flux. A small amount of methanol was removed at the head of the column as an azeotropic mixture with benzene. Subsequently, one mole of dibutyl hydrogen phosphite (b. p. 103–104° at 6.5 mm.) was added to the hot mixture and methanol was removed at the head of column again as an azeotrope with benzene (b. p. 58–59°). Analysis of the distillate showed that only 75–80% of the theoretical amount of methanol could be recovered in this way. The clear benzene solution of sodium dibutyl phosphite was allowed to cool to room temperature and one mole of freshly distilled allyl bromide was added dropwise over a period of 1.5 hours to the benzene solution with stirring keeping the temperature between 50–60°. A precipitate of sodium bromide appeared five minutes after the addition of allyl bromide had begun. After addition was complete, the mixture was heated at 60° for an additional 2.5 hours. The cooled reaction mixture was poured into 500 ml. of water, the benzene layer separated and washed again with 150 ml. of water. The benzene layer was again separated and benzene together with residual water were removed by distilling at normal pressure.

The residual yellowish-orange liquid was fractionated and yielded the diphosphonate as the main fraction (96 g.) boiling at 231–232° at 7 mm. pressure which possessed the following characteristics: $n^{20}\text{D}$, 1.4495; $d^{20}{}_4$, 1.028; *MR* calcd., 111.44; *MR* found, 111.90; mol. wt. calcd. for either II or III, 428.5; mol. wt. found, 409. *Anal.* Calcd. for $C_{19}H_{42}O_6P_2$: C, 53.3; H, 9.8; P, 14.5. Found: C, 53.2; H, 9.9; P, 14.7.

TECHNICAL COMMAND
ARMY CHEMICAL CENTER, MARYLAND
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Structure of the Silver Perchlorate–Benzene Complex[1]

BY R. E. RUNDLE AND JEANNE H. GORING

Benzene acts as a Lewis base under a number of circumstances, but it is as yet unknown whether the acid is bonded to one carbon, or by π-bonds, to two, or as more often suggested,[2] equally to six carbons. The problem is interesting due to possible implications in organic reaction mechanisms.[3] We have examined the silver perchlorate–benzene complex to aid in settling this question.

Crystals, $AgClO_4 \cdot C_6H_6$, prepared by crystallization of $AgClO_4$ from benzene, are orthorhombic, $a_0 = 7.96$, $b_0 = 8.34$, $c_0 = 11.7$ Å., $\rho_{\text{obsd.}} = 2.4$, $Z = 4$, space group Cmcm, Cmc or C2cm. Patterson and, subsequently, Fourier projections on (100), (010) and (001) have been made. On Fouriers, carbon and oxygen peaks are resolved, leading to the structure of Fig. 1, based on Cmcm. Ag and Cl are in 4(c) with $y_{\text{Ag}} = 0.04$, $y_{\text{Cl}} = 0.44$. Benzene centers are in 4(a) with the normal to the ring making an angle of about 40° with c_0. Bond lengths C–C and Cl–O appear normal. The complete structure, after refinement, will be published elsewhere.

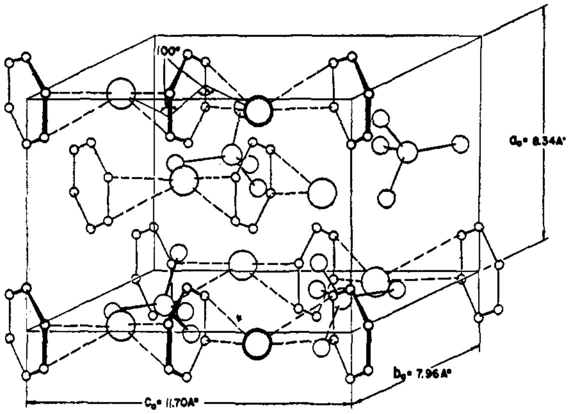

Fig. 1.—Structure of the silver perchlorate–benzene complex.

Definite, though weak, Ag–benzene interactions are indicated by Ag–C distances of 2.6 Å., leading to an electron density of 0.15 pair per bond by Pauling's rule and radii.[4] Each silver is bonded equally to two carbons of each of two rings, lying above and below the rings, suggesting π-bonding. The perchlorates are pushed away from one side of Ag^+ to make room for benzene.

Benzene may act differently with other Lewis acids or with Ag^+ in solution. But if the silver positions in the crystals are influenced by the availability of π-electrons from benzene, as appears to be the case, then the axial position cannot be materially more favorable than a position over two carbon atoms, and it may be considerably less favorable.

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[1] Paper No. 106 from the Institute for Atomic Research and the Department of Chemistry, Iowa State College, Ames, Iowa. Work performed in the Ames Laboratory, Atomic Energy Commission.

[2] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

[3] See, for example, the speculation of M. Dewar in "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949.

[4] L. Pauling, THIS JOURNAL, **69**, 542 (1947).

DEPARTMENT OF CHEMISTRY
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A Methoxyl-containing Lignin-like Component of the Mold *Trametes Pini*[1]

BY WALTER J. SCHUBERT AND F. F. NORD

Information on the occurrence of lignin in fungi is scanty, and it has been stated that definite proof for the presence of true lignin in fungi is not available. However, since lignin is characteristically resistant to concentrated mineral acids, residues obtained in this way from fungi have arbitrarily been considered as "lignin," without supporting analytical data. For example, 25% of the weight of the mycelium of *Polyporus fomentarius* was designed as "lignin,"[2a] although this material did not contain the characteristic methoxyl groups.[2b] Similarly, high percentages of fuming HCl-resistant "lignin-like" materials, have been claimed to be present in certain "bracket" fungi,[3] but no methoxyl determinations were reported on the products. On

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[1] For the previous communication of this series, see reference (5b). Contribution No. 202 from the Department of Organic Chemistry and Enzymology, Fordham Univ.

[2] F. O. Kucher, Dissertation, München, 1929. Cited by L. Kalb in G. Klein's "Handbuch der Pflanzenanalyse," Springer, Wien, 1932, (a) Vol. III, No. 1, p. 191; (b) *ibid.*, p. 201.

[3] C. Thom and M. Phillips, *J. Wash. Acad. Sci.*, **22**, 237 (1932).

the other hand, the methoxylated ester, methyl *p*-methoxycinnamate, is a known metabolic product of the wood-rotting fungus, *Lentinus lepideus*.[4]

Hence, since it seemed possible that substances might be formed by fungi which, while not chemically identical with the lignin of higher plants, at least have certain properties sufficiently characteristic to be considered as "lignin-like," it was of interest to determine the nature of this fraction of a fungus and to attempt to isolate this product by less drastic means, such as have recently been employed to isolate native lignin from white Scots pine wood.[5a,b]

The wood-rotting fungus, *Trametes pini*, was selected for this purpose, since it was reported[3] to produce 54.08% of "lignin."

Experimental

Fifty-ml. portions of the nutrient medium employed in previous experiments,[6] contained in 125-ml. erlenmeyer flasks, were sterilized by autoclaving for 20 min. at 15 lb. pressure. Each flask was inoculated with a 3-ml. spore-mycelial suspension of *Trametes pini* (obtained from Centraalbureau voor Schimmelcultures, Baarn, Holland), and incubated in the dark at 27–28°. After one month of growth, the mycelia were filtered off, dried and ground to 60 mesh in a mill.

The dried powder was analyzed for its "lignin" content by a standard method,[7] and was found to contain 23.7% of "sulfuric acid lignin." This "lignin" was subjected to analysis, with the results reported in Table I.

Since extraction of sawdust with ethyl alcohol in a Soxhlet apparatus has been demonstrated to be an efficient method of isolating an unaltered lignin from wood,[8] this procedure was also applied to the ground *Trametes pini* mats. Thus, the dried powder was extracted for 24 hours in a Soxhlet apparatus with 95% ethyl alcohol. The extract was concentrated by distillation, whereby a reddish-brown residue remained. This was dissolved in dioxane and precipitated by filtering into ether. It amounted to about 1% of the weight of the dry mats. The resulting powder was purified by repeated precipitations from dioxane into ether. The product was submitted to microanalysis, and these results are also recorded in Table I.

TABLE I

COMPOSITION OF LIGNIN-LIKE COMPONENT OF *Trametes pini*

	Prod. isolated with H_2SO_4, %	Prod. extracted with EtOH, %
C	54.12	55.21
H	4.33	5.78
OCH_3	1.55	12.76

Like native white Scots pine lignin,[5a,b] the product isolated from *Trametes pini* with ethyl alcohol reduces Fehling solution, is soluble in ethyl alcohol, methyl alcohol, dioxane, pyridine, dil. sodium hydroxide and glacial acetic acid, and insoluble in water, ether, benzene and petroleum ether. However, unlike native white Scots pine lignin, it does not give the characteristic color reactions with phloroglucinol or aromatic amine reagents.

Thus, the enzymatic formation from carbohydrate of a fungal product containing 12.66% methoxyl and resembling true lignin in many respects, has been demonstrated in the wood-rotting fungus, *Trametes pini*.

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[4] F. F. Nord and J. C. Vitucci, *Arch. Biochem.*, **14**, 243 (1947); *ibid.*, **15**, 465 (1947).

[5] (a) W. J. Schubert and F. F. Nord, THIS JOURNAL, **72**, 977 (1950); (b) W. J. Schubert and F. F. Nord, *ibid.*, **72**, 3835 (1950).

[6] W. J. Schubert and F. F. Nord, *Arch. Biochem.*, **20**, 465 (1949).

[7] "Methods for the Chemical Analysis of Pulps and Pulpwoods," Forest Products Laboratory, Madison, Wis., 1939.

[8] F. F. Nord and W. J. Schubert, *Holzforschung*, **5**, No. 1 (1950).

Heterocyclic Basic Compounds. XIII. 4-Aminocoumarin Derivatives

BY DAVID P. SPALDING,[1] HARRY S. MOSHER[2] AND FRANK C. WHITMORE

The preparation of 4-aminocoumarin derivatives was undertaken to supply samples for testing as antimalarial drugs. The starting point in these syntheses was 4-hydroxycoumarin obtained from methyl acetylsalicylate by the method of Stahmann.[3] Anschütz[4] successfully prepared 4-chlorocoumarin by the action of phosphorus pentachloride on 4-hydroxycoumarin, but he failed to report the yield. In the present work phosphorus oxychloride was found to be a superior reagent. 4-Chlorocoumarin was found to react vigorously with morpholine to produce 4-morpholinocoumarin in good yield. The reaction with 3-diethylaminomethyl-4-hydroxyaniline was not so vigorous, and resulted in the product 4-(4′-hydroxy-3′-diethylaminomethylanilino)-coumarin, an analog of the quinoline antimalarial Camoquine,[5] in much lower yield. Neither of these last two compounds showed any indication of antimalarial activity in the *P. gallinaceum* infection in chicks.[6]

Experimental

4-Chlorocoumarin.—4-Hydroxycoumarin (25 g.) was refluxed with 15 ml. of phosphorus oxychloride for two hours. After hydrolyzing the mixture in ice-water, the reaction product was separated and extracted with 500 ml. of ethanol and the purified product obtained by crystallization. The yield was 27.7%, 7.7 g., m. p. 89–91°. Anschütz[4] reports m. p. 91–92°.

4-Morpholinocoumarin.—A mixture of 6 g. of morpholine and 4.1 g. of 4-chlorocoumarin produced a deep red solution; a vigorous reaction immediately followed solution. On standing the reaction mixture set to solid. After thorough washing with cold water the product was crystallized from 50-ml. portions of ethanol to a constant melting point of 139–141°. The yield was 71% (3.8 g. light orange colored plates).

Anal. Calcd. for $C_{14}H_{13}O_3N$: N, 6.12. Found: N, 6.06.

4-(4′-Hydroxy-3′-diethylaminomethylanilino)-coumarin.—2-Diethylaminomethyl-4-acetylphenol[5] (11.8 g.) was hydrolyzed by heating two hours with 50 ml. of water and 50 ml. of concentrated hydrochloric acid. After

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[1] Parke, Davis Research Fellow, The Pennsylvania State College, 1943–1945; S. C. Johnson and Son, Inc., Racine, Wis.

[2] Department of Chemistry, Stanford University, Stanford, Calif.

[3] Stahmann, *et al.*, THIS JOURNAL, **65**, 2285 (1943).

[4] Anschütz, *Ann.*, **367**, 200 (1909).

[5] Burckhalter, *et al.*, THIS JOURNAL, **70**, 1363 (1948).

[6] We are greatly indebted to Dr. R. J. Porter of the University of Michigan for these results.