

This, perhaps, is the manner in which inosite is formed. Since the pinite occurring in some resins has been proven by L. Maquenne<sup>1</sup> to be the monomethyl ether of an inosite, and, as the latter, by the symmetrical splitting off of three molecules of water, yields phloroglucinol, and the former, by losing two molecules of water, yields dihydroiretol, which can be converted into iretol by the removal of two atoms of hydrogen, the general relation of iridin to the sugars is better understood.

Our thanks are due to Dr. Paul Krüger, and to Dr. Richard Schmidt, for their valuable assistance in prosecuting this investigation.

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### BOTRYTIS BASSIANA AND ITS CRYSTALLINE PRODUCTS.<sup>2</sup>

BY E. VERNON.

**A**MONG the alterations produced by *botrytis bassiana* almost all authors note an abundant crystalline efflorescence which very often covers the small mummified bodies of the muscardin worms.

M. Dandolo in note 21 of his book, "*l'Art d'élever le verif à soie*," 1814, has written on this subject as follows: "As soon as I had observed attentively the worms or muscardin chrysalides I affirmed without hesitation that all this must be the consequence of chemical attractions and combinations."

It was in fact difficult to be mistaken after having seen the animal tissue altered in this manner and converted into a substance more or less hard and unalterable while before it was an animal substance easily decomposed. I put away with care the white saline substance which enveloped the so-called muscardin worms and afterwards analyzed it. Not being satisfied with my work I asked my learned friend, M. Brugnatelli, professor of chemistry at Pavia, to make an analysis of the material.

"The muscardin which covers the mummy of the worm or the chrysalide in the cocoon is composed principally of magnesium ammonium phosphate."

A like opinion was given by M. Lomeli (*Variétés agraires*

<sup>1</sup> *Ann. chim. phys.*, [6], 22, 264.

<sup>2</sup> Read before the World's Congress of Chemists, Thursday, August 24, 1893.

*économiques et technologiques*, 3, 1835), who says: "The chemical analysis of this substance has proved to M. Dandolo and to the late Professor Brugnatelli that the efflorescence of the muscardin is a combination of magnesia, phosphoric acid, and ammonia. Professor Balsamo thinks also that the whitish efflorescence by which the worms are enclosed is entirely inorganic."

Mr. Charles Vittadini in his celebrated work, *Della natura del calcino o mal del segno* (*Journal de l' T. R. Istituto Lombardo di Sc. L. A.*, 3), expresses an entirely different opinion on this subject.

"The cadavers of the muscardin worms," he says, "after being deprived of their efflorescence and kept in a humid state become covered, after several days, with a second efflorescence which has also the appearance of a muscardin; but this is formed by myriads of fine crystals produced by the final chemical metamorphosis of the cadaver. These crystals observed by the naked eye have the form of diverging bunches of needles like a brush or of rounded masses which resemble the sea-urchin. They are transparent, colorless, or slightly reddish. The crystals dissolved in warm water show a decidedly acid reaction which becomes more sensible by evaporating the solution; on being treated with caustic potash it gives off a strong ammoniacal odor; the geometrical figure consists of long prisms with a rectangular base with cuneiform extremities."

"The reaction obtained by M. Cardoné on a small quantity of the crystals indicates a combination of alloxanic acid and ammonia with small quantities of potassium and calcium. In fact during the new process of crystallization a thick reddish liquid, generally alkaline, of a strong ammoniacal odor, flows off the cadaver of the worm and deposits a considerable quantity of crystals."

This secondary efflorescence, which takes place not only on the surface of the cadaver but extends to all the interior tissues by giving them an almost vitreous appearance, explains to a certain extent the doubt expressed by some observers that the *botrytis* is nothing else than simple crystallization.

I cite only these three authors who agree with what the literature furnishes on the nature and composition of the efflorescence

and do not mention others who have investigated the crystalline efflorescence and its different properties.

The worms mummified by the muscardin, consist always of a plentiful crystalline substance which, dispersed between all the tissues, is accumulated in considerable quantities in the inside of different parts of the somatic cavity. But it is to be remarked that the crystals do not always have the same exterior appearance; this depends on the humidity of the surrounding atmosphere. When kept perfectly dry from the beginning the crystalline substance remains inside of the cutaneous integument and consists of very fine needles which impregnate all the tissues. In an atmosphere more or less humid the cadaver when it begins to dry, exudes on the surface a dense reddish humor, which forms a crust of an earthy appearance. The microscope shows that the exuded substance notwithstanding its amorphous appearance is mostly of a crystalline nature and is not different from the substance left and dispersed between the interior viscera.

Finally, if we place the fresh cadaver in a warm place, more or less closed and saturated with moisture we will see after a certain time the crystallization in the sea-urchin forms which rupture the superficial integument. Often they are disposed without order in different parts of the body but generally are to be found in both extremities and where the visceral volume does not hinder a larger expansion of the somatic cavity.

It is to be remarked that the formation of the sea-urchin crystallizations is not limited to the time immediately following the death of the worm. I was able to obtain it from cadavers mummified some months before by placing and keeping the cadavers during some weeks in a humid warm place. By means of two needles these crystals can be removed from the cadaver like the stone from a dried fruit.

By this method I was able to provide myself with a certain quantity of material though not free from mechanical impurities and of reddish appearance. By dissolving it in warm water, filtering, and concentrating the filtrate at a moderate temperature I obtained a crystalline mass which on being redissolved, recrystallized two or three times, and separated from the mother-liquor, were obtained perfectly pure. I may remark here that

although the warm water is of a moderate temperature ( $50^{\circ}$ - $60^{\circ}$  C.) the solution of the crystals is always accompanied by the formation of very small bubbles which are probably carbon dioxide; in repeating this operation an insoluble residue always perceptible though very light is noticed. This is the reason which led us to believe that the crystals are not stable and liable to decompose even by dissolving in distilled water. That belief is fortified by the fact that I was never able to obtain the crystals in the sea-urchin form though under the microscope the crust of the second and third crystallization seemed to be composed of ordinary prisms with dihedral extremities.

The crystals of the sea-urchin form are easily soluble in distilled water and react decidedly acid. Dried and heated in a small test-tube which is covered by a piece of paper moistened with litmus solution they produce the following phenomena: without any visible change of appearance, they expel ammoniacal vapors which turn the litmus blue; by further heating they melt to an ash-colored, foamy mass, the bubbles expelling whitish vapors. On the neck of the tube small drops of a condensed liquid can be seen; in the upper part of the test-tube a ring of crystalline needles sublimes; the odor is strong and excites a cough; on the bottom remains a whitish compact residue with little carbon.

The solution obtained from the crystals does not show any change with hydrochloric and sulphuric acids; ammonium chloride, ammonia, and sodium phosphate form an abundant precipitate. Ammonium carbonate and caustic ammonia do not produce any visible reaction.

The solution remains clear on concentrating with platinum chloride or even with potassium antimoniate; calcium hydroxide sets free an abundant quantity of ammoniacal vapors. The residue left from evaporation on the salt-bath dissolved in nitric acid produces some insoluble flocks; the result is almost absolutely negative with molybdic acid.

Another portion of the liquid was treated with barium chloride and gave an abundant precipitate, soluble in hydrochloric acid; a white precipitate is obtained by treating with silver nitrate; calcium chloride gave a white precipitate on being added to the

alkaline solution; ferric chloride precipitates voluminous reddish flocks.

A portion of the solution of crystals obtained was precipitated with lead acetate; the precipitate was decomposed by hydrogen sulphide; the filtered solution after evaporating, left on the bottom rhombic prisms which, on redissolving, produced a white precipitate with calcium chloride insoluble in acetic acid. Heated in a small tube they sublime without residue, while heated with strong sulphuric acid they effervesce and evolve carbon dioxide and carbon monoxide.

Finally I investigated the residue of the calcined crystals of the sea-urchin form. This, when dissolved in hydrochloric acid, does not give any appreciable precipitate unless by adding ammonia, ammonium chloride, and sodium phosphate. After all the reactions I have mentioned above there can not be any doubt about the composition of the crystals. Not taking into consideration the impurities which can not be entirely removed and remain as undeterminable traces of potassium, phosphoric, silicic, and succinic acid, the crystals are composed mostly of *oxalic acid, ammonium, and magnesium*.

I have also determined the percentage composition of the crystals as completely as the small amount of material permitted.

I. Purified crystals, 0.0784 gram; dried at 100° C., 0.0686 gram; difference = 0.0098; equal to 12.47 per cent. Dissolving the crystals in distilled water and treating the acidified solution with calcium acetate I obtained by the regular method 0.054 gram calcium carbonate which corresponds to 0.0389 gram oxalic acid or 49.62 per cent.

II. Purified crystals, 0.2572 gram; dried at 100° C., gave 0.2243 gram; difference 0.0329, equal to 12.80 per cent. Dissolved in distilled water and treated with calcium acetate gave 0.1727 gram calcium carbonate which corresponds to 0.1243 gram oxalic acid or 48.33 per cent.

III. Purified crystals, 0.1571 gram; dried at 100° C., 0.1376 gram; treated with milk of lime (Schloesing's method). After forty-eight hours the ten cc. of normal sulphuric acid was neutralized by only 8.06 cc. of normal caustic soda or 1.94 cc. of

normal sulphuric acid was neutralized by the ammonium of the crystals, which corresponds to 22.23 per cent.

IV. Purified crystals, 0.2560 gram; dried at 100° C., left 0.2243 gram; Schloesing's method for determination of ammonium gave 0.0576 gram of ammonium, equal to 22.50 per cent.

V. Purified crystals, 0.0789 gram; dried at 100° C., left 0.0690 gram. The hydrochloric acid solution precipitated with ammonium chloride, ammonia, and sodium phosphate, gave 0.0066 magnesium pyrophosphate, equal to 0.0015 magnesium or 1.9 per cent.

After the above determinations I conclude that the sea-urchin crystals of the muscardin after being purified by repeated crystallization, contain on an average:

	Per cent.
Water .....	12.635
Oxalic acid .....	48.975
Ammonium .....	22.365
Magnesium .....	1.900
	85.875

I regret that the amount of material was not sufficient for further investigations in order to find the fourteen per cent. necessary to complete the analysis. We could then establish whether the crystals contain any water which is separated at higher temperature than 100° C. We could also determine the carbon dioxide given off while dissolving the crystals in water and ascertain from comparative analysis the products of different successive crystallizations.

Nevertheless I believe the data we possess are sufficient cause to accept in full certainty that the crystals represent a double salt of oxalate of magnesium and ammonium.

I find described in the literature five double oxalates of the following formula of constitution:<sup>1</sup>

1.  $C_2O_4Mg, 7C_2O_4(NH_4)_2 + 8H_2O.$
2.  $3(C_2O_4Mg), C_2O_4(NH_4)_2 + 2H_2O.$
3.  $C_2O_4Mg, 6C_2O_4(NH_4)_2 + 9H_2O.$
4.  $5(C_2O_4Mg), 13C_2O_4(NH_4)_2 + H_2O.$
5.  $C_2O_4Mg, 5C_2O_4(NH_4)_2 + 10H_2O.$

of which the percentage compositions are as follows:

<sup>1</sup> Souchay et Lussen, Kayser in *Poggend. Ann.*, 60.

For the first formula :—

	Per cent.
Oxalic acid.....	63.30
Magnesium.....	1.08
Ammonium.....	22.66
Water.....	12.95
	99.99

	For the Second, Per cent.	Third, Per cent.	Fourth, Per cent.	Fifth, Per cent.
Oxalic acid.....	76.52	61.23	62.26	58.66
Magnesium.....	7.82	1.19	2.36	1.33
Ammonium.....	7.82	21.47	18.40	20.00
Water.....	7.82	16.10	16.98	20.00
	99.98	99.99	100.00	99.99

Comparing the results obtained from our analysis with these figures we have to exclude without hesitation formulas 2 and 4 in which there is a considerably larger amount of magnesium than we have found. Taking into consideration the fact mentioned on the first pages of this investigation, that the crystalline spheres radiated from the muscardin worms are partly decomposed by dissolving in distilled water and the phenomena by which this decomposition is accompanied I believe there is no doubt that the essential cause of the change must be in the oxalic acid.

But as oxalic acid is rapidly diminishing the amount of ammonium and magnesium must increase in the products of each renewed crystallization.

This consideration compels me to lay aside also formulas 1 and 3 and prefer formula 5 as more nearly approaching the results obtained than any of the others.

I have already emphasized at the beginning of this work that the crystals of the sea-urchin form whose nature I have established, are only formed under certain circumstances. But if we enclose the cadaver in a warm and humid place we can on the contrary determine their development at our will.

It seems to me that this fact authorizes us to make a very interesting conjecture; namely, that the immediate action of the *botrytis* is limited to the production of oxalic acid. This remains principally free, being combined generally with very small quantities of lime and magnesia.

But if the surrounding circumstances produce the putrefaction of the cadaver and the development of ammonia, ammonium

oxalate is formed at the same time, which dissolves a certain amount of magnesium oxalate forming the double oxalate; only it then forms that peculiar crystallization to which we wished to confine our attention.

It is very remarkable that *botrytis bassiana* cultivated on nutritive gelatine produces oxalic acid in large quantities which I have separated in a crystalline form.

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## CLOSING ADDRESS DELIVERED BEFORE THE WORLD'S CONGRESS OF CHEMISTS, AUGUST 26, 1893.

BY ALBERT B. PRESCOTT.

I N this closing hour of the Congress the chair would congratulate its members upon the great interest and value of its transactions. In the wide attendance of European and American chemists, in the weight of the papers in the several divisions of chemical science, in the constant and increasing attendance through the sessions of six crowded days, and in the hearty spirit of brotherly sympathy which has given life and happiness to all our labors, we have been favored beyond the most sanguine expectations. We in the United States know the chemists of Europe better than we did before this Congress. Surely we have the best of encouragement for the union of the chemists of the world in a series of great meetings of profit and acquaintance, the first one of which is now being concluded.

I know that I voice the sentiment of every member when I give our united thanks to those whose active and untiring exertions have carried so well all the arrangements of this meeting. Our thanks are due, first, to the American Chemical Society, who instituted the call for the Congress and now opens its journal to our proceedings. To our general chairman of the joint committee, Professor Wiley, of the United States Department of Agriculture, we have been indebted for most efficient attention in details. He took the position when it was not easy to find one to accept its labors and to face its uncertainties. The chairman of the committee on papers, Professor William McMurtrie, and assuredly the chairman of the committee from the Congress Auxiliary, Professor John H. Long, the local