A COMPARATIVE STUDY OF TANNIC ACID, U. S. P.*,[1]

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This investigation was initiated with a survey of the prior work done by others on the chemistry of tannic acid in the hope of finding the best method of developing an assay procedure. The published records of Mitchel (1) and Forbes (2) are typical of these previous studies. It seemed mandatory after careful scrutiny of the work of Mitchel and Forbes that a general study of tannic acid be made in order to determine the logical method of developing an assay for tannic acid. This paper describes that portion of the work.

Eleven samples of U. S. P. Fluffy Tannic Acid were obtained and used for this investigation. The tests for purity as outlined by the Pharmacopœia yielded results which were not congruent with the anticipated values. The amount of moisture was found to vary from 4.50 to 9.52 per cent and the ash from 0.01 to 0.16 per cent. A number of the samples gave positive tests for gums, dextrins and resinous substances.

The acetylation of tannic acid was attempted, using a mixture of tannic acid, acetic anhydride and pyridine. This mixture was placed in a shaking machine for two hours, and allowed to stand at room temperature for three days. The resulting yellowish-brown liquid was poured into ice water and the acetylated tannic acid liberated by the addition of dilute sulfuric acid. A grayish-white powder was obtained which, upon fractional crystallization, did not give a product of any definite purity as evidenced by the formation of resinous masses and in several cases products which melted from 118° C. to 135° C. We concluded, therefore, that if the above method be taken as typical of those available, the acetylation of tannic acid does not yield a definite compound.

In order to obtain some idea of the comparative values of the different tannic acids in terms of gallotannin, they were analyzed using the Lowenthal Method as modified by the A. O. A. C. (3). This method involves permanganate titration and gelatin precipitation. From the calculated results it was quite evident that the samples are not of the same purity and the non-tannin portion as found by the gelatin precipitation is high. A possible explanation of this variation of the non-tannin portion is that such factors as strength of solution, rate of filtration and time of shaking influence the precipitation of the tannins.

The determination of the melting point, effect of heat, hydrolysis with acids and fusion of tannic acid with alkalies gave results which suggest that tannic acid has an indefinite composition. The determination of various physical constants such as refractive index, surface tension, optical activity, titratable acidity, spectroscopic analysis were made with the idea perhaps that an assay might be developed from one of them but disappointing results were obtained.

Nierenstein's (4) results on the effect of various color reagents with tannic acid were confirmed and further elaborated in making a systematic comparison of the tannic acid with seventy-two color reagents. As this work progressed it became apparent that one of the major difficulties encountered in assays making use of color reactions was the inability to accurately estimate the slight variation in color between the various samples with any given color reagent.

In attempting to obviate this difficulty, a photoelectric colorimetric comparison was made of freshly prepared aqueous solutions of tannic acid from one-tenth of one per cent to one per cent in concentration. These solutions were prepared from stock solutions by diluting aliquots with distilled water to make the required concentrations. All readings were made at 25° C. A number 7-089 Fisher Electrophotometer was used in this investigation. A 125-mm. cell was used for

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* Presented before the Scientific Section, A. PH. A., Atlanta meeting, 1939.

[1] Abstracted from a thesis submitted to the Graduate School of the University of Washington by Clifton E. Miller, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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all samples. The variance for each sample over the range of concentration used and the variable reduction units demonstrate that colorimetric assays of tannic acid cannot be accomplished due to the inconsistency of the sample and difference in color. The numerical results are given in the following table.

TABLE I.—RANGE ONE. CONCENTRATION IN PER CENT.

Sample.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.	1.0.
1	4.50	11.00	18.75	21.25	25.25	29.25	32.75	35.75	38.75	41.25
2	3.25	4.25	7.75	9.25	11.50	12.75	15.00	16.00	18.25	19.50
3	2.50	7.00	10.25	12.25	15.25	17.75	20.75	22.00	25.00	26.75
4	6.25	11.25	15.50	19.25	23.00	27.00	29.75	33.00	34.50	37.25
5	3.75	6.00	8.00	10.75	15.00	15.25	18.00	19.50	21.50	23.00
6	7.75	14.25	20.00	25.00	29.50	33.00	36.50	39.75	42.50	45.50
7	6.25	11.00	15.25	18.25	21.50	25.25	28.25	31.00	33.75	35.75
8	4.75	7.00	9.25	11.00	13.50	16.25	17.50	19.75	21.50	23.25
9	4.25	7.00	10.00	12.75	15.00	17.00	19.00	21.75	23.25	25.25
10	7.50	10.25	12.75	15.00	17.25	19.00	21.25	22.75	25.25	27.00
11	9.75	13.50	19.00	23.75	28.25	32.00	34.25	37.25	40.25	42.75

CONCLUSIONS.

1. The available samples of U. S. P. Fluffy Tannic Acid were purchased and compared by the tests for purity as outlined by the Pharmacopœia. The wide variation in these results gave proof of the variable composition of Tannic Acid Fluffy, U. S. P.

2. The determination of the melting point, refractive index, surface tension, optical activity, titratable acidity and spectroscopic analysis have been made with the hope that an assay might be developed making use of one of these constants.

3. A critical study of the various color reactions of tannic acid has been made together with an electrophotometric analysis, and as a result we conclude that an assay making use of color reactions is at present impractical.

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THE VOLATILE OIL OF POLIOMINTHA INCANA.*

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Among the species of southwestern plants under cultivation and observation at the Nursery of the Soil Conservation Service of the U. S. Department of Agriculture at Tucson, Arizona, one of particular interest to the senior writer while visiting the nursery in May 1938 was *Poliomintha incana* (Torr.), A. Gray (*Hedeoma incana* Torr.), N. O. *Labiatæ*. The one-and-a-half acre plot of this species was in full bloom and the strong odor of the foliage and flowers suggested the advisability of making a preliminary study of the volatile oil, inasmuch as a search of the litera-

* Presented before the Scientific Section, A. PH. A., Atlanta meeting, 1939.

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