

PROCEEDINGS
OF THE
CHEMICAL SECTION,
OF THE
FRANKLIN INSTITUTE.

[*Stated meeting, held at the institute, Tuesday, December 16, 1890.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, December 16, 1890.

Mr. T. C. Palmer, president, in the chair.

Members present: Prof. E. F. Smith, Prof. L. B. Hall, Dr. Wm. H. Wahl, Mr. Lee K. Frankel, Mr. H. Pemberton, Jr., Mr. Reuben Haines, Dr. S. C. Hooker, Prof. Henry Trimble, and several visitors.

Dr. Wahl, as chairman of the committee to prepare a circular to be addressed to the chemists of the country, reported progress, and the committee was continued. The secretary read his annual report to the section, which was accepted.

The election of officers followed, and, on motion, it was decided that the secretary cast the vote of the section for the ticket nominated at the November meeting. Dr. Wahl was escorted to the chair by the retiring president, and, on taking his seat, made a brief address appropriate to the occasion.

On motion of Dr. Hall, it was voted that the officers, president, secretary and treasurer, constitute three of the seven members of the committee on admissions.

The following gentlemen were then nominated and elected to fill the remaining vacancies in the committee, viz: Mr. H. Pemberton, Jr., Dr. S. E. Hooker, Prof. E. F. Smith, Dr. L. B. Hall.

The president appointed Messrs. Haines and Frankel to act with the secretary as members of the finance committee.

Dr. Wahl referred to the approaching convention of chemists, to be held shortly in this city, stating what had been done by the local committee to arrange for the event, and expressed the wish that the members of the section would second the efforts of the local committee to make the visitors welcome.

Dr. Greene exhibited specimens of the alloys of sodium and lead, discussed in the paper by himself and Dr. Wahl at the last meeting. They were examined with much interest.

Adjourned.

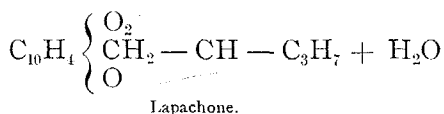
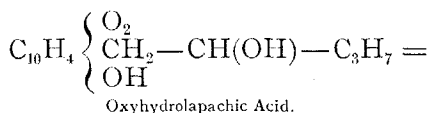
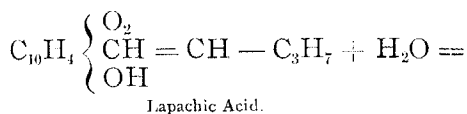
WM. C. DAY, *Secretary.*

ON SOME DERIVATIVES OF LAPACHIC ACID (I).

By SAMUEL C. HOOKER and WM. H. GREENE.

[Read before the Chemical Section, March 18, 1890.]

In a preliminary paper* published by the authors, it was shown that the conversion of lapachic acid into lapachone,† by the action of strong mineral acids, probably occurs in two stages, as indicated in the following equations:



In support of this view it was stated that lapachone can be readily converted into oxyhydrolapachic acid, and that this acid, under the influence of mineral acids, again readily passes into its anhydride lapachone.

The details of these experiments, which have not yet been printed, will be published in this paper.

CONVERSION OF LAPACHONE INTO OXYHYDROLAPACHIC ACID.

The action of aqueous potash on lapachone has been studied by Paterno,‡ who writes as follows: "In aqueous potash of medium concentration lapachone does not dissolve in the cold; on heating it passes into a fine purple-red

* This *Journal*, **128**, 142.

† *Gazz. chim. Ital.*, **12**, 372.

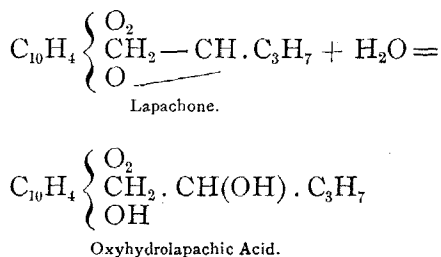
‡ *Gazz. chim. Ital.*, **12**, 372.

solution which, filtered while hot, deposits on cooling beautiful orange needles of silky lustre, recognized by their fusing point (154° – 155°) to be lapachone. On the addition of hydrochloric acid the alkaline filtrate yields a precipitate, which, purified by recrystallization, was similarly found to be lapachone."

This statement is misleading. The facts are these: Lapachone dissolves with some difficulty in hot aqueous potash, but in so doing undergoes a change. A new compound, an acid, is formed, and this, and not lapachone, exists in the solution obtained. If hydrochloric acid, in very slight excess, be added to the cold alkaline solution, the new compound separates as a yellow oil, which gradually assumes a crystalline form. If, however, a larger quantity of hydrochloric acid be employed, the color of the turbid solution is seen gradually to change. The bright yellow gives place to orange, and finally red crystals of lapachone may be observed floating in the liquid.

The new compound has, in fact, been reconverted, by the excess of hydrochloric acid employed, into lapachone. The experiment has been repeated a number of times, but the authors have not once observed the separation of crystals of lapachone from the alkaline solution as described by Paterno.

The action of potash on lapachone is shown in the following equation:



In order to prepare oxyhydrolapachic acid, eight grams of lapachone, four grams of caustic potash and 150 cc. of water are heated together. If the crystals of lapachone be large, they should be first powdered. As the lapachone is

dissolved, the color of the solution becomes very intense, being similar to that of the salts of lapachic acid.

After boiling several minutes, the solution is filtered to remove any crystals which may have escaped the action of the potash, and an excess of acetic acid is then added. A yellow oil is immediately precipitated, which collects in the bottom of beaker, and then appears considerably darker than when first seen in a fine state of division. In the course of an hour or so, it solidifies to a yellow crystalline mass which, after some hours, may be separated and washed well with water. The acid, as thus obtained, though slightly colored at the surface, is in a very pure condition and can be rendered absolutely so by crystallization once or twice from alcohol, in which it dissolves very readily and from which it separates slowly in monosymmetric crystals. The yield is theoretical; eight grams of lapachone gave 8.4 grams of the crude acid; that required by theory being 8.59 grams.

The following figures were obtained on analysis:

(I)	1.965 gram	gave	1.4970 CO ₂	and	—	H ₂ O
(II)	1.4932	"	"	1.2510 CO ₂	"	1.2743 H ₂ O
(III)	1.2093	"	"	1.5306 CO ₂	"	1.1160 H ₂ O

	I.	Found. II.	III.	Calculated for C ₁₂ H ₁₆ O ₄ .
C,	68.96	69.18	69.13	69.23
H,	lost	6.18	6.15	6.15

Oxyhydrolapachic acid melts at 125°. It is readily soluble in most of the ordinary solvents, from which it crystallizes after standing some time; if, however, the solvent be allowed to evaporate rapidly, the acid is left as a yellow oil. Under ordinary conditions it is a perfectly stable body, which can be crystallized from acetic acid unchanged; but in contact with mineral acids, even when dilute, it is readily converted into its anhydride lapachone, which was identified by its fusing point and other properties, and by analysis.

The barium salt is extremely characteristic, separating from a claret-colored solution in bright orange, silk-like needles, grouped together in wavy tufts. In order to prepare it, the acid was dissolved in a solution of baric hydrate,

from which the excess of barium was precipitated at the boiling temperature by means of carbon dioxide. The solution was then concentrated to the crystallizing point. As the evaporation proceeds, a film of the salt, in an amorphous condition, and of the *same* color as the solution, forms at the edge of the liquid, on the evaporating basin. The salt is much more soluble in hot than in cold water. After recrystallization, the orange needles gave the following figures on analysis:

(I)	2152	gram substance	gave	0744	BaSO ₄ .
(II)	2883	"	"	0987	"
(III)	2478	"	"	0854	"

	Found.			Calculated for	
	I.	II.	III.	(C ₁₅ H ₁₅ O ₄) ₂ Ba, H ₂ O.	(C ₁₅ H ₁₅ O ₄) ₂ Ba.
Ba (per cent.),	20.32	20.12	20.26	20.35	20.91

The above figures were obtained from different preparations, dried over sulphuric acid, and also at 110°.

The salt evidently contains one molecule of water of crystallization, although the attempts to determine this by loss were unsuccessful. Heated to 110° for several hours, no change in weight occurred, and decomposition commenced at somewhat higher temperatures. It was, however, observed that the orange crystals, when rubbed, became dark magenta-red, and analysis proved the altered salt, dried at 105°–110°, to be anhydrous. Under the microscope, it showed no definite structure, and when moistened with water it became immediately orange, at the same time swelling up and then passing into solution. On evaporation, the characteristic orange needles of the salt, as above described, were again obtained.

The anhydrous salt was prepared for analysis by thoroughly grinding the orange crystals, in small quantities at a time, in an agate mortar. The conversion was not easily accomplished, and it seemed as if a resinous substance were being dealt with. The ground substance was heated to 110° until constant in weight.

(I)	3368	gram substance	gave	1182	BaSO ₄ .
(II)	2834	"	"	1002	"

	Found.			Calculated for	
	I.	II.		(C ₁₅ H ₁₅ O ₄) ₂ Ba.	
Ba,	20.63 p.c.	20.78 p.c.		20.91 p.c.	

The two determinations were made with different preparations.

The calcium salt is entirely different from the barium salt just described. It separates from its solution on evaporation in small dark-red crystals, and is only very sparingly soluble in both hot and cold water. After drying over sulphuric acid, it did not lose in weight when exposed for over an hour to a temperature of 105° – 110° . Analysis shows it to be anhydrous.

(I) .3113 gram gave .0808 CaSO_4
 (II) .2594 " " .0635 "

	Found.		Calculated for ($\text{C}_{15}\text{H}_{15}\text{O}_4$) $_2\text{Ca}$.
	I.	II.	
Ca.,	7.63 p.c.	7.19 p.c.	7.16 p.c.

The preparations analyzed were different. (I) was obtained by adding the theoretical quantity of calcium chloride to the slightly ammoniacal solution of the acid; on expelling the excess of ammonia by heat, the salt separated. (II) was prepared as above described for orange variety of the barium salt.

The silver salt was obtained by precipitating a concentrated neutral solution of the ammonium salt with the calculated quantity of silver nitrate. It separates in a semi-resinous condition, becoming granular after some time. It is decidedly soluble in water, also in dilute alcohol, from which it separates, on spontaneous evaporation, in small dark-red needles. The figures it gave on analysis lie between those required for $\text{C}_{15}\text{H}_{15}\text{O}_4\text{Ag}$ and $\text{C}_{15}\text{H}_{15}\text{O}_4\text{Ag} + \text{H}_2\text{O}$. It is probable, therefore, that the compound was not obtained in a pure condition.