BIBLIOGRAPHY

(1) Freda, *Gazz. chim. ital.*, 8 (1878), 9; through Dekker, "Die Gerbstoffe, 1913, page 26, Berlin.

(2) Biddle, H. C., *J. Am. Chem. Soc.*, 34 (1912), 918.

(3) Knecht, E., *J. Chem. Soc.*, 125 (1924), 1537.

Tannic Acid, U. S. P.

III. Hydrogen-Ion Studies of Tannic Acid Solutions

By Clifton E. Miller and L. Wait Rising†*

It is well known that freshly prepared solutions of tannic acid in water, irrespective of concentration, show a marked change in color, formation of bacterial growth, formation of an odor and, in some cases, deposition of a residue when kept over a prolonged period of time. These changes appear to be the result of decomposition. Engels (1) and Fantus (2) introduced various stabilizing agents in an attempt to prevent these changes. Therefore it was desired to measure the degree of decomposition of the stabilized and unstabilized solutions if possible. One way to do this on a comparative basis is to measure the resultant changes in hydrogen-ion concentration.

Surprisingly little work has been done on the hydrogen-ion value of tannic acid solutions. Johnson (3) in his survey of hydrogen-ion studies makes no mention of tannic acid-p_{H} relationship; Glasstone (4) proposed the limits of p_{H} in which it was possible to obtain a violet color by the addition of ferrous tartrate solution to solutions of tannic acid. This was another reason why the study seemed worth while.

EXPERIMENTAL

As tannic acid is water-soluble and does ionize, it seemed of interest to make a relative study of the hydrogen-ion concentration of freshly prepared solutions and stabilized solutions of tannic acid over varying intervals of time.

Therefore freshly prepared one per cent aqueous solutions were tested at varying intervals for a period of 96 hours. The hydrogen-ion value was determined using a saturated calomel-quinhydron, electrode. All readings were made at 250° C.

Table I.—p_{H} Values of Freshly Prepared Tannic Acid Solutions

Sample	Hours			
	0	24	72	96
1	2.5	2.5	2.6	2.8
2	2.6	3.1	2.9	3.0
3	2.6	2.8	3.1	3.2
4	2.4	2.6	2.8	3.1
5	2.8	2.8	3.0	3.4
6	2.7	2.7	3.3	3.2
7	2.8	2.7	3.2	3.1
8	3.8	3.4	3.6	3.5
9	3.6	2.9	3.6	3.0
10	3.6	2.9	3.2	3.2
11	3.4	3.2	3.1	3.4
12	3.2	2.9	3.0	3.4

It is quite evident that aqueous solutions of tannic acid are unstable on standing and their internal constitution is not only constantly changing but generally toward the alkaline side.

As mentioned earlier, Fantus brought forth a formula for the stabilized solutions of tannic acid in which he proposed the use of stabilizers such as salicylic acid and sodium chloride. Solutions were prepared using the formula suggested by Fantus which is given herewith.

Potassium chloride	0.42 Gm.
Calcium chloride	0.84 Gm.
Salicylic acid	1.00 Gm.
Sodium chloride	10.50 Gm.
Tannic acid	100.00 Gm.
Distilled water *q. s.*	1000.00 Gm.

The p_{H} of the solutions was determined upon preparation and at two-month intervals over a period of 12 months. There was a general darkening of the solutions as time progressed. Generally the acidity decreased in proportion to the increase in time. A sediment was noted in the bottoms of the containers which were kept under ordinary laboratory conditions.

Table II.—p_{H} Values Using Fantus Formula at Two-Month Intervals

Sample	Months						
	0	2	4	8	8	10	Av.
1	3.0	2.7	2.4	2.5	2.6	2.6	2.6
2	2.9	3.3	2.8	2.9	3.2	3.4	3.1
3	3.1	4.3	4.0	4.4	4.2	4.1	4.0
4	2.8	4.0	3.2	3.6	3.2	3.2	3.3
5	3.1	3.9	3.8	2.2	4.0	3.9	3.5
6	2.7	4.4	3.7	4.0	3.8	4.0	3.8
7	2.5	4.0	3.6	4.2	3.5	3.9	3.6
9	2.9	4.2	3.6	4.1	3.6	4.1	3.7
10	2.9	4.3	3.7	4.2	4.2	3.7	3.9
11	2.9	4.5	3.6	3.7	3.8	3.8	3.7
12	2.9	4.2	3.7	3.9	3.5	3.7	3.7

Since Sample No. 8 presented difficulties in getting a clear solution using the formula of Fantus no results are given.

Solutions were also prepared using Engels' formula, which is given herewith.

Alkyl or aryl *p*-hydroxy benzoate	0.1000 Gm.
Sodium bisulfite	2.5000 Gm.
Tannic acid	50.0000 Gm.
Distilled water *q. s.*	1000.0000 Gm.

---

* Instructor in Pharmacy, North Dakota State College, Fargo.

† Professor of Pharmacy, University of Washington, Seattle.

Four sets of solutions were made up according to the above formula using methyl, ethyl, propyl and benzyl *p*-hydroxy benzoates as stabilizers. No similarity in color could be detected and after standing for a period of 10 months the samples had noticeably darkened in color. p_{H} determinations were made at two-month intervals.

Table III.—p_{H} Values, Methyl Para Hydroxy Benzoate as Stabilizer

	Months						
Sample	0	2	4	6	8	10	Av.
1	5.2	3.6	4.8	5.0	5.0	2.6	4.4
2	5.7	3.6	5.3	5.1	5.0	4.5	4.9
3	5.5	3.5	5.4	5.4	5.1	4.6	4.9
4	5.6	3.1	5.7	5.3	4.9	4.3	4.8
5	6.1	3.4	5.6	5.5	5.0	3.5	4.8
6	5.9	3.3	5.8	5.7	5.3	4.5	5.1
7	6.0	2.8	5.7	5.5	5.1	4.5	4.9
8	6.1	3.8	6.0	6.0	5.4	4.2	5.2
9	6.1	3.3	5.6	5.5	5.2	4.6	5.1
10	6.1	3.4	5.5	5.4	5.0	4.5	5.0
11	5.9	3.3	5.7	5.4	5.0	4.5	5.0
12	5.9	2.8	6.0	5.5	5.3	4.5	5.0

Table IV.—p_{H} Values, Ethyl Para Hydroxy Benzoate as Stabilizer

	Months						
Sample	0	2	4	6	8	10	Av.
1	5.3	3.8	6.1	5.7	5.5	4.6	5.3
2	6.1	4.0	5.7	5.6	5.1	4.5	5.2
3	5.9	4.7	6.2	5.6	5.5	4.6	5.4
4	5.9	4.0	5.9	5.4	5.1	2.8	4.8
5	5.8	4.2	5.9	5.5	5.2	4.2	5.1
6	5.5	4.1	6.1	5.6	5.3	4.3	5.1
7	5.6	4.3	6.2	5.5	5.3	2.8	4.9
8	7.9	5.2	6.7	6.3	5.9	4.5	5.9
9	6.3	4.4	6.2	5.7	4.8	3.7	5.2
10	5.9	4.5	5.9	5.5	5.2	4.1	5.2
11	6.0	4.4	6.6	5.4	5.2	4.3	5.3
12	6.2	4.1	6.1	5.9	5.3	4.2	5.3

Table V.—p_{H} Values, Propyl Para Hydroxy Benzoate as Stabilizer

	Months						
Sample	0	2	4	6	8	10	Av.
1	6.0	3.0	6.5	5.6	5.2	4.4	5.1
2	6.3	3.2	6.2	5.4	5.2	3.2	4.9
3	6.5	3.8	6.5	5.7	3.9	3.3	4.9
4	6.0	3.5	6.0	5.3	4.9	4.3	5.0
5	6.5	3.7	5.9	5.6	5.1	3.3	5.0
6	6.2	3.8	5.0	5.8	6.0	4.5	5.2
7	6.1	3.9	6.2	5.6	2.9	2.2	4.5
8	6.7	4.7	6.6	6.2	5.3	3.4	5.5
9	6.1	3.9	6.3	5.7	5.1	3.2	5.0
10	6.6	3.8	6.2	5.6	5.0	4.2	5.2
11	6.9	3.9	6.5	5.6	5.0	4.5	4.9
12	6.3	3.6	6.3	5.7	5.3	4.5	4.8

Table VI.—p_{H} Values, Benzyl Para Hydroxy Benzoate as Stabilizer

	Months						
Sample	0	2	4	6	8	10	Av.
1	6.3	2.4	6.3	5.7	4.8	3.4	4.8
2	6.2	2.9	5.8	5.7	5.1	4.3	5.0
3	6.5	3.2	6.2	5.7	5.4	4.3	5.2
4	5.9	2.5	5.8	5.0	2.9	2.4	4.1
5	6.1	2.9	6.1	5.6	4.9	4.3	5.0
6	5.7	3.0	6.8	5.7	4.8	4.4	5.1
7	6.7	3.5	6.3	5.8	5.0	4.4	5.3
8	6.5	3.8	6.8	6.3	5.7	4.9	5.7
9	6.4	3.7	6.1	5.4	4.4	2.7	4.8
10	5.6	2.9	6.0	5.7	5.4	4.6	5.0
11	5.9	3.9	5.9	5.7	5.2	4.8	5.2
12	5.6	4.2	6.1	3.9	4.3	3.8	4.6

CONCLUSIONS

1. A study of the rate of change of hydrogen-ion concentration of tannic acid solutions has been made.
2. Ethyl and propyl para hydroxy benzoates exhibited a stronger stabilizing power on tannic acid than the corresponding methyl and benzyl esters.
3. We believe that the recommended stabilizing agents do not produce the desired effect with respect to hydrogen-ion concentration.

BIBLIOGRAPHY

(1) Engels, Wm., U. S. Patent 2,088,570, Aug. 3, 1937.

(2) Fantus, B., *Jour. Am. Med. Assoc.*, 109 (1937), 220.

(3) Johnson, F. F., *Jour. A. Ph. A.*, 24, (1935), 397.

(4) Glasstone, S., *Yearbook A. Ph. A.*, 14, (1925), 355.

Adaptation of Assay Methods for Some N. F. Ointments. Ointment of Zinc Stearate*

By Wm. B. Baker and D. I. Kutzly

Many ointments in the N. F. VI do not have assay methods given for the determination of their active constituents. In the case of a number of these ointments, it has been found (1) that suitable assay procedures for the quantitative determination of certain medicinal ingredients are possible by adaptation of the assay methods that already exist for certain of the drugs and chemicals contained in the formulas.

OINTMENT OF ZINC STEARATE

The assay method for Zinc Stearate, U. S. P. XI, may be successfully adapted for use in the assay of Ointment of Zinc Stearate, N. F. VI, as shown by the satisfactory results reported in this article.

"Zinc Stearate is a compound of zinc with variable proportions of stearic acid and palmitic acid, corresponding to not less than 13 per cent and not more than 15.5 per cent of ZnO" (2). Therefore, the criterion of

---

* From the Sutliff & Case Pharmaceutical Laboratories, Peoria, Illinois.

Read before the Scientific Section, A. PH. A., Richmond meeting, 1940.