and after resolidification, the slides rubbed against each other. It was observed that this procedure lowered the proportion of liquid phase to that of solid phase for mixtures containing less than 60 mole per cent. cholic acid and raised by some 40–60° the thaw point of mixtures richer in cholic acid. Thaw points for the latter mixtures shown in the diagram are averages of several determinations and are of rather poor accuracy.

p-Aminoazobenzene showed in sodium cholate solution practically the same spectrum as in sodium desoxycholate solution. With the N-dimethyl derivative in sodium cholate solution considerable changes, such as a shift toward longer wave length, were observed.[8]

Experimental

p-Dimethylaminoazobenzene, cholesterol and cholic acid were several times recrystallized from ethyl alcohol. The former two were dried in vacuum and showed m.p. 117–118° and m.p. 147.5–148.5°, respectively. Cholic acid was dried in Abderhalden drying apparatus at 94° until constant weight; m.p. 198–200°; desoxycholic acid (m.p. 171–173°). *p*-Aminoazobenzene (m.p. 123.5–124.5°) and its choleic acid (m.p. 180–183°) were described in a previous note.[2] Solid–liquid equilibrium diagrams were carried out according to Rheinboldt.[9] Thaw points were determined in a microscope equipped with a heating stage. *p*-Dimethylaminoazobenzene choleic acid was repeatedly prepared by the current method[2]; m.p. 201–204°. Analyses were carried out by the method previously described.[2] Percentages were computed from the optical densities D measured in 1.002 cm. silica cells at 410 mμ, which was, approximately, the wave length of the absorption maximum of *p*-dimethylaminoazobenzene. Alcoholic solutions of this azo compound showed, in average, $D/c = 0.1304$, c being the concentration in mg. per liter. Analyses of various samples are summarized in Table I. Calculated percentages of azo dye for a tetra-, penta- and hexacholeic acid were 12.5, 10.3 and 8.7, respectively.

TABLE I

ANALYSES OF VARIOUS SAMPLES OF *p*-DIMETHYLAMINOAZOBENZENE CHOLEIC ACID

	Choleic acid solution		
Sample	Mg./liter	D_{410}	Acholic in choleic, %
A[a]	103.1	1.219	9.0
B[a]	97.2	1.261	9.9
C[a,b]	50.9	0.722	10.8
	51.2	0.724	10.8
C[c]	49.8	0.728	11.2
	49.2	0.722	11.2
D[c]	68.4	0.951	10.6
	102.8	1.459	10.8
E[c]	118.5	1.620	10.5
	96.6	1.364	10.8

[a] Unrecrystallized. [b] Prepared from alcoholic solutions of butter yellow and desoxycholic acid in such concentrations that even if no choleic were formed on mixing them, there would not be precipitation of any reactant upon cooling. [c] Recrystallized.

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[8] All solutions were prepared in 0.1 N sodium hydroxide and had arbitrary concentrations of azo dye and bile acid.

[9] H. Rheinboldt, *et al.*, *J. prakt. Chem.*, [2] **111**, 242 (1925); **112**, 187, 199 (1926); **113**, 348 (1926); *Ber.*, **74**, 756 (1941).

Cleavage of Dimercaptols of Acetonylacetone by Mercuric Chloride

BY R. A. DINERSTEIN

When sugar mercaptals are treated with mercuric chloride in alcohol, the sulfur precipitates as the alkylmercapto mercuric chloride, RSHgCl, and the aldehyde is regenerated.[1] That this cleavage is general for mercaptals and mercaptols has been recognized in this Laboratory. To demonstrate the effect of treating dimercaptols with mercuric chloride, the dimercaptols of acetonylacetone were prepared from three different mercaptans according to the method of Rietz, Chapman and Fernandez[2] and then treated with mercuric chloride. The precipitates were analyzed for sulfur and compared by mixing melting point with the RSHgCl compound prepared directly from the mercaptan and mercuric chloride.[3] Mixed melting points (Table I) and sulfur analyses (Table II) demonstrated that the products are identical. Thus, cleavage takes place in the reaction of dimercaptols and mercuric chloride.

TABLE I

MELTING POINTS OF RSHgCl COMPOUNDS

R	From RSH and $HgCl_2$	From dimercaptol and $HgCl_2$	Mixed	Reported by Rietz[4] for "addition product"
n-Amyl	183–184	181–182	182–183	184–185
n-Decyl	155–156	154–155	154–155	155–156
n-Dodecyl	153–154	152–153	152–153	153–154

TABLE II

SULFUR CONTENTS (% S) OF RSHgCl COMPOUNDS

R	Obsd. from RSH and $HgCl_2$	Obsd. from dimercaptol and $HgCl_2$	Calcd. for RSHgCl	Calcd. for "addition product"
n-Amyl	9.4	9.7	9.5	6.9
n-Decyl	7.7	7.6	7.8	6.9
n-Dodecyl	7.1	7.2	7.3	6.5

This conclusion differs from that of Rietz, *et al.*,[4] regarding the same reaction. In a study of the dimercaptols of acetonylacetone prepared from mercaptans containing one to twelve carbons, these authors described the "mercuric chloride addition products" derived from each member of the series. Carbon and hydrogen analyses led the authors to assume that four to eight mercuric chloride molecules were attached to each dimercaptol molecule, the exact number being a function of chain length; two cases in which this number was 4.5 were considered "anomalous."

Identification of the reaction products as the RSHgCl compounds permits a simpler explanation. Confirmation is provided by the sulfur analyses (Table II). Furthermore, the calculated carbon and hydrogen contents of the RSHgCl compounds

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[1] H. Gilman, "Organic Chemistry," second edition, John Wiley and Sons, Inc., New York, N. Y., 1943, Vol. II, pp. 1562, 1575.

[2] E. G. Rietz, R.D. Chapman and J. B. Fernandez, THIS JOURNAL, **70**, 3486 (1948).

[3] S. Blackburn and F. Challenger, *J. Chem. Soc.*, 1872 (1938).

[4] E. G. Rietz, J. B. Fernandez, L. T. Snider and T. K. Todsen, THIS JOURNAL, **71**, 3433 (1949).

are in agreement with the observed data reported by Rietz.[4]

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Investigations on Lignin and Lignification. V. Lignin of Cork[1]

BY ROBERT M. DEBAUN AND F. F. NORD

Two procedures have been successfully applied to the isolation of authentic native lignin preparations from wood.[2,3a,b,4] Although several lignins have been isolated by chemical means from cork and bark,[5-11] no native product has been obtained from these sources. We wish to report on the isolation and fractionation of the native lignin of cork.

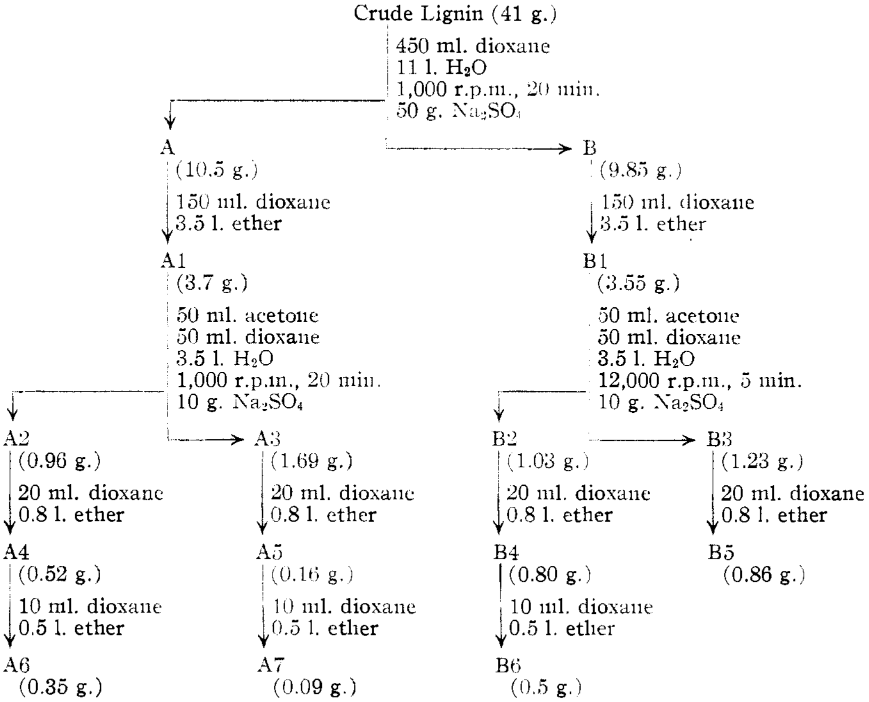

Fig. 1.—Fractionation of the cork native lignin.

This material was fractionated according to the scheme summarized in Fig. 1, and the various fractions were studied with regard to their composition, ultraviolet and infrared absorption spectra, their reaction with the "phenol" reagent,[12,13] and with the phloroglucinol-HCl test.[14,15,16]

An alkali lignin of cork was also prepared.

The dissimilarity of the composition of our native lignin from the alkali lignin, and from the other cork lignins[10,11] suggested to us that our product might be admixed with phenolic extractive materials such as tannin and/or phlobaphene. This supposition was verified by paper chromatography.

Experimental

Native Lignin.—One and one-half kilograms of "männlicher Kork",[10] the bark of *Quercus suber*, ground to 40–60 mesh, was extracted with alcohol in a percolator-type extractor[17] until the extract no longer gave the phloroglucinol-HCl test. The solution was evaporated to dryness *in vacuo* at 40°. The residue (120 g.) was washed with ether several times, and again with water by centrifugation and resuspension with fresh solvent until the supernatant became opalescent. The residual material (41 g.) was then treated as outlined in Fig. 1. Solutions in purified dioxane[18] were added to the ice-cold non-solvents, slowly with stirring. Anhydrous sodium sulfate was used as the salting agent throughout.

Alkali Lignin.—Ether- and then methanol-preextracted cork was autoclaved for 8 hours at 23 pounds pressure in the presence of ten times its amount of 3% sodium hydroxide. The filtered hot mixture was acidified with hydrochloric acid, and the resulting precipitate was redissolved in base and reprecipitated with acid. It was then reprecipitated from acetone solution with ether until a constant methoxyl value (12.40%) was obtained.

Spectra.—The ultraviolet absorption spectra were obtained with a Beckman model DU quartz ultraviolet spectrophotometer, absolute ethanol being used as the solvent. The infrared absorption spectra were determined in an experimental model of the Baird double beam recording spectrophotometer. The wave length accuracy of the instrument was 0.04 μ. The samples were run as mulls in mineral oil.

Colorimetry.—The colorimetric readings were taken in an Evelyn Photoelectric Colorimeter. A 550 mμ filter was used in the phloroglucinol-HCl test. Isolated native white Scots pine lignin was used as the standard, and the reaction is accurate to ± 3 γ in the range 20–120 γ/ml. The production of color is reported to be due to the presence of coniferyl aldehyde groups.[16,19a,b,c] The cork native lignin on contact with phloroglucinol and HCl gives a color similar in spectrum to that obtained with the softwood lignin. The results of the phloroglucinol-HCl test are expressed as per cent. of lignin, the white Scots pine native lignin being taken as 100%. A 600 mμ filter was used for the study with the Mehta reaction. The cork alkali lignin was applied as the standard, and the reaction could be conducted with an accuracy of ± 5 γ in the range 50–200 γ/ml. Addition of 15% Na_2CO_3 is necessary for full development of the color.

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(4) Kudzin and Nord, *ibid.*, **73**, 690 (1951).

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(6) Hilpert and Knackstedt, *Ber.*, **72**, 1582 (1939).

(7) Clothofski, Weikert and Nick, *ibid.*, **74B**, 299 (1941).

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