XVII.—*On some of the Products of Oxydation of Chinese Wax.*

By G. B. BUCKTON, Esq., F.L.S., F.C.S.

SOME years have elapsed since Gerhardt first pointed out the analogy and connection which exists between the monobasic, so called, fatty acids, and the series of bibasic acids, represented respectively by the formulæ $C_{2n}H_{2n}O_4$ and $C_{2n}H_{2n-2}O_8$.

He showed that by careful fusion with hydrate of potassa,

several members of the one series may be converted into those of the other. Thus, oxalates are well known to yield formiates by dry distillation, whilst by treatment with nitric acid, butyric and stearic acids have been proved to yield succinic acid.

More recently Dr. Hofmann has pointed out the existence of a series of similar bibasic acids which correspond to the monobasic aromatic acids. These substances are likewise produced by the action of oxydation upon the monobasic acids. The bibasic group, corresponding to the aromatic acids, is far from being complete, but the group connected with the fatty acids exhibits at present but two gaps between oxalic and sebacic acids, the terms with four and eighteen carbon being wanting.

There appeared some hope of filling these vacancies, and perhaps of extending the series by studying the action of nitric acid upon some of the fatty and waxy bodies, which have not yet been examined with this view.

Professor Brodie,* in his memoir read before the Royal Society, has already demonstrated Chinese wax to be a fatty ether, compounded of cerotic acid, with its corresponding base ceryl, $C_{54}H_{53}(C_{54}H_{55})O_4$, and that by fusion with hydrate of potash, the ceryl gives up part of its hydrogen and passes by oxydation into cerotic acid.

As therefore little new offered itself in this direction, I have in this paper wholly confined myself to a description of the products eliminated by the action of nitric acid.

The wax was broken into lumps and introduced into a capacious retort, and heated, at first gently, with from four to five times its bulk of acid, which, for this purpose, must be in a concentrated form. The strongest ordinary nitric acid of commerce has a sp. gr. of 1.39 or 1.40, and will be found sufficient for the purpose. A condensing apparatus was attached, but not in such a manner as to permit the more volatile portions to return on the wax, which would have prevented the action of the acid in its full strength. When ebullition commenced, a large quantity of red vapour passed over, and in an hour's time, the contents of the retort frothed much from the increased viscosity of the waxy stratum. After a while, the action calmed, and when the digestion had been continued for three hours, it was arrested, the distillate having been once returned to the retort during the interval.

I have found a close adherence to one mode of operation very

* Phil. Trans. Roy. Soc. 1848. Part I., p. 161.

desirable. A comparatively slight alteration in the density of the acid employed, or an increase in the time of digestion, modifies the results and eliminates products of a simpler character than those desired for study.

After agitating the contents of the retort with a moderate quantity of boiling water, the whole was poured into a beaker and set aside for twelve hours. The upper stratum, which had the consistence of tallow, was removed, and the liquid separated from the greasy flakes which were suspended, by filtration through asbestos. The acid liquid was then concentrated to about $\frac{1}{3}$ of the bulk of the nitric acid originally used, and allowed to stand for twelve hours, after the expiration of which a crust had formed upon the surface, which, when removed from the liquid, was plentifully washed with cold water. The mass was then rubbed to a paste in a mortar, and again washed until the rinsings had but a feeble acid taste.

The washings were added to the first filtrate for subsequent concentration and examination.

From a hot aqueous solution, the new substance crystallises in soft nodular masses, of a snowy whiteness, which are, however, contaminated with an oily substance, very difficult to separate by simple crystallization from water. The mass was therefore placed in paper and subjected to a screw press, and after being thoroughly dried was fused in a porcelain dish. When cold it was powdered and agitated with a little ether, which reduced the quantity, but removed the oily matter. The substance remaining on the filter was pressed and allowed to dry spontaneously. Another crystallisation from water furnished the substance pure.

The crystals are very minute, and are but slightly acid to the taste, which character is due to their little solubility in cold water. The aqueous solution easily reddens litmus paper. Hot water dissolves the acid to an almost unlimited extent, and the solution becomes densely white and semifluid on cooling.

The melting point of the dry acid was taken from two separate preparations, one of which liquefied at 114° and the other at 116° . From the fact that a minute trace of moisture depresses the melting point of suberic acid in a marked degree, I am inclined to believe the latter figure to be the most correct. When a film of the melted acid is allowed to cool under the microscope, it crystallises very distinctly and shoots into short needles in all directions. The fused mass, when cold, may be readily reduced to powder under the pestle.

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For analysis, a portion of the substance was retained at the melting point until all bubbles of air and moisture had disappeared, and then burnt with oxide of copper.

0·2015 grms. of substance gave
 0·4215 „ carbonic acid and
 0·1575 „ water

From the percentage composition is deduced the formula

$C_9H_8O_4$; or regarding the acid as bibasic,

This, therefore, represents the acid, hitherto, I believe, unknown, intermediate to suberic and sebacic acids. For comparison I annex the percentages obtained by experiment and those required by theory:—

Suberic acid.			New acid.			Sebacic acid.			
			Theory.		Experiment.				
C ₁₆	96	55·17	C ₁₈	108	57·44	57·02	C ₂₀	120	59·45
H ₁₄	14	8·04	H ₁₆	16	8·51	8·68	H ₁₈	18	8·91
O ₈	64	36·79	O ₈	64	34·05	34·30	O ₈	64	31·64
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174 100·00			188 100·00		100·00		202 100·00		

The substance under examination, when strongly heated, partly decomposes and partly sublimes in white vapours, which, although inodorous, exert a painful choking sensation in the chest when inhaled.

This property, which, however, is common to all the known acids in the oxalic series, with the exception of pyrotartaric, has suggested a name.

I propose to call the acid *Anchoic Acid*, and its salts *Anchoates*, from the Greek word $\alpha\gamma\chi\omega$, I suffocate. Apart from the varied constitution of this acid, it will be found to differ both in crystalline appearance, in its solubility in water and in ether, and also in its melting point, from either of the acids immediately preceding and following it.

The salt first analysed was the

ANCHOATE OF SILVER.

This substance is easily prepared by precipitating with nitrate of silver an aqueous solution of anchoic acid which has been previously neutralized by ammonia.

It is white and flocculent, and when dry will bear, without decomposition, a temperature of 120° . It is soluble in dilute acid, but little soluble in water. The dry salt becomes highly electrical when rubbed in a warm mortar.

I.	0.2650	gms. dried at 110° when ignited gave
	0.1415	„ of metallic silver.
II.	0.2075	„ at 120° gave
	0.1115	„ of metallic silver.
III.	0.3520	„ at 120° gave
	0.1890	„ of metallic silver.

These numbers correspond to the following percentages*—

	I.	II.	III.
Silver	53.35	53.73	53.69

and to the formula

The mean of the experiments compared with theory is:—

	Theory.		Experimental mean.
C_{18}	108	26.86	—
H_{14}	14	3.48	—
Ag_2	216	53.73	53.57
O_8	64	15.93	—
	402	100.00	

ANCHOATE OF BARIUM.

An aqueous solution of anchoic acid acts but feebly upon carbonate of barium, and the liquid can only be neutralized by a continued boiling with an excess of base. The neutral salt, however, is readily obtained by substituting hydrate of baryta. The solution, when evaporated on the water bath, forms a pellicle which is at first transparent, but becomes opaque at 100° from the loss of water. It is insoluble in alcohol and in ether, but very soluble in water.

* The percentages of silver in the two nearest allied salts are:—

	Suberate of silver.	Sebacate of silver.
Silver	55.67	51.91.

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The dry salt becomes pasty by a strong heat, but does not wholly fuse. It blackens and burns with a smoky flame, leaving a residue of carbonate of barium.

Samples from different preparations were used for analysis.

- I. 0.3920 gms. dried at 110° gave with sulphuric acid
 0.2808 „ of sulphate of barium
 II. 0.3460 „ dried at 115° gave
 0.2513 „ sulphate of barium

representing in 100 parts,

	I.	II.
Barium	42.12	42.68

the mean of which closely accords with the formula,

	Theory.		Mean of Experiment.
C_{18}	108	33.43	—
H_{14}	14	4.33	—
Ba_2	137	42.41	42.40
O_8	64	19.83	—
	323	100.00	

This solution does not exhibit definite crystals, even when concentrated and viewed by a lens.

I have not been able to prove the bibasic character of anchoic acid by an analysis of an acid barium salt. A weighed portion of acid was exactly neutralized with hydrate of baryta and added to a similar quantity of acid. The substance, however, which was obtained by evaporation, was found to give up the whole excess of acid when digested with alcohol, and the neutral salt remained alone in the filter.

This fact accords with the observation of M. Dœpping, who failed in obtaining the acid succinate of barium by a like method.

ACID ANCHOATE OF POTASSIUM.

That anchoic acid may be made to combine with either one or two equivalents of base, can be shown by the preparation of the acid potassium salt. The above process of semi-neutralization was adopted, carbonate of potassium being substituted for the barium salt, and the liquid was evaporated on the water-bath to

dryness. The crystalline residue was agitated with a small quantity of cold water, and then filtered from a few flakes of acid, which was, intentionally, in slight excess. The solution concentrated over sulphuric acid gave a colorless salt, which differed in appearance from the neutral anchoate, presenting the form of circular or tubercular grains under the microscope. They are soluble in about three parts of cold water, but exceedingly soluble in hot water. Methylated spirit also dissolves them without difficulty. They are not deliquescent, they have a cooling acid taste, and bear a temperature of 140° without change. They begin to lose their whiteness at 160° , and, when further heated, give off white fumes and burn with a smoky flame and deposit of carbon.

For analysis, the salt was calcined, and afterwards converted into chloride of potassium, by boiling with chloride of ammonium.

0.2634 gms. of substance dried at 110° gave, when ignited,
0.0895 ,, chloride of potassium

a result which accords sufficiently well with the formula

as may be seen by comparing the experimental percentage with that required by the acid and neutral salt.

Neutral anchoate of potassium.			Acid anchoate of potassium.			Experiment.
C_{18}	108	40.90	C_{18}	108	47.78	—
H_{14}	14	5.30	H_{15}	15	6.63	—
K_2	78	29.54	K	39	17.25	17.78
O_8	64	24.26	O_8	64	28.34	—
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	264	100.00		226	100.00	

The composition of the neutral anchoates is therefore represented in a general manner by the expression

and the acid anchoates by the formula

The other salts of anchoic acid are so similar in appearance and properties to the sebacates, that a few words only need be said regarding them.

Neutral anchoate of Potassium. This substance is very soluble in water. It gives on evaporation a confused crystalline mass, destitute of regular forms.

Anchoate of Ammonium is very soluble in water and in alcoholic spirit. The solid salt is amorphous and loses ammonia when gently heated.

Anchoate of Sodium is more crystalline than the potassium salt. Sulphuric acid throws down anchoic acid in a solid form, from moderately strong solutions.

Anchoate of Zinc is a white precipitate formed when sulphate of zinc is added to anchoate of potassium.

Anchoate of Copper forms a copious, blue, insoluble precipitate when a neutral anchoate is decomposed by a copper salt. Anchoic acid gives no precipitate under similar circumstances.

Anchoate of Lead. This substance appears in a white bulky form when anchoate of ammonium is treated with acetate of lead. It is quite insoluble in water, but soluble in dilute nitric acid, from which solution anchoic acid is deposited on cooling.

Anchoate of Mercurousum may be obtained by precipitating the corresponding nitrate, by either anchoic acid or any of its soluble salts.

Anchoate of Mercuricum may be obtained by adding a neutral anchoate to a solution of chloride of mercury. It forms a white and curdy precipitate.

Anchoate of Ethyl. When an alcoholic solution of anchoic acid is saturated with hydrochloric acid gas, the liquid rises in temperature and the ether is formed, together with abundance of chloride of ethyl vapour. A moderate heat drives off the excess of hydrochloric acid, and, after washing with water, the ether may be purified by rectification.

It is an unctuous liquid, with rather a pleasant odour, but hot and persistent taste.

It is almost wholly insoluble in water, upon which it floats. It readily mixes with both alcohol and ether. Its boiling point is about 325° .

EXAMINATION OF THE MOTHER LIQUID AFTER REMOVAL OF ANCHOIC ACID.

This liquid, which also contained the washings from the former acid, was evaporated so as to drive off a further portion of nitric

acid, a little water being added from time to time, and the whole being stirred to prevent the substances in solution becoming brown.*

When sufficiently concentrated, a small portion of water was added and the fluid set apart for twelve hours to crystallise. The crop of crystals was removed, washed with a little water, and after draining on a tile, was dried at a gentle heat. Traces of anchoic acid were removed by agitation with a little ether, and afterwards the substance was purified by two crystallisations from water.

The crystals, which were much larger than those obtained from anchoic acid, were also much more soluble in water. Ether, on the contrary, exhibited a less solvent action upon them. They had a strong acid taste, and the dry acid had a melting point of 126° .

0.1924	gms. of substance gave
0.3878	„ carbonic acid and
0.1420	„ water

The substance, therefore, was clearly suberic acid, the formula calculated from the percentage being

The numbers required by theory and obtained by experiment are

Suberic acid.				Experiment.
C ₁₆	96	55.17		54.93
H ₁₄	14	8.04		8.19
O ₈	64	36.79		36.88
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	174	100.00		100.00

As a check upon the foregoing analysis, a barium salt was prepared from a portion of the acid, and afterwards decomposed by sulphuric acid.

0.3235	gms. dried at 115° gave
0.2633	„ sulphate of barium.

* If the concentration be carried too far, a violent reaction sets in; red vapours are produced, and the mass, if large, is liable to take fire spontaneously.

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Suberate of barium $C_{16}H_{12}Ba_2O_8$ contains in 100 parts,

	Theory.	Experiment.
Barium . . .	44·33	44·42

There can, therefore, be no doubt that suberic acid is one of the chief products of the action of nitric acid on Chinese wax. The greater or less amount eliminated depends mainly upon the duration of the action.

EXAMINATION OF THE LIQUID AFTER THE SEPARATION OF SUBERIC ACID.

This filtrate obviously contained other substances more soluble and less crystalline than either of the two acids above described. By further evaporation and draining the mother liquor from the mass, and by subsequent pressure between paper, a crystalline substance was obtained, which was exceedingly soluble in ether and in alcohol. I could procure only a small portion in a state of purity, finding it very difficult to remove other acid bodies, which had the consistence of tallow.

The sample taken for analysis had a melting point of 110° . By combustion with oxide of copper,

0·3204	gms. of substance gave
0·6202	„ carbonic acid and
0·2226	„ water.

indicating the formula,

which is that of pimelic acid, obtained by Laurent from bees'-wax, spermaceti, and other fatty bodies.

Annexed are the percentages required by theory and found by experiment :—

	Theory.		Experiment.
C_{14}	84	52·50	52·46
H_{12}	12	7·50	7·70
O_8	64	40·00	39·84
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	160	100·00	100·00

I have not further examined the remaining acids contained in the mother liquid, since it would scarcely repay the tedium and

labour of separating them from each other. Also the fact that adipic and other lower acids have been already obtained by both Malaguti and Laurent from similar sources, made a more extended inquiry in this direction unnecessary.

I have found that no advantage is gained in preparing anchoic and similar acids by substituting cerotic acid for Chinese wax. Cerotic acid is more inert to the action of nitric acid than either cerylic alcohol or the wax itself; and I am inclined to believe that the elimination of these acids is principally due to the decomposition of the ceryl in the wax.

Experiment proves that a prolonged digestion with nitric acid, such as for twenty-four hours, resolves both Chinese wax and cerotic acid into an oily body slightly soluble in hot water. This oil does not appear to yield anchoic acid by further treatment.*

On the other hand, cerylic alcohol, $C_{54}H_{56}O_2$, produces the soluble acids of the class without difficulty.

Before dismissing this portion of the subject, a few remarks may be offered upon the melting points obtained, which, in the case of anchoic acid, is perhaps somewhat different from what we might have expected. It cannot, we think, be doubted that there is a relationship between the composition and the points of liquefaction in these bodies.

There is, however, an apparent anomaly in the various acids of the class. Thus succinic acid, with eight equivalents of carbon, melts at 180° ; adipic, with fourteen of carbon, at 145° ; suberic, with sixteen carbon, at 125° ; anchoic acid, with eighteen carbon, at 118° ; and sebacic acid, with twenty carbon, as high as 127° .

Gottlieb and Heintz† have shown that any two fatty acids may form a mixture with a melting point much lower than that of either of them in a state of purity, an observation which also applies to several alloys. Heintz‡ has even been led to believe in a sort of allotropism in stearin, from its having two constant melting points. As therefore a comparatively minute impurity varies the scale so remarkably, I think the fusing points, by themselves, can be little relied upon as a distinctive character.

* I have only slightly examined the nature of this oil. It is heavier than water and obviously is a mixture of several bodies, which decompose at a temperature below that at which they can be distilled *per se*.

† Bericht der Akad. der Wiss. zu Berlin, 1854, p. 207. Chem. Gazette, vol. xii p. 373.

‡ Poggendorff Annalen, vol. xciii. p. 431.

ON THE VOLATILE ACIDS PRESENT IN THE DISTILLATE FROM
CHINESE WAX AND NITRIC ACID.

When the red vapours which are abundantly disengaged at the commencement of the reaction are passed through a condenser, a bright emerald green liquid is obtained, upon which a few drops of a highly volatile oil float, having a pleasant odour and peculiar aromatic taste. It was too small in quantity for close examination, but as it distilled unchanged from weak potash it might have been one of the higher alcohols. The green colour of the distillate was very evanescent, and appeared to be due to traces of the oil (which Mr. Brodie states may be extracted in small quantity from Chinese wax), being acted upon by hyponitric acid. Messrs. Boudet and Fauré have shown that a variety of tints may be produced by the combination of hyponitric acid with different fatty bodies.

During the early stages, whilst little nitric acid passes over, a distinct odour of hydrocyanic acid is perceptible, but as the heat is raised it disappears, and gives place to a strong rancid smell of butyric acid. The first distillate was placed in a retort, and again distilled, until nitric acid began to pass somewhat freely. The second distillate was then filtered from a small quantity of oil which floated, and neutralized with carbonate of barium, the nitrate of barium being parted by crystallisation. The mother-liquor was carried nearly to dryness on the water-bath, and digested with alcohol, which separated a small quantity of caprylate of barium.

The two next crops of crystals which appeared from spontaneous evaporation were removed and purified by recrystallisation.

0.2528 gms. of substance gave
0.1500 „ of sulphate of barium,

proving this salt to be cenantylate of barium, the formula of which is

and requires

	Theory.	Experiment.
Barium . .	34.16	34.53

Although the number obtained is a little high, the salt cannot be confounded with that next in the series. Caprylate of barium is quite insoluble in alcohol. With dilute sulphuric acid an oil was disengaged, which was soluble in an excess of water.

The mother-liquor from the œnanthylate of barium, gave, on further evaporation, a transparent pellicle, which was also analysed. The substance was dried at 105° , and the amount of barium, estimated in the usual manner, was found to accord with that required for anhydrous butyrate of barium, within five-tenths of a per cent.

As I had plenty of the salt at my disposal, it was distilled with dilute sulphuric acid, and the acid distillate was partially neutralized with potash and again distilled. The condensed liquid which had the well known odour of butyric acid, was neutralized with ammonia and precipitated with a solution of nitrate of silver.

0.3094 gms. when ignited, gave
0.1710 „ of reduced silver.

The percentage composition is almost identical with that required by the formula

	Theory.	Experiment.
Silver in butyrate of silver . .	55.38	55.34

Lastly, the oil separated by filtration from the distillate was examined. It had all the properties of caprylic acid. It was distilled with water, the vapour of which carried over a sufficient quantity to form a silver salt.

0.4404 gms. dried in vacuo, gave
0.1890 „ of reduced silver,

which corresponds to the formula

	Theory.	Experiment.
Silver in caprylate of silver . .	43.02	42.91

I am disappointed not to be able to prove pelargonic acid to be one of the products of decomposition of Chinese wax by nitric acid. The fact that acetic acid may be transformed into oxalic acid, and butyric into succinic, would lead us to expect, that pelargonic acid, by assuming oxygen and eliminating water would similarly yield anchoic acid. The list of products, however, is by no means complete, and probably a careful separation of the fatty

mass which is insoluble in water, and which remains after digestion with nitric acid may bring it to light.

In conclusion, I may express a doubt as to pyrotartaric acid being really a member of the series $C_{2n}H_{2n-2}O_6$. From its well known constitution, several chemists have included it in the group, yet its general properties show but little accordance with those of either succinic or adipic acids between which it is placed. If we consider its different mode of production, its fluidity at so low a temperature as $10^{\circ}C.$, its volatility without decomposition, and the non-irritability of its vapour when inhaled—characters the reverse of those exhibited by the rest of the series, there is room to believe it to be only a polymeric body, and that the true term is still a desideratum.*

* M. Schlieper seems to have obtained an acid with the composition of pyrotartaric, by acting on sebacic acid with nitric acid. The reaction, however, has failed in the hand of M. Bouis, who simply obtained succinic acid.

Ann. der Chem. LXX. 121, and Gerhardt's *Traité de Chem.* vol. 2, p. 64.