exposure to air. The distilled liquid had a marked odor of oil of lemons and this with its rotation suggest that it must be identical with the product described by Berthelot as iso-terebenthene, which may be obtained also from the laevo-rotatory French oil. While the ordinary product of long heating of turpentine-oil seems to be inactive dipentene we have here a very stable active product which is probably mainly laevo-limonene.

CHICAGO, October 22, 1894.

IRIDIN, THE GLUCOSIDE OF THE IRIS ROOT.

BY G. DE LAIRE AND FERD. TIEMANN.

[TRANSLATED AND ABRIDGED BY S. S. EMERY.]

(Continued from Page 411 of Volume XV.)

Iretol.—Iretol, the third decomposition product of irigenin, may be separated from the alkaline solution of the three by supersaturating with dilute sulphuric acid (1 : 2), neutralizing with potassium carbonate, and, after filtering from the separated potassium sulphate, shaking ten to twelve times with ether, which dissolves only the iretol. The ether can not be completely distilled from this extract, as the crude iretol forms condensation products which are insoluble in water and ether; hence the last portion of the ether must be allowed to evaporate in the air. The iretol thus obtained is a crystalline mass, easily soluble in water, alcohol, ether, and acetic ether. By fractional precipitation by chloroform from the acetic ether solution it is obtained as white needles, melting at 186°.

Its molecular weight was found to be:

1. By the lowering of the freezing-point of a glacial acetic acid solution. (Raoult's method.)	2. By the raising of the boiling-point of an alcoholic solution.	Calculated for $C_7H_8O_4$.
181.2	159	156

It contains one methoxyl group, as shown by the following determinations:

ANALYSIS.

	Per cent. (OCH_3).
Calculated for $C_6H_5O_3(OCH_3)$	19.87
Found	17.26—19.22

Tribenzoyliretol, $C_7H_6O_4(CO.C_6H_5)_3$. — Tribenzoyliretol is obtained by treating an absolute alcohol solution of one molecule of iretol and three molecules of sodium ethylate with a slight excess of benzoyl chloride and letting stand several days in the cold. It is separated by removing the alcohol by steam, extracting with ether, and, after shaking with dilute soda solution, evaporating, when it is obtained as an oily substance, which solidifies after several weeks to a transparent resin, easily soluble in alcohol, ether, acetic ether, benzene and chloroform, but insoluble in water and ligroin.

ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated for $C_{28}H_{20}O_7$	71.79	4.27
Found	71.03	4.68

From the foregoing, it is evident that iretol contains one methoxyl and three hydroxyl groups, and that its empirical formula is $C_6H_2(OCH_3)(OH)_3$, according to which iretol appears to be the monomethyl ether of a tetroxybenzene. The correctness of this view is established by the conversion of iretol into phloroglucinol.

This is accomplished by treating the cold dilute (1 : 10) aqueous solution with sodium amalgam, and, after destroying the excess of amalgam by heating on the water-bath, adding a slight excess of sulphuric acid and then distilling. The distillate consists of very dilute methyl alcohol with traces of acetone. The ether extraction of the residue, on evaporating, gave pure phloroglucinol, melting at 208°, its identity being established by the following:

ANALYSIS.

	Per cent. water of crystallization.
Calculated for $C_6H_6O_3.2H_2O$	22.22
Found	22.38, 22.92

	Per cent. C.	Per cent. H.	
Calculated for $C_6H_6O_3$	56.98	4.76	In the anhydrous phloroglucinol.
Found	59.94, 56.71	4.64, 4.70	

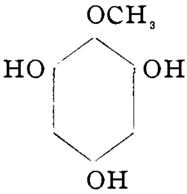
	Molecular weight.
Calculated	126
Found (raising of boiling-point of alcoholic solution)	121

The triacetyl derivative formed from the phloroglucinol melted at 106° (104°–106° according to Hlasiwetz[1] and Herzig[2]). Finally, we prepared tribenzoylphloroglucinol $C_6H_3(OCOC_6H_5)_3$, crystallizing from alcohol and melting at 172°.

ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated for $C_{27}H_{18}O_6$	73.97	4 11
Found	73.40	4.10

The phloroglucinol is formed from the iretol according to the equation $C_7H_8O_4 + 2H = C_6H_6O_3 + CH_3OH$, from which it is evident that iretol is a methoxyphloroglucinol, having the constitutional formula



Properties and Reactions of Iretol:—Melts at 186°; easily soluble in water.

(*a*) *In Aqueous Solution.*—Violet color, changing to brownish red, with ferric chloride.

Red precipitate of benzeneazoiretol with anilin nitrate, sodium nitrite, and a few drops of strong acid.

(*b*) *In Alcoholic Solution.*—A white, crystalline condensation product with a solution of benzaldehyde in six times its volume of concentrated hydrochloric acid. Substitution of vanallin for benzaldehyde gives violet-colored solution before precipitation.

The last three tests are characteristic, although also given by resorcinol and phloroglucinol.

(*c*) *With Bromine.*—In ethereal solution, gives bromine substitution products.

In ethereal solution in the presence of water gives hexabromacetone, $Br_3C.CO.CBr_3$.

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[1] *Liebig's Annalen*, 119, 201.

[2] *Wiener Monatshefte für Chemie*, 6, 838.

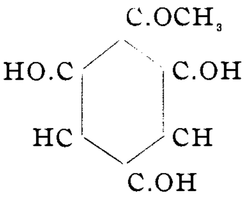
Bromine in caustic alkali, instead of free, gives bromoform, the hexabromacetone first formed being readily decomposed by the alkali into carbon dioxide and bromoform.

Sodium nitrite, with acetic acid in slight excess, converts it into the sodium salt of dinitrosoiretol, $C_7H_3NaN_2O_5.2H_2O$, separating in red crystals.

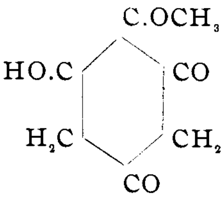
Tetroxybenzene 1.2.3.5.—The methyl in the methoxyl group of iretol can be easily replaced by hydrogen, by heating with dilute hydrochloric acid in a closed tube. Monochlormethane is given off. After removing the hydrochloric acid with lead and silver carbonate, and the water by evaporation in a partial vacuum, the tetroxybenzene was obtained as an amorphous substance, soluble in water, alcohol, ether, acetic ether, but insoluble in benzene, chloroform, and ligroin.

Isomerism of Iretol.—The properties and reactions of iretol, and also the difficulty in obtaining pure the corresponding tetroxybenzene, are explained by its isomerism, its two forms being

I.



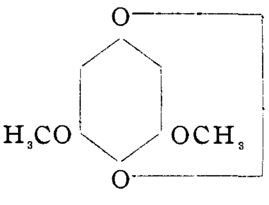
II.



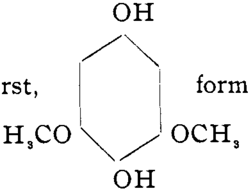
Form II undergoes hydrolysis on treating with alkali, acetone, and acetic acid being found.

This isomerism is substantiated by the following :

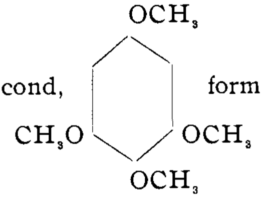
Methyl Derivatives of Iretol.—Tetroxybenzene yields a di- and tetra-methyl ether, prepared from the dimethoxyquinol



the first,



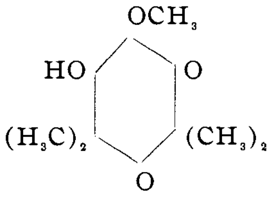
formed by reduction of the quinol, and the second,



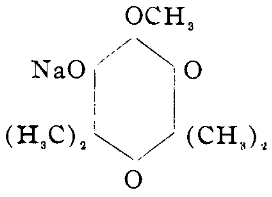
formed by methylating the dimethyl product.

We have not succeeded in preparing this last from iretol.

Tetramethyliretol



is prepared by treating the methyl alcohol solution of iretol (five grams) in an atmosphere of hydrogen, with sodium (three grams) dissolved in methyl alcohol, and with iodomethane (twenty grams). The methylation is induced by shaking the flask, and is accompanied by a rise of temperature. The sodium salt of tetramethyliretol is separated by evaporating and precipitating with concentrated caustic soda. The yield is about one-third of the theoretical, the remainder of the iretol being converted into oily methyl derivatives. The salt crystallizes in long white needles, with three molecules of water, and suffers efflorescence, at ordinary temperatures, in a partial vacuum. Its constitutional formula is



ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. Na.	Per cent. H_2O.	Per cent. OCH_3.
Calculated for $C_{11}H_{15}NaO_4.3H_2O$ $(=C_{11}H_{21}NaO_7)$..	45.83	7.29	7.98	18.75	10.76
Found	45.57, 45.50	6.94, 6.99	7.76, 7.75	18.82, 18.20	10.74
In the anhydrous salt:					
Calculated for $C_{11}H_{15}NaO_4$	56.41	6.41	9.83		
Found............	56.55, 56.04	7.17, 7.18	9.70		

Sulphuric acid liberates free tetramethyliretol, insoluble in ligroin, but soluble in hot water, alcohol, ether, acetic ether, benzene, and chloroform. It crystallizes in glistening white needles, with one molecule of water, melting at 97°; effloresces in a partial vacuum, the anhydrous substance melting at 104°.

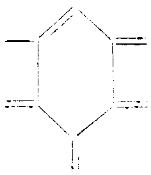
ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. H_2O.
Calculated for $C_{11}H_{16}O_4.H_2O,(=C_{11}H_{18}O_5)$.....	57.39	7.83	7.83
Found	56.98	7.86	8.06
In the anhydrous substance:			
Calculated for $C_{11}H_{16}O_4$.....................	62.27	7.55	
Found	62.41	7.51	

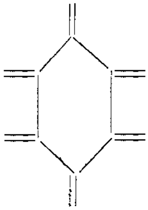
Benzoyltetramethyliretol, $C_{11}H_{15}(COC_6H_5)O_4$, formed by the action of benzoylchloride on the sodium salt of tetramethyliretol in alcoholic solution, crystallizes therefrom in white tablets, melting at 84°.

From the constitutional formula of tetramethyliretol (page 851), it is evident that by oxidation it breaks up into dimethylmalonic acid, isobutyric acid, and formic acid. By fusion with caustic potash, these products were actually obtained.

Dihydrotetramethyliretol.—Tetramethyliretol is a derivative of tetrahydrobenzene.



On treating with sodium amalgam, at ordinary temperature, it takes up two atoms of hydrogen, apparently passing into the hexahydrobenzene form

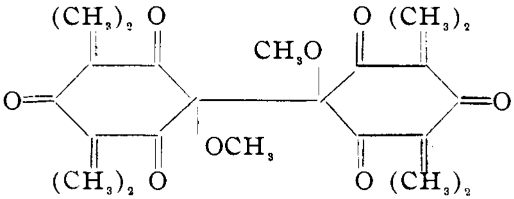


and this view is substantiated by the conversion of iretol into phloroglucinol. After destroying the excess of amalgam by heating on a water-bath, the sodium salt of dihydrotetramethyliretol may be crystallized out, or the free dihydrotetramethyliretol may be obtained by acidifying before crystallizing, when it forms transparent, rhombohedral crystals, containing one molecule of water, which is slowly given off on standing in a partial vacuum. The crystallized substance melts at 107°, the anhydrous at 139°. It is easily soluble in water, alcohol, ether and chloroform, and is precipitated from the latter by ligroin. It is not attacked by bromine nor permanganate, and, in general, does not differ widely from the tetramethyliretol.

ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated for $C_{11}H_{18}O_4.H_2O$	56.90	8.62
Found	56.90	8.67
In the anhydrous substance:		
Calculated for $C_{11}H_{18}O_4$	61.68	8.41
Found	61.71	8.72

Dehydroditetramethyliretol, $C_{22}H_{30}O_8$.—

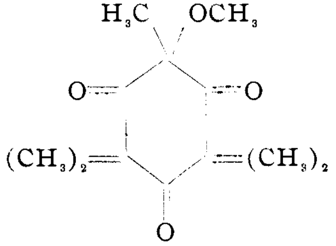


This is formed by the action of ferric chloride on the aqueous solution of sodium tetramethyliretol, two molecules, of which unite, each losing one atom of hydrogen. The precipitation is attended with a change of color of the solution into deep violet, passing into olive-brown, and finally clear green. It forms white needles, melting at 133°, easily soluble in alcohol, ether, benzene, and chloroform, but insoluble in water. It is very stable, having, in general, the properties of a saturated compound.

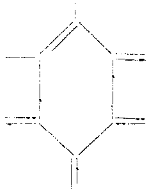
ANALYSIS.

	Per cent. C.	Per cent. H.	Molecular weight.
Calculated for $C_{22}H_{30}O_8$	62.64	7.11	422
Found	62.49	7.14	367

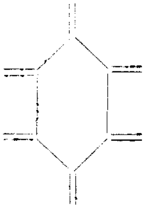
Pentamethyliretol, $C_{12}H_{18}O_4$.—



This is formed by further methylation of the sodium tetramethyliretol by means of methyl iodide. According to this, it is a derivative of tetrahydrobenzene,



and not of hexahydrobenzene.



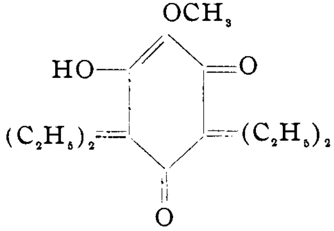
As it has, in general, the properties of a saturated compound, it was thought that rearrangement of the atoms in the molecule of the tetramethyliretol must have taken place in the above process, and this is proved by the methoxyl determination, which shows the presence of but one methoxyl group.

ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. OCH_3.	Molecular weight.
Calculated for $C_{11}H_5(OCH_3)O_3$	63.72	7.97	13.72	226
Found	63.62	7.98	13.63	190

It crystallizes from a methyl alcohol solution in long white needles, melting at 62°, boiling at 240°, and slowly subliming at ordinary temperatures.

Tetraethyliretol, $C_{16}H_{24}O_4$.—



This was prepared similarly to the corresponding methyl compound. That its constitutional formula is analogous to the latter is shown by the methoxyl determination in the following

ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. OCH_3.
Calculated for $C_{14}H_{21}(OCH_3)O_3$	67.16	8.95	11.57
Found	67.21	9.19	13.81

Its sodium salt being somewhat soluble in caustic soda, it is difficult to isolate from the other products of the reaction, but it may be accomplished by first removing them with ether, when it may be crystallized from the chloroform and acetic ether extraction of the residue by precipitating with ligroin. It forms white, anhydrous prisms, melting at 168°–169°.

Analogous to the trimethylether of phloroglucinol,

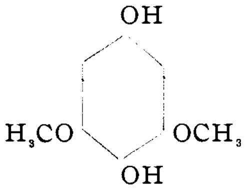
$$C_6H_3(OCH_3.1.3.5)_3$$

(prepared by saturating the methyl alcohol solution of phloroglucinol with hydrochloric acid gas, and then further methylating the dimethyl product thus formed by using methyl iodide in alkaline solution), we have attempted to prepare the trimethylether of iretol, the tetramethylether of asymmetrical tetroxybenzene, but as yet, without success.

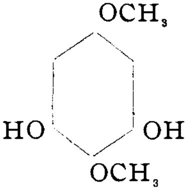
Monomethyliretol, $C_6H_2(OCH_3)_2(OH)_2$.—This is the dimethylether of asymmetrical tetroxybenzene. It is formed by the action of hydrochloric acid gas on the methyl alcohol solution of iretol at 0°. When freshly prepared it is of oily appearance but slowly solidifies to a crystalline mass. When crystallized from boiling benzene it forms white tablets, melting at 87°, easily soluble in water, alcohol, and ether, but less soluble in benzene and chloroform.

It may be further methylated by the action of methyl iodide on its sodium salt, but instead of obtaining thus a normal asymmetrical tetroxybenzene ether, polymethyl derivatives of methyliretol result, since the methylation takes place in the benzene ring.

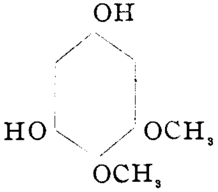
The dimethylether,



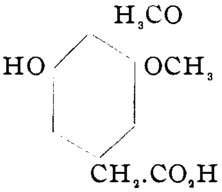
prepared from the unsymmetrical tetroxybenzene differs completely from the monomethyl iretol. Hence, the latter conforms to one of the two formulas:



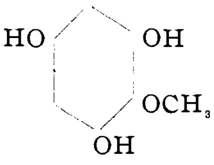
or



Constitution of Irigenin and Iridin.—Irigenin has the formula $C_{15}H_{16}O_8$. By hydrolysis it takes up three molecules of water and breaks up into



CH_2O_2 and



Iridinic acid. Formic acid. Iretol.

Iridin, also, can undergo hydrolysis.

The presence of two phenol groups in irigenin is demonstrated by the formation of the dibenzoylirigenin and the diacetylirigenin; the unstability of diacetyl derivative relative to the monoacetyl derivative, indicates that these phenol groups are not similarly situated in the irigenin molecule.

We have not yet been able to crystallize the hydrolyzed irigenin, but, by converting it into its potassium or sodium salt (accomplished by treating its absolute alcohol solution with sodium or potassium ethylate) we have thus been able to effect its isolation. From the analysis of these salts is made clear the reaction of the hydrolysis.

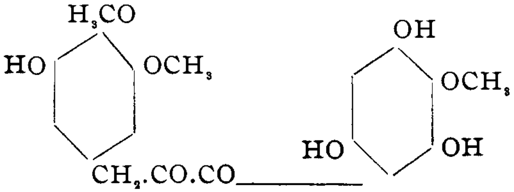
ANALYSIS.

($C_{24}H_{25}K_3O_{14}$ and $C_{24}H_{25}Na_3O_{14}$.)

	Per cent. K.	Per cent. Na.
Calculated	17.96	11.39
Found	18.32	11.69

If, now, instead of using an *excess* of potassium ethylate, only the amount sufficient to form the tribasic salt be taken, a *di*-basic salt is always the result, which indicates that one of the hydroxyl groups of the hydrolyzed irigenin is of a weaker acid character than the other two. Consequently, the first product in the hydrolysis of iridin is $C_{18}H_{14}O_5(OH)_3(OC_6H_{11}O_5)$, and, for irigenin, is $C_{18}H_{14}O_5(OH)_4$.

Since the hydrolyzed irigenin is a relatively sable compound, not being attacked by reagents which effect the saponification of ether, we conclude that the two portions of the irigenin molecule, representing respectively iridinic acid and iretol, are not linked together by an oxygen atom, but are held together by a chain of carbon atoms, as shown in the following formula:



According to this formula, the hydrolyzed irigenin is an α di-ketone. This is further proved by the similarity of its reactions with alkali reagents and those of benzene, the latter, in the presence of potassium cyanide, yielding benzaldehyde, and benzoic acid, while the former yields iridinic acid, or aldehyde, and a carboxyl derivative of iretol.

This is more particularly shown by the formation of the same aldehyde by the decomposition of irigenin, and also synthetically from iretol. In the first case, the hydrolysis of the irigenin was effected by dilute caustic soda. After precipitating with sulphuric acid and filtering, soda solution and potassium cyanide were added to the solution. After standing some eight days, it was acidified and extracted with ether. The aldehyde was separated from the ether extract by sodium bisulphite. By cautiously decomposing with sulphuric acid, and shaking with ether, the aldehyde was obtained as a syrup, which, on digesting six hours with alkali, gave the theoretical amount of formic acid.

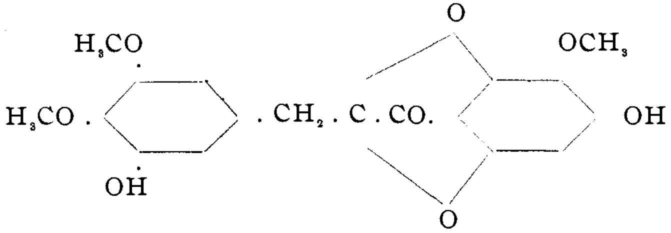
The synthesis of the aldehyde from iretol was effected by the action of chloroform and caustic soda on iretol in an atmosphere of hydrogen. After removing the chloroform by evaporation, the aldehyde was separated as above, it was also, in like manner decomposed, yielding iretol and formic acid.

The hydrolyzed irigenin, by taking up the elements of water, breaks up into iridinic acid and iretol aldehyde, this latter subsequently being converted into iretol and formic acid. Analogous to this is the decomposition of phloroglucinolcarboxylic acid into phloroglucinol and carbon dioxide, by boiling its aqueous solution.

From the foregoing, we feel justified in giving irigenin the formula

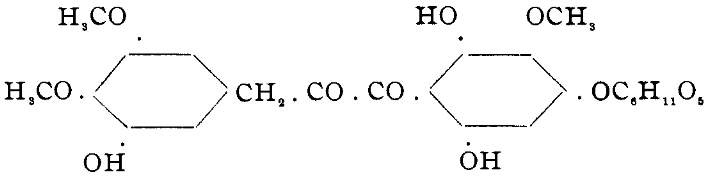
$$(H_3CO)_2(HO)C_6H_2.CH_2.CO.CO.C_6H_2(OCH_3)(OH)_2.$$

The irigenin itself contains one less molecule of water, and, in accord with all the reactions described, has the following constitution:

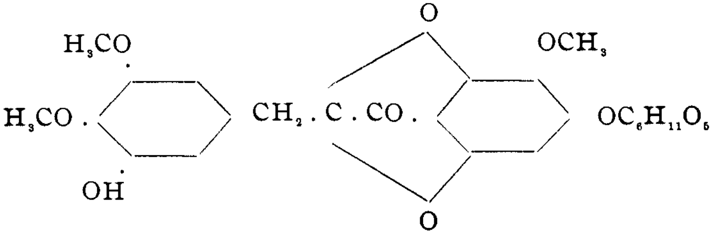


The iridin contains the glucoside residue, $OC_6H_{11}O_6$, in place of one of the two hydroxyls of irigenin.

We have previously noted the weaker acid character of one of the three hydroxyls of hydrolyzed iridin relative to the other two; we have also remarked that in titrating iridinic acid, $(H_3CO)_2.C_6H_2(OH)(CO_2H)$, with caustic soda and litmus, the end-point is obtained as soon as the hydrogen of the carboxyl group has been replaced by the alkali. From these two considerations we conclude that in the hydrolyzed iridin, the hydroxyl having the weakest acid character is found in the iridinic acid nucleus. Consequently, the constitution of hydrolyzed iridin is



Finally, if the above results and conclusions are correct, iridin itself has the constitutional formula



In closing, we would add a word regarding the probable relation of iridin and irigenin to the sugars; both are carbohydrates, and, as without doubt, the sugars are the first products changes of the plant matter, it appears probable that iridin and irigenin are formed from three and four molecules of sugar respectively, by the splitting off of eleven and ten molecules of water. In reviewing the possible methods of the formation of sugars from benzene derivatives, our attention is called to "cyclo" sugars, formed by an aldol condensation between the first and sixth groups of the chain in hexanpentolal

$$\mathrm{HO\overset{1}{C}.\overset{2}{C}HOH.\overset{3}{C}HOH.\overset{4}{C}HOH.\overset{5}{C}HOH.\overset{6}{C}H_2OH.}$$

This, perhaps, is the manner in which inosite is formed. Since the pinite occurring in some resins has been proven by L. Maquenne[1] 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.

BOTRYTIS BASSIANA AND ITS CRYSTALLINE PRODUCTS.[2]

BY E. VERSON.

AMONG 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' elêver le verf 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. Lomeni (*Variétés agraires*

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[1] *Ann. chim. phys.*, [6], **22**, 264.

[2] Read before the World's Congress of Chemists, Thursday, August 24, 1893.