the presence of an impurity to the extent of about 25% of the total protein. Figure 3 was obtained with horse serum (diluted one to four) and indicates a marked overlapping of the gradients corresponding to the albumin and the α-, β- and γ-globulins.[3]

In obtaining the records illustrated by Figs. 2 and 3 the plate was geared to travel 7.5 times as fast as the diaphragm. The lenses D and O, Fig. 1, had 36″ (91-cm.) focal lengths, the aperture ratio of the latter was F/36 and unit magnification was used. With a 0.2 × 25 mm. slit illuminated by an "H4" mercury lamp and a 0.2 mm. masking slit a plate travel of 15.1 mm. per minute adequately exposed an Eastman contrast lantern slide. Thus only about three minutes were required to make the exposures.

The modification of the schlieren method outlined here has an advantage over that described by Philpot[4] in that the position of the base line is definite even in the presence of linear gradients in the column. Moreover, the method is rapid and flexible in its application. The quantitative comparisons that have been made indicate that the precision attainable is comparable with that of the scale method. As Philpot has suggested, the photographic record thus obtained lends itself readily to a direct photometric determination of the area under the contour and hence of the protein concentration.

(3) Tiselius, *Biochem. J.*, **31**, 1464 (1937).
(4) Philpot, *Nature*, **141**, 283 (1938).

THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH
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The Reconversion of an "Extracted" Lignin into its Primary Building Units

BY QUINTIN P. PENISTON, JOSEPH L. MCCARTHY AND HAROLD HIBBERT

It has been found possible partially to reconvert a lignin, extracted from oak wood meal by a mild process of acetylation and fractionation, into what are considered to be its primary building units.

This was effected by refluxing, for fifteen hours, an acetylated, carefully purified oak lignin (8.7% OCH_3, 35.0% $COCH_3$) with anhydrous ethanol containing 2% hydrogen chloride. The reaction products were isolated in the manner described in the accompanying communications (this series, parts 35 and 36)[1] on the ethanolysis of spruce and maple wood, respectively.

(1) Cramer, Hunter and Hibbert, THIS JOURNAL, **61**, 509 (1939); Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939).

The yield of crude oils obtained amounted to 36% of the acetyl-free lignin content of the starting material. These crude oils were separated into four fractions, the percentage of each fraction, based on the weight of the crude oils, being

Fraction I	Bisulfite soluble	4.8%
Fraction II	Bicarbonate soluble	6.3%
Fraction III	Sodium hydroxide soluble	49.2%
Fraction IV	Neutral	20.2%

The characteristics of these fractions are very similar to those of analogous fractions obtained by the action of ethanol–hydrochloric acid on maple wood.[1] It seems probable that considerably higher yields may be obtained from further experiments now in progress.

In this investigation, for the first time, an "extracted" lignin has been reconverted into what are apparently primary building units.

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Yields of Stibines and Arsines

BY JOSEPH SEIFTER

The following observations have been made on trimethyl and tri-*n*-butylstibines, and on tri-*n*-butylarsine.

The attempt to make a simple distillation of trimethylstibine from the Grignard reaction carried out in di-*n*-butyl ether was unsuccessful. A constant boiling mixture with a minimum at 72–74° (uncorr.) resulted.

Dyke, Davies, and Jones[1] prepared tri-*n*-butylstibine from $^1/_2$ mole of Grignard reagent and $^1/_6$ mole of antimony trichloride. They refluxed the mixture for one hour after adding the antimony trichloride. Isolation was effected by removing the ether and octane at atmospheric pressure, and then distilling the product *in vacuo*. The yield of stibine was about 22.5%. By varying the conditions, we isolated a 70% yield of tri-*n*-butylstibine from a run involving 3.3 moles of Grignard reagent and 1.0 mole of antimony trichloride. The reaction mixture was not refluxed, and the ether and reaction products were removed *in vacuo*.

Dyke and Jones,[2] applying their stibine methods, prepared tri-*n*-butylarsine in yields of 23%.

(1) Dyke, Davies and Jones, *J. Chem. Soc.*, 463 (1930).
(2) Dyke and Jones, *ibid.*, 2426 (1930).

This compound had already been obtained in 70% yield by Gryszkiewicz and Trochimovski,[3] who used As_2O_3 instead of $AsCl_3$. By application of our method used in preparing the stibine, the yield of tri-*n*-butylarsine was about 50%. Gryszkiewicz and Trochimovski record the boiling point of the arsine as 102–104° at 8 mm. Our product boiled at 113–115° at 10 mm.

(3) Gryszkiewicz and Trochimovski, *Roczniki Chem.*, **8**, 250 (1928).

DEPARTMENT OF PHARMACOLOGY
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WESTERN RESERVE UNIVERSITY
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Some Esters of 3,5-Dihydroxybenzoic Acid

BY C. M. SUTER AND ARTHUR W. WESTON

The well-known preservative action of benzoic and salicylic acids[1] has led to the investigation of numerous related substances. Sabalitschka and co-workers[2] in particular have been active in this field. Methyl, *n*-propyl and benzyl *p*-hydroxybenzoates were found to be useful preservatives, and later[3] certain dihydroxybenzoic acids and their esters were observed to exhibit considerable activity in this direction. Alkyl 3,5-dihydroxybenzoates, however, were not investigated and hence the availability of 3,5-dihydroxybenzoic acid[4] has induced us to prepare a series of these esters.

The *n*-alkyl 3,5-dihydroxybenzoates from ethyl to *n*-heptyl inclusive were prepared from the alcohol and acid. The 3,5-dihydroxybenzoic acid was prepared according to the procedure outlined previously.[4] The alcohols were the purest commercial products. Preparation of the *n*-propyl ester is described. A mixture of 20 g. (0.13 mole) of 3,5-dihydroxybenzoic acid, 100 g. of absolute *n*-propyl alcohol and 10 ml. of concentrated sulfuric acid was refluxed for nine hours. About 20 ml. of benzene was added and the mixture distilled very slowly until the distillate amounted to 100 ml. The residue was dissolved in ether, washed with dilute bicarbonate and distilled. There was obtained 21 g. (82%) of a slightly yellow viscous oil, b. p. 217° (3 mm.), which slowly solidified upon standing. By freezing an aqueous solution and then allowing the ice to melt slowly, the ester was obtained as fine white needles, m. p. 67–68°.

After preliminary purification by distillation it was possible to obtain all of the esters in crystalline form except the *n*-amyl compound. With the exceptions of the ethyl and *n*-heptyl derivatives, which were crystallized from water and toluene, respectively, the esters were unusually difficult to purify. The *n*-propyl and *n*-butyl compounds finally were obtained by freezing their aqueous solutions. The *n*-hexyl derivative first crystallized after standing for eight months. When precipitated as an oil from ether by ligroin crystals slowly formed in the supernatant solvent. The ethyl and *n*-butyl esters were obtained as hemihydrates, the *n*-propyl as the monohydrate.

The esters were analyzed by titration with standard potassium bromide–bromate solution according to the modified procedure already described.[4] The *n*-amyl ester, which was not obtained crystalline, did not give reproducible results by this method but gave a satisfactory carbon and hydrogen analysis.[5]

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.25; H, 7.20. Found: C, 64.36; H, 7.44.

The results of the other analyses are listed in the last two columns of Table I.

TABLE I

n-ALKYL 3,5-DIHYDROXYBENZOATES

Alkyl	Yield	B. p. °C.	Mm.	M. p., °C. Anhyd.	Hyd.	Mol. wt. Calcd.	Found
Methyl[a]	..	.....	..	163–165	....	...	...
Ethyl[b]	81	.....	..	128.5	*ca.* 80	182	182.5
n-Propyl	82	215–217	3	.....	67–68	214[c]	213.4
n-Butyl	84	209–210	2	62.5–63.5	39–40[d]	219[e]	218.6
n-Amyl	90	225–227	4	.....	....	...	...
n-Hexyl	82	220–221	2	65–66.5	....	238	237.5
n-Heptyl	74	235–237	2	74–75	....	252	252.6

[a] Prepared by Herzig and Epstein, *Monatsh.*, **29**, 668 (1908). [b] Reported by Barth and Senhofer, *Ann.*, **159**, 222 (1871) to melt below 100°. [c] Analyzed as monohydrate. [d] Drying of the hydrate indicated 0.5 H_2O. [e] The crude tribromo derivative melted at 59–60°.

The ethyl, *n*-butyl and *n*-heptyl esters were tested for bactericidal properties and toxicity.[6] The modified phenol coefficients were run against *Staph. aureus* at 37°, stock solutions being made up in 20% alcohol. The toxicities are reported in terms of mg. per kg. of body weight for mice, the compounds having been administered orally in dose levels at 250-mg. intervals. In Table II the value following LD indicates the percentage of the animals that died from the amount of ester given in the column.

TABLE II

PROPERTIES OF *n*-ALKYL 3,5-DIHYDROXYBENZOATES

Alkyl	P. C. *Staph. aureus* at 37°	Toxicity, mg./kg. LD 0	LD 50	LD 100	Sol. H_2O at 25° g./100 g.
Ethyl	<10	750	1250	1875	0.6
n-Butyl	<10	2000	2375	3000	.14
n-Heptyl	38	2500	2750	..	.02

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(1) See Serger, *Chem.-Ztg.*, **35**, 1194 (1911), for an earlier review of common bacteriostatic agents.

(2) Sabalitschka, Dietrich and Böhm, *Pharm. Ztg.*, **71**, 834 (1926); Sabalitschka and Dietrich, *Desinfektion*, **11**, 67 (1926); Sabalitschka, *Apoth. Ztg.*, **43**, 670 (1928); Schweiz, *ibid.*, **65**, 169 (1927); *Z. angew. Chem.*, **42**, 936 (1929); *Pharm. Acta Helv.*, **5**, 286 (1930); and many later references.

(3) Sabalitschka and Tietz, *Arch. Pharm.*, **269**, 545 (1931).

(4) Suter and Weston, THIS JOURNAL, **61**, 232 (1939).

(5) This analysis was made by Mr. Robert Schuetz of this Laboratory.

(6) We are indebted to Dr. Maurice L. Moore, Research Laboratories, Sharp and Dohme, for these data.