were allowed to react with 2.3 g. of ethyl iodide for one week. 5 g. of a light yellow oil were obtained.

0.4658 g. gave 20 cc. N_2 at 21° and 745 mm.
Calc. for $C_{17}H_{17}O_4N$: N, 4.68. Found: N, 4.81%.

Summary.

1. In the course of experiments which had in view the preparation of mixed oximidocarbonic esters, RO.C(NOH).OR′ several new hydroxyurethanes, including the methyl, isopropyl, isobutyl, isoamyl and benzyl derivatives were prepared, and their benzoyl esters studied.

2. The silver salts of some of these benzoyl esters were obtained in two modifications, white and yellow, of the same composition and mutually transformable. While the methyl, ethyl and isopropyl derivatives were prepared only as yellow salts, the compounds with larger radicals, *viz.*, isobutyl, isoamyl, and benzyl, were obtained in two forms.

3. These silver salts have been found to yield derivatives with the alkyl groups bound to *nitrogen* instead of to *oxygen*. This unforseen reaction prevented us from obtaining the acyl derivatives of mixed oximidocarbonic esters, which would otherwise have resulted from the action of various alkyl halides upon these silver salts.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE, LABORATORY OF CLINICAL RESEARCH, RUSH MEDICAL COLLEGE.]

THE ISOLATION OF CRYSTALLINE *dl*-GLYCERIC ALDEHYDE FROM A SYRUP OBTAINED BY THE OXIDATION OF GLYCEROL.

BY EDGAR J. WITZEMANN.

Received August 7, 1914.

dl-Glyceric aldehyde is a compound of considerable importance. In the various more or less theoretical discussions of the break-down and synthesis of the hexoses, either in the chemical laboratory or in the living organism, *dl*-glyceric aldehyde, along with dihydroxyacetone, assumes a prominent place. The collection of facts with regard to its behavior in the body has been retarded by the difficulty of obtaining sufficient quantities with which to work. The only method now known of preparing the pure substance is that of Wohl, and this method is extremely laborious. For physiological experiments in man, quantities are required which make Wohl's method well nigh prohibitive. The method of Fenton and Jackson is simple and undoubtedly gives a large yield of glyceric aldehyde, although admixed with impurities. Dr. R. T. Woodyatt, of this laboratory, sometime ago published a preliminary report on the use of glyceric aldehyde, prepared according to the latter method, in diabetes mellitus.[1] The nature of these results was such as to emphasize the necessity of determining

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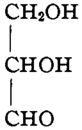
[1] *J. Am. Med. Assoc.*, 55, 2109–2112 (1910).

more definitely than has yet been done the composition of the crude glyceric aldehyde syrup employed and if possible to develop a method for purifying it.

The only known compound of glyceric aldehyde which would serve for its identification, and which could also be subsequently used as a source of free glyceric aldehyde, is glyceric aldehyde diethyl acetal. If, therefore, glyceric aldehyde diethyl acetal could be made from the Fenton and Jackson reaction mixture it would at once prove, more conclusively than has yet been done, the presence of glyceric aldehyde and also serve for its isolation. The following paper is a report on the successful execution of the plan outlined above, as suggested by Dr. Woodyatt.

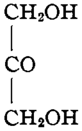
When glycerol is acted upon by one atom of oxygen two oxidation products are theoretically possible, namely:



$$\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CHO\end{array}$$

Glyceric aldehyde.

and



$$\begin{array}{c}CH_2OH\\ |\\ CO\\ |\\ CH_2OH\end{array}$$

Dihydroxy acetone.

The preparation of pure *dl*-glyceric aldehyde, or any derivative from which pure glyceric aldehyde itself can be isolated, from an oxidation product of glycerol has apparently been frequently tried but without success. In fact, in most cases in which the presence of glyceric aldehyde has been reported its identity was established through the formation of phenylglycerosazone with phenylhydrazine, which, however, is produced by both of the oxidation products given above.[1] This reagent will, therefore, not help in deciding which of the above compounds, or whether both, are present in a reaction mixture.

Since the literature on the formation of glyceric aldehyde by oxidation methods is very scattered it may be well to give a brief history of this subject at this point. J. van Deen[2] observed that either an electrical current or nitric acid acting on glycerol gave an optically inactive, fermentable syrup, which reduced cupric oxide in alkaline solution and which he considered to be a sugar. Huppert,[3] Kirchner and Meissner,[4] Heynsius,[5] Perl[6] and G. Werther[7] all disputed v. Deen's results as a whole or in part.[8] Przibytek[9] found that prussic acid acting on glycerol gives some glyceric

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[1] Fischer and Tafel, *Ber.*, **20**, 1088 (1887).

[2] *Nederl. Tydschr. v. Geneesk.*, **4**, Aug., 1860.

[3] *Arch. f. Heilkunde*, **3**, 289 (1862).

[4] *Z. ration. Med.*, [3] **16**, 289 (1862).

[5] *Nederl. Tydschr. v. Geneesk.*, **6**, 641 (1862).

[6] *Konigsberger Med. Jahrb.*, **8**, 84 (1862); *J. prakt. Chem.*, **88**, 148 (1862).

[7] *J. prakt. Chem.*, **88**, 151 (1862).

[8] For a good account see *Chem. Zentr.*, **1863**, 833–41; or *Jahrb. f. Chem.*, **1863**, 501.

[9] *J. Russ. Chem. Soc.*, **12**, 214 (1887); **13**, 330 (1888).

aldehyde in addition to meso-tartaric and saccharic(?) acids. Grimaux[1] oxidized glycerol with platinum black and states that he obtained "glyceric aldehyde" which was fermentable. Fischer and Tafel[2] oxidized glycerol with nitric acid and got a compound which reduced Fehling's solution in the cold and gave the phenylglycerosazone. They challenge Grimaux's right to priority on the ground that he identified his so-called glyceric aldehyde only by its ability to reduce alkaline copper solutions. A short time later they synthesized acrose[3] by hydrolyzing acrolein bromide and concluded that glyceric aldehyde must be an intermediate in the synthesis of this compound. Later[4] they prepared a product which they declared was probably glyceric aldehyde, (1) by the oxidation of glycerol with bromine in the presence of soda and (2) by the oxidation of lead glycerate with bromine vapors. They subsequently decided that these products were chiefly dihydroxyacetone[5] without definitely proving that there was any glyceric aldehyde present at all. Later Wohl and Neuberg[6] showed by means of the phloroglucinol test that the product obtained in (1) is mainly, if not solely, dihydroxyacetone, while the product obtained in (2) is also mainly dihydroxyacetone but contains a little glyceric aldehyde, since it gave a slight positive phloroglucinol test. Piloty and Ruff[7] had previously shown that the product in the latter case gave a large amount of dihydroxyacetoxime, from which they likewise concluded that this crude oxidation syrup consisted for the most part of dihydroxyacetone. W. E. Stone and McCoy[8] probably obtained traces of glyceric aldehyde or dihydroxyacetone, as shown by qualitative tests when solutions of glycerol containing sulfuric acid or sodium nitrate were electrolyzed. Likewise Fonzes-Diacon[9] obtained detectable quantities of "glycerose" by the action of mercuric chloride on glycerol. Lobry de Bruyn[10] found that the hydrolysis of dibromoacrolein gave detectable quantities of "glyceric aldehyde." Wohl[11] synthesized glyceric aldehyde from acrolein by preparing acrolein diethyl acetal which, when oxidized with potassium permanganate under the prescribed conditions, gave glyceric-

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[1] *Compt. rend.*, 104, 1276 (1887); *Chem. Zentr.*, **1887**, 629; *Bull. soc. chim.*, 45, 481 (1886).

[2] *Ber.*, **20**, 1088 (1887); *Chem. Zentr.*, **1887**, 691.

[3] *Ibid.*, **20**, 2566 (1887); **1887**, 1491.

[4] *Ibid.*, **20**, 3384 (1887); **21**, 2634 (1888); **1888**, 277, 1303.

[5] *Ibid.*, **22**, 106 (1889); **1889**, I, 278.

[6] *Ber.*, **33**, 3098, 3109 (1900).

[7] *Ibid.*, **30**, 1663 (1897).

[8] *Am. Chem. J.*, **15**, 656 (1893); *Chem. Zentr.*, **1894**, I, 199.

[9] *Bull. soc. chim.*, [3] **13**, 862 (1895); *Chem. Zentr.*, **1895**, II, 676.

[10] *Rec. trav. chim.*, **17**, 258 (1898); *Chem. Zentr.*, **1898**, II, 964.

[11] *Ber.*, **31**, 1796, 2394 (1898); *Chem. Zentr.*, **1898**, II, 419, 1008; see also Wohl and Neuberg, *Ber.*, **32**, 1352 (1899); **33**, 3095 (1900); *Chem. Zentr.*, **1899**, I, 1272; **1900**, II, 1197.

aldehyde diethyl acetal. Glycericaldehyde diethyl acetal on hydrolysis in 0.1 *N* sulfuric acid gave *dl*-glyceric aldehyde. This was the first time that this compound had been prepared in pure form. The next year (1899) Fenton and Jackson[1] reported on the oxidation of glycerol with hydrogen peroxide in the presence of 10% of ferrous sulfate. The syrup product of this reaction reduced Fehling's solution in the cold, gave the reaction for aldehydes with Schiff's reagent and yielded phenylglycerosazone with phenylhydrazine. They treated a portion with prussic acid according to the method of Fischer and Tafel.[2] Trihydroxyisobutyric acid, which should have been formed if dihydroxyacetone was present, could not be found. When another portion was treated with the calculated quantity of hydroxylamine there was no sign of the formation of dihydroxyacetoxime crystals.[3] Fenton and Jackson, therefore, concluded that the product obtained by them probably consisted chiefly of *dl*-glyceric aldehyde. Ciamician and Silber[4] observed that glycerol is oxidized to "glycerose" by quinone, which is simultaneously reduced to quinhydrone. By the action of ozone on glycerol Harries[5] obtained glyceric aldehyde or dihydroxyacetone as shown by the formation of phenylglycerosazone with phenylhydrazine. Seyewetz and Gibello[6] found that trioxymethylene and sodium sulfate gave a sugar-like compound in which "formose" and "glycerose" have been found. When glycerol is treated with sodium hypochlorite in the presence of cobalt chloride,[7] or sodium hypochlorite and chlorine in the presence of cobalt chloride "glycerose," identified as the phenylosazone, is formed. Neuberg[8] obtained some *dl*-glyceric aldehyde by the electrolysis of *dl*-erythronic acid, and in similar products from *d*-galactonic acid, *d*-lyxose, *dl*-erythronic acid[9] and *l*-arabonic acid.[10] Neuberg also found[11] that a 5% aqueous solution of glycerol, containing 0.8% of uranium sulfate, when exposed for six hours to June sunlight developed a reducing power equal to 2.1% solutions of glucose, which corresponds to a 42% transformation. Glyceric aldehyde was identified by the formation of the phenylosazone, by a re-

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[1] *J. Chem. Soc.*, **75**, 4 (1899); *Chem. News*, **78**, 187 (1898); *Chem. Zentr.*, **1898**, II, 1011; **1899**, I, 249, 521.

[2] *Ber.*, **22**, 106 (1889).

[3] Piloty, Ruff, *Ibid.*, **30**, 1663 (1897).

[4] *Atti accad. Lincei*, [5] **10**, I, 92 (1901); *Chem. Zentr.*, **1901**, I, 770.

[5] *Ber.*, **36**, 1933 (1903); *Chem. Zentr.*, **1903**, II, 189.

[6] *Compt. rend.*, **138**, 150 (1904); *Chem. Zentr.*, **1904**, I, 581.

[7] Tarugi, *Gazz. chim. ital.*, **36**, I, 332 (1906); *Chem. Zentr.*, **1906**, II, 558.

[8] *Biochem. Ztschr.*, **7**, 527 (1907); *Chem. Zentr.*, **1908**, I, 1165; *C. A.*, **2**, 1724.

[9] Neuberg, Scott, Lachmann, *Biochem. Ztschr.*, **24**, 152 (1910); *Chem. Zentr.*, **1910**, I, 1231; *C. A.*, **4**, 1474.

[10] Neuberg and Hirschberg, *Biochem. Ztschr.*, **27**, 327 (1910); *Chem. Zentr.*, **1910**, II, 1455; *C. A.*, **5**, 313.

[11] *Biochem. Ztschr.*, **13**, 307 (1908); *Chem. Zentr.*, **1908**, II, 1485; *C. A.*, **3**, 2142.

duction of Fehling's solution in the cold, by the absence of the characteristic reaction with resorcinol and by the formation of a glucoside-like crystalline compound with phloroglucinol.[1]

Experimental Part.

The crude glyceric aldehyde syrup was prepared essentially as described by Fenton and Jackson.[2] 100 g. of glycerol in 100 cc. of water, to which 5 or 10 g. of ferrous sulfate—previously dissolved in 15 cc. of water—have been added, are placed in a two liter flask. 771 cc. of 6% hydrogen peroxide (1.25 mols hydrogen peroxide for 1 mol glycerol) were added at the rate of about 100 cc. in an hour, care being taken to avoid a rise in temperature of more than 5° to 7°. After adding a portion of 50 to 100 cc. of the hydrogen peroxide, it seems desirable to wait before adding subsequent portions until the red color of the reaction mixture has faded somewhat. When all of the hydrogen peroxide has been added the mixture is allowed to stand 24 hours in order to allow the oxidation to continue until the solution becomes clear and pale yellow in color.[3]

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[1] See also Neuberg, *Z. physiol. Chem.*, **31**, 564 (1900); *Zt. ver. Rub.-Ind.*, **1901**, 270.

[2] *Loc cit.*

[3] The result obtained in the oxidation of glycerol with hydrogen peroxide may vary quite widely. On one occasion the attempt was made to prepare some of this syrup in a shorter time. The same quantities of materials were used as given above; the mixture was kept constantly in an ice-water bath. The only difference in procedure was that the hydrogen peroxide was all added a little at a time in the course of 5 hours. This reaction mixture did not become pale yellow in color on standing for 2 days; it remained quite red. The reaction mixture was strongly acid and showed, by titration with Fehling's solution, some 22% of the sugar theoretically derivable from 100 g. of glycerol. In the meantime Dr. Nef, of the University of Chicago, had become interested in these experiments and was conducting a series of quantitative experiments in order to determine something more about the limits of this reaction. His quantitative data would indicate that the amount of acid formed increases, and the amount of sugar formed decreases as the length of time is diminished during which the hydrogen peroxide is added. Likewise, he found that, if the hydrogen peroxide is added very slowly (drop by drop for example), much acid and little sugar are formed. In order, therefore, to get more definite data on the best mode of procedure in this oxidation, the following experiment was made:

100 grams of glycerol (pure double distilled) and 10 grams of ferrous sulfate (precipitated by alcohol) in 100 cc. of water were treated with 784 cc. of 5.89% hydrogen peroxide (or 1.25 molecules), at the following rate: 45 cc. were added in the first hour, 65 cc. in the 2nd hour, 70 cc. in the 3rd hour, 85 cc. in the 4th hour, 100 cc. in the 5th and 6th each, 110 in the 7th, 120 cc. in the 8th, and the remainder (90 cc.) in 40 minutes more. All of the hydrogen peroxide was added in one working day. The mixture was kept in ice-water throughout the experiment. The temperature of the reaction mixture was, as a rule, 10°, sometimes 8°, rising usually to 12°, but sometimes to 15°, on adding the hydrogen peroxide. The peroxide was added in small portions at first (2–3 cc.) but in the later stages as much as 10 cc. were added at one time. This mixture, on standing in the refrigerator over night, had become pale yellow in color and gave a negative test for hydrogen peroxide. It had a perceptible odor of formaldehyde

This solution is then neutralized at room temperature as completely as possible by simply shaking with an excess of powdered calcium carbonate.[1]

The sediment (chiefly excessive calcium carbonate) is filtered off by means of a suction filter. The filtrate is then concentrated to a syrup by distilling *in vacuo* (bath temperature 40–45°), during which process a considerable quantity of calcium salts separate in the bottom of the flask (mostly calcium sulfate). The residue from the distillation is then mixed with four to five volumes of absolute alcohol containing some ether. This solution is then freed from its precipitate by sedimentation and filtration and again reduced to a thick, clear, pale yellow syrup by distilling *in vacuo* (bath temperature not over 45°). The total yield of syrup is 70 to 80 g. By extracting the sediment of calcium salts, etc., with another portion of alcohol somewhat more material may be recovered.

The final product has a sweet taste accompanied by a slightly aromatic sour or sometimes a bitter taste. This latter taste is probably due in part to the diethyl acetal of glyceric aldehyde. The amount of it seems to increase with the amount of free acid left unneutralized by the calcium carbonate and the time during which the aldehyde remains in the absolute alcohol solution. The syrup, on heating, gives the odor of burnt sugar and leaves a slight residue on ignition. Fehling's solution is reduced slowly in the cold, in a minute or two at room temperature and instantly at 50°. If 10 cc. of a 1% solution are treated with 1 cc. of 20% potassium hydroxide and the alkaline mixture allowed to stand for half an hour, or if it is heated to boiling, its ability to reduce Fehling's solution at room temperature is lost but the solution retains its power to reduce Fehling's solution on boiling. The above change indicates acrose (hexose) formation. The reducing power of the syrup, as determined with Fehling's solution, is frequently 52–58% of that of pure glucose. With Schiff's reagent it gradually gives the characteristic color tests for aldehydes. By treating with phenylhydrazine in the usual way an osazone is readily formed, which, after recrystallization from 50% alcohol and then from benzene, gives a melting point of 130–1° (phenylglycerosazone). When several drops of a 0.25% solution of this sugar-containing syrup were warmed with

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and when titrated with Fehling's solution showed a glucose equivalent corresponding to 38% of that which could occur if all the glycerol had been converted into glucose.

A parallel experiment in which only 1.0 molecule of hydrogen peroxide was added during the same period showed about the same amount of sugar and less formaldehyde and free acids. These solutions were turned over to Dr. Nef.

It is quite possible that a further variation of conditions might serve to increase the yield in sugar by 5 to 15%. Experiments will be made on this point.

[1] If this material is not to be used for physiological experiments it is better to use barium carbonate to neutralize the free acid because barium sulfate is so much less soluble.

0.5 cc. of a cold saturated phloroglucinol solution, in the presence of a trace of sulfuric acid, a flocculent precipitate was formed in about one minute when the mixture was placed in hot water. This precipitate corresponds well with the description of the glucoside-like compound between phloroglucinol and glyceric aldehyde as given by Wohl and Neuberg.[1]

All of the above stated facts harmonize well with the supposition that the syrup contains chiefly *dl*-glyceric aldehyde, as maintained by Fenton and Jackson, but they do not prove it conclusively since a mixture of aldo- and keto-trioses would give similar reactions.

A method of separating the glyceric aldehyde from any dihydroxyacetone or other impurities that may be present in the mixture, was needed. It was thought that the acetal derivative would enable this to be done. Wohl not only synthesized glyceric aldehyde by the hydrolysis of its acetal but also demonstrated that the aldehyde could be converted back into the acetal[2] by the method used by Fischer and Giebe,[3] which consists in dissolving the aldehyde in absolute alcohol containing 1% of dry hydrochloric acid gas, and allowing the mixture to stand five days in the cold, after which it is worked up for the acetal. Ketones react very much more difficultly to form acetals under these conditions.[4] In fact the acetal of dihydroxyacetone is not known as yet. It was hoped, therefore, to convert the glyceric aldehyde of the Fenton and Jackson mixture into the acetal by the method of acetylating used by Fischer and Giebe, to remove and purify the acetal by fractional distillation and finally to liberate pure glyceric aldehyde from the acetal so formed in accordance with the method used by Wohl.

The following is a brief record of the experiments made in the preparation of *dl*-glyceric aldehyde diethyl acetal:

(*a*) Ten grams of the crude glyceric aldehyde were dissolved in 87 cc. of absolute alcohol and cooled to 0°. 13 cc. of 8.5% dry hydrochloric acid gas in absolute alcohol were added and the mixture placed in a refrigerator at 0°. The reducing power of this solution was tested, from time to time, with Fehling solution and finding no further loss at the end of three weeks, it was worked up as follows: The solution was treated with an excess of lead carbonate in order to remove the hydrochloric acid. On filtering, a clear, reddish yellow solution was obtained, which was concentrated by distilling *in vacuo* at 21–22°. No tar was formed. A hot ceresin bath (150°) was now placed around the flask. Distillation began at a low temperature and the rise in temperature was slow up to 60°, rapid from 60° to 110°, and slow from 110° to 144°, at which point it

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[1] *Ber.*, **33**, 3095 (1900).

[2] *Ibid.*, **33**, 3103.

[3] *Ibid.*, **30**, 3055; **31**, 545.

[4] Meyer u. Jacobson, "Lehrb. d. Org. Chem.," 2nd Ed., Vol. I, 1, p. 64.

remained a moment before dropping quickly to 138°. The pressure was 22 to 25 mm. throughout the distillation. The distillate between 110° to 144° showed a strong acid reaction and reduced Fehling's solution in the cold. The drop of colorless liquid on the thermometer did not reduce Fehling's solution in the cold. The unsatisfactory results of this experiment are due largely to the presence of acid, as will appear in the following experiments:

(*b*) Sixty grams of the crude aldehyde were treated as in (*a*) and after remaining at 0° for one month the reaction mixture was worked up. The addition of a little water made it possible to completely neutralize the solution with lead carbonate. The alcohol was removed by distilling *in vacuo* as before. The residue was diluted with an equal volume of water and saturated with finely powdered potassium carbonate.[1] The mixture was cooled from time to time as it became perceptibly warm. Toward the end the solution separated in two layers, the upper one of which was a red oil. Sufficient ether was then added to dissolve the upper layer. The solution was extracted four more times with ether. The ether solution was filtered through a dry filter and dried over night with anhydrous sodium sulfate. After driving off the ether this oil distilled at 134° at 15 mm. pressure (ceresin bath at 150°). The thick oily distillate had only a very slight yellowish tinge and an acrid burning taste. Yield, estimated 4 or 5 g.

(*c*) The experiment was repeated as in (*b*) except that the residue after distilling off the alcohol was extracted at once with ether and not treated with water and potassium carbonate as in (*b*). This gave 19.5 g. of a thick, golden yellow oil. When this oil was distilled *in vacuo* two fractions were obtained, one boiling mostly below 80°, the other between 132–40° at 18 mm. The latter weighed 4 g. and subsequently proved to be nearly pure glyceric aldehyde diethyl acetal. A large quantity of a dark red, tarry liquid remained in the flask. Subsequently a higher boiling fraction of unknown composition, boiling mostly at 155–70° at 18 mm., was obtained from this residue. This method is less satisfactory than that used in (*b*).

(*d*) Experiment (*b*) was repeated using 320 g. of crude aldehyde. In the distillation two fractions were collected. The first consisted of 11.5 g. of material distilling below 120° at 11 mm. pressure. The second was 41 g. distilling between 120° and 140° at the same pressure. When the low boiling or first distillate was redistilled 10.1 g. distilled below 110° at 11 mm. When the high boiling or second distillate was placed in the flask containing the small residue of the previous distillation it was found that distillation began at 112° at 11 mm. pressure. The temperature arose rapidly to 119°, then slowly to 121° at which point the larger part

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[1] Wohl, *Ber.*, 31, 1796 (1898); 33, 3099 (1900).

of the distillate passed over. The temperature then rose fairly rapidly to 123°, and the distillation was interrupted at this point. The temperature of the ceresine bath throughout was never above 140° and was at 127° when distillation was interrupted. The oily distillate was almost transparent like water, had a burning taste and weighed 29.5 g. The boiling point of *dl*-glyceric aldehyde diethyl acetal as given by Wohl[1] is 136° at 27 mm. pressure. The above material was redistilled subsequently and was found to distil freely at 132° at 22 mm. pressure with an outside bath temperature of 140°. The boiling points observed (121° at 11 mm.; 132° at 22 mm.), therefore, coincide very closely with those of *dl*-glyceric aldehyde diethyl acetal as observed by Wohl.[2]

In order to complete the identification of this oil as *dl*-glyceric aldehyde acetal, it now remained only to show that it yields *dl*-glyceric aldehyde upon hydrolysis. 1.6 g. of the above oil were dissolved in ten parts of 0.1 *N* sulfuric acid[3] and allowed to stand at room temperature for two days. The mixture was then carefully neutralized with barium hydroxide, filtered and reduced to a thick syrup in a desiccator over sulfuric acid. A few days after stirring with a glass rod the thick syrup showed signs of crystallization, and in about two months assumed the form of an opaque, brittle nearly white, solid mass. When particles of this mass were dissolved in water the solution reduced Fehling's solution within a minute in the cold and gave the characteristic aldehyde test with Schiff's reagent. The taste resembled that of the original acetal of which no doubt a considerable amount was still left unchanged.

A 10 g. portion was similarly hydrolyzed and after concentrating to a syrup *in vacuo*, when treated with ammoniacal lead acetate solution, gave the characteristic precipitate of the lead compound of *dl*-glyceric aldehyde which turned yellow on exposure to the air as described by Wohl and

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[1] *Ber.*, **33**, 3103 (1900).

[2] In one experiment a considerable quantity of syrup was treated as in (*d*) except that it was allowed to stand in the laboratory instead of in the refrigerator. When worked up I was greatly surprised to obtain about 30 g. of a low-boiling liquid and no *dl*-glyceric aldehyde diethyl acetal whatever. This compound, boiled at 97–100° at 12 mm. or 93–96° at 8 mm. pressure. When it is recalled that experiment (*d*), in which the hydrochloric acid was not neutralized, quickly gave 10 g. of a similar low-boiling distillate and that experiment (*e*), in which I took special pains to neutralize quickly, gave none of this low-boiling compound whatever, it seemed clear that the compound is in some way related to glyceric aldehyde. Further experiments will determine whether or not it is, as is suspected, the β-ethyl glucoside of *dl*-glyceric aldehyde.

(Since the above was written Emil Fischer (*Ber.*, **46**, 1983) has published a paper on glucosides in which he has expressed the belief that a glucoside of glyceric aldehyde is formed under the conditions here described and in which he has promised to investigate this possibility, so that it will no doubt shortly be known whether an ethyl glucoside of glyceric aldehyde is formed here or not.)

[3] Wohl, *Ber.*, **31**, 1800; **33**, 3103.

Neuberg.[1] The original crude material also gave this test. When several drops of a 0.25% solution of this syrup were mixed with 0.5 cc. of a cold saturated solution of phloroglucinol, in the presence of a trace of sulfuric acid, the flocculent precipitate described by Wohl and Neuberg[1] was formed at once when the mixture was immersed in hot water. This syrup also gave the Fehling solution test and the Schiff test described above. The syrup with which these tests were made did not crystallize and had a bitter taste so that it clearly lacked some of the essential characteristics of pure *dl*-glyceric aldehyde.

These experiments had reached this point when they were interrupted in order to synthesize *dl*-glyceric aldehyde according to Wohl's method.[2] In the light of the experience gained here, the experiments were then taken up again and completed as described below.

(*e*) Six hundred grams of the glycerol oxidation syrup, which had been standing in the laboratory for six months, were dissolved in 6 liters of absolute alcohol containing 1% of dry hydrogen chloride and kept in an ammonia-cooled refrigerator for three months. This solution was worked up in three equal portions of 2 liters each as follows: Each portion was treated with 200 cc. of water and then shaken vigorously with an excess of $PbCO_3$ for an hour or more. Finally the last portions of acid were removed by adding small amounts of sodium bicarbonate until the solution was no longer acid to moist litmus paper. This solution was then concentrated *in vacuo* to a rather thick syrup. About two volumes of water were added in which the syrup was readily dissolved. The whole was now saturated with potassium carbonate. A dark red upper layer separated which was taken up in ether. The remaining solution was then extracted four or five times more with ether. A very thick, almost black, tar remained as the residue of the top layer. The orange colored ether solution was dried with potassium carbonate and concentrated, which gave 125 g. of a red oil. This distilled *in vacuo* gave 50 g. of a colorless distillate boiling between 100° and 140° at 8 mm. pressure. On redistilling, 37 g., distilling between 108° and 125° (mostly 118° to 122°) at 8 mm. pressure were obtained. This was dissolved in 370 cc. 0.1 *N* sulfuric acid and allowed to stand at room temperature for one week. Two grams of glacial acetic acid were added and then 170 cc. of 0.212 *N* barium hydroxide. After filtering off the barium sulfate the solution was adjusted by the addition of small amounts of 0.1 *N* sulfuric acid until only a slight positive test for barium could be obtained. This solution was freed from barium sulfate by filtering through a filter containing a pinch of washed animal charcoal. The filtrate was freed from water by distilling *in vacuo*. The yellow gum was taken up in absolute alcohol, treated with ether to

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[1] *Loc. cit.*

[2] Cf. THIS JOURNAL, 36, 1908 (1914).

remove inorganic matter, and concentrated *in vacuo*. The syrup obtained was inoculated with a few particles of crystalline *dl*-glyceric aldehyde. In a week crystallization was complete. The crystals were filtered off, washed freely with absolute alcohol and dried in the air for one day and then three days *in vacuo* over concentrated sulfuric acid. These crystals melted at 142°. When mixed with *dl*-glyceric aldehyde, obtained by Wohl's method and similarly dried, the melting point (142°) was unchanged. A second crop of 1 g. made the total quantity obtained 5 g., *i. e.*, about 25% of the amount theoretically possible if all of the material hydrolyzed was glyceric aldehyde acetal.

It was thus definitely established that this oxidation syrup contains *dl*-glyceric aldehyde; furthermore, it is also clear from the data given that this method, at least in its present form, is valueless as a practical method of preparing *dl*-glyceric aldehyde. Wohl and Neuberg[1] succeeded in converting only 11% of their *dl*-glyceric aldehyde into the diethyl acetal when they used the pure sugar. In Experiment (*d*) only 5.1% of the crude material was obtained as the acetal. In another experiment 7.5% was obtained as crude acetal. If these acetals had been absolutely pure this would be a very favorable result, but they were no doubt mixed with small amounts of other acetals or acetal-like compounds of glycerol, etc., which either failed to hydrolyze, or form products of hydrolysis which prevent the crystallization of the *dl*-glyceric aldehyde present to a large extent. Such acetals and acetal-like derivatives of aldehyde with glycerol and the higher alcohols are known to be formed[2] and especially in the presence of hydrogen chloride.[3]

The results just presented make it clear that it ought to be possible[4] to obtain crystalline *dl*-glyceric aldehyde directly from the glycerol oxidation syrup by seeding the absolute alcohol solution with the crystallized material. All my efforts in this direction have thus far met with practically negative results. In each test in which it was tried a very small amount crystallized out on long standing, but the amount thus obtained was negligible for practical purposes. The dihydroxyacetone of which there is no doubt some present, and possibly the glycerol appear to hinder crystallization. Further experiments with this syrup are, however, still being made.

Summary.

It has been shown that the reaction mixture, obtained on oxidizing

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[1] *Loc. cit.*

[2] Cf. Meyer and Jacobson's "Lehrbuch der Org. Chemie," I, II, pp. 157 and 171 for references.

[3] Schultz, Tollens, *Ann.*, **289**, 29 (1895); Nef, *Ibid.*, **335**, 215 (1904); and Fischer, *Ber.*, **28**, 1169 (1895).

[4] Cf. also the paper on the preparation of glyceric aldehyde according to Wohl's method, THIS JOURNAL, **36**, 1908 (1914).

glycerol with hydrogen peroxide in the presence of ferrous iron, contains *dl*-glyceric aldehyde:

(1) By converting the aldehyde into glyceric aldehyde diethyl acetal, which was separated by extraction with ether and subsequent distillation and was identified by its color, taste, boiling point, and,

(2) By liberating and crystallizing pure glyceric aldehyde from the syrup obtained on hydrolyzing the above acetal in 0.1 *N* sulfuric acid.

The presence or absence of glycolaldehyde and dihydroxyacetone was not established by these experiments.

This is the first time that either *dl*-glyceric aldehyde or its acetal have been isolated from an oxidation syrup or in fact from any source, except by the synthetic method devised by Wohl. It is likewise the first time that a sugar has been isolated from a reaction mixture by converting it into the acetal.

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NEW BOOKS.

Introduction to Modern Inorganic Chemistry. By J. W. MELLOR, D.Sc. 1914. pp. xvi + 657. 8vo. Longmans, Green & Co., London, New York. Price, $1.30.

The earlier and similar work by the same author, "Modern Inorganic Chemistry," 1912, has been reviewed in THIS JOURNAL, **35**, 494. In the preface to the present book the author says: "I have prepared a smaller introductory volume to suit students who want to start with a rather simpler book, and I have been persuaded to introduce some pages dealing with a few of the more important compounds which the inorganic chemist borrows from the organic chemist. My larger book can now be regarded as a kind of sequel to the present work."

We all believe that good teaching requires us to arouse and hold the attention of the student, but those of us who have to perform this task for freshmen may well be discouraged over our feeble efforts on reading such an exciting book as this. Our attempts to keep the students awake by such crude means as strange smells and explosions are here supplanted by poetry and drama. Who ever suspected that chemistry afforded such opportunities for literary effect as we find on page one? "Wind is air in motion, and wind has sufficient energy to propel our sailing ships, to drive the machinery of our windmills, and, when stirred by cyclonic blast, to uproot trees, sweep away buildings, and lash the surface of the ocean into wild monster waves." Again, how the student will be aroused by the paragraph commencing "Let us assume the function of a judge in a law court and sum up the evidence for the jury," etc. How many of us have ever thought of reciting stanzas from Shelley's poem "The Cloud" to enliven our lecture on water? We find a paragraph headed, "Nature Abhors