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# ON THE BEHAVIOR OF ALLYLMALONIC, ALLYLACETIC, AND ETHYLIDENEPROPIONIC ACIDS WHEN BOILED WITH CAUSTIC SODA SOLUTIONS.

## CONTRIBUTIONS TO THE KNOWLEDGE OF PROPYLIDENEACETIC ACID.[1]

BY JOHN G. SPENZER.

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DURING the preparation of hydropiperic acid, Fittig and Buri,[2] in 1883, discovered that in the reduction of piperic acid by means of sodium amalgam, two very different isomeric hydropiperic acids were formed, according as the reducing fluid was kept almost neutral, or allowed to become strongly alkaline by not adding acid. In the first procedure they obtained the already known and now designated $\alpha$ hydropiperic acid, while in the second process together with the $\alpha$ acid, larger or smaller quantities of the new isomeric $\beta$ hydropiperic acid appeared, which seemed to have been produced from the $\alpha$ acid through the agency of the caustic soda formed in the reducing fluid.

In fact it was proven experimentally, by heating the $\alpha$ hydropiperic acid, with caustic soda on the water-bath, that $\beta$ hydropiperic acid could be obtained.

Weinstein[3] and Regel[4] were induced by Fittig to examine the two isomeric acids further, and because of its behavior on substituting bromine and hydrobromic acid as also in the oxidation with potassium permanganate they came to the interesting con-

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[1] Read before Section C., American Association for Advancement of Science, Brooklyn, N. Y., August 20, 1894.

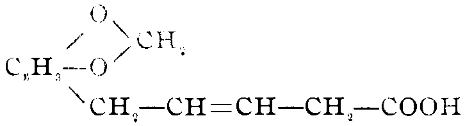
[2] *Ann. Chem.*, 216, 171.

[3] Ibid. 227, 31.

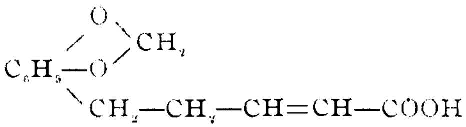
[4] *Ber. d. Chem. Ges.*, 20, 414.

clusion that the α hydropiperic acid was a β γ unsaturated acid, and that the β hydropiperic acid must be an α β unsaturated acid.

Therefore, by the conversion of the α hydropiperic acid into the β hydropiperic acid, under the influence of hot caustic soda, a moving of the double bond of union towards the carboxyl group takes place as follows:

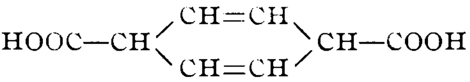


α hydropiperic acid (β γ)

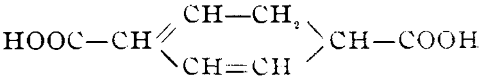


β hydropiperic acid (α β)

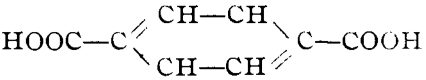
Other such displacements of the double bonds of union through the agency of alkalies and even by boiling water were soon found. Baeyer[1] observed, that the $\delta^{2.5}$ dihydroterephthalic acid, became the $\delta^{1.5}$ dihydroterephthalic acid, when boiled with water, and the latter, in turn, when boiled with caustic soda, produced the $\delta^{1.4}$ dihydroterephthalic acid, according to the following scheme:



$\delta^{2.5}$ dihydroterephthalic acid.



$\delta^{1.5}$ dihydroterephthalic acid.



$\delta^{1.4}$ dihydroterephthalic acid.

Further $\delta^{2}$ tetrahydroterephthalic acid when treated with hot caustic soda produces $\delta^{1}$ tetrahydroterephthalic acid as follows:

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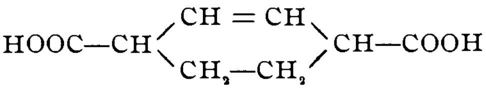
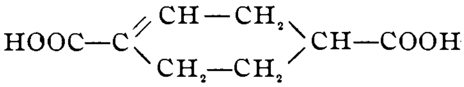
[1] *Ann. Chem.*, 251, 257.



δ²



δ¹

Finally hydromuconic acid according to Baeyer and Rupe[1] by the same treatment is changed into an isomeric α β acid, as:

$HOOC—CH_2—CH{=}CH—CH_2—COOH$

β γ hydromuconic acid.

$HOOC—CH_2—CH_2—CH{=}CH—COOH$

α β hydromuconic acid.

Even previous to this Fittig[2] had been led to the conclusion, that in the potassa-fusion of hydrosorbic acid a moving of the double union from the β γ to the α β position must also take place, since the splitting, thereby occasioned, occurs at the α β position with the production of butyric and acetic acids, still the hydrosorbic acid is unquestionably a β γ unsaturated acid, which, therefore, must split into two molecules of propionic acid.

All these observations but favored the belief, that the shoving of the double union in the unsaturated acids towards the carboxyl group when boiled with caustic soda was a general one.

To prove the correctness of this point, Fittig began with his pupils, on a series of β γ unsaturated acids, and in all the researches as yet made, no exception has been found. Of the aromatic acids, aside from hydropiperic acid the following have been examined:

Phenyl β γ pentinic acid, which gives, according to T. Hoffmann, with boiling caustic soda, the isomeric phenyl α β pentinic acid.

$C_6H_5—CH_2—CH{=}CH—CH_2—COOH$

β γ

$C_6H_5—CH_2—CH_2—CH{=}CH—COOH$

α β

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[1] Ibid, 256, 1.

[2] Ibid, 255, 13.

Phenylisocrotonic acid is changed, after Luib, by a like treatment into benzylacrylic acid.

$$C_6H_5-CH\underset{\beta\ \gamma}{=}CH-CH_2-COOH$$

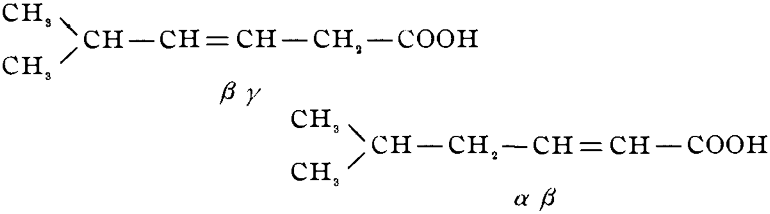
$$C_6H_5-CH_2-CH\underset{\alpha\ \beta}{=}CH-COOH$$

In the "fatty series" this change takes place regularly. Baker obtained from hydrosorbic acid by boiling with caustic soda $\beta$ propylacrylic acid.

$$CH_3-CH_2-CH\underset{\beta\ \gamma}{=}CH-CH_2-COOH$$

$$CH_3-CH_2-CH_2\underset{\alpha\ \beta}{=}CH-COOH$$

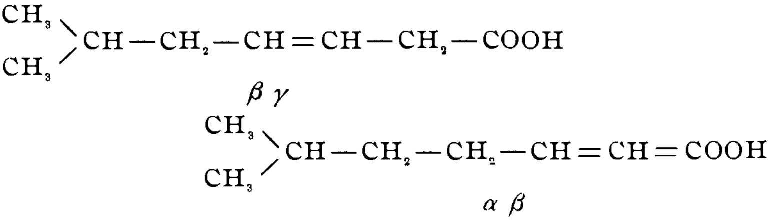
Feurer, from isoheptylic obtained isobutylacrylic acid.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH\underset{\beta\ \gamma}{=}CH-CH_2-COOH$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH_2-CH\underset{\alpha\ \beta}{=}CH-COOH$$

Weill, from $\beta$ $\gamma$ isoctylic the $\alpha$ $\beta$ isoamylacrylic acid.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH_2-CH\underset{\beta\ \gamma}{=}CH-CH_2-COOH$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH_2-CH_2-CH\underset{\alpha\ \beta}{=}CH=COOH$$

The present work was taken up with a view of extending these researches by including acids of the "$\gamma$ $\delta$ series."

The supposition of Zincke and Kuester[1] that the $\gamma$ $\delta$ unsaturated acids would, when boiled with caustic soda, also allow of a displacement of their double bonds, can be given as one of the principal reasons for beginning the investigations.

If the supposition of Zincke and Kuester is correct, then the following, which they looked upon as very probable, would

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[1] *Ber. d. chem. Ges.*, 24, 909.

have been most interesting: that is, if the γ δ acids should suffer their double bond to be moved, then it would be an easy matter to produce a β γ and in turn an α β acid, for example, from allylacetic acid, ethylidenepropionic acid, and finally propylideneacetic acid should be obtained by boiling with caustic soda, according to the following:

$$CH_2=CH-CH_2-CH_2-COOH$$
$$\beta\ \delta$$
$$CH_3-CH=CH-CH_2-COOH \rightarrow$$
$$\beta\ \gamma$$
$$CH_3-CH_2-CH=CH-COOH$$
$$\alpha\ \beta$$

The first part of this paper is taken up in the description of the results of the experiments, on two γ δ acids, allylmalonic and allylacetic acids.

In the case of both of these acids, the following surprising results were obtained. On boiling with caustic soda no conversion into the corresponding β γ and α β unsaturated acids could be detected. This passive behavior, of both of these representatives of the "γ δ series," is, therefore, the more remarkable, since from analogy, taken from the already observed inclination of terminal methylene radicals, to form methyl groups, as for instance, Faworsky[1] found in the unsaturated hydrocarbons, a complete change might be expected here. On the other hand Baeyer[2] has verified these exceptions to Faworsky's rule in the case of the hydrated phthalic acids.

Finally, if this difference to boiling caustic soda should be asserted in other γ δ acids and become a general characteristic of this series, then through this means a sharp and decided distinguishing property has been discovered between the γ δ and the β γ unsaturated acids, which, moreover, behave alike in the substitution of hydrobromic acid and the decomposition of the product, by means of water and alkalies (Messerschmidt[3]); as also in the substitution of bromine (Urban[4]); and in the treatment with potassium permanganate (Urban[5]).

The second part of this research is given to a description of the

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[1] J. *prakt. Chem.*, 44, 212.

[2] *Ann. Chem.*, 269, 150.

[3] Ibid, 208, 93.

[4] Ibid, 268, 60.

[5] Ibid, 268, 32.

results obtained in the treating with caustic soda the $\beta\ \gamma$ acid corresponding to allylacetic acid, that is, ethylidenepropionic acid.

As a result it was found that this $\beta\ \gamma$ unsaturated acid, like all the others, which have as yet been investigated, on boiling with caustic soda, allowed the double union to be shoved to the $\alpha\ \beta$ position, with the formation of propylideneacetic acid, formerly known, but until now only in the impure state.

Even from the first, investigators on the moving of the double bond of union, through the influence of boiling caustic soda, busied themselves with efforts to explain the mechanism of the reaction.

Based on analogous reactions Weinstein[1] suggested that by warming the $\beta\ \gamma$ unsaturated acids with caustic soda the elements of water are taken up and an oxy acid formed, and this in turn, giving it up again, an $\alpha\ \beta$ unsaturated acid results, as follows:

1. $R{-}CH{=}CH{-}CH_2{-}COOH \quad + H_2O =$

$\beta\ \gamma$ unsaturated.

$$R{-}CH_2{-}CH(OH){-}CH_2{-}COOH$$

$\beta$ oxy acid.

2. $R{-}CH{-}CH(OH){-}CH{-}COOH \quad - H_2O =$

$$R{-}CH_2{-}CH{=}CH{-}COOH$$

$\alpha\ \beta$ unsaturated.

This meanwhile purely hypothetical $\beta$ oxy acid, forms, therefore, the intermediate step between the two isomeric unsaturated acids.

Although Weinstein himself could not isolate this oxy acid still it has been formed repeatedly since then, thus:

Luib obtained from phenylisocrotonic acid phenyl $\beta$ oxybutyric acid $C_6H_5{-}CH_2{-}CH(OH){-}CH_2{-}COOH$.

Hoffmann from phenyl $\beta\ \gamma$ pentinic acid produced phenyl $\beta$ oxyvalerianic acid.

$$C_6H_5{-}CH_2{-}CH_2{-}CH(OH){-}CH_2{-}COOH.$$

However, just through Hoffmann's careful investigations, the idea that the $\beta$ oxy acid was the middle link, in the change

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[1] *Ann. Chem.*, **227**, 31.

from the $\beta$ $\gamma$ unsaturated, to the $\alpha$ $\beta$ acids was made somewhat doubtful.

He found for example that the $\beta$ $\gamma$ acid after six hours boiling with caustic soda gave fifty per cent. of $\alpha$ $\beta$ acid without any trace of $\beta$ oxy acid, and that further, the formation of the oxy acid required a very long and protracted treatment with the alkali, and that finally, the $\beta$ oxy acid can be most easily produced, by boiling the $\alpha$ $\beta$ acid with caustic soda. Briefly, his observations leave the impression as if the $\beta$ oxy acid is not the intervening middle link between $\beta$ $\gamma$ and $\alpha$ $\beta$ acids, but is a secondary one to, and resulting from the $\alpha$ $\beta$ acid.

In the "fatty series," on the contrary, the reaction seems to follow the course of the above scheme of Weinstein even if it has certain restrictions.

Baker's work pointed to, and Feurer's observations made it certain, that the three acids which he examined $\beta$ $\gamma$ isoheptylic, $\beta$ oxydimethylvalerianic, and $\beta$ isobutylacrylic acids, when boiled with caustic soda, gave certain quantities of both of the others; the reaction does not, however, proceed smoothly in every sense of the term, but only to a certain limit, the $\beta$ oxy acid always forming the intermediate product of the two unsaturated isomers.

These observations also cover the results described in the second part of this paper, they having been also noticed in the examination of the $\beta$ oxy valerianic acid obtained from ethylidenepropionic acid.

PART I.

*On the behavior of allylmalonic and allylacetic acids when boiled with caustic soda solutions.*

PART II.

*On the behavior of ethylidenepropionic acid when boiled with caustic soda.*

*Contributions to the knowledge of propylideneacetic acid.*

## PART I.

*Preparation of Allylmalonic Acid.*—The allylmalonic acid was produced according to Conrad and Bischoff,[1] from malonic acid, ethyl ester, and allyl iodide.

[1] *Ann. Chem.*, **204**, 168.

The malonic acid ethyl ester was obtained from Claisen and Crismer's[1] modification of Conrad's[2] method; the allyl iodide in turn was prepared after Kannonikoff and Saytzew[3] and Wagner's[4] improved suggestions of Berthelot and Luca.[5]

Since the purity of the allylmalonic acid depends principally on the absolute purity of the allyl iodide, a few precautionary hints, which have recommended themselves during the course of preparation, may not be amiss here.

1. Some ignited sand was put into the retort, thereby overcoming, on the one hand, the danger of breaking the latter through the phosphorus or iodine becoming attached to the bottom of the retort, and on the other, the action of the phosphorus is rendered more uniform and regular.

2. The retort was filled to one-half or at least one-third of its capacity.

3. It is particularly desirable that the phosphorus react directly as it is brought into the retort and that the allyl iodide distill over at once; this is facilitated by covering the upper part of the bowl and beak of the retort with a cloth to guard against cooling.

If the allyl iodide is not carried over as soon as formed, then much isopropyl iodide is produced, which is only with the greatest difficulty separated from the allyl iodide. Through repeated careful fractional distillations a preparation boiling between 99° and 102° C. and possessed of only a light-red color, was obtained.

To prepare the allylmalonic acid ester, the allyl iodide was run as rapidly as possible into the well-cooled sodium malonic acid ester and the product obtained after two hours boiling, separated by shaking with ice-water, and fractioning without further drying. The fractions were collected at every 5° from 150° to 200°, and at every 2° from 200° to 235° C.

After repeated and successive fractioning the four portions from 218° to 226° were taken to be pure and so used.

The saponification of the ester, which Conrad and Bischoff[6] performed with potassium hydroxide was in this case accomplished with barium hydroxide, in which the four fractions from

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[1] Ibid., 218, 131.

[2] Ibid., 204, 131.

[3] *Ann. Chem.*, 185, 191.

[4] *Ber. d. chem. Ges.*, 9, 1810.

[5] *Ann. Chem.*, 204, 168.

[6] *Ann. Chem.*, 204, 168.

218° to 226° were separately treated. After the saponification was complete, the contents of the flask were diluted with hot water and the excess of barium hydroxide removed by means of carbonic acid gas; it was now filtered, and the filtrate evaporated to obtain the crystalline barium allylmalonate in fractions, the several crystallizations of the original fractions being held separate, until the subsequent decomposition by means of hydrochloric acid proved them to be pure.

Thanks, to this careful and protracted process of fractioning, a white, almost perfectly pure acid was obtained, from which through the aid of the acid barium salt, an absolutely pure acid melting at 105° C. was prepared. The production of pure acid amounted to thirty-three per cent. of the theory.

*Boiling Allylmalonic Acid with Caustic Soda Solution.*—Two experiments were performed.

In the first one, ten grams of pure allylmalonic acid were boiled for twenty hours (in a copper flask connected with a return condenser) with ten times the amount of caustic soda necessary for neutralization in a ten per cent. aqueous solution. Allowed to cool, the alkaline liquid was strongly acidified with sulphuric acid and shaken out with ether; after distilling off the ether a faintly yellow-colored oil remained behind, hardening to a white crystalline mass in a vacuum over sulphuric acid, and melting at 103° C. when crystallized out of benzene; after being purified by means of the acid barium salt the melting-point was raised to 105° C.; the substance was, therefore, pure and unaltered allylmalonic acid; it represented 9.591 grams or 95.9 per cent. of the acid originally used.

In the second test 7.3305 grams of allylmalonic acid were boiled in the same manner for twenty hours with a twenty per cent. solution of caustic soda representing ten times the necessary amount of alkali for neutralization; allowing to cool, acidifying, shaking out with ether, recrystallizing out of benzene, and purifying by means of the acid barium salt, 7.1345 grams of pure allylmalonic acid melting at 105° C. was recovered, corresponding to 97.3 per cent. of the amount used.

The loss of four and one-tenth per cent. in the first and two and seven-tenths per cent. in the second is explained by the fact that it is impossible to recover the last portions of the acid from its solutions by means of ether.

The identity of the acid obtained, with allylmalonic acid, was not only proven by the melting-point, but also by other physical properties, as also by its deportment on distillation.

*Preparation of Allylacetic Acid.*—Zeidler[1] first obtained allylacetic acid from allylacetic acid ester and dry sodium ethylate, and stated its boiling-point to be 182° C. Conrad,[2] who got it by distilling allylmalonic acid, found the boiling-point to be 184° C.

According to Messerschmidt,[3] who used a modification of Zeidler's method, it boiled at 187° to 189° C.

Finally Marburg[4] studied the acid obtained by means of the Conrad as well as the Zeidler-Messerschmidt methods in both their physical and chemical properties and definitely settled the boiling-point at 186° to 187° C.

The allylacetic acid used in these researches was made after Conrad's process; it boiled constantly at 186° to 187° C. The production was about sixty-two per cent. of the theory.

*Boiling of Allylacetic Acid with Caustic Soda Solution.*—Ten grams of pure allylacetic acid boiling at 186° to 187° C. was boiled (in a copper flask connected with a return condenser) with ten times the amount of caustic soda necessary to neutralize it, in ten per cent. solution for twenty hours.

The cold contents of the flask were then strongly acidified with sulphuric acid and shaken out with ether, after distilling off the latter the residual acid was distilled with steam.

According to the statement given in the beginning of this paper one must consider the presence of $\beta\ \gamma$, and $\alpha\ \beta$, as well as of an oxy acid, and the use of steam was considered the better means of effecting their separation.

The distillation was continued until the distillate reacted neutral, the residual liquid in the distillation flask being then shaken out with ether; by this latter process nothing could be extracted; no oxy acid had, therefore, been formed.

The aqueous distillate was neutralized with barium carbonate

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[1] *Ann. Chem.*, 187, 4.

[2] Ibid. 204, 170.

[3] Ibid. 208, 93.

[4] Dissertation, Strassburg, *1887*.

in the cold, boiled, filtered, and evaporated to dryness; in this manner 15.85 grams of barium salt dried at 100° was obtained. The finely powdered salt was repeatedly extracted with hot absolute alcohol, thereby one and a half grams dissolved, remaining as an amorphous yellow-colored transparent mass, upon distilling off the alcohol. Redissolved in alcohol and allowed to evaporate in a desiccator it was again deposited amorphous. This experiment gave, therefore, 90.5 per cent. of barium salt insoluble in alcohol.

In order to obtain a larger amount of the soluble salt a second trial was begun under the same conditions as the first with ten grams of allylacetic acid; it gave 16.52 grams of dry barium salt of which one gram was soluble in hot alcohol leaving ninety-four per cent. undissolved. The two portions of insoluble barium salt were mixed, and a careful fractional crystallization begun. This process allowed of the eventual separation of the $\beta$ $\gamma$ and $\alpha$ $\beta$ acids from the barium allylacetate. To this end the salt was dissolved in the least possible amount of hot water, filtered, evaporated to a pellicle, and allowed to crystallize.

The first crystals obtained were flat and lanceolate prisms, later flat curved needles and leaves were shot out; an easily soluble salt could, however, not be detected.

The difference in appearance of the crystals would not necessarily point to the presence of different salts, since, on the one hand, pure barium allylacetate separates out in entirely different forms according as it crystallizes out more rapidly or slowly, and on the other hand, the last fractions could, when dissolved in water, adding alcohol until precipitation began, warming and then allowing to cool slowly, be obtained in small needle-shaped crystals of exactly the same appearance.

To examine the acid the several crystallizations together with their mother-liquors were mixed, the alcohol distilled off, and the organic acid set free and removed by successive treatments with hydrochloric acid and ether, the ethereal solution shaken with calcium chloride, filtered, and distilled from a small flask, the principal portion passed over from 186° to 187° C., a higher boiling fraction not occurring.

Because the barium salt had lost considerable in weight in the successive evaporations (due to a slight decomposition) a third trial of boiling the allylacetic acid with caustic soda was made, in order to exclude any doubt of its conversion into $\beta\ \gamma$ or $\alpha\ \beta$ acid.

13.65 grams of allylacetic acid boiling at 186° to 187° C. and which had been recovered from former trials, were boiled with twenty per cent. sodium hydroxide for twenty-two hours, in the same manner as the others had been; also here the ether extract was entirely volatile, leaving no trace of an oxy acid.

The aqueous acid distillate was made slightly alkaline with sodium carbonate, evaporated to dryness, the sodium salt so obtained decomposed with sulphuric acid and extracted with ether. The ètheral extract was dried and gave 11.96 grams of an acid boiling at 186° to 187° C.; portions of a higher boiling-point were not present.

To more closely characterize the distillate 2.96 grams of the fraction boiling at 186° to 187° C., were subjected to the well-known "Lactone Reaction." For this purpose the acid was mixed with five times its weight of dilute sulphuric acid (one volume concentrated sulphuric acid and one volume water) in a small flask and heated just to boiling for fifteen minutes with constant agitation. The organic acid, which at first swam on the surface of the mixture, soon dissolved with a yellow coloration of the liquid; the contents of the flask was diluted with an equal volume of water and boiled for fifteen minutes, then cooled and extracted with ether.

The ethereal extract was dissolved in a little water, made slightly alkaline with sodium carbonate and at once shaken out with ether, a yellow-colored neutral liquid resulting, which, after drying, boiled constantly at 206° C., proving it to be pure valerolactone produced from the unaltered allylacetic acid.

The alkaline solution freed from lactone was, after removing the ether, acidified with sulphuric acid and distilled with steam; the distillate after neutralizing with calcium carbonate, filtering, and evaporating to dryness gave 0.1352 gram of a gray residue equivalent to 4.57 per cent. of the acid used.

From these three trials one can certainly conclude that by boiling allylacetic acid with caustic soda, neither propylideneacetic acid, nor ethylidenepropionic acid, nor an oxy acid is formed in any quantity, which can be detected.

If a change does at all occur it is almost imperceptible. The small quantities of a barium salt soluble in alcohol were not sufficient to settle the question, whether it was the salt of the $\alpha$ $\beta$ acid.

## PART II.

The ethylidenepropionic acid, $CH_3—CH{=}CH—CH_2—COOH$ was prepared according to Fraenkel[1] by the distillation of methylparaconic acid.

*Preparation of Methylparaconic Acid.*—Methylparaconic acid was first made by Gantter[2] from acetosuccinic acid ester, by reducing with sodium amalgam and described under the name of ethylidene hydroxysuccinic acid. Fraenkel,[3] however, was the first one who obtained it pure; he prepared it by the condensation of acetaldehyde with sodium succinate; he also described it more closely.

The acid used in the present research was prepared according to Gantter's method, and since the preparation is somewhat difficult it may not be amiss to give it more than a casual description here.

1. Monochloracetic acid ester, was obtained after the Conrad[4] process; it gave a yield of eighty-five per cent. of the theoretical amount.

2. The acetosuccinic acid ester, was prepared according to Conrad's[5] process, which by fractioning under reduced pressure gave upwards of sixty per cent. of the theory.

In the acetosuccinic acid ester synthesis, it is of advantage to add the acetic acid ester, as well as the monochloracetic acid ester as rapidly as possible through a stoppered funnel into a flask containing the sodium ethylate and connected with a return condenser; by so doing the violent bumping of the contents of the flask is prevented; this can only otherwise be accomplished by filtering off the sodium chloride, which separates out in the reaction.

After the two esters have been brought together, the contents

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[1] *Ann. Chem.*, 255, 24.

[2] Dissertation, Wuerzburg, *1878*.

[3] Ibid, 255, 18.

[4] Ibid, 188, 218.

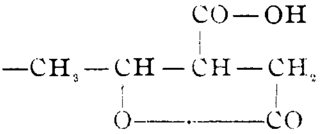
[5] *Ann. Chem.*, 188, 218.

of the flask are kept boiling on the water-bath for two hours, allowed to cool, mixed with ice-water, and extracted with ether; a reddish-brown crude ester is obtained, which, after being shaken with small portions of water, is subjected to fractional distillation. Drying by the use of calcium chloride is not to be recommended, since the salt dissolves, and when distilled, causes a decomposition of the ester, as Gottstein[1] and Young[2] have also observed in similar esters.

To free the crude ester of ether, alcohol, water, unaltered acetic acid ester, and monochloracetic acid ester, it was heated to 200° C. That portion, which did not distil off at this temperature, was then fractioned in a rarefied atmosphere under fifty mm. pressure and this repeated three times, gave an ester boiling at 180° to 183° C.

This was accepted as pure acetosuccinic acid ester; it presented a colorless pleasant smelling liquid almost as thick as glycerol. By fractioning under the ordinary pressure it was never found possible to obtain an ester as colorless, nor boiling as constantly, and notwithstanding the statements of Conrad[3] it is the author's opinion that it can not be distilled under ordinary pressure even when perfectly pure, without a decomposition more or less slight, taking place.

*Methylparaconic Acid.*—



$$\begin{array}{ccccccc} & & & & CO-OH & & \\ & & & & | & & \\ CH_3 & - & CH & - & CH & - & CH_2 \\ & & | & & & & | \\ & & O & - & - & - & CO \end{array}$$

Pure acetosuccinic acid ester, in portions of twenty-five grams each, was mixed with a like quantity of absolute alcohol, and water added to a turbidity, then four per cent. sodium amalgam was added, the vessel being frequently agitated. At the beginning the sodium amalgam melted in a short time without any perceptible evolution of gas; when the reaction diminished in consequence of the concentration of the liquid more water was added until turbidity again appeared and the reaction renewed.

The mercury resulting from the decomposition of the amalgam was taken out from time to time with a pipette, washed with water, and the wash-water added to the original reducing fluid.

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[1] Ibid, 216, 31-36.
[2] Ibid, 216, 43.
[3] *Ann. Chem.*, 188, 218.

The latter was, during the process of reduction, neutralized with dilute sulphuric acid to prevent the accumulation of a large excess of alkali. The entire process was continued until three times the theoretical amount of sodium amalgam had been added.

It is necessary in the reduction to observe that the solution does not become too warm (for this reason it may be well to set the vessel containing it, into ice-water at the beginning), also that it does not become too alkaline, otherwise a splitting of the acetosuccinic acid ester can easily occur, which, according to Wislicenus,[1] can follow in two directions.

When the sodium amalgam had ceased to act the liquid was, after removing and washing the mercury, exactly neutralized with dilute sulphuric acid, filtered, evaporated to a small volume, and allowed to crystallize, the mother-liquor drained off from the crystals of sodium sulphate, acidulated with sulphuric acid, and extracted with ether ; the ethereal residue at first a yellow oil, soon becomes a solid mass when placed in a vacuum over sulphuric acid. This solid mass relieved of the oily matters by suction with a filter pump and pressure between bibulous paper gave, when broken into small pieces and kept over sulphuric acid in a vacuum, a perfectly dry white powder ; this was the desired methylparaconic acid.

It was crystallized out of benzene in the following manner : A flask containing the powdered acid and some benzene, and fitted with a perforated cork, through which passed a long glass tube, was heated by plunging it into boiling water, it being constantly agitated, so as to bring the now melted underlying acid into intimate contact with the supernatant solvent ; allowed to settle, and the clear solution decanted (from the liquid and still undissolved acid) into flasks, which were at once stoppered and set aside to crystallize. To the still undissolved acid in the first flask more benzene was added and the same process continued until no more was dissolved.

If before being dissolved in the benzene the acid was perfectly dry and therefore free from all oily matters then it dissolves completely and crystallizes out in hard dry crystals ; if, however,

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[1] Ibid, 190, 275.

the oil has not been entirely removed, then the acid separates out as a sticky mass; should this be the case then it must be freed from the solvent, the oil thoroughly removed by pressing between bibulous paper, drying, and again crystallizing out of benzene.

The production of pure acid was twenty per cent. of the theoretical.

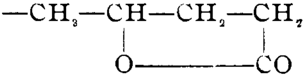
*Preparation of Ethylidenepropionic Acid.*—The ethylidenepropionic acid was made according to Fraenkel.[1] Pure methylparaconic acid, in portions of fifteen grams each, was carefully heated in a small distillation flask; at first the acid melted to a colorless fluid, but took on a yellowish-red coloration as the operation advanced. When the temperature of the molten acid had reached 200° C. a slight evolution of carbon dioxide had begun and as the immersed thermometer indicated 240° to 260° C. the evolution of gas was a very regular one.

The thermometer bulb was now drawn up to the opening of the exit tube and the distillation continued to the end, the vapors passing over at 210° to 220° C. A slight carbonaceous residue representing nine-tenths per cent. of the acid used, alone remained behind.

The distillate, a yellowish oil of a strong empyreumatic odor contains:

1. Valerolactone.
2. Ethylidenepropionic acid.
3. Methylcitraconic acid.
4. Methylitaconic acid, and
5. Unaltered Methylparaconic acid.

1. *Valerolactone.*—



$$\begin{array}{ccccccc} CH_3 & — & CH & — & CH_2 & — & CH_2 \\ & & | & & & & | \\ & & O & — & — & — & CO \end{array}$$

The empyreumatic distillate, mixed with five times its volume of water, was made slightly alkaline with sodium carbonate in the cold, and rapidly extracted with ether; a reddish-yellow oil resulted, which, after removing the ether and water, could be easily characterized as valerolactone.

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[1] *Ann. Chem.*, 255, 24.

2. *The Acids.*—The alkaline solution, from which the lactone had been extracted, was acidulated with sulphuric acid and completely extracted with ether; the acid mixture so obtained was distilled with steam until the distillate ceased to be acid. The slightly turbid distillate was made faintly alkaline with barium hydroxide, treated with carbonic acid gas, boiled, and filtered; in this manner a solution of barium ethylidenepropionate and methylcitraconate was obtained, which can be separated by fractional crystallization.

The acid residue left in the distillation flask after distilling with steam, was evaporated to a small bulk, when it solidified to a yellow crystalline mass on being placed over sulphuric acid in a vacuum.

By treating this mass with cold chloroform the unaltered methylparaconic acid was easily extracted, while the methylitaconic acid, which was present only in small quantities, remained undissolved as a powder; the latter, like the methylcitraconic acid, was not used further.

To separate the barium methylcitraconate from the barium ethylidenepropionate, the solution containing both was simply evaporated when the barium methylcitraconate difficultly soluble in the heat separated out; it was then filtered again, evaporated, and so continued until no more salt difficultly soluble in the heat, separated out. The mother-liquors deposited upon further evaporation, when cold, the barium ethylidenepropionate in the form of flat lanceolate prisms grouped together into stars. To remove every trace of barium methylcitraconate, the barium ethylidenepropionate was recrystallized three times. It was then exactly decomposed with a weak solution of sodium sulphate, and thereby, after filtering and evaporating, sodium ethylidenepropionate obtained, in which form it was later mostly used.

200 grams of methylparaconic acid gave about forty-five grams, or twenty-two and one-half per cent. of ethylidenepropionic acid.

*Preparation of Propylideneacetic Acid.*—By the action of propionaldehyde on malonic acid Komnenos[1] obtained a monobasic unsaturated acid with five atoms of carbon, which he called pro-

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[1] *Ann. Chem.*, 218, 166.

pylideneacetic acid. In the same manner Zincke and Kuester,[1] as well as Ott[2] and Viefhaus,[3] prepared their propylideneacetic acid.

Zincke and Kuester[4] also obtained, in an entirely different manner, an acid which they recognized to be identical with Komnenos's propylideneacetic acid.

Starting with hexachlordiketo R hexane obtained from catechol, orthoamidophenol and chlorine they prepared successively tetrachlorcatechol or tetrachloramidophenol, and then pentachlorbutane carbon dioxide, and by treating the latter with sodium amalgam, procured their acid.

Fittig and Fraenkel,[5] however, suspected that the above acid of Zincke and Kuester was identical with ethylidenepropionic acid, obtained from methylparaconic acid; this supposition was, through the later researches of Zincke and Kuester,[6] made very probable, inasmuch as these investigators obtained small quantities of lactone by treating the bromhydric acid addition product of their acid with water, from which it would appear that the acid must be ethylidenepropionic acid or at least contain it as an impurity, since pure propylideneacetic acid can produce no lactone.

Such acids as have been prepared and described under the name of propylideneacetic acid are no homogeneous bodies. It was not until the writer, in July, 1892, procured the acid in its crystalline form by boiling ethylidenepropionic acid with caustic soda; and Mackenzie,[7] in February, 1893, secured it after the method of Komnenos that pure propylideneacetic acid had been made and characterized.

*Boiling of Ethylidenepropionic Acid with Sodium Hydroxide.*—Sodium ethylidenepropionate, in portions of ten grams each, was boiled with thirty-three grams of sodium hydroxide dissolved in 295 grams of water for fifteen hours in a copper flask connected with a return condenser. The cold alkaline solution was now acidulated with ether, the ethereal extract distilled with steam until the distillate came over perfectly neutral; the milky acid

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[1] *Ber. d. chem. Ges.*, **22**, 494. Ibid, **23**, 818. Ibid, **24**, 909.

[2] Ibid, **24**, 2,600.

[3] Ibid, **26**, 915.

[4] Ibid, **21**, 2,719.

[5] Ibid, **255**, 33.

[6] *Ber. d. chem. Ges.*, **24**, 909.

[7] Dissertation, Strassburg, 1894.

distillate was neutralized with barium carbonate in the cold, filtered, and evaporated to dryness.

From the liquid remaining in the distillation flask the $\beta$ oxyvalerianic acid was obtained (see $\beta$ oxyvalerianic acid).

To separate the ethylidenepropionic acid and expected propylideneacetic acids, the dry barium salt was repeatedly extracted with hot alcohol and filtered hot each time; the barium salt remaining undissolved was perfectly white and proved to be unaltered barium ethylidenepropionate; it was through double decomposition with sodium sulphate changed to the sodium salt, in which form it was again boiled with caustic soda. In the alcohol another barium salt had been dissolved; on distilling off the solvent a light yellow-colored, amorphous varnish-like mass was left behind; this was supposed to be the barium salt of the newly formed $\alpha$ $\beta$ acid.

To remove every trace of $\beta$ $\gamma$ acid from it, the barium salt was decomposed with sodium sulphate forming the sodium salt, and this mixed with a quantity of dilute sulphuric acid (one volume concentrated sulphuric acid and one volume of water), corresponding to five times the amount of organic matter present, plus a sufficiency to neutralize the sodium of the sodium salt and heated in a flask almost to boiling, with constant agitation for fifteen minutes, then mixed with a like bulk of water and boiled for thirty minutes. Allowed to cool, the acid solution is extracted with ether, the ethereal extract again rapidly boiled with some water, and a few drops of dilute sulphuric acid to again change into lactone any oxy acid, which may have been formed, rapidly cooled off, sodium carbonate added to an alkaline reaction, and the lactone at once shaken out with ether. The alkaline solution free from lactone was again acidified, extracted with ether, and the ethereal residue distilled with steam, the acid distillate neutralized with sodium carbonate anew, and the sodium salt obtained, again treated with sulphuric acid as above. The entire operation was repeated until no more lactone was formed; this was accomplished after repeating it two or three times, when every trace of $\beta$ $\gamma$ acid had surely been removed.

Propylideneacetic acid: $CH_3—CH_2—CH=CH—COOH$.

After no more lactone could be detected in shaking the alkaline liquid after boiling with sulphuric acid, the solution was acidified and distilled with steam, and from the acid distillate the sodium or calcium salt of the α β acid produced. On decomposing the sodium salt with sulphuric acid, or the calcium salt with hydrochloric acid in a narrow tube, the pure α β acid was obtained as an almost colorless oily layer; it was drawn off, the last portions extracted with ether, and the ethereal solutions dried by means of dried sodium sulphate or calcium chloride, filtered, and the ether evaporated, leaving a colorless oil, which congeals in a freezing mixture at once and remaining solid indefinitely in ice-water, since it melts at 7¼° to 8¼° C.

In cold winter weather it is extremely easy to obtain the acid perfectly pure and of the correct melting point.

The acid from the ethereal extract is poured into a watch-glass and placed in a desiccator at a low temperature; it then solidifies in flat rhombohedral tables or leaves, which can, with the aid of a cold platinum wire, be brought upon a piece of filter paper, to there give up the last traces of moisture, remaining behind as flat, glistening crystals. The acid is therefore the α β acid, corresponding to the ethylidenepropionic acid; its melting-point, compared with a specimen of the acid subsequently prepared, after the method of Komnenos,[1] which was purified and crystallized in a like manner, gave the following results.

A specimen of each was placed on the bulb of the same thermometer and plunged into a freezing mixture for a minute and then into cold water, the temperature of which was gradually raised.

At 6½° C. they both remained solid.

At 7° C. likewise so.

At 7¼° C. both samples began to melt slightly.

At 7½° C. both were about half melted.

At 8° C. only a small quantity of each still remained solid.

At 8¼° C. both were completely melted.

The melting-point determinations were made by placing the acid in thin-walled melting-point tubes two mm. in diameter, and closed at both ends; this allowed of a repetition of the esti-

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[1] Ann. Chem., 218, 166.

mations without any danger of loss by evaporation or inaccuracy from the absorption of water.

During some recent work on propylideneacetic acid by the Komnenos' process, Mackenzie[1] found the melting-point to be 9½°–10½° C.

It is much more difficult to obtain the solid acid of a constant melting-point in summer; to this end the following method was used: The acid freed, as much as possible, from ether and water, contained in a small flask held horizontally, was moved backwards and forwards through a water-bath of 65° C., in order to remove the last traces of ether. The flask was then closed with a stopper and calcium chloride tube, and plunged into a freezing mixture of ice and salt, in such a manner that the acid congeals on one side of the flask; the flask was now placed upright in a vessel of ice-water for an hour; the mother-liquor draining out was poured off; finally the crystalline cake was itself slightly warmed, so that the last low melting portions of the acid percolated out what remained congealed in a freezing mixture completely and did not remelt in ice-water.

Pure propylideneacetic acid becomes solid at 0° C.; if the melted acid be placed in ice-water, it solidifies in half an hour. If a crystal of the acid be dropped in, it congeals at once. The smallest quantities of water or ether have a decided effect on its melting-point.

At the ordinary temperature pure propylideneacetic acid is a mobile colorless liquid with a faint, pleasant odor of acetic acid. It is so volatile, that even at 45° C. it passes over with the ether vapors, and in summer a considerable loss is not to be prevented when working with this substance.

About sixty per cent. of the ethylidenepropionic acid is converted into propylideneacetic acid by boiling with caustic soda. For analysis the acid melting at 7¼° to 8¼° C. was used.

1. 0.2716 gram acid gave 0.1915 gram $H_2O$, and 0.595 gram $CO_2$.

2. 0.2965 gram acid gave 0.2125 gram $H_2O$, and 0.6508 gram $CO_2$.

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[1] Dissertation, Strassburg, 1894.

| | Calculated for $C_5H_8O_2$. | Found. 1. | 2 |
|---|---|---|---|
| C | 60.00 | 59.75 per cent. | 59.86 per cent. |
| H | 8.00 | 7.84 " | 7.96 " |

*Salts of Propylideneacetic Acid.*—Barium Salt. The barium salt of propylideneacetic acid is very characteristic; it was prepared by neutralizing propylideneacetic acid with barium carbonate suspended in water; the neutral solution was boiled, filtered, and evaporated to a pellicle; after cooling, the pellicle was removed from the surface of the solution and the liquid placed in an ice-chest (for when allowed to evaporate at the ordinary temperature a sticky mass only separates out) to undergo a very slow evaporation. After some weeks the salt is deposited in needles grouped to rosettes; these were washed and subjected to analysis.

The salt contains considerable water of crystallization, but effloresces easily, becoming anhydrous in a desiccator over sulphuric acid.

1. The salt pressed between filter paper and allowed to remain in an ice-chest on a piece of filter paper over night, was on the following morning weighed into an open crucible, and allowed to remain in a desiccator to constant weight.

0.2102 gram lost 0.0170 gram $H_2O$ or 8.10 per cent.

2. The pressed salt was, after remaining for fifteen minutes on a piece of filter paper in the ice-chest, weighed into an open crucible and allowed to remain to constant weight in a desiccator.

0.6470 gram lost 0.1028 gram $H_2O$ or 15.88 per cent.

3. The pressed salt was placed for twenty-five minutes in the air at 14° C. and then treated as above.

0.2493 gram lost 0.0203 gram $H_2O$ or 8.14 per cent.

4. 0.1932 gram of the salt dried in a desiccator gave 0.1335 gram $BaSO_4$, 0.0785 gram Ba.

| Calculated for $(C_5H_7O_2)_2Ba$. | Found. |
|---|---|
| 40.89 per cent. Ba. | 40.63 per cent. Ba. |

It follows from these determinations that because of the disposition of this salt to effloresce, it is impossible to make an exact estimation of the water; the difference in amount seems to depend on the temperature at which the crystallization takes place.

It was found impossible to examine the crystals optically; one can only see that they are tables with end faces, but to which system they belong can not be said.

To observe the deportment of the crystallized salt at a higher temperature, a portion which had crystallized out in the ice-chest was placed together with its mother-liquor in a stoppered vessel and allowed to remain several days at a temperature of 20° C.; a part of the crystals were thereby dissolved; the other portion, however, remained crystalline and did not become sticky.

Calcium Salt. The calcium salt was made by neutralizing an aqueous solution of the acid with calcium carbonate in the cold; the solution boiled, filtered, and evaporated to a pellicle; on cooling, the salt crystallized out in moderately long, flat, glistening prisms; they were collected on a platinum cone, washed, dried, and laid on filter paper for twelve hours at 6° C. The salt gives off all its water of crystallization in a desiccator.

0.4155 gram gave 0.0985 gram $H_2O$.

| Calculated for $(C_5H_7O_2)_2Ca+4H_2O$. | Found. |
|---|---|
| 23.22 per cent. $H_2O$. | 23.71 per cent. |

0.2263 gram of salt dried at 100° C. gave 0.1298 gram $CaSO_4$.

| Calculated for $(C_5H_7O_2)_2Ca$. | Found. |
|---|---|
| 16.81 per cent. Ca. | 16.87 per cent. Ca. |

The calcium salt crystallizes much easier than the barium salt, since it can be obtained at a temperature of 16° C. in nice prisms, while the barium salt always becomes sticky at this temperature. Calcium propylideneacetate like the barium salt is easily soluble in water and alcohol.

*Propylideneacetic acid dibromide.*

$\alpha$ $\beta$ dibromvalerianic acid.

$\alpha$ $\beta$ pentinic acid dibromide.

$CH_3-CH_2-\dot{C}HBr-CHBr-COOH$.

To further characterize the acid, the bromine and bromhydric acid addition products were made.

To prepare the dibromide, the vessels and reagents used were carefully dried.

The acid was dissolved in a little carbon disulphide and then with exclusion of air the calculated amount of bromine in a ten per cent. carbon disulphide solution was added through a dropper funnel-tube. A violent reaction was not noticed even at the commencement, the decolorization being slow and incomplete. The experiment was conducted in diffused daylight.

After a small excess of bromine had been added, the whole was cooled off and allowed to remain quiet for twenty-four hours; the most of the carbon disulphide was then removed by aspirating a current of dry air through the bottle; the remaining solution was placed on a large watch-glass in a desiccator, and the disulphide entirely removed by frequent stirring with a glass rod. The desiccator placed in a refrigerator soon caused the dibromide to crystallize out in large leaves.

After the disulphide had been completely removed by alternate stirring, and evacuation of the desiccator, the solid dibromide was dissolved in the least possible quantity of petroleum ether, and the solution allowed to stand in a corked test-tube for several hours. Here the dibromide was deposited in rosettes of flat prisms on the sides of the tube. The mother-liquor was rapidly decanted and the crystals washed two or three times with cold (0° C.) petroleum ether, and again crystallized out of the latter, when the preparation was considered pure.

The dibromide seems not adapted for crystallographic study; the crystallization is probably monosymmetric; it melts without coloration at 56° C.; it is very soluble in carbon disulphide and benzene; in petroleum ether it is easily soluble.

0.2040 gram of the dibromide dried in a vacuum gave 0.2957 gram of $AgBr = 0.1258$ gram Br.

| Calculated for $C_5H_8Br_2O_2$. | Found. |
|---|---|
| 61.54 per cent. Br. | 61.68 per cent. Br. |

$\beta$ Bromvalerianic acid. $CH_3-CH_2-CHBr-CH_2-COOH$.

The hydrobromic acid addition product of propylideneacetic acid was prepared as follows: To one volume of the pure acid contained in a small cylinder having a well-ground stopper, one and a half volumes of hydrobromic acid saturated at 0° C. were added; on shaking, a clear solution resulted; it was allowed to remain quietly for twenty-four hours at the ordinary temperature; the monobromide had now risen to the surface of the hydrobromic acid as a light brown-colored layer. The cylinder was now vigorously shaken from time to time, to bring any unaltered propylideneacetic acid which might be dissolved in the monobromide, into intimate contact with the hydrobromic acid. After this occasional shaking had been continued four or five days, the contents of the cylinder formed two distinct layers; the reaction was ended and all the propylideneacetic acid had been quantitatively changed into β bromvalerianic acid. The cylinder, still stoppered, was now placed in ice-water to cause the new acid to solidify, this, however, did not occur. It was then placed in a freezing mixture of ice and salt, and on agitating slightly, the monobromide at once congealed to a mass of fine needles lying on the surface of the hydrobromic acid. The cylinder stood for fifteen hours at a temperature of 15° C.; then the crystalline cake was broken through with a glass rod, distributed through the hydrobromic acid, and brought into a platinum cone where it was allowed to dry, being washed with small successive portions of ice-water, in order to remove the greater part of the mineral acid. The contents of the cone were now brought upon a watch-glass and placed in a vacuum over sulphuric acid and potassium hydroxide; a dry sandy-white substance resulted, which was powdered and recrystallized out of petroleum ether. So produced, the β bromvalerianic acid is, after drying, perfectly pure, as the analysis proves.

0.233 gram of the substance dried in a vacuum gave 0.2410 gram AgBr.

| Calculated for $C_5H_9BrO_2$. | Found. |
|---|---|
| 44.20 per cent. Br. | 44.20 per cent. Br. |

β bromvalerianic acid melts at 59° to 60° C., the melting-point not altering in the least by repeated determinations on the same sample.

It dissolves readily in ether, chloroform, carbon disulphide, less easily in benzene and petroleum ether, and is almost insoluble in water of 0° C.

If the cold, saturated solution of the monobromide in petroleum ether be allowed to evaporate spontaneously it crystallizes out in beautiful, colorless, eight-sided prisms.

The crystals set up after Naumann's system give the following crystallographic measurements:

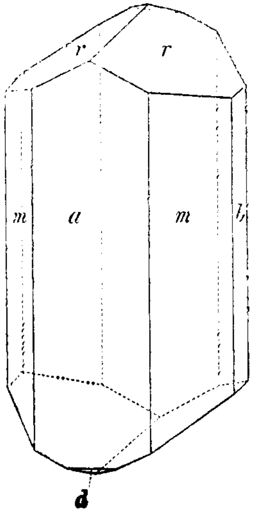
## $\beta$ BROMVALERIANIC ACID.

Crystal system : Monosymmetric.

$\acute{a} : \bar{b} : \grave{c} = 1.4688 : 1 : 0.4900$

$\beta = 79^\circ 58' 45''$

Observed forms: $m = \{110\} \infty P$, $a = \{100\} \infty \bar{P}\infty$, $b = \{010\} \infty \grave{P}\infty$, $r = \{011\} \grave{P}\infty$, $d = \{\bar{1}01\} + \bar{P}\infty$, $e = \{101\} - \bar{P}\infty$.



The crystals are mostly two to five mm. long by one to two mm. wide, and possess a valerianic acid-like odor.

Some crystals are minus $[\bar{1}01] + \bar{P}\infty$, as also $[100] \infty \bar{P}\infty$, while $[10\bar{1}] - \bar{P}\infty$ was only observed once.

The faces were almost always smooth and polished, giving excellent reflexes.

The following angles were measured and calculated:

| | | Measured. | Calculated. |
|---|---|---|---|
| r : r | = (011) : (011) = | *51° 31′ | ...... |
| a : m | = (100) : (110) = | *55° 20′ 30″ | ...... |
| r : m | = (011) : ($\bar{1}$00) = | *99° 1′ | ...... |
| m : m | = (110) : (1$\bar{1}$0) = | 110° 43′ | 110° 41′ |
| m : b | = (110) : (010) = | 34° 47′ | 34° 39′ 30″ |
| r : b | = (011) : (010) = | 64° 6′ | 64° 14′ 30″ |
| a : b | = (100) : (010) = | 89° 58′ | 90° |
| a : d | = (100) : ($\bar{1}$01) = | 99° 2′ | 99° 12′ |

| | Measured. | Calculated. |
|---|---|---|
| r : m = $(011) : (1\bar{1}0)$ = | 74° 2′ | 74° 26′ |
| a : e = $(100) : (101)$ = | 61° 59′ | 62° 44′ |
| r : d = $(101) : (\bar{1}01)$ = | 36° 33′ | 36° 29′ |
| r : m = $(011) : (110)$ = | 63° 33′ | 63° 28′ |
| r : d = $(011) : (\bar{1}01)$ = | 31° 8′ | 31° 45′ |
| d : m = $(\bar{1}01) : (\bar{1}00)$ = | 80° 11′ | 80° 48′ |

A cleavage could not be found. The plane of the optical axes stands at right angles to the klinopinacoid and is only slightly inclined towards the orthopinacoid.

Obtuse bisectrix = b axis.

$\beta$ Oxyvalerianic acid, $CH_3—CH_2—CH(OH)—CH_2—COOH$. The acid mixture from the treatment of ethylidenepropionic with caustic soda was not completely volatile with steam.

The residue left in the distillation flask, after the ethylidenepropionic and propylideneacetic acid had been driven over, had a strong acid reaction and gave up a yellow oil when shaken with ether. It was purified by dissolving in ether and precipitating with petroleum ether as a thick colorless liquid. This syrup could not be solidified either by allowing it to remain in a desiccator or at a temperature of 18° C. for several hours, aided by frequent stirring with a platinum wire. A portion of the acid, which had been prepared from the perfectly pure barium salt, was dried in a desiccator to constant weight; it then presented an absolutely colorless liquid, which, when put into a narrow test-tube and placed in a freezing mixture, would not become solid with frequent stirring by means of a platinum wire. At best it remained a colorless molasses-like liquid, although the barium salt from which it was obtained as well as the acid itself, as far as purity is concerned, left nothing to be desired as the analyses show.

0.2745 gram obtained from the pure barium salt contained in a platinum boat and dried in a desiccator gave 0.2073 gram $H_2O + 0.5105$ gram $CO_2$.

| | Calculated for $C_5H_{10}O_3$. | Found. |
|---|---|---|
| C ................ | 50.85 per cent. | 50.72 per cent. |
| H.... ........... | 8.47 " | 8.39 " |

$\beta$ oxyvalerianic acid is easily soluble in cold water, ether, benzene, and in chloroform; in carbon disulphide and petroleum ether it is insoluble.

From forty-five grams of ethylidenepropionic acid, which was boiled with caustic soda, 16.5 grams or thirty-six per cent. of $\beta$ oxyvalerianic acid was produced.

*Salts of $\beta$ Oxyvalerianic Acid.*—Calcium Salt. The still yellow-colored acid was diluted with water and heated on the water-bath until the mixture reacted neutral; it was then filtered and the yellow-colored filtrate decolorized with animal charcoal; the filtered solution was now evaporated until a pellicle formed on the surface and was then allowed to cool; the pellicle was dissolved and after remaining at the ordinary temperature for some time there was deposited on the bottom of the vessel a collection of white opaque warts of porcelain-like appearance, which, when powdered and dried in the air, was analyzed.

1. 0.43 gram of air-dried salt lost 0.0263 gram $H_2O$ at 175° C.

| Calculated for $(C_5H_9O_3)_2Ca+H_2O$. | Found. |
|---|---|
| 6.16 per cent. $H_2O$. | 6.12 per cent. |

2. 0.1889 gram anhydrous salt gave 0.0915 gram $CaSO_4$.

| Calculated for $(C_5H_9O_3)_2Ca$. | Found. |
|---|---|
| 14.59 per cent. Ca. | 14.30 per cent. |

The salt retains its water of crystallization very tenaciously and gives it up when heated for some time at 175° C. At 180° C. it begins to melt and acquire a yellow tint, whereby it loses considerable in weight and at 200° C. a yellow transparent molten mass filled with bubbles results, with an increase in the amount of decomposition, which began at 180° C. The salt is quite soluble in water and insoluble in alcohol. Still the aqueous solution, to which three volumes of absolute alcohol has been added, remains perfectly clear at first, only becoming cloudy after the lapse of some hours, and after a longer period the salt is deposited as a sandy indistinctly crystalline mass.

Treated with alcohol on a slide and examined under the microscope the following was observed:

The precipitate consists of small, mostly irregularly formed, double refracting leaves, stretched at times in one direction, and which present an oblique obliteration of light, parallel to this principal direction of development. Because of this oblique obliteration the crystals probably belong to the monoclinic system.

Barium Salt.—The barium salt was prepared in exactly the same manner as the preceding, by warm neutralization of barium carbonate; the solution evaporated to a pellicle, was allowed to cool, the pellicle not dissolving; after about an hour it became cloudy, and deposited small, fine needles, which gradually accumulated on the bottom of the beaker as a sandy crystalline mass.

This crystalline mass treated with alcohol and examined under the microscope, showed a colorless, strongly double refracting homogeneous number of crystals, grouped to a half ball; they were tables of rhombic or right angular form, with an oblique obliteration and were, therefore, probably monoclinic.

0.1983 gram of the air-dried salt lost 0.0093 gram $H_2O$ at 105° C. and gave 0.1193 gram $BaSO_4$.

| | Calculated for $(C_5H_9O_3)_2$ Ba+$H_2O$. | Found. |
|---|---|---|
| $H_2O$ | 4.63 per cent. | 4.67 per cent. |
| Ba | 35.22 " | 35.36 " |

At 105° C. the salt melts without decomposition to a colorless transparent mass; even, on the water-bath, when covered with a little water a thick syrup results. It is insoluble in alcohol.

Silver Salt.—The silver salt was obtained by the double decomposition of a warm concentrated solution of the calcium salt with silver nitrate, as slightly violet-colored crystals or a powder according as it separated out rapidly or slowly. When recrystallized from hot water it is nearly white and is but little affected by light.

0.1037 gram of the salt dried at 50° to 55° C. gave in the combustion 0.0497 gram Ag.; 0.1018 gram $CO_2$; and 0.0390 gram $H_2O$.

| | Calculated for $(C_6H_9O_3)$Ag. | Found. |
|---|---|---|
| Ag | 48.00 per cent. | 47.93 per cent. |
| C | 26.67 " | 26.86 " |
| H | 4.00 " | 4.27 " |

Microscopically the crystalline powder appeared to be fine, flat, at times, corroded needles, which had an oblique obliteration in their long direction.

*Boiling β Oxyvalerianic Acid with Sodium Hydroxide.*—For this very interesting experiment 6.240 grams of calcium β oxyvalerianate (representing five grams of acid) was used; through double decomposition with sodium carbonate sodium β oxyvalerianate was formed and this boiled for thirty hours in a copper flask connected with a return condenser and containing 17.1 grams, of sodium hydroxide in 154 grams of water.

After cooling, the solution was acidified with sulphuric acid and extracted with ether. The ethereal residue rapidly boiled with water and a few drops of dilute sulphuric acid, to change any $\gamma$ oxy acid present (which could have originated from the $\beta$ oxy acid with ethylidenepropionic acid and valerolactone as intermediate steps) into lactone, was then made slightly alkaline with sodium carbonate, and shaken out with ether; nothing was taken up by the latter, consequently, the presence of $\gamma$ oxy acid must be excluded.

The alkaline solution, after the ether had been removed, was acidulated with sulphuric acid and distilled with steam until the distillate passed over the neutral. The unaltered $\beta$ oxy acid remained behind in the distillation flask, which, when shaken with ether, allowed of its removal from the contents of the same; it was converted into the calcium salt, which amounted to three and four-tenths grams or more than one-half of the acid originally employed.

The acid distillate was neutralized with barium carbonate, but since the barium salts thus obtained do not allow a good separation with alcohol, they were converted into the sodium salts through the aid of sodium sulphate, and now the $\beta$ $\gamma$ acid converted into lactone by boiling with sulphuric acid, made alkaline with soda solution, the lactone was shaken out with ether, and characterized by boiling with barium hydroxide for thirty minutes, thus converting it into the barium salt of $\gamma$ oxyvalerianic acid. After precipitating the excess of barium with carbon dioxide in the heat, the evaporated filtrate gave 1.973 grams of an amorphous substance easily soluble in alcohol and water, from which it was deposited as a gummy mass, and proved in all its conduct to be the barium salt of $\gamma$ oxy acid. Finally by exactly precipitating with sulphuric acid in the heat, and adding potassium carbonate to the cold filtrate in a narrow tube the valerolactone was obtained as a supernatant layer.

The alkaline solution freed from lactone was acidulated with sulphuric acid and distilled with steam; from the acid distillate through neutralization with calcium carbonate 0.94 gram of calcium propylideneacetate was obtained, from which the acid itself was freed. After purifying in the manner already mentioned it melted at $7\frac{1}{4}°$ to $8\frac{1}{4}°$ C.

In the process of boiling with caustic soda, there was obtained from the β oxy valerianic acid:

56.6 per cent. of unaltered oxy acid.
21.26 per cent. of ethylidenepropionic acid.
14.64 per cent. of propylideneacetic,
with a loss of 6.5 per cent.

*Distillation of the β Oxyvalerianic Acid.*—A portion of the thick, almost colorless, acid was so distilled from a small distillation flask that it passed over slowly and in drops. As the boiling began, the thermometer with its bulb in the liquid indicated 190° C.; it was now raised until its bulb was just beneath the exit tube; it sank to 180° C., but rapidly rose to 190° C., where it remained constant for a short time, gradually rising to 195° C., and then to 200° C., where the principal portion went over, and finally to 203° C.; the last drops of the distillate were colored yellow, and a small tarry residue only remained in the flask. The distillate, which had the same empyreumatic odor as that from methylparaconic acid, was mixed with five times its volume of water and sufficient sodium carbonate to render it distinctly alkaline after a vigorous shaking; nothing could be extracted by means of the ether, consequently, the distillate contained no lactone and a conversion of β oxyvalerianic acid into γ oxy acid respectively γ lactone had not taken place. The salt solution, free from ether, was now acidulated and distilled with steam, in order to separate the unsaturated acids from the oxy acid. The milky distillate was neutralized with barium carbonate and thereby the mixed barium salts of the volatile acids obtained; as, however, these can not be satisfactorily separated with alcohol, the above-described process used to effect their separation when produced by boiling the oxy acid with caustic soda was employed and the β γ acid separated as lactone from the α β acid; the latter was characterized by means of its melting-point.

From the residue of the distillation with steam a small amount of the β oxy acid could be extracted.

The principal product in the distillation of the β oxyvalerianic acid was propylideneacetic acid; only a small quantity of ethylidenepropionic was found, and a like small portion of oxy acid went over unaltered.

The three isomers allylacetic, ethylidenepropionic, and propylideneacetic acids, can, as the accompanying table shows, be easily characterized and distinguished.

But recently Fittig and Mackenzie[1] have for the sake of simplicity, applied the terms $\gamma\ \delta$, $\beta\ \gamma$, and $\alpha\ \beta$ pentinic acids to the allylacetic, ethylidenepropionic, and propylideneacetic acids, respectively.

| | Allylacetic acid. | Ethylidenepropionic acid. | Propylideneacetic acid. |
|---|---|---|---|
| Free acid. | Fluid, boiling-point 186°-187° C., characteristic odor resembling that of valerianic acid. | Fluid, boiling-point 193°-194° C. | Solid melts at 7¼-8¼° C. |
| Calcium salt. | Crystallize out of a hot saturated aqueous solution with one molecule of water in flat pointed prisms, which are insoluble in alcohol. | | Crystallizes out of the aqueous solution in the cold, with four molecules of water of crystallization<br>Soluble in hot absolute alcohol. |
| Barium salt. | Crystallize out of a hot saturated aqueous solution with one molecule of water in flat pointed prisms. Insoluble in alcohol. | | Crystallizes in the cold out of the aqueous solution with two and four molecules of water.<br>Soluble in hot absolute alcohol. |
| Monobromide. | Both acids produce the same γ bromvalerianic acid with hydrobromic acid. Fluid and not solid at—16° C. | | Gives with hydrobromic acid β bromvalerianic acid. This crystallizes out of petroleum ether in monoclinic prisms with the following forms:<br>$\infty P\infty, \infty P, \infty \grave{P}\infty, \grave{P}\infty, +P\infty, -P\infty$, melts at 59°-60° C.<br>Insoluble in water, becomes liquid in water of 45°-50° C. |
| Dibromide. | Thin four-sided monoclinic tables melting at 58°.<br>Difficultly soluble in petroleum ether. | Monoclinic prisms developed in the direction of the C axis. Readily soluble in warm petroleum ether; less so in cold. Melting-point 65°; dissolves in water with a gyratory motion. Becomes fluid under water of 50°-55° C. | Monoclinic prisms melting at 56°, becoming liquid under water of 15° C.<br>Very readily soluble in petroleum ether at the ordinary temperature. |

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[1] Dissertation, Strassburg, 1894.