[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE STRUCTURE OF DIMERIC 3-C-PHENYLGLYCERALDEHYDE AND ITS REACTIONS WITH AMINES

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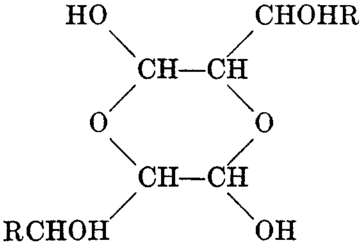
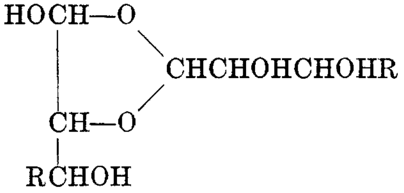
Under certain circumstances, glyceraldehyde exists as a dimer (1). It has been reported (2) that the dimer persists in solutions of glyceraldehyde in organic solvents, although the monomeric form exists in aqueous solutions.

It has now been found that β-phenylglyceraldehyde exhibits an analogous behavior. In aqueous solution, this triose exists in the monomeric form, but in organic solvents the triose exists as a dimer. The reactions of the monomer with amines have been discussed in the previous paper (3); the present paper constitutes a report of the reactions of the dimer in organic solvents.

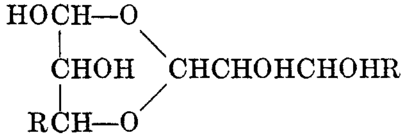
Structure I (R = H) has been proposed (1) for the dimer of glyceraldehyde, but structures II and III (R = H) may also reasonably represent this substance. The three analogous structures (I, II, III, R = C_6H_5)



I. R = H or C_6H_5



II. R = H or C_6H_5.
V. R = C_6H_5; OH replaced by —NHC_6H_5.



III. R = H or C_6H_5

may likewise represent dimeric β-phenylglyceraldehyde.

Hall and Stern (4) showed that the diacetate (IV) of the dimer of β-hydroxypropionaldehyde underwent hydrolysis in two well-defined steps: one acetyl group was removed within five minutes by action of dilute (0.05 *N*) hydrochloric acid at 70°, whereas the second acetyl group was not entirely removed after two hours. This showed that the two acetyl groups in IV were situated differently within the molecule and lent considerable support to structure IV.

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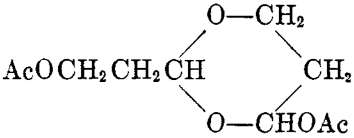
[1] Abstracted from a thesis by Ray H. Anderson, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, July, 1950.



IV

$[C_6H_5CHOHCHOHCHOH]_2NC_6H_5$

VI

Acetylation of dimeric β-phenylglyceraldehyde produced a crystalline tetraacetate, as required by structures I, II, and III. Depending upon the structure of the dimer, this tetraacetate would possess two different pairs of acetyl groups (I) or three acetyl groups alike, and one different (II, III). However, the rate of hydrolysis of the tetraacetate by action of dilute (0.05 *N*) hydrochloric acid at 70° showed no variation from the beginning to the end of the hydrolysis. It is not possible to write a structure for a dimer of β-phenylglyceraldehyde which contains four equivalent hydroxyl groups, so no choice as to the structure I, II, or III can be made on the basis of these results.

Reaction of the dimer with aniline in dioxane at room temperature resulted in a product (V) which separated in crystalline form when petroleum ether was added to the solution. The composition of V was that required by direct combination of one molecule of the dimer with one of aniline. The same substance V resulted when other conditions were used—other solvents (ethanol, etc.), temperatures varying from 20° to 85°, and excess aniline. The substance was unstable in water solution, and was very sensitive toward acids. It reduced Fehling's solution and an alkaline solution of methylene blue. The substance was not a Schiff base, nor was any carbonyl group present, for it was unaffected by action of hydrogen in the presence of a platinum catalyst. When V was subjected to prolonged drying under reduced pressure, slightly less than one molecule of water was evolved, and the composition agreed well with that required for a phenylglycosylamine. It has been reported several times (5) that crystalline glycosylamines usually contain water of crystallization which is held tenaciously. The properties of V therefore indicate that the substance is a phenylglycosylamine.

Since only one molecule of aniline is involved in the formation of V, it would appear that structures analogous to II and III, with the glycosidic hydroxyl group replaced by C_6H_5NH, would be most logical for V, and this, in turn, would indicate that dimeric β-phenylglyceraldehyde is best represented by II or III. The glycosylamine V cannot possess structure VI for this substance (V in the previous paper, 3) melts at 68° whereas V melts at 105°, and V (anhydrous) has the composition $C_{24}H_{25}NO_5$ as compared with $C_{24}H_{27}NO_6$ required for VI. Moreover, VI cannot be an intermediate in the formation of V, for VI decomposes under the conditions which lead to formation of V from aniline and dimeric β-phenylglyceraldehyde. No attempt was made to investigate the action of periodic acid upon V in view of the reports in the literature (6) that action of this reagent upon glycosylamines derived from sugars and primary aromatic amines, purines, or pyrimidines results in excessive consumption of periodic acid and leads only to tarry products.

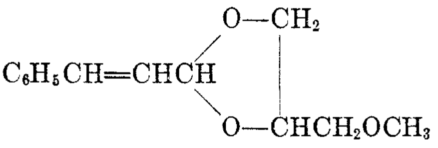
Acetylation of V by action of acetic anhydride in pyridine led to a tetraacetate VII. Measurement of the rate of hydrolysis of VII by action of dilute (0.05 *N*) hydrochloric acid at 70° indicated that three of the acetyl groups were removed at approximately the same rate—70 minutes for each acetyl group. No more acetic acid was produced by continuing the hydrolysis for two hours longer. This behavior indicates that of the four acetyl groups present in VII, three are structurally similar whereas one is different, and is in agreement with a structure for V related to II and III, but not to I. However, no acetanilide could be isolated from the tarry products of this hydrolysis.

Neither methyl iodide nor methyl sulfate could be used for alkylation of V, because V decomposed in solutions of these materials in dioxane at room temperature. A solution of V and methyl *p*-toluenesulfonate in benzene deposited a crystalline material (VIII) on standing at room temperature. This product, after crystallization from benzene, melted at 90°; it appeared to be a tetramethyl derivative of V, although the analytical value for hydrogen was somewhat low. Hydrolysis of VIII by the action of boiling aqueous sulfuric acid (15%) for six hours led to a brown solution from which neither methylaniline nor aniline could be isolated. Action of warm ethyl iodide upon V led to a solid melting at 127°. The analytical values for this material did not agree with any simple ethyl derivation of V nor could any ethylaniline be obtained from it by hydrolysis.

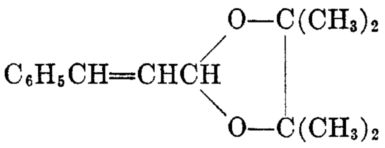
Dimeric β-phenylglyceraldehyde reacted with the ethyl ester of phenylalanine in dioxane at room temperature to give a crystalline material melting at 61–62°. The composition of this material indicated that it was derived from one molecule each of the dimer and the amine ester. It was thus analogous to V; the material appeared to be hydrated, but it was impossible to obtain it in anhydrous form for it was unstable above 30°. The substance was unstable in water, reduced Fehling's solution and an alkaline solution of methylene blue, and was very sensitive toward acids. It was recovered essentially unchanged when subjected, for six hours, to the action of hydrogen under 50 lbs. pressure at room temperature in the presence of a platinum catalyst.

The infrared absorption spectra of several compounds having a dioxolane ring were examined and compared with those of dimeric β-phenylglyceraldehyde and of V.[2] Cinnamaldehyde was converted into the cyclic acetals (dioxolanes) IX and X by reaction with the α-methyl ether of glycerol and pinacol, respectively. These unsaturated acetals were then hydroxylated using the method of Rüber (7), resulting in the hydroxy compounds XI and XII. The infrared absorption spectra of IX and XII, V, and the dimeric aldehyde were examined. The infrared spectra of the dimer, V, and XII showed a strong absorption, characteristic of hydroxyl groups, and which, in V, masked the characteristic frequencies of the amino group. None of the spectra showed any absorption characteristic of the carbonyl group.

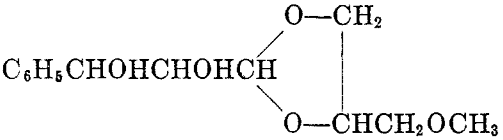
[2] We wish to thank Dr. B. L. Crawford, Jr., and Mr. J. E. Lancaster of this laboratory for their kindness in measuring and interpreting the infrared spectra of these compounds. The complete curves are included in the Ph.D. thesis of R. H. Anderson, University of Minnesota, 1950.



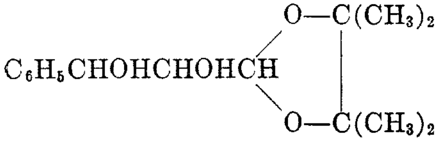
IX



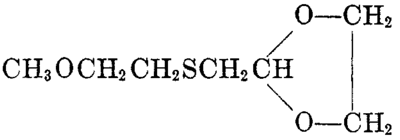
X



XI



XII



XIII

$C_6H_5N(CH_3)CH_2COCHOHC_6H_5$

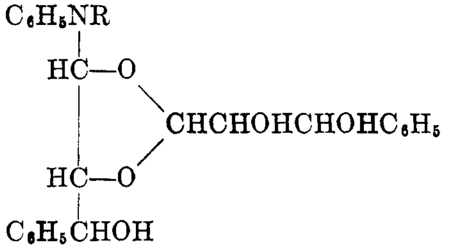
XIV

Comparison of these spectra with the spectrum of XIII (8) showed that all, except that of the dimer, possessed a strong adsorption band at 9.6 μ in common with the spectrum of XIII. The data in the literature (9) do not include any group, common to all the compounds examined in this work, which has an absorption bond at 9.6 μ. It is therefore likely that the presence of a peak at 9.6 μ in the spectrum of V indicates the presence of a dioxolane ring in V and hence the best structure for V is II with the glycosidic hydroxyl group replaced by —NHC_6H_5. The spectrum of the dimer of β-phenylglyceraldehyde showed a strong absorption band at 9.65 μ indicating a dioxolane ring, but absorption is also strong at 9.55 μ, and the latter is the position of an absorption band of dioxane. Hence, a definite choice among structures I and II for the dimer cannot be made.

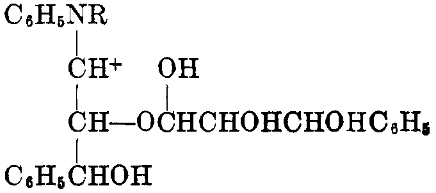
Hydrolysis of XI produced a crystalline material identical in melting point and analysis with dimeric β-phenylglyceraldehyde. Hydrolysis of XII was so difficult that any conditions severe enough to bring about hydrolysis also brought about complete decomposition of the resulting triose.

A solution of dimeric β-phenylglyceraldehyde in dioxane did not react with methylaniline during 24 hours at room temperature. But a solution of the dimer and methylaniline in ethanol containing acetic acid, refluxed for 30 minutes and then cooled, deposited a crystalline solid. This material, after crystallization from ethanol, melted at 103–104°. The substance was soluble in ether, alcohol, and dioxane and was only slightly soluble in water. It rapidly reduced Fehling's solution or a cold alkaline solution of methylene blue. Analytical values of the substance agreed well with those required by an aminoketol of structure XIV (or of the isomer with the carbonyl and hydroxyl groups interchanged); in agreement with such a structure, the substance formed a white hydrochloride melting at 117–119°, and a pale yellow semicarbazone melting at 145–146°.

In the preceding paper (3) it was shown that action of aniline and other primary aromatic amines upon monomeric β-phenylglyceraldehyde led to benzylglyoxal; action of methylaniline did not bring about this transformation. The ketol XIV, therefore, must have been derived from dimeric β-phenylglyceraldehyde, and most likely by way of the glycosylamine, XV.

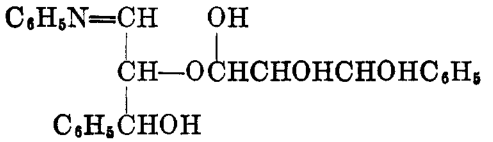


XV R = CH_3



$$\begin{array}{l} C_6H_5NR \\ \quad | \\ \quad CH^+ \quad OH \\ \quad | \qquad\ \ | \\ \quad CH{-}OCHCHOHCHOHC_6H_5 \\ \quad | \\ C_6H_5CHOH \end{array}$$

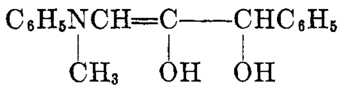
XVI



$$\begin{array}{l} C_6H_5N{=}CH \quad OH \\ \qquad\quad | \qquad\ \ | \\ \qquad\quad CH{-}OCHCHOHCHOHC_6H_5 \\ \qquad\quad | \\ C_6H_5CHOH \end{array}$$

XVII

The question then arises as to why and how this glycosylamine XV is transformed into the ketol XIV, whereas the analogous product V (XV, R = H) derived from aniline, is not transformed into an analog of XIV. The salient differences between the two glycosides lie in the presence of a hydrogen atom on the nitrogen atom of one, and not the other, and in the basicity of the nitrogen atom itself. Both glycosides can give rise to a cation XVI; when R = H, this cation may change to the Schiff base XVII. When R = CH_3 a Schiff base cannot form; instead, a proton may be expelled from the adjacent carbon atom, leading eventually to XVIII and then to XIV. The Schiff base XVII, on the other hand, may decompose in some other manner, either directly or by reversion to XV (R = H) which is itself very sensitive toward acids.



$$\begin{array}{llll} C_6H_5N & CH{=} & C{-\!-} & CHC_6H_5 \\ | & & | & | \\ CH_3 & & OH & OH \end{array}$$

XVIII

EXPERIMENTAL PART[3]

Dimeric β-phenylglyceraldehyde. The aldehyde (0.1 g.) prepared as described in the previous paper (3), was dissolved in dioxane (10 cc.), and the molecular weight was determined by Rast's (10) modification of the method of Barger (11), using pinacol as the reference compound.

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[3] Microanalyses by R. W. Amidon, Jay S. Buckley, William Cummings, R. E. Kelly, and H. W. Turner.

Anal. Calc'd for $C_{18}H_{20}O_6$: M. W., 322. Found: M. W., 325, 316.

Tetraacetate (VII). The aldehyde (0.5 g.) was dissolved in anhydrous pyridine (2 cc.), acetic anhydride (2 cc.) was added, and the solution was boiled for three minutes. The cooled solution was poured into water (50 cc.), the solid was removed, washed successively with hydrochloric acid (2%) and water, and crystallized from ethanol. The acetate weighed 0.69 (60%) and melted at 89–91°.

Anal. Calc'd for $C_{26}H_{28}O_{10}$: C, 62.40; H, 5.64.
Found: C, 62.60; H, 6.00.

Hydrolysis. The tetraacetate (0.1206 g.) was mixed with hydrochloric acid (100 cc., 0.05 N) and the resulting solution was kept at 70°. At periodic intervals, 5-cc. aliquots were removed and titrated with aqueous sodium hydroxide (0.01 N) using phenolphthalein as the indicator. There was no preferential hydrolysis which would differentiate among the acetyl groups.

Reaction of the dimer with aniline: *Product* V. A solution of the aldehyde dimer (0.5 g.), and aniline (0.3 g.) in dioxane (10 cc.) was heated on the steam-bath for 20 minutes, cooled, and diluted with petroleum ether. The yellow solution, after a day at 15°, deposited 0.22 g. (36%) of solid which was crystallized from a mixture of dioxane and petroleum ether. The product, dried under reduced pressure at room temperature, melted at 102–104°. It was stable at 0°, but became yellow after standing for two weeks at room temperature. The instability was increased markedly by traces of the yellow impurity.

Anal. Calc'd for $C_{24}H_{25}NO_5$: C, 70.76; H, 6.19; N, 3.44.
Calc'd for $C_{24}H_{25}NO_5 \cdot H_2O$: C, 67.78; H, 6.35; N, 3.3.
Found: C, 68.16; H, 6.53; N, 3.22.

The experiment was duplicated, but the solution was not heated; instead, it was allowed to stand for four hours at room temperature. Petroleum ether was then added and the mixture was processed as above. The crystalline material weighed 0.37 g. (60%) and melted, after crystallization, at 101–105°. If the solution was allowed to stand for longer than four hours, it became progressively more yellow, and it was difficult to isolate the solid from it.

Anal. Found: C, 68.19; H, 6.56; N, 3.12.

The product from experiment 2 was dried for eight hours under reduced pressure at 65°; it then melted at 103–104°.

Anal. Found: C, 69.67; H, 6.62; N, 3.51.

The experiment was duplicated except that ethanol was used in place of dioxane. The mixture was refluxed for 20 minutes and then set aside at −15°, no petroleum ether being added. The solid (0.12 g., 20%) was recrystallized from ethanol and dried at 65° for eight hours under reduced pressure; m.p. 104–106°.

Anal. Calc'd for $C_{24}H_{25}NO_5$: C, 70.76; H, 6.19; N, 3.44.
Found: C, 70.43; H, 6.24; N, 3.61.

Each of the products obtained from the above experiments reduced Fehling's solution and alkaline methylene blue at room temperature. The material (0.3 g.) from the second experiment was dissolved in dioxane (10 cc.) and the solution was subjected to the action of hydrogen under 50 lb. pressure for six hours at room temperature in the presence of a platinum catalyst. The catalyst was removed and the product was isolated as above and crystallized from a mixture of dioxane and petroleum ether. It was then dried at 65° for eight hours under reduced pressure, when it melted at 99–102°. It reduced Fehling's solution, and was unchanged V.

Anal. Found: C, 69.39; H, 6.68; N, 3.62.

Substance V (0.1 g.) was dissolved in dioxane (10 cc.) and the molecular weight was determined by the Rast-Barger method (10, 11) using pinacol as the reference compound.

Anal. Calc'd for $C_{24}H_{25}NO_5$: M. W., 407. Found: M. W., 425, 414.

Tetraacetate VII. Substance V (0.5 g.) was dissolved in dry pyridine (5 cc.), acetic anhydride (2 cc.) was added, and the solution was allowed to stand overnight at room temperature. It was poured into ice-water (50 cc.), and the amorphous product was removed by ether extraction. The extract was washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate, and water, and was dried and concentrated to a volume of 5 cc. Petroleum ether (2 cc.) was added and the solution was set aside at −15°. After a day, the solid was removed and crystallized from a mixture of petroleum ether and ether, when it weighed 0.37 g. (53%) and melted at 136–138°.

Anal. Calc'd for $C_{32}H_{33}NO_9$: C, 66.78; H, 5.78; N, 2.43.
Found (dried 8 hrs. at 74° under reduced pressure): C, 66.15; H, 6.30.
Found (dried 24 hours at 74° under reduced pressure): C, 66.30; H, 6.15; N, 2.36.

The analytical sample decomposed when it was dried for four hours at 100° under reduced pressure.

Hydrolysis. The tetraacetate VII (0.1387 g.) was mixed with hydrochloric acid (100 cc., 0.05 *N*) and the solution was kept at 70°. Aliquots of 5 cc. were removed at periodic intervals and titrated with aqueous sodium hydroxide (0.01 *N*) using phenolphthalein. The data showed that three acetyl groups were removed in regular sequence, 70 minutes for each, but that no further removal of acetyl groups occurred during an additional 2½ hours. No acetanilide separated from the solution during the hydrolysis, nor from the cooled solution remaining after hydrolysis.

Tetramethyl derivative (VIII) of V. A solution of V (0.5 g.) and methyl *p*-toluenesulfonate (1 g.) in benzene (30 cc.) was allowed to stand overnight at room temperature. The solid was crystallized, first from benzene, and then from aqueous ethanol, when it weighed 0.4 g. and melted at 90°.

Anal. Calc'd for $C_{28}H_{33}NO_5$ (tetramethyl): C, 72.33; H, 7.17; N, 3.05.
Found: C, 72.64; H, 6.53; N, 2.97.

This material was refluxed for six hours with aqueous sulfuric acid (15%). The brown solution was extracted with ether; the aqueous layer was neutralized with sodium bicarbonate and again extracted with ether. The solvent was evaporated from the second ether extract and the residual oil was subjected to the action of acetic anhydride and alkali. No N-methylacetanilide could be isolated from the tarry product.

Ethylation of V. No reaction occurred when V (0.3 g.) and ethyl iodide (0.3 g.) were dissolved in dioxane (2 cc.) and the solution was allowed to stand at room temperature for a day. Unchanged V was recovered. But when V (0.5 g.) was warmed with ethyl iodide (5 cc.), solution occurred and then a solid was quickly deposited. This solid began to decompose to a brown oil after about ten minutes in the refluxing ethyl iodide, so the experiment was interrupted, and the solid was removed and washed thoroughly with ether. The product obtained in this way weighed 0.45 g. and melted at 127°.

Anal. Calc'd for $C_{26}H_{29}NO_5$ (monoethyl): C, 71.72; H, 6.68; N, 3.22.
Found: C, 69.91; H, 6.23; N, 3.55.

After crystallization from aqueous ethanol, the substance melted at 124° and was evidently undergoing decomposition.

Anal. Found: C, 69.34; H, 6.54; N, 3.45.

The analytical values of this substance agree well with those required by V from which it was derived, yet the melting points of the two substances are quite different. Action of sulfuric acid (15%) upon this product led only to a brown tar; no ethylaniline could be isolated from the product.

2-Styryl-4-methoxymethyl-1,3-dioxolane (IX). In agreement with Hibbert and Whelen (12), it was found that reaction between cinnamaldehyde and a glycol led to very small yields of cyclic acetals. But by modifying the procedure of Hibbert and Whelen, a good yield of IX was obtained. Cinnamaldehyde (13 g.) and glycerol-α-methyl ether (12 g.) were dissolved in benzene (100 cc.), *p*-toluenesulfonic acid (0.5 g.) was added, and the mixture was refluxed in an apparatus which included a water trap. After the calculated amount of water (1.8 cc.) had collected in the trap (one hour), the solution was washed with aqueous sodium bicarbonate, dried, and the solvent was removed. The residual liquid was distilled at 6 mm., and the fraction boiling at 155° was collected. This weighed 21 g. (90%); n_D^{25} 1.5440, as reported by Hibbert and Whelen (12).

2-(β-Phenyl-α,β-dihydroxyethyl)-4-methoxymethyl-1,3-dioxolane (XI). The unsaturated dioxolane (IX) (13.5 g.) was dissolved in ethanol (750 cc.) and hydroxylated at −40° according to Rüber (7) by the slow addition of a solution of potassium permanganate (12 g.) in water (400 cc.). The mixture was allowed to come to room temperature, and the *brown* manganese dioxide was removed. The filtrate was concentrated to a volume of 100 cc. and extracted with four 50-cc. portions of ether. The combined extracts were dried, concentrated to a volume of 25 cc., diluted with petroleum ether, and cooled to −15°. The product separated as an oil which could not be crystallized. The oil was distilled to give XI (1.5 g.), b.p. 190°/0.7 mm.

The acetal XI (0.5 g.) was stirred with dilute sulfuric acid (5 cc., 1%) at 60° for three hours and the solution was kept overnight at room temperature. The crystalline material was removed; it reduced Tollens' solution, melted at 123–125°, and was β-phenylglyceraldehyde, although the analytical values for carbon were low, as is always the case for this compound.

Anal. Calc'd for $C_9H_{10}O_3$: C, 65.06; H, 6.03.
Found: C, 62.96; H, 6.40.

2-Styryl-4,4,5,5-tetramethyl-1,3-dioxolane (X). Cinnamaldehyde (13 g.) and pinacol (13 g.) were dissolved in benzene (100 cc.), *p*-toluenesulfonic acid (0.5 g.) was added, and the reaction was conducted as described for the preparation of IX above. The product was a colorless liquid (22 g., 90%), b.p. 142°/4 mm. and n_D^{25} 1.5265.

Anal. Calc'd for $C_{15}H_{20}O_2$: C, 77.58; H, 8.68.
Found: C, 77.34; H, 8.81.

2-(β-Phenyl-α,β-dihydroxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (XII). The unsaturated dioxolane X (13.5 g.) was hydroxylated as described above for the preparation of XI. The product, crystallized from aqueous ethanol, weighed 6 g. (37%) and melted at 120°.

Anal. Calc'd for $C_{15}H_{22}O_4$: C, 67.67; H, 8.34.
Found: C, 67.78; H, 8.45.

The acetal XII (1 g.) in dioxane (10 cc.) was heated to 60° and stirred for four hours with aqueous sulfuric acid (8 cc., 2%). No hydrolysis of XII occurred; the cooled solution deposited unchanged XII, m.p., 120°.

3-Phenylmethylamino-1 (or 2)-hydroxy-1-phenyl-2 (or-1-)-propanone (XIV). β-Phenylglyceraldehyde (0.5 g.) and methylaniline (0.4 g.) were dissolved in dioxane (10 cc.) and the solution was allowed to stand at room temperature for one day. Petroleum ether was added, and the pale yellow solution was set aside at −15° for one day. The crystalline solid was unchanged aldehyde but was impure. It melted at 101–103°, and contained no nitrogen.

β-Phenylglyceraldehyde (0.5 g.) and methylaniline (0.4 g.) were dissolved in dry ethanol (10 cc.) containing acetic acid (0.5 cc.). The solution was refluxed for 30 minutes, then cooled, diluted with water, and set aside at −15°. The white crystalline material (0.3 g., 45%) was crystallized from dry ethanol, m.p. 103–104°. The amino ketone reduced Fehling's solution and alkaline methylene blue at room temperature.

Anal. Calc'd for $C_{16}H_{17}NO_2$: C, 75.28; H, 6.72; N, 5.50.
Found: C, 75.20; H, 6.87; N, 5.36.

Hydrochloride. Addition of hydrogen chloride to an ethereal solution of XIV resulted in precipitation of the white hydrochloride. It melted at 117–119°, and was only slightly soluble in cold water.

Anal. Calc'd for $C_{16}H_{18}ClNO_2$: C, 66.00; H, 6.23; N, 4.81.
Found: C, 65.82; H, 6.39; N, 4.71.

Semicarbazone. A solution of XIV (0.3 g.) in ethanol (5 cc.) was added to an aqueous solution of semicarbazide hydrochloride and potassium acetate, and the mixture was warmed for two minutes on the steam-bath. The pale yellow semicarbazone separated when the solution was cooled. It was recrystallized from ethanol, m.p. 145–146°.

Anal. Calc'd for $C_{17}H_{20}N_4O_2$: C, 65.38; H, 6.46; N, 17.95.
Found: C, 65.46; H, 6.70; N, 17.67.

Reaction of dimeric β-phenylglyceraldehyde with phenylalanine ester, The aldehyde

(0.7 g.) and phenylalanine ester (0.87 g.) were dissolved in dioxane (10 cc.) and the solution was allowed to stand at room temperature for six hours under nitrogen. Dioxane was removed at 0° under reduced pressure until the volume of the solution was about 2 cc. This residue, set aside at 0° for one day, solidified. The dioxane was allowed to melt, and the remaining solid was removed and crystallized from a mixture of dioxane and petroleum ether. The material weighed 0.52 g. (46%), m.p. 61–62°. It reduced Fehling's solution and alkaline methylene blue, and was very unstable at room temperature—standing for longer periods than about one hour at room temperature, even under reduced pressure, resulted in decomposition and the resulting yellow impurity, if present even in traces, greatly accelerated the decomposition.

Anal. Calc'd for $C_{29}H_{33}NO_7$: C, 68.64; H, 6.56; N, 2.76.
Found: C, 67.20; H, 6.97; N, 2.39.

The experiment was duplicated except that the solution of the reagents, after standing for six hours at room temperature, was diluted with petroleum ether (40 cc.) and then cooled to −15°. The product in this case was an oil from which no crystalline material could be obtained.

The solid product (0.4 g.) in dioxane (20 cc.) was subjected for six hours to the action of hydrogen under 50 lb. pressure at room temperature in the presence of a platinum catalyst. The catalyst was removed, the filtrate was concentrated at 0° under reduced pressure to a volume of 4 cc., diluted with petroleum ether (10 cc.), and set aside at −15°. The solid was removed and crystallized from a mixture of dioxane and petroleum ether, when it melted at 56–59° and was identical with the starting material. No reduction occurred.

Anal. Found: C, 66.92; H, 7.53; N, 2.31.

SUMMARY

1. β-Phenylglyceraldehyde has been found to exist in a dimeric form in organic solvents. The structure of the dimer has been investigated; three structures have been considered, and some evidence has been obtained favoring structure II for the dimer.

2. Aniline, as well as phenylalanine ethyl ester, react with the dimer in organic solvents, giving crystalline products to which structures have been assigned.

3. Reaction of the dimer with methylaniline in organic solvents produces a crystalline aminoketol, XIV.

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