

maintained with entropy and heat values obtained by Ishikawa or by Ueda who measured the temperature coefficient of a different cell, disagree-

ment is found with entropy and heat values obtained by Larson.

EAST LANSING, MICHIGAN

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. L. Fractionation of Acetylated Cell Wall Constituents of Red Oak Wood¹

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

It is not yet known whether in the plant cell wall the lignin exists in the free state or whether it is in partial or complete chemical combination with carbohydrate substances. Considerable indirect evidence² is at hand indicating the presence of such a combination although Klason,^{3a} Freudenberg,^{3b} and Brauns^{3c} have shown independently that a very small part of what is apparently protolignin can be extracted from wood by neutral organic solvents at room temperature, indicating that this extracted fraction probably has a relatively simple structure and is not combined with carbohydrates.

It is possible that a chemical combination between lignin and carbohydrate exists, perhaps as a glycosidic or an ether linkage between a phenolic hydroxyl group of the lignin and some hydroxyl grouping in the pentosans or cellulose. The acetolysis of such a compound might be expected to result in changes in general similar to those experienced in the case of acetolysis of cellulose wherein a simultaneous acetylation and hydrolytic reaction occurs, so that the resulting degree of polymerization depends upon the extent to which the acetolysis change has proceeded.⁴

Several previous investigators⁵ elsewhere and

in these Laboratories have studied the acetylation of wood from the point of view of preventing complex condensation or polymerization changes in the individual cell wall constituents by means of a prior acetylation of reactive hydroxyl groups. Success in application of the method in this connection, a matter of considerable importance in the investigation being reported, is shown by the preparation of an oak lignin soluble in sodium bisulfite solution⁶ and also partially convertible into lignin building units on ethanolysis.⁷

In the present research an attempt has been made to employ a hydrolytic acetylation, *i. e.*, an acetolysis reaction, in order to obtain an acetylated oak wood, soluble in organic solvents, which by mixed solvent fractionation could be examined for the presence of a lignin-carbohydrate complex. It was hoped that fission of any existing linkages would not proceed to the extent of rupture of all bonds, and that at least a small fraction of a lignin carbohydrate compound would be preserved in the soluble state. It also was desirable to devise a method of purification of acetylated lignin which would avoid the laborious and inefficient acetone extraction step of Suida and Titsch.^{5d}

Thus resin-free, alkali-extracted red oak wood meal was acetylated with acetic anhydride in glacial acetic acid solution, using sulfuric acid as the catalyst. The "crude acetylated wood" was recovered by pouring the reaction mixture into water.

In a series of experiments in which the maximum temperature of acetylation was varied, it was established that the solubility of "crude acety-

(1) From a thesis presented to the Faculty of Graduate Studies and Research, McGill University, by Quintin P. Peniston, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, May, 1939.

(2) (a) Erdmann, *Liebigs Ann. Chem. Suppl.*, **5**, 223 (1867); (b) Cross, *J. Chem. Soc.*, **55**, 199 (1889); (c) Klason, *Ber.*, **56**, 300 (1923); (d) Harris, Sherrard and Mitchell, *THIS JOURNAL*, **55**, 889 (1934); (e) Norman and Shrikhande, *Biochem. J.*, **29**, 2259 (1935). See also recent reviews: (f) Hagglund, "Holzchemie," Akad. Verlag., Leipzig, 1939, p. 206; (g) Norman, "The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.," Clarendon Press, Oxford, 1937, p. 59; (h) compare Freudenberg, "Tannin, Cellulose, Lignin," J. Springer, Berlin, 1933, p. 145; (i) Cross and Bevan, "Researches on Cellulose," Vol. 4, Longmans, Green, London, 1922, pp. 152, 170.

(3) (a) Klason, "Beitrage zur Kenntnis der chemische Zusammensetzung des Fichtenholzes," Berlin, 1911, pp. 34-36; (b) Freudenberg, Janson, Knopf, and Haag, *Ber.*, **69**, 1415 (1936); (c) Brauns, *THIS JOURNAL*, **61**, 2120 (1939).

(4) Freudenberg, *Ber.*, **54**, 767 (1921).

(5) (a) Fuchs, *ibid.*, **61**, 948 (1928); (b) Horn, *ibid.*, **61**, 2542 (1928); (c) Suida and Titsch, *ibid.*, **61**, 1599 (1928); (d) Suida and

Titsch, *Monatsh.*, **54**, 700 (1929); (e) Lieser and Schwind, *Ann.*, **532**, 104 (1937); (f) Steeves, Ph.D. Thesis, McGill University, 1936; (g) Lief, *ibid.*, 1938; (h) Hawkins, *ibid.*, 1938.

(6) (a) Hibbert and Steeves, *THIS JOURNAL*, **59**, 1768 (1937); (b) Steeves and Hibbert, *ibid.*, **61**, 2194 (1939); (c) Hawkins, Wright and Hibbert, *ibid.*, **59**, 2247 (1937).

(7) Peniston, McCarthy and Hibbert, *ibid.*, **61**, 530 (1939).

lated wood" in chloroform increased with increase in the maximum temperature as follows:

EFFECT OF ACETYLATION TEMPERATURE ON SOLUBILITY OF CRUDE ACETYLATED WOOD

Max. temp. during acetylation, °C.	Solubility in chloroform, %		
	Individual expts.		
25	47.7		
28	71.2	79.0	75.5 67.4
35	76.1	80.0	79.0
			Average
			47.7
			73.3
			78.4

Since in these experiments the yields in the acetylation step (156–161%), and the acetyl contents of the products (40–41% COCH₃) were practically the same, it can be concluded that the acetylation was substantially complete, and that, in agreement with previous views,^{5d,e} the solubility of acetylated wood in organic solvents is largely dependent upon the extent to which the acetolysis has proceeded during the acetylation reaction. This concept is in harmony with the experience of the authors and others^{5d} that, in the absence of hydrolytic catalysts such as sulfuric acid, acetylation does not proceed to the above degree, and the product is not appreciably soluble in organic solvents.

Since the presence of a chemical linkage between lignin and carbohydrate in the products isolated can be proven only by first showing that the materials cannot be separated, various methods of solvent fractionation were considered. That of Suida and Titsch,^{5d} involving acetone extraction of the chloroform-soluble fraction of the crude acetylated wood, gives^{6b} an acetone-soluble "lignin fraction," containing 35 to 37% acetyl and 8 to 11% methoxyl, which may be further separated by fractionation procedures. The authors found this method unsatisfactory for their purposes, and therefore developed a more effective method based on the mixed solvent fractionation scheme which Schulz⁸ has found so useful in studies of the distribution function of polymer homologous series. Although chloroform seemed to be the best solvent for the crude acetylated wood, it was not possible to obtain satisfactory flocculation of the product from it into any other "non-solvent" investigated. Dioxane, however, proved to be almost as good a solvent as chloroform, and gave a workable flocculent precipitate on addition of methanol. Therefore the crude acetylated wood was fractionated with dioxane and methanol according to the procedure outlined in the experimental section.

Analytical and calculated results indicating the

(8) Schulz, *Z. Physik. Chem.*, **30**, 390 (1935).

changes undergone by the wood on extraction, acetylation and fractionation are summarized in Table I. From these data, it is apparent that in the course of the alkali extraction of the resin-free wood meal, about two-thirds of the pentosans and one-fourth of the lignin present in the original wood are dissolved away. This is significant because both Suida and Titsch^{5d} and Lieff^{5g} have shown that this hydrolytic step is necessary if satisfactory acetylation and solubility of the acetylated wood in organic solvents is to be achieved. Little change in the gross composition of the wood is caused in the acetylation step.

It is of interest that the methoxyl-containing constituents in a fraction ("dioxane-chloroform-insoluble") of the crude acetylated wood, despite the fact that substantially complete acetylation has been attained, dissolve neither in dioxane nor chloroform, although Steeves and Hibbert^{6b} have shown that isolated lignin acetates are readily soluble in these solvents. A similar condition seems to prevail in the *dioxane-soluble* "carbohydrate" fractions (I, II and III) in that here a nearly constant composition is maintained, even after the three re-precipitations. Two further reprecipitations, making five in all, yielded a fraction (IIaa) still containing methylated materials, pentosans and cellulose in nearly the same ratio as before. These results, and particularly the latter derived from soluble materials, strongly indicate the chemical combination of the methoxyl-containing substances in these fractions with both the cellulose and the pentosans.

The "lignin" fraction (V) was not isolated by the Schulz re-precipitation technique, but instead, when the concentrated mother liquor from IV was diluted with methanol and allowed to stand, V formed spontaneously as an oily film clinging to the sides of the precipitation vessel, thus leaving the precipitation residue, VI, to be recovered by evaporation of the mother liquor. Two re-precipitations of this oil yielded a fraction (Vaa) containing a very high concentration of lignin, a small amount of probably uncombined pentosans, and practically no cellulose.

It is to be noted that the lignin content of the several fractions shown in Table I is estimated from the results of methoxyl analyses on the arbitrary assumption of 23.0% methoxyl in the lignin. There is some evidence⁹ that methylated carbo-

(9) (a) O'Dwyer, *Biochem. J.*, **22**, 381 (1928); (b) Ritter and Kurth, *Ind. Eng. Chem.*, **25**, 1250 (1933).

hydrates occur in plant tissue. If present, they would be expected, in these cases, to contribute to the apparent lignin content of the fractions. However, the dioxane-soluble, carefully fractionated I and IIa were analyzed¹⁰ and found to contain 4.3 and 2.4% Klason lignin, respectively, when calculated on an acetyl-free basis, comparable to the calculated values given in Table I. These results, as well as those from solvent-extracted wood meal, alkali- and solvent-extracted wood meal, and crude acetylated wood, show that the Klason lignin content of the materials is lower than the lignin value calculated from the methoxyl analyses, perhaps partially due to the presence of methylated substances soluble in 72% sulfuric acid, to the influence of the acetyl groupings present, and also to the uncertainty as to what methoxyl content to assume. This difference is generally encountered with acetylated, lignin-containing materials. Methoxyl analyses on the Klason lignin preparations from I and IIa gave values, 18.2 and 18.6% methoxyl, respectively, which are somewhat lower than those usually found, although still of the proper order of magnitude expected for extracted lignins. The fact that lower values are obtained in these two fractions as compared with the extracted lignin from VI (23.8% OCH₃) may be due to the greater importance of non-methylated carbohydrate humification products in the former case. However, within the limitations of our present knowledge, it can be concluded that the methoxyl groupings of the dioxane soluble fractions are united largely to the lignin.

In general the results of this investigation are in harmony with the concept that the acetylation reaction is one of acetolysis of intercombined cell wall constituents. The apparent necessity of the preliminary hydrolytic alkaline extraction, as well as the fact that methoxyl-containing materials could not be removed from either soluble or insoluble fractions by solvents in which such constituents when isolated are known to be soluble, points to the existence of a general combination between the lignin and perhaps both the pentosans and the cellulose. This view can be used to explain satisfactorily several previously reported results^{11,5c} although there are serious objections to

extending it to include *all* of the cell wall constituents since good evidence¹² has been presented showing that portions of lignin and carbohydrate are highly localized in certain areas of the plant cell wall.

Experimental

Extraction of Wood Meal.—Air-dry red oak (*Quercus rubra*) wood meal (60–80 mesh) was extracted with ethanol-benzene (1:1), ethanol-water (60°) and finally was washed with ethanol, then air-dried at 25°. *Anal.*¹³ Found: hot water extractives, 0.9%; alcohol-benzene extractives, 0.2%; Klason lignin, 20.9%; Cross and Bevan cellulose, 57.8%.

Under a nitrogen atmosphere the extracted red oak wood meal was then subjected to four forty-eight-hour treatments with aqueous alkali (2 liters of 5% sodium hydroxide per 100 g. of wood meal at 25°). Following each treatment the wood meal was washed exhaustively with water at 60°, finally with acetic acid (1%), water, and ethanol, and then air-dried at 25°; yield, 72.8%. *Anal.* Found: Klason lignin, 21.4%; Cross and Bevan cellulose, 68.1%.

Acetylation of the Wood Meal.—Acetic anhydride (1800 g.), glacial acetic acid (1600 g.), and sulfuric acid (14 g.) were mixed and cooled to 0°. Extracted wood meal (205 g. or 200 g. oven-dry basis) was slowly added with stirring. A nitrogen atmosphere was maintained through the whole reaction period. The mixture was allowed to come to room temperature over a period of three hours, and then held at 28° for five hours. The dark green viscous suspension was allowed to stand twelve hours at approximately 25° and then poured slowly into ice water (20 liters) to which sodium hydroxide was added as needed to maintain neutrality. The light cream-colored curdy acetylated wood was washed in a linen sack for forty-eight hours with cold running water to remove all traces of sulfuric acid. The product was air-dried at room temperature; yield, 322 g. *Anal.* Found: Klason lignin, 11.6%; chloroform solubility, 76.1%. By means of the sodium fusion test, sulfur was shown to be absent.

Fractionation of the Acetylated Wood.—Crude acetylated wood (50 g.) was triturated in a mortar with anhydrous dioxane (750 cc.). The insoluble portion was removed in the centrifuge, washed with two additional portions of dioxane (750 cc.), and with ligroin¹⁴ and finally dried¹⁵ to give the *Dioxane Insoluble Fraction*, yield 18.8 g.

A portion (9.4 g.) of this fraction was triturated with chloroform (200 cc.), allowed to stand in this solvent for twelve hours, and the mixture then filtered through a solid sodium chloride filter, yielding a light yellow chloroform solution and a gelatinous residue. The latter was washed four times by stirring with distilled water (one hour) and decanting the aqueous sodium chloride solution, then dried and analyzed as the *Chloroform Insoluble Fraction*; yield, 5.97 g.

(12) Bailey, *Ind. Eng. Chem., Anal. Ed.*, **8**, 52, 389 (1936).

(13) In all cases analyses are expressed on the oven dry basis. Methoxyl, acetyl, pentosan, and approximate chain length of cellulose results are not shown in the experimental section but instead are given in Table I.

(14) In all cases ligroin of b. p. 30–50° was used.

(15) In all cases mentioned below samples were dried over phosphorus pentoxide in an Abderhalden pistol at 64° and 15 mm. pressure.

(10) Ritter, Seborg and Mitchell, *Ind. Eng. Chem. Anal. Ed.*, **4**, 202 (1932).

(11) (a) Urban, *Cellulosechem.*, **7**, 73 (1926); (b) Wacek, *Ber.*, **61**, 1604 (1928); (c) Harris, Sherrard and Mitchell, *This Journal*, **56**, 889 (1934).

TABLE I
 ANALYSES OF ACETYLATED WOOD FRACTIONS

Fraction	Analytical results						Approx. cellulose chain length, glucose units	Calculated ^b composition of— CH ₃ CO free fraction		
	Calcd. yields, ^a g. Found	CH ₃ CO free	CH ₃ O, %	CH ₃ CO, %	Pentosan, %	Cellulose, %		Pentosans, %	Lignin, %	
Solvent-extracted wood meal	100	96.5	6.1	3.5	28.4	...	59.5 ^d		21.5 ^e	
Alkali-solvent extr. wood meal	72.8	72.7	5.9	0.1	13.2	...	43.1	29.4	27.5	
Crude acetylated wood	117	70.1	3.91	40.1	7.16	...	68.1 ^d		21.4 ^e	
Dioxane insol. fraction	44.0	27.6	4.59	37.3	3.62	...	61.0	13.2	25.8	
CHCl ₃ insol.	28.0	17.3	4.84	38.1	2.67	...			19.3 ^e	
CHCl ₃ sol.	3.2	(2.0)	1.14	37.3 ^e	1.98	...	59.6	12.0	28.4	
Dioxane soluble							62.4	5.8	31.8	
I	16.3	9.4	0.85	42.6	2.08	178	61.7	4.3	34.0	
II	20.5	11.5	.70	43.4	1.73	168	88.9	(3.2)	(7.9)	
IIaa	18.1	(10.2)	.77	43.4 ^e	1.15	...	89.9	3.6	6.5	
III	6.1	3.4	.84	44.0	2.10	99	91.5	3.1	5.4	
IV	4.2	2.5	4.14	39.8	2.35	69 ^f	(92.1)	(2.0)	(5.9)	
V	6.6	4.7	12.34	28.9	12.3	...	89.7	3.8	6.5	
Va	4.1	..	13.25	69.3	3.9	29.8	
Vaa	3.4	2.4	14.00	29.9	9.18	...	7.2	17.3	75.5	
VI	15.5	10.4	6.73	32.8	17.0	81.0	
							0.0	13.0	87.0	
							31.2	25.3	43.5	

^a Calculated on a basis of 100 g. of solvent-extracted wood meal. ^b See remarks in experimental section regarding method of calculation. ^c Not analytical, but assumed values of acetyl content from which parenthesized data were calculated. ^d Experimental Cross and Bevan cellulose values calculated on acetyl-free basis. ^e Experimental Klason lignin values calculated on acetyl-free basis. ^f Value uncertain because of large amount of lignin present.

The chloroform solution from which the above *Chloroform Insoluble Fraction* had been separated was concentrated to 50 cc., then precipitated into a mixture (500 cc.) of equal volumes of dioxane and methanol (no precipitation occurring with dioxane alone). The precipitate was removed by centrifuging, redissolved in chloroform (50 cc.), and precipitated as before. It was then washed twice in the centrifuge cup with portions (100 cc.) of ligroin, dried and analyzed as the *Chloroform Soluble Fraction*; yield, 0.68 g.

The dioxane solutions and washings from which the above *Dioxane Insoluble Fraction* had been separated were combined, concentrated, under reduced pressure to 500 cc., and then fractionated by mixed solvent precipitations. For example, in the case of the isolation of *Fraction I*, anhydrous methanol (500 cc.) was added in a fine stream with vigorous stirring to the *Dioxane Soluble Fraction* (500 cc.). The resulting white, flocculent precipitate, after removal in the centrifuge, was twice more re-precipitated from dioxane solution (500 cc.) by addition of methanol (500 cc.), and the final precipitate washed with ligroin and dried as *Fraction I*; yield, 6.97 g.

In a similar manner the liquors from the precipitations and washings of *Fraction I* were concentrated and thrice re-precipitated as *Fractions II, III, and IV*, except that the dioxane-methanol ratios were 1:1.43, 1:2, and 1:5, respectively, and the yields were 8.78, 2.61, and 1.81 g., respectively. In the extraction of the *Crude Acetylated Wood* and the precipitations of *Fractions I to IV*, the ratio of dioxane to solute was approximately 15:1 (cc./g.) in each case.

A portion (5.82 g.) of *Fraction II* was re-precipitated by

first dissolving it in anhydrous dioxane (58 cc.). It was difficultly soluble and, after standing for twenty-four hours, more dioxane (42 cc.) was added and the mixture shaken for twelve hours, yielding a slightly turbid solution. *Fraction IIa* was re-precipitated by addition of methanol (150 cc.) and recovered by centrifuging. This product was redissolved in dioxane (100 cc.), again re-precipitated with methanol (150 cc.), collected in the centrifuge, washed with ligroin and dried to give *Fraction IIaa*; yield, 5.14 g.

The liquors from the precipitation of *Fraction IV* were concentrated under reduced pressure to 100 cc., methanol (1400 cc.) was added and the mixture allowed to stand for forty-eight hours at 0°. An oily film which separated out clinging to the sides of the precipitation vessel was dissolved in chloroform, precipitated into ligroin, washed with ligroin and dried as *Fraction V*; yield, 2.83 g.

A portion (1.83 g.) of *Fraction V* was re-precipitated by dissolving it in dioxane (15 cc.) and slowly pouring the solution into methanol (120 cc.), the precipitate forming a white, fine oily suspension. This mixture was allowed to stand for forty-eight hours at 0°, during which period the solution became almost clear and a yellow oil settled to the bottom of the container. The solution was removed by decantation and then centrifuged, which increased its clarity and caused further precipitation of oil as a film on the sides of the vessel. The precipitated oils were combined, dissolved in chloroform, and precipitated into ligroin, washed with ligroin, and dried as *Fraction Va*; yield, 1.17 g.

A portion (0.87 g.) of *Fraction Va* was dissolved in dioxane (10 cc.) and again precipitated by methanol (80

cc.). After standing for forty-eight hours at 0°, the oily product was recovered by the same method as used for *Fraction Va* to give finally *Fraction Vaa*; yield, 0.72 g.

The liquors remaining from the separation of *Fraction V* were evaporated to dryness at reduced pressure. The residue was taken up in chloroform, precipitated into ligroin, filtered, washed with ligroin and dried to give *Fraction VI*; yield, 6.63 g.

Portions of *Fractions I* and *Iia* on analysis¹⁰ for Klason lignin gave 4.3 and 2.4%, respectively, calculated on an acetyl-free basis. Methoxyl analyses¹⁶ on these materials gave 18.2 and 18.6% methoxyl, respectively.

A portion (1.404 g.) of *Fraction VI* heated at 100° with 3% sulfuric acid (200 cc.) for twelve hours in a flask fitted with a reflux condenser gave a brown, amorphous precipitate and a bright yellow solution, the latter showing a positive test for furfural with aniline hydrochloride paper. The insoluble residue was filtered off, washed with hot distilled water and dried; yield, 0.2556 g. *Anal.* Found: OCH₃, 23.8%.

The estimations of methoxyl,¹⁶ acetyl,¹⁷ pentosan,¹⁸ and viscosity¹⁹ (0.100% solutions in chloroform at 25°) were carried out by standard methods. The data are given in Table I, the pentosan yield being taken as 1.71 times the percentage of furfural, and the chain length being deduced from the viscosity by means of the value²⁰ $K_m = 5.3 \times 10^{-4}$.

The composition of the fractions on an acetyl-free basis as shown in Table I was calculated from the results of the acetyl, methoxyl and pentosan analyses (arbitrarily assuming 23.0% methoxyl in lignin) exemplified for *Fraction I* as follows:

$$\frac{(0.85)(100)(100)}{(100-42.6)(23.0)} = 6.5\% \text{ lignin}$$

$$\frac{(2.08)(100)}{(100 - 42.6)} = 3.6\% \text{ pentosan}$$

$$100 - (6.5 + 3.6) = 89.9\% \text{ cellulose}$$

(16) Vieböck and Schwappach, *Ber.*, **63**, 2818 (1930).

(17) Friedrich and Rapoport, *Biochem. Z.*, **251**, 432 (1932).

(18) (a) Powell and Whittaker, *J. Soc. Chem. Ind.*, **43**, 36T (1924);

(b) see also Kline and Acree, *Bur. Standards J. Research*, **8**, 25 (1932).

(19) Fordyce and Hibbert, *THIS JOURNAL*, **61**, 1912 (1939).

(20) Staudinger and Daumiller, *Ann.*, **529**, 219 (1937).

Summary

1. Red oak wood meal previously extracted with alcohol-benzene followed by aqueous alkali was subjected to acetolysis at temperatures of 25, 28 and 35° using acetic anhydride, glacial acetic acid and a catalyst, sulfuric acid; the crude acetylated wood was isolated and investigated.

2. The solubility in chloroform of crude fully acetylated wood increases with the temperature of acetylation, indicating that the extent of acetolysis determines the degree of solubility of the crude acetylated wood in organic solvents.

3. The crude acetylated wood was separated by differential solubilities into the following fractions: (a) dioxane insoluble; (b) dioxane-chloroform insoluble, and (c) dioxane insoluble-chloroform soluble. The dioxane soluble material, using the Schulz re-precipitation technique with increasing methanol to dioxane ratios, was divided into six fractions. Methoxyl, acetyl, pentosan content and yield of the several fractions were determined.

4. Methoxyl-containing substances, apparently lignin, were retained in the dioxane-chloroform insoluble fraction and also in certain dioxane soluble fractions in spite of numerous attempts to remove such materials from both the insoluble and soluble fractions.

5. The results are in apparent harmony with the concept of the reaction as one of acetolysis of intercombined cell wall constituents, the latter involving perhaps a general combination between the lignin and both pentosans and cellulose. Not all these three latter products can be thus united.

MONTREAL, CANADA

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[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Reactions of Aldehydes with Amines. I. With *o*-Aminophenol

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In an investigation being undertaken in this Laboratory it became necessary to prepare a series of azomethine derivatives in which *o*-aminophenol constituted the amine portion of the molecule. A search of the literature revealed several discrepancies. Levi¹ states that only *p*-aminophenol has been reported as condensing with aldehydes. We found twelve compounds from *o*-aminophenol listed. According to Möhlau and

Adam,² the compounds obtained from the three nitrobenzaldehydes and *o*-aminophenol are addition compounds containing the group -NH-CHOH- instead of the usual -N=CH- group. They assumed that the presence of the nitro group inhibits the loss of water. Pope³ found that the usual azomethine compound formed when meta- and para-nitrobenzaldehyde were

(2) Möhlau and Adam, *Chem. Zentr.*, **78**, 107 (1907).

(3) Pope, *J. Chem. Soc.*, **93**, 532 (1908).

(1) Levi, *Gazz. chim. ital.*, **59**, 544 (1929); *C. A.*, **24**, 351 (1930).