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XXV.—*Researches on Acids of the Acrylic Series.*—No. 1. *Transformation of the Lactic into the Acrylic Series of Acids.*

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The acrylic or oleic series of acids, represented as it is by a rather numerous list of members, has hitherto received a remarkably small share of the attention of chemists, and such is more especially the case as regards the constitution of these acids. This comparative neglect is doubtless due to the circumstance that these acids have hitherto maintained a very isolated position, having few points of attachment to other families of organic compounds, from which any probable hypothesis as to their internal architecture could be formed. We trust, however, that the opening of a new path admitting of ready access to this series will materially contribute to the completion of the history of these acids, especially as it discloses at the same time a view of their structure, which scarcely leaves any doubt regarding their atomic constitution.

Action of Terchloride of Phosphorus upon Ethylic Leucate or Diethoxalate.

When terchloride of phosphorus is gradually added to ethylic leucate, a considerable elevation of temperature takes place, and torrents of hydrochloric acid are evolved. The reaction is not, however, completed until the mixture has been submitted to upward distillation for several hours, during which operation a considerable quantity of amorphous phosphorus separates. As soon as the evolution of hydrochloric acid has ceased, the contents of the retort must be distilled nearly to dryness, and the distillate cautiously mixed with water. A layer of ethereal liquid collects on the surface, which, after repeated washing, first with water, and then with dilute solution of carbonate of soda, boils between 162° and 168° C.

Several ounces of ethylic leucate so treated, gave about two-thirds of its volume of this ethereal product. After drying with chloride of calcium, the greater part of it passed over on rectification at 165° C. It was perfectly free from chlorine, and yielded on analysis the following numbers :—

·2885 grm. burnt with oxide of copper, gave ·709 grm. carbonic acid, and ·2549 grm. water.
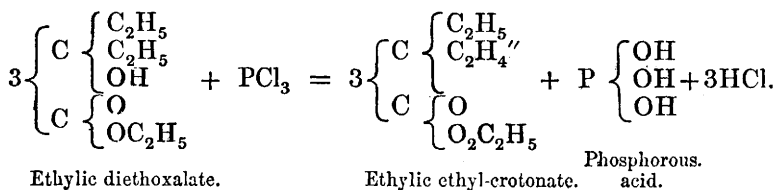
These numbers agree closely with the formula—

$$C_8H_{14}O_2,$$
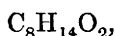
as seen in the following comparison :—

	Calculated.		Found.
C_8	96	67·60	67·02
H_{14}	14	9·86	9·82
O_2	32	22·54	——
	142	100·00	

From considerations mentioned below, we regard this body as the ethylic ether of ethyl-crotonic acid, the latter consisting of crotonic acid in which one atom of hydrogen has been replaced by ethyl :

$$C_4H_6O_2 \qquad\qquad C_4H_5(C_2H_5)O_2$$

Crotonic acid.   Ethyl-crotonic acid.
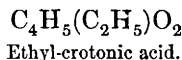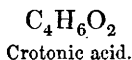
Ethylic Ethyl-crotonate is therefore produced by the action of terchloride of phosphorus upon ethylic diethoxalate, according to the following equation :—

$$3\left\{\begin{matrix}C\begin{cases}C_2H_5\\C_2H_5\\OH\end{cases}\\C\begin{cases}O\\OC_2H_5\end{cases}\end{matrix}\right. + PCl_3 = 3\left\{\begin{matrix}C\begin{cases}C_2H_5\\C_2H_4''\end{cases}\\C\begin{cases}O\\O_2C_2H_5\end{cases}\end{matrix}\right. + P\begin{cases}OH\\OH\\OH\end{cases}+3HCl.$$

Ethylic diethoxalate.   Ethylic ethyl-crotonate.   Phosphorous. acid.

Ethylic ethyl-crotonate is a colourless, transparent, mobile liquid, possessing a burning taste and a very penetrating odour, recalling at the same time the smell of oil of peppermint and that of mushrooms. It is almost insoluble in water, to which, how-ever, it communicates its peculiar taste and odour in a very high degree. Alcohol and ether dissolve it in all proportions. Its specific gravity is ·9203 at 13° C. It does not oxidize on expo-sure to air, and is not decomposed by water. Ethylic ethyl-crotonate boils at 165° C., and distils without decomposition. A determination of its vapour density by Gay-Lussac's method gave the following data :—

Weight of ethylic ethyl-crotonate	..	..	..	·1725 grm.
Observed volume of vapour	..	..	..	.. 54·66 cbc. c.
Temperature of bath	..	..	..	190° C.
Height of barometer	..	..	..	752 m.m.
Height of mercury inside of tube above that outside				94·5 m.m.
Equivalent of spermaceti column in millimetres of mercury ..	..	.	..	.. 15·7 m. m.

From these data the specific gravity was calculated to be 4·83, the theoretical number for a two-volume vapour ($H_2O = 2$ vols.) of the above formula being 4·90.

Boiled with alcoholic potash, ethylic ethyl-crotonate is completely decomposed, yielding alcohol and potassium ethyl-crotonate. After treating the solution with water, and evaporating off the alcohol, the potassium ethyl-crotonate was treated with excess of sulphuric acid and submitted to distillation. An oily liquid, together with a large quantity of water, passed over and solidified before leaving the condenser, which required to be kept warm to prevent its being obstructed by the crystalline product. The whole of the distillate on being warmed, presented the appearance of a colourless oil floating on the surface of water, and on cooling, the oily layer solidified to a mass of splendid crystals, some of which were continued downwards through the water to the depth of 4 inches. These crystals, after pressing between folds of blotting paper and drying over sulphuric acid in vacuo, are specifically heavier than water, although the oil which they form when melted floats upon that liquid. They gave the following analytical results:—

·2524 grm. gave ·5799 grm. carbonic acid, and ·2002 grm. water.

These numbers correspond well with those calculated from the formula of ethyl-crotonic acid,

$$C_2 \begin{cases} C_2H_5 \\ C_2H_4'' \\ O \\ OH \end{cases}$$
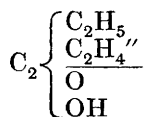
|	Calculated.		Found.
C_6	72	63·15	62·66
H_{10}	10	8·77	8·81
O_2	32	28·08	——
	114	100·00	

Ethyl-crotonic acid crystallises very readily from fusion in large and brilliant quadrilateral prisms, which melt at 39·5° C., and possess a peculiar odour, somewhat resembling that of a mixture of pyrogallic acid and benzoic acids. It sublimes at ordinary temperatures, is very soluble in alcohol and ether, but sparingly so in water. Its aqueous solution reddens litmus powerfully, and neutralises the strongest bases. The salts of ethyl-crotonic acid are generally distinguished by the facility with which they become basic on the evaporation of their solutions. The potassium, sodium, and barium salts are of a soapy nature, especially the two former, which separate from their concentrated solutions, and float on the surface. The silver, copper, and lead salts are very sparingly soluble in water.

Silver Ethyl-crotonate is obtained as a white crystalline precipitate, by mixing tolerably concentrated solutions of ammonium ethyl-crotonate and silver nitrate. Thrown upon a filter, well washed with water, and then dried in vacuo, it yielded on analysis the following numbers :—

I. ·4022 grm. gave ·4796 grm. carbonic acid and ·1464 grm. water.

II. ·3380 grm. gave ·1654 grm. metallic silver.

The following comparison shows that these numbers agree closely with the formula—

$$C_2 \begin{cases} C_2H_5 \\ C_2H_4'' \\ \overline{O} \\ OAg. \end{cases}$$
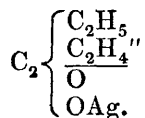
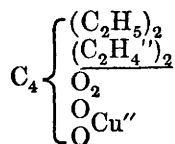|	Calculated.		I.	II.
C_6	72	32·58	32·52	——
H_9	9	4·07	4·05	——
O_2	32	14·48	——	——
Ag	108	48·87	——	48·93
	221	100·00		

Silver ethyl-crotonate crystallises from water in minute scales, which are only slightly discoloured by light, or by a temperature of 100° C. By boiling, or even by evaporation of its solution over sulphuric acid in vacuo, this salt loses acid ; a specimen so obtained in vacuo gave on analysis 30·78 per cent. of carbon, 4·04 of hydrogen, and 49·95 per cent. of silver.

Cupric Ethyl-crotonate is readily obtained as a beautiful greenish blue precipitate, by adding a solution of cupric sulphate to one of ammonium ethyl-crotonate. This precipitate, well washed, and afterwards dried in vacuo, gave the following analytical results:—

I. ·3052 grm. gave ·5442 grm. carbonic acid and ·1748 grm. water.

II. ·2127 grm. gave ·0570 grm. cupric oxide.

These numbers correspond sufficiently with those calculated from the formula

$$C_4 \begin{cases} (C_2H_5)_2 \\ (C_2H_4'')_2 \\ \overline{O_2} \\ O \\ O Cu'' \end{cases}$$

	Calculated.		Found.	
			I.	II.
C_{12}	144	49·74	48·63	——
H_{18}	18	6·22	6·36	——
O_4	64	22·11	——	——
Cu	63·5	21·93	——	21·41
	289·5	100·00		

The deficiency in the amount of carbon in the above analysis is doubtless due to the extreme facility with which this salt loses acid. A sample, which had been boiled for only a few minutes, gave 43·54 per cent. of carbon, 5·66 of hydrogen, and 27·07 per cent. of copper.

Lead Ethyl-crotonate was prepared by mixing solutions of lead acetate and ammonium ethyl-crotonate. It falls as a brilliant white curdy precipitate, which is perfectly insoluble in water. Submitted to analysis, ·4265 grm. gave ·5149 grm. carbonic acid, ·1647 grm. water, and ·2169 grm. lead oxide; numbers which closely correspond with the formula

$$C_4 \begin{cases} (C_2H_5)_2 \\ C_2H_4'')_2 \\ \overline{O_2} \\ O \\ O Pb'' \end{cases}$$
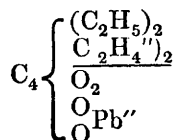
as is seen from the following calculation :—

	Calculated.		Found.
C_{12}	144	33·26	32·93
H_{18}	18	4·16	4·29
O_4	64	14·78	15·58
Pb	207	47·80	47·20
	433	100·00	100·00

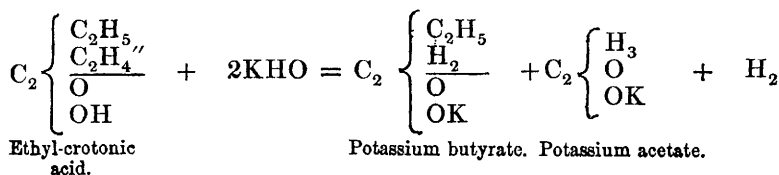## *Action of Potassic hydrate upon Ethyl-crotonic Acid.*

When ethyl-crotonic acid is mixed with a large excess of potassic hydrate and heated to about 180° C., hydrogen gas is evolved in large quantity, and the residual mass, when treated with water and excess of sulphuric acid, gives an acid distillate, which, by L i e b i g's process of semi-saturation, is completely resolved into two acids ; the silver salt of one of these yielded on analysis the following results :—

·2904 grm. gave ·2599 grm. carbonic acid, ·0959 grm. water, and ·1613 grm. metallic silver.

These numbers shew that this salt is silver butyrate, as seen from the following comparison of the experimental with the calculated percentage quantities :—

|	Calculated.		Found.
C_4	48	24·61	24·41
H_7	7	3·59	3·67
O_2	32	16·42	16·38
Ag	108	55·38	55·54
	195	100·00	100·00

The silver salt of the second acid is silver acetate ; it crystallises in needles, which left on incineration 63·82 per cent. of silver. Silver acetate contains 64·64 per cent. Ethyl-crotonic acid is therefore decomposed by potassium hydrate into the potassium salts of butyric and acetic acids, with evolution of hydrogen, according to the following equation :—

$$C_2\begin{cases} C_2H_5 \\ C_2H_4{}'' \\ O \\ OH \end{cases} + 2KHO = C_2\begin{cases} C_2H_5 \\ H_2 \\ O \\ OK \end{cases} + C_2\begin{cases} H_3 \\ O \\ OK \end{cases} + H_2$$

Ethyl-crotonic   Potassium butyrate. Potassium acetate.
acid.

These are also the results of the action of the same reagent upon pyroterebic acid, which is isomeric with ethyl-crotonic acid. The cause of this identity of products from isomeric compounds we have explained below.

*Action of Terchloride of Phosphorus upon Ethylic Ethomethoxalate.*

When ethylic ethomethoxalate is treated with terchloride of phosphorus, the same phenomena are observed as in the corresponding reaction just described. After the complete cessation of the evolution of hydrochloric acid, the liquid was distilled, and the distillate washed, first with water, and then with dilute solution of sodium carbonate. An ethereal liquid separated as before, which, after drying over chloride of calcium, was submitted to rectification. We have not analytically proved the composition of this ether, but from the mode of its formation and the result of its decomposition by alcoholic potash, there can be no doubt that it is homologous with ethylic ethyl-crotonate, and that its formula is

$$C_7H_{12}O_2.$$
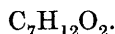
The same considerations which led us to regard the ethereal product of the previous reaction as ethylic ethyl-crotonate demand for this ether, the name *ethylic methyl-crotonate,* and the formula

$$C_2 \begin{cases} CH_3 \\ \underline{C_2H_4''} \\ O \\ OC_2H_5 \end{cases}$$
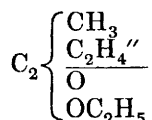
Ethylic methyl-crotonate is a colourless, transparent, mobile liquid, boiling at 156° C., possessing an insupportable and very persistent odour of decaying mushrooms, and a burning taste. It is lighter than, and nearly insoluble in, water. Alcohol and ether dissolve it in all proportions. Treated with boiling alcoholic potash, it is readily decomposed, yielding alcohol and potassium methyl-crotonate. An aqueous solution of the latter, mixed with excess of dilute sulphuric acid, and submitted to distillation, yields a beautifully crystalline body, which is methyl-crotonic acid,

$$C_2 \begin{cases} CH_3 \\ \underline{C_2H_4''} \\ O \\ OH \end{cases}$$
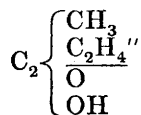
*Methyl-crotonic acid* fuses at 62° C., and crystallizes on cooling

in splendid needles, which are considerably more soluble in water than ethyl-crotonic acid. It possesses the same aromatic odour as ethyl-crotonic acid, but more intense, and in its other properties closely resembles the latter. Its salts have a strong tendency to become basic on the evaporation of their solutions. We have examined the barium and silver salts.

Barium Methyl-crotonate is readily obtained by adding barium carbonate to a hot solution of methyl-crotonic acid, filtering and evaporating in vacuo over sulphuric acid. The salt which separates is difficultly crystallisable; dried in vacuo it gave on analysis 39·90 per cent. of barium. The formula—

$$C_4 \begin{cases} (CH_3)_2 \\ \dfrac{(C_2H_4'')_2}{O_2} \\ O \\ O \end{cases} Ba''$$
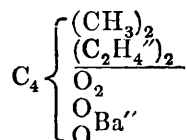
requires 40·89 per cent. of barium. Barium methyl-crotonate is very soluble in water.

Silver methyl-crotonate is best prepared by precipitating a moderately concentrated solution of barium methyl-crotonate with nitrate of silver. The silver methyl-crotonate falls as a white crystalline powder, which is little affected by light, and very slightly soluble in water. Well washed with water and dried in vacuo, ·2246 grm. gave, when burnt with oxide of copper, ·2417 grm. carbonic acid, ·0735 grm. water, and ·1167 grm. metallic silver. These numbers agree sufficiently with the formula

$$C_2 \begin{cases} CH_3 \\ \dfrac{C_2H_4''}{O} \\ OAg \end{cases}$$
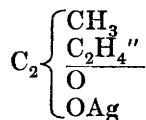
as is seen from the following calculation:—

	Calculated.		Found.
C_5	60	28·99	29·35
H_7	7	3·38	3·63
O_2	32	15·46	15·06
Ag	108	52·17	51·96
	207	100·00	100·00

Action of Potassium Hydrate upon Methyl-crotonic Acid.

Heated with an excess of potassium hydrate, methyl-crotonic acid evolves abundance of hydrogen, and the residue yields, on distillation with dilute sulphuric acid in excess, an acid mixture, which the process of fractional saturation resolves into propionic and acetic acids. The barium salts of these acids yielded respectively 47·86 and 51·97 per cent. of barium. The formula of barium propionate requires 48·41 per cent., and that of barium acetate 52·73 per cent of barium.

Methyl-crotonic acid is therefore decomposed by potassium hydrate into propionic and acetic acids, with the evolution of hydrogen, according to the following equation :—

$$C_2 \begin{cases} CH_3 \\ C_2H_4{''} \\ O \\ OH \end{cases} + \quad 2KHO \; = \; C_2 \begin{cases} CH_3 \\ H_2 \\ O \\ OK \end{cases} + \quad C_2 \begin{cases} H_3 \\ \overline{} \\ O \\ OK \end{cases} + \quad H_2$$

Methyl-crotonic acid.   Potassium propionate.   Potassium acetate.
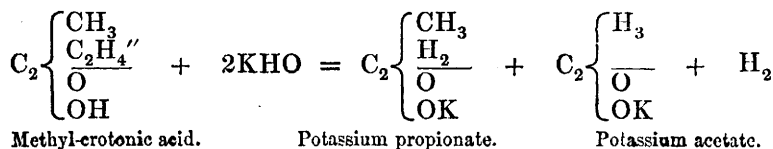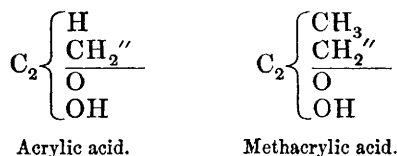
These results of the action of potassium hydrate upon methyl-crotonic acid are identical with those obtained by Chiozza in acting the same reagent upon angelic acid,[*] with which methyl-crotonic acid is isomeric. They show that the conversion into water, of the atom of peroxide of hydrogen in ethylic etho-methoxalate, is effected at the expense of the constitutional ethyl exclusively, the methyl remaining intact.

Action of Terchloride of Phosphorus upon Ethylic Dimethoxalate.

Ethylic dimethoxalate is readily attacked by terchloride of phosphorus, even at ordinary temperatures, but to complete the reaction it is necessary to heat the mixture to ebullition in a flask, with an inverted condenser, for several hours, taking care to employ a large excess of the terchloride. When the evolution of hydrochloric acid has completely ceased, the contents of the flask may be distilled from an oil-bath nearly to dryness, the distillate mixed cautiously with water, and the ethereal layer floating on the surface removed by decantation. After washing with water and solution of carbonate of soda, drying over chloride of calcium

[*] Ann. Ch. Phys. [3], xxxix, 435.

and rectification, the new ether possesses the following properties. It is a colourless, transparent, and very mobile liquid, having the nauseating odour of decaying mushrooms in a very high degree. This odour becomes more powerful as the atomic weight of these ethers is lowered, and reaches its climax in the body we are now describing. From the mode of its formation and the composition of the acid obtained from it, there can be no doubt that this ether possesses the composition of ethylic crotonate, but the decomposition which the acid suffers when heated with potassium hydrate, proves that it is metameric, and not identical with ethylic crotonate. We shall state at the conclusion of this paper our reasons for regarding this ether as the ethylic salt of methacrylic acid, the latter being acrylic acid in which an atom of hydrogen has been replaced by methyl—

$$C_2 \begin{cases} H \\ CH_2'' \\ O \\ OH \end{cases} \qquad C_2 \begin{cases} CH_3 \\ CH_2'' \\ O \\ OH \end{cases}$$

<div align="center">Acrylic acid.   Methacrylic acid.</div>

Ethylic methacrylate is readily decomposed by boiling alcoholic potash, yielding alcohol and the potassium salt of methacrylic acid, which crystallises from the alcoholic solution in beautiful scales. Distilled with excess of dilute sulphuric acid, potassium methacrylate yields methacrylic acid, which at first separates as an oily layer on the surface of the distillate, but afterwards dissolves in the water, which passes over with it.

Methacrylic acid is a colourless oil, which does not solidify at $0°$ C., and possesses a faint odour, like pyrogallic acid. It has a powerful acid reaction, and its salts have the same tendency to lose acid by evaporation, as those of the other members of the acrylic family.

Silver methacrylate is best obtained pure by precipitating ammonium methacrylate with nitrate of silver. It falls as a white precipitate, but slightly soluble in water, and not much affected by light. After washing and subsequent drying in vacuo over sulphuric acid, ·3038 grm. of this salt gave, on combustion with oxide of copper and free oxygen, ·2785 grm. carbonic acid, ·0780 grm. water, and ·1705 grm. metallic silver, numbers which correspond closely with those calculated from the formula

$$C_2 \begin{cases} CH_3 \\ \dfrac{CH_2''}{O} \\ OAg \end{cases}$$
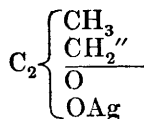
	Calculated.		Found.
C_4	48	24·87	25·00
H_5	5	2·59	2·85
O_2	32	16·54	16·03
Ag	108	56·00	56·12
	193	100·00	100·00

Barium methacrylate is very soluble in water, and on the evaporation of its solution, either in vacuo or by heat, it solidifies to a transparent gum-like mass.
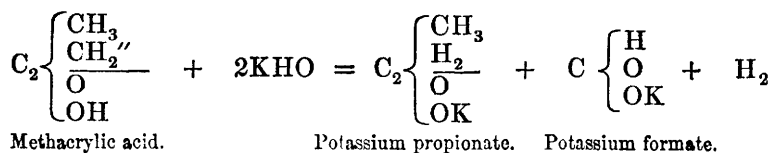
Cupric methacrylate, unlike its isomer, cupric crotonate, is tolerably soluble in water.

Action of Potassium Hydrate upon Methacrylic Acid.

When methacrylic acid is heated with excess of potassium hydrate, nearly to the temperature of boiling oil, much hydrogen is given off, and the residual mass, on distillation with dilute sulphuric acid, gives an acid distillate, which, boiled with mercuric oxide, does not reduce the latter, thus proving the absence of formic acid. The acid distillate was converted into a silver salt, and dried in vacuo. ·3163 grm. of this salt gave on analysis, ·2299 grm. carbonic acid, ·0802 grm. water, and ·1874 grm. metallic silver. The salt was therefore propionate of silver, as will be seen from the following comparison of calculated and experimental numbers :—

Calculated from $C_3H_5AgO_2$.			Found.
C_3	36	19·89	19·83
H_5	5	2·76	2·82
O_2	32	17·68	18·10
Ag	108	59·67	59·25
	181	100·00	100·00

Heated with potassium hydrate, therefore, methacrylic acid is transformed, with evolution of hydrogen, into propionic and formic acids, according to the following equation :

$$C_2 \begin{cases} CH_3 \\ CH_2'' \\ O \\ OH \end{cases} + 2KHO = C_2 \begin{cases} CH_3 \\ H_2 \\ O \\ OK \end{cases} + C \begin{cases} H \\ O \\ OK \end{cases} + H_2$$

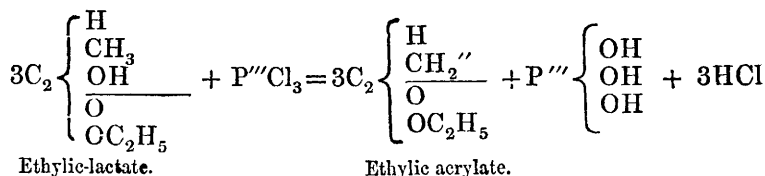Methacrylic acid.   Potassium propionate.   Potassium formate.

The absence of formic acid from the acid distillate is by no means incompatible with the foregoing explanation of the reaction, and need not create surprise, when it is remembered that this acid is readily converted into oxalic acid, with evolution of hydrogen, on being heated with potassium hydrate; and it must also be mentioned that the temperature required for this decomposition of methacrylic acid is much higher than that necessary for either ethyl or methyl-crotonic acid. Although oxalic acid is, in turn, also converted into carbonic acid, with evolution of hydrogen, by the same agent, at a more elevated temperature, still we expected to find at least traces of oxalic acid amongst the products of decomposition; but in this we were disappointed, and it therefore became necessary to examine the behaviour of formic acid itself, under the influence of an excess of potassium hydrate at the same temperature. We also simultaneously exposed oxalic acid with excess of potassium hydrate in the same bath. The latter acid was not in the least acted upon at the temperature employed for the decomposition of methacrylic acid; on the other hand, a very copious evolution of hydrogen took place from the formic acid, the residual product of which did not, however, at the conclusion of the reaction, contain a trace of oxalic acid. It is therefore evident that, at the temperature necessary for the decomposition of methacrylic acid by potassium hydrate, formic acid itself is converted at once into carbonic acid without any intermediate formation of oxalic acid.

This result of the action of potassium hydrate upon methacrylic acid proves the isomerism of the latter with crotonic acid, which yields under the same treatment acetic acid only.

Action of Terchloride of Phosphorus upon Ethylic Lactate.

If the reactions described in the foregoing pages were homologously continued to ethylic lactate, there ought to be produced ethylic acrylate, according to the following equation :—

$$3C_2 \begin{cases} H \\ CH_3 \\ \underline{OH} \\ O \\ CC_2H_5 \end{cases} + P'''Cl_3 = 3C_2 \begin{cases} H \\ CH_2'' \\ \overline{O} \\ OC_2H_5 \end{cases} + P''' \begin{cases} OH \\ OH \\ OH \end{cases} + 3HCl$$

Ethylic-lactate.   Ethylic acrylate.

There is, however, frequently a difficulty in carrying a general reaction of this nature to the extreme lower limit of the series; thus, for instance, the reactions for the production of ketones and anhydrides cannot be extended to formic acid, and we were therefore not altogether unprepared for failure, in attempting the production of acrylic from lactic ether. We find, in fact, that this reaction, sharp and definite as it is in the case of diethoxalic, ethomethoxalic, and dimethoxalic ethers, fails utterly when attempted with ethylic lactate or methydroxalate.

When terchloride of phosphorus is added to ethylic lactate, the action is even more energetic than in the former cases, and torrents of hydrochloric acid are evolved, in fact, to all appearance, the action is the same as with the other ethers of the lactic family ; but on separating and purifying the ethereal product, as before, it is found to burn with a green-fringed flame, characteristic of the presence of chlorine. Submitted to analysis, this ether gave the following results :—
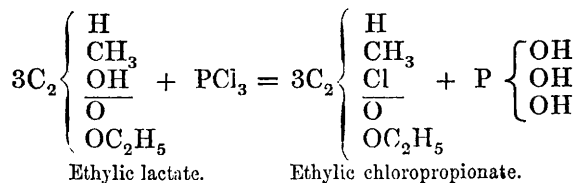
·2889 grm. gave ·4598 grm. carbonic acid and ·1736 grm. water.

These numbers agree closely with those calculated from the formula of ethylic chloropropionate, first prepared by Wurtz, from lactyl chloride and sodium ethylate, as seen from the following comparison :—

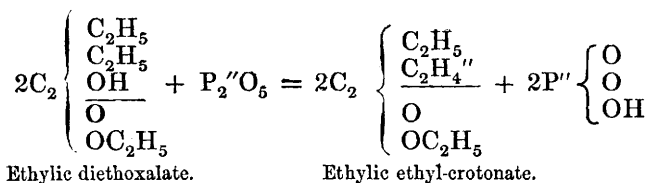|	Calculated from $C^3H^4Cl(C^2H^5)O^2$		Found.
C_5	60	43·95	43·41
H_9	9	6·59	6·68
Cl	35·5	26·01	
O_2	32·0	23·45	
	136·5	100·00	

The ether has the same boiling point (144° C.) as Wurtz's compound, and is in every respect apparently identical with it. The formation of ethylic chloro-propionate in the above reaction

is explained by the following equation, which, however, does not take cognizance of the hydrochloric acid which was evolved :—

$$3C_2 \begin{cases} H \\ CH_3 \\ \overline{OH} \\ O \\ OC_2H_5 \end{cases} + PCl_3 = 3C_2 \begin{cases} H \\ CH_3 \\ \overline{Cl} \\ O \\ OC_2H_5 \end{cases} + P \begin{cases} OH \\ OH \\ OH \end{cases}$$

Ethylic lactate.   Ethylic chloropropionate.

There can be little doubt that the single atom of hydrogen in ethylic lactate plays an important, though unknown, part in this reaction ; and it is not improbable that, in the first instance, this atom of hydrogen is removed along with peroxide of hydrogen, from the ethylic lactate, and escapes as hydrochloric acid. The exigencies of atomicity, however, require that the place of this hydrogen should be occupied by some other monatomic body : this is probably a compound of phosphorus, the presence of a considerable quantity of which in the crude ether was proved. The ultimate production of ethylic chloro-propionate may be explained on the assumption that this phosphorus compound becomes again replaced by hydrogen, during the subsequent washing of the ether. This point, however, we hope to elucidate in a future communication.

In connection with this reaction, we have to mention that phosphoric anhydride appears to dehydrate the ethers of the lactic series, in the same manner as terchloride of phosphorus. Thus ethylic dithoxalate is at once transformed into ethylic ethyl-crotonate, when it is gently heated with phosphoric anhydride, the reaction being :—
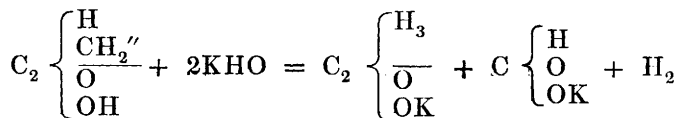
$$2C_2 \begin{cases} C_2H_5 \\ C_2H_5 \\ \overline{OH} \\ O \\ OC_2H_5 \end{cases} + P_2''O_5 = 2C_2 \begin{cases} C_2H_5 \\ C_2H_4'' \\ \overline{O} \\ OC_2H_5 \end{cases} + 2P'' \begin{cases} O \\ O \\ OH \end{cases}$$

Ethylic diethoxalate.   Ethylic ethyl-crotonate.

We are not without hopes that by the application of this re-agent to lactic ether, we shall be able to transform the latter into acrylic ether.

The Relations of the Artificial to the Natural Acids of the Acrylic Series.
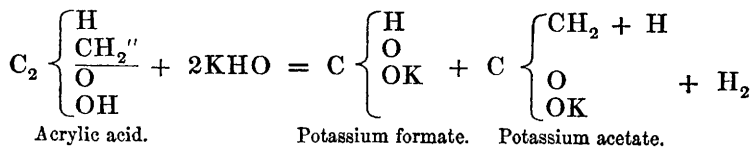
In the foregoing pages we have described the transformation of three synthesized acids of the lactic, into acids of the acrylic series. We have indicated that these transformed acids are isomeric, and not identical with certain natural acids of the same composition; but it is now necessary that we should inquire somewhat more minutely into the relations existing between the transformed and natural acids, and into the cause of their isomerism.

If the formula of acrylic acid given above be examined, it will be found that this acid must be the lowest possible term of the series, and that it is incapable of isomeric change, unless an alteration in the position of the atoms, with regard to the grouping carbon, determines such isomerism—an assumption which is at present totally unsupported by facts. It is, therefore, certain that acrylic acid is incapable of isomeric modification from a change in the composition of its constituent radicals.

By heating with potassium hydrate, acrylic acid, as is well known, yields acetic and formic acids, with evolution of hydrogen, according to the following equation :—

$$C_2 \begin{cases} H \\ CH_2'' \\ \overline{O} \\ OH \end{cases} + 2KHO = C_2 \begin{cases} H_3 \\ \overline{O} \\ OK \end{cases} + C \begin{cases} H \\ O \\ OK \end{cases} + H_2$$
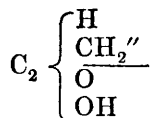
This mode of decomposition assumes the simple replacement of diatomic methylene by two atoms of hydrogen, the expelled methylene being at the same time oxidized to formic acid. But there is also another and by no means improbable mode of viewing this reaction, viz., that the molecule of acrylic acid is entirely broken up by the separation of the two dominant atoms of carbon, in fact, by a transformation of the hexatomic into the tetratomic carbon type, according to the equation :—

$$C_2 \begin{cases} H \\ CH_2'' \\ \overline{O} \\ OH \end{cases} + 2KHO = C \begin{cases} H \\ O \\ OK \end{cases} + C \begin{cases} CH_2 + H \\ \\ O \\ OK \end{cases} + H_2$$

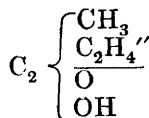Acrylic acid.　　　　　　Potassium formate.　Potassium acetate.

It is impossible to decide between these views, so long as the two radicals above the horizontal line of the formula differ by one

atom of carbon, as in the case of acrylic and methyl-crotonic acids.

$$C_2 \begin{cases} H \\ \underline{CH_2''} \\ O \\ OH \end{cases} \qquad\qquad C_2 \begin{cases} CH_3 \\ \underline{C_2H_4''} \\ O \\ OH \end{cases}$$

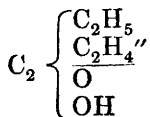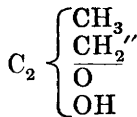<div align="center">Acrylic acid.   Methyl crotonic acid.</div>

Both these acids would exhibit with potassium hydrate exactly the same products of decomposition, no matter which view of the reaction be the correct one, acrylic acid yielding acetic and formic acids, whilst methyl-crotonic acid would give, under both schemes of decomposition, acetic and propionic acids. Fortunately, however, the behaviour of an acid in which both the radicals just alluded to contain an equal number of carbon atoms, definitely decides between the two hypotheses. Two such acids synthetically prepared, and the nature of whose atoms is therefore known, have been described above, viz., ethyl-crotonic and methacrylic acids.

$$C_2 \begin{cases} C_2H_5 \\ \underline{C_2H_4''} \\ O \\ OH \end{cases} \qquad\qquad C_2 \begin{cases} CH_3 \\ \underline{CH_2''} \\ O \\ OH \end{cases}$$
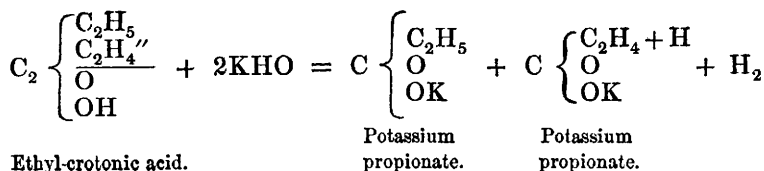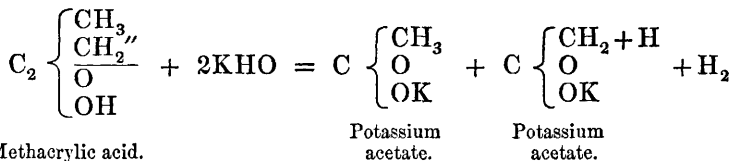
<div align="center">Ethylcrotonic acid.   Methacrylic acid.</div>

According to the view which assumes the conservation of the hexatomic type of the original acid, ethyl-crotonic acid ought to yield, by heating with potassium hydrate, butyric and acetic acids, whilst methacrylic acid should give, under like conditions, propionic and formic acids. We have already proved that these are actually the products obtained from these acids. But if the view which assumes the change from the hexatomic to the tetratomic type were correct, then ethyl-crotonic acid ought to yield two atoms of propionic acid; and in like manner methacrylic acid should give two atoms of acetic acid, according to the following equations :—

$$C_2 \begin{cases} C_2H_5 \\ \underline{C_2H_4''} \\ O \\ OH \end{cases} + 2KHO = C \begin{cases} C_2H_5 \\ O \\ OK \end{cases} + C \begin{cases} C_2H_4 + H \\ O \\ OK \end{cases} + H_2$$

<div align="center">Ethyl-crotonic acid.   Potassium   Potassium
                             propionate.   propionate.</div>

$$C_2 \begin{cases} CH_3 \\ CH_2'' \\ \overline{O} \\ OH \end{cases} + 2KHO = C \begin{cases} CH_3 \\ O \\ OK \end{cases} + C \begin{cases} CH_2+H \\ O \\ OK \end{cases} + H_2$$

Methacrylic acid.   Potassium   Potassium
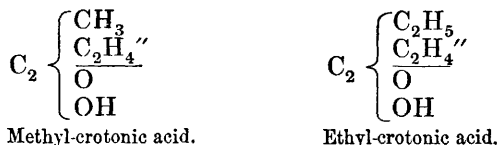   acetate.   acetate.

Having thus definitely established the nature of the reaction which takes place when the acids of the acrylic series are heated with potassium hydrate, we can now apply the information so acquired for the purpose of determining the constitution of those natural acids of this series, besides acrylic acid, whose products of decomposition have thus been determined, viz., crotonic acid, angelic acid, pyroterebic acid, and oleic acid.
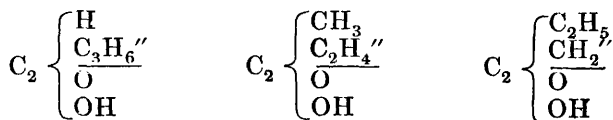
For crotonic acid the two following formulæ are alone possible :—

$$C_2 \begin{cases} H \\ C_2H_4'' \\ \overline{O} \\ OH \end{cases} \qquad\qquad C_2 \begin{cases} CH_3 \\ CH_2'' \\ \overline{O} \\ OH \end{cases}$$

and of these the first only could be made to exhibit the products of decomposition yielded by that acid when treated by potassium hydrate. Hence crotonic acid contains, as basylous radicals, hydrogen and ethylene, and hence the names which we have applied to the two homologous synthesized acids, methyl-crotonic and ethyl-crotonic acids, the products of whose decomposition by potassium hydrate prove them to contain respectively ethyl and methyl in the place of the hydrogen-radical of crotonic acid.

$$C_2 \begin{cases} CH_3 \\ C_2H_4'' \\ \overline{O} \\ OH \end{cases} \qquad\qquad C_2 \begin{cases} C_2H_5 \\ C_2H_4'' \\ \overline{O} \\ OH \end{cases}$$

Methyl-crotonic acid.   Ethyl-crotonic acid.

As we ascend the series, the number of possible metameric acids increases, and the next higher compound, angelic acid, admits of being expressed by three formulæ, viz. :—
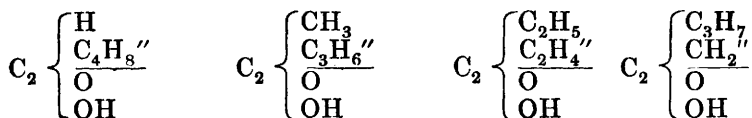
$$C_2 \begin{cases} H \\ C_3H_6'' \\ \overline{O} \\ OH \end{cases} \qquad C_2 \begin{cases} CH_3 \\ C_2H_4'' \\ \overline{O} \\ OH \end{cases} \qquad C_2 \begin{cases} C_2H_5 \\ CH_2'' \\ \overline{O} \\ OH \end{cases}$$

Of these the first only can be the rational formula of angelic acid,

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because that acid yields, when heated with potassium hydrate, propionic and acetic acids, which excludes the third of the above formulæ. The two remaining formulæ both exhibit the same results, when they are used in an equation representing the action of potassium hydrate upon this acid; but one of these formulæ, viz., the second, is known by synthesis to be that of methyl-crotonic acid, from which angelic acid differs by $17°$ C. in its melting point, the former melting at $62°$ C., whilst the latter fuses at $45°$ C.   Hence, unless unknown causes of isomerism be assumed,

$$C_2 \left\{ \begin{array}{l} H \\ \underline{C_3H_6''} \\ \underline{O} \\ OH \end{array} \right.$$
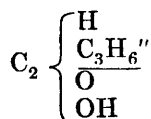
must be the rational formula of angelic acid.

Pyroterebic acid has no less than four possible formulæ, viz. :—

$$C_2 \left\{ \begin{array}{l} H \\ \underline{C_4H_8''} \\ \underline{O} \\ OH \end{array} \right. \qquad C_2 \left\{ \begin{array}{l} CH_3 \\ \underline{C_3H_6''} \\ \underline{O} \\ OH \end{array} \right. \qquad C_2 \left\{ \begin{array}{l} C_2H_5 \\ \underline{C_2H_4''} \\ \underline{O} \\ OH \end{array} \right. \quad C_2 \left\{ \begin{array}{l} C_3H_7 \\ \underline{CH_2''} \\ \underline{O} \\ OH \end{array} \right.$$

Of these the second and fourth are excluded by reason of the products of decomposition which acids of such constitution would give in the test reaction. These products would be, for the second, two atoms of propionic acid, and for the fourth, valerianic and formic acids, whilst pyroterebic acid has been proved by Chautard* to yield butyric and acetic acids.   The two remaining formulæ indicate acids both of which would give the same products of decomposition by potassium hydrate.   The third represents ethyl-crotonic acid, with which pyroterebic acid cannot be identical, since the latter is liquid at $-20°$ C., whilst the former solidifies sharply at $+39·5°$ C.

Hence the rational formula of pyroterebic acid must be—

$$C_2 \left\{ \begin{array}{l} H \\ \underline{C_4H_8''} \\ \underline{O} \\ OH \end{array} \right.$$
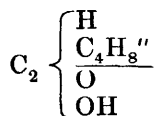
The rational formula of oleic acid cannot be determined with the same degree of certainty, owing to the want of a synthesized acid with which to compare it.   Of the sixteen possible formulæ for
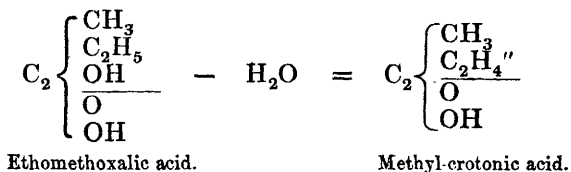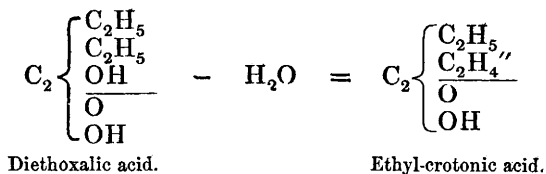
* J. Pharm. [3], xxviii, 192.

this acid (the number of possible formulæ for any acid of this series being equal to the number of constituent atoms of carbon less two) fourteen are excluded by the nature of the products of decomposition by potassium hydrate, which acids of such a constitution would yield; leaving consequently only two which can express the internal architecture of oleic acid. These are—

$$C_2 \begin{cases} H \\ \dfrac{C_{16}H''_{32}}{O} \\ OH \end{cases} \qquad\qquad C_2 \begin{cases} C_{14}H_{29} \\ \dfrac{C_2H_4''}{O} \\ OH \end{cases}$$
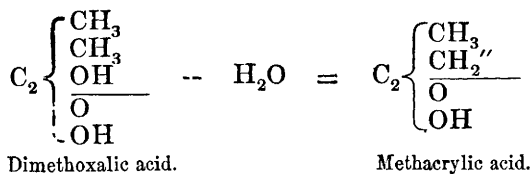
each of which expresses the composition of an acid, which, heated with potassium hydrate, would yield the same products as oleic acid, namely, acetic and palmitic acids. Further data are required to decide between these two formulæ, but from the circumstance that the remaining natural acids of this series, whose constitution is known, contain only one compound organic radical—a mode of construction which also seems to prevail in the natural acids of the lactic and acetic series—we believe that the first will eventually be found to be the rational formula of oleic acid.

The relations of the Acrylic to the Lactic Series of Acids.

The transformation of the lactic into the acrylic series of acids establishes a very simple relationship between the two series; in fact, it has been shown that the abstraction of the elements of one atom of water, from the basylous portion of an acid of the lactic family, converts that acid into the corresponding one of the acrylic family, thus—

$$C_2 \begin{cases} C_2H_5 \\ C_2H_5 \\ \underline{OH} \\ O \\ OH \end{cases} \quad - \quad H_2O \quad = \quad C_2 \begin{cases} C_2H_5 \\ C_2H_4'' \\ O \\ OH \end{cases}$$

Diethoxalic acid.   Ethyl-crotonic acid.

$$C_2 \begin{cases} CH_3 \\ C_2H_5 \\ \underline{OH} \\ O \\ OH \end{cases} \quad - \quad H_2O \quad = \quad C_2 \begin{cases} CH_3 \\ C_2H_4'' \\ O \\ OH \end{cases}$$

Ethomethoxalic acid.   Methyl-crotonic acid.

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$$C_2 \begin{cases} CH_3 \\ CH_3 \\ \underline{OH} \\ O \\ OH \end{cases} \quad -- \quad H_2O \quad = \quad C_2 \begin{cases} CH_3 \\ \underline{CH_2''} \\ O \\ OH \end{cases}$$

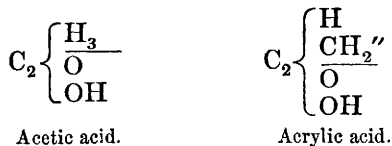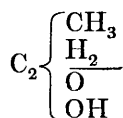Dimethoxalic acid.   Methacrylic acid.

It will be seen from these equations, that, in the passage from the one series to the other, the hexatomic carbon type is preserved, since the abstraction of one atom of hydrogen, from one of the monatomic radicals of the original acid, converts the latter into a diatomic radical, thus filling up the atomicity vacated by the withdrawal of the atom of peroxide of hydrogen.

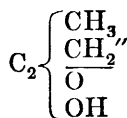### The relations of the Acrylic to the Acetic Series of Acids.

Simple as are the relations between the lactic and acrylic families, those connecting the acetic with the acrylic are even still more easily expressed. Rendered intelligible by the light which synthesis throws upon the constitution of the acrylic series, the action of potassium hydrate upon these latter acids proves, that they are derived from acids of the acetic family, by the substitution of a diatomic radical such as methylene, ethylene, &c., for two atoms of hydrogen. Thus acrylic acid is derived from acetic acid by the substitution of two atoms of hydrogen in the latter by one of methylene.

$$C_2 \begin{cases} \underline{H_3} \\ O \\ OH \end{cases} \qquad\qquad C_2 \begin{cases} H \\ \underline{CH_2''} \\ O \\ OH \end{cases}$$

Acetic acid.   Acrylic acid.

Although this transformation has not yet been realised, the inverse process is well known in the reaction of potassium hydrate upon acrylic acid, by which the latter is converted into acetic acid by the exchange of its methylene for two atoms of hydrogen. So far as the natural acids of the acrylic series have been studied, they all appear to derive from acetic acid, since they all yield this acid when heated with potassium hydrate. The artificial acids, on the other hand, all derive from acids in the acetic series higher than acetic acid. Thus methacrylic is methylene-propionic acid—
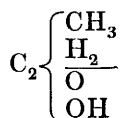
$$C_2 \begin{cases} CH_3 \\ \underline{H_2} \\ O \\ OH \end{cases}$$

Propionic acid.

$$C_2 \begin{cases} CH_3 \\ \underline{CH_2''} \\ O \\ OH \end{cases}$$

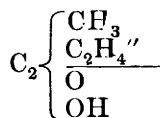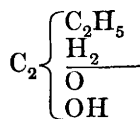Methacrylic acid.

And in like manner, methyl and ethyl crotonic acids are respectively ethylene-propionic, and ethylene-butyric acids; thus—
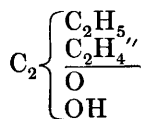
$$C_2 \begin{cases} CH_3 \\ \underline{H_2} \\ O \\ OH \end{cases}$$

Propionic acid.

$$C_2 \begin{cases} CH_3 \\ \underline{C_2H_4''} \\ O \\ OH \end{cases}$$

Methyl-crotonic acid.

$$C_2 \begin{cases} C_2H_5 \\ \underline{H_2} \\ O \\ OH \end{cases}$$

Butyric acid.

$$C_2 \begin{cases} C_2H_5 \\ \underline{C_2H_4''} \\ O \\ OH \end{cases}$$
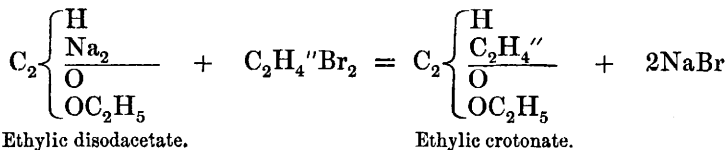
Ethyl-crotonic acid.

This extremely simple relation between the acetic and acrylic series, once pointed out, cannot fail to suggest appropriate reactions for the direct transformation of the former into the latter series. We may, in passing, suggest that the action of the haloid compounds of the diatomic radicals, upon the disodium compounds, recently described by us,* of the ethereal salts in the acetic series, could scarcely fail to effect the desired transformation. Thus dibromide of ethylene and ethylic di-sodacetate would probably yield ethylic crotonate.

$$C_2 \begin{cases} H \\ \underline{Na_2} \\ O \\ OC_2H_5 \end{cases} + C_2H_4''Br_2 = C_2 \begin{cases} H \\ \underline{C_2H_4''} \\ O \\ OC_2H_5 \end{cases} + 2NaBr$$

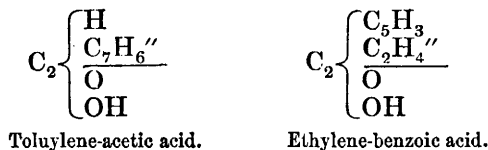Ethylic disodacetate.   Ethylic crotonate.

The nature of the change, by which acetic acid is converted into the acids of the acrylic series, suggests the existence of another family of acids, derived from acetic acid by the substitution of a triatomic radical for three atoms of hydrogen in the basylous part of acetic acid. The first acid of this series would be formyl-acetic acid with the formula—

$$C_2 \begin{cases} \underline{CH'''} \\ O \\ OH \end{cases}$$
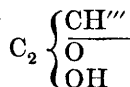
* Proceed. Roy. Soc., vol. xiv, p. 198.

The Extension of the Acrylic form of Acids to the Benzoic Series.

The close relations known to exist between the benzoic and acetic series of acids, scarcely leave a doubt that there must be a family of acids, holding the same position with regard to the benzoic series as the acrylic maintains by the side of the acetic ; in fact, the probable existence of such acids has already been pointed out by Chiozza,* who names cinnamic acid as one of the series, and proves that this acid, when treated with potassium hydrate, yields benzoic and acetic acids. This reaction, however, still leaves it undecided whether cinnamic acid is toluylene-acetic acid or ethylene-benzoic acid.

$$C_2 \begin{cases} H \\ C_7H_6'' \\ O \\ OH \end{cases} \qquad\qquad C_2 \begin{cases} C_5H_3 \\ C_2H_4'' \\ O \\ OH \end{cases}$$

Toluylene-acetic acid.   Ethylene-benzoic acid.

An acid possessing either of these formulæ would yield acetic and benzoic acids on treatment with potassium hydrate. Any method of general application for the production of the members of the acrylic family from acetic acid would, doubtless, when applied to benzoic acid, furnish an extensive benzacrylic series by the introduction of the various olefines into benzoic acid.
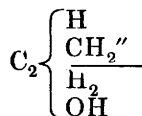
Constitution of the Allylic Series.

The obvious analogy that exists between the relations of acrylic acid and allylic alcohol on the one hand, and of acetic acid and vinic alcohol on the other, permits us to draw certain conclusions regarding the constitution of allylic alcohol, from what we now know of that of acrylic acid. If, in accordance with the notation adopted in this paper, we formulate vinic alcohol and acetic acid thus—

$$C_2 \begin{cases} H_3 \\ \overline{H_2} \\ OH \end{cases} \qquad\qquad C_2 \begin{cases} H_3 \\ O \\ OH \end{cases}$$

Alcohol.   Acetic acid.
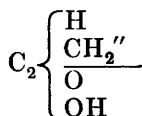
it follows that allylic alcohol and acrylic acid ought to be expressed as follows :—

* Ann. Ch. et de Phys., xxxix, 435.

$$C_2\begin{cases}H \\ CH_2'' \\ \overline{H_2} \\ OH\end{cases} \qquad C_2\begin{cases}H \\ CH_2'' \\ \overline{O} \\ OH\end{cases}$$

Allylic alcohol.   Acrylic acid.

Such a generalization must, however, be received with great caution, until the habits of allylic compounds, and especially their relation to the triatomic compounds of allyl, have been further investigated.

In conclusion, the extension of this reaction to the ethers of other acids, in which the so-called atomicity is greater than the basicity, such as malic and tartaric acids, can scarcely fail to throw light upon the constitution of these acids, and we propose further to prosecute our inquiries in this direction.

We append a table of the acids of the acrylic series already known, giving the rational formulæ, where these have been ascertained :—

Acids of the Acrylic Series.

Name.   Formula.

Acrylic acid. . . . . , ... $C_2\begin{cases}H \\ CH_2'' \\ O \\ OH\end{cases}$

Methacrylic acid . . . . $C_2\begin{cases}CH_3 \\ CH_2'' \\ O \\ OH\end{cases}$

Crotonic acid . . . . $C_2\begin{cases}H \\ C_2H_4'' \\ O \\ OH\end{cases}$

Methyl-crotonic acid . . . . $C_2\begin{cases}CH_3 \\ C_2H_4'' \\ O \\ OH\end{cases}$

Angelic acid . . . . $C_2\begin{cases}H \\ C_3H_6'' \\ O \\ OH\end{cases}$

Ethyl-crotonic acid. . . . . $C_2 \begin{cases} C_2H_5 \\ \dfrac{C_2H_4''}{O} \\ OH \end{cases}$

Pyroterebic acid. . . . . $C_2 \begin{cases} H \\ \dfrac{C_4H_8''}{O} \\ OH \end{cases}$

Damaluric acid . . . . $C_7H_{12}O_2$

Moringic acid. . . . . $C_{15}H_{28}O_2$

Physetoleic acid . . . . $C_{16}H_{30}O_2$

Oleic acid   . . . . $C_2 \begin{cases} H \\ \dfrac{C_{16}H_{32}''}{O} \\ OH \end{cases}$?

Doeglic acid . . . . $C_{19}H_{36}O_2$

Erucic acid . . . . $C_{22}H_{42}O_2.$