

TABLE I
THE SYSTEM $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 - \text{CaO} \cdot \text{P}_2\text{O}_5$

No.	Weight fraction $\text{CaO} \cdot \text{P}_2\text{O}_5$	Liquidus, °C.	Crystalline
1	0	627.6	$\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$
	0.046	625	Eutectic
		661	$2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{P}_2\text{O}_5$
2	.094	696	$2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{P}_2\text{O}_5$
3	.258	734 ^a	$2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{P}_2\text{O}_5$
4	.328 (2:1)	738 ^b	$2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{P}_2\text{O}_5$
5	.404	734 ^b	$2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{P}_2\text{O}_5$
6	.448	728 ^c	$2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{P}_2\text{O}_5$
7	.492	739	$\text{CaO} \cdot \text{P}_2\text{O}_5$
8	.700	834	$\text{CaO} \cdot \text{P}_2\text{O}_5$
9	.898	927	$\text{CaO} \cdot \text{P}_2\text{O}_5$
10	1.0	977	$\text{CaO} \cdot \text{P}_2\text{O}_5$

^a No. 3 and 4 together at 733°; 3, very few crystals; 4, hardly sintered. ^b No. 3 and 5 together at 734°; 3, hardly sintered; 5, very few crystals. ^c The eutectic is near; 4° below liquidus both kinds of crystals were present.

is at 625°. The composition was not determined exactly, but it is assumed to be about 0.01 weight fraction CaP_2O_6 . The eutectic between $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{P}_2\text{O}_5$ is at 725°, 0.46 weight fraction CaP_2O_6 . The eutectic composition was obtained by extra-

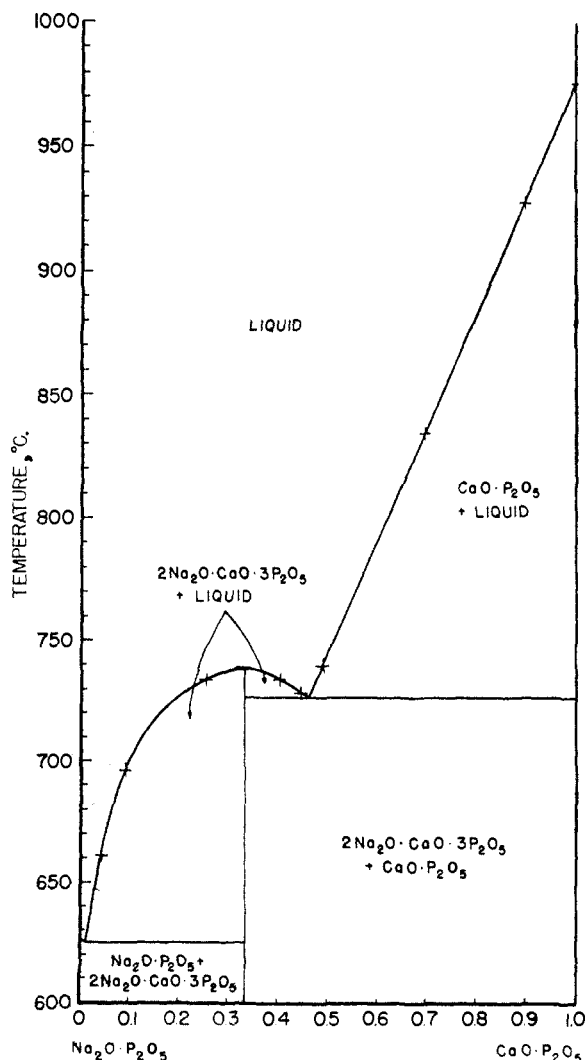


Fig. 1.—The binary system $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 - \text{CaO} \cdot \text{P}_2\text{O}_5$.

polating the two liquidus curves to their intersection.

GEOPHYSICAL LABORATORY
WASHINGTON, D. C.

Color Reactions of Lignin in Solution Compared to Similar Reactions in the Solid State

BY JOHN C. PEW

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In previous work, the color reactions of lignin with phenols¹ and with strong acids² were found to be caused by the presence of a substituted coniferylaldehyde group in the lignin. The colors developed with Brauns' spruce "native lignin" in solution had absorption maxima at the same wave length as those produced with coniferylaldehyde and the respective reagent. With spruce wood sections, the maxima occurred at higher wave lengths, comparable to those resulting with the reagent and solutions of coniferylaldehyde substituted in the 5-position with a propenyl group. This was believed to indicate the presence of a side chain in the 5-position in the color-reacting group of the lignin in spruce wood. Adler,³ however, found absorption at a higher wave length when certain dyestuffs were measured in the solid or adsorbed state than in solution and a similar effect when wood, in which the color reacting group had been destroyed, was impregnated with the colored solution produced by the reaction of coniferylaldehyde with phloroglucinol and then dried. Similar results were obtained with impregnated filter paper. In view of these observations, it seemed desirable to re-examine the color reactions described in the above papers.

The maximum absorption of the colored solution formed by the condensation of coniferylaldehyde with resorcinol was found at a higher wave length (from 579 to 590 $m\mu$) when measured on filter paper that had been impregnated with the solution and dried. The situation with wood sections, however, may not be comparable, since in this case the chromophoric groups developed are probably more or less dispersed throughout the wood substance.

In order to avoid any effects of the solid state on the measurement of the resorcinol color with spruce wood, an attempt was made to put the chromophoric groups into solution. By using spruce wood ground in a vibratory ball mill⁴ and a suitable mixture of concd. hydrochloric acid and ethanolic hydrogen chloride for the reaction vehicle, it was possible to develop and extract concurrently a portion of the colored substance. This extract had a maximum absorption at 586 $m\mu$ as compared to 579 $m\mu$ for spruce "native lignin" or coniferylaldehyde when reacting with resorcinol. Wood sections under the same conditions had a maximum at 593 $m\mu$.

The proportion of the coloring matter from the

- (1) J. C. Pew, *THIS JOURNAL*, **73**, 1678 (1951).
- (2) J. C. Pew, Abstract of Papers, XIIth International Congress of Pure and Applied Chemistry, 616 (1951).
- (3) E. Adler, private communication.
- (4) F. H. Forziati, W. K. Stone, J. W. Rowen and W. D. Appel, *J. Research Natl. Bur. Standards*, **45**, 109 (1950).

ground spruce wood that went into solution was unknown. For this reason, a method was developed to dissolve the wood entirely by stirring fuming hydrochloric acid into finely milled wood that had been moistened with an ethanol solution of resorcinol. In 10 minutes, a purple solution with only a slight haze was obtained. The maximum absorption then occurred at 588 $m\mu$. The solution probably was colloidal in nature, however, and, because the cellulose still was present, the situation actually may not have differed much from that with the wood sections.

The resorcinol staining of "native lignin" in the solid state was investigated as another approach to the problem. To a suspension of spruce "native lignin" in a benzene solution of resorcinol was added hydrogen chloride to develop the color. The stained lignin was filtered off and made into a paste with tricresyl phosphate. A maximum absorption of 587 $m\mu$ was obtained. When a transparent film of the "native lignin" containing resorcinol was stained with hydrogen chloride gas to produce a color, a maximum absorption of 585 $m\mu$ resulted. In both experiments, the colored material was dissolved in a mixture of 1 volume of concd. hydrochloric acid and 2 volumes of ethanol. The resulting solutions had normal maxima at 579 $m\mu$. On the other hand, when "native lignin" suspended in concd. hydrochloric acid was stained with resorcinol, the maximum in the solid state was practically at the same wave length (591 $m\mu$) as that of the material subsequently put into solution. This indicated that some secondary condensation may have occurred.

The color produced by strong acid alone on spruce wood was also reinvestigated. Solutions in which the first color produced (yellow) was partially leached from the milled wood had a maximum absorption in ethanolic hydrogen chloride of 453 $m\mu$, as contrasted to 449 $m\mu$ for coniferylaldehyde solutions and 463 $m\mu$ for wood sections. A solution of the milled wood in fuming hydrochloric acid became emerald green on standing, and the blue component of this color had a maximum absorption at 628 $m\mu$, exactly the same as that obtained with wood sections.

These data indicate that, in spite of the excellent correlation obtained with absorption spectra in previous work^{1,2} further confirmation is required of the type of substitution in the coniferylaldehyde groups responsible for the color reactions of lignin in spruce wood.

Experimental

Measurement of the Coniferylaldehyde-Resorcinol Color on Filter Paper.—A mixture of 0.5 ml. of a 0.01 molar solution of coniferylaldehyde in ethanol, 0.5 ml. of a 0.01 solution of resorcinol in ethanol and 1 ml. of a 38% ethanolic solution of hydrogen chloride was allowed to stand 5 minutes to develop the purple color. After 0.75 ml. of water was added, filter paper was dipped in the solution and air-dried. A portion of the stained paper was mounted in tricresyl phosphate, and, using a similarly mounted piece of unstained paper as a reference, the absorption spectrum was measured as in previous work.¹

Measurement of Resorcinol Color Partially Extracted from Wood.—Resin-free spruce wood meal was dried over anhydrous magnesium perchlorate and then ground 1 hour in a vibratory ball mill.⁴ To 0.03 g. of the resulting powder was added 0.5 ml. of 0.01 molar solution of resor-

cinol in aqueous ethanol, 2.5 ml. of a 38% ethanolic solution of hydrogen chloride, and 2.5 ml. of concd. hydrochloric acid. The mixture was stirred at room temperature for 15 minutes, 2 ml. of water added, and the mixture diluted to 15 ml. with ethanol and filtered with suction on an asbestos mat. The absorption spectrum was measured on the filtrate at 2°.

Measurement of Resorcinol Color Produced with Wood in Solution.—A portion of the powdered spruce wood weighing 0.012 g. was moistened with 0.3 ml. of a 0.001 molar ethanol solution of resorcinol and 5 ml. of fuming hydrochloric acid added with stirring. After standing 10 minutes with occasional stirring, the solution was diluted to 15 ml. with concd. hydrochloric acid, and the color measured as with the extracted resorcinol color.

Resorcinol Staining of "Native Lignin" in the Solid State.—Spruce "native lignin" (0.05 g.) was suspended in 5 ml. of benzene containing 0.005 g. of resorcinol in solution, and a stream of hydrogen chloride was bubbled through the mixture for 5 minutes. The mixture was allowed to stand an additional 5 minutes before the lignin was filtered on a fritted glass crucible. The benzene was then allowed to evaporate from the filtrate, and a portion of the stained powder residue was rubbed up with tricresyl phosphate. A film of this paste was spread on a glass slide for measurement of the absorption spectrum. When the reaction was conducted in hydrochloric acid suspension, the same amount of "native lignin" was stirred into a solution of 0.005 g. of resorcinol in 1 ml. of concd. hydrochloric acid. After the solution stood for 5 minutes, the lignin was filtered off, air-dried, and made into a paste as before.

In the film experiment, one or two drops of a solution of 0.1 g. of "native lignin" and 0.01 g. of resorcinol in a mixture of 1 ml. of ethanol and 1 ml. of Cellosolve were placed on a glass slide, and the solvent was allowed to evaporate. The color was developed by placing the slide in an atmosphere of hydrogen chloride for a few minutes.

Colors Produced by Action of Acid on Spruce Wood.—Powdered spruce wood (0.03 g.) was moistened with 2 drops of ethanol, the mixture cooled to -30°, and 4 drops of cold fuming hydrochloric acid were stirred into the moistened powdered wood. The resulting yellow gel was diluted to 10 ml. with a 38% ethanolic solution of hydrogen chloride. Glass beads were added, and the mixture was shaken for 5 minutes, allowed to stand for an additional 5 minutes, and filtered by gravity on a fritted glass crucible. All these operations were carried out at -30°. The absorption spectrum of the clear yellow solution was determined at -10°.

To produce an emerald-green solution of the wood, 0.03 g. of the powdered substance was moistened with 0.2 ml. of ethanol, 9.8 ml. of fuming hydrochloric acid stirred in, and the mixture allowed to stand for 10 minutes. The operation was carried out at -30°. To develop the green color, this yellow solution was warmed to 2° and maintained at that temperature for 2 hours.

FOREST PRODUCTS LABORATORY, FOREST SERVICE
U. S. DEPARTMENT OF AGRICULTURE
UNIVERSITY OF WISCONSIN
MADISON 5, WISCONSIN

The Stereochemistry of the 3-Carboxycyclohexaneacetic Acids

BY FAUSTO RAMIREZ AND JOHN W. SARGENT¹
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Only one diastereoisomeric form of 3-carboxycyclohexaneacetic acid, of unknown configuration, has been reported.² This substance, m.p. 156-158°, was obtained by Komppa³ from the catalytic

- (1) From part of the Ph.D. thesis of J. W. Sargent.
- (2) Both *cis*- and *trans*-2-carboxycyclohexaneacetic acids, of known configurations have been prepared (E. G. Davis, Ph.D. dissertation (1942) in "Summaries of Theses," Harvard Graduate School (1946)). Only one form of 4-carboxycyclohexaneacetic acid appears to be known; G. Komppa (*Ber.*, **68B**, 1287 (1935)) assigned to this substance, which formed no anhydride, the *trans* configuration.
- (3) G. Komppa, T. Hirn, W. Rohrmann and S. Beckmann, *Ann.*, **521**, 242 (1936).