Experimental

The first three of the following syntheses are representative of the preparation of compounds listed in Tables I and II.

Dimethyl Carbamate of (3-Hydroxy-2-pyridylmethyl)-dimethylamine Dihydrochloride.—A solution containing 43 g. of (3-hydroxy-2-pyridylmethyl)-dimethylamine in 30 cc. of pyridine and 32 cc. of dimethylcarbamyl chloride was heated on a steam-bath for 2 hours. Most of the pyridine was then removed by distillation *in vacuo*. The residue was dissolved in cold water, made alkaline with sodium hydroxide, and extracted with ether. The ether layer was washed with water and dried over anhydrous sodium sulfate. After removal of the ether by distillation, the residue was heated on a steam-bath under a vacuum of 1 mm. to remove traces of pyridine. The residue was dissolved in ether and saturated with anhydrous hydrogen chloride. A light brown crystalline solid separated. This was dissolved in hot ethanol, decolorized with charcoal, and crystallized on addition of anhydrous ether. After recrystallization from a mixture of ethanol and ether or from acetonitrile, the dihydrochloride melted at 163–167°; yield 47%.

Dimethyl Carbamate of (3-Hydroxy-2-pyridylmethyl)-trimethylammonium Bromide.—The esterification product obtained in the above example, after removal of traces of pyridine *in vacuo*, was dissolved in a cold acetone solution of methyl bromide. Crystals of the quaternary ammonium salt began to separate in a short time. After recrystallization from a mixture of ethanol and ether, the product melted at 175–177° dec.; yield 60%.

Phenylmethyl Carbamate of (3-Hydroxy-2-pyridylmethyl)-diethylamine Monohydrochloride.—To a solution of 10 g. of (3-hydroxy-2-pyridylmethyl)-diethylamine in 10 cc. of pyridine, there was added 10 g. of phenylmethylcarbamyl chloride. In about two minutes, the acid chloride dissolved with considerable evolution of heat and bubbling. The solution was cooled in water and kept for about 16 hours at room temperature. The large crystals of the monohydrochloride which formed were filtered and washed with pyridine and anhydrous ether. After recrystallization from a mixture of isopropyl alcohol and ether, the product melted at 142–144°; yield 52%.

(3-Hydroxy-2-pyridylmethyl)-diisopropylamine.—A mixture of 24.7 g. of (3-hydroxy-2-pyridylmethyl)-trimethylammonium bromide and 60 g. of diisopropylamine was stirred and refluxed. There did not seem to be any reaction at the reflux temperature. On heating the above mixture in a rocking autoclave at 125° for 2 hours, reaction took place. After boiling off excess diisopropylamine, the residue was extracted with benzene and the benzene layer then washed with water. The residue after removal of benzene, was distilled. This gave 13.7 g. of (3-hydroxy-2-pyridylmethyl)-diisopropylamine, b.p. 98–101° (1.2 mm.); yield 66%.

(3-Hydroxy-2-pyridylmethyl)-diisopropylmethylammonium Bromide.—A cold solution of (3-hydroxy-2-pyridylmethyl)-diisopropylamine in acetone containing methyl bromide gave crystals of the quaternary salt. After two crystallizations from a mixture of methanol and ether, it melted at 171–172° dec.; yield 82%.

Anal. Calcd. for $C_{13}H_{23}ON_2Br$: C, 51.49; H, 7.64; N, 9.24. Found: C, 51.19; H, 7.49; N, 8.96.

2-Benzylaminomethyl-3-pyridol Dihydrochloride.—On addition of 60 g. of benzylamine to 24.7 g. of (3-hydroxy-2-pyridylmethyl)-trimethylammonium bromide, the temperature rose to 33°. The reaction mixture was then stirred and heated at 50° for 1.5 hours, during which time the originally milky mixture became clear. After removal of excess benzylamine by distillation *in vacuo*, the residue was dissolved in 10% sodium hydroxide. The insoluble oil that separated was extracted with ether. On neutralization of the alkaline layer with hydrochloric acid to about *p*H 8, an oil separated that was extracted with benzene. The residue after removal of benzene was dissolved in ethanol and alcoholic hydrogen chloride added. The crystalline dihydrochloride separated in 71% yield. After two crystallizations from methanol, it melted at 236–241°.

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Investigations on Lignin and Lignification. IX. The Relationship Between the Action of Brown Rot Fungi, Cellulose Degradation and Lignin Composition in Bagasse

BY GEORGE DE STEVENS AND F. F. NORD

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A comparative study of the effect of four wood-destroying fungi of the "brown rot" type on the dissimilation of cellulose in bagasse has been carried out. The lignins liberated by the cellulolytic action of each of these molds have been characterized. Their identity with bagasse native lignin is discussed.

The importance of wood-destroying fungi of the "brown rot" type as agents of cellulose degradation for the isolation of additional amounts of unaltered lignin from woody tissues has been well established.[1,2] However, these molds reveal a certain amount of specificity with respect to the type of wood attacked and their rate of growth when cultivated on a wood species. That is, certain "brown rots" thrive better when softwoods are used as substrates, whereas others show optimum activity with hardwoods.[3] In a recent report from this Laboratory,[4] the isolation and characterization of the native lignin and enzymatically liberated lignin from bagasse, the supporting fiber from the annual plant, sugar cane, was described. Since bagasse cannot be assigned to either the softwood or hardwood class, the problem of the choice of the "brown rot" fungus which would give rise to the highest rate of cellulose depletion necessarily presented itself. The resolution of this problem is, in part, reported in this paper.

(1) W. J. Schubert and F. F. Nord, THIS JOURNAL, **72**, 977, 3835 (1950).

(2) S. F. Kudzin and F. F. Nord, *ibid.*, **73**, 4619 (1951).

(3) M. K. Nobles, *Can. J. Research*, **26C**, 281 (1948).

(4) G. de Stevens and F. F. Nord, THIS JOURNAL, **73**, 4622 (1951).

Experimental

The wood species investigated in this study was virgin bagasse, and the "brown rot" organisms employed to effect the decay were the softwood molds, *Poria vaillantii* and *Lentinus lepideus*, and the hardwood fungi, *Daedalea quercinia* and *Polyporus sulphureus*.

Sterilization and Inoculation of Bagasse Samples.—Ten gram samples of the virgin bagasse were weighed into each

of forty 500-ml. Fernbach-type culture flasks, and to each flask was added a 25-ml. portion of a nutrient medium consisting of: neopeptone, 1.0 g.; KH_2PO_4, 1.5 g.; $MgSO_4 \cdot 7H_2O$, 0.5 g.; thiamine hydrochloride, 2.0 mg.; tap water to, 1 liter.

The flasks were plugged with cotton, and, to avoid thermal destruction of the woody tissue, sterilized with streaming steam at 100° for 60 minutes on three successive days. After cooling, each flask was inoculated with a 5-ml. spore–mycelial suspension of a pure culture of one of the organisms referred to above. The inoculated flasks were incubated in the dark at 27–28°. The decayed bagasse was analyzed periodically.

Analytical Methods.—After separation of the fungal mycelia from the decayed bagasse,[1] the latter was collected and dried. Lignin was determined according to the standard method,[5] and the percentage solubility of the decayed residue in 1% NaOH determined according to the method outlined.[6] All values were corrected for moisture content.

Isolation of Native Lignin.—The Brauns method[7] of extraction was used. This consists essentially of first extracting the ground bagasse with water and with ether. It was then extracted thoroughly with 95% ethyl alcohol at room temperature. Upon removal of the ethyl alcohol at reduced pressure, the remaining resinous material was dried, dissolved in dioxane, centrifuged, filtered and precipitated into thirty times its volume of ice-cold distilled water. Hereupon, the precipitate was dried, redissolved in dioxane, centrifuged, filtered and precipitated now into thirty times its volume of ether. This procedure was repeated until a constant methoxyl value was obtained. This method of purification must be applied in order to obtain a uniform lignin of maximum purity. The enzymatically liberated lignin was extracted from the decayed bagasse and purified in the same manner. Needless to say, the fungal mycelia were separated from the decayed bagasse before extraction.

Results and Discussion

According to Bray,[8] an increase in alkali solubility serves as a definite index of cellulose degradation. The percentage solubility in 1% sodium hydroxide of the decayed bagasse samples is listed in Table I.

TABLE I

ALKALI SOLUBILITY OF BAGASSE DECAYED FOR THREE MONTHS

Organism	Solubility in 1% NaOH,[a] %
Uninoculated control	23.72
Daedalea quercina	24.6
Polyporus sulphureus	28.1
Lentinus lepideus	38.6
Poria vaillantii	69.6

[a] Average of three determinations.

Thus, with the exception of the case of *Daedalea quercina*, the selected organisms demonstrated a marked efficiency for cellulolytic decay within a three-month period. This was verified by periodic analyses of the resulting bagasse residues. The data in Table II express this change with respect to the increase in the relative lignin content of the samples.

It appears, therefore, that the softwood as well as the hardwood "brown rot" molds will decay bagasse, although *Poria vaillantii* causes the most rapid dissimilation of cellulose. A possible understanding of this observation can be derived from the high pentosan content of bagasse, *e.g.*, 31.3%

TABLE II

LIGNIN CONTENTS OF DECAYED BAGASSE

Organism	Period of decay (mo.)	Klason lignin,[a] %
Daedaela quercina	3	22.8
	8	23.9
Polyporus sulphureus	3	26.3
	10	32.2
Lentinus lepideus	3	30.7
	10	35.2
Poria vaillantii	3	46.0
	8	50.4
Control	0	21.3

[a] Average of two determinations.

as compared to the pentosan content of some softwoods, such as spruce, having 12.1%.[9,11] Rege[11] suggested that the ability of a wood to undergo decomposition is directly proportional to its pentosan content, since it may be regarded as an energy source.

A recent report of Erdtman, *et al.*,[12] purports to the non-identity of the native and enzymatically liberated lignins from spruce wood, the argument being based, in part, on the lowering of the methoxyl content of the Klason lignins and more so on the increase of reducing ability of the enzymatically liberated lignin with respect to the native lignin. These authors determined the copper numbers on the total, *i.e.*, unpurified benzene–alcohol extract from the decayed spruce wood. However, this residue contains contaminants and cellulose degradation products, and this fact must be kept in mind when these results are considered since it is known that the benzene–alcohol mixture is a suitable deresinifying agent.[13]

On the other hand, we have purified our ethyl alcohol extract from decayed bagasse according to Brauns. In Table III are recorded the chemical compositions of the purified enzymatically liberated lignins obtained from bagasse. Their identity attests to the necessity of using pure preparations for comparative studies. Furthermore, if the methoxyl content of the Klason lignins decreases with the time of decay, then one would expect the methoxyl contents of the enzymatically liberated fractions to show the same trend. We have found no such change. Moreover, since the bagasse lignins liberated by three different molds underwent no fundamental change in chemical composition, their

TABLE III

COMPARISON OF BAGASSE NATIVE LIGNIN WITH BAGASSE LIGNINS LIBERATED BY VARIOUS FUNGI

		Native lignin	*Poria vaillantii*	*Polyporus sulphureus*	*Lentinus lepideus*
Analyses, %	C	61.5	61.6	61.1	61.8
	H	5.7	5.9	5.5	5.6
	OCH_3	15.3	15.4	15.0	15.2

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(11) R. D. Rege, *Ann. Applied Biol.*, **14**, 1 (1927).

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identity with bagasse native lignin is well founded. This identity may be further recognized in their infrared and ultraviolet absorption spectra.[4] In a forthcoming communication this conclusion will be further supported by means of oxidation studies with nitrobenzene and alkali and also by identifying their lignosulfonic acids.

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NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XVIII. Preparation and Properties of 1,1,3-Trichloro-2-fluoro-1-propene and 1,1,2,3-Tetrachloro-1-propene[1]

BY LEWIS F. HATCH AND DAVID W. MCDONALD[2]

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The following compounds have been prepared and characterized for the first time: 3-bromo-1,1-dichloro-2-fluoro-1-propene, 3,3-dichloro-2-fluoro-2-propen-1-ol, 1,1,3-trichloro-2-fluoro-1-propene, 2,3,3-trichloro-2-propen-1-ol and 1,1,2,3-tetrachloro-1-propene. The reactions of 1,1,3-trichloro-2-fluoro-1-propene and 1,1,2,3-tetrachloro-1-propene with potassium iodide and with sodium ethoxide have been studied.

The study of the influence of various groups and atoms on the reactivity of the allylic chlorine atom of substituted allyl chloride has been extended to include 1,1,3-trichloro-2-fluoro-1-propene and 1,1,2,3-tetrachloro-1-propene. Both of these compounds are of the type $CCl_2{=}C(Y){-}CH_2Cl$, a type which shows a marked difference in its reaction with potassium iodide in acetone from the similar type $CH_2{=}C(Y){-}CH_2Cl$.

The 1,1,3-trichloro-2-fluoro-1-propene was synthesized from 1,1-dichloro-2-fluoro-1-propene by the use of N-bromosuccinimide followed by hydrolysis of the 3-bromo-1,1-dichloro-2-fluoro-1-propene to 3,3-dichloro-2-fluoro-2-propen-1-ol and conversion of this allylic alcohol to the desired allylic chloride in a manner similar to that previously used to prepare the 1,3-dichloro-2-fluoropropenes from the 1-chloro-2-fluoro-1-propenes.[1] The 1,1,2,3-tetrachloro-1-propene was obtained by the dehydrochlorination of 1,1,2,2,3-pentachloropropane.

The pentachloropropane was prepared by the low temperature addition of chlorine to 1,2,3-trichloropropene.[3] Apparently no substitution occurred which conforms with the generalizations of Taft[4] on non-activated, low temperature chlorination reactions. The pentachloride obtained by the addition of chlorine to 1,2,3-trichloropropene is considered to be 1,1,2,2,3-pentachloropropane, although the physical constants of this compound do not agree very closely with those reported by Stevens,[5] which disagreement, however, is probably due in part to the higher purity of our sample.

The structure of 1,1,3-trichloro-2-fluoro-1-propene was related to 1,1-dichloro-2-fluoro-1-propene by replacement of the allylic chlorine atom by a hydrogen atom using lithium aluminum hydride.[6] The structure of 1,1,2,3-trichloro-1-propene was also confirmed in the same manner by its conversion to the known 1,1,2-trichloro-1-propene.[7]

The relative reactivities of 1,1,3-trichloro-2-fluoro-1-propene and 1,1,2,3-tetrachloro-1-propene with sodium ethoxide in ethanol (Table I) show the same relationship between the electron-attracting ability of the substituent on the number two carbon atom and reactivity as do those compounds having two hydrogen atoms on the number one carbon atom.[8] In both series the replacement of the hydrogen atom on the number two carbon atom by an electron attracting atom (Br, Cl or F) causes a decrease in reactivity. This similarity does not

TABLE I

RELATIVE REACTIVITY OF 1,1,3-TRICHLORO-2-FLUORO-1-PROPENE AND 1,1,2,3-TETRACHLORO-1-PROPENE WITH SODIUM ETHOXIDE IN ETHANOL AT 50°

1,1,3-Trichloro-2-fluoro-1-propene

Time, hr.	6.50	8.50	10.5	12.5	22.0
Reacted, %	58.6	63.3	67.4	70.7	81.9
k, hr.$^{-1}$ mole^{-1} l.	4.37	3.88	3.87	3.81	3.83
Av. k			3.95±0.16		
Relative reactivity[a]			3.3		

1,1,2,3-Tetrachloro-1-propene

Time, hr.	1.00	1.50	2.00	3.00	4.00
Reacted, %	36.1	43.5	50.7	60.7	67.9
k, hr.$^{-1}$ mole^{-1} l.	11.3	10.2	10.3	10.4	10.6
Av. k			10.6±0.3		
Relative reactivity[a]			9.0		

[a] Allyl chloride as 1.00 with k = 1.18.

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