PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XI.—*On the Products of Decomposition of Castor Oil*, No. I.—*Sebacic Acid, No.* 1.

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When castor oil is gently heated with sodium hydrate, the whole solidifies, after much frothing, to a soft yellowish waxy mass of sodium ricinoleate. On raising the heat, this salt melts and decomposes, an oily distillate passing over, and the residue yields sebacic acid. This acid, discovered in 1802 by Thénard, and considered identical with benzoic acid by Berzelius, an opinion corrected by Dumas and Peligot, has been examined by Bouis and Redtenbacher, the latter alone analysing the salts; and since its discovery it has been the subject of some uncertainty, owing to the varying accounts given in different researches.

The method which proved to be best adapted to yield a large amount of sebacic acid, was a modification of Schorlemmer's process for the preparation of octyl alcohol.

500 grams of sodium hydrate in fine powder was well mixed with 500 grams of castor-oil; 50 grams of water well mixed with the pasty mass; and the whole gently heated with constant stirring until it solidified to a soft waxy mass of a pale yellow colour. This was placed in a copper flask, two-thirds of a litre in capacity, in quantities of 200 grams at a time, and quickly distilled by the direct heat of a powerful Bunsen burner. The distillation was continued until dense white fumes were evolved violently, and a thick yellow green oil came over. The residue in the flask was dissolved out by hot water, and after filtration, allowed to cool.

The process of separating the sebacic acid from this solution may be advantageously varied according to its condition. If the distillation has been carried too far, and the residue partly carbonised, the resulting solution will be of a dark-greenish, almost black colour, and the first method of separating the acid will be found most satisfactory. This plan will also be found most suitable when the distillation has not been carried far enough, and the resulting solution has a pale yellow-brown colour, and froths much. If, on the other hand, the distillation has been pushed to the right stage, the solution will have a dark brown colour, the yield of sebacic acid will be greatest, and the second method of separation will give the best results with the least trouble.

First Method.—The solution, when cold, is treated directly with hydrochloric acid, and the solution well stirred. A precipitate soon forms, which is only partially re-dissolved by stirring, and the addition of hydrochloric acid is continued until the solution suddenly turns greyish-white; an indication that all the tarry matters and undecomposed ricinoleic acid have been separated. After filtration, excess of hydrochloric acid precipitates the sebacic acid from the filtrate, as a yellowish-white gelatinous mass, which is dissolved in boiling water; the small quantity of yellow oil removed by filtration; and the filtrate yields crystals of sebacic acid on cooling.

Second Method.—The solution when cold is precipitated directly by excess of hydrochloric acid, the precipitate well washed and boiled with water, the tarry matters removed by filtration, and the filtrate yields crystals of sebacic acid on cooling.

The sebacic acid, as obtained by either process, must be purified by washing and recrystallisation from boiling water. The yield is, however, small, as 1 kilogram of oil gives about 50 grams of sebacic acid at the outside.

It having been found that the volatile products of the decomposition varied both according to the proportion of alkaline hydrate used, and to the degree and duration of the temperature of distillation, the result was examined with regard to the residue in the retort, more especially as to changes in the acid which might be formed, and which had been supposed to vary by Bouis (*Compt. rend.*, xxxiii, 141).

Accordingly, twenty series of experiments were made in which the proportion of alkaline hydrate and the degree of heat used, and duration of distillation were varied, but with a result showing that sebacic acid was always formed, although partially decomposed if the heat was prolonged. On this point, therefore, the details of these experiments are unimportant.

Sebacic acid usually crystallises in a multitude of long, fine, feathery crystals, which, when dry, have a peculiar pearly lustre, or from dilute saline solution in long thin needles; but, under certain conditions, it separates from the ammonium sebates in very thin brilliant laminæ, with a peculiar bright lustre.

Soluble in 1500 parts of water at 10°; in 1000 parts at 15°; in 700 parts at 20°; in 400 parts at 40°; in 240 parts at 50°; in 130 parts at 80°; in 100 parts at 85°; and easily in 50 parts at 100°. By prolonged boiling, it is possible to dissolve it in 22 parts of water, of which 1 part in 45 remains in solution at 96°. It is readily soluble in cold alcohol and ether, easily dissolved by hot ether, and extremely soluble in hot alcohol. It crystallises from hot ether in short, transparent needles, and from hot alcohol in the same manner as from hot water.

It is readily soluble in hot nitric acid, and not decomposed by boiling therewith for a moderate time, but separates out when cold; easily soluble in hot hydrochloric acid without change, crystallising out on cooling, readily soluble in cold sulphuric acid, extremely soluble in sulphuric acid at 100°, and separates out unaltered on dilution with water; not sensibly attacked by digestion with nitrohydrochloric acid, potassium bichromate and sulphuric acid, or potassium permanganate and sulphuric acid.

Aqueous sebacic acid reddens litmus strongly, tastes acid and bitter, completely neutralises the alkaline hydrates, decomposes the carbonates of potassium, sodium, barium, strontium, and magnesium, and precipitates solutions of lead acetate and silver nitrate if dilute, but neither mercuric nor calcium chloride, nor silver nitrate if strong, but precipitates the silver-ammonio nitrate.

Even after being twice recrystallised, it is apt to retain traces of a white solid hydrocarbon melting below 100°, and a pale yellow hydrocarbon, which can be removed only by repeated recrystallisation. A trace of hydrochloric acid is also frequently retained, even after a second recrystallisation, and is also best removed by repeated crystallisation; but it is probably to this trace of retained hydrochloric acid that one or two of the discrepancies in the earlier descriptions are due.

Of the two classes of salts formed by sebacic acid in its capacity of a bibasic acid, the neutral salts would appear to be the more stable, the second class, or the acid salts, being apparently decomposed more readily, and even in some instances by prolonged boiling of their concentrated solutions. The acid salts seem to be all more or less soluble in water, and the neutral salts of the heavy metals and of calcium insoluble in water, while the rest are soluble.

After careful purification, the acid dried at 100° was analysed as under:—

1st. Taken 0·2960 gram., giving 0·2390 gram of H_2O, and 0·6502 gram of CO_2.

2nd. Taken 0·3120 gram, giving 0·2530 gram of H_2O, and 0·6800 gram of CO_2.

		Found.	
Percentage for	Theory.	I.	II.
C_{10}	59·41	58·89	59·46
H_{18}	8·91	8·98	9·01
O_4	31·68	32·13	31·53
	100·00		

Ammonium Sebates can be obtained in solution by the processes described for the potassium sebates, which they resemble in properties, but they are invariably partially decomposed, with loss of ammonia, on attempting to obtain them in the solid state, whether the evaporation is conducted *in vacuo*, at the heat of a water-bath, over sulphuric acid, or spontaneously in a current of dry air.

Potassium Hydrogen Sebate $\{K.H.C_{10}H_{16}O_4\}$ was prepared by the addition of a hot alcoholic solution of potassium hydrate to a hot alcoholic solution of sebacic acid, keeping the latter in excess; owing to its slight solubility, the salt is at once precipitated in minute crystals readily purified by washing with hot alcohol.

Thus prepared, acid potassium sebate is obtained in white, anhydrous, microscopic, short, slender needles, not deliquescent in the air, easily soluble in water, still more readily in hot water, and moderately in alcohol, yielding strongly acid solutions.

It was analysed by ignition and conversion into sulphate, giving the following results:—

Taken, 1st, 0·3260 gram; 2nd, 0·5630 gram.

		Found.	
For $K.H.C_{10}H_{16}O_4$.	Theory.	I.	II.
K per cent...	16·25	16·19	16·24

By using dilute alcoholic solutions of potassium hydrate and sebacic acid, no immediate separation of the salt takes place, but after standing the salt crystallises out in magnificent groups of large feathery crystals radiating from a small nucleus, and over an inch in length. After washing with alcohol and drying at 100°, they were analysed by the same method, with the following results:—

Taken, 1st, 0·2644 gram; 2nd, 0·2910 gram.

		Found.	
$K.H.C_{10}H_{16}O_4$.	Theory.	I.	II.
K per cent...	16·25	16·52	16·46

It was found that, unless the potassium hydrate was in excess, this acid sebate was always formed, the reaction being in this respect in notable contrast to that which takes place with sodium hydrate. Several attempts were made to obtain a pure crystalline salt from aqueous solutions, with but indifferent success, owing to the ease with which mixtures of the two sebates were formed. Prolonged boiling apparently tends to break up the acid sebate, if the solutions are concentrated, into the neutral salt and free sebacic acid, probably from the superior solubility of the neutral sebate. This, perhaps, accounts for the failure of Redtenbacher (*Ann. Pharm.*, xxxv, 188), to obtain this salt, as he used aqueous solutions of sebacic acid and potassium carbonate.

Potassium Sebate $\{K_2C_{10}H_{16}O_4\}$ was obtained by adding a hot alcoholic solution of sebacic acid to a large excess of a hot alcoholic solution of potassium hydrate, boiling well with alcohol, washing well with hot alcohol, and drying. Thus formed, potassium sebate is a white, anhydrous, crystalline powder, consisting of minute granules, non-deliquescent, readily soluble in cold, and still more soluble in hot water, but only with difficulty in alcohol, the solutions being neutral to litmus.

Analysed in the same manner as the last, it gave the following result:—

Taken 0·3228 gram.

For $K_2C_{10}H_{16}O_4$.	Theory.	Found.
K, per cent.	28·06	28·05

Sodium Hydrogen Sebate $\{Na.H.C_{10}H_{16}O_4\}$ was obtained by addition of an alcoholic solution of sodium hydrate to a large excess of a hot alcoholic solution of sebacic acid, and boiling the mixed sebates which separated out with excess of alcoholic sebacic acid. By this means a small quantity of pure acid sodium sebate was obtained, as a very finely divided semi-crystalline powder, readily soluble in water, and moderately soluble in alcohol, giving solutions with a strongly marked acid reaction. Unless care is taken, not only to have a large excess of sebacic acid present, but to boil the mixed solutions well, the resulting sebate always contains a large percentage of the neutral sebate, and consequently it is only with difficulty that the pure acid salt is obtained.

It was analysed in the same manner as the corresponding potassium salt, 0·0600 gram being taken.

For $Na.H.C_{10}H_{16}O_4$.	Theory.	Found.
Na per cent.	10·27	10·26

Sodium Sebate $\{Na_2C_{10}H_{16}O_4\}$ was obtained by mixing hot alcoholic solutions of sodium hydrate and sebacic acid, the salt then separating out at once in small crystals, which were purified by washing with hot alcohol. By this process the salt is obtained in very fine microscopic crystals, consisting of thin, broken, anhydrous needles, not deliquescent, very readily soluble in water, and slightly so in hot alcohol. It was analysed like the corresponding potassium salt.

Taken, 1st, 0·4660 gram; 2nd, 0·3865 gram.

For $Na_2C_{10}H_{16}O_4$.	Theory.	Found.	
		I.	II.
Na per cent.. .	18·70	18·73	18·21

It is to be remarked that there is a striking difference between the action of sebacic acid upon potassium and sodium hydrates under these conditions. With potassium hydrate, the neutral salt is difficult to obtain, even by the use of a large excess of the hydrate, while with sodium hydrate it is the acid salt that presents the difficulty in formation, as it is extremely liable to contain the neutral sodium sebate even in presence of large quantities of free sebacic acid.

By adding sodium hydrate to sebacic acid, both dissolved in hot alcohol, and keeping the acid in large excess, a separation of a white curdy precipitate of sodium sebate was obtained, which, on analysis, gave 16·50 per cent. of sodium, or consisted of nearly pure neutral sebate. Addition of more sodium hydrate to the filtrate threw down the pure neutral sebate.

An attempt was made to obtain the sebates in crystals from their aqueous solutions, but without satisfactory results, as even by spontaneous evaporation only a crystalline crust was obtained, a result confirmatory of the observations of Redtenbacher, who, by this method, succeeded only in obtaining granules.

Barium Hydrogen Sebate $\{Ba.H_2(C_{10}H_{16}O_4)_2\}$ was obtained by boiling barium carbonate with excess of aqueous sebacic acid, and after cooling to separate excess of sebacic acid, the filtered solution was concentrated and crystallised. Thus prepared, it is a white anhydrous confusedly crystalline salt, not deliquescent, readily soluble in water, still more soluble in hot water, giving solutions which have an acid reaction; but insoluble in alcohol, which precipitates it from its aqueous solutions. From dilute solutions it crystallises in short, thin, transparent, anhydrous needles, whereas from strong hot concentrated solutions, it separates in irregular glistening white needles and granules.

It was analysed by direct ignition and conversion into carbonate.

Taken 0·2005 gram.

$BaH_2(C_{10}H_{16}O_4)_2$.	Theory.	Found.
Ba per cent.	25·42	25·08

No sebacic acid separates, as in the potassium salt, by long boiling of concentrated solutions.

Barium Sebate $\{BaC_{10}H_{16}O_4\}$ was prepared by prolonged boiling of sebacic acid with excess of barium carbonate, and crystallised after filtration. By rapid crystallisation from concentrated solutions, it is obtained in white anhydrous crystalline crusts, easily soluble in water and forming a perfectly neutral solution, but insoluble in alcohol and ether.

Analysed as the last, it gave the following results, two different specimens being used.

Taken 1st, 0·1370 gram; 2nd, 0·1635 gram.

		Found.	
For $BaC_{10}H_{16}O_4$.	Theory.	I.	II.
Ba per cent..	40·95	40·59	40·98

Unless the solution be long boiled with excess of barium carbonate, mixtures of the two sebates are always obtained. Two specimens in which this had occurred gave 37·35, and 36·64 per cent. of barium, but by redigestion with barium carbonate, the pure salt was obtained.

Strontium Hydrogen Sebate $\{Sr.H_2(C_{10}H_{16}O_4)_2\}$ was formed in the same manner as the corresponding barium salt, and obtained in white crystalline crusts readily soluble in water to an acid solution, and nearly insoluble in alcohol.

Analysed as the barium sebates the result giving:

Taken 0·0460 gram.

For $Sr.H_2(C_{10}H_{16}O_4)_2$.	Theory.	Found.
Sr per cent.	17·87	18·21

Strontium Sebate $\{SrC_{10}H_{16}O_4\}$ was obtained, by a similar process to the neutral barium sebate, as a white granular, anhydrous crystalline powder, dissolving easily in water, and forming a neutral solution. It was analysed by direct ignition and conversion into carbonate, 0·1185 grm. being taken.

For $Sr.C_{10}H_{16}O_4$.	Theory.	Found.
Sr per cent.......	30·43	30·05

There would seem to be a tendency, noticed also with the analogous salts, to form a mixed salt approximately of the formula $Sr_3.H_2(C_{10}H_{16}O_4)_4$, which requires 24·66 per cent. of strontium, and in two separate specimens the proportion was found to be 25·53 and 25·59 per cent. Even prolonged boiling with a slight excess of sebacic acid was found to leave this percentage sensibly the same, being about from 25·00 to 25·50 per cent.

Calcium Hydrogen Sebate $\{Ca.H_2(C_{10}H_{16}O_4)_2\}$ was prepared, by addition of a hot solution of acid potassium sebate to calcium chloride solution, as a dense white precipitate, somewhat soluble in water, having an acid reaction, and partially decomposed by prolonged boiling into sebacic acid and the neutral salt.

It was analysed by direct ignition and conversion into carbonate, 0·2726 gram being taken, with the result as under:—

For $Ca.H_2(C_{10}H_{16}O_4)_2$.	Theory.	Found.
Ca per cent.......	9·05	8·94

Calcium Sebate $\{CaC_{10}H_{16}O_4\}$ was obtained by the addition of the neutral sodium sebate to calcium chloride solution, as a white, amorphous, dense precipitate. A certain amount of either sebacic acid or the last salt would appear likewise to be contained in the precipitate, and to be but partially separated by washing or digestion with hot alcohol. Analyses were made of two separate specimens with the following results:—

No. 1. Taken, 1st, 0·3620 gram; 2nd, 0·3150 gram.

		Found.	
For $Ca.C_{10}H_{16}O_4$.	Theory.	I.	II.
Ca per cent...	16·66	16·13	16·20

No. 2. Taken, 1st, 0·3470 gram; 2nd, 0·3020 gram.

		Found.	
For $Ca.C_{10}H_{16}O_4$.	Theory.	I.	II.
Ca per cent...	16·66	16·42	16·36

Magnesium Hydrogen Sebate $\{Mg.H_2(C_{10}H_{16}O_4)_2\}$ was formed by the long continued boiling of a large excess of sebacic acid with magnesium carbonate, separating the excess of acid by cooling, and after concentration nearly to dryness, allowing to crystallise. It then consists of white, anhydrous, crystalline granules, composed of aggregations of short thick needles, dissolves very easily in water, forming a solution which has a strong acid reaction; very slightly soluble in alcohol. Like the corresponding sodium salt, it appears usually to retain traces of the neutral salt.

Of the two specimens analysed, that used for analyses 1st and 2nd was prepared by the use of a very large excess of free sebacic acid; while that used for analyses 3rd and 4th, was obtained by the more prolonged boiling with a smaller excess.

Taken, 1st, 0·0005 gram; 2nd, 0·2760 gram.
3rd, 0·2475 gram; 4th, 0·3596 gram.

		Found.			
For $Mg.H_2(C_{10}H_{16}O_4)_2$.	Theory.	I.	II.	III.	IV.
Mg per cent.....	5·63	6·00	6·08	6·54	6·40

Magnesium Sebate $\{MgC_{10}H_{16}O_4\}$ was obtained in exactly the same manner as the corresponding barium salt, in thin white anhydrous crystalline crusts; dissolving easily, soluble in water to form a neutral solution, and very slightly soluble in hot alcohol. It is apt to retain a trace of the acid salt, unless the boiling be long continued with excess of the magnesium carbonate.

It was analysed by direct ignition, 0·1415 gram being taken, and gave the following result:—

For $MgC_{10}H_{16}O_4$	Theory.	Found.
Mg per cent.	10·72	10·81

As with the strontium salt, there is a tendency to form a double sebate.

Zinc Sebate $\{ZnC_{10}H_{16}O_4\}$ was prepared by precipitation of zinc sulphate with sodium sebate, as a compact heavy powder slightly soluble in water and in dilute ammonia.

Analysed by direct ignition, 0·2636 gram being taken, it gave—

For $ZnC_{10}H_{16}O_4$.	Theory.	Found.
Zn per cent.	24·34	24·26

Aluminium Hydrogen Sebate $\{Al.H_3(C_{10}H_{16}O_4)_3\}$ was prepared by precipitating a concentrated solution of alum with a solution of acid potassium sebate, and washing and drying the white curdy precipitate at 100°. Thus formed, it consists of a white friable powder, slightly soluble in cold water, easily in hot water, separating out on cooling in white anhydrous semi-crystalline scales. The solution has a marked acid reaction.

It can also be obtained by boiling freshly precipitated aluminium hydrate with excess of sebacic acid, removing the excess of sebacic acid from the salt which separates out on cooling, by means of alcohol, and drying at 100 centigrade.

The dried salt was analysed by direct ignition, 0·8090 gram being taken, and gave the result as under :—

For $Al.H_3(C_{10}H_{16}O_4)_3$.	Theory.	Found.
Al per cent.	4·54	4·78

Cobaltous Sebate $\{Co.C_{10}H_{16}O_4\}$ was formed by dissolving freshly precipitated cobaltous hydrate in aqueous sebacic acid with the aid of heat; evaporating the solution to dryness; and after digestion with boiling alcohol, drying at 100°. When thus prepared, it is obtained in vivid purple-blue thin scales, anhydrous, and sparingly soluble in cold, somewhat more easily in hot water, and forming a rose red solution. By cautious evaporation it may be obtained in thin red scales, containing water of crystallisation, but always mixed with a small quantity of the blue scales. Solutions of cobalt salts are not precipitated either by sebacic acid or by soluble sebates.

It was analysed by direct ignition and conversion into the protosesquioxide.

Taken for analysis, 1st, 0·1040 gram; 2nd, 0·1650 gram.

		Found.	
$Co.C_{10}H_{16}O_4$.	Theory.	I.	II.
Co per cent...	22·69	23·18	22·28

Nickel Sebate $\{NiC_{10}H_{16}O_4\}$ was formed by dissolving freshly precipitated nickel hydrate in hot aqueous sebacic acid, filtering, and evaporating to dryness the solution obtained, then freeing the residue from excess of sebacic acid by digesting with hot alcohol. Thus prepared, it forms pale green anhydrous crystalline crusts, soluble with some difficulty in cold water to a pale green solution, and but slightly more soluble in hot water; insoluble in alcohol. Solutions of nickel salts are not precipitated either by solution of sebacic acid, or by the alkaline sebates, even if both solutions are concentrated. It was analysed by direct ignition.

Taken for analysis 0·2360 gram.

For $Ni.C_{10}H_{16}O_4$.	Theory.	Found.
Percentage of Ni	22·62	22·15

The nickel sebate does not appear to crystallise like the cobaltous sebate with water of crystallisation.

Lead Sebate $\{Pb.C_{10}H_{16}O_4\}$ was prepared, by precipitation of lead acetate solution with sodium sebate, as a heavy white amorphous powder, insoluble in hot and cold water and alcohol, not changed by boiling with sebacic acid.

Analysed by ignition and conversion into oxide, 0·1795 gram being taken, it gave the following result:—

For $PbC_{10}H_{16}O_4$.	Theory.	Found.
Pb per cent.	50·85	50·43

Lead acetate is also precipitated by hot aqueous sebacic acid, giving a substance identical in appearance and properties with that above; but on analysis it appears that a certain amount of sebacic acid is carried down with the precipitate, as the resulting lead salt contained, according to two analyses, 49·60 and 49·71 per cent. of lead. It thus resembles the corresponding calcium salt, in which a similar result is found, and to about the same extent.

Cupric Sebate $\{Cu.C_{10}H_{16}O_4\}$ was prepared, by precipitation of cupric sulphate solution with sodium sebate, as a light emerald-green bulky precipitate, shrinking much on drying, and then forming a green light powder. It is insoluble in hot or cold water, alcohol, or in aqueous sebacic acid. By prolonged digestion with aqueous sebacic acid, it is possible to produce a solution containing the merest trace of copper. On gently heating, it melts to a dark brown transparent liquid, at once decomposed by slightly increasing the heat.

Analysed by direct ignition and conversion into oxide, it gave the following results.

Taken 1st, 0·1380 gram; 2nd, 0·2195 gram.

		Found.	
For $CuC_{10}H_{16}O_4$.	Theory.	I.	II.
Cu per cent. .	24·09	23·81	24·37

Cupric sebate is readily soluble in ammonia, forming a dark purple blue solution, which yields by spontaneous evaporation a bluish green mass containing ammonia, and possibly a cupric ammonium sebate.

Mercurous Sebate $\{Hg_2C_{10}H_{16}O_4\}$ was prepared by precipitation of mercurous nitrate with potassium sebate, washing cautiously with water and drying at 100°.

By this means it is obtained as a heavy white amorphous powder, resembling calomel in appearance; it is slightly soluble in water, both hot and cold, and very slightly soluble in alcohol.

Analysed by boiling with aqua regia to convert it into mercuric chloride, and estimated volumetrically by the ammonia and potassium cyanide process, it gave the following result:

Taken 1st, 0·05180 gram; 2nd, 0·05180 gram.

		Found.	
For $Hg_2C_{10}H_{16}O_4$.	Theory.	I.	II.
Hg per cent. ..	66·67	66·96	66·79

Mercuric Sebate $\{Hg.C_{10}H_{16}O_4\}$ was obtained from the decomposition of mercuric chloride with potassium sebate, as a white insoluble precipitate. If the acid potassium sebate is used instead of the neutral, the same salt only is obtained, the excess of sebacic acid separating out. Sebacic acid in hot aqueous solution does not precipitate mercuric chloride, the acid separating on cooling free from mercury.

Analysed directly volumetrically, it gave the following result:

Taken 1st, 0·0528 gram; 2nd, 0·0620 gram.

		Found.	
For $HgC_{10}H_{16}O_4$.	Theory.	I.	II.
Hg per cent. ..	50·00	50·19	50·22

Silver Sebate $\{Ag_2.C_{10}H_{16}O_4\}$ was formed by precipitation of potassium sebate with silver nitrate, and cautious washing of the precipitate. White powder, rapidly turning pink when exposed to the light, and readily soluble in nitric acid. Insoluble in cold water, slightly soluble in hot water, and very slightly in alcohol.

It was analysed by direct ignition, the salt fusing to a brown liquid, and decomposing somewhat energetically.

Taken 0·1060 gram.

For $Ag_2C_{10}H_{16}O_4$.	Theory.	Found.
Ag per cent.	51·92	51·53