I. The Reduction of Tartaric Acid.

II. The Heats of Combustion of Anhydrous Oxalic Acid, Malonic Acid, dl-Malic Acid, Glutaric Acid, Adipic Acid, Azelaic Acid and Sebacic Acid.

Thesis

by

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Summary

I. In order to correlate the configuration of threo-2,3-butanediol with the sugar series we have attempted to prepare an optically active 2,3-butanediol by the reduction of tartaric acid.

l-threo-γ-Carbomethoxy-*α*,*β*-diacetoxybutyryl chloride can be obtained by the action of thionyl chloride on monomethyl diacetyltartrate. This acid chloride is easily reduced to methyl diacetyl-*l*-threuronate with hydrogen in the presence of palladinized barium sulfate.

Methyl diacetyl-*l*-threuronate can be reduced in basic solution to *l*-threonic acid by sodium amalgam. Reduction of *l*-threonic acid in acid solution by sodium amalgam yields *l*-threitol, the configuration of which is established by this synthesis.

Unsuccessful attempts were made to reduce ethyl tartrate, isobutyl tartrate, ethyl isopropylidenetartrate, and isobutyl isopropylidenetartrate. Also, the reduction of methyl diacetyl-*l*-threuronate was attempted by other means, but without success.

II. The isothermal heats of combustion at 25° of anhydrous oxalic acid, malonic acid, dl-malic acid, glutaric acid, adipic acid, azelaic acid, and sebacic acid have been determined. These data are compared with the existing values.

Using the experimental data and the heats of formation of water and carbon dioxide, the heats of formation of the compounds have been calculated.

The free energies of formation have been calculated making estimates of the entropies.

The Reduction of Tartaric Acid.

Within recent years there has been a marked revival of interest in the tetroses and related compounds. Aside from the ozonolysis of diacetyl-*d*-xylal[1] the tetroses have been prepared mainly from the pentoses by the well known degradation methods of Ruff[2a], Wohl[2b,c,3] and Weermann.[4]

The desirability of using the tartaric acids as sources for tetroses and related compounds was recognized by Emil Fischer[5]--who was unsuccessful in attempts to reduce tartaric acid. Following the realization that the lactones, rather than the acids themselves, are the compounds which undergo reduction he planned to reduce esters of tartaric acid[6]. Since no subsequent statement has appeared, it is presumed that results were negative.** This report is made now, since the synthesis of *ℓ*-threitol has been accomplished.

The extension of the Rosenmund[7] method to sugar chemistry by Cook and Major[8] and by Glattfeld and coworkers[9], who have reduced the acid chlorides of acetylated hydroxy acids to acetylated hydroxy aldehydes with hydrogen in the presence of palladinized barium sulfate, suggested a similar method of attack here.

When tartaric acid, I, is heated with acetic anhydride[10] or with benzoyl chloride[11], it is converted into diacetyltartaric anhydride, II, or dibenzoyltartaric anhydride. The dibenzoyl anhydride is converted by

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* Dextrorotatory tartaric acid, *ℓ*-(+)-*threo*-dihydroxysuccinic acid, is referred to simply as tartaric acid.

** The method of Bouveault and Blanc, *Compt. rend.* **136**, 1676 (1903); **137**, 60 (1903) has been applied to the reduction of isobutyl tartrate, ethyl isopropylidenetartrate andisobutyl isopropylidenetartrate without success. Glattfeld and Mochel, *J.Am.Chem.Soc.* **60**, 1001 (1938) have shown that esters of α,β-dihydroxyisobutyric acid cannot be reduced this way.

water into dibenzoyltartaric acid monohydrate. The anhydride was obtained when attempts were made to convert the acid to the acid chloride, as noted by others.[12] Diacetyltartaric acid was not obtained in satisfactory yields from the diacetyl anhydride.*

An acid chloride can be prepared from a half ester, obtained from one of the anhydrides through a reaction with an alcohol. Although dibenzoyltartaric anhydride reacts readily with primary alcohols, the resulting products are liquids. Moreover, they cannot be distilled without decomposition. However, diacetyltartaric anhydride, II, reacts vigorously with methanol to give the easily purifiable solid monomethyl diacetyltartrate, III.[13] This with thionyl chloride is converted into the crystalline acid chloride of monomethyl diacetyltartrate, IV.

The acid chloride can be reduced by the Rosenmund method in xylene at a temperature of 130° to 135°. When the reaction mixture stands at room temperature, methyl diacetyl-*l*-threuronate, V, separates in fifty-five to sixty percent yield.

The threuronate has a mild aldehyde odor, reduces warm Benedict's solution and gives the characteristic uronic acid test with naphthoresorcinol.[14] The color of the resulting dye in ether is reddish violet and it has a strong absorption in the range 5200° to 6000° Å, similar to that of the dye from glucuronic acid, which absorbs in the region of the D line. The threuronate reacts with phenylhydrazine, *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine, yielding solid derivatives with the last two.

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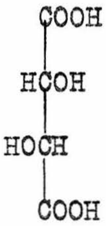
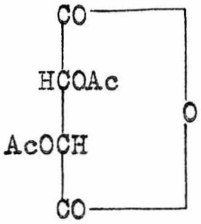
* Austin and Park, *J. Chem. Soc.* **127**, 1926 (1925) state that diacetyltartaric acid results from the action of water in acetone. No yield is given.



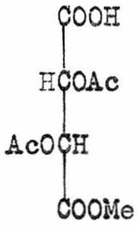
$$\begin{array}{c}\text{COOH}\\ |\\ \text{HCOH}\\ |\\ \text{HOCH}\\ |\\ \text{COOH}\end{array}$$

I



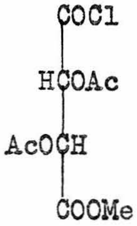
$$\begin{array}{c}\text{CO}-\\ |\\ \text{HCOAc}\quad \text{O}\\ |\\ \text{AcOCH}\\ |\\ \text{CO}-\end{array}$$

II



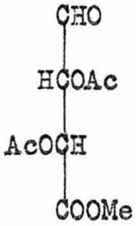
$$\begin{array}{c}\text{COOH}\\ |\\ \text{HCOAc}\\ |\\ \text{AcOCH}\\ |\\ \text{COOMe}\end{array}$$

III



$$\begin{array}{c}\text{COCl}\\ |\\ \text{HCOAc}\\ |\\ \text{AcOCH}\\ |\\ \text{COOMe}\end{array}$$

IV

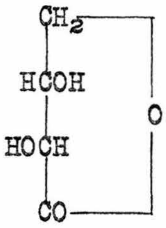


$$\begin{array}{c}\text{CHO}\\ |\\ \text{HCOAc}\\ |\\ \text{AcOCH}\\ |\\ \text{COOMe}\end{array}$$

V

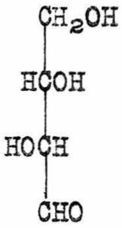
$$\begin{array}{c}\text{CH}_2\text{OH}\\ |\\ \text{HCOH}\\ |\\ \text{HOCH}\\ |\\ \text{COOH}\end{array}$$

VI



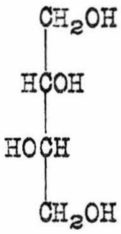
$$\begin{array}{c}\text{CH}_2-\\ |\\ \text{HCOH}\quad \text{O}\\ |\\ \text{HOCH}\\ |\\ \text{CO}-\end{array}$$

VII



$$\begin{array}{c}\text{CH}_2\text{OH}\\ |\\ \text{HCOH}\\ |\\ \text{HOCH}\\ |\\ \text{CHO}\end{array}$$

VIII



$$\begin{array}{c}\text{CH}_2\text{OH}\\ |\\ \text{HCOH}\\ |\\ \text{HOCH}\\ |\\ \text{CH}_2\text{OH}\end{array}$$

IX

In contact with water, hydrolysis of V takes place easily, for essentially three equivalents of sodium hydroxide must be added before the solution becomes alkaline. When an aqueous solution of V is concentrated, darkening gradually takes place. Finally a dark gum is obtained, from which no crystalline product could be isolated.

This is the first tetruronic acid of which the structure is definitely established. A few previously described compounds may be teturonic acids, but some doubt exists as to the structures. Thus from the oxidation of meso-erythritol[15] Neuberg isolated an acid, $C_4H_6O_5$, in the form of the barium salt. Schmidt et al isolated the calcium salt of 3-methylthreuronic acid by hydrolyzing the ozonolysis product of the unsaturated methylation product resulting from the action of diazomethane on saccharic acid, and on saccharolactonic acid.[16]

Reduction of the uronic ester, V, was attempted with aluminum isopropoxide and with hydrogen in the presence of a Raney nickel catalyst.* In neither case was any reduction product isolated. However, V can be reduced in aqueous solution by sodium amalgam, keeping the solution slightly basic. The reduction is stopped when the reducing power is lost. The reduction product was a syrup which could not be obtained crystalline. The procedure of Gätzi and Reichstein[17], who obtained *l*-threonolactone, VII, in a crystalline form by means of high vacuum distillation at 0.3 mm., gave a syrup which would not crystallize. However the acid, VI, was characterized as the brucine salt. This salt has been described previously.[17,18]

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* E. Baer and H. O. L. Fischer, J. Biol. Chem. 128, 463 (1939), have reduced isopropylidene glyceric aldehyde to isopropylidene glycerol at room temperature and at high pressure. The latter was not available here.

Reduction of _ℓ_-threonic acid with sodium amalgam was carried out under acidic conditions. Under these conditions the compound undergoing reduction presumably is the lactone, VII, which is in equilibrium with the acid. No attempt was made to isolate the first reduction product _ℓ_-threose, VIII, the presence of which was indicated by reducing action of the solution towards Benedict's solution. The reaction was continued until the solution had no reducing action. The final reduction product, _ℓ_-threitol, was isolated as dibenzylidene-_ℓ_-threitol, and from this _ℓ_-threitol was obtained.

The synthesis of _ℓ_-threitol from tartaric acid is a confirmation of the configuration of the threitols, as determined by others. Thus Maquenne[19] obtained d-threitol from _d_-xylose through _d_-threose, and Hockett[2] obtained dibenzylidene-_d_-threitol from _d_-xylonic acid and _d_-xylose, through _d_-threose. The formation of _ℓ_-threitol by the reduction of erythrulose does not establish its configuration.[20].

Experimental

Isobutyl Tartrate.---A mixture of 250 g. (1-2/3 moles) of tartaric acid and 450 g. (5.3 moles) of isobutyl alcohol containing 3% hydrogen chloride was heated so as to obtain a slow distillation of the azeotropic mixture of the alcohol and water through a fractionating column until anhydrous alcohol came over. After excess alcohol had been distilled out, the product, which solidifies on cooling, distilled at 155-160° (5 mm.). Yield 350 g. (80%).

Reduction of Tartaric Esters.--The isobutyl ester in absolute alcohol was added slowly to a mixture of sodium and absolute alcohol. After the sodium had disappeared, the alcohol was distilled off and the residue was taken up in water. The solution was neutralized with sulfuric acid, boiled with charcoal and the colorless solution was evaporated to dryness. From this residue no organic compound could be extracted with alcohol.

The reduction was repeated, except that the alkali was neutralized by potassium bisulfite in one case, and by carbon dioxide in another. The results were negative.

Alkyl Isopropylidenetartrates.--When ethyl tartrate was heated with acetone and anhydrous copper sulfate for thirty-six hours, as in the method of Tsuzuki[21], no reaction product was obtained. However, reaction took place when a small amount (a few drops per liter) of sulfuric acid was added. The yield was 50%. It was found preferable to carry out the reaction at room temperature on the shaking machine. Thus the isobutyl derivative was obtained in 60% yield by shaking for about twelve hours, 131 g. (0.5 mole) of isobutyl tartrate, 800 ml. (10 moles) of acetone and 195 g. (1.2 mole) of anhydrous copper sulfate. The product distilled at 125° (2mm.). The yield from ethyl tartrate was similar.

It was thought that blocking of the hydroxyl groups in the isopropylidene compounds would facilitate reduction of the ester groups. However, no reduction product could be isolated when the ethyl or isobutyl isopropylidenetartrate was reduced as above.

Dibenzoyltartaric Anhydride.--This was prepared in practically quantitative yield by the procedure of Butler and Cretcher[11]. The melting point, 193°, was higher than values reported previously (173°).

The monohydrate of the free acid, resulting when water is added to the anhydride, was reconverted into the anhydride by thionyl chloride or phosphorus pentachloride, thus confirming the observations of Zetzsche and Hubacher.[12] Thionyl chloride in the presence of a small amount of zinc chloride acts similarly, although it converts phthalic, succinic and fumaric acids into the respective acid chlorides.[22]

A crystalline half ester could not be prepared by dissolving the anhydride in methyl alcohol, followed by removal of excess methanol at reduced pressure. The residual oil would not crystallize. This substantiates the results of Zetzsche and Hubacher, who however, heated the reactants. The syrupy product from the action of the anhydride on benzyl alcohol was converted into the anhydride with thionyl chloride.

Diacetyltartaric Anhydride, II.--This was obtained in 95% yield when 220 g. (1.5 moles) of tartaric acid was heated at 60° for 20 hrs. with 530 g. (5 moles) of acetic anhydride containing 3% of hydrogen chloride. The solid after removal of acetic acid and excess acetic anhydride, was crystallized from benzene, m.p. 134°.

The neutralization equivalent was determined by titration in aqueous solution at room temperature, the saponification equivalent by the method of Redemann and Lucas.[23]

Anal. Calcd. for $C_8H_8O_7$: Neutralization equiv., 108. Found: neutral. equivl., 110. Saponification equiv., 54. Found: Sapon. equiv., 53.5.

Monomethyl Diacetyltartrate, III.--When 40 ml. (1 mole) of methanol is added to 108 g. (0.5 mole) of diacetyltartaric anhydride, the solid dissolves with heating. After removal of excess methanol at reduced pressure, 93 g. (75% yield) of monomethyl diacetyltartrate is obtained after crystallization from isopropyl ether; m.p. 124.7° (corr).* $[\underline{\alpha}]^{25}$ D, -18.4° (α, -0.75°; l, 2; c, 2.32; MeOH)

Anal. Calcd. for $C_9H_{12}O_8$: C, 43.6; H, 4.84. Found: C, 43.4; H, 4.88. Neutralization equiv., 248. Found: 244. Saponification equiv., 62. Found: 63.

The Acid Chloride of Monomethyl Diacetyltartrate, IV (ℓ-threo-γ-Carbomethoxy-α,β-diacetoxybutyryl Chloride).--Under a reflux condenser a mixture of 45 g. of III and 45 ml. of redistilled (but yellow) thionyl chloride (b.p. 75°-78°) was heated at 60° for about two hours, by which time all of the solid had dissolved. The excess thionyl chloride was removed at reduced pressure, and the residue was recrystallized twice from isopropyl ether, which had been carefully purified from water and peroxide, and stored over sodium. It separated as fine needles, yield 75%; m.p., 108.5° (corr). The solid is not very stable, for it slowly liquefies even in a sealed tube, or in a desiccator. The compound was analyzed for chlorine by first hydrolyzing, and then determining chloride ion by the Volhardt method.

Anal. Calcd. for $C_9H_{11}O_7Cl$: C, 40.5; H, 4.12; Cl, 13.3. Found: C, 40.15; H, 4.18; Cl, 13.1. Saponification equiv., 52.4. Found 57 to 59.

Other Half Esters and Acid Chlorides.--Diacetyltartaric anhydride with ethyl, isopropyl or isobutyl alcohol gives a liquid which could not be crystallized. The ethyl and isobutyl esters were converted to acid chlorides with thionyl chloride as above. Analysis for chlorine was made as above. The slightly low values are due to the tendency of the compounds to decompose slowly.

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* Wrobel[13] reports m.p., 102°.

ℓ-threo-γ-Carbethoxy-*α,β*-diacetoxybutyryl chloride, b.p., 137.5° at 6 mm. *Anal.* Calcd. for $C_{10}H_{13}O_7Cl$: Cl, 12.65. Found: 11.8.

ℓ-threo-γ-Carbisobutoxy-*α,β*-diacetoxybutyryl chloride, b.p. 147° at 6.5 mm. *Anal.* Calcd. for $C_{12}H_{17}O_7Cl$: Cl, 11.5. Found: 10.9.

Methyl Diacetyl-ℓ-threuronate, V.--Hydrogen was passed vigorously into 60 ml. of xylene in which 32 g. of IV was dissolved and 5 g. of palladinized barium sulfate was suspended.* The temperature was 130° to 135° and the time, three to four hours. The reaction was stopped when the evolution of hydrogen chloride slackened, by which time the reduction was 75 to 80% complete. The rate of evolution was followed by passing the exit gas through aqueous sodium hydroxide. The catalyst was removed by centrifuging. On standing the threuronate crystallized in yields of 55 to 60%. An additional crop resulted when the xylene was removed at reduced pressure and the product was distilled at 3 mm. (b.p., 120 to 130°). The total crude yield was 65 to 70%.

The yield was lower when the acid chloride or the xylene was not pure, or when the reduction took longer, as was the case if the catalyst was not well suspended, if it became less active, or if the reduction was carried on towards completion. The purity of the product in some cases was so reduced that no solid separated. When the reduction was satisfactory, the solution was colorless, or nearly so. Whenever the solution was dark colored the yield was low. Distillation at low pressures was necessary whenever the product failed to crystallize, or was dark colored.

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* Technical xylene, previously refluxed with metallic sodium for some time and distilled, was satisfactory. The catalyst was prepared as described in Gattermann, Wieland, "Laboratory Methods of Organic Chemistry," 22nd edition, The Macmillan Co., N.Y., 1932, p. 369.

The ester crystallizes in nodules from toluene or from isopropyl ether, m.p. 84°. The former is preferable, for the loss is much less. Rotations were observed in water, in methanol and in methanol containing one percent of hydrogen chloride. The initial rotations (about five minutes was required for dissolving) were: $[\underline{\alpha}]^{25}$ D = -34.4 (*α*, -2.23°; *l*, 2; *c*, 3.259; H_2O); $[\underline{\alpha}]^{25}$ D = -55.2 (*α*, -3.68°; *l*, 2; *c*, 3.314; MeOH); $[\underline{\alpha}]^{25}$ D = -35.4 (*α*, -1.12°; *l*, 1; *c*, 3.171; MeOH, HCl).

Anal. Calcd. for $C_9H_{12}O_7$: C, 46.5; H, 5.18. Found: C, 46.6; H, 4.96.

It gives a positive uronic test with naphthoresorcinol,[14] and the resulting reddish violet dye in ether absorbs strongly in the range, 5200 to 6000 Å.

The threuronate has a mild aldehyde-like odor, reduces Benedict's solution when warmed, and reacts with phenylhydrazine, *p*-nitrophenylhydrazine and with 2,4-dinitrophenylhydrazine. In the case of the last two, the derivatives were solids. These were prepared by carrying out the reactions in hot glacial acetic acid and adding water to throw out the products. These were recrystallized from hot alcohol. The respective melting points were: p-nitrophenylhydrazone, 143° (corr); 2,4-dinitrophenylhydrazone, 148° (corr).

Anal. Calcd. for $C_{15}H_{17}O_8N_3$: C, 49.05; H, 4.63; N, 11.43. Found: C, 49.11; H, 4.39; N, 11.06.

Anal. Calcd. for $C_{15}H_{16}O_{10}N_4$: C, 43.6; H, 3.88; N, 13.5. Found: C, 43.96; H, 4.5; N, 13.4.

The rotation in aqueous solution remained constant for about twelve hours, then descreased slowly thereafter. After twenty days

$[\underline{\alpha}]^{D}$ was -4°. Color developed after two or three days. After twenty days the solution was dark brown.

In methanol the rotation decreased slowly from the start and after five days reached a constant value of -38°. By this time the solution was colored slightly, but not so much as the aqueous solution.

In methanol containing hydrogen chloride the rotation dropped rapidly, reaching zero in about one day. Then it became positive and in four more days then +22°. The solution was quite dark by this time.

Some attempts at reduction of the methyl diacetylthreuronate were unsuccessful. It was heated three to four hours with an excess of aluminum isopropoxide. The original material was recovered by distillation. The failure here to effect reduction agrees with the experience of others[24] with hydroxyaldehydes.

Hydrogenation was tried in methanol and dioxane as solvents. Neither low pressure hydrogenation with palladium oxide, nor high pressure hydrogenation with Raney nickel was successful. The recovery of the tetruronate in the first case by distillation was essentially quantitative. In the second case the reaction product was a dark colored solution, from which a small amount of the uronate could be recovered. The maximum pressure available was about 80 atmospheres. The temperature was 100° to 120°. Probably the hydrogenation would be possible at higher pressures and room temperature. High temperatures should be avoided.because of polymerization.

l-Threonic Acid, VI, was obtained by reducing V with sodium amalgam in aqueous solution. When 23 g. (0.1 mole) of the crystalline methyl uronate was suspended in 150 ml. of water and cooled, the addition of approximately 0.3 mole of sodium hydroxide was required to make the solution alkaline. This shows that removal of the methyl and the two acetyl groups takes place easily, and that the compound being reduced was sodium l-threuronate. Reduction was accomplished by the addition of 3% sodium amalgam in 50 g. batches, keeping the liquid slightly alkaline to phenolphthalein by neutralizing the excess of base with sulfuric acid, and cooling to keep the temperature in the range, 0 to 25°. After about twelve hours, when about twice the theoretical amount of sodium had been used, the solution no longer reduced Fehling's solution. The solution was filtered, evaporated to dryness under reduced pressure, enough 6 N sulfuric acid was added to liberate the organic acid and the solution was poured into five times its volume of hot absolute alcohol. The mixture was allowed to stand some hours, the voluminous precipitate of sodium sulfate was removed by filtration, and the filtrate was concentrated by reduced pressure evaporation to a small volume. This was taken up in a second volume of alcohol and then after filtering, concentration was effected as before. The residue was a pale colored syrup, presumably l-threonolactone, VIII.

This was converted to the brucine salt by dissolving in warm water, adding brucine until alkaline, cooling, removing excess brucine with chloroform, and evaporating to dryness. After crystallizing from alcohol, the solid recovered weighed 33 g., which is 62% of the theory, calculated from V. The solid melted at 203-204°, dec. $[\underline{\alpha}]^{25}$ D = -23° (*α*, -0.95°; *l*, 1; *c*, 4.13; H_2O).

Anal. Calcd. for $C_{27}H_{34}O_9N_2$: C, 61.25; H, 6.60; N, 5.52; CH_3O, 11.7. Found: C, 61.32; H, 6.6; N, 5.22; CH_3O, 11.8.

When the reduction of V was attempted under acidic conditions, the reaction was much slower. Even when a larger amount of amalgam was used, the reduction was not complete. This shows the importance of keeping the medium slightly alkaline, rather than acidic.

Dibenzylidene-ℓ-threitol.--The syrup from the reduction of V was dissolved in water, cooled to 0°, and with good agitation sodium amalgam was added at intervals. The mixture was kept acid to Congo Red by means of frequent additions of dilute sulfuric acid. After a short time a test portion reduced Benedict's solution, indicating the presence of *ℓ*-threose. No attempt was made to isolate this. Instead, the reduction was continued until the test was negative, requiring about 200% excess of sodium. After filtering, the filtrate was concentrated to a small volume (about 50 ml.) but not to dryness, and poured into a large volume (about 300 ml.) of absolute alcohol. After standing for some time, the solid was removed by filtration, the filtrate was evporated under reduced pressure and the residue was taken up in alcohol. This was saturated with hydrogen chloride and a 10% excess of benzaldehyde added.* After a time, dibenzylidene-*ℓ*-threitol crystallized in fine needles. It was allowed to stand in the cold over night, collected by centrifuging and washed

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* Since benzaldehyde is an excellent solvent for the product, only a slight excess was taken. Preliminary experiments on test portions were made to determine the proper amount.

with alcohol. Yield 15% from V. When crystallized from hot benzene, the melting point was 221-223° (corr) $[\underline{\alpha}]^{25}$ D = + 79° (*α*, +0.62°; *l*, 1; *c*, 0.78, $CHCl_3$).*

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.05. Found: C, 72.5; H, 6.27.

ℓ-Threitol, IX.--When 0.45 g. (0.0015 mole) of dibenzylidene-*ℓ*-threitol was heated with 20 ml. of 20% aqueous acetic acid, solution took place slowly and was complete after one hour. The solvent was removed at reduced pressure, the residue was dissolved in a small amount of water, the solution was filtered and the solvent was removed as before. The residue was dissolved in a small amount of absolute alcohol, the insoluble matter centrifuged down and the solution was cooled in a "dry ice" bath. Crystallization was induced by scratching. Colorless, thread-like needles separated. These were centrifuged down and recrystallized from a small volume of absolute alcohol as above, to give 0.137 g. (0.0011 mole) of *ℓ*-threitol, m.p. 88°. An additional amount of less pure material was recovered by evaporating the mother liquors. The yield of *ℓ*-threitol is 73% for this step, 6.6% on the acid chloride, IV, and 4.6% on tartaric acid, I.

$[\underline{\alpha}]^{25}$ D = -4.2 (*α*, -0.32; *l*, 1; *c*, 7.63; H_2O).**

Anal. Calcd. for $C_4H_{10}O_4$: C, 39.34; H, 8.19. Found: C, 39.28; H, 8.25.

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* Previous values for dibenzylidene-*d*-threitol: Hockett[2], m.p. 220-222°; $\underline{\alpha}^{D}$, -77.9° (-78.2°). Maquenne[19], m.p. 231°.

** Bertrand[20] found for *ℓ*-threitol, $\underline{\alpha}^{D}$, -4.4, m.p. 88°; Maquenne found for *d*-threitol, $\underline{\alpha}^{D}$, + 4.3, m.p. 88°.

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Attempted Reduction of Erythritol to 2,3-Butanediol

The reduction of 1,2,3,4-butanetetrol to 2,3-butanediol was attempted but has not yet been accomplished. Since l-threitol which is prepared by the reduction of tartaric acid[1], is too valuable a material erythritol was used as a model to study the reaction.

We proposed to convert erythritol into 1,4-ditosyl 2,3-butanediol. It has been pointed out by Oldham and Rutherford[2] that p-toluenesulfonylchloride, called for shortness "tosylchloride", is a reagent which attacks preferably primary alcoholic groups. The tosylesters of primary alcohols react with sodium iodide in acetone at 80° - 100° replacing the tosylgroup by iodine. This reaction has been used in the preparation of desoxysugars,[3a] since the iodine can easily be reduced off by hydrogen and Raney nickel.

Unfortunately the reaction of erythritol with tosylchloride is not clear cut. When the reaction is allowed to proceed without cooling, the temperature of the mixture rose and no uniform product can be isolated. If, however, the reaction is carried out at 0°, we were able to obtain a single crystalline compound, which melted sharply at 165°. The analysis of this compound indicated that more than two molecules of tosylchloride have reacted with erythritol. This was confirmed by a molecular weight determination.

When the tosylester of erythritol is shaken with acetone and anhydrous coppersulfate, there is no reaction indicating the absence of free hydroxyl groups.

The tosylester was heated with sodium iodide in acetone at 100° in an autoclave for several hours. The product contained large amounts of free iodine, and no crystalline product was isolated from the gummy reaction mixture. Supposedly the iodine has replaced more than the two terminal tosylgroups, and in the course of the reaction iodine was split off and unsaturated compounds were formed.

Experimental

Tosylester of Erythritol.--4.88 g. erythritol (1 mole) are suspended in 20 ml. anhydrous pyridine (6 moles) and cooled to 0°. To this mixture is slowly added 16 g. tosylchloride (2 moles) so that the temperature never rose above 5°. The reaction mixture is kept at 0° for 24 hours and then poured into ice water. The precipitate was filtered, washed with aqueous hydrochloric acid and crystallized from ethyl acetate. The compound melted sharply at 165° and crystallized in fine needles. The yield was 7 g.

Anal. Calc. for ditosyl-erythritol $C_{18}H_{22}O_8S_2$: C, 50.25; H, 5.12; S, 14.88.

Calc. for tetratosyl-erythritol $C_{32}H_{34}O_{12}S_4$: C, 52.0; H, 4.62; S, 17.3. Found: C, 51.94; H, 4.68; S, 18.60.

The molecular weight determined by a modified Rast method[4] was found approximately as 700. The molecular weight of the tetratosyl-erythritol is 738. The result of the analysis and the molecular weight determination seem to leave little doubt that the compound in question is actually the tetratosylester of erythritol.

Attempted Acetonization of Tosyl Erythritol. A glass-stoppered bottle containing 2.15 g. tosylerythritol, 50 ml. acetone, 20 g. anhydrous coppersulfate and a few drops of concentrated sulfuric acid are shaken for 24 hours. The coppersulfate is filtered off, washed with acetone and then shaken with potassium carbonate for half an hour. After filtration the acetone is distilled under reduced pressure in the presence of a small amount of potassium carbonate. The residue is boiled with ethyl acetate. Nearly 2 g. of the starting material were recovered.

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The Heats of Combustion of Anhydrous Oxalic Acid, Malonic Acid, dl-Malic Acid, Glutaric Acid, Adipic Acid, Azelaic Acid and Sebacic Acid.

Introduction.

During the second half of the last century Berthelot and Thomsen accumulated a vast amount of data on the heat of combustion of organic compounds. Their aim was to obtain the chemical affinities of organic compounds purely from heat data. With the general acceptance of the second law of thermodynamics their data lost its usefulness, since it was shown that ΔF and not ΔH is the driving force of a chemical reaction.

However, with the formulation of the third law of thermodynamics the values of the heats of combustion and the heats of formation derived therefrom attained new interest. The third law allows the calculation of absolute entropies from heat capacity measurements or spectroscopic data, thus the free energy can be evaluated by the combination of ΔH and ΔS in the second law equation

$$\Delta F = \Delta H - T\Delta S \quad .$$

In the last twenty or thirty years there has been a renewed interest in thermal data due to its applicability to structural questions and reaction mechanisms. This has made more accurate values of the heats of formation desirable.

While the data of the older investigators are remarkably good for their time, newer chemical and physical methods allow us today to attain greater accuracy. In the last few years the investigation of the heat of combustion of organic compounds has been undertaken in this laboratory. This report presents the heat of combustion of seven organic dicarboxylic acids.

Method and Apparatus.

The determination of the heat of combustion of liquid and solid material is carried out most conveniently in the bomb calorimeter. Two methods of bomb calorimetry are in use at the present time. It has been shown that the ordinary and the adiabatic method give results of essentially the same accuracy. The ordinary method has been employed by Huffman and coworkers[1a-g] in this laboratory. In this method the rise in temperature of the calorimeter is observed while surrounded by a constant temperature jacket, and a correction is applied for the heat lost to the surroundings. The calorimetric system is essentially that of Dickinson[2]. It consists of three parts, the constant temperature jacket, the calorimeter proper, and the bomb. The calorimeter is completely surrounded by a double-walled metallic vessel, the jacket, containing a large mass of water. This water jacket (Fig. 1 pg. 25) is well stirred and the temperature kept constant within ± 0.002° by means of a thermoregulator. The calorimeter proper (Fig. 2 pg. 25) is stirred by a propeller driven at 380 r.p.m. by a constant speed motor.

There are four possible causes for heat interchange between the calorimeter and the jacket: radiation, convection, conduction, and evaporation or condensation. About one-fifth of the heat is transferred by radiation, about four-fifths by convection and conduction, and only very little by evaporation. In calculating the correction for the heat transfer Newton's law of cooling is assumed to hold over the small range of temperature. This assumption is only approximately true.

The heat transfer by convection and conduction depends largely upon the shape and size of the surfaces involved. For small temperature differences, however, Newton's law is a close enough approximation.

The heat loss due to evaporation does not follow a simple law. However, with proper precautions evaporation losses can be reduced to insignificant values; for this purpose the stirrer, thermometer, and electrical leads were brought into the calorimeter through water-tight seals. Furthermore the main portion of the calorimeter is provided with a cover which fits the calorimeter vessel closely and has only one opening for the thermometer. The heat transfer due to radiation is proportional to the difference to some high power of the absolute temperatures of the two surfaces. To eliminate transfer of this kind the calorimeter is nickel plated to reduce radiation to a minimum.

A Parr bomb (Fig. 3 pg. 25) with a capacity of 380 ml. is used. It was modified in such a way that it is made gas tight by means of a gold washer. The standard illium electrodes were replaced by platinum electrodes equipped with threaded binding posts for making the electrical connections to the fuse wire. The bomb is placed in the calorimeter and is completely surrounded by water, the same amount of water being used in the calorimeter each time within 0.1 g. The bomb is mounted on small ivory pegs; this permits the calorimeter liquid to pass below the bomb and so facilitates the circulation.

Fig. 1

Fig. 2

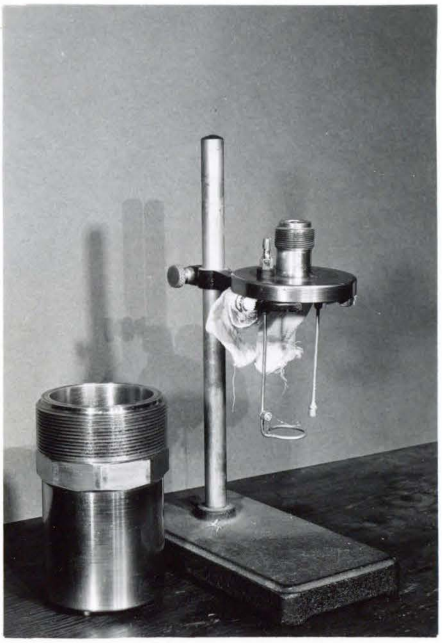

Fig. 3

The temperature is measured by means of a calibrated platinum resistance thermometer, in conjunction with a Mueller type thermometer bridge, and a high sensitivity galvanometer all supplied by Leeds and Northrup Co., the sensitivity of the system being such that 0.00001 ohm (0.0001°) was equivalent to about 0.5 mm. on the galvanometer scale. The galvanometer was used as a null point instrument. The times at which a predetermined series of resistances were reached were recorded on a drum type chronograph with a precision of 0.2 seconds.

The charge is fired by heating a platinum wire, electrically, which ignites a paper fuse which in turn ignites the charge. The energy[1a] required for firing was found to be 1.4 ± 0.2 calories. Since the filter paper is hygroscopic it is kept in a desiccator at constant humidity approximately that of the air in the room. The weight of the fuse is adjusted to 4 ± 0.3 mg. but the weight is actually determined to the nearest 0.01 mg. The heat of combustion of the filter paper has been determined as 3,893.2 cal/g.[1a].

In the experiments with anhydrous oxalic acid and dl-malic acid an auxiliary substance was found necessary for complete combustion. For this purpose Cenco vacuum pump oil was used. Its heat of combustion had been determined as 10,825 ± 2 cal/g.[1a]

The combustion samples are pressed into pellets to simplify handling and transferring. They are then dried. Great care has to be taken that the samples are as dry as possible. For this purpose the drying process is varied in length of time and intensity. First the samples are dried to constant weight at room temperature in a desiccator over phosphorus pentoxide. They are then subjected to different treatments. Some are dried at elevated temperatures in air, others in a vacuum desiccator over phosphorus pentoxide. Finally some of the samples are fused, provided no decomposition occurs during the process. When more strenuous treatment did not change the heat of combustion, there was reasonable assurance the drying of the samples was complete.

Before the combustion the samples are weighed on a Kuhlmann micro balance to 0.01 mg. A small amount of water is placed in the bomb, the platinum crucible with pellet inserted, the bomb evacuated to a few millimeters and filled with oxygen at a pressure of 30 atmospheres. The water is placed in the bomb to saturate the space with water vapor, thus making the correction for the vaporization of the water formed during the combustion negligible. It is furthermore necessary to evacuate the bomb, since the nitrogen of the air is partially burned to nitric acid, and it is advisable to keep this correction as small as possible. The method of determining this correction will be discussed later.

The constant range method has been adopted in this laboratory. All the combustions are started at the same initial temperature of 24°, and the mass of the samples are adjusted to give a rise in temperature of 2°. An auxiliary heater in the calorimeter is used to facilitate the attainment of the initial temperature.

The Calibrations.

Either of two methods may be used for the calibration of the calorimeter. The electrical energy equivalent of a calorimetric system, consisting of calorimeter, bomb, oxygen, electrical heater, thermometer, and a weighed amount of water, is determined by supplying a measured quantity of energy electrically and observing the resultant rise in temperature. The conditions in these experiments should be as nearly identical as possible to those in the combustion experiments. The results of such observations give directly the energy equivalent of the calorimeter and its contents, in joules per degree.

In this laboratory the energy equivalent of the calorimetric system, consisting of calorimeter, bomb, electric thermometer, and a weighed amount of water, but without the bomb contents, is determined by use of the second method in which a standard sample of benzoic acid (sample 39 e) supplied by the Bureau of Standards is burned. Its isothermal heat of combustion under standard conditions at 25° is given as $-\Delta U_B/m$ = 26,419 international joules per gram true mass[3]. The sample is burned at 25° in oxygen under an initial pressure of 30 atmospheres absolute, in a bomb of constant volume, the mass of sample and the mass of water placed in the bomb each being 3 g. per liter of bomb volume. Since our conditions differ from these standard ones, we have calculated 26,418 international joules are evolved by the combustion of one gram of benzoic acid under our bomb conditions.

While this work was in progress a new calorimeter was installed. Furthermore we decreased the amount of water added to the bomb from

1 ml. to 0.1 ml. Under these bomb conditions we calculated with the formula given by Jessup and Green[3] for the heat of combustion of benzoic acid at 25° the value 26,416 international joules per gram true mass.

The energy equivalent of the calorimeter was determined at frequent intervals during this work. We have found 3,153.2 ± 0.3 cal. for the old and 3,222.72 ± 0.25 cal. for the new calorimeter.

A small amount of nitric acid is always formed during the combustion. The amount was determined by titration with standard sodium hydroxide using brom cresol green as the indicator. For the heat of formation of nitric acid at 25° and constant volume the value 13,960 cal. Mole^{-1} is used.[4]

Our results are expressed in the conventional calorie which is derived from the absolute joule by the arbitrary definition 4.185 absolute joule = 1 calorie. Since 1 international joule = 1.0004 absolute joule was accepted as the true relation between the international joule and the absolute joule it follows that :
4.1833 international joule = 4.185 absolute joule = 1 calorie.

All the thermal data are given for the isothermal process at 25° and true mass. The calorimetric determination is carried out between the temperatures of 24° and 26°. To correct the experimental heat of reaction to that of the isothermal reaction at 25° we applied equations given by Washburn[5] involving the heat capacities of the bomb contents consisting of the platinum crucible, oxygen, and water added to the bomb and the reactants and products in the initial and final state.

The molecular weights are based on the 1940 table of atomic weights.

Preparation and Purification of Combustion Samples.

Anhydrous Oxalic Acid. The anhydrous acid is prepared from Baker's Acid Oxalic Special for Standardizing by dehydration in the vacuum of the oil pump over concentrated sulfuric acid at approximately 65°C. Sample A is the commercial sample treated as described, sample B was recrystallized once from water prior to dehydration. The dehydrated oxalic acid contained small amounts of formic acid; this impurity, however, could be removed by maintaining the sample in a vacuum desiccator over phosphorus pentoxide. It should be noted that no decomposition of oxalic acid to formic acid occurred at temperatures as high as 45° C.

Malonic Acid. Samples A and B were prepared from Phanstiehl c.p. malonic acid by 4 and 3 crystallizations from redistilled water in the usual manner. Samples E and F were Eastman's malonic acid 3 and 4 times crystallized from water, respectively.

dl-Malic Acid. Eastman's practical dl-malic acid was dissolved in water at 80° and after filtration the clear solution was allowed to stand at room temperature until crystallization was complete. The acid separates in very hard crystals. The mother liquor was decanted off and this whole process repeated. Samples A and B were crystallized 4 and 3 times respectively.

Glutaric Acid. The samples A, B, and H were prepared from trimethylene cyanide by the method of Organic Syntheses[6]. Sample A was crystallized 5 times, sample B 6 times from water. Sample H was a composite from the samples A and B and was crystallized 5 times from water. Samples E and K were Eastman's c.p. glutaric acid crystallized twice from water. The differences in the last two samples were that they originated from two different batches of material.

Adipic Acid. The combustion samples were prepared from Eastman's adipic acid. They were purified by successive crystallizations from water in the usual manner. Sample A was twice, sample B three times and sample C six times crystallized from water.

Azelaic Acid. Two combustion samples were prepared from Eastman's azelaic acid by three and five crystallizations from redistilled water respectively.

Sebacic Acid. Two combustion samples A and B were prepared from Eastman's sebacic acid by three and five crystallizations from redistilled water respectively.

Results.

The results of the combustion experiments are given in tables 1 to 7. The observed temperature rise of the calorimeter was corrected for heat transfer and heat of stirring by Dickinson's method[2]. The heat produced by the combustion of the sample was calculated by multiplying the corrected temperature rise by the energy equivalent of the system. From the total heat evolved were subtracted the energy of firing, the heat evolved by the combustion of the fuse, the energy of formation of the nitric acid formed during the combustion, and the energy of the oil when an auxiliary substance was used. Since the mean temperature of the combustion is 25°, the experimental data have been corrected to

Table 1

Anhydrous Oxalic Acid

Sample		Desiccation P_2O_5 vacuum	Hours in vacuum oven 45°	True mass	Total heat evolved cal.	Cal. from HNO_3	Cal. from oil	Cal. from carbon	Cal. from paper EIT	$-\Delta U_B/m$ cal/g	Deviation cal.
1	B		42 hrs.	2.14191	6,512.60	1.0	5,081.80	2.72	17.17	664.85	+ .59
2	B	60 hrs.		2.54717	6,524.13	1.0	4,829.68	4.00	16.54	663.33	- .93
3	B		100 hrs.	1.66347	5,767.77	.5	4,655.29	4.08	18.25	664.90	+ .64
4	B		100 hrs.	2.09934	6,506.32	.6	5,109.51	4.4	16.14	663.62	- .64
6	A		45.5 hrs.	2.28124	6,567.29	.7	5,044.02	3.84	19.35	664.43	+ .17
7	A		45.5 hrs.	2.22752	6,464.33	.7	4,978.31	3.44	17.41	664.44	+ .18
									Mean	664.26	± .53

Table 2

Malonic Acid

Sample		Desiccation P_2O_5 vacuum	Hrs. in vacuum 50-55°	true mass	Total heat evolved cal.	Cal. from HNO_3	Cal. from paper EIT	$-\Delta U_B/m$ cal/g	Deviation cal.
2	A	816		3.27418	6,511.04	.3	17.32	1,986.34	- .36
3	A	600		3.18074	6,326.71	.2	17.99	1,986.47	- .23
8	A	816	40	3.17622	6,321.72	.3	19.23	1,987.30	+ .60
10	A	912	87	3.16725	6,300.79	.3	18.54	1,986.53	- .17
4	B	528		3.21394	6,394.78	.1	18.11	1,987.16	+ .46
7	B	576	40	3.20421	6,374.41	.1	20.26	1,986.15	- .55
9	B	528		3.16778	6,299.59	.1	17.35	1,986.26	- .44
11	B*	528	52	3.11318	6,194.48	.00	17.01	1,987.08	+ .35
13	E*	96	120	3.12217	6,212.33	.2	16.34	1,986.88	+ .18
14	F*	96	168	3.23220	6,430.54	.2	17.45	1,986.83	+ .13
							Mean	1,986.70	± .35

*Combustions done with new calorimeter and with 0.1 ml. water in bomb. Corrected by + 0.0135% to be comparable with other data in set. Where ash observed was greater than 0.07 mg. the observed weights were corrected by subtracting the ash found.

Table 3

dl-Malic Acid

Sample		Desiccation hours in		True mass	Total heat evolved cal.	Cal. from HNO_3	Cal. from oil	Cal. from paper + EIT	$-\Delta U_B/m$ cal/g	Deviation cal.
		P_2O_5 vacuum	vacuum oven P_2O_5 55°							
11	A		432	2.52467	6,553.10	.4	572.10	18.17	2,364.82	- .25
16	A		34	2.45963	6,285.52	.4	457.35	18.21	2,365.02	- .05
18	A		70	2.50705	6,456.44	.6	515.38	18.17	2,365.34	+ .27
20	A		70	2.56084	6,464.17	.5	399.77	18.57	2,365.26	+ .19
10	B	504	360	2.57488	6,543.47	.3	443.83	18.13	2,364.79	- .28
12	B	168		2.58727	6,398.86	.2	270.41	17.21	2,364.92	- .16
17	B	1296		2.59720	6,505.59	.4	353.33	16.34	2,365.36	+ .29
								Mean	2,365.07	± .21

Table 4

Glutaric Acid

Sample		Desiccation hours in P_2O_5 vacuum	vacuum oven P_2O_5 55°	oven 85°	True mass	Total heat evolved cal.	Cal.from HNO_3	Cal.from paper + EIT	$-\Delta U_B/m$ cal/g	Deviation cal.
3	A	336			1.60825	6,268.56	.2	17.39	3,892.48	+ .24
4	A	360	44		1.61976	6,314.09	.8	18.19	3,892.11	- .13
14	A	888	44		1.60804	6,267.43	.8	17.08	3,892.11	- .13
1	B	288			1.58149	6,166.46	.35	19.02	3,892.56	+ .32
19	B	1032	44		1.61980	6,312.45	.4	17.75	3,891.52	- .72
21	B	1344	44		1.62240	6,322.20	.3	18.98	3,890.61	-1.63
7	E	144			1.62607	6,339.98	.3	19.23	3,892.62	+ .38
15	E	456			1.62459	6,332.10	.3	17.75	3,892.22	- .02
22	H	312			1.61971	6,313.56	.4	18.03	3,892.25	+ .01
25	H	336	26		1.61739	6,304.35	.4	17.87	3,892.23	- .01
26	H	360	26		1.62569	6,336.61	.4	18.27	3,891.98	- .26
27*	K	192			1.67648	6,537.62	1.4	17.69	3,893.20	+ .96
28*	K	192		55	1.64558	6,417.58	.4	18.98	3,893.18	+ .94
								Mean	3,892.24	± .44

*These combustions were carried out with the new calorimeter and .1 ml. water in bomb. Corrected by + 0.0117% to be comparable with other data.

Table 5

Adipic Acid

Sample		Desiccation hours in P_2O_5 vacuum	vacuum oven P_2O_5 55°	vacuum oven P_2O_5 75°	Oven 105°	True mass	Total heat evolved cal.	Cal. from HNO_3	Cal. from paper+EIT	$-\Delta U_B/m$ cal/g	Deviation cal.
6	A	1676	65.5		68	1.40566	6,442.99	1.2	18.05	4.575.77	+ .77
9	A	288	65.5		25	1.40932	6,457.91	2.0	17.45	4.574.34	- .66
7	B	1580			68	1.36883	6,276.47	2.0	21.13	4.574.25	- .75
11	B	192	65.5		150	1.40128	6,420.56	1.0	18.45	4.573.93	-1.07
5	C	648			25	1.40231	6,430.52	2.2	17.97	4.577.13	+2.13
12	C				94	1.41311	6,472.77	.6	16.58	4.574.19	- .81
13	C			65		1.37730	6,310.50	.8	17.93	4.574.08	- .92
14	C				94	1.39882	6,409.09	.8	17.09	4.574.83	- .17
15	C	960			94	1.38149	6,334.71	2.0	18.77	4.576.22	+1.22
10	A		fused at 165°			1.40893	6,456.53	2.5	15.42	4.575.70	+ .70
8	C		fused at 165°			1.45703	6,677.41	2.0	18.65	4.514.55	- .45
									Mean	4,575.00	± .88

Table 6

Azelaic Acid

Sample		Desiccation hours in P_2O_5 vacuum	vacuum oven P_2O_5	oven 56°	oven 65°	oven 98°	True mass	Total heat evolved cal.	Cal. from HNO_3	Cal. from paper+EIT	$-\Delta U_B/m$ cal/g	Deviation cal.
1	A	216					1.14212	6,905.40	1.5	16.70	6,037.97	- .81
4	A	336				44	1.06462	6,437.56	.4	17.25	6,037.50	-1.28
5	A	336				44	1.06882	6,464.08	.4	16.34	6,039.44	+ .66
8	A	264	139				1.07448	6,499.66	.5	16.58	6,039.48	+ .70
2	B	312					1.06998	6,472.52	.6	17.97	6,039.06	+ .28
3	B	264			46		1.07541	6,505.10	.4	17.41	6,039.57	+ .79
6	B	264			46		1.06321	6,431.11	.4	18.21	6,038.53	- .25
7	B	408				24	1.05276	6,368.01	.6	17.73	6,038.74	- .04
			fused in oven 115 for							mean	6,038.78	± .60
9	B				35 min.		1.07793	6,520.93	.6	15.98	6,041.28	
10	A				20 min.		1.08848	6,587.38	1.0	17.41	6,042.25	
11	A				5.5 hrs.		1.13945	6,889.90	.6	18.45	6,037.59	
12	A				24 hrs.		1.12911	6,815.03	.4	19.24	6,026.09	
										mean 9,10	6,041.75	± .60

Table 7

Sebacic Acid

Sample	Desiccation hours in P_2O_5 vacuum	vacuum oven P_2O_5 70°	oven 106°	True mass	Total heat evolved cal.	Cal.from HNO_3	Cal.from paper_n+EIT	$-\Delta U_B/m$ cal/g	Deviation cal.
9 A		114		.99664	6,380.47	2.0	16.62	6,390.86	+ .83
10 A	1176		32	.99849	6,389.20	.3	17.17	6,388.98	-1.05
12 A	864	280	79	.98496	6,300.93	.2	16.10	6,388.21	-1.82
7 B			18.5	.98267	6,291.43	1.0	18.29	6,390.35	+ .32
8 B			91.5	.98018	6,277.28	.8	18.77	6,391.87	+1.84
11 B			32	.99878	6,392.39	.5	17.97	6,389.32	- .71
13 B	624	282		.99240	6,352.94	1.0	17.49	6,390.63	+ .60
							Mean	6,390.03	± 1.02

the isothermal process at this temperature by applying the equations of Washburn[5] as described above in the case of benzoic acid. When the heat capacity of the compounds were not known estimates have been made. The energy evolved in the isothermal bomb process per mole is represented by the sumbol $-\Delta U_B$.

In contrast to the actual bomb process Washburn[5] proposed an analogous process. It consists in the reaction of unit quantity of the substance with an equivalent amount of pure oxygen gas, both under a pressure of 1 atmosphere and at the temperature t_H, to produce pure carbon dioxide gas and pure liquid water, both under a pressure of 1 atmosphere and the same temperature t_H, the reaction taking place without the production of any external work. The energy change in this hypothetical process is a definite thermodynamic quantity and is equal to $-\Delta U_R$, the decrease in energy for the reaction at t_H:

$$C_aH_bO_c(s) \text{ or } (\ell),\ 1 \text{ atm.} + a + \frac{b-2c}{4}\ O_2(g),\ 1 \text{ atm.}$$

$$= a\ CO_2(g),\ 1 \text{ atm.} + \frac{b}{2} H_2O(\ell),\ 1 \text{ atm.}$$

The quantity $-\Delta U_R$ is calculated by means of the correction factor given by Washburn. From this quantity $-\Delta H_R$, the energy evolved in the isobaric reaction at 1 atmosphere, is calculated by the addition of the proper work term. Finally the heat of formation $-\Delta H_f^\circ$ is calculated from $-\Delta H_R$ by using 94,030 calories for the heat of formation of carbon dioxide and 68,317 calories for the heat of formation of liquid water[7].

Rossini[8] has pointed out the advisability of a uniform procedure for the determination of the precision error assigned to the different values. This uniform comparison will be concerned, however, only with the precision, the reproducibility, of the various sets of data and not with their actual accuracy. The accuracy will depend largely upon the magnitude of the unknown or unaccounted for systematic errors. Serious errors may arise from impure combustion samples and from incomplete combustion experiments.

Jessup and Green[3] have assigned an accuracy uncertainty of 0.023% to the determination of the heat of combustion of benzoic acid. From the result of the calibration experiments the calculated calibration error is 0.005%. From the data on the combustions the reaction errors have been determined.

The only additional error which will affect the absolute accuracy of the final values is the presence of impurities. Any error due to this cause should be very small, and therefore the precision error has been assumed to be the same as the accuracy error.

In calculating the error in $-\Delta U_R$ a 10% uncertainty is arbitrarily allowed for in the Washburn correction.

In table 8 the derived values $-\Delta U_B$, $-\Delta U_R$, $-\Delta H_R$, and $-\Delta H_f^{\circ}$ are compiled. The temperature coefficients of the heat of combustion $d\Delta U_B/dT$ are calculated by making use of Washburn's[5] equation and the known or estimated heat capacities.

Table 8

Summary of Derived Data at 25.0°

Substance	Formula	M.W.	Density	$-\Delta U_B$	$-\Delta U_R$	$-\Delta H_R$	$-\Delta H_f$	$\frac{d\ \Delta U_B}{dt}$
Oxalic acid	$C_2H_2O_4$	90,036	2.0	59,807 ± 49.9	59,508 ± 54.9	58,620 ± 54.9	197,757 ± 60	+ 4.4
Malonic acid	$C_3H_4O_4$	104,062	1.6305 (15°)	206,740 ± 5.6	206,316 ± 69	205,720 ± 69	213,004 ± 78	+18
Malic acid	$C_4H_6O_5$	134,088	1.601 (20°)	317,128 ± 78	316,665 ± 92	316,073 + 92	264,998 ± 106	+36
Glutaric acid	$C_5H_8O_4$	132,114	1.429 (14.5°)	514,219 ± 129	513,730 ± 139	513,730 ± 139	229,668 ± 154	+41
Adipic acid	$C_6H_{10}O_4$	146,14	1.5*	668,591 ± 181	668,115 ± 187	668,411 ± 187	237,534 ± 204	+55
Azelaic acid	$C_9H_{16}O_4$	188,218	1.03	1,137,166 ± 284	1,136,597 ± 295	1,137,781 ± 295	255,019 ± 320	+92
Sebacic acid	$C_{10}H_{18}O_4$	202,244	1.5*	1,292,345 ± 362	1,291,902 ± 370	1,293,382 ± 370	261,771 ± 395	+104

*Estimated

Discussion of Results.

The acids of the oxalic acid series have been burned by Verkade[9] and coworkers. They have obtained their data under conditions which are different from those of this investigation and in addition have used a different calorie. For the calibration of his calorimeter Verkade uses as the isothermal heat of combustion of benzoic acid at 19.5° 6324 $cal_{15°}$ per gram benzoic acid (not corrected to true mass). Their value is corrected to true mass and by application of the temperature coefficient of benzoic acid to the isothermal heat of benzoic acid at 25° per gram true mass. It follows by comparison of the value for benzoic acid used by Verkade and the one obtained by Jessup and Green, that Verkade's calorie has to be multiplied by the factor 0.99959 to make it comparable to the conventional calorie used in this laboratory. In table 9 the values so corrected are compared with our results.

Becker and Roth[4] have determined the heat of combustion of the dihydrate of oxalic acid and have found $-\Delta H_R = 52.23$ Kcal/mol. They have also measured the heats of solution of both the anhydrous and the dihydrate of oxalic acid. From these data $-\Delta H_R$ of anhydrous oxalic acid can be calculated. This calculation gives $-\Delta H_R = 58.8$ Kcal/mol. We found from our combustion data the value 58.6 Kcal/mol. The comparison is very favorable. Verkade found for anhydrous oxalic acid $-\Delta H_R = 59.7$ Kcal/mol. Why his value differs so largely can not be stated with certainty. Paessler[10] has also determined the heat of combustion of anhydrous oxalic acid and found $-\Delta H_R = 58.4$ Kcal/mol.

Table 9

Comparisons of Verkade's and Our Data at 25.0° and for Standard Conditions

Values of $-\Delta H_R$ at 25°C.

Substance	Verkade	This research	%	Deviation, Cal.
Oxalic acid	59,675 cal.	58,620 cal.	+ 1.8	+ 1,055
Malonic acid	205,935	205,720	+ .10	+ 215
Glutaric acid	514,072	513,730	+ .067	+ 342
Adipic acid	668,000	668,411	- .062	- 411
Azelaic acid	1,140,930	1,137,781	+ .28	+ 3,149
Sebacic acid	1,296,242	1,293,382	+ .22	+ 2,860

No details concerning the bomb conditions are given which makes a comparison impossible.

We have not been able to find a value for the heat of combustion of dl-malic acid in the literature. In Landolt-Boernstein Tabellen[11] a value for l-malic acid is given.

It is interesting to note that the higher homologues in the dicarboxylic acid series contain a small percentage of water which is rather difficult to remove. Both adipic and sebacic acid lose the last trace of water only when dried at 105°, as indicated by the higher heat of combustion of samples dried at the elevated temperature. Azelaic acid due to its lower melting point (105°) was dried at 96°. However fused samples gave a higher heat of combustion. Since only two combustions with fused samples were carried out, the heat of combustion of the samples dried below the melting point were used in the calculation of the precision error.

When azelaic acid, however, is fused over a long period of time, the heat of combustion decreases. It is seen from the experimental data in table 6 that the longer the time of fusion, the greater is the decrease in the heat of combustion. It is assumed that this drop in the heat of combustion is due to the formation of an unsaturated substance.

With glutaric acid a similar effect is observed. Since glutaric acid is known to occur in two crystal structures it might be possible that the lowering of the heat of combustion is due to isomorphism.

In Table 10 the free energies of formation of the seven organic acids are compiled. Oxalic and succinic acid are the only members of the oxalic acid series with known entropies. The entropies of the other compounds have been estimated by the method described by Parks and Huffman[12]. The uncertainty is probably as high as three entropy units. The values of the free energies are probably uncertain to at least ± 1,000 calories.

Table 10

Thermal Data at 298.1° K.

Substance	$S_{298.1}$ E.U.	$\Delta H_{f298.1}$	$T\Delta S$	$\Delta F_{298.1}$
Oxalic acid	28.7	-197,757	-30,725	-165,925
Malonic acid	35.4	-213,004	-38,582	-174,422
Succinic acid[1f]	42.0	-224,829	-46,269	-178,560
Glutaric acid	49.0	-229,668	-53,950	-175,718
Adipic acid	57	-237,534	-61,283	-176,251
Azelaic acid	79	-255,019	-83,878	-171,141
Sebacic acid	86	-261,771	-91,508	-170,213
dl-Malic acid	40.5	-264,998	-54,088	-210,910

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Propositions Submitted by Werner Baumgarten.

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Committee: Lucas (Chairman), Buchman, Dickinson, Huffman, Koepfli,
Niemann, Pauling, Zechmeister.

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1. An explanation for the optical stability of some biphenyls with only two ortho substituents has been given by Calvin. We may expect however that similar optically active biphenyls exist where resonance of the type postulated by Calvin is not possible.

   Calvin, J. Org. Chem. 4, 256 (1939).

2. The unreactivity of certain p-toluenesulfonic esters can be attributed to steric hindrance.

   Levene and Tipson, J. Biol. Chem. 120, 607 (1937)

   Mueller and Reichstein, Hel. chim Acta. 20, 1529 (1937).

3. Contrary to the statement of Raymond, Bergmann's glucal-hydrobromide-diacetate is likely to be 1-bromo-2-desoxy-diacetylglucose.

   Raymond, Organic Chemistry, John Wiley and Sons; pg. 1500.

   Fischer, Bergmann and Schotte, Ber. 53, 518 (1920).

4. The results of the ozonization experiments of Shriner and Moffet as well as of the nitration of flavylium salts can be explained by assuming a resonating structure for these salts.

   Shriner and Moffet, J. Am. Chem. Soc. 62, 2711 (1940).

   LeFevre and LeFevre, J. Chem. Soc. 1988 (1932).

5. Freudenberg and Brauns state: "Der Vorschlag die linksdrehende Glycerinsäure und Milchsäure der d-Reihe zuzurechnen ist umso berechtigter als die Salze, Äther and Ester dieser beiden Säuren nach rechts drehen." They propose two independent

stereochemical families for the hydroxy acids and the sugars themselves. This inconsistency should be eliminated.

Freudenberg and Brauns, Ber. 55, 1339 (1922)

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Müller and Reichstein, Hel. chim. Acta 21, 251 (1938).

6. A course showing the historical development of chemical concepts would be especially beneficial if given to graduate students.

7. Only 2- and ω -desoxysugars are easily synthesized. A method is proposed by which other desoxysugars can be obtained.

8. The phenomena of alternation in homologous series may be more adequately expressed by a comparison of the ΔF than of the ΔH for the alternating increments per CH_2 group. To show that the alternation is a property of the crystal lattice it is proposed to compare the free energies of formation in a dilute aqueous solution.

9. The formation of γ -bromoacetoacetyl bromide by the action of bromine on diketene is best explained by assuming vinylaceto-β-lactone as the structure of diketene.

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10. The reaction between an optically active acid chloride and diazomethane can be directed to yield a homologous acid which is still optically active. This may be compared with the Hofmann or Curtius degradation clarifying if retention or inversion occurs during the degradation.

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11\. Clarke and Stegeman determined the molal heat of combustion of α-lactose monohydrate to be larger by 9 Kcal. than that of β-lactose. Their results are contrary to the known stability relationships.

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