

CLXXIV. *On a Common Origin of the Acids  $(\text{CH})_n \text{O}_4$  with a Boiling-point under  $300^\circ$  Centigrade.* By Dr. JOSEPH REDTENBACHER. (Translated by E. F. TESCHEMACHER.)

UNDER this head I include not merely the volatile acids of butter, but also acetic acid, metacetic acid, valerianic acid, &c. ; and, in short, all those acids, according to the above formula, beginning at  $n = 4$  to  $n = 20$ , and including all the intervening members whose values are even numbers of  $n$ . These are acetic acid, metacetic acid, butyric acid, valerianic acid, caproic acid, cænanthyllic acid, caprylic acid, pelargonic acid (a new acid,  $n = 18$ ), and capric acid.

By former examinations, it is known that they occur and are formed under the most varying circumstances. They are found partly in plants and in animals, in small quantities, as mixtures of solid and fluid fats ; their more immediate origin in these cases has not yet been clearly shown. They may be produced from bodies resembling aldehyd,  $(\text{CH})_n \text{O}^2$ , by simply withdrawing the oxygen. The similar theoretical origin of acetic acid, metacetic, butyric, valerianic and cænanthyllic acids has been already proved. That the same has not been accomplished with capric, caprylic and pelargonic acids, is owing to the want of a sufficient quantity for examination. It is not probable that the origin would be found in the organism of the corresponding aldehydes. The different aldehydes by decomposition have been heretofore represented by complex atoms ; they have been produced from organic bodies, but not found in them, although the possibility cannot be denied that they may be formed by organic bodies. Another

## 236 Dr. Redtenbacher on a Class of Organic Acids.

mode of origin has been made known by Pelouze, namely the production of butyric acid by the decomposition of the hydrate of carbon, of decayed cheese, and of similar bodies; and the production of butyric acid has been detected by Marchand in sour krout and in cucumber-water; and also by Wurz in tainted meat.

Iljenko and Laskowsky, in Liebig's laboratory, have found a considerable quantity of valerianic acid in half-decayed cheese. Cheese which consists of the ingredients of the milk contains only fat and casein; the valerianic acid could only be formed out of these two ingredients. Fresh butter contains no valerianic acid; Liebig has however obtained by the action of caustic alkali on cheese valerianic and butyric acid. But these last two modes cannot be the ordinary way in which these acids exist in organic bodies. It is not especially to be referred to putrefaction or to cheese.

It is probable that nature follows a more general course in producing so great a variety of the easily volatile fatty acids. They are combined with the base lipyloxyde, the constant companion of all the fixed and volatile fatty bodies of the vegetable and animal kingdom. The different fatty bodies may be submitted to the same process by which the volatile acids are separated from butter, but in every case a very small quantity of these acids is found.

It is very possible that they proceed either from the fixed acids or from the oily acids of the fat.

The solid acids, stearic, margaric, palmitic, cocinic, myristic, contain carbon and hydrogen in the same proportions; they may merely combine with oxygen in order to be converted, in several equivalents, into acids volatile under  $300^{\circ}$  Centig.,  $(CH)_n O_4$ .

But these solid acids are in themselves permanent, and do not undergo change by exposure to the air; on the contrary, oleic acid is by the action of the oxygen of the atmosphere, and also by other oxidizable agents, a body subject to changes. According to the formula  $C_{36} H_{34} O_4$  of Gottlieb, two atoms of carbon must be given off in order that it may be converted into the acid  $(CH)_n O_4$ .

Laurent and Bromeis having examined the oxidizing action of nitric acid on the oily acids, the one considered he had found in them œnanthic acid, the other that he had found butyric acid. Tilley, by the action of nitric acid on castor oil, also produced an acid of this class; and still later, Gottlieb, by dry distillation, which is partly an oxidizing process, obtained capric and caprylic acids from oleic acid.

The foregoing considerations have induced me to study the

oxidizable products arising from the action of nitric acid upon oleic acid, but not with the view of repeating or controlling the experiments of Laurent and Bromeis: I have not occupied myself with the products which these two chemists have obtained, but only examined the volatile substances given off on oxidation by the action of nitric acid; I have discovered the before-mentioned series of acids volatile under  $300^{\circ}$  Centigrade. The oleic acid which served for my experiments was obtained from the stearine factory of this place; it is exclusively obtained from the fat of oxen. It contained some tallow and margaric acid, which did not essentially interfere with the following experiments. When pure stearine is acted upon by soda, and the solution very much concentrated, the decomposition, which is subsequently effected by an acid, gives off the smell of butyric acid; the separated oleic acid melts under  $70^{\circ}$  C., so that there remains no doubt that even the fixed acids by oxidation give off acids volatile at  $300^{\circ}$  C.,  $(\text{CH})_n \text{O}_4$ .

I made use of a very spacious tubulated retort to effect the oxidation of about 10 gallons contents, the neck of which was furnished with a cooling apparatus. 5 lbs. of the strongest brown fuming acid were poured in, and a funnel provided, whose lower opening dipped into the nitric acid. The acid was slightly warmed, and the oil carefully introduced in small portions at a time. Upon each addition of oil a violent action took place; it was necessary to wait until the previous action had subsided before any fresh addition of oil was made. The thick brown fumes condensed partly in the water of the receiver through which it passed. Sometimes drops of oil appeared on it, and the passing nitrous gas smelt strongly of volatile fatty acids. After 2 or 3 lbs. of oleic acid had been added, the further oxidation was assisted by heat. When, after long heating, a quantity of oil remains on the surface, a fresh portion of nitric acid may be added, using the same precautions as when the oil was added. In this way I have digested 3 or 4 lbs. of oleic acid for several days with nitric acid. At last I obtained, by the addition of water and redistillation, all the volatile products contained in the retort. The products of the distillation were partly saturated with potash and subjected to a fresh distillation. In the retort there remained nitrate of potash; the colourless distilled product had floating upon the surface strata of volatile fatty acids, and the easily soluble acids were dissolved in the water. The oily portion was drawn off by a siphon and neutralized by baryta water, the different acids separated by crystallization. It contained all the acids, from the valerianic to the capric. The

## 238 Dr. Redtenbacher on a Class of Organic Acids.

solution of the easily soluble acids was neutralized by carbonate of soda and evaporated to a syrup. Acetate of soda first crystallized out. The mother-liquor was decomposed by sulphuric acid, the floating oily stratum drawn off, and the acetic, metacetic and butyric acids were partly separated from one another by their boiling-points; the acetic acid and the metacetic were determined by a silver salt, and the butyric acid by a barytic salt. It may be conceived that the separation of these nine acids, possessing such similar properties, was effected with much difficulty. It is already troublesome to separate the four volatile acids of butter by means of the crystallization of the barytic salts; nearly one-third of the barytic salts remain as an inseparable mixture. The volatile acids of butter differ in the amount of the factor  $n$ , but not more than 4, while the series with which I was occupied differed only 2. The similarity of the properties of the barytic salt, or, what is the same thing, the difficulty of their separation, was therefore twice as great. I had therefore a large quantity of the mixed barytic salts which was unfit for examination; it would have been impossible to exhibit separately all the acids unless I had had 4 oz. of the mixed volatile acids.

Before I made use of the barytic salts I tried the separation of the hydrated acids by means of their boiling-point. According to recent experiments of Kopp and Fehling, it appears that the hydrated acids  $(CH_n)O_4$  increase in their boiling-point about  $20^\circ C.$  when the factor  $n$  is augmented by 2. But when I undertook the distillation, the thermometer rose so regularly from degree to degree that I soon discovered the futility of this mode of separation. A portion of the acid hydrates which came over at the boiling-points of butyric acid,  $164^\circ C.$  and about  $4^\circ$  lower, were converted into silver salts; they proved to be upon examination a mixture of three acids, —the butyric acid, the next lower, the metacetic, and the next higher, the valerianic acid. Therefore, as a complete separation could not be effected by distillation of the hydrated acids, I did not attempt the separation by means of the ethyl compounds, which would in all probability have acted in the same manner.

For the less volatile acids, from valerianic to capric acids, I had recourse to the barytic salts. By gentle evaporation and crystallization I obtained a series of about twenty crystallizations, and by means of an examination according to their known atomic weights, I was enabled to refer the separate crystallization to their different acids, and by subsequent recrystallization of the different portions to separate them

perfectly from one another, taking only the middle portion of each.

I had originally intended only to undertake the examination of the volatile acids of butter, but the form of the barytic salts led me to the expectation and to the discovery of the intervening acids. If the crystallization of the four volatile acids of butter be compared, it is found that they all crystallize in forms which are only of different sizes and differently grouped. The prisms of caprate of baryta are microscopical, and appear like fine powder. Those of caprylate of baryta are united in small grains; the groups of the caproate of baryta are much larger; and the baryta salts of the butyric acid crystallize in groups as large as hazel-nuts. The other three intervening acids, whose factor  $n$  is not divisible by 4 but by 2, crystallize in scaly clusters of a pearly lustre, as is already known to be the case with valerianic acid and cœnanthylic acid.

I will now give the analytical results of the series, beginning with the lowest. It is to be observed, that in the analysis of bodies presenting so many difficulties, the results cannot be expected to agree perfectly with the theory.

1. *Acetic Acid*.—The silver salts were formed from crystallized acetate of soda; it gave 69·19 per cent. of oxide of silver; theory requires 69·46 per cent.

2. *Metacetic Acid*.—As before mentioned, the mother-liquor, from which the acetate of soda was crystallized, was decomposed by sulphuric acid. An oily stratum was produced, which was distilled over. It began to boil at 110° C.; what came over from 120° to 140° was neutralized by ammonia and precipitated with nitrate of silver, then boiled until completely dissolved. On cooling, the silver salt was deposited in small hard grains and druses, which blackened at 100° C., and at a higher temperature fused and decomposed. It had all the other properties of metacetate of silver. 0·242 grm. dried in vacuum gave 0·144 grm. silver; and further, 0·203 grm. gave 0·1525 grm. carbonic acid and 0·057 grm. water.

		Theory.	Experiment.
6 eqs. Carbonic acid.	. . . . . 450·0	19·89	20·49
5 ... Hydrogen . . . . .	62·5	2·76	3·12
3 ... Oxygen . . . . .	300·0	13·26	12·47
1 ... Oxide of silver . . . .	1450·0	64·09	63·92
1 ... of Metacetate of silver	2262·5	100·00	100·00

3. *Butyric Acid*.—The oily acid just mentioned under metacetic acid as passing over at 140° to 164° C. was saturated with baryta and crystallized. The first two crystal-

## 240 Dr. Redtenbacher on a Class of Organic Acids.

lizations still contained valerianic acid; the third and fourth crystallizations had all the properties of butyric acid, and were again crystallized; upon analysis it gave the following result. This, as well as all the following analyses, was made with chromate of lead.

0.415 grm. butyrate of baryta gave 0.261 grm. carbonate of baryta; 0.4697 grm. of the same salt gave 0.5265 grm. carbonic acid and 0.1955 grm. water.

	Calculated.	Found.
8 eqs. Carbonic acid. . .	600.0      30.86	30.57
7 ... Hydrogen . . .	87.5      4.50	4.62
3 ... Oxygen . . .	300.0      15.43	15.95
1 ... Baryta . . .	956.9      49.21	48.86
1 ... Butyrate of barytes	1944.4      100.00	100.00

As already stated, the oily stratum which floated on the liquid in the receiver, and which contained the less soluble acids, was saturated with caustic baryta, and a series of crystallizations of the baryta salts thus produced.

4. *Valerianic Acid*.—The soluble salts below crystallized in clusters of large plates, with the known properties of valerianate of barytes.

0.268 grm. valerianate of barytes gave 0.154 grm. carbonate of barytes; 0.394 grm. gave 0.506 grm. carbonic acid and 0.1935 grm. water.

	Calculated.	Found.
10 eqs. Carbonic acid . . .	750.0      35.38	35.03
9 ... Hydrogen . . .	112.5      5.31	5.46
3 ... Oxygen . . .	300.0      14.15	14.87
1 ... Baryta . . .	956.9      45.16	44.64
1 ... Valerianate of baryta	2119.4      100.00	100.00

5. *Caproic Acid*.—The foregoing second and third crystallizations of the valerianate of baryta appeared in small semiglobular druses, which were made up of small prismatic crystals. These were now recrystallized, and had then all the appearance and properties of caproate of barytes.

0.282 grm. gave 0.149 carbonate of barytes; 0.5085 grm. gave 0.7255 carbonic acid and 0.270 grm. water.

	Calculated.	Found.
12 eqs. Carbonic acid . . .	900.0      39.22	38.92
11 ... Hydrogen . . .	137.5      5.99	5.90
3 ... Oxygen . . .	300.0      13.08	14.14
1 ... Baryta . . .	956.6      41.71	41.04
1 ... Caproate of barytes	2294.4      100.00	100.00

6. *Enanthylic Acid*.—Between the crystallization of ca-

proate of baryta and the foregoing fine granular crystals of caprylate of baryta, there appeared crystals in large plates, with a mother-of-pearl lustre, which recrystallized several times in the same form. It appeared from analogy that it could only contain an acid whose composition was between the caproic and caprylic acids, or it rather was presumed to be with certainty the œnanthylic acid discovered by Tilley. The quantity of the salt obtained was very small, only a few grammes, nevertheless it was necessary to recrystallize it in order to take only the middle portions. I obtained only about 400 milligrammes of the pure salt for examination, of which a part was used for qualitative analysis. The properties however agreed in every respect with the œnanthylate of baryta of Tilley. There remained only sufficient for the determination of the atomic weight of the salt.

0·3273 grm. œnanthylate of baryta gave 0·162 grm. carbonate of baryta; this gave œnanthylate of baryta :—

	Calculated.	Found.
Atomic weight . . . . .	2469	2489
Anhydrous acid . . . . .	1413	1413
In 100 parts,—Baryta . . .	38·73	38·45

7. *Caprylic Acid*.—The before-mentioned very small fine granular crystals from œnanthylate of baryta were decomposed by sulphuric acid; they gave out the odour of sweat, and formed the known properties of caprylic acid. I have obtained crystals of caprylate of baryta in other forms. I left a cold saturated solution of this salt for eight months in a glass vessel covered with blotting-paper to spontaneous evaporation. During this time the solution had evaporated to three-quarters of its former bulk, and at the bottom were deposited prismatic crystals, above one-quarter of an inch in length, very hard, with a waxy lustre. The atomic weight showed me that they were pure caprylate of baryta.

Of the above fine granular crystals, 0·493 grm. gave 0·229 grm. carbonate of baryta; 0·3265 grm. gave 0·545 grm. carbonic acid and 0·212 grm. water.

	Calculated.	Found.
16 eqs. Carbon . . . . .	1200·0	45·38
15 ... Hydrogen . . . . .	187·5	7·09
3 ... Oxygen . . . . .	300·0	11·35
7 ... Baryta . . . . .	956·9	36·18
1 ... Caprylate of baryta	2644·4	100·00
		100·00

8. *Pelargonic Acid*.—Between capric and caprylic acids no  
*Chem. Soc. Mem.* VOL. III.



## 242 Dr. Redtenbacher on a Class of Organic Acids.

other acid was previously known to exist. When the crystallizations of the mixed barytic salts were made, crystals of caprylate of baryta formed on the powder of the caprate. I have already mentioned in my work upon the products of the oxidation of choloidic acid, that a barytic salt in large plates, with a mother-of-pearl lustre, was formed between the caprate and caprylate of baryta, which, from its variable composition, I considered as a mixture of the two salts. But during my proposed examination I obtained between caprate and caprylate of baryta, in the third and fourth crystallizations, a salt of barytes in large plates, which remained the same after repeated crystallization; they were purified in the same manner as the other salts, by taking only the middle portions of the crystals. I consider I am not hasty, even with so imperfect a knowledge, to admit the existence of a new acid, and which analysis confirms to contain the factor  $n=18$ . I name it, upon grounds which I shall subsequently state, pelargonic acid.

Pelargonate of baryta crystallizes, as I have already stated, similarly to valerianate and cœnanthylate of baryta, but is much less soluble in water and in alcohol; it is considerably more soluble than caprate of baryta, and, as it crystallizes out before caprylate of baryta, it is therefore less soluble than this latter salt. It has properties between these two salts. In its other properties it naturally corresponds with the barytic salts of all the volatile fatty acids. It gave out at  $100^{\circ}\text{C}$ . a very small quantity of water, so that its crystals are anhydrous.

0.3395 grm. gave 0.148 grm. carbonate of baryta; 0.316 grm. gave 0.5485 grm. carbonic acid and 0.212 grm. water.

	Calculated.	Found.
18 eqs. Carbon . . . . .	1350.0	47.88
17 ... Hydrogen . . . . .	212.5	7.54
3 ... Oxygen . . . . .	300.0	10.64
1 ... Baryta . . . . .	946.9	33.94
1 ... Pelargonate of baryta	2809.4	100.00

The mother-liquor from which the above barytic salts were crystallized, and which doubtless still contained caprylic acid, as a trial of it proved, was precipitated by nitrate of silver. A white curdy precipitate fell, which was with difficulty soluble in hot water. The precipitate was dried at  $100^{\circ}\text{C}$ .

0.198 grm. pelargonate of silver gave 0.0815 grm. silver; 0.3845 grm. of the salt gave 0.5635 grm. carbonic acid and 0.219 water.



## Dr. Redtenbacher on a Class of Organic Acids. 243

		Calculated.	Found.	Pless*.
18 eqs. Carbon . . . . .	1350·0	40·75	39·98	40·88
17 ... Hydrogen . . . . .	212·5	6·42	6·33	6·46
3 ... Oxygen . . . . .	300·0	9·06	9·48	8·89
1 ... Oxide of silver . . .	1450·0	43·77	44·21	43·77
1 ... Pelargonate of silver	3312·5	100·00	100·00	100·00

A small quantity of caprylic acid contained in it decreased the carbon and the water, but increased the quantity of oxide of silver.

9. *Capric Acid*.—Of all the foregoing acids, the action of nitric acid upon the oily acids produces the smallest quantity of this acid, it being the strongest combination, and containing the smallest quantity of oxygen; and also from possessing the highest boiling-points, during the distillation with the nitric acid and water, the smallest quantity is distilled over. Having dissolved all the barytic salt in water, the first crystallization had all the appearance of caprate of baryta. The atomic weight was considerably higher than that of the pelargonate of baryta, but not so high as that of the caprate of baryta. By means of crystallization, redissolving the first-formed crystals and recrystallizing, I at last raised the atomic weight to 2950; but pure caprate of baryta possesses an atomic weight of 2990. Although I had not enough of the substance to submit it to combustion, still there is no doubt that capric acid had been formed. With this is closed the series of these volatile fatty acids, which are obtained by the action of nitric acid upon the oily acids. The largest in quantity formed are the caproic, valerianic and acetic acids; the next in quantity are caprylic, butyric and metacetic acids; and the least in quantity formed are the capric, pelargonic

\* H. Pless undertook some time ago the examination of the volatile ingredients of the plant *Pelargonium roseum*, (so called from the known scent of the rose), but could not complete it for want of sufficient material. He distilled the plant with water; the product had the scent of the plant, and an oil swam at the top. The liquid had a sour reaction. It was neutralized by baryta water, and the neutral, strongly-scented oil was distilled over. The solution evaporated to dryness contained fatty acids. It was boiled in alcohol, and the first product precipitated by nitrate of silver.

0·284 grm. gave 0·1157 grm. silver; another portion of 0·354 grm. gave 0·5305 grm. carbonic acid and 0·2058 grm. water.

The calculation of this analysis is given above under the head of Pless. This is the reason, for want of a better, that I gave it the name pelargonic acid. Respecting the properties of the hydrates of pelargonic acid, I have little to notice, as the quantity of it I possessed was too small. It is an oily, greasy acid, slightly soluble in water, but easily soluble in alcohol and æther. With regard to its other properties, as far as experiments lead, it may be considered to hold a middle place in the hydrates between the capric and caprylic acids.

## 244 Dr. Redtenbacher on a Class of Organic Acids.

and cœnanthylic acids. Before I make any further observations in connection with these acids, I will refer to a non-volatile body, which is also obtained by the oxidation of the oily acids, and which appears as a middle member that first originates from oily acids and then changes, on the one hand, into suberic and pimelic acids, and, on the other, by the presence of water into the volatile fatty acids. If the oxidation is not carried so far that the last trace of the fatty stratum in the retort does not disappear, there floats on the surface of the water on cooling an oily stratum of an unguent consistency, which, after washing with water, possesses a strong odour of sweat. This unctuous body is heavier than water, easily soluble in alcohol and æther, but not capable of being distilled over. If heated to above  $100^{\circ}$  C., a kind of combustion takes place of its elements, giving out an odour of cinnamon and nitrous acid; volatile fatty acids distil over, and the remainder becomes quite black and tough; suberic acid may be detected in it; when acted upon by an alkali it is dissolved with a blood-red colour, and can be again separated unchanged by an acid. When boiled with water in a retort it undergoes decomposition, and volatile fatty acids distil over into the receiver; suberic and pimelic acid remain dissolved in the water in the retort, and the first acid may be crystallized out. These bodies therefore appear to consist of that portion of the atom of the oily acids combined with nitrous acid which produce suberic and pimelic acids,  $(\text{CH})_n \text{O}_4$ .

As it was not possible to obtain it free from mixture, I did not submit it to any further examination. The common origin of the volatile fatty acids from the oily acids clearly accounts for the wide-spread occurrence of these with the oily acids in all fat.

As before stated, I have for many years examined, partly myself and partly by means of others, the volatile acids contained in animal fat, namely, the fat of fowls, of geese, snakes, badgers, hares, particularly human fat, and several others, and in every one, without exception, I have discovered small portions of volatile fatty acids. The most common appear to be the caprylic, caproic and valerianic acids.

Human fat, which M. Lerch very carefully examined, and in large quantities, gave, with the known margaric and oleic acids, a considerable quantity of volatile fatty acids besides caprylic acid, so that the barytic salt of the latter could be clearly established. As before stated, the weakened odour of caprylic acid brings to my mind the ordinary odour of the perspiration of a healthy man; and it is therefore probable

## Dr. Kolbe on the Formation of Nitric Acid, &amp;c. 245

that this acid passes off with the perspiration of the body after strong exercise and heating.

According to the knowledge we possess concerning the fat of plants and of animals, the combinations of the volatile and non-volatile acids are with lipyloxiide. A person the least accustomed can with ease distinguish by their smell the difference between the fat of oxen, of pigs, or of fowls, particularly when the fat is heated to the melting-point, but still the composition of them all is the same. If the fat is washed and the acids separated, it is no longer possible to distinguish between them (butter is an exception). During the washing the substances disappear which are characteristic of the different fats; they appear to have volatilized or to be decomposed. The substance to which the peculiar smell of the fat is due has not yet been isolated. It is possible that it is the corresponding lipyloxiide combination of the volatile fatty acids.

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