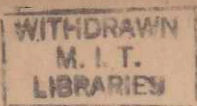


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Notes on Anthony Jannate

1878

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Notes on Antimony Tannate. No. II; by ELLEN SWALLOW RICHARDS and ALICE W. PALMER.

THE next point of interest was to determine whether the method of titration as given in the preceding paper (this Journal, p. 196) was applicable to tannin-holding substances other than nut-galls and sumac. The following tests were made for this purpose:

	Tannin. Per cent.
Leaves of sweet-fern (<i>Comptonia asplenifolia</i>) from near Boston, gathered the middle of May	7.56
The same, gathered on the Kennebec River, Maine, the last of July	8.00
Sample of ground hemlock-bark from Vermont	7.07
Sample of catechu	29.70
Sample of kino	41.50
Crushed quercitron bark	7.00
Congo tea	4.60
Cinchona flavor	9.60
Ground cloves	7.03
Chestnut-oak from Careyville, Tenn.	3.00

We also prepared a quantity of antimony-tannate from each of these substances in the same manner as we had prepared it from commercial tannin and sumac. The composition is given as follows:

	Sb. Per cent.	C. Per cent.	H. Per cent.
Sweet-fern (May)	15.30	45.09	3.40
Sweet-fern (July)	15.06	44.90	3.90
Quercitron	12.80	49.50	3.42
Chestnut-oak	15.50	47.51	3.63
Cloves	12.50	43.30	3.09
Hemlock-bark, No. I.	13.60	51.02	3.85
Hemlock-bark, No. II.	13.50	49.86	
Catechu	13.70	51.13	3.84
Kino	15.00	50.71	3.72
Cinchona flava	11.20	53.56	4.56
Congo tea	11.40	47.30	4.00

These analyses showed that the composition of the precipitate was influenced by one of two causes: either the formula of the so-called tannin which united with the antimony contained more C and H than di-gallic acid,—that is, it must be something like $SbOC_{38}H_{33}O_{17}$ or $Sb_2(C_{25}H_{21}O_{12})_3$ —or the antimony-tannate, which was formed in the solution, acted as a mordant, and carried down with it coloring matters which might or might not affect the titration, but which did affect the combustion.

To determine how far this latter cause could be held respon-

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sible, we prepared antimony tannate from the sample of tannin which we used for all our experiments, and having washed by decantation so as to keep the gelatinous precipitate in the best condition for absorbing color, we treated solutions of several of these substances with a quantity of antimony tannate corresponding to the estimated quantity of tannin contained in the solution, so as to have the conditions the same as in the previous precipitations; in one case we increased the amount of antimony tannate. The composition of the antimony tannate thus treated in the different solutions, together with the average composition of antimony tannate as we have already obtained it from tannin, sumac and nut-galls is given as follows:

	Sb. Per cent.	C. Per cent.	H. Per cent.
Sweet-fern + antimony tannate	15.70	46.21	3.73
Quercitron + antimony tannate	9.54	45.90	3.80
Hemlock + antimony tannate		63.30	3.60
Hemlock + five times the required amount of antimony tannate	13.40	43.40	3.90
Antimony-tannate	20.00	38.21	2.86

In the case of sweet-fern and quercitron, the results are very nearly those obtained by direct precipitation with tartar emetic. The possible reason for this will be considered later.

We were greatly surprised by the behavior of the solution of hemlock-bark. In all cases after treating the solution with the previously prepared antimony-tannate, we precipitated the remaining tannin by tartar emetic as usual, and noted the quantity required as compared with that required for the precipitation of tannin in the titration. The sweet-fern and quercitron gave a precipitate about one-third less than that from the original solution. In the case of hemlock there was scarcely a trace of a precipitate, showing that the antimony tannate had dragged down or united with all the substance which had been supposed to be tannin.

In order further to test the character of the supposed coloring matter in these substances, we made a series of trials with mordanted yarn. A brown-red color was obtained from hemlock on wool mordanted with tin chloride, and on cotton mordanted with alumina. A brilliant yellow color nearly equal to that from quercitron was obtained from sweet-fern on both the wool and the cotton.

We then tested solutions of all the substances upon which we had been working with cloth mordanted in the usual way for calico-printing (with iron and alumina in alternate stripes), in order to show the presence of tannin and coloring matter at the same time. This test divided the substances into two classes, the one showing the deep black of tannin on the iron stripe, and a yellow more or less intense on the alumina; the

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other giving on the iron stripe a faint brownish-black, corresponding in dullness to that produced by gallic acid, and on the alumina a dull reddish-brown. To the first class belong nut-galls, sumac, sweet-fern leaves, bark of quercitron, black oak, white oak and chestnut oak and bearberry leaves; to the other, hemlock, catechu, kino, fever bark, cinchona bark and congo tea. For our further investigation we took sweet-fern as the type of the former, and hemlock as that of the latter class.

The yellow in sweet-fern seems closely allied to, if not identical with the quercetin derived from oak-bark. A solution of sweet-fern guarancined (i. e., boiled with very dilute sulphuric acid), behaves like a solution of quercitron-bark,—a black gummy mass being formed, and the solution depositing yellow flakes which dye intensively.

Two pieces of cloth of equal size, the one dyed with one gram of sweet-fern leaves, the other with one gram of quercitron-bark, showed rather more tannin and less yellow for the sweet-fern, and more yellow and less tannin for the quercitron.

A single trial of the amount of yellow in sweet-fern, by weighing the antimony-tannate which had carried down the yellow with it, and which had been added in known quantity gave 2.5 per cent, and the amount of tannin in the filtrate had decreased about three of the eight per cent. This indicates that the antimony combines with a portion of the coloring matter, as well as with the tannin. This is further shown by the fact that the quercetin-like color obtained by guarancining was precipitated by antimony. The formula of this portion of the color must be very near to that of di-gallic acid, since the per cent of C and H in the precipitate from sweet-fern after the original solution had been treated with antimony tannate and the tannin then precipitated by tartar emetic was C 44.32 and H 3.39, and the composition of the precipitate when tartar emetic had been added directly to the solution without previous treatment with the antimony tannate was C 44.9 per cent and H 3.9 per cent.

Heppe (Die chemischen Reactionen) gives the formula of quercetin as $C_{27}H_{18}O_{12}$ and that of quercetin acid as $C_{15}H_{10}O_7$, which, corresponding to our formula of antimony tannate, would give respectively :

	Sb.	C.	H.
$Sb_2(C_{27}H_{18}O_{12})_3 + 6H_2O$	12.52	50.00	3.08
$Sb_2(C_{15}H_{10}O_7)_3 + 6H_2O$	19.49	43.13	2.87
Antimony-tannate,			
$Sb_2(C_{14}H_8O_9)_3 + 6H_2O$	18.59	38.41	2.74

The result of this is that the process of titration with tartar emetic, when applied to the class of substances holding this

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yellow coloring principle, would give too high results. We have not yet succeeded in isolating this yellow coloring matter unchanged, in order to test its effect on the accuracy of the iodine process or Löwenthal's method.

As to the brown-red obtained from the fresh hemlock, it seems to belong to a different class of substances. It is precipitated by gelatine, is acted on by iodine, is precipitated by antimony, and on fusion with potassium hydrate it is decomposed, and a substance is formed which blackens the iron stripe like tannin. We have not yet obtained a sufficient quantity to determine its composition or to deduce a theory for its relation to di-gallic acid. Our experiments go to show that the red-brown is decomposed in the slow process of fermentation, and the iron-blackening substance thus formed may possibly be the agent of the tanning.

Massachusetts Institute of Technology, Woman's Laboratory, August, 1878.