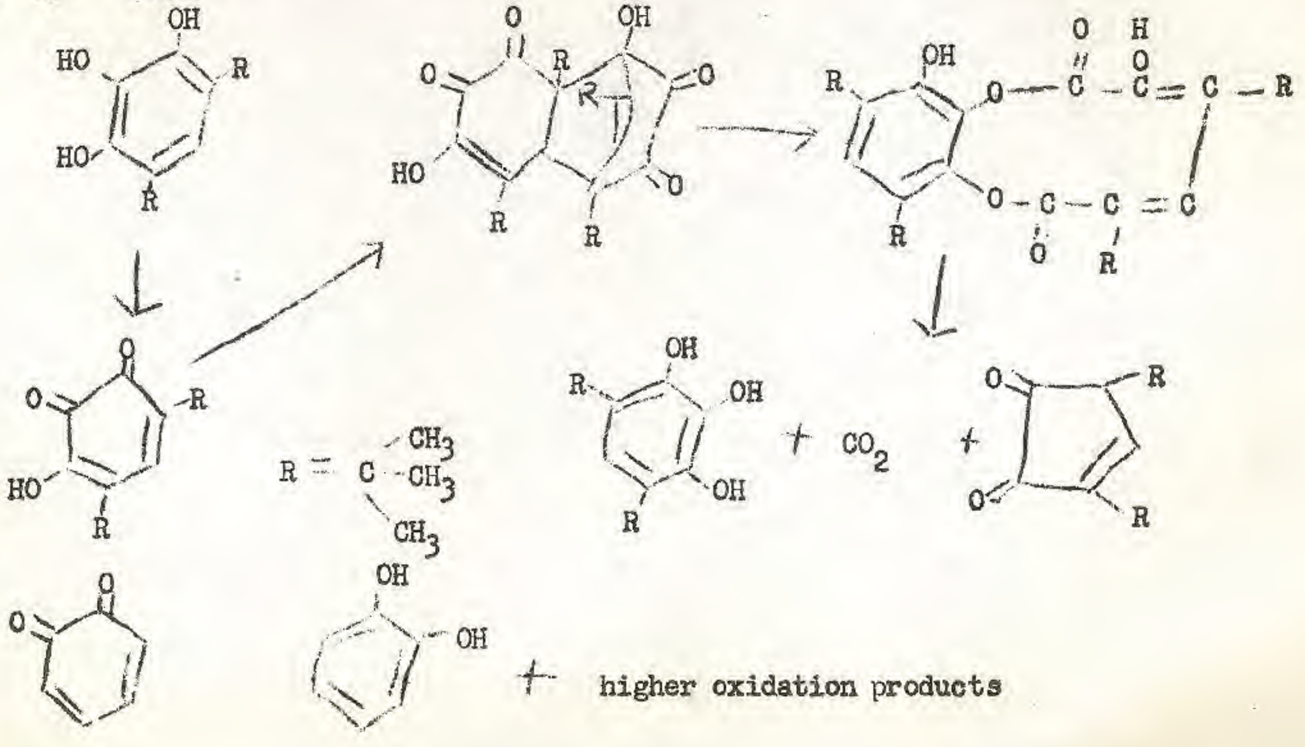
In recent time we have investigated the oxidation of pyrogallol more intensively (W. Flaig and co-workers, unpublished; J. C. Salfeld, Zum Reaktionsmechanismus der Purpurogallinbildung - Hauptversammlung der GDCh. Berlin 4, 10, 1957). For nearly 100 years, it has been known that purpurgallolin is formed under very different conditions by the oxidation of pyrogallol. But the course of this peculiar reaction has not been elucidated and only hypothetical conceptions have been made. Summarizing, the formation of purpurogallin is an oxidative dimerization of pyrogallol by splitting off carbon dioxide. For a long time it has been presumed that the first step of the reaction is an oxidation of pyrogallol 2,3-hydroxy-o-benzoquinone which finally dimerizes and is oxidized. (Compare the following references for the chemistry of purpurogallin). (Girard: - C. R. hebd. Seances Acad. Sci. 69, 865, (1869) - Haworth, R. D., B. P. Boore u. P. L. Pauson: - J. chem. Soc. 1948, 1045 - Haworth, R. D., B. P. Boore u. P. L. Pauson: - J. chem. Soc. (1950), 1631 - vgl. P. L. Pauson "Tropones and Tropolones" Chem. Rev. 55, 9-136 (1955) 111 and the following pages. - Critchlow, A., R. D. Haworth u. P. L. Pauson: - J. chem. Soc. (1951) 1318 - Dewar, J. M. S.: - Chem. Society London Symposium on Tropolones, London (1950) zit.: nach Chem. and Ind. (1951), 30 - Willstatter, R. u. H. Heiss: - Liebigs Ann. Chem. 433, 17 (1923)).

3-hydroxy-o-benzoquinone is not known till now. It is too unstable. Pyrocatechol and pyrogallol derivatives form indeed dark colored, mostly violet solutions which are changed very rapidly. In the case of 4,6-di-tert.-butylpyrogallol we have followed up this reaction.

S 22 125 (Slide cannot be reproduced on stencil)

The freshly prepared deep blue violet colored oxidation solution, 4,6-di-tert.-butyl-pyrogallol in carbon tetrachloride shows in the ultraviolet and infrared typical o-quinone spectra. These go over in the spectra of the dimers with a velocity depending on the concentrations. The dimer can be isolated in a preparative manner. The acetate and the methyl ether of the monomer 3-hydroxy-4,6-di-tert.-butyl-o-benzoquinone can be prepared by the oxidation of the corresponding pyrogallol mono acetate or mono methyl ether.

S 23 126



The properties of the dimer, 3-hydroxy-4,6-di-tert.-butyl-o-benzoquinone, can be explained satisfactorily by analogy to the dimer 4,5-di-methyl-o-benzoquinone formulated as a dien-adduct as before. The yellow dimer isomerizes very easily by heating or by treatment with small amounts of alkali to a colorless isomer with the constitution of an ester of 2,4-di-tert.-butyl-4-oxalo-crotonic acid. This product can be split off by further treatment with alkali to 4,6-di-tert.-butyl-pyrogallol, 3,5-di-tert.-butyl-cyclopenta-en-4-dion and CO_2. Overlooking the whole course of reaction, disproportionation of 3-hydroxy-4,6-di-tert.-butyl-o-benzoquinone takes place in 3 defined steps to 4,6-di-tert.-butyl-pyrogallol and a higher oxidation product, cyclopenta-en-dion. This reaction is of a certain analogy to the disproportionation of the unsubstituted o-benzoquinone. In this case pyrocatechol and oxidation products with higher molecular weight are found.

S 24 110 (Slide cannot be reproduced on stencil)

While in the case of the oxidation of 4,6-di-tert.-butyl-pyrogallol the corresponding hydroxy-o-benzoquinone as a primary oxidation product at least spectroscopically could be identified, in the case of unsubstituted pyrogallol, the secondary reactions are too fast. From the first product of these reactions, it can be concluded that the first steps of the oxidation of pyrogallol are principally similar to those of di-tert.-butyl-pyrogallol. So it has been possible to isolate in a low yield a dimer, hydroxy-o-benzoquinone, after oxidation of pyrogallol in alcohol with acetic acid and iso-amyl nitrite. The constitution of this dimer could be found analogously as the one of the dien-adduct of the dimer 3-hydroxy-4,6-di-tert.-butyl-o-benzoquinone.

Perkin has also found a dimer hydroxy-o-benzoquinone but he did not succeed to elucidate its constitution (compare: Perkin, A. G. u. A. B. Steven, J. Chem. Soc. 89, 802 (1906); Perkin, A. G., J. Chem. Soc. 103, 650, 661 (1913); Perkin, A. G., Proc. Chem. Soc. 29, 354 (1913); Perkin, A. G.u. A. B. Steven, J. Chem. Soc. 83, 192 (1903)).

Furthermore, we (J. C. Salfeld, in press) succeeded to isolate the ethyl ester of the still unknown purpuro-gallin-γ-carbonic acid during oxidation of pyrogallol in ethanol solution with p-benzoquinone or sodium iodate. If methanol is used, the methanol ester is formed.

After saponification in acid solution, the corresponding acid is formed, and by decarboxylation, purpurogallin.

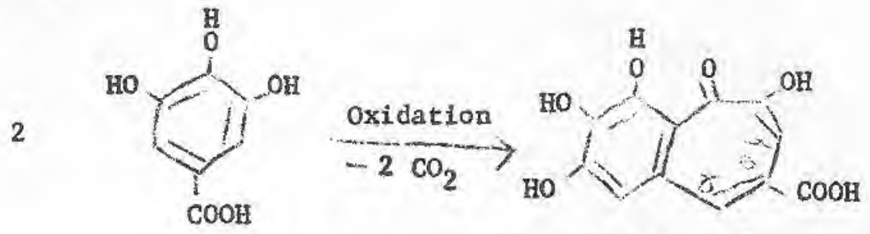
There is also another way to the ethyl ester of purpurogallin-γ-carbonic acid from the dimer hydroxy-o-benzoquinone. The ester is also formed in alcoholic solution in the presence of sodium acetate.

If the dimer o-benzoquinone is treated with aqueous dicarbonate solution, purpurogallin is formed by decarboxylation with a yield of 45%.

The best yield of purpurogallin by the formation of pyrogallol is obtained in aqueous solution with sodium iodate; the yield is 78%.

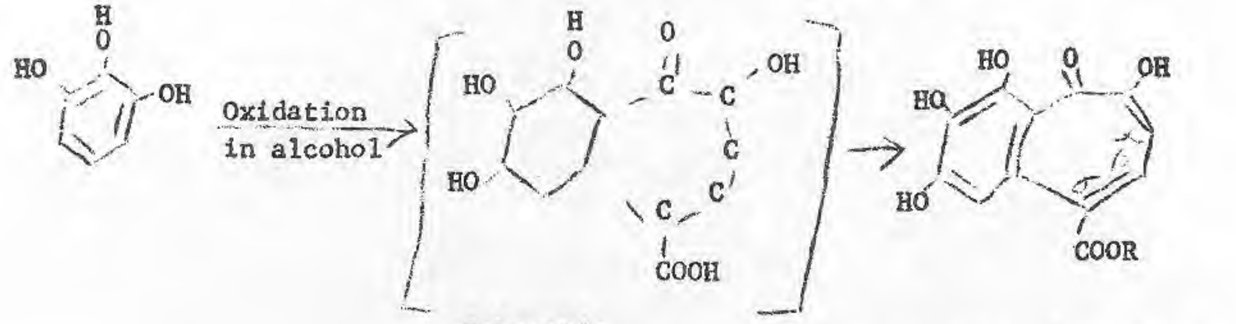
If gallic acid is oxidized, the purpurogallin-β-carbonic acid, known since a long time, is formed. This reaction can also be done with phenoloxidases in vitro. The best yield of purpurogallin-β-carbonic acid is obtained by the oxidation with sodium iodate.

S 25 151



Purpurogallin-β-carbonic Acid

2)



Schematic

Purpurogallin γ-carbonic acid

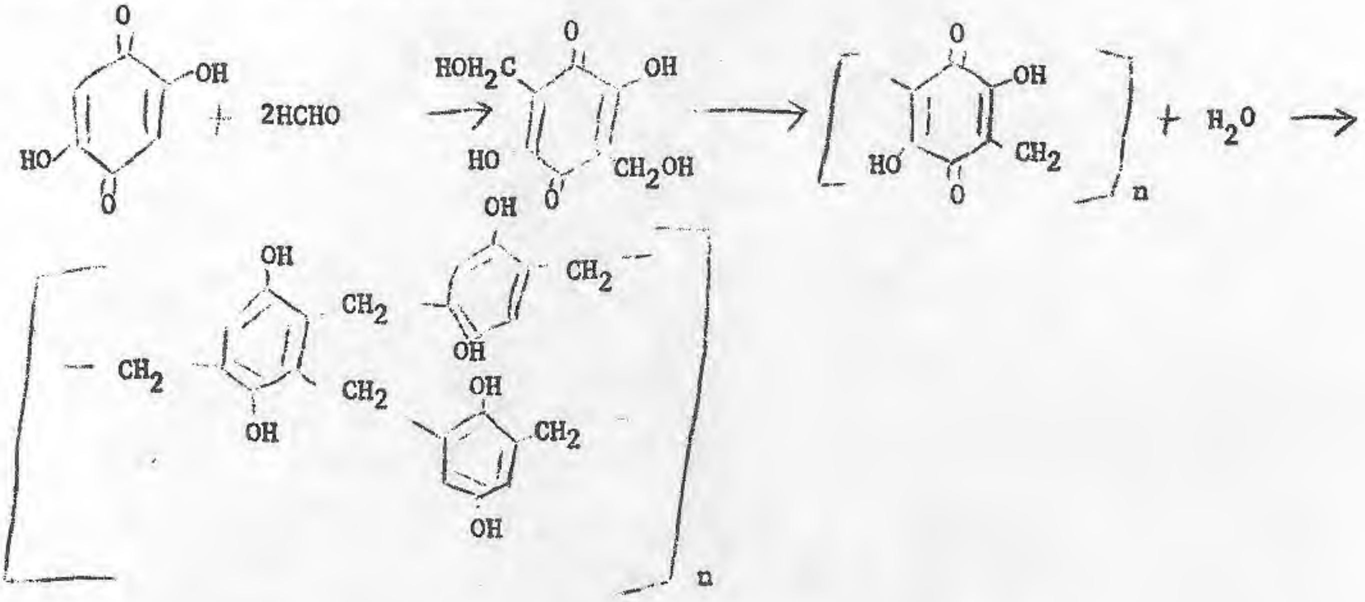
Vergleich der Schmelzpunkte von
Purpurogallin-β und-γ-carbonsaure und Derivaten

	Carbonsaure	Penta-acetat	Methylester	Methylester tetra-acetat	Athylester	Athylester tetra-acetat
Carbonsaure	uber 320 Z.	156-57	268-74 Z.	199-201	237-38.5 252-56	181-82.5
Carbonsaure	308 Z.	193 Z.	280-86 Z.	177-78	218-19	143-44

In the next slide, data of the two different acids and their derivatives are given.

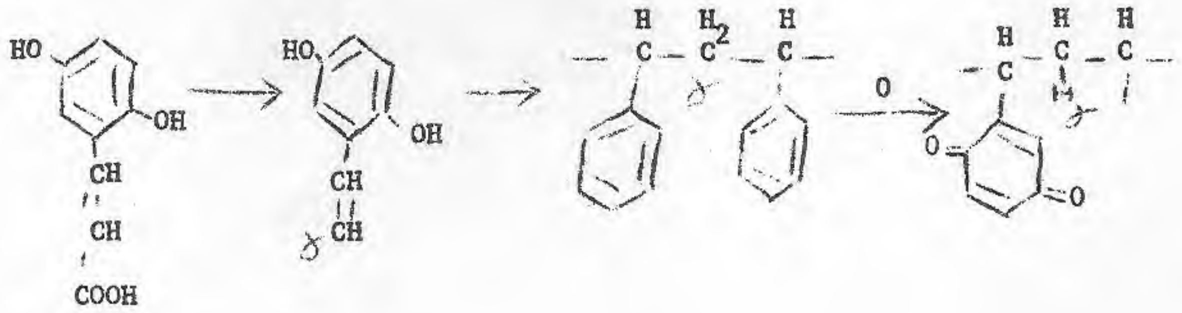
Until now we have only discussed the dimerization of polyphenols and quinones. In former lectures we talked also about the cleavage of the ring and the compounds being formed by it. It is rather improbable that the humic acids are formed only by polymerization of quinone. In the case of lignin fragments, and by the cleavage of the ring, reactions of the side chains of the lignin components and of the newly formed decomposition products of the ring with the quinones must be discussed. In other words, different kinds of bridges can be formed to connect the quinonic compounds. It can be expected that these different bridges are in fact reactions in different directions. The formation of three-dimensional products can be understood to be built up easily.

Products which occur during the condensation of phenol and formaldehyde, can be considered as model substances. For instance, we succeeded (unpublished) to isolate a crystallized compound formed by the reaction between 2,5-dihydroxy-p-benzoquinone and formaldehyde. In the presence of diluted acid, condensation to a polymer occurs at once. A scheme of the three-dimensional connection of phenol-formaldehyde-condensation products is given. (Hultzsch, K.: Chemie der Phenolharze, Springer-Verlag, Berlin-Göttingen, Heidelberg (1950)).



In connection with the type of higher molecular substances of quinonic character, electron exchanging substances must be considered. As a model for this purpose, the polymerized vinyl-hydroquinone prepared by Cassidy must be mentioned. (Cassidy, H. G.: J. Am. Chem. Soc. 71, 402 (1949)). Polyvinyl-hydroquinones can be oxidized stepwise to polyvinyl-quinones. These kind of polymers are interesting as they are electron-exchange resins like the humic acids. Furthermore, they possess more ability for formation of semiquinones than the monomers.

S 26 178



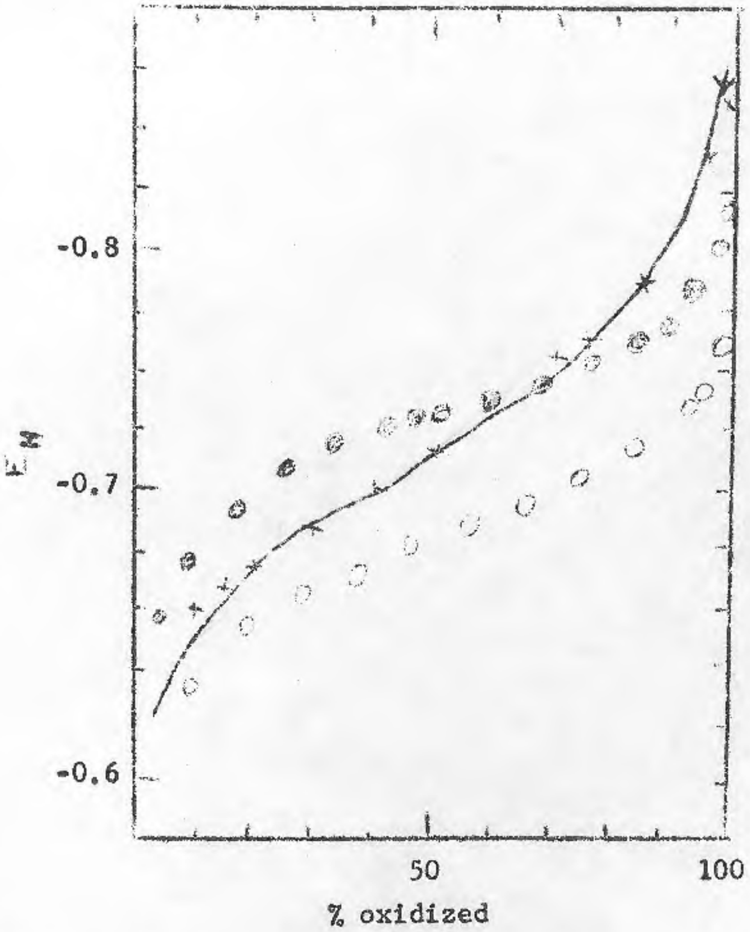
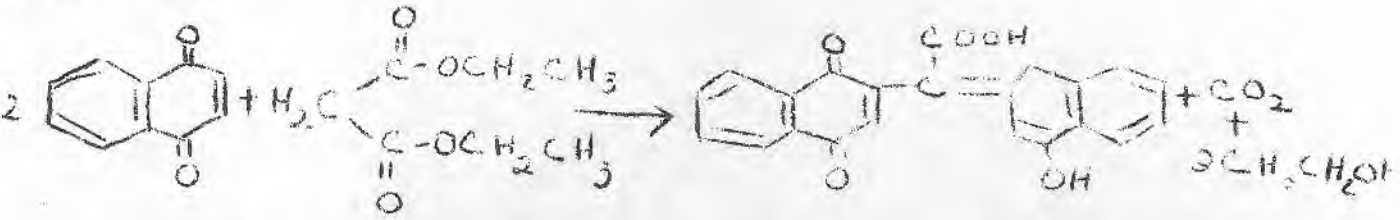


Fig. 1.-Oxidation of polymerized vinylhydroquinone, of hydroquinone and of ethylhydroquinone in solution in aqueous acetic acid with bromine in the same solvent: E_H potential in volts referred to the normal hydrogen electrode: X, polymerized vinylhydroquinone; pH, -0.45 to -0.6; temperature 23°. The line is drawn through the points to improve visualization of the curve. $\overset{\times}{\downarrow}$, this point showed a slight downward drift. ●, hydroquinone, pH 0.0 to -0.4, temperature 24°; O, ethylhydroquinone, pH -0.45 to -0.6, temperature 23°.

Cassidy could show that the curves of the potentiometric titration of the polymers have a steeper slope than the monomers. This fact means, according to Michaelis, that they form semiquinones more easily than the monomers. (Michaelis, L.: Oxydations-Reduktions-Potentiale. Monographien aus dem Gesamtgebeit der Physiologie der Pflanzen und der Tiere, Band 17, 107 (Berlin 1933)). Also the observed intermediary deepening of the color during the oxidation of the poly-vinyl hydroquinone to the corresponding quinone supports this consideration.

S 28 191



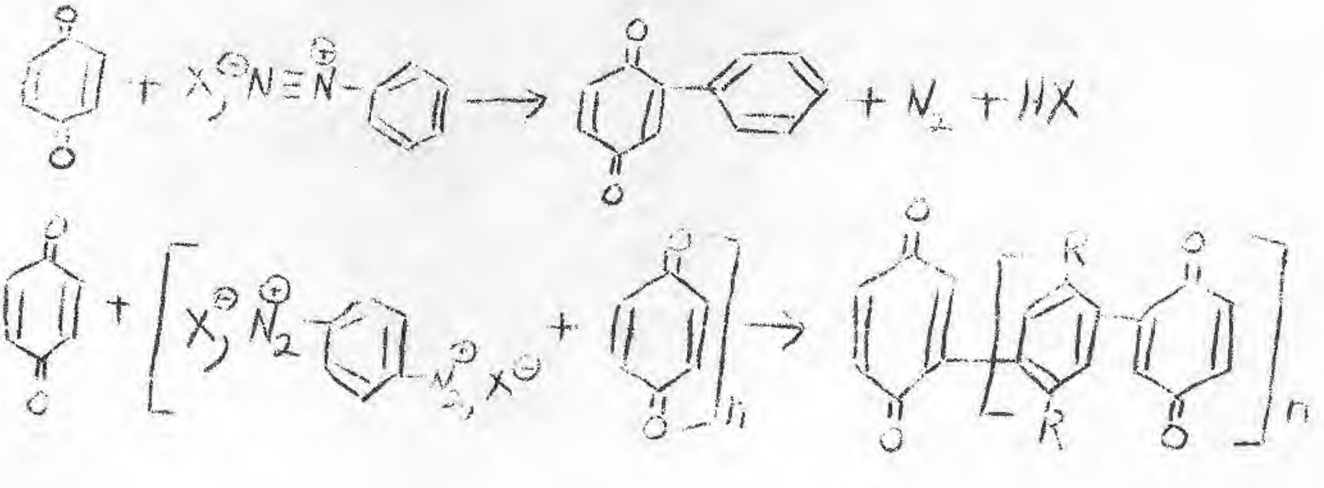
A further model which is interesting in the case of o-p-tautomery of quinoid substances is the condensation product of malonic acid-di-ethylester with quinones. According to Pratt,* E. F., und Boehme, W. E.: J. Am. Chem. Soc. 73, 444 (1951)). After saponification and decarboxylation a product is formed, in which, on the basis of aromatization tendency, one part of the α-naphthoquinone is transformed in an o-quinonic form.

*two mols of naphtho-quinone react with one mol malonic acid-ester.

Furthermore, we investigated another model in which the bridge between the two rings of quinones is a system of conjugated double-bounds. Summarizing, I will mention the investigations with di-quinoyl-benzene. (Ploetz, Th.: Polymere Chinone als Humin-säuremodelle. Z. Pflanzenernähr., Düng., Bodenkunde 69, 50-58 (1955)).

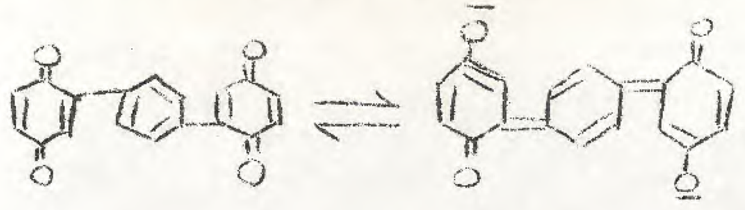
Some lectures before, I mentioned the reaction between quinones and diazonium salts. (Compare: Kvalnes, D. E.: J. Am. Chem. Soc. 56, 667, 2478 (1934)).

S 29 179



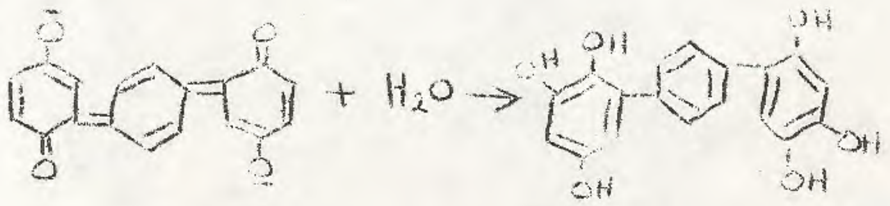
Ploetz succeeded to carry out these reactions with bis-azo-benzenes. In the most simple case, diazotated phenylen-diamine with benzoquinone results in 1,4-di-quinoyl-benzene. The aromatization tendency is here yet higher than in the case of the condensation product of malonic acid-ester and α-naphthoquinone. The UV-spectra showed maxima which belong to an o- and p-quinoid configuration.

S 30 183



1,4-Di-quinoyl-benzene exists therfore in two tautomeric forms, from which one is extremely reactive and can be considered as a diradical. The red color of 1,4-di-quinoyl-benzene supports this fact. Comparatively, 2,5-di-phenyl-p-benzoquinone is yellow.

S 31 185



The addition of water leads to hydroxy-hydroquinones which can be dehydrated to hydroxyquinones, which are strong acid products. Only with this acidity the acid nature of humic acids could be explained sufficiently.

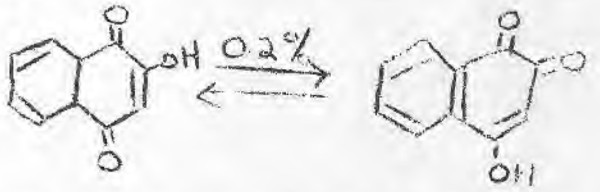
Oxidation- and reduction-reactions show that this kind of quinone can form intermolecular quinhydrones. This means that one ring in the molecule of di-chinoyl-benzene is in hydroquinone and the other in the benzoquinone form. The usual quinhydrone is formed by hydroquinone and quinone and is an intermolecular quinhydrone.

S 32 184 (Slide cannot be reproduced on stencil)

In dioxane 1,4-di-quinoyl-benzene disproportionates by treatment with light. The absorption curve becomes more and more a straight line. It is easy to imagine that a mixture of these products results in more or less only a straight line. I remember the UV-spectra of natural humic acids or fulvic acids which are also only a straight line without specific maxima. (Compare: Frömel, W.: Bodenkunde und Pflanzenernährung 6, (51), 93 (1938); Frömel, W.: Bodenkunde und Pflanzenernährung 11, 129 (1938); Frömel, W.: Bodenkunde und Pflanzenernährung 25, (70), 345 (1941); Scheffer, F., und Welte, E.: Landwirtsch. Forsch. 1, 190 (1950); Scheffer, F., und Welte, E.: Landwirtsch. Forsch. 3, 1 (1950).

Summarizing these experiments in connection with the chemistry of natural humic acids, it can be said that, if in natural humic acids there are quinone rings combined by systems of conjugated double bounds, the pure quinoid state is very improbable. The conglomeration of the conjugation effects a strongly enlarged oxidation potential. The transformation of the tautomer-autoquinonic radicals in hydroxy-hydroquinones can be explained by an addition of water only without the mechanism of formation of hydrogen peroxide, according to Weissberger. (James, T. H., Snell, J. M., und Weissberger, A.: J. Am. Chem. Soc. 60, 2084 (1938)).

Some words must be said about the tautomery of 2-hydroxy-1,4- and 4-hydroxy-1,2-quinones.



Fieser and Peters worked on the tautomery of the different hydroxy-naphthoquinones (L. F. Fieser, u. M. A. Peters, J. Am. Chem. Soc. 53, 793 (1931)).

The compound with less energy content must be predominant in solutions; it possesses also the lower normal redox potential. Some details we shall hear later on. In the case of 2-hydroxy-1,4-naphthoquinone and 4-hydroxy-1,2-naphthoquinone, Fieser determined that the o-quinonic form is only in equilibrium for 0.2%. In the case of humic chemistry, it is interesting to study the conditions in the case of hydroxy-benzoquinones. One method for this purpose are the UV-spectra.

Not only for this reason but also to have the possibility to compare model substances with natural products such as lignin precursors, fragments of lignin, their methylation products and phenols and quinones which can be found as metabolism products of plants and microorganisms. We investigated the UV-spectra of the different methylated quinones, mono-hydroxy-methyl-, monomethoxy-methyl- and the methylated quinones. With these combinations most of the important quinones in connection with humic chemistry are included.

We investigated the ultraviolet spectra of the mentioned quinones to find out if there are some regularities which can help to elucidate the processes of formation of humic acids and their chemical constitutions. (Flaig, W., Th. Ploetz, u. A. Kullmer: - Uber Ultraviolettspektren einiger Benzochinone. Z. Naturforsch. 10b, 668-676 (1955); Flaig, W. u. J. Ch. Salfeld: - UV-Spektren und Konstitution von p-benzochinonen. Liebigs Ann. Chem. 618, 117-139 (1958)).

The different solubility of the substances made it necessary that in some cases, the measurements be done in different solvents. Later on we will speak about the influence of the solvents on absorption.

S 33 197 (Slide cannot be reproduced on stencil)

In this slide are the different spectra of the methyl substituted p-benzoquinones. All these quinones have three maxima. They are marked with the numbers 1 to 3 from the shorter to the longer waves. For the first impression it is to see that the first maximum is shifted only a small amount, the third nearly none following the substitution. The second maximum shows the largest differences.

S 34 132 (See S#9 of Introduction to Work of the Institute for Soil Biochemistry)

The shift of the second maximum depends upon the number of substituents. The unsubstituted p-benzoquinone and the quinones which have one or two substituents are nearly the same as those with the mono- and di-substitutions on the one and the tri- and four substituted quinones.

S 35 133 (Slide cannot be reproduced on stencil)

If we consider the three different di-substituted p-benzoquinones, we see that the maxima of the m- and p-disubstituted quinones are at the same place as the monosubstituted but the maximum of the o-disubstituted is at the same place as those of the tri- and four substituted benzoquinones. This regularity is applicable also for the other substituted quinones.

S 36 198 (Slide cannot be reproduced on stencil)

In the case of the monomethyl substituted methoxy benzoquinones, the first maximum is less and the second more shifted to longer wave lengths; consequently the third maximum which does not or only in a very small amount, is shifted to shorter wave lengths, is overlapped with its small extinction by the second maximum.

S 37 199 (Slide cannot be reproduced on stencil)

The same observations are made in the case of monohydroxy substituted methyl p-benzoquinones. This kind of spectra are relatively similar to those of the monomethoxy substituted methyl p-benzoquinones.

S 38 200 (Slide cannot be reproduced on stencil)

In the case of the different methoxyl-p-benzoquinones the same observation can be made. The type of this spectra shows some differences in the shift of the first maxima.

Before showing the general regularities, I will give you some different others.

S 39 243 (Slide cannot be reproduced on stencil)

By the substitution with aliphatic compounds the number of carbon atoms in the substituent does not make as much difference in the shift as the position. The second maximum of p-xyloquinone is at 309 mμ, that of cyclohexyl at 316 mμ, that of 2,5-di-cyclohexyl-p-benzoquinone 316, and that of 2,5-di-tert.-butyl-p-benzoquinone 310 mμ. This means that p-xyloquinone with 2 carbon atoms in the side groups and the 3 other benzoquinones with 6, 8, and 12 carbon atoms in the substituents give only a shift effect of 1 to 6 mμ.

While 1 carbon atom more than in p-xyloquinone as a new side-chain, e.g., pseudocumoquinone, gives a shift of 24 mμ.

S 40 245 (Slide cannot be reproduced on stencil)

In the case of the monohydroxy-dimethyl-benzoquinone there are always 2 substituents in o-position. The second maximum of 2-hydroxy-5,6-dimethyl-benzoquinone has the same position as, for instance, 2-hydroxy-5-methyl or 2-hydroxy-6-methyl-p-benzoquinone.

A shift can occur in the case of 2-hydroxy-3,5-dimethyl and 2-hydroxy-3,6-dimethyl-p-benzoquinone. This means that the shift to longer wave lengths, effected by the o-position of two substituents can only be observed when the second substituent is in o-position to that which is responsible for the absorption.

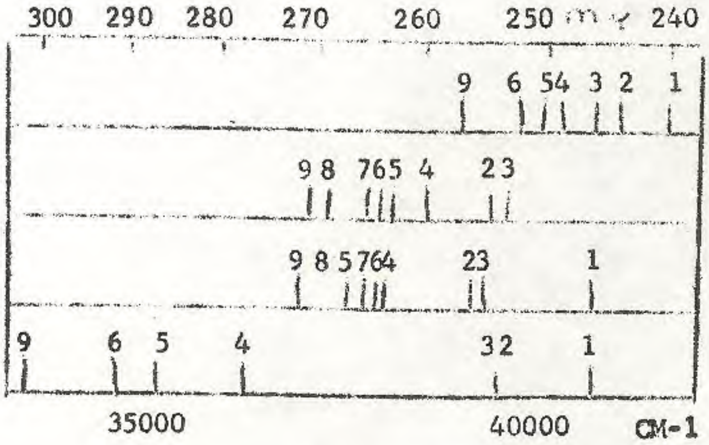
After these details the general regularities will be discussed.

It is not always possible to write all the formula and therefore I will give a scheme for an abbreviation.

S 41 201 (On next page)

The first maximum is shifted by the substituents in the order CH_3, OCH_3, OH increasing to longer waves.

S 42 202



I: $R_1,R_2 = CH_3$; in n-Hexan

II: $R_1 = OCH_3$, $R_2 = CH_3$; in CCl_4

III: $R_1 = OH$, $R_2 = CH_3$; in $CHCl_3$

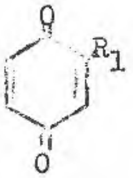
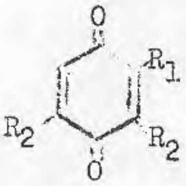
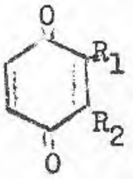
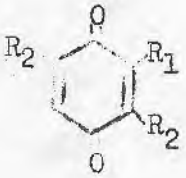
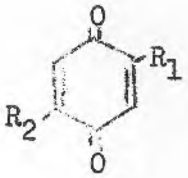
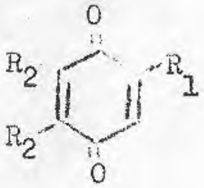
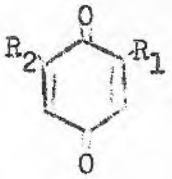
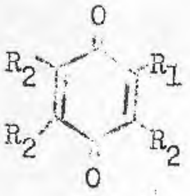
IV: R_1, $R_2 = OCH_3$; in $CHCl_3$

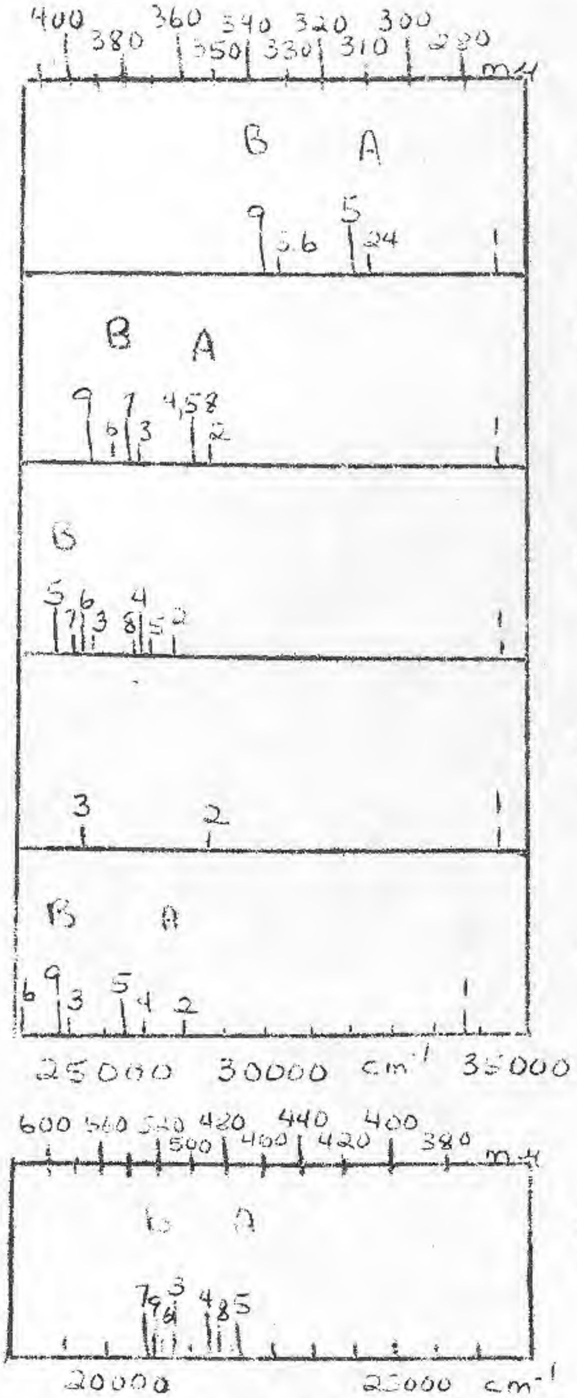
Length of the 1 Maxima of Substituted p-Benzoquinone

The first maximum of the methyl substituted p-benzoquinones is shifted in n-hexane 4 m per methyl group to longer waves. In the case of the three dimethyl-p-benzoquinones (I/3,4 and 5) effects occur in addition by the position of the substituents.

In the case of the dimethoxy-p-benzoquinones the difference between 2,3- and 2,5-dimethoxy-p-benzoquinones (IV/3, IV/4, respectively) 24 mμ, between 2,5- and 2,6-dimethoxy-p-benzoquinone (IV/4, IV/5, respectively) 9 mμ. In all cases, the 2,3-disubstituted compound I/3 to IV/3) absorbs in a shorter wave region than the 2,5-(I/4 to IV/4) and the 2,6- disubstituted. In the rows with two different substituents (II and III) there are also in the case of the tri-substituted p-benzoquinone, 3 isomers. The maxima of those compounds, which possess in o-position a methyl group to the substituent which is determining for the absorption (OH, OCH_3, respectively) are closer together and in the region of shorter waves (II/6 and 7, III/6 and 7, respectively) the third isomer (II/8, III/8, respectively) absorbs in a larger distance in a region of longer waves. This seems to be remarkable because this "o-effect" in the case of the second maxima causes a shift to longer wave lengths.

Abbreviation Scheme
p-Benzoquinone = I/1 bzw. II/1, III/1, IV/1

R_1 =	CH_3	OCH_3	OH	OCH_3	R_1 =	CH_3	OCH_3	OH	OCH_3
R_2 =	CH_3	CH_3	CH_3	OCH_3	R_2 =	CH_3	CH_3	CH_3	OCH_3
	I/2	II/2	III/2	IV/2		I/6	II/6	III/6	IV/6
	I/3	II/3	III/3	IV/3		I/6	II/7	III/7	IV/6
	I/4	II/4	III/4	IV/4		I/6	II/8	III/8	IV/6
	I/5	II/5	III/5	IV/5		I/9	II/9	III/9	IV/9



I: R_1, R_2 = CH_3 in CCl_4

II: R_1 = OCH_3, R_2 - CH_3 in CCl_4

IIIa: R_1 = OH, R_2 = CH_3 in CCl_4

IVa: R_1, R_2 = OCH_3, in CCl_4

IVb: R_1, R_2 = OCH_3 in $CHCl_3$

IIIb: R_1 = OH, R_2 = CH_3 in 0.01 n methanol. KOH

Lage der 2. Maxima von substituierten p-Benzochinonen

Verschiebung des 2. Maximums von p-Benzochinon in CCl_4 Durch verschiedene Substituenten

		CH_3	OCH_3	OH
Gruppe A	1. Substituent	+27	+69	+82 m
	2. Substituent	m-und p-Substitution zum 1. Substituenten hat nur "sekundaren" Einfluss		
Gruppe B*)	CH_3	+23	+23	+26 m
	OCH_3		+41	

*) Inkremente fur o-Stellung von Substituenten zueinander

In the next slide the wave lengths of the second maxima of the four groups of quinones are summarized. The regularities concerning the position and the extinction of the second maxima can be formulated as follows.

The frequency of wave length of each row form always two groups (A and B). To the group B belong the o-substituted p-benzoquinones with two and more substituents, to the group A the non o-substituted. In the case of two different substituents (row II and III) the o-positions of the substituents determining the shifting is decisive. The values are nearly the same for all investigated solvents.

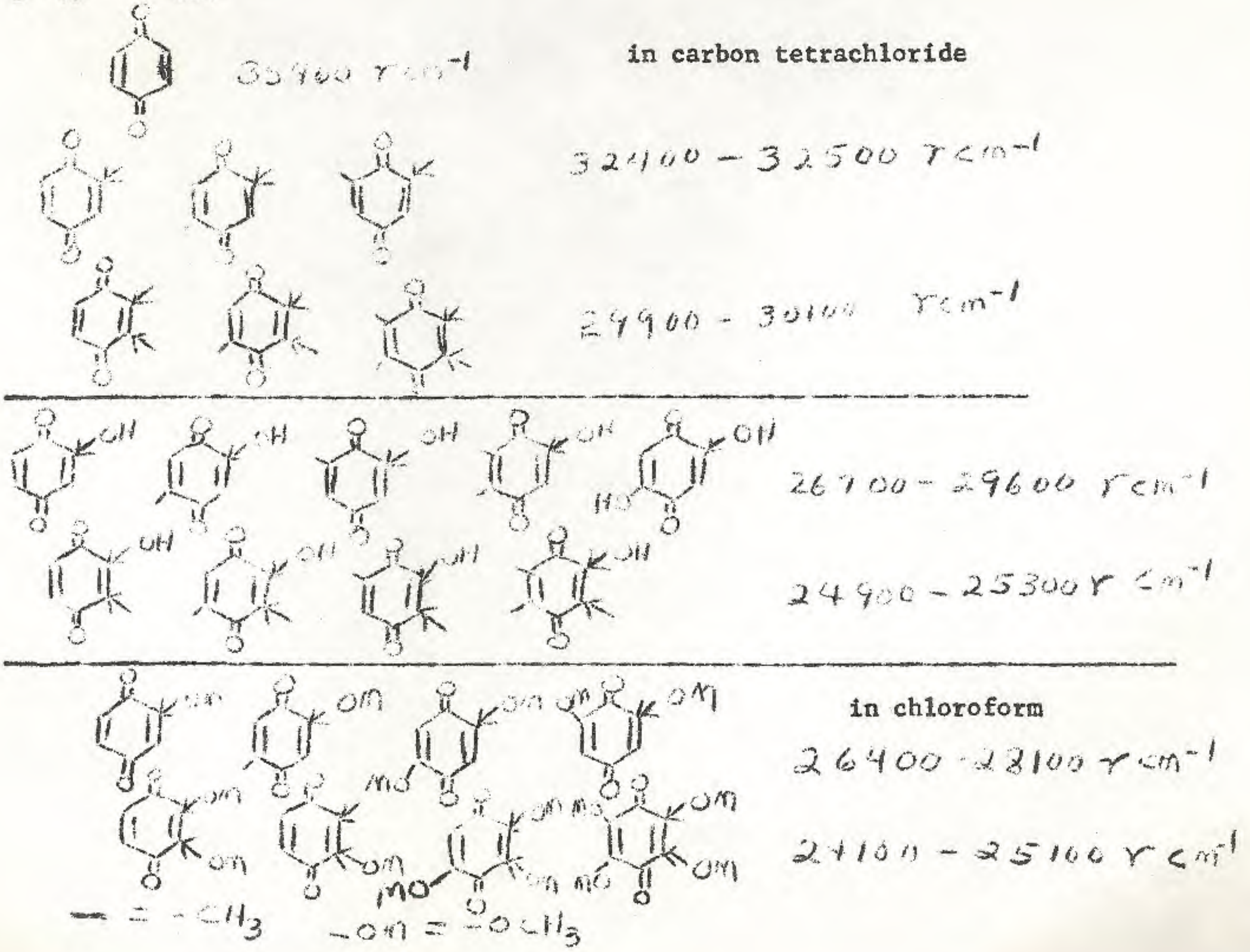
In the group A and B there can be observed secondary effects concerning the kind and the position of the substituents.

In the group A, a second substituent shifts the maximum in the case of CH_3 + 27, OCH_3 + 69, and OH group + 82 m u. In the group B, the maxima are shifted by a second CH_3 group + 23, in the case of introducing a methyl group in methoxybenzoquinone for also + 23 in the case of hydroxy quinone, also 26 and by introducing a methoxyl group in methoxybenzoquinone + 41.

S 44 205 (See next page)

The differences between the values which can be calculated by the mentioned numbers for shifting and the measured values are given in this table in the case of methoxybenzoquinone. It must be remarked that the secondary effect produced by the substitution in the case of tetramethoxy-p-benzoquinone is nearly missing. It may be that this is connected with a symmetry of the molecules.

S 45 134



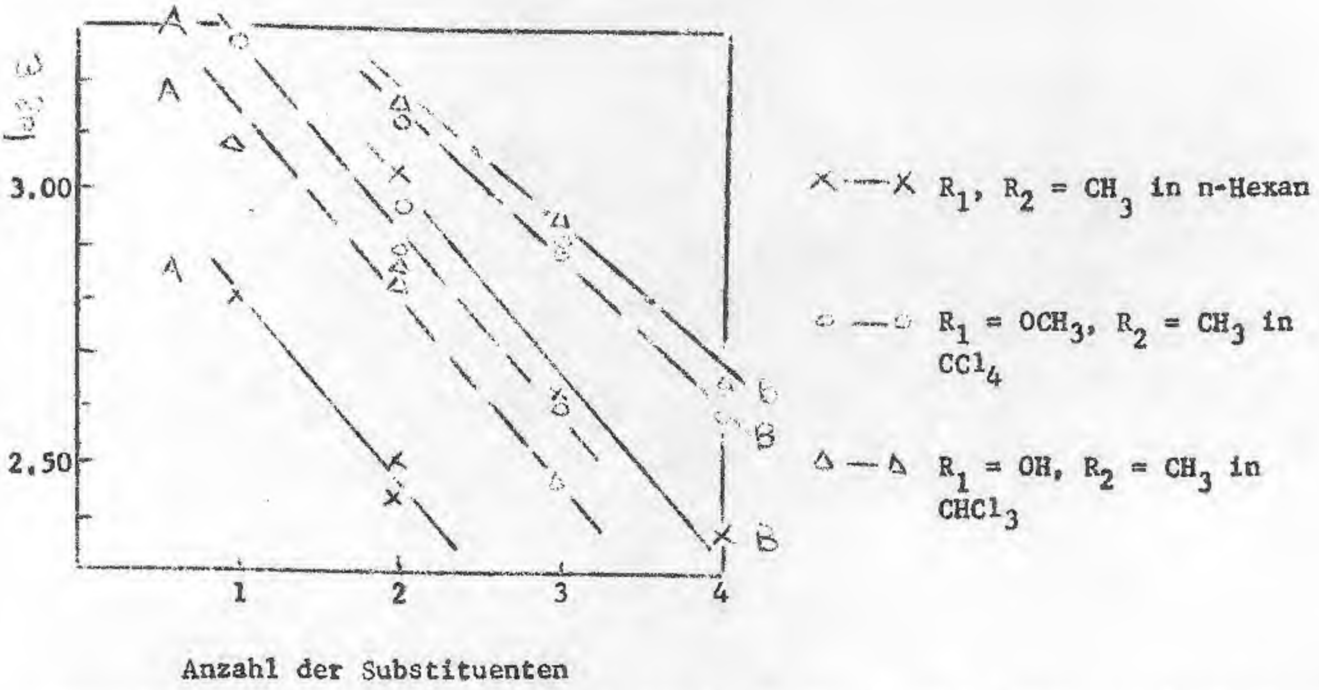
Differenzen zwischen den aus den Werten der Tabelle 4 berechneten und den gemessenen Werten der 2. Maxima der Reihe IV in mμ ;
Losungsmittel $CHCl_3$

Chinon	Ber.	Gef.	Diff.
II/2	-	357	-
IV/3	398	398	0
IV/4	357	370	+13
IV/5	357	377	+20
IV/6	398	418	+20
IV/9	398	400	+2

These results give the possibility to differentiate hydroxy quinones which have a substituent in o-position to the hydroxy group. The maxima of the anions of the hydroxy-p-benzoquinone are shifted into the visible region. Alkyl substituted p-benzoquinones which have no substituent in o-position to the hydroxy group are red in alkaline solution, those which have a substituent in o-position to the hydroxy group are violet. This possibility to differentiate the hydroxy-p-benzoquinones by this color reaction may help in different analytical investigations which belong to oxidized lignin precursors, lignin fragments, or other natural quinones.

Corresponding groups show also the extinctions of the second maxima as well as the wave lengths.

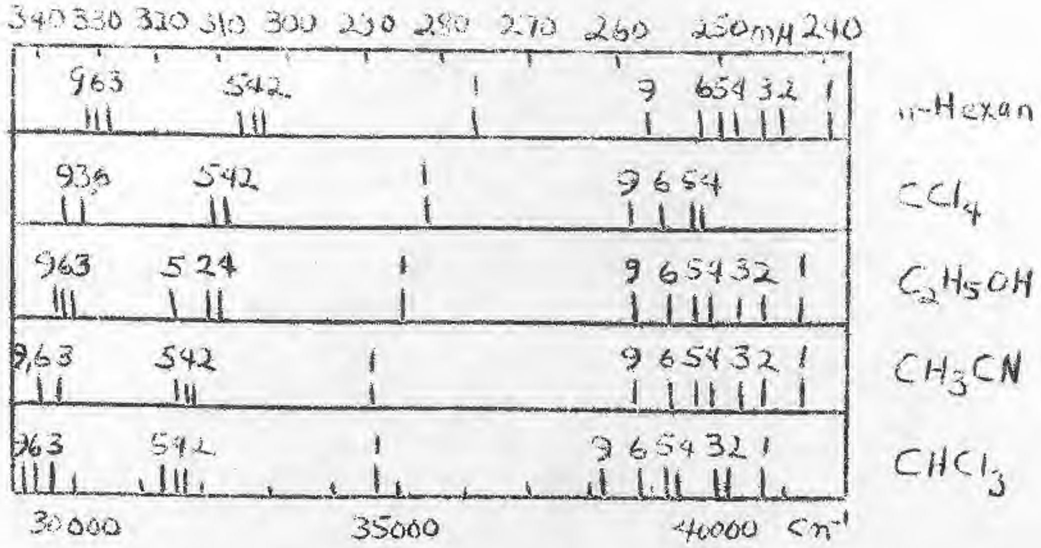
S 46 206



Abhangigkeit der Extinktion (log) der 2. Maxima der UV-Spektren substituierter-p-Benzochinone (I-III) von Anzahl und Stellung der Substituenten

The next table shows the extinction of the second maxima of the rows I to III as log ε plotted against the number of the substituents. Within the groups A and B, given by the position of the maxima, the extinction decreases nearly linearly with the number of substituents. In all three rows the decreasing is log ε = 0.25 to 0.35 per substituent. The extinction, therefore, decreases with the introduction of a further methyl group by nearly half.

S 47 207



Length of the 1 and 2 Maxima of methyl substituted p-Benzoquinone (I) in various solvents

We examined also the influence of different solvents. For this purpose, for instance, the methyl-substituted p-benzoquinones (I/2, 3, 4, 5, 6 and 9) were measured in n-hexane, carbon tetrachloride, ethanol, acetonitrile and chloroform. In the mentioned order, the first and the second maxima are shifted to longer wavelengths. The shift of the first and second maxima is nearly independent of the number and the position of the methyl groups in the different solvents. Therefore, it is possible to calculate with an average value.

S 48 208

Mittelwerte fur die Verschiebung der 1. und 2. Maxima der methylsubstituierten p-Benzochinone (1) in verschiedenen Losungsmitteln gegenuber n-Hexan in m

Losungsmittel	CCl_4	C_2H_5OH	CH_3CN	$CHCl_3$
1. Maximum	3	2	2	5 m
2. Maximum	4	7	10	11 m

Lage des 1. und 2. Maximums von Durochinon in verschiedenen Losungsmitteln

Losungs-mittel	1. Max. (m)	2. Max. (m)	Dipol-moment*)	Dielektrizitats-konstante*)	Loslichkeit in g/100ccm bei 20
n-Hexan	257,266	331	0	1.88	2.38
CCl_4	259,269	335	0	2.25	13.82
C_2H_5OH	259,267	338	1.70	25.8	2.32
CH_3CN	259,267	340	3,4	38.8	7.22
$CHCl_3$	269	342	1.10	5.14	30.23

*) entnommen aus J.D' Ans und E. Lax, Taschenbush fur Chemiker und Physiker, Springer-Verlag, Berlin 1943.

Lage der 1. und 2. Maxima der methylsubstituierten Hydroxy-p-benzochinone in CCl_4 und ihre Verschiebung gegenuber der Losung in $CHCl_3$ (vgl. Tab. 2)

Maxima in CCl_4	III/2	III/3	III/4	III/5	III/6	III/7	III/8	III/9	
1. Maximum	254	-	262	265	262	264	270 277		270 m 278 m
2. Maximum	365	391	373	372	395	396	375		403 m
Verschiebung								Mittelwert	
1. Maximum	2	-	2	3	3	2	2	2	2 m
2. Maximum	4	5	9	8	7	6	3	6	6

Furthermore, the shift of the first and second maxima has been investigated in the case of duroquinone in connection with some physical properties of the solvents. With increasing values of the dielectric constant of the solvent the shift increases. The values in chloroform are exceptions. It may be that there are other interactions in addition. Results of a similar kind are described. (M. Pestemer and D. Bruck in Houben-Weyl-Muller, Methoden der organischen Chemie, 4. Aufl., Band 3/2, S. 736 ff., Thieme Verlag, Stuttgart 1955).

In this table are also given the values of the dipolemoment. The different solubility in the solvents can be seen in the last row.

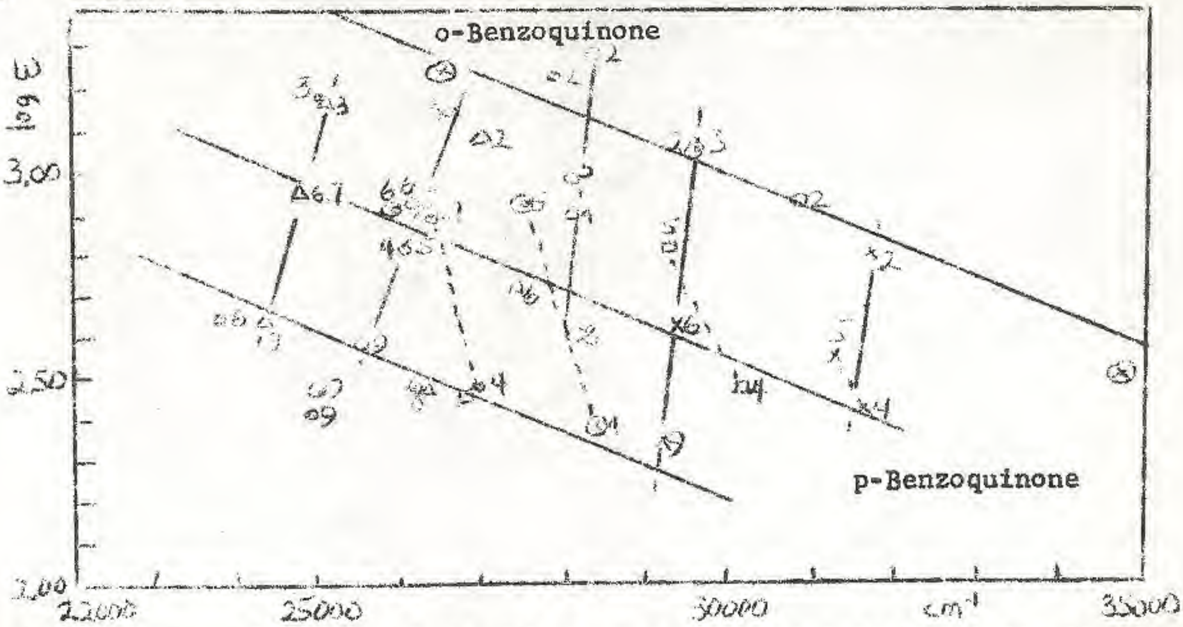
The shift of the first and second maxima of the methyl substituted monohydroxy-p-benzoquinones is between carbon tetrachloride and chloroform of the same order as of the methyl substituted p-benzoquinones.

Methoxy-p-benzoquinone- and 2-methoxy-5-methyl-p-benzoquinone have a slightly stronger shift in carbon tetrachloride, acetonitrile and chloroform than in the rows I and III compared to hexane.

The extinction of the second maxima of row I are nearly independent of the solvent.

For our further considerations, it is of interest to study the correlation between the position and the extinction of the second maxima. I will remember that the position of the second maxima depends upon the distribution of the electrons in the ring of the quinones. Therefore, the substitution must have a specific influence.

S 49 209



Log ε of the second maxima of the UV-spectra of substituted p-benzoquinones as related to the frequency. The dashed straight lines connect the values of the 2,5- and 2,6-disubstituted derivates of each row. The numbers are analogous to the scheme of abbreviation. The values of the halogenated p-benzoquinones according to E. A. Braude. (E. A. Braude; J. Chem. Soc. (London) 1945. 490. Since Dr. E. A. Braude died in the meantime, the reason for the different values cannot be explained). The values for the o-benzoquinones according to H. J. Teuber and co-workers. (H. J. Teuber and G. Jellinek, Chem. Ber. 85, 95 (1952); H. J. Teuber and N. Gotz, ibida 89, 2654 (1956)). x row I in $CHCl_3$ o row II in CCl_4 △ row III in $CHCl_3$ ▪ row IV in $CHCl_3$ ⊆ chlorosubstituted and ⊛ bromosubstituted quinones in $CHCl_3$

Due to the position and extinction of the second maxima, the substituted benzoquinones of one row can be divided in each case into two groups. The classification of these two groups depends upon the substitution in o-position. In one group belong quinones which have a hydrogen atom in o-position to the substituents determining the absorption and in the other group those which have another substituent. Benzoquinones which belong to one and the same group have the maxima in nearly the same position, but an extinction decreasing with the number of substituents.

The frequencies (cm^{-1}) of the maxima are plotted against $\log \varepsilon$. The points of p-benzoquinone and the mono-substituted p-benzoquinones are situated nearly on a straight line with a slope; $\log \varepsilon = -0{,}834 \times 10^{-4}$. Also the value for the unsubstituted o-benzoquinone is situated near this straight line. Later on, we will hear more about this.

The m- and p-disubstituted and trisubstituted compounds with <u>one</u> substituent in o-position to the substituent determining the absorption (case a) on the one hand, the trisubstituted with <u>no</u> substituent in o-position to the substituent determining the absorption (case b) and the tetra-substituted p-benzoquinones on the other hand are also of different straight lines with the same slope. To test the equation of these straight lines

$$(1) \qquad \log \varepsilon = -0.834 \cdot \bar{\nu} \cdot 10^{-4} + k = k - 834/\lambda$$

The extinctions of the measured λ-values were calculated with the different constants, depending upon the substitution, and compared with the measured extinction.

The different constants are

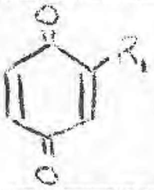
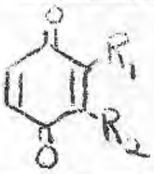
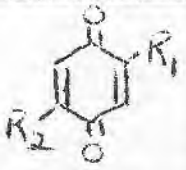
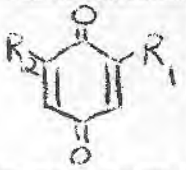
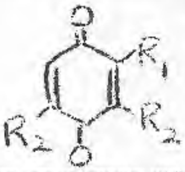
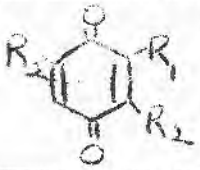
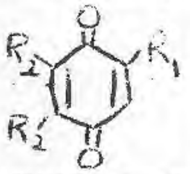
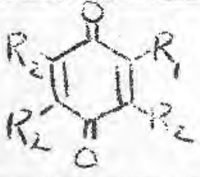
quinones	k	
unsubstituted monosubstituted and o-disubstituted	5.49	1,2,3
p- and m-disubstituted, trisubstituted (case a)	5.06	4,5,6
trisubstituted (case b) and tetrasubstituted	4.72	7,8,9

Zur Prufung der Gleichung dieser Geraden

(1) $\log \varepsilon = -0.834 \cdot \bar{v} \cdot 10^{-4} + k = k - 834/\lambda$

wurden mit den in Tabelle 10 angegebenen Konstanten k die Extinktionen aus den gemessenen λ -Werten berechnet und mit den gemessenen Extinktionen verglichen.

Tabelle 11. Differenz zwischen den gemessenen und nach Gleichung (1) berechneten Werten fur log der 2. Maxima der UV-Spektren von substituierten p-Benzoquinone in CH(

R_1 = R_2 =	CH_3 CH_3	OCH_3 CH_3	OH CH_3	OCH_3 OCH_3	Cl Cl	Br Br
	+0.02	+0.06	-	+0.06	0.00	-0.01
	+0.03	-	-0.23	-0.23	-	-
	0.00	+0.10	-0.06	-0.33	-0.06	-0.30
	+0.09	-	0.00	-0.07	+0.18	+0.15
	0.00	-	-0.05	-0.41	-0.06	-0.07
	-	-	0.05	-	-	-
	-	-	-0.06	-	-	-
	+0.06	-	-0.03	-0.22	-0.03	-0.04

In the next table the differences between the measured and calculated values according to the equation (1) for log ε of the second maxima of the UV-spectra of substituted p-benzoquinones in chloroform are summarized. From the summary, it can be concluded: the equation (1) is significant to some extent in the case of the mono- tri- and tetra-chloro- respectively, bromo-substituted p-benzoquinone and the dimethyl-p-benzoquinone. There are relatively large deviations in the case of the disubstituted p-benzoquinones with electromeric substituents as well as in the cases of tri- and tetra-methoxy-p-benzoquinone.

We also investigated the methyl-substituted o-benzoquinones. It seems to me to be sufficient that there is a similar relation between position and extinction of the second maxima. It is very remarkable that there is good conformity between the calculated and the measured values, if one calculates the extinctions of the second maxima with the measured wavelengths of o-benzoquinones with a constant k determined for p-benzoquinone.

From slide 209, it can be seen furthermore that the points of o-substituted p-benzoquinones on the one hand and the non-o-substituted on the other hand are also on straight lines which are nearly parellel to the methyl-substituted p-benzoquinones.

In the case of methyl-substituted p-benzoquinones, the equation of this straight line is the following:

$$\log \varepsilon = 16{,}5 \cdot \overline{\nu} \cdot 10^{-4} - n \qquad (2)$$

In this equation the constant n for the non-o-substituted compounds is 49.6; for the o-substituted 46.0.

With the equations (1) and (2) the values for λ and ε can be determined:

$$\lambda = 17330/(k + n) \qquad (3)$$

and

$$\log \varepsilon = 0.95\ k - 0.048\ n \qquad (4)$$

With the equations (3) and (4), the values have been calculated and compared with the measured. The values for the position and the extinction of the second maxima of the methyl-substituted p-benzoquinones, calculated and measured, are the following:

substituted p-benzoquinone	(m) calculated	measured	log calculated	measured
methyl-	314	315	2,83	2,79
2,3-dimethyl-	337	337	3,00	3,05
2,5-dimethyl-	317	316	2,43	2,42
2,6-dimethyl-	317	319	2,43	2,54
trimethyl-	340	340	2,60	2,61
tetramethyl-	342	342	2,28	2,34

The position as well as the extinction of the second maxima of the methyl-substituted p-benzoquinones can be represented as a linear function of the characteristic constant k for the number and position of the substituents. In the case of methyl-substituted methoxy- and hydroxy-p-benzoquinone the representation is not so significant. The straight line according to equation (2) is no longer completely parallel and also the differences between the p- and m-disubstituted derivatives can no more be neglected.

For the explanation of the influences of substituents on the position of the second maxima, some short considerations about the spectra of o-quinones must be made.

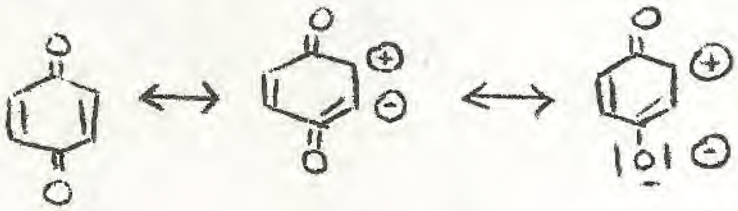
S 51 242

In this summarizing drawing, it will be mentioned that the influence of substituents in the same position has no remarkable effect on the shift of the second maxima. The maxima of 2,5-di-tert.-butyl- and 2-methyl-5-isopropyl-p-benzoquinone have nearly the same position.

The relatively stable 3,5-di-tert.-butyl-o-benzoquinone has its second maximum in a range of longer wavelengths. The second maxima of the o-quinones are always in a range of longer wavelengths. By substitution of a hydroxy group in o-position to another substituent, there is also a shift to longer wavelengths.

The influence of the substituents on the position of the second maximum can be explained approximately as follows:

It has been shown that usually o-benzoquinone absorbs in a range of longer wave lengths than p-benzoquinone.



In the same manner as an o-quinoid structure takes part in the basic state of a p-benzoquinone molecule its second maximum is in a range of longer wavelengths. From the three possible basic structures, A (p-quinoid), B and C (o-quinoid), B and C do not take part much as polaric structures on the mesomery of the unsubstituted p-benzoquinone, while this polaric structure takes part in a remarkable amount on the mesomery in the case of the anion of the hydroxy-p-benzoquinone.

Therefore, the second maximum of the anion of the hydroxy-p-benzoquinone has a 220 mμ longer wavelength than the p-benzoquinone. In the case of the undissociated hydroxy-p-benzoquinone, the structures B and C are favored against the unsubstituted p-benzoquinone due to the electromeric effect. In this case, polaric structures are discussed. They contribute a remarkably lower effect to the mesomery than in the case of the anion. Therefore, the second maximum of the undissociated hydroxy-p-benzoquinone is only shifted 82 mμ toward longer wavelengths. The other substituents can be classified in a corresponding row according to the electromeric effects.

If one considers the different possibilities of structure a second substituent with a + E effect in 3-position must have a stronger influence on the relationship of the p- and o-quinoic structure. This can be observed. The measurements show that in these cases the o-quinoic part increases. Corresponding substituents in 5- or 6-position should have nearly no influence on the mentioned distribution of electrons.

Substituents in these positions have only a "secondary" effect on the shift of the maximum. This effect increases with an increasing electromeric effect of the substituents.

These investigations can help to elucidate the constitution of unknown quinones. I will show you these facts by an investigation of a diquinone, which we have done.

It may be suggested that ultraviolet spectra of steric hindered diquinones are made up by addition of the spectra of the single parts of the molecule, like those of steric hindered derivatives of diphenyls.

S 52 212

If one compares the spectra of phoenicin with that of 2-hydroxy-6-methyl-p-benzoquinone and 2-hydroxy-3,6-dimethyl-p-benzoquinone, it can be seen that among the π-electrons there are no interactions. But one part of the molecules has an effect on the other in the sense of a substituent without electromeric effects. The spectrum of phoenicin is not comparable with that of 2-hydroxy-6-methyl-p-benzoquinone but with that of 2-hydroxy-3,6-dimethyl-p-benzoquinone. Especially the position of the second maximum is the same. In the diagram are the wave lengths and the doubled extinctions of 2-hydroxy-3,6-dimethyl-p-benzoquinone compared with those of pheonicin. The second maximum of phoenicin shows an increasing of $\Delta \log \varepsilon = 0.12$.

Substance	1.Maximum		2.Maximum	
	λ (mμ)	$\log \varepsilon$	λ (mμ)	$\log \varepsilon$
Phoenicin	268	4.52	406	3.36
2-Hydroxy-3,6-dimethyl-p-benzoquinone	266	4.54*	402	3.24*

*Extinction duplicated.

During the alkaline oxidation of 6-hydroxy-thymoquinone with oxygen a dimer product $C_{20}H_{22}O_6$ has been isolated. It could be presumed by reason of its formation that it possesses the constitution of a steric hindered diquinone. Some lectures before, we had mentioned this reaction.

This assumption of a steric hindered diquinone could be ascertained by the ultraviolet spectra. The spectrum of 2-hydroxy-3-isopropyl-5,6-trimethyl-p-benzoquinone had not been available for the comparison. In our experience this spectrum differs very little from that of 2-hydroxy-3,5,6-trimethyl-p-benzoquinone.

Substance	1.Maximum		2.Maximum	
	λ(mμ)	log ε	λ(mμ)	log ε
Di-(6-hydroxy-thymoquinone)	272	4.46	410	3.17
	(280	4.41)		
2-hydroxy-3,5,6-trimethyl-p-benzoquinone	272	4.59*	409	2.95*
	280	4.60*		

*Extinction duplicated.

In the table the values for 2-hydroxy-3,5,6-trimethyl-p-benzoquinone for extinction of the first and second maxima are given and compared with those of di-(6-hydroxy-thymoquinone). The position of the maxima are the same. The extinction of the first maximum is in the case of di-(6-hydroxy-thymoquinone) $\Delta \log \varepsilon = 0.12$ lower. The extinction of the second maximum is in the comparable spectrum $\Delta \log \varepsilon = 0.22$ higher.

Meanwhile we are working more about this point and the regularities of the ultraviolet spectra of the different substituted quinones are helpful.

These investigations have been made not only as a help for elucidating oxidized lignin precursors or lignin fractions but also to elucidate the structure of natural occuring quinones.

On the other hand, these studies give ideas about how much the isolated products are perhaps transformed during isolation. After the isolation, it may be that different reactions, which must be used for the elucidation of the natural products are done in media in which changes or transformations of the compounds can occur. These methods may be helpful to study in which direction the one or the other reaction has gone.

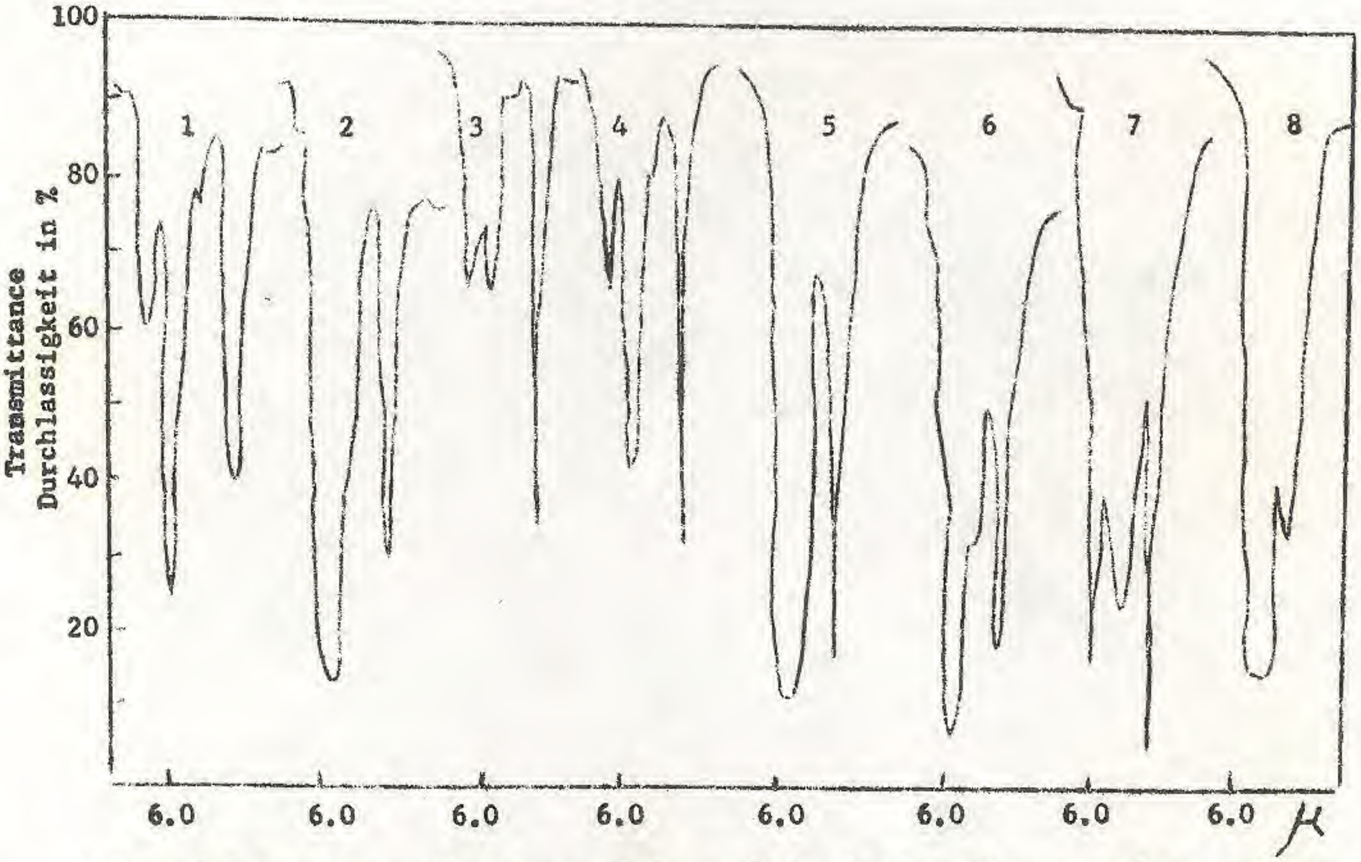
Other possibilities to work out regularities are investigations with infrared. Also in this case I will mention only some facts which seem to be interesting for the chemistry of humus. (Flaig, W. and Johann-Christoph Salfeld: Infrarotspektren von p-Benzochinonen, in press).

Only recently, some infrared spectra of several p-benzoquinones were investigated. (Yates, P. I. M. Ardao u. L. F. Fieser, J. Am. Chem. Soc. 78, 650 (1956)). We made extensive studies with methylsubstituted and methylsubstituted monomethoxy-p-benzoquinones, methylsubstituted monohydroxy p-benzoquinones and methoxysubstituted p-benzoquinones. We found also here some regularities but I will only discuss that which is interesting in connection with the problems of the transformation of organic substances in soils.

Summarizing, it can be said that by the relatively long wave position of the sharp absorption bands of the hydroxy-valency vibrations of the methylsubstituted monohydroxy-p-benzoquinones (2.92 - 2.95μ) it can be concluded that the hydrogen atoms are orientated to the quinone carbonyl group. Furthermore, there could be found similiar regularities corresponding to the groups A and B and new regularities. I will only give some data which seem to me to be the most important.

The most characteristic absorption bands of the IR-spectra of all quinones is the range between 5.9 and 6.3 μ. Numerous single investigations have been made to determine the carbonyl bonds of the p-benzoquinones, but systematically they have not been studied. (Hadzi, D. u. N. Shephard, J. Am. Chem. Soc. 73, 5460 (1951); Tatibonet, F. u. P. Souchay, C. R. Acad. Sci, 236, 1652 (1953); Hoyer, H.: Ber. Bunsenges. physik. Chem. 60, 381 (1956); Josien, M. L. u. J. Deschamps, C. R. hebd. Seances Acad. Sci. 242, 3067 (1956); Hadni, A., J. Deschamps, u. M. L. Josien, C. R. hebd. Seances Acad. Sci. 242, 1014 (1956); J. Deschamps, Theses Bordeaux (1956).

S 53 897



C=O- and C=C-valency vibrations of the methyl substituted mono-methoxy-p-benzoquinones in CCl_4 (methoxy-p-benzoquinone (1), 2-methoxy-3-methyl-p-benzoquinone (2), 2-methoxy-5-methyl-p-benzoquinone (3), 2-methoxy-6-methyl-p-benzoquinone (4), 2-methoxy-3,5-dimethyl-p-benzoquinone (5), 2-methoxy-3,6-dimethyl-p-benzoquinone (6), 2-methoxy-5,6-dimethyl-p-benzoquinone (7), methoxy-trimethyl-p-benzoquinone (8)).

In the case of the methyl-substituted mono-methoxy-p-benzoquinones there is a dependency of the relative intensity of these absorption bands on the chemical constitution. In the case of those quinones which have a hydrogen atom besides the methoxyl group, the bands are in the range of longer wave lengths, which means the C=C-bonds are stronger. In the case of those compounds which have a methyl group besides the methoxyl group, the bands are in the range of the shorter wave lengths, indicating that the carbonyl bonds are weaker.

The compound no. 1 is methoxy-p-benzoquinone.

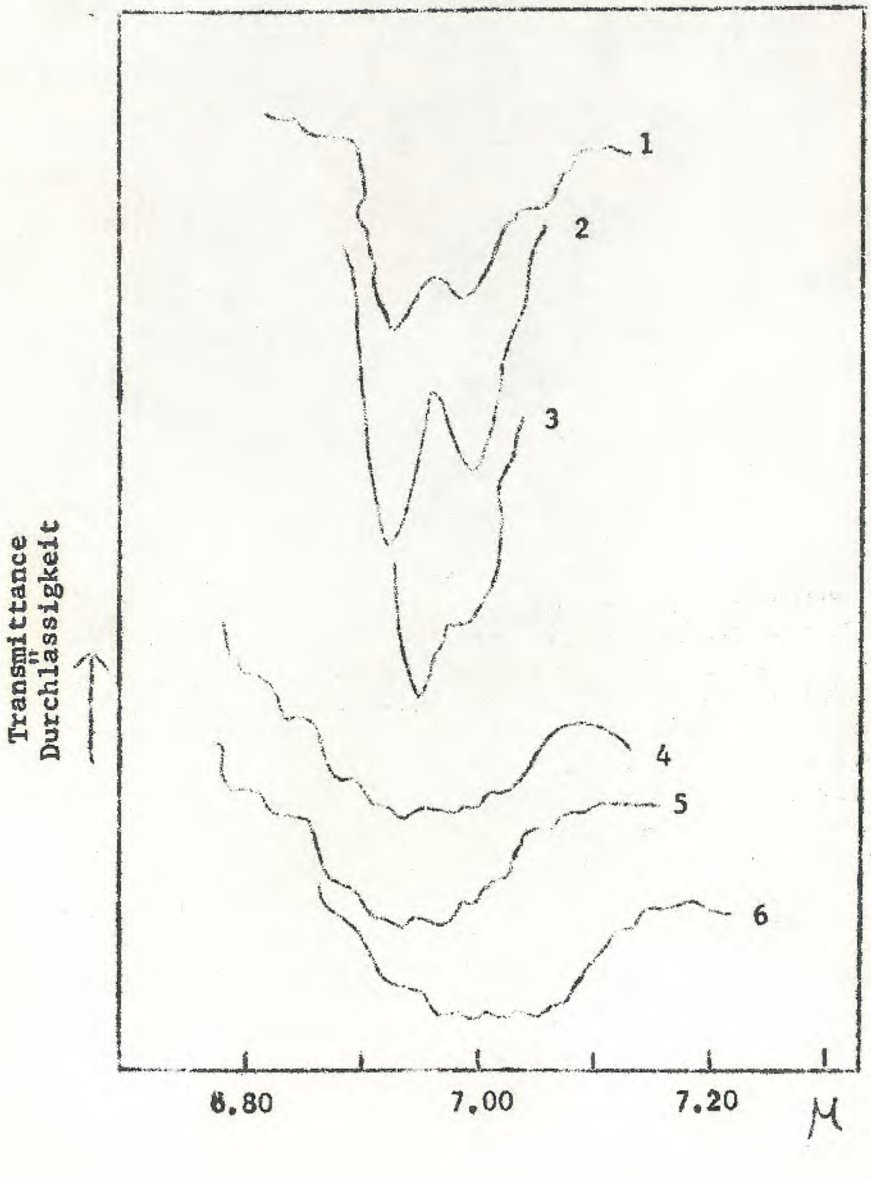
The cases in which a hydrogen atom is besides the methoxy group are the compounds no. 3, 4 and 7. The C=C -bands are higher than the carbonyl bands.

The cases in which the hydrogen atom is not beside the methoxy group, the o-position being substituted with a methyl group, are the compounds no. 2, 5, 6, and 8. The carbonyl bands are higher than the C=C bands.

The first kind of compounds belongs to the group A and the second to the group B. I remember that we had in this case a shift of the second maxima in the UV-spectra, depending upon the substitution in o-position to the methoxy group.

In the range from 6.8 to 7.3 μ there are the asymmetrical and the symmetrical CH-deformation vibrations of the methyl groups. In the row of the methyl-substituted p-benzoquinones, the band of the asymmetrical CH-deformation vibration (6.8 to 7.0 μ) show a remarkable enlargement in the case of the o-di-substituted compounds. Acetone and acetophenone show similar bands. The positions of the individual maxima of the bands are nearly the same. The structure of the bands is determined by the different relative intensity of the individual maxima.

S 54 900



Asymmetrical CH-deformation vibrations of toluquinone (1), 2,5-dimethyl-p-benzoquinone (2), 2,6-dimethyl-p-benzoquinone (3), 2,3-dimethyl-p-benzoquinone (4), tetramethyl-p-benzoquinone (5) and acetone (6) in CCl_4.

Table 5. Asymmetrical CH-deformation vibrations of the methyl groups of methyl substituted p-benzoquinones, acetone and aceto-phenone in CCl_4 in μ (strongest maxima are underlined).

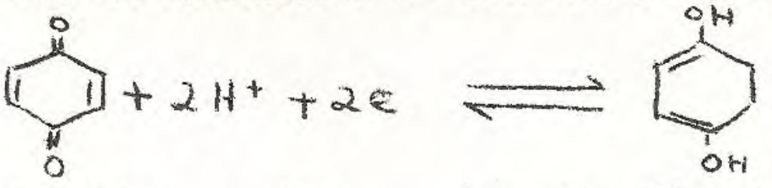
Methyl-p-benzoquinone		$\underline{6,929}$		$\underline{6,993}$		7,053	
2,5-dimethyl-p-benzoquinone		$\underline{6,922}$		$\underline{6,933}$	7,027		7,066
2,6-dimethyl-p-benzoquinone			$\underline{6,948}$	$\underline{6,997}$	7,034	7,057	
trimethyl-p-benzoquinone	6,909		$\underline{6,938}$		7,026		
2,3-dimethyl-p-benzoquinone	6,912		$\underline{6,940}$	7,003	7,029		7,066
tetramethyl-p-benzoquinone	6,913	6,922	$\underline{6,939}$	7,001	7,029		7,063
acetone			$\underline{6,941}$	$\underline{7,001}$	$\underline{7,026}$		$\underline{7,064}$
acetophenone			6,940	$\underline{7,002}$	$\underline{7,028}$		$\underline{7,065}$

Another regularity can be observed in the case of monohydroxy-p-benzoquinone. These have in contrast to the p-benzoquinone without hydroxy-group in the range of 7.09 to 7.18 μ a strong band, which can presumably be an OH-deformation vibration. The position of this band shows also a dependency on the constitution. The bands of the quinones of the group A occur at shorter wavelength than those of the group B.

Table 7. CH-deformation vibration of the methyl-substituted monohydroxy-p-benzoquinones in CCl_4 in μ

hydroxy-p-benzoquinone	7,099	2-hydroxy-3-methyl-p-benzoquinone	7,163
2-hydroxy-5-methyl-p-benzoquinone	7,110	2-hydroxy-3,5-dimethyl-p-benzoquinone	7,178
2-hydroxy-6-methyl-p-benzoquinone	7,128	2-hydroxy-3,6-dimethyl-p-benzoquinone	7,754
2-hydroxy-5,6-dimethyl-p-benzoquinone	7,086	hydroxy-trimethyl-p-benzoquinone	7,155

Another characteristic for quinones is the redox normal potential. The reduction of quinones to hydroquinones is in aqueous solution a reversible process which is quick and quantitative. It can be compared with a reduction of ferric ions to ferrous ions and formulated as an electrochemical reduction:



$$Fe^{+++} + 1e \rightleftarrows Fe^{++}$$

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A platinum electrode in a solution with quinoic or hydroquinoic substances of a certain concentration of hydrogen ions has a certain potential. The potential is measured by connecting the electrode with a comparison electrode. This can be a calomel-or a hydrogen electrode. According to the following equation, the potential of the electrode E of the organic half cell depends on the concentration of the components which are in equilibrium; in our case the quinone, the hydroquinone and the hydrogen ions:

$$E^{25^\circ} = E_o + 0.05912 \log (H^+) + 0.02956 \log \frac{(\text{Quinone})}{(\text{Hydroquinone})}$$

E_o is a characteristic normal potential for a certain system consisting of a quinone and a hydroquinone. E_o is the potential of a half cell in which the concentration of hydrogen ions is one and the concentration of quinone equals that of hydroquinone. The second expression on the right side of the equation becomes 0 when the hydrogen ion concentration is 1. Also the third expression disappears if the concentration of quinone equals that of hydroquinone. The only variable is the hydrogen ion concentration which can be measured if quinone and hydroquinone are in equal amounts in the solution.

The expression 0.05912 log (H+) is a potential of a hydrogen electrode or half cell. The normal potential can be measured therefore in a primitive arrangement: the half cell with quinone and hydroquinone in molar relation in a certain buffer solution and a hydrogen electrode in the same buffer solution connected with the solution bridge. The potential of hydrogen is then equal on both sides. Furthermore, the concentration of quinone must be equal to that of hydroquinone. The difference of the potential between these two half cells is therefore the normal potential of the quinone or hydroquinone system.

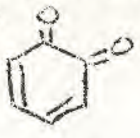
In different laboratories the normal potential for p-benzoquinone system in aqueous solution has a value of 0.699 V.

In certain cases the corresponding quinhydrone is not always available. The redox normal potential therefore is determined in this way. The solution of the quinone is titrated with a reducing agent or the hydroquinone solution with an oxidizing reagent potentiometrically. The point of intersection of the two titration curves corresponds to the equivalents of oxidation- and reduction agents.

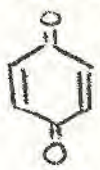
The normal potential can be determined also in alcoholic solution of unknown concentration of hydrogen ions if as a correspondent half cell a hydrogen electrode is used with the same solvent as in the case of the organic compounds. In this way, quinones not soluble in water can be determined by a potentiometric method.

The normal potential is a characteristic constant for a certain quinone-hydroquinone mixture. The redox normal potential describes the ability for reduction of a quinone or the ability for oxidation of a hydroquinone. Some values for different quinones shall be mentioned.

E_o^{alc} 0.954 V

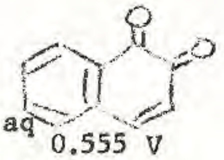


E_o^{aq} 0.792 V



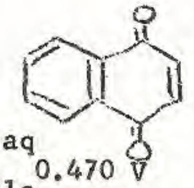
E_o^{aq} 0.699 V

E_o^{alc} 0.715 V



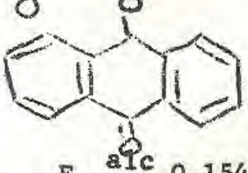
E_o^{aq} 0.555 V

E_o^{alc} 0.576 V



E_o^{aq} 0.470 V

E_o^{alc} 0.484 V



E_o^{alc} 0.154 V

Diphenoquinone has an unsaturated, conjugated, quinoic system over 2 rings. It possesses a very high potential and is therefore a strong oxidation agent. In other words, another substance with a higher normal potential is necessary for the oxidation of the corresponding hydroquinone. Presumably this kind of quinones do not occur very often in the soil as a product derived from lignin or natural phenols during the formation of humus.

The potential of the o-quinones of the benzene and naphthalene type are on the average 85 to 95 mV higher than the isomeric p-quinones. The o-quinones have, therefore, a higher content of energy than the p-quinones. Comparing the o- and p-benzoquinones with the corresponding naphthoquinones the difference is in every case between 230 to 240 mV. The bicyclic compounds have therefore a much lower content of energy than the monocyclic compounds. By the condensation of a benzene ring with a double bond on the o- or p-benzoquinone a stabilization occurs. This can be explained by the fact that the double bond is connected with an aromatic nucleus and therefore relatively more stable.

In the anthraquinone both reactive quinoic double bonds belong to a benzoic ring system. Therefore, this kind of quinones has a low oxidation potential. Vice versa, the reduction product, the anthrahydroquinone, is a strong reducing agent.

The substituents often increase or decrease the redox potential remarkably. Fieser and Fieser (1935) determined the change of the redox normal potential of naphthoquinones differently substituted in the 2-position.

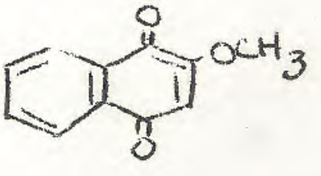
Substituent	Potential Change in mV	Substituent	Potential Change in mV
$NHCH_3$	-252	$NHCOCH_3$	-67
NH_2	-210	C_6H_5	-32
$N(CH_3)_2$	-181	$OCOCH_3$	-9
OH	-128	Cl	+24
OCH_3	-131	SO_3Na	+69
CH_3	-76	$SO_2C_6H_4CH_3$	+121

Substituents which influence a substitution in meta-position such as -NO_2, -CH, -SO_2Ar, -COAr, -COOH, -SO_3H, and halogen increase the potential of the unsubstituted quinone. Substituents such as -NHR, -NH_2, -$N(CH_3)_2$, -OH, -OR, -CH_3, -$NHCOCH_3$ -C_6H_5, and -$OCOCH_3$ decrease the potential in the mentioned row.

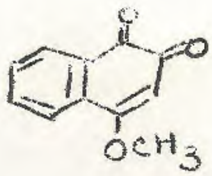
Strongly unsaturated groups and atoms of halogen are generally electron-attractive. They increase the attractive power of the two oxygen atoms for other electrons. By this process, the quinone is transformed in the hydroquinone-ion. The hydroquinone-ion combines in a second process with protons. The second process depends in its velocity on the acidity of the solution. At relatively high pH-values, i.e., in alkaline solution, the reduction is only a process of transfer of electrons. No association of protons to the hydroquinones occurs.

The redox potential has a special value to explain the behavior of hydroxy- and amino-quinones. One of these cases is the tautomery between the 2-hydroxy-1,4- and 4-hydroxy-1,2-quinones.

Some lectures before, I mentioned that 4-hydroxy-1,2-naphthoquinone exists in an amount of 0.2% in the mixture of the hydroxy-naphthoquinones. Now we can say more about this tautomery.



2-methoxy-1,4-naphthoquinone
(yellow, Fp. 183.5°, E_0alk. 0,353V.)



4-methoxy-1,2-naphthoquinone
(orange-yellow, Fp. 190°, E_0alk. 0,433V.)

The two different methyl-ethers were prepared. The potential of the B-quinone ether is 80 mV higher than that of the α-isomer. The difference of the normal-potential is a difference of 3.7 Kcal for the free reduction energy. The relation of the amount of the tautomeric forms is given approximately by the following equation:

$$\log K^{25^\circ} = \frac{E_0(\text{B-form}) - E_0(\alpha\text{-form})}{0{,}02956}$$

$$K = \frac{\alpha\text{-form}}{\text{B -form}}$$

Also in the case of the hydroxynaphthoquinones, there is a difference of 80 mV. Therefore only 0.2% of the B-form is present at equilibrium.

Since the potential of the solution of a substance depends on the nature and the degree of dissociation of functional groups, it is possible to recognize from the pH-dependence of the change of the potential which tautomeric form is predominant.

In the case of 4-amino-1,2-naphthoquinone, it is possible to determine to which extent this compound reacts as hydroxy-quinone-imine. The amino-quinone has a basic substituent, the hydroxy-quinone-imini an acid one. It could be determined that the amino-quinone exists in a pH-range from 0 to 11 and the hydroxy-quinone-imine from 11 to 13.

We investigated the redox potential of a greater number of quinones, besides the ones mentioned in the abbreviation scheme. The half-step potentials are dependent on the hydrogen ion concentration. With the formula of Nernst, the redox-normal-potentials are calculated.

$$E = E_0 - \frac{0.058m}{n} \text{ pH} + \frac{0.058}{n} \log \frac{(Ox)}{(red)}$$

For the determination of the redox-normal-potential, the dependency of pH must be known. This can be obtained by differentiation of the eqation according to Nernst

$$\frac{dE}{dpH} = \frac{0.058\ m}{n} \quad pH$$

where m is the number of protons and n is the number of electrons which take part in the reaction.

We (unpublished , diploma thesis by E. Kalke, 1956) measured the half-step potentials of different quinones at different pH-values.

S 55 93 (see next page)

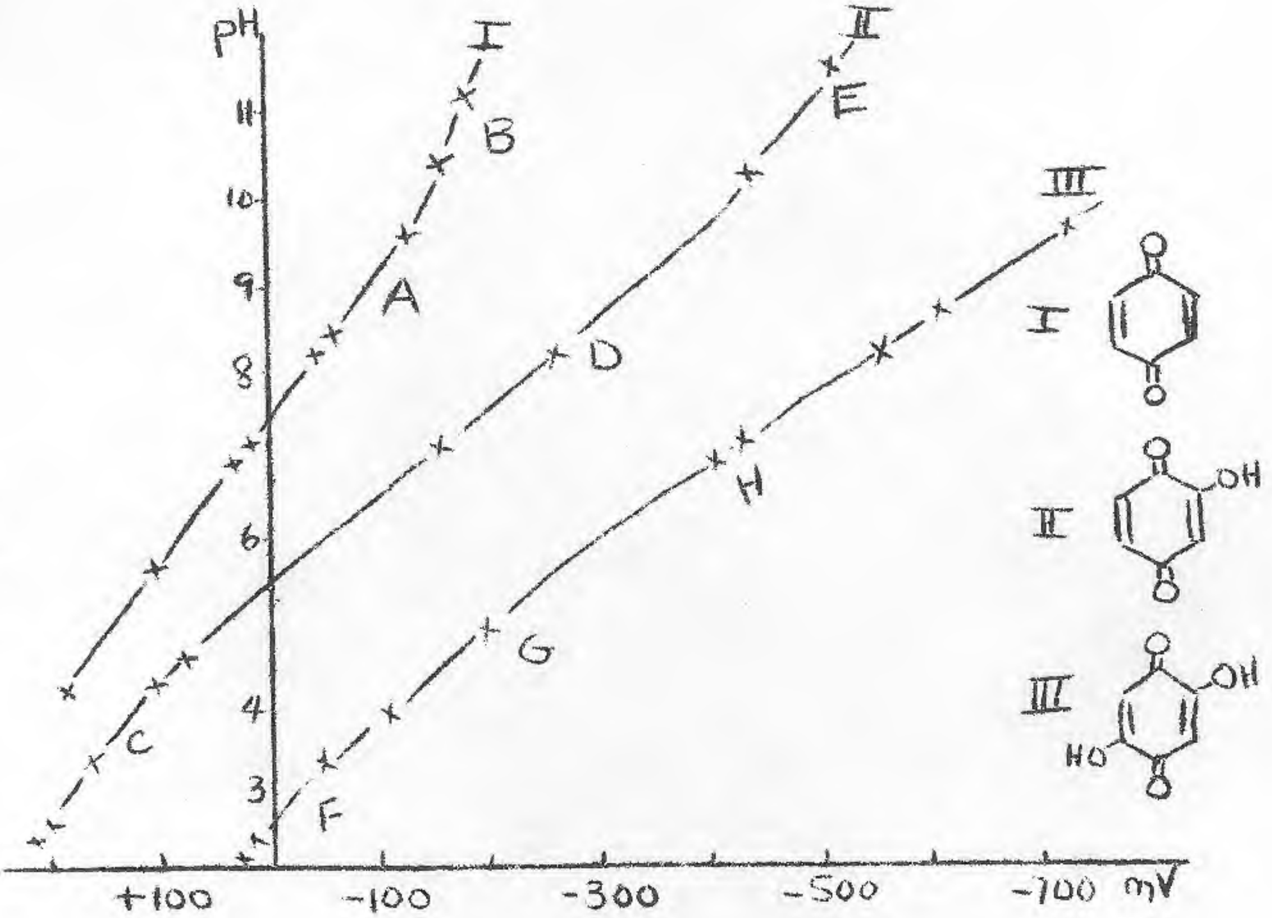
In the case of hydroquinones and hydroxy-quinones, the dissociation must be considered. Therefore, a supplement of the equation is necessary which contains the dissociation constant K. The most simple form of the supplement is

$$\Delta E = + 0.058 \log (K + (H+))$$

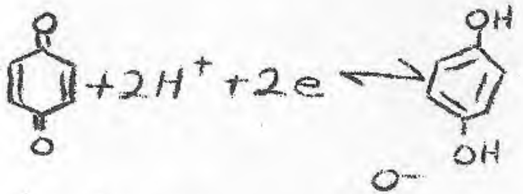
The pH-dependency of the potential of the quinones has been measured. The half-step potentials at different pH-values have been plotted against pH. Straight lines with different slopes are found according to the dissociation at different pH-values. The slopes of the straight lines are higher in the case of the dissociation of the hydroxyquinones and lower in the case of the dissociation of the hydroquinones. The cross-section of the straight lines indicates the constants of dissociation.

According to the diagram shown, the pH-dependency of the quinones varies within certain limits. The slopes of the straight lines are either 58 mV, 87 mV, 116 mV or 29 mV per-pH-unit. The slopes depend on the participation of protons during the reaction. Semiquinones could not be identified. Therefore, the slopes can only be dependent on the change in the number of protons which take part.

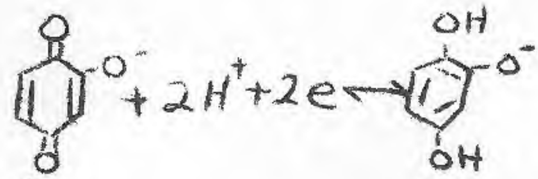
For the explanation of the given example, the following remarks are made. In the case of p-benzoquinone or other methyl- or methoxy- substituted quinones, the straight line has two slopes, at first 58 mV per pH-unit and then 29 mV per pH-unit, according to the equation of the slope of the straight line: $dE/dpH = 0.058\ m/n$. During the first section of the determination of the half-step potential two protons and two electrons participate. During the second section only one proton and two electrons participate, since one electron of the hydroquinone dissociates. The curves determined experimentally show no sharp bend (break). To determine the cross-section and with it the dissociation constant, the lines are drawn out.


pH
11
10
9
8
6
4
3
I
II
III
A
B
C
D
E
F
G
H
+100
-100
-300
-500
-700
mV
I
II
III
OH
OH
HO

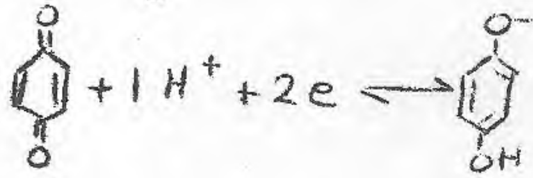
A)


+2H+ +2e
OH
OH

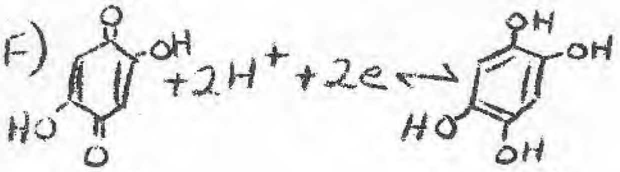
E)


O-
+2H+ +2e
OH
O-
OH

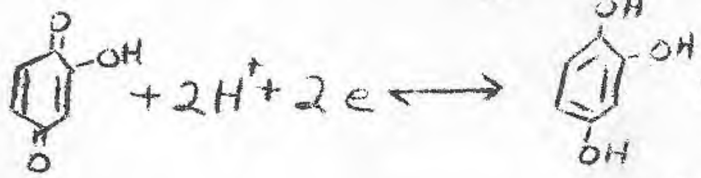
B)


+1 H+ +2e
O-
OH

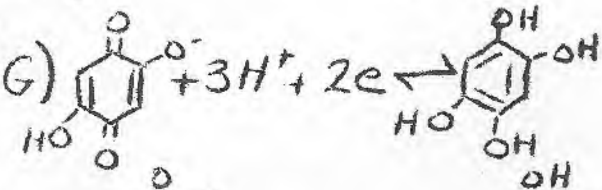
F)


OH
HO
+2H+ +2e
OH
OH
HO
OH

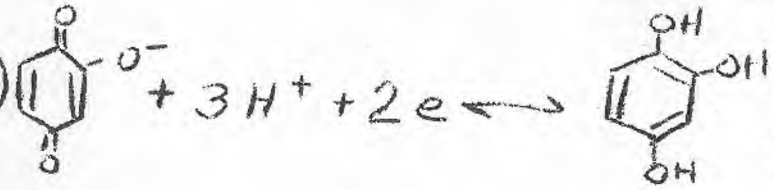
C)


OH
+2H+ +2e
OH
OH
OH

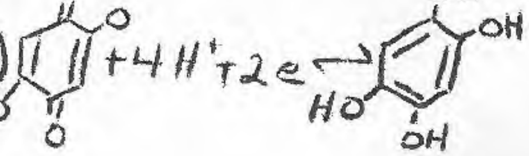
G)


O-
HO
+3H+ +2e
OH
OH
HO
OH

D)


O-
+3H+ +2e
OH
OH
OH

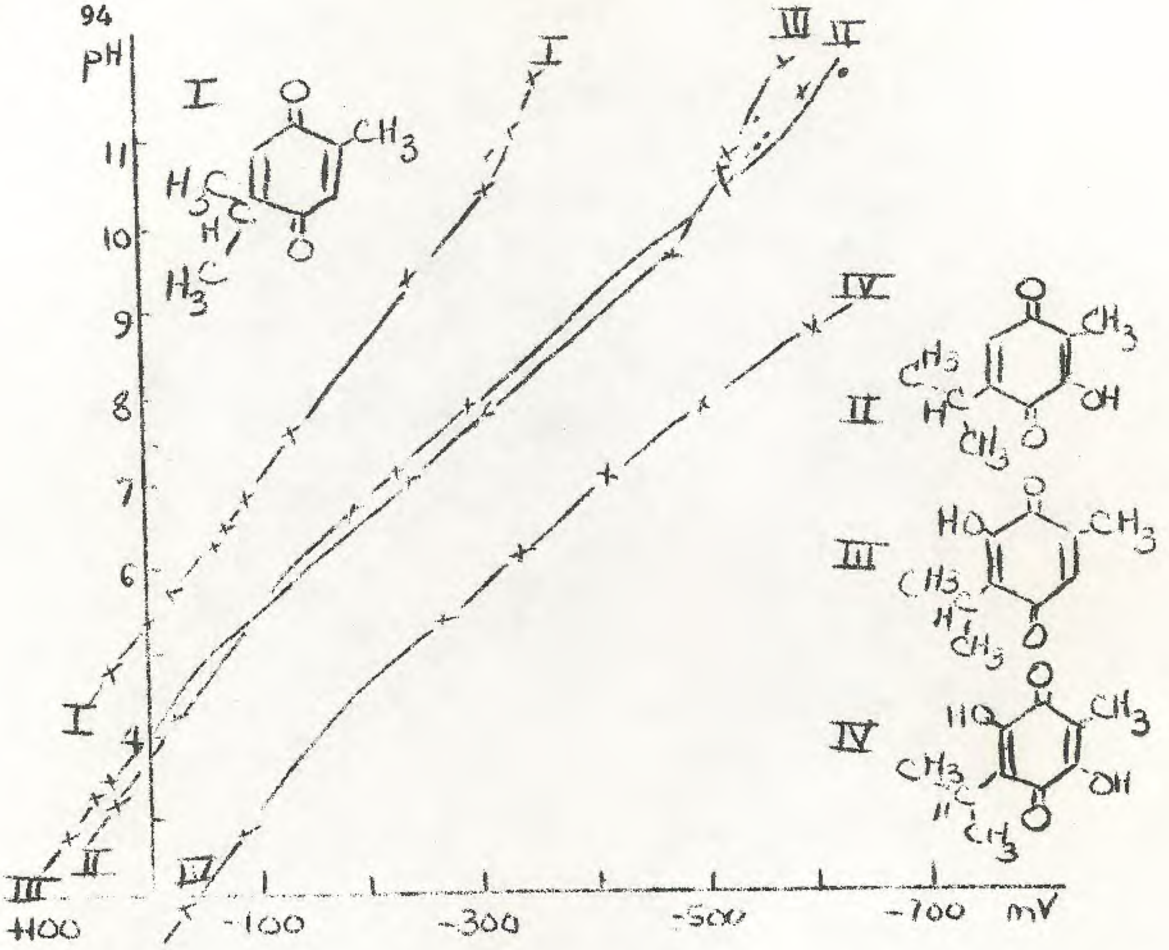
H)


O
-O
+4H+ +2e
OH
OH
HO
OH

In the case of hydroxyquinone, we have two times a slope of 58 mV per pH-unit, in the beginning and at the end. And a slope of 87 mV per pH-unit in the middle depending on the participation of protons and electrons.

In the case of 2,5-di-hydroxy-p-benzoquinone, we have also three different types of slopes. First 58 mV per pH-unit, then 87 mV per pH-unit, and 116 mV per pH-unit.

S 56 94



Dependency of half-step potentials on the pH of thymohydroquinone and its hydroxy-derivatives.

This diagram shows that the curves of the differently substituted quinones are principally the same, but the dissociation constant and the value of the half-step potential vary with the pH. Furthermore, this diagram shows that differences such as 3-hydroxy- and 6-hydroxy-thymo-hydroquinone could be found.

To calculate the redox-normal-potential from the measured half-step potentials, the equation of Nernst must be enlarged in these cases, in which the straight lines show different slopes. The number of the members of the equation depends on the number of slopes.

$$E = E_o - \frac{0{,}058\ m_1 \cdot pH_1}{n} - \frac{0{,}058\ m_2}{n} (pH_2 - pH_1) \ldots\ldots\ldots$$

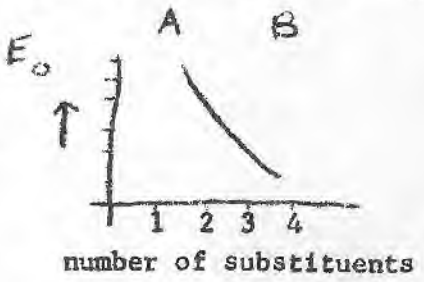
$$\ldots\ldots - \frac{0.058\ m_x}{n} (pH_x - pH_{(x-1)}) + \frac{0{,}058}{n} \log \frac{[Ox]}{[Red]}$$

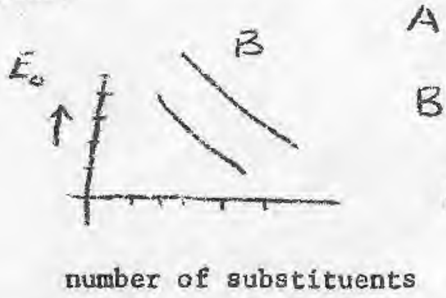
m_1 is the number of the protons taking part in the range of the curve with a slope of 58 mV per pH-unit. I.e., in the acid range, pH_1 is the pH-value of the cross-section of the two straight lines. m_2 is the number of the protons in the range of the following straight line, pH_2 is the pH-value of the measured potential.

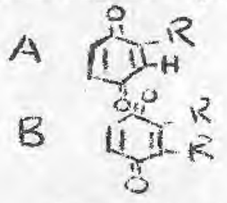
If there are three different slopes, a further member for the calculation of the redox-normal-potential is necessary. In this case, pH_2 is the pH-value of the second cross-section of the straight line, i.e., the cross-section between the second and third straight line, and pH_3 the pH-value of the measured potential, and m_3 is the number of protons in the range of the upper curve section.

As an example, the redox-normal-potential at the different values of pH of 3-hydroxy-thymoquinone is 489 mV ± 1,23.

Also in the case of the redox potentials of the investigated quinones, there can be observed some regularities.







R = substituent other than hydrogen

If the number of the substituents of the different quinones is plotted against the value of the redox-normal-potential, the methyl-substituted and the monohydroxy-methyl-substituted quinones are in each case on one line with a slope of 60 mV per substituent.

In the case of mono-methyl-substituted and that of methoxy-substituted there are in each case two nearly parallel straight lines, one of which contains the quinones of the group A, the other the group B. The slope is in the case of the methyl-substituted monomethoxy-p-benzoquinones 52 mV per methyl group and in the case of the methoxy-p-benzoquinones 100 mV per methoxy group.

Furthermore, there are some regularities if E_o in mV-values are plotted against the log ε of the second maximum of the UV-spectra. Four lines are found:

1) methyl-substituted p-benzoquinones of group A.

2) the methyl-substituted, monomethoxy-methyl-substituted and methoxy-substituted of group B.

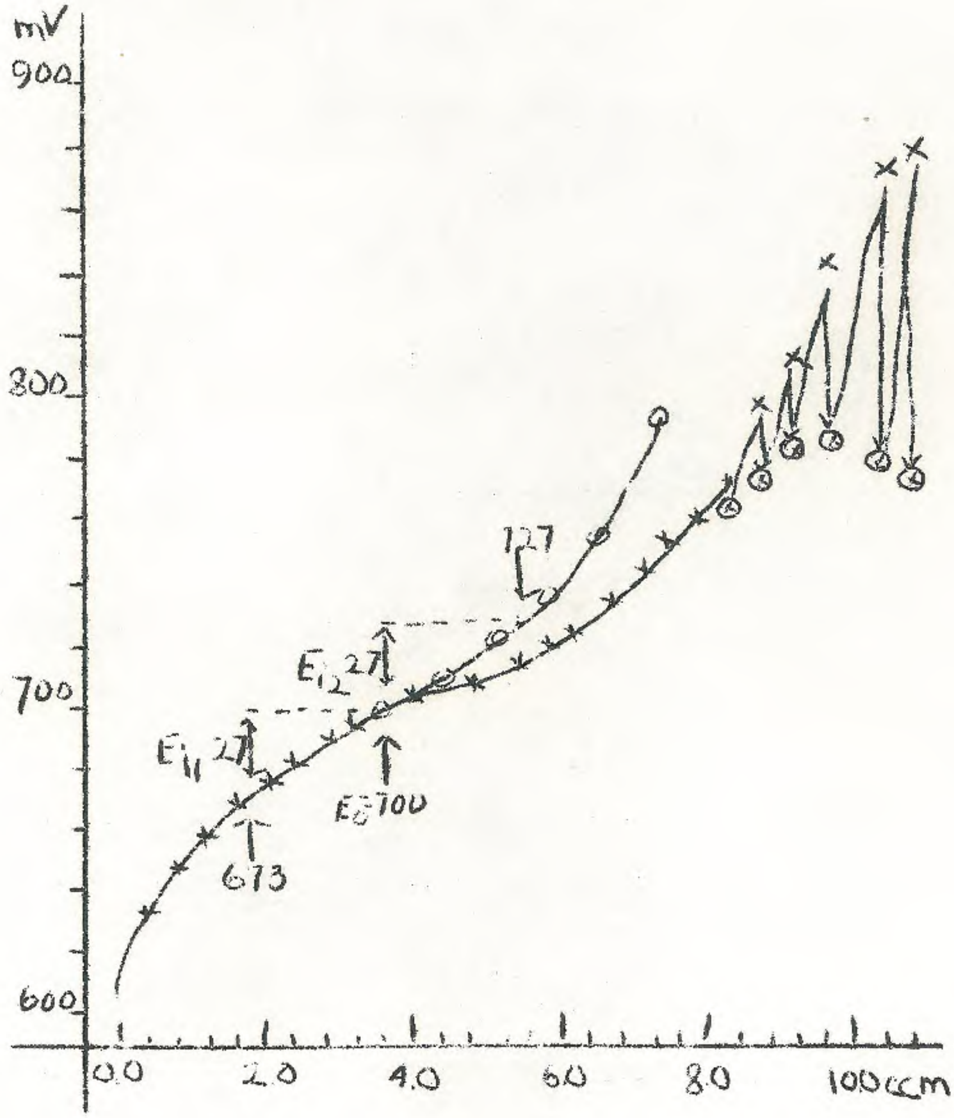
3) the mono-methoxy-methyl-substituted, monohydroxy-methylsubstituted and methoxy-substituted p-benzoquinones of group A.

4) the monohydroxy-methyl-substituted p-benzoquinones of group B.

There exists also a linear function between log ε of the second maximum of the UV-spectrum among the single groups and their redox-normal-potential.

In some cases we started the oxidation-reaction of different quinones. So it has been possible to identify, during the alkaline oxidation of 2,3-dimethyl-p-benzoquinone, hydrogen peroxide in accordance with the work of Weissberger and co-workers. Furthermore, another polymerization product could be found. With this method, it is possible to determine the oxidation rate and depending on it, the formation of the different reaction products. In the case of thymo-hydroquinone during alkaline oxidation, quinone and hydrogen peroxide could not be found, but the step of the corresponding hydro- quinone could be determined. The reaction between quinone and hydrogen peroxide must be very quick.

S 57 389



Investigations of this kind are of interest as we found that the system which determines the potential in the soils, the system Fe^{+++}/Fe^{++}, can be influenced by the fraction of fulvic acids. Even by titration in weak acid solutions, there are deviations from the normal curve of Fe^{+++}/Fe^{++}. The organic substances lower the potential. In the fraction of fulvic acids, the lignin fragments and similar products of phenolic, quinoid, structure, respectively, can occur. The investigations with the different phenols or quinones are therefore model reactions.

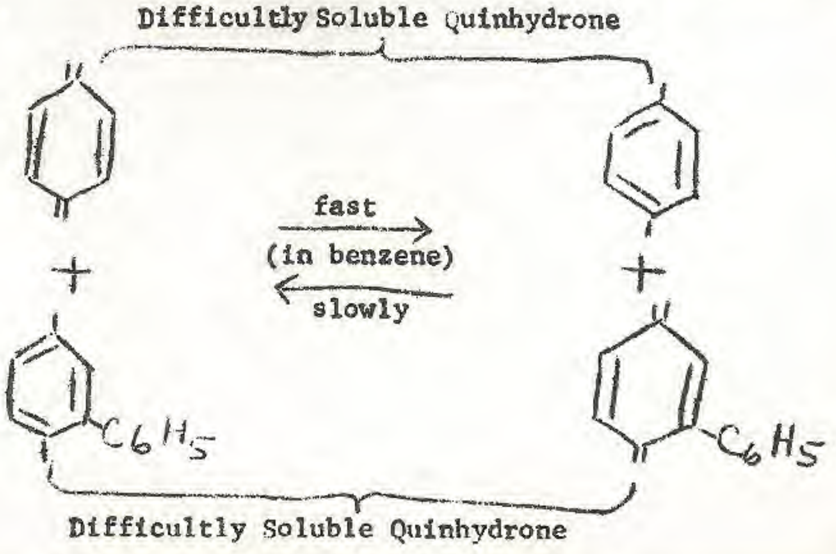
Something must be said about the formation of quinhydrones. If a yellow alcoholic solution of quinone is mixed with a colorless solution of hydroquinone in the same solvent, the color of the mixture is immediately dark brown red. Dark green crystals are separated with a melting point of 171° C. The melting point of quinone is 115° C and that of hydroquinone is 170° C. This compound named quinhydrone has a composition of an equimolecular mixture of quinone and hydroquinone. By oxidation quinone is formed, by reduction hydroquinone. The complex is much less soluble in water and in organic solvents than both of the components. Its dissociates, however, to a certain equilibrium.

Some lectures before, we spoke about the humic acids as electron exchange materials. Under natural conditions there would, therefore, exist always quinone- and hydroquinone systems. If the possibility for the formation of the usual, intermolecular quinhydrone complexes exist, the humic acids of the soils would be one single quinhydrone complex.

Therefore, it is necessary to discuss the preposition of the formation of quinhydrones in connection with the chemistry of humic acids. Not much is known about this point. There are only investigated quinhydrones out of analagous components. Bothner-By (Bothner-By, A. A.: J. Amer. Chem. Soc. 73, 4223, (1951)) could show with an example of quinhydrone from duroquinone and durohydroquinone by labeling with C^{14} of one component, that in the case of solved quinhydrone, a quick exchange of the oxidation step occurs but not in the case of unsolved components. In the case of humic chemistry, it is interesting to study this process with mixed systems.

We observed that after mixing of solutions of benzoquinone and phenylhydroquinone in petroleum ether, a nearly insoluble, dark blue quinhydrone is immediately precipitated. After changing the oxidation steps and mixing solutions of hydroquinone with phenyl quinone, the solution remains clear and only after hours, or after heating the precipitation of quinhydrone began. Further investigations of the quinhydrone showed that in this mixture, there is no mixed quinhydrone but a mixture of two quinhydrones. Therefore, the process can be formulated as follows:

S 58 727

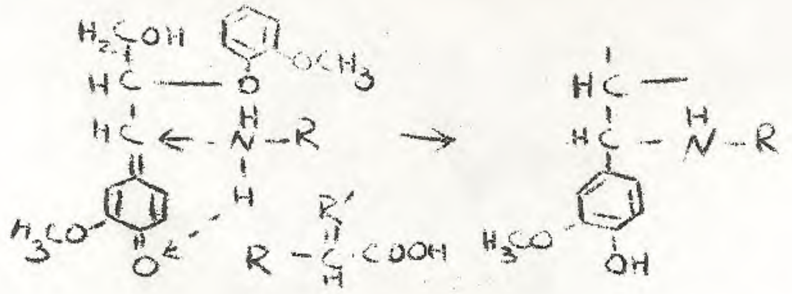


All four components could be isolated from the precipitate. Due to the low solubility of both quinhydrones in benzene the process is nearly complete. Benzoquinine has a higher oxidation potential, 711 mV, phenyl quinone 698 mV, therefore, the process is in one direction quick and in the other slow.

Therefore, it may be that the mixed quinhydrones described in the literature are mixtures of quinhydrones. The importance of the redox potential for the cause of reactions of this kind and therefore for the formation of humic substances can be seen by this type of investigations. In connection with these experiments a method to determine the redox potential in non-aqueous solutions, in solutions of organic solvents, has been worked out. (Ploetz, Th.: - Zur Bestimmung des Redoxpotentials reversibler organischer Systems. Z. Naturforsch. 9b, 753-755 (1954)).

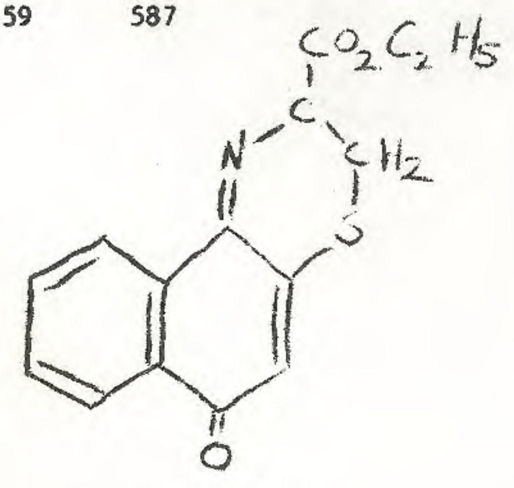
Now the possibilities for nitrogen entering the molecule of humic acids must be discussed. The knowledge about these processes is still incomplete. Model reactions have shown that ammonia and primary amines can enter the molecule only at the time when the oxidation reactions take place and not afterwards. Furthermore it has been proved that secondary amines do not react. About these model reactions which have been made by the oxidizing of hydroquinones in ammoniacal solution, we must speak later on.

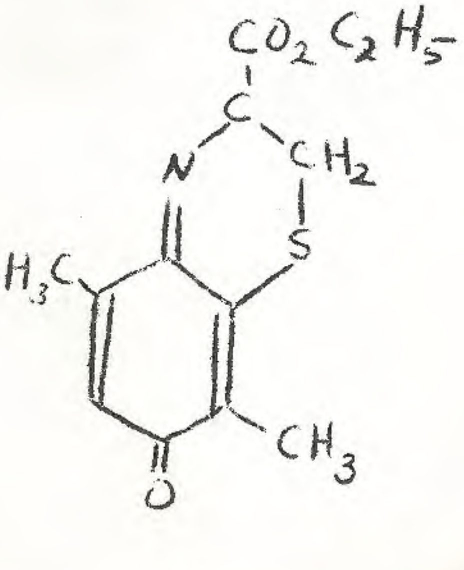
During the considerations about chemistry of lignin it has been mentioned that an additive coupling of different substances in dehydrogenated coniferyl alcohol in its p-quinone-methide structure can occur.



So it would be possible that amine components are fixed in the first stage of oxidation. It may be that these condensed amino components give further reactions which form three dimensional products by condensation.

S 59 587

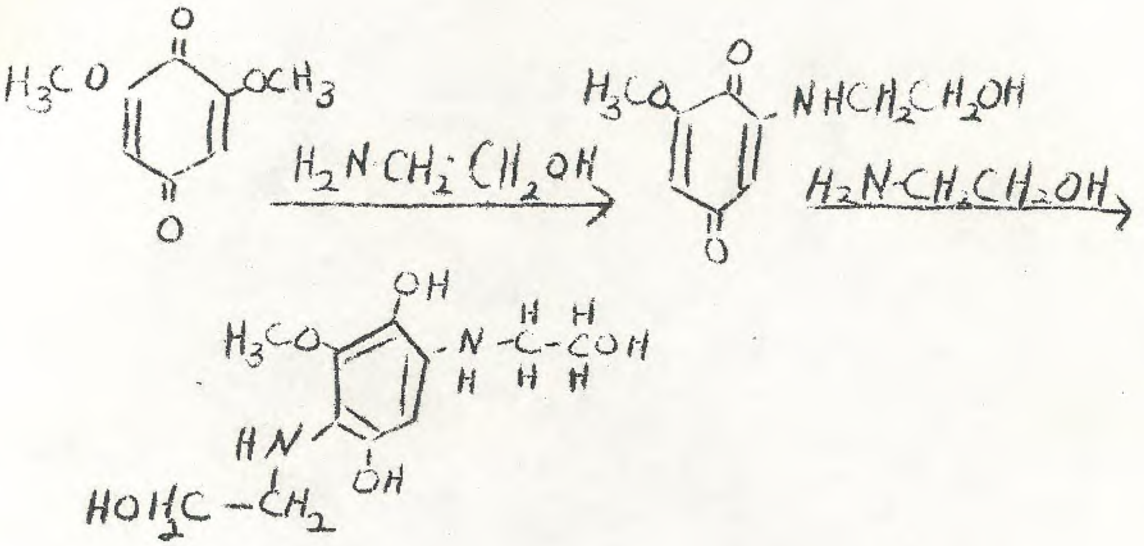


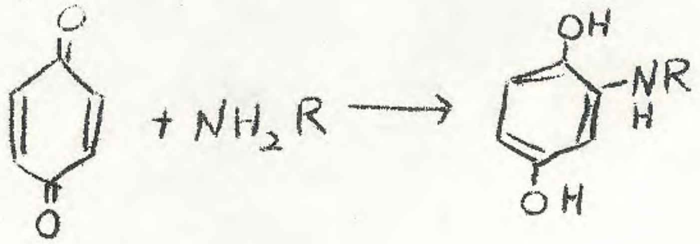


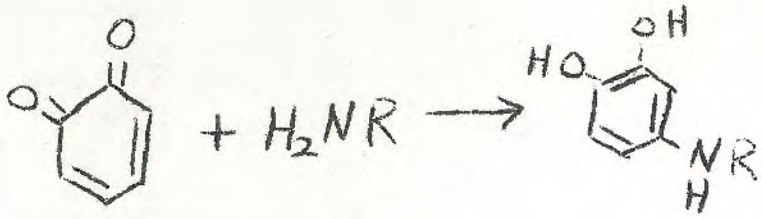
Another possibility is the reaction of compounds such as cysteine-ester-chlorohydrate with α -naphthoquinone and p-xyloquinone. (Kuhn, R., und Beinert, H.: Ber. dtsch. chem. Ges. 77-79, 606 (1944-46) - Kuhn, R., und Hammer, J.: Ber. dtsch. chem. Ges. 84, 91 (1951)).

In this case a fixation of the nitrogen compounds takes place.

S 60 129





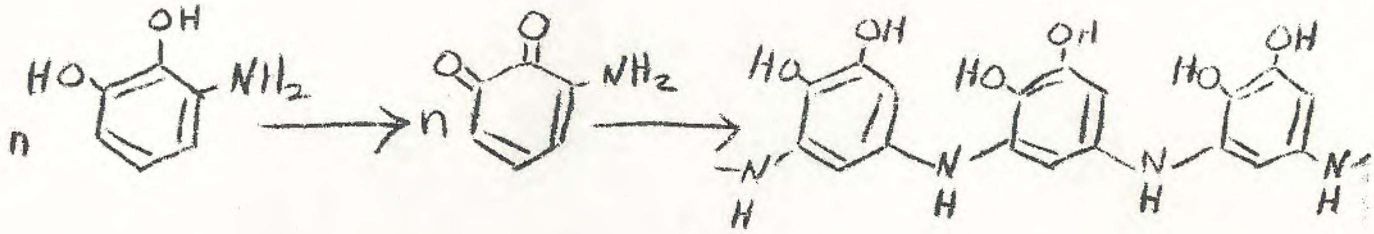


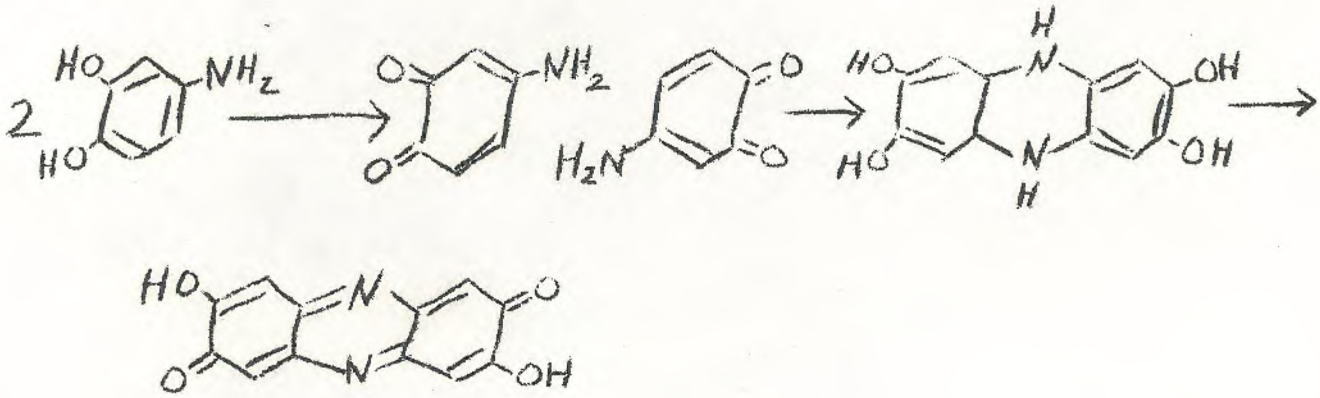
About the mechanism of the building in nitrogen components in lignin fragments or other quinoic compounds to form humic acid there is not very much known. As principles, two reactions can be mentioned. One is the exchange of a functional oxygen groups (OH or OR) for that of amino groups. The other is the addition of amino compounds on the system of double bonds.

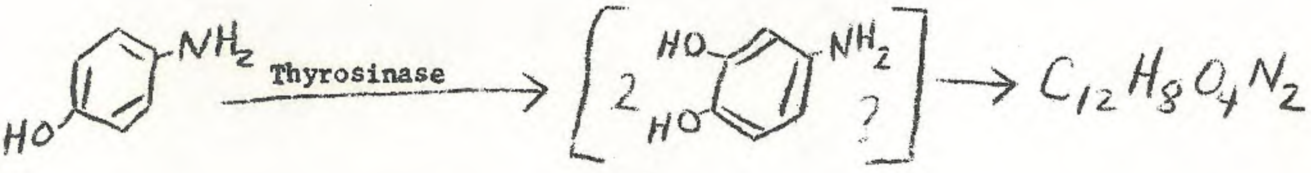
The first will be relatively rare. As an example, the reaction of 2,6-dimethoxy-p-benzoquinone with ethanolamine is mentioned. In this case both types of reactions occur. But the substitution of a methoxy group by the group of ethanolamine occurs only by heating to 40 to 50° C.

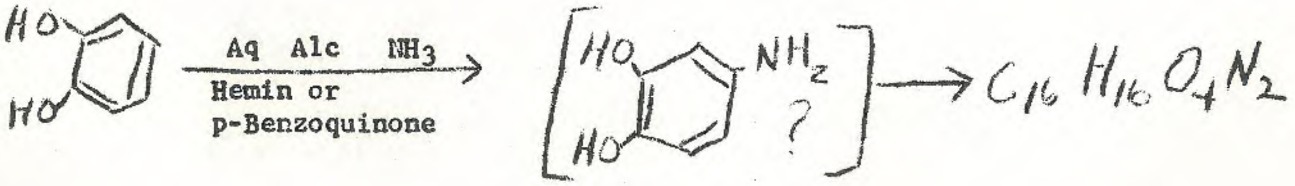
Compounds with amino groups are known to be added very easily on o- and p-quinones in common.

S 61 130









(Horner, L., und Sturm, K.: Zur Kenntnis der o-Chinone. X. Modellreaktionen zur Melaninbildung. Liebigs Ann. Chem. 608, 128 (1957)). Horner oxidized 4-amino-pyrocatechol to a melanin-like product. The same author described also the oxidation of 4-amino-pyrocatechol to a product which he described as a phenazin.

The next example shows how the reactions can go in numerous directions in such cases. By oxidation of p-amino-phenol with tyrosinase prepared from meal worm, there was isolated a product of the formula $C_{12}H_8O_4N_2$ of unknown constitution. One should also presume that p-amino-phenol is oxidized by the enzyme at first to 4-amino-pyrocatechol and the phenazin isolated by Horner could have been formed.

By oxidation of pyrocatechol in alcoholic ammonia with hemin or p-benzoquinone a well defined compound of the formula $C_{16}H_{16}O_4N_2$ is found with unknown constitution Also in this case, one would presume that at first 4-amino-pyrocatechol is formed. Presumably phenoxazones are formed during this reaction.

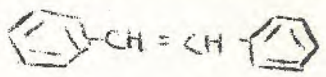
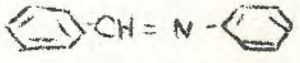
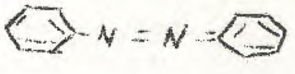
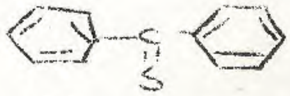
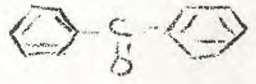
In other cases, Musso could find phenoxazones by the oxidation of orcinol in ammonia solution. (Musso, H., Matthies, H. G., Beecken, H. und Kramer, H.: Zur Konstitution der Orceinfarbstoffe. Angew. Chem. 69, 178 (1957)). The mentioned possibilities show how many varieties of reactions can occur. It may be that the reaction from 3-amino-pyrocatechol to melanin gives an idea of the formation of polymeric substances and the possibility to give a formula for an undefined dark product.

This is formed from only one initial material and by way of one known reaction. The situation in nature is much more difficult because of the possible reaction conditions. The products which are formed must be much more complicated. The elucidation therefore is very difficult, especially regarding the different reactions which can happen. These possible ways of reaction give only a suggestion about how to formulate those dark colored products. Only careful work taking all circumstances and conditions into consideration, may help to solve these complicated problems.

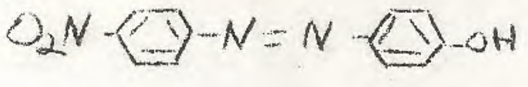
On the other hand, these questions are quite important with regard to the utilizability of the nitrogen which is in the humic substances. In many cases, it is mentioned that the so-called heterocyclic nitrogen of humic substances can be utilized by microorganisms or plants scarcely or not at all. However, this effect exists;that a yearly supply of organic matter gives a definite content of organic bound carbon in the soil. In the first lectures, I showed that there is a balance of organic carbon in the soils depending on the climate, i.e., supplied organic matter decomposes always to a certain extent. This means also that heterocyclic compounds, too, have to be degraded and they cannot remain unchanged in the soil. Later on we will hear something about the decomposition of definite heterocyclic compounds by the microorganisms of the soil, in some cases depending on the chemical constitution.

Some words must be said about the color of the humic substances. Principally, the color of substances can be caused by addition of conjugated double bonds. These systems are very sensitive to oxidation. Therefore, it is nearly impossible to find such combinations in the soil.

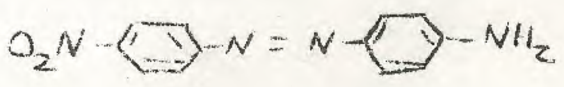
But the combination with atoms other than carbon atoms, such as nitrogen or sulfur, increase the color of the chemical compounds. In the table some examples are given,

		λ(mμ)	color
Stilben		295	none
Benzalanilin		330	none
Azobenzene		450	orange
Thiobenzophenon		620	blue
Benzophenon			none

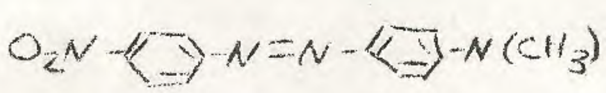
Also the substitution of different substances increases the color. This can be shown by the substitution of the different nitro-azo-benzenes.



(dark yellow)

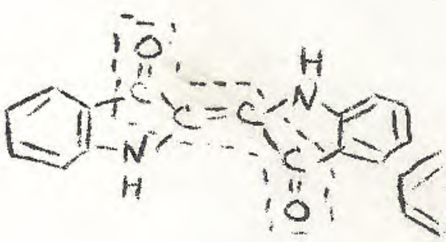


(yellow-red)

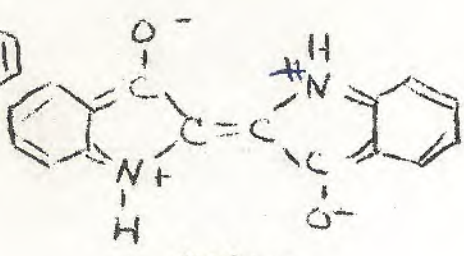


(dark red)

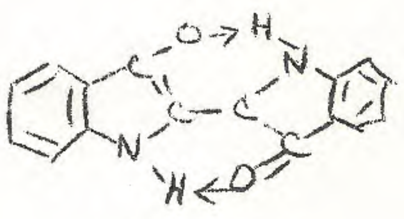
A good example to explain all these factors is the well investigated indigo. By x-ray diffraction it could be ascertained that indigo possesses transfiguration.



λ = 590 mμ



ionic -

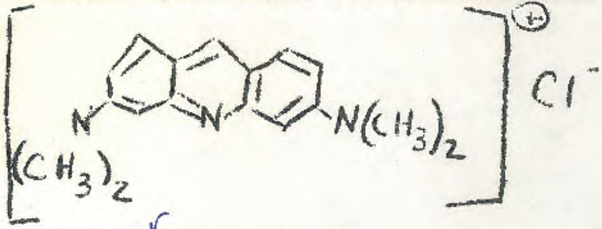


chelat-formula

The transorientation can be explained by a tetrapolar- ionic structure. In this case, the different charged oxygen- and nitrogen-atoms of the two halves of the molecule attract each other. The conjugated system of the double bounds is in this case larger than in the usually written formula. The heteropolar character has a large effect deepening the color. This dipole complex can aggregate in a way so the molecules with their four charges are one over the other. The dark blue color of indigo in polar solvents can be explained in this way.

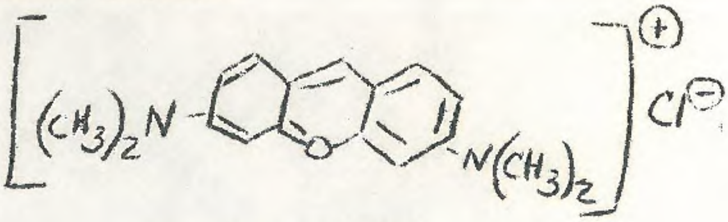
In non-polar solvents, the color of indigo is red; this means that no aggregation has taken place.

The effect of light absorption by the different combinations of nitrogen, oxygen, and sulfur atoms in hetero-cyclic compounds, which are comparable with those of humic substances, are given in some formulas. Humic acids as well as these dye-stuffs can be reduced to colorless compounds.



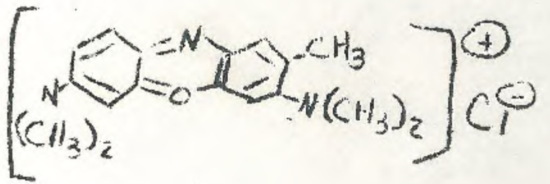
Acidine orange

$\lambda = 496 + 467$ mμ



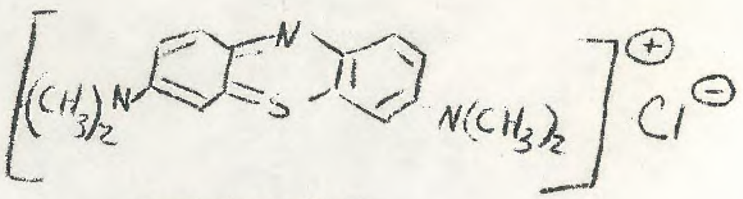
Pyronin~~g~~e (red)

$\lambda = 543 + 501$ mμ



Capri blue

$\lambda = 665 + 607$ mμ



Methylene blue

$\lambda = 668 + 610$ mμ

According to our present knowledge, the dark color of humic acids can be caused by quinhydronic systems or different heterocyclic compounds comparable with the mentioned dye-stuffs.