conditions, is proportional to the copper content of these preparations. Since it has been shown by Keilin and Mann, and confirmed in these laboratories, that the activity toward catechol, in the case of these high catecholase preparations, is also proportional to the copper content, it follows that the Adams and Nelson values would also be proportional to the catecholase activity.

Summary

1. Evidence is offered indicating that the action of tyrosinase on hydroquinone resembles the action of the enzyme on monohydric phenols.

2. When hydroquinone is oxidized by tyrosinase, in the presence of a small amount of catechol, the reaction and the product formed are different from those occurring when hydroquinone is oxidized by means of laccase.

3. A greater total oxygen uptake occurs in the oxidation of hydroquinone by tyrosinase when the ratio of the activity toward monohydric phenols over the activity toward *o*-dihydric phenols is large.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Aldehyde–Resorcinol Condensations[1]

BY JOSEPH B. NIEDERL AND HEINZ J. VOGEL[2]

A crystalline condensation product of acetaldehyde with resorcinol has been reported by several investigators[3,4,5] but the statements relative to the constitution of this compound are conflicting. Thus the conventional alkylidene-diphenol[3] as well as the acetal[4] structure has been suggested. It is the purpose of the present investigation to contribute to the elucidation of the structure of not only this disputed compound, but also of its derivatives and homologs and to compare the products with the recently established structures of certain crystalline ketone–resorcinol condensation products[6] which involved multiple alkylation of the resorcinol.

Quantitative elementary analysis of the crystalline, water-free acetates and propionates of the acetaldehyde–, propionaldehyde– and iso-valeraldehyde–resorcinol condensation products indicated an equimolar ratio of the reactants, the same as encountered in the aldehyde–phenol and cresol condensations.[7] However, molecular weight determinations indicated that the ratio of reactants is 4:4. The compounds are insoluble in water, yet seem to possess eight free phenolic hydroxyl groups as indicated by the formation of crystalline octa-acetates, octa-propionates and octa-methyl ethers. The original condensation products, as well as their methyl ethers, retain various amounts of water of crystallization very tenaciously, which may explain the difference in the analytical results obtained by the previous investigators. The condensation products do not appear to undergo hydrolysis upon refluxing with alcoholic sulfuric acid (absence of acetal linkages) nor with hydriodic acid (absence of ether linkages). Thus carbon to carbon linkages throughout are strongly indicated.

In the condensation of resorcinol with ketones, two alkyl radicals always enter the resorcinol molecule. Undoubtedly a similar behavior must be anticipated when an aldehyde is used instead of a ketone in such condensations. On the other hand, equimolar condensation of aldehydes with phenols as previously observed also has to be considered. Of the few structural formulas which would satisfy the above enumerated physical and chemical behavior, as well as that of analogous compounds, open chain as well as ring structures have to be taken into consideration. An open chain structure would imply polymerization and there would be no reason why polymerization should stop at exactly the tetrameric stage, regardless of the aldehyde used, or of the reaction conditions employed. Also the crystalline state and the high melting points of the compounds do not favor such a structure.

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[1] This communication is part of a paper entitled: "Syntheses of New Polycyclics" which was presented before the Division of Organic Chemistry at the Detroit meeting of the American Chemical Society, September, 1940.

[2] Abstracted from the thesis submitted by Heinz J. Vogel to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science.

[3] Michael and Comey, *Am. Chem. J.*, **5**, 349 (1883).

[4] Moehlau and Koch, *Ber.*, **27**, 2887 (1894).

[5] Causse, *Ann. chim.*, [vii] **1**, 90 (1894).

[6] J. B. Niederl and V. Niederl, THIS JOURNAL, **61**, 348 (1939).

[7] J. B. Niederl and co-workers, *ibid.*, **59**, 1113 (1937).

TABLE I

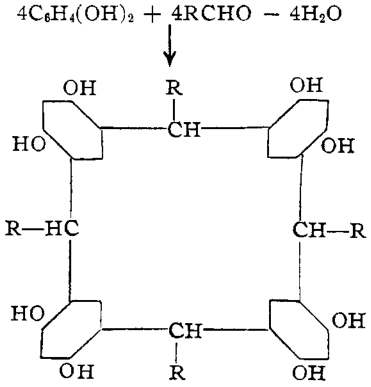
CHEMICAL CONSTANTS AND ANALYSES OF COMPOUNDS

	Compound	M. p. °C. (uncor.)[a]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. wt.[9] Calcd.	Mol. wt.[9] Found
	Acetaldehyde–Resorcinol Condensation Product								
I	Mono-hydrate	>300	$C_{32}H_{34}O_9$	68.33	68.37	6.05	6.06		
	(a) Acetate[10]	282	$C_{48}H_{48}O_{16}$	65.45	65.15	5.45	5.72	800	1021 880
	(b) Propionate	222	$C_{56}H_{64}O_{16}$	67.61	67.61	6.45	6.68	992	1165 950
	(c) Methyl ether (mono-hydrate)	256	$C_{40}H_{50}O_9$	71.21	71.60	7.41	7.30	688	
	Propionaldehyde–Resorcinol Condensation Product								
II	Mono-hydrate	>300	$C_{36}H_{42}O_9$	69.90	69.84	6.80	7.08	618	
	(a) Acetate	242	$C_{52}H_{56}O_{16}$	66.67	66.73	5.98	6.16	936	975
	(b) Propionate	114	$C_{60}H_{72}O_{16}$	68.70	68.41	6.87	7.22	1048	1191
	(c) Methyl ether (mono-hydrate)	227	$C_{44}H_{58}O_9$	72.33	72.86	7.94	7.96		
	Isovaleraldehyde–Resorcinol Condensation Product								
III	Di-hydrate	>300	$C_{44}H_{60}O_{10}$	70.58	70.44	8.02	7.98		
	(a) Acetate	>300	$C_{60}H_{72}O_{16}$	68.70	68.66	6.87	6.42	1048	1189

[a] All substances melt with decomposition.

Ring structures possessing four times the same molecular aggregates are widely encountered in the heterocyclic series (porphyrins, hemin, chlorophyll, etc.). A similar type of structural pattern for the aldehyde–resorcinol condensation products would be in harmony with the physical and chemical properties of these compounds. Such a structure would not only involve a most simple type of condensation but would also indicate that resorcinol can react like pyrrole under similar circumstances. Also the requirements of "equimolar condensation"[7] as well as "multiple alkylation"[6] appear fulfilled. This type of structure would involve the simple reaction mechanism of a fourfold self-condensation through intermolecular dehydration, of the intermediate "resorcinol-hydrin"[8] as shown

$4C_6H_4(OH)_2 + 4RCHO - 4H_2O$



R = CH_3 (I); C_2H_5 (II); $CH(CH_3)_2$ (III)

Experimental

Method of Condensation

With Acetaldehyde and Propionaldehyde (I and II).—Fifty grams of resorcinol was dissolved in 500 cc. of 10% sulfuric acid in a round-bottomed flask placed on a steam-bath. A solution of acetaldehyde in dilute sulfuric acid was prepared by slowly adding 110 cc. of 10% aqueous sulfuric acid to 190 cc. of a 10% solution of the aldehyde in water. The mixture was kept cool and was added to the resorcinol solution at the rate of 5 cc. every five minutes. The reaction mixture was then allowed to stand for several days, after which time the condensation product was filtered off and recrystallized from alcohol.

With Isovaleraldehyde (III).—The above procedure was modified by using 50% alcohol instead of water for both the resorcinol and the aldehyde solutions. After the addition of the aldehyde solution the reaction mixture was allowed to stand in a loosely covered vessel for several weeks. The condensation product was then filtered off, washed thoroughly with water and recrystallized from alcohol.

Acetates (Ia, IIa, IIIa).—Five grams of the condensation product was refluxed with 50 cc. of acetic anhydride for two hours. The solution was then poured into 100 cc. of water and was allowed to stand for one hour. The precipitate was collected on a filter and recrystallized from dilute alcohol.

Propionates (Ib, IIb).—Two-tenths gram of condensation product was refluxed with 10 cc. of propionic anhydride for two hours. The solution was then poured into 100 cc. of water. A semi-solid separated which gradually solidified after boiling with water. The solid was filtered off and recrystallized from dilute alcohol.

Methyl Ethers (Ic).—Thirty-eight grams of condensation product I was dissolved in 400 cc. of 30% sodium hydroxide solution. The solution was placed in a two-liter 3-necked round-bottomed flask fitted with a dropping funnel. One hundred and forty cc. of dimethyl sulfate was added fairly rapidly and the temperature was allowed to rise. After some time the reaction mixture was filtered and the precipitated methylated product was washed with water and recrystallized from dilute alcohol.

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(8) M. E. McGreal and J. B. Niederl, "Abstracts of Papers, 97th meeting, Am. Chem. Soc.," Baltimore, Md., 1939, pp. M5–7.

(9) Performed according to R. Rast, as described in J. B. Niederl and V. Niederl, "Micro-methods of Quantitative Organic Elementary Analysis," J. Wiley and Sons, Inc., New York, N. Y., 1938, p. 175.

(10) Acetyl: calcd., 39.09; found, 40.62.

(IIc) One gram of condensation product II was dissolved in 5 cc. of 20% sodium hydroxide solution and 2 cc. of dimethyl sulfate added. The mixture was shaken vigorously and allowed to stand for some time. The methylated product was then filtered off, washed with sodium hydroxide solution, and recrystallized from alcohol.

Summary

Crystalline condensation products and their derivatives of resorcinol and saturated aliphatic aldehydes were investigated and subjected to extensive quantitative elementary analysis and molecular weight determinations. The results obtained seem to indicate that resorcinol in these condensations reacted like pyrrole under similar circumstances, giving rise also to crystalline condensation products which seem to possess a similar structural pattern as the "porphyrins" obtainable in pyrrole-carbonyl compounds condensations, but possessing "benzene" instead of "pyrrole" rings.

WASHINGTON SQUARE COLLEGE
NEW YORK, N. Y.
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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Studies in the Biphenyl Series. IV. Some *o*-Biphenyl Derivatives of Phosphorus, Arsenic and Antimony

BY DAVID E. WORRALL

It has been shown previously[1] that *p*-chlorobiphenyl condenses smoothly with the chlorides of phosphorus, arsenic and antimony in the presence of sodium, that the products exhibit the usual properties of these organo derivatives and that they are unusually tractable. The corresponding reactions in part have been studied with *o*-chlorobiphenyl. While the ortho derivatives react less smoothly and undergo hydrolysis more easily, only minor differences in chemical behavior were discovered.

Tri-*o*-biphenylphosphine (I).—A mixture containing 9 g. of granulated sodium, 25 g. of 2-chlorobiphenyl and 6.1 g. of phosphorus trichloride in 200 cc. of benzene, after adding a crystal of antimony trichloride, was heated to boiling for two hours. It was filtered while still warm, concentrated to a small bulk and mixed with an equal volume of alcohol. An oil separated at first but it became crystalline on standing; yield after washing with alcohol, 8.3 g. After several crystallizations, small colorless plates were obtained, m. p. 151–152°. As with most of the *o*-derivatives, the melting point was not sharp and preliminary softening took place.

Anal. Calcd. for $C_{36}H_{27}P$: P, 6.3. Found: P, 6.3.

Tri-*o*-biphenylphosphine Oxide.—The gummy product obtained by the action of bromine or chlorine on I was heated for a few minutes with alcoholic potassium hydroxide, poured into water and dissolved in a small volume of dilute alcohol. Clumps of tiny needles appeared, m. p. 184–185°.

Anal. Calcd. for $C_{36}H_{27}PO$: P, 6.1. Found: P, 6.1.

Tri-*o*-biphenyl Methylphosphonium Iodide.—On dissolving a portion of I in methyl iodide, bundles of tiny needles almost immediately began to form; yield after several hours, nearly quantitative. It melted indefinitely with decomposition above 250°.

Anal. Calcd. for $C_{37}H_{30}PI$: I, 20.1. Found: I, 20.0.

The odor of biphenyl on heating the phosphonium compound with silver oxide was indicative of the conventional change into dibiphenylmethylphosphine oxide.

Tri-*o*-biphenylarsine (II).—Arsenic chloride, 0.1 g. mole, was heated to boiling for two hours with corresponding quantities of *o*-chlorobiphenyl and sodium in benzene. The filtrate, concentrated to a small volume and mixed with alcohol, yielded 33–34 g. of product. Small glittering plates separated from a benzene–alcohol mixture on recrystallization, m. p. 190°.

Anal. Calcd. for $C_{36}H_{27}As$: As, 14.0. Found: As, 13.9.

Tri-*o*-biphenylarsine Dihydroxide.—Attempts to convert II into the dibromide or dichloride gave gummy products which were heated with alcoholic potassium hydroxide, evaporated to dryness and extracted with water. The residue crystallized in the form of stout needles from alcohol, m. p. 237–238°.

Anal. Calcd. for $C_{36}H_{29}O_2As$: As, 13.2. Found: As, 13.4.

Tri-*o*-biphenylmethylarsonium Iodide.—II dissolved in methyl iodide and heated for a few minutes changed quantitatively into the arsonium iodide. Needle-like crystals separated on crystallization from a small volume of alcohol. It dissociated on heating into methyl iodide and II at approximately 154° when it partially melted and then hardened.

Anal. Calcd. for $C_{36}H_{30}AsI$: I, 18.8. Found: I, 18.5.

Chlorine converted this substance into the corresponding iodochloride, sparkling yellow platelets, m. p. 172–174°, with decompn. A satisfactory analysis for combined halogens was made.

Tri-*o*-biphenylstibine (III).—To a solution of 50 g. of *o*-chloro-biphenyl in 250 cc. of benzene containing 20 g. of

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(1) Worrall, THIS JOURNAL, 52, 2933 (1930).