ELECTROMETRIC TITRATION OF TANNIC ACIDS.

PART I. ELECTROMETRIC TITRATION OF ELLAGIC, ELLAGITANNIC AND CHEBULINIC ACIDS.

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INTRODUCTION.

Freudenberg (*Collegium,* 1921, No. 618, 353) regards the combination of collagen and tannin as analogous to that of a weak base, like aniline, with phenol. He showed that phenolic hydroxyl groups can interact with amino- and imino-groups and has pointed out that the larger and more complicated the phenol and the larger and more complicated the amine or imine, the more readily the reaction takes place and the more stable the resulting product.

As the tannins are characterised by the possession of one or more hydroxyl groups, they precipitate gelatin from solution, very probably through the formation of insoluble gelatin tannate, or they adhere to the collagen present in hide in such a way that, the resulting product is not decomposed by water. The tannins are weakly acidic in their behaviour and collagen behaves as a base in acid solutions of hydrogen-ion concentration greater than about pH 5.

A variation in the pH of vegetable tanning liquors has a pronounced effect on their colours and consequently on the resulting leathers. Thomas and Kelly (*Ind. Eng. Chem.,* 1923, **15**, 1148) studied the influence of hydrogen-ion concentration, the concentration of tanning liquors and the time allowed for tanning. The minimum fixation is seen to have occurred at pH 5, which is approximately the isoelectric point of collagen. It is shown from the curves that an increase in the fixation of tannin occurred from pH 5 to pH 2; a fact which is in harmony with the acid nature of the true tanning agent.

Thomas and Kelly (*loc. cit.,* 1924, **16**, 800) studied the rate of tanning of purified gallotannic acid as a function of pH, and found a minimum rate of tanning in the region of isoelectric point of collagen. The rate of tanning drops rapidly on the alkaline side of pH 7, while the commercial extracts show a definite tanning action on the alkaline side of pH 8. The results of their experiments prove the correctness of the idea that in the case of pure gallotannic acid, very little or no material of the nature of gallic acid, quinone-like bodies, etc., is present and consequently there is comparatively no fixation in the alkaline solutions. The slight amount of fixation found, is due to traces of impurities and to the products formed by hydrolysis and oxidation of tannic acid in alkaline solution.

The part played by hydrogen-ion concentrations in vegetable tanning has been investigated by Gordon and Gilman (*Jour. Soc. Leather Trades' Chemists*, 1927, **11**, 213). They found an increased tannin fixation when the liquors were about pH 2, but the resulting leather was of little commercial value, as it was harsh and brittle. At pH 2.5 the leather was found to be firm and not brittle. Tanning at pH 3 gave rise to a leather which appeared to have properties most desired in sole leather, *viz.*, firmness without brittleness, good substance and colour and a fairly high percentage of tannin. The increase in pH tended to promote "bloom" deposition.

Humphreys (*Jour. Soc. Leather Trades' Chemists*, 1934, **18**, 178) dealing with the factors influencing the tanning properties of tan liquors, postulates that the pH value, buffer index of the liquors, the size of the particles or the degree of dispersion are the controlling factors. By means of freezing point determinations he obtained figures for the apparent average molecular size of certain commonly used tanning materials and concluded that the average apparent molecular weights of the liquor fall in approximately the same order as that in which the tanner would place the liquors from their properties, *i.e.*, in order of their *astringencies*. He found the apparent average molecular weights of two myrobalan extracts (*a*) and (*b*) and gallotannic acid, to be 181, 256 and 1302 respectively.

The use of myrobalan in reducing the viscosity of the Rotary Drilling Mud has been investigated in this laboratory, the results of which are under publication. Of all the tannin-bearing materials, myrobalan powder brings about the greatest reduction in viscosity, the lowest value being only 6% of the original, which remained constant with larger additions of myrobalan. Metha and Jatkar (*This Journal*, 1935, **18A**, 101) showed that the addition of myrobalan powder changed the pH of the mud in the manner analogous to its effect on viscosity, the range of constant viscosity corresponding to 7.5 pH. And they also showed that the initial effect of adding small quantities of myrobalan was equivalent to the tannic and ellagitannic acids content of the myrobalan which was estimated by electrometric titration.

From the foregoing discussion it is abundantly clear that the pH of the solution of the tannic acids is a very important consideration in considering the relative merits of the acids for tanning purpose as well as for purpose of treating the clays in order to control the viscosity, plasticity, etc. The object of the present paper was, therefore, to measure the initial pH of the myrobalan tannic acids in solutions and when the acids were neutralised to different stages. It was also thought that a knowledge of the dissociation constants of these acids and their equivalent weights as determined by potentiometric titration, would throw light on the structure of these tannic acids about which there is considerable controversy.

EXPERIMENTAL.

The apparatus used for measuring the E.M.F. of the hydrogen-saturated calomel electrodes, consisted of a cylindrical glass vessel fitted with an air-tight rubber stopper with a number of holes for admitting hydrogen electrodes, calomel half cell, bubbler, thermometer and the burette tip. Purified hydrogen gas was bubbled through the solution which was kept stirred by a mechanical stirrer made air-tight by using a mercury seal. A simple type of potassium chloride bridge was used which consisted of a tube having a ground glass stopper at one end dipping in the solution, the calomel half cell being introduced at the other end. E.M.F. was measured by Tinsley's vernier type of potentiometer. A sensitive mirror galvanometer was used as an indicating instrument.

The same type of apparatus was used for the differential titration with tungsten wires, the only difference being the electrodes used were two polished tungsten wires, one of which was kept dipping directly in the solution, while the other was kept in an ink-filler, the tip of which was dipping in the solution. A small quantity of the titrated liquid was sucked up in the ink-filler and emptied successively. All the measurements were made on the vacuum tube circuit developed in our laboratory which consisted of two P_2 valves in push-pull, the electrodes being directly connected to the grids of the respective valves. A sensitive unipivot galvanometer was used as an indicating instrument.

Hydrogen-ion concentration and pH are calculated according to the following formula:

$$-\log [H^{\bullet}] = pH = \frac{E_{ob.} - E_{cal.}}{2{\cdot}303\ RT/F}$$

where $E_{ob.}$ is the observed E.M.F. and $E_{cal.}$ is the E.M.F. of the saturated calomel half cell.

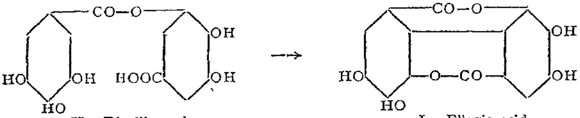
A monobasic acid dissociates in the following manner:

$$HR \rightleftharpoons H^{\bullet} + R' \qquad K_1 = \frac{[H^{\bullet}] \times [R'].}{[HR]}$$

The various concentrations were calculated from the molality of the acid and from the quantity of the alkali added at every point.

ELLAGIC ACID $C_{14}H_6O_8, 2H_2O$.

Schiff (*Berichte,* 1879, **12**, 1534) produced ellagic acid from digallic acid II and suggested the formula I.

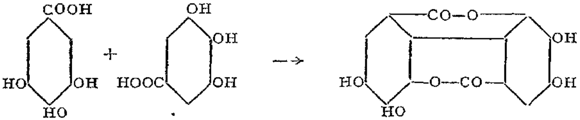


II. Digallic acid. I. Ellagic acid.

Zölffel (*Arch. der. Pharm.,* 1891, **229**, 123–60) found that on heating Algerobilla and Myrobalan extract with dilute sulphuric acid, ellagic acid is formed in addition to gallic acid.

Nierenstein (*Chem. Ztg.,* 1909, 87) investigated the "bloom" produced on sole leather tanned with Valonia, myrobalans, etc., and has shown it to consist of ellagic acid.

Schiff's formula was synthetically confirmed by Perkin and Nierenstein (*Jour. Chem. Soc.,* 1905, **87**, 1415) who oxidised gallic acid in acid solution to ellagic acid.



1 gallic acid + 1 gallic acid 1 ellagic acid.

In the present investigations, ellagic acid was prepared by boiling the aqueous myrobalan extract with dilute acid. This crude acid was purified by dissolving in dilute caustic soda and precipitating with carbon dioxide. After washing with water, it was dissolved in dilute alkali and decomposed by dilute sulphuric acid. The free acid was thoroughly washed and dried in desiccator.

Ellagic acid is practically insoluble in all ordinary solvents. It dissolves in alkali and pyridine. When heated it does not melt below 360° C. and at higher temperatures sublimes with considerable carbonisation. On acetylating, colourless needles of tetra-acetyl ellagic acid were formed, having m.p. 344–46° C.

Marklein and Wohler (*Ann. Chem.,* 1845, **55**, 129) prepared dipotassium salt $K_2C_{14}H_4O_8$ from the acetylated ellagic acid.

As the acid is insoluble in water, it was suspended in water and then titrated electrometrically using hydrogen and saturated calomel electrodes and also differentially by using tungsten wires, in hydrogen atmosphere.

The results of the titration are given in Table I.

TABLE I.

Potentiometric Titration of Ellagic Acid.

Wt. taken = 0·4280 gm. NaOH = 0·089 N.
Electrodes (i) H—Cal. sat. (ii) Polished tungsten wires.

	I		II	
c.c. NaOH	E.M.F.	$\frac{dE}{dC} \times 10^3$	Deflection	$\frac{dE}{dC}$
0·0	0·58542	..	..	..
5·0	..	..	320	64
10·0	·65500	27·0	−65	−13
11·0	..	..	−75	−75
12·0	·68873	16·6	−20	−20
13·0	·69487	6·1	0·0	0·0
14·0	·70048	5·6	40	40
14·3	·70527	*16·0*	34	113
14·5	·70809	14·1	20	100
14·8	·70895	2·9	30	100
15·0	·71179	14·2	42	210
15·5	·71529	7·0	42	84
17·0	·72218	4·6	77	51
19·0	·73635	7·1	150	75
20·0	·74748	11·1	125	125
21·0	·77145	*24·0*	115	115
23·0	·81561	22·1	155	77
25·0	·83789	11·1	93	47
26·0	·83969	0·2	60	60
27·0	·84257	4·7	45	45
28·0	·84867	*6·1*	40	40
29·0	·85276	4·1	36	36
29·5	·85545	5·4	42	84
30·0	·85733	3·8	32	64
31·0	·86329	6·0	31	31
32·0	·87018	*6·9*	−10	−10
34·0	·87739	3·6	+ 5	+ 2·5

Fig. 1 contains two curves, E.M.F. and dE/dC against c.c. The dE/dC curve shows four prominent peaks. The peaks 1 and 2 are obtained on adding 14.2 and 27.5 c.c. of 0.089 N alkali, corresponding to the equivalent weights of 338.6 and 174.9.

The results of the differential titration with tungsten electrode are plotted in Fig. 2, as c.c. of NaOH against dE/dC. Here also three peaks are prominent. Peaks 1 and 2 correspond to the equivalent weights of 338.6 and 164.6 when 14.2 and 29.25 c.c. of the alkali are added. The first peak in the direct differential is in agreement with the previous value and also with the theoretical value (Schiff, $C_{14}H_6O_8 \cdot 2H_2O$, 338).

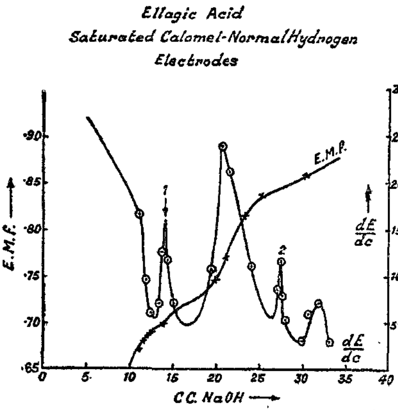


FIG. 1.

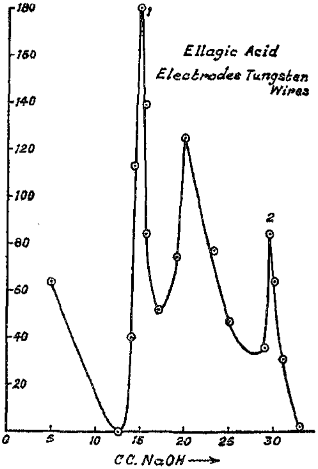


FIG. 2.

The existence of the intermediate peaks in both the figures can only be accounted for, if the structure of the acid is assumed to be bimolecular. Then, in this case, it should be possible to get one more value on adding 7.0 c.c. of the alkali which was apparently missed. The next peaks should be obtained on adding 14, 21, 28 and 35 c.c. of the alkali. This assumption is confirmed by the actual titration results which show that the peaks in Fig. 1 are obtained on adding 14.2, 20.5, 27.5 and 31.5 c.c. of the alkali approximately. Further points were not investigated.

As there is no free carboxyl group in the acid, the acidity seems to be due to only cumulative effect of the four hydroxyl groups. Out of the four OH groups, only two seem to be strongly acidic. It will be shown later in the case of gallic acid, that out of three OH groups, only one seems to behave as fairly strong acid. As 2 mols of gallic acid are oxidised to ellagic acid, one can infer that one OH group from each of the two mols of gallic acid should behave as strongly acid group in the molecule of ellagic acid.

The following table shows the dissociation constant K_A of ellagic acid as calculated from the titration results.

Dissociation Constant of Ellagic Acid.

Wt. taken = 0·4280 gm. in 250 c.c. 0·005064 Molal concentration.

Mol. Wt. = 338. NaOH = 0·089 N.

C.C. NaOH	E.M.F.	pH	H-ion concentration $\times 10^8$	Free acid $\times 10^4$	Undissociated Acid $\times 10^4$	NaR $\times 10^3$	$K_1 \times 10^7$
10	·6550	6·956	11·07	14·44	14·439	3·423	2·65
12	·6887	7·534	2·924	7·56	7·559	4·077	(1·58)
13	·6948	7·632	2·333	4·159	4·158	4·398	2·47
							2·56

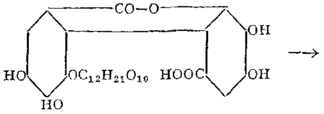
ELLAGITANNIC ACID $C_{26}H_{28}O_{19}\cdot 3H_2O$.

G. Zolffel (*Archiv Pharm.,* 1891, 155–9) isolated ellagitannic acid from myrobalans and assigned the formula $C_{14}H_{10}O_{10}$. The constitutional formula suggested by him was

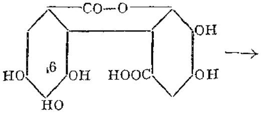
$$O_6H_2\ COOH(OH)_2O-C_6H_2\ COO(OH)_3.$$

He prepared a penta-acetyl derivative $C_{14}H_5O_{10}\ (C_2H_3O)_5$. The ready solubility of this acid in water, together with the ease with which it is hydrolysed to ellagic acid leads one to infer that it is a glucoside of ellagic acid.

Nierenstein obtained ellagitannic acid (I) present in myrobalans (*Berichte*. 1910, 43, 1267) in the form of crystals which on hydrolysis produced luteoic acid (II) and two molecules of glucose which are probably attached to the hydroxyl group marked 6. The diglucoside residue also obviously prevents the closing of luteoic acid to ellagic acid in the plant.



I. Ellagitannic acid.



II. Luteoic acid.

We prepared ellagitannic acid by Zolffel's method and purified it further by precipitating the concentrated alcoholic solution of purified acid with ether as suggested by him. The acid is hygroscopic, and optically active, the specific rotation in 1% solution in water being $[\alpha]^{27}$ 20.0° which compares with Nierenstein's value $[\alpha]_D^{17}$ 18.02° in ½% solution.

Equivalent weight was determined by electrometric titration using hydrogen and saturated calomel electrodes. The results are given in Table II.

On pointing the graph of dE/dC against c.c. of NaOH solution as co-ordinates (Fig. 3), it is found that there is a sharp peak after the addition of 8.45 c.c. of 0.089 N NaOH to 0.4889 grams of acid. This corresponds to 650 as the equivalent weight of the acid ($C_{26}H_{28}O_{19}$) 644, Nierenstein (*loc. cit.*).

Next peak is obtained when 42.3 c.c. of NaOH are added, corresponding to the neutralisation of the last hydroxyl group, the equivalent weight being 129.7, which is one-fifth of the value obtained above. The results obtained are in agreement with the fact that there are four hydroxyl groups and one free carboxyl group in the acid. The other hydroxyl groups are also shown by small intermediate peaks. The last peak cannot be accounted for, and appears to be due to the failure of the hydrogen electrode in that range of pH.

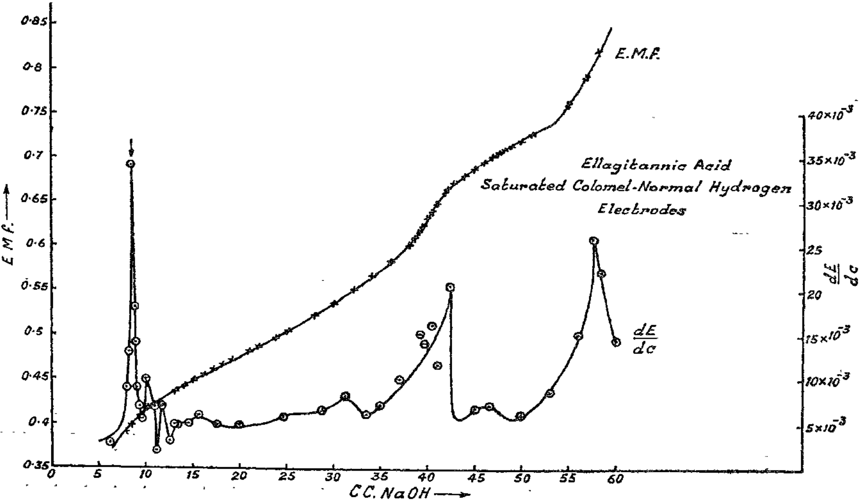

E.M.F.
Ellagitannic Acid
Saturated Colomel-Normal Hydrogen
Electrodes
dE/dc
E.M.F. →
0·35
0·4
0·45
0·5
0·55
0·6
0·65
0·7
0·75
0·8
0·85
0
5
10
15
20
25
30
35
40
45
50
55
60
CC. NaOH →
5×10⁻³
10×10⁻³
15×10⁻³
20
25
30×10⁻³
35×10⁻³
40×10⁻³
dE/dc

FIG. 3.

TABLE II.

Saturated Calomel-normal Hydrogen Electrodes.

Ellagitannic acid. Wt. taken = 0·4889 gm.
In Hydrogen Atmosphere. NaOH = 0·089 N.

c.c. NaOH	E.M.F.	$\frac{dE}{dC}$	c.c. NaOH	E.M.F.	$\frac{dE}{dC}$	c.c. NaOH	E.M.F.	$\frac{dE}{dC}$
0·0	·38632	..	11·5	·43005	·00670	39·5	·62403	·01520
2·0	·39072	·00221	11·7	·43147	·00710	40·0	·63134	·01462
4·0	·38162		12·1	·43403	·00640	40·5	·63955	·01642
6·0	·38652	·00245	12·5	·43546	·00375	41·0	·64681	·01452
8·0	·39591	·00469	13·0	·43809	·00526	42·0	·65857	·01176
8·2	·39778	·00935	14·0	·44352	·00543	42·2	·66233	·01880
8·4	·40055	·01385	15·0	·44903	·00551	42·4	·66641	*·02040*
8·5	·40395	*03400*	16·0	·45508	·00605	42·6	·67003	·01810
8·6	·40584	·01890	17·0	·46097	·00589	42·8	·67013	·00055
8·7	·40733	·01490	18·0	·46607	·00510	43·0	·67173	·00795
8·8	·40905	·01720	19·0	·47130	·00523	43·2	·67527	·01770
8·9	·41083	·01780	21·0	·48291	·00580	43·5	·67622	·00320
9·0	·41174	·00910	22·0	·48744	·00453	44·0	·68051	·00858
9·2	·41350	·00880	23·0	·49324	·00580	44·5	·68527	·00952
9·4	·41464	·00570	24·0	·49917	·00593	45·0	·68872	·00690
9·6	·41599	·00675	24·5	·50226	·00618	46·0	·69587	·00715
9·8	·41729	·00650	25·0	·50509	·00566	47·0	·70196	·00609
10·0	·41932	·01015	25·5	·50799	·00580	48·0	·70939	·00743
10·1	·41992	·00600	26·0	·51081	·00564	49·0	·71473	·00534
10·2	·42089	·00970	28·0	·52350	·00634	51·0	·72854	·00690
10·3	·42209	·00120	30·0	·53657	·00653	55·0	·76303	·00862
10·4	·42305	·00960	32·0	·55321	·00832	57·0	·79359	·01528
10·5	·42381	·00760	34·0	·56617	·00648	58·0	·82040	·02681
10·6	·42437	·00560	36·0	·58105	·00744	59·0	·84254	·02214
10·8	·42589	·00760	38·0	·60217	·01056	60·0	·85750	·01496
11·0	·42744	·00775	38·5	·60813	·01192	61·0	·86867	·01117
11·2	·42803	·00295	39·0	·61643	·01660	62·0	·87682	

Dissociation Constant of Ellagitannic Acid.

Mol. Wt. 129·7. NaOH = 0·089 N.

c.c. NaOH	E.M.F.	pH	H-ion concentration	Free acid $\times 10^4$	Undissociated acid $\times 10^4$	NaR $\times 10^3$	$K_1 \times 10^5$
32	·55321	5·216	$6·081 \times 10^{-6}$	30·84	30·78	10·1	1·99
34	·56617	5·436	$3·664 \times 10^{-6}$	24·35	24·32	10·65	1·60
36	·58105	5·690	$2·042 \times 10^{-6}$	17·98	17·96	11·2	1·3
							1·6

CHEBULINIC ACID.

Fridolin (Dissertation Dorpat 1884; *pharm. Zeitss fur Russland,* 1884, **23**, 393) discovered a crystalline Tannin in *Terminalia chebula* myrobalans and assigned to it a formula $C_{28}H_{24}O_{19} + H_2O$. Further he showed that on hydrolysis, gallic acid and new tannin are produced. His investigations were partly confirmed by Adolphi (*Arch. der. Pharm.,* 1892, **230**, 694–705) who found its specific rotation in alcoholic solution and determined its molecular weight by rise in boiling point of acetone and showed it to be in agreement with Fridolin's formula. He described numerous salts from which he concluded that chebulinic acid is a *monobasic acid* forming a neutral salt with zinc, ZnO, $Zn\,(C_{28}H_{23}O_{19})_2$.

Freudenberg and Fick (*Berichte,* 1920, **53**, 1728) assigned to this acid the formula $C_{34}H_{30}O_{23}$, in support of which, they found molecular weights by (*a*) potentiometrically titrating the acetone-water solution, and by (*b*) the boiling point method using acetone as solvent in agreement with the theoretically calculated values. [Found (*a*) 800, (*b*) 788. Theoretical ($C_{34}H_{30}O_{23}$), 806.]

Freudenberg and Frank (*Liebig's Annalen,* 1927, **452**, 303–15) in their third contribution to the chemistry of chebulinic acid, assigned to this acid the formula $C_{41}H_{34}O_{27}$. They argued in support of this formula as follows: (1) Loss of water of crystallisation at 78° C. under 15 mm. pressure was 14.5% which agrees with the calculated quantity according to the formula $C_{41}H_{34}O_{27}\cdot 9H_2O$. (2) Equivalent weight by alkalimetry, *i.e.,* dissolving in excess of alkali and titrating back the excess of alkali by hydrochloric acid, making due correction for the solubility of chebulinic acid, was found to be 962 (calculated 958). (3) Equivalent weight by electrometric titration of the anhydrous acid using hydrogen and saturated calomel electrodes was 977. However (4) the molecular weights found in acetic acid (K = 38.9) varied from 879 to 911, and in succinic acid methyl ester (K = 55.5), from 814–99. Summarising they came to the conclusion from the synthesis of the acid that it consists of three gallic acid molecules, one glucose and one new tannin $C_{14}H_{14}O_{11}$

$$\begin{array}{llll} C_{41}H_{34}O_{27} + 5\,H_2O & = 3\,C_7H_6O_5 & + C_6H_{12}O_6 & + C_{14}H_{14}O_{11} \\ \text{Chebulinic acid} & \text{3 gallic acid} & + \text{1 glucose} & + \text{1 new tannin.} \end{array}$$

In the following table the summary of the data worked out by different workers is given (B.P.R. rise in the Boiling Point Method).

Reference	Formula	Molecular calculated	Weight found	Water of crystallisation	Optical Rotations
1. Adolphi .. (*Arch. pharm.*, **230**, 1892)	$C_{28}H_{24}O_{19}$ + 1 H_2O	682	634–756 (B.P.R.)	1 H_2O	60·5° – 66·9° (in alcohol)
2. H. Thomas .. (*Chem. Zentral*, 1906, **1**, 1829)	$C_{28}H_{22}O_{19}$ + 1 H_2O	680		1 H_2O	61·7° – 66·9°
3. Freudenberg and Fick (*Berichte*, 1920, **53**, 1728)	$C_{34}H_{30}O_{28}$	806	800 (Alkalimetry) 788 (B.P.R.)		
4. Freudenberg and Frank (Liebig's *Ann.*, 1927, **452**, 303)	$C_{41}H_{34}O_{27}$	958	962 (Alkalimetric) (Electrometric) 977 879–911 814–899 (B.P.R.)	9 H_2O (14·5%)	65·1° (alcohol+ water) 3 : 1
5. Authors ..		914	915 930	6 H_2O	60·6° – 65·5° (alcohol+ water)

Preparation of Chebulinic acid.—Chebulinic acid was prepared in three ways as follows:—

(1) By Adolph's method (*Archiv. Pharm.*, 1892, **230**, 684) Myrobalans were extracted with cold 95% alcohol. After distilling off the solvent, the dry extract was dissolved in water and filtered from the gummy and resinous matter. The filtrate was salted out when tannin was precipitated. The precipitated mass after washing with

saturated salt solution, was dissolved in water and extracted with ethyl acetate. The solvent was distilled off and the dry extract was dissolved in water, filtered and kept in a cool place for about 8–10 days, when a crystalline substance separated. This was crystallised out twice from hot water and dried in desiccator over calcium chloride.

(2) Myrobalans were extracted with acetone in soxhlet apparatus. Solvent was distilled off and the dry extract was dissolved in water and filtered. The filtrate was kept in a cool place for about 8–10 days, when a crystalline substance separated, which was recrystallised twice from hot water and dried in desiccator over calcium chloride.

(3) In preparing myrobalani tannic acid by fractional precipitation with neutral lead acetate, it was observed that, when the middle fraction of lead tannate, after decomposing with either hydrogen sulphide or sulphuric acid was kept for some days, the crystals obtained were identical with those prepared by the two methods previously described. It was crystallised twice from hot water and dried in desiccator over calcium chloride.

In all the three acids prepared by three different methods, water of crystallisation was found to be 14% by drying at 100° in vacuum.

Phenyl hydrazine derivatives of the three acids were prepared (m.p. 170° C. in all cases). The acid was optically active. Specific rotations of the acids in a mixture of alcohol and water (3 : 1 by volume) were determined as follows. The specific rotation changed up to seventh day and then remained constant as found by Adolphi (*loc. cit.*).

$[\alpha]_D^{25}$.

I	II	III	
60·2°	60·6°	60·6°	1st day
61·5	61·8	61·5	2nd day
63·4	63·5	63·5	3rd day
65·5	65·7	65·8	7th day
65·5	65·7	65·8	8th day

Equivalent weight was determined by electrometric titration using acetone and water mixture with Ag (+) and W (−) electrodes. The results of titrations are given in the following table (Table III) and shown graphically in Fig. 4.

TABLE III.

Potentiometric Titration of Chebulinic Acid.

Wt. taken = 0·3580 gm. (air dried). NaOH = 0·0127 N.
Electrodes Ag^+ and W^-.

c.c. NaOH	E.M.F.	$\frac{dE}{dC}$	c.c. NaOH	E.M.F.	$\frac{dE}{dC}$	c.c. NaOH	E.M.F.	$\frac{dE}{dC}$
0·0	0·151		5·3	−0·008	−0·004	21·0	0·001	+ 0·001
0·2	0·131	−0·100	6·3	−0·011	−0·003	22·0	0·003	0·002
0·4	0·107	−0·120	6·5	−0·008	0·015	23·0	0·004	0·001
0·6	0·087	−0·100	7·0	−0·006	0·004	24·0	0·008	0·004
0·8	0·063	−0·120	7·5	−0·006	0·0	25·0	0·020	0·012
1·0	0·041	−0·110	8·0	−0·007	−0·002	26·0	0·025	0·005
1·2	0·035	−0·030	8·5	−0·007	0·0	27·0	0·033	0·008
1·3	0·010	−0·250	9·0	−0·008	−0·002	28·0	0·045	0·012
1·4	0·0085	−0·015	9·5	−0·008	0·0	29·0	0·053	0·008
1·5	0·0075	−0·010	10·5	−0·010	−0·002	30·0	0·067	0·014
1·6	0·0085	−0·010	11·5	−0·009	0·001	31·0	0·118	*0·051*
1·7	0·005	−0·035	12·5	−0·007	0·002	31·5	0·129	0·022
1·9	0·003	−0·010	13·5	−0·007	0·0	32·0	0·137	0·016
2·1	0·002	−0·005	14·5	−0·005	0·002	32·5	0·141	0·008
2·5	0·0	−0·005	16·0	0·002	0·005	33·0	0·145	0·008
2·7	0·0	0·0	17·0	0·003	0·001	34·0	0·150	0·005
2·9	0·002	0·010	18·0	0·002	−0·001	35·0	0·155	0·005
3·1	0·001	−0·005	19·0	0·00	−0·002	36·0	0·157	0·002
3·3	0·0	−0·005	20·0	0·00	0·00	37·0	0·159	0·002
4·3	−0·004	−0·004						

The curve was plotted with c.c. of NaOH and dE/dC as co-ordinates (Fig. 4, iii). It can be seen from the curve that the highest peak is obtained on adding 30.8 c.c. of 0.0127N NaOH, corresponding to the equivalent weight of 915 ($C_{34}H_{30}O_{23}\ 6H_2O = 914$).

The acid was dissolved in a mixture of acetone and water as above and titrated potentiometrically using hydrogen-sat. calomel electrodes. The results are given in Table IV.

The curve was plotted with dE/dC and c.c. of NaOH as co-ordinates (Fig. 4, ii). The first peak is obtained when 6.0 c.c. of 0.0772N NaOH are added which corresponds to equivalent weight of 930. The second peak is at 11.9 c.c., third at 17.8 and the fourth at 23.7, all the peaks being equally prominent. The quarter basic nature of this acid and the equivalent found are in accordance with the original digalloyl structure given by Freudenberg and Fick (*loc. cit.*) with 6 mols. water of crystallisation.

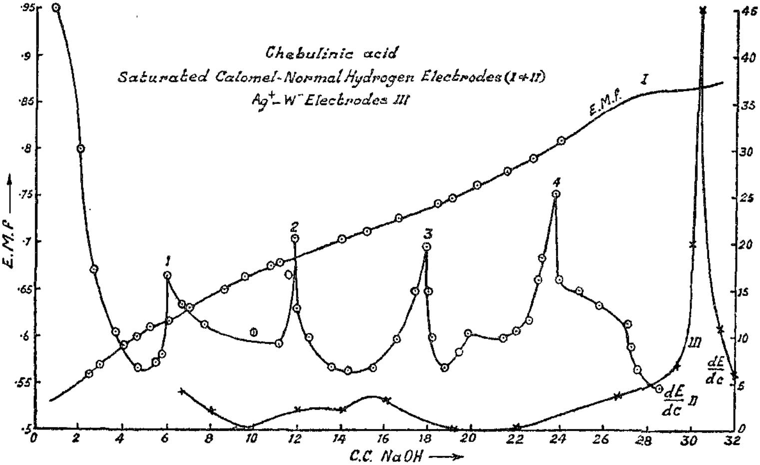


FIG. 4.

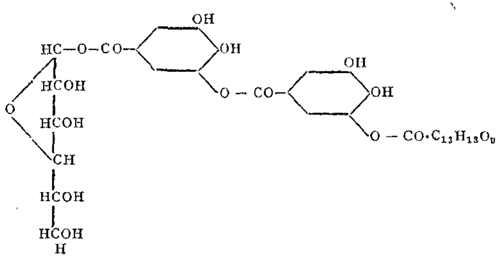


TABLE IV.

Potentiometric Titration of Chebulinic Acid.

Wt. taken = 0·4306 gm. NaOH = 0·0772 N.

H_2 — Sat. Calomel Electrodes. In Hydrogen Atmosphere.

c.c. NaOH	Cell C.°	Calomel C.°	E.M.F.	$\frac{dE}{dC} \times 10^3$	c.c. NaOH	Cell C.°	Calomel C.°	E.M.F.	$\frac{dE}{dC} \times 10^3$
0·00	24·9	27·0	·46161		13·95	27·1	28·6	·70516	6·7
1·80	25·0	,,	·54277	45·0	15·05	,,	,,	·71463	8·6
2·40	25·1	,,	·56087	30·2	15·8	27·2	28·7	·71954	6·6
2·9	25·6	27·2	·56923	16·7	16·3	,,	,,	·72557	12·1
3·3	25·7	,,	·57641	17·9	16·6	,,	28·8	·72847	9·7
3·7	,,	,,	·58552	22·7	17·1	27·3	,,	·73139	5·8
3·94	25·8	27·4	·59235	28·3	17·5	,,	,,	·73737	15·0
4·3	25·9	27·5	·59752	14·3	18·05	27·4	,,	·74183	8·1
4·7	,,	,,	·60187	10·9	18·45	,,	,,	·74476	7·4
5·0	26·0	,,	·60841	21·8	19·1	,,	,,	·74883	6·1
5·3	26·1	27·6	·61017	5·9	19·5	,,	,,	·75454	14·3
5·7	,,	,,	·61329	8·2	20·1	,,	,,	·76067	10·2
5·95	,,	,,	·61521	7·7	20·55	27·5	28·7	·76737	14·8
6·2	26·2	27·8	·61945	17·0	21·0	,,	,,	·77250	11·4
6·55	,,	,,	·62425	13·7	21·6	27·6	,,	·77815	9·4
6·75	,,	,,	·62760	16·8	22·2	,,	,,	·78435	10·3
7·1	26·3	27·9	·63260	14·3	22·8	,,	,,	·79131	11·6
7·3	,,	,,	·63623	18·2	23·4	27·7	,,	·80181	17·5
8·0	26·4	28·0	·64437	11·6	23·8	,,	,,	·80823	16·1
8·45	26·5	,,	·65027	13·1	24·3	,,	,,	·81607	15·7
8·85	26·6	,,	·65583	13·9	25·0	,,	28·6	·82595	14·1
9·2	,,	,,	·66064	13·7	25·4	,,	,,	·83376	19·5
9·5	,,	28·2	·66460	13·2	25·9	,,	,,	·84052	13·5
10·45	26·7	28·4	·67453	10·4	26·55	27·8	,,	·84867	12·5
11·1	26·8	28·5	·68052	9·2	26·9	,,	28·5	·85515	18·5
11·45	,,	,,	·68352	8·6	27·4	,,	28·4	·85950	8·7
11·75	,,	,,	·68843	16·5	27·85	27·7	,,	·86245	6·5
12·1	26·9	,,	·69131	8·1	30·2	27·6	28·0	·86927	2·9
12·38	27·0	,,	·69241	4·0	30·9	,,	29·7	·87361	6·2
12·68	,,	,,	·69534	9·8	32·4	,,	27·8	·88183	5·5
13·08	27·1	,,	·69935	10·0	33·9	27·5	27·7	·88957	5·2

The following table shows the dissociation constant of chebulinic acid as calculated from the titration results.

Dissociation Constant of Chebulinic Acid.

Mol. Wt. = 914. NaOH = 0·0772 N.

c.c. NaCH	E.M.F.	pH	H-ion concentration $\times 10^6$	Free acid $\times 10^4$	Undissociated acid $\times 10^4$	NaR $\times 10^4$	K $\times 10^6$
1·8	·5427	5·015	9·64	13·19	13·09	5·52	(4·07)
2·4	·5609	5·321	4·78	11·32	11·27	7·34	3·12
2·9	·5692	5·461	3·47	9·736	9·7	8·85	3·16
3·3	·5764	5·581	2·63	8·545	8·3	10·06	3·19
							3·16

The following tables show the initial pH and the pH at different stages of neutralisation of the various tannic acids used in concentrations mentioned.

pH of Tannin Solutions.

Saturated Calomel-H Electrodes.

Acid	Molality	Initial pH	1st stage pH	2nd stage pH
Ellagic ..	0·00506	5·77	7·8	
Ellagitannic ..	0·0148	2·3	2·6	7·14
Chebulinic ..	0·00188	3·6	6·2	7·4

Saturated Calomel-Quinhydrone Electrodes.

Acid	Molality	Initial pH
Ellagic	0·00516	6·4
Ellagitannic	0·0148	4·03
Chebulinic	0·00185	4·29
Myrobalan extract ..	..	3·6

The following table summarises the values of the dissociation constants of the various tannic acids.

Acid	Dissociation constant
Ellagic ..	$2{\cdot}6 \times 10^{-7}$
Ellagitannic ..	$1{\cdot}6 \times 10^{-5}$
Chebulinic ..	$3{\cdot}16 \times 10^{-6}$

The divergence in the results for the initial pH obtained by the hydrogen and the quinhydrone electrodes may be due to the disturbing influence of the tannin which is often met with in estimating the pH of the tan liquors. In the case of the pure tannic acids, these factors should not be present and it is believed that the results with quinhydrone electrode are more reliable than those of the hydrogen electrode for the initial pH. It is intended to confirm these results by using a glass electrode in the near future. The results show that the myrobalan tannic acids which are represented by the ellagitannic acid, are half as strong as gallic acid (K, 3.8×10^{-5}) and stronger than gallotannic acid (K, 1.3×10^{-5}) *cf.* Part II.

As the isoelectric point of collagen is pH 5 and there is rapid increase in the fixation of tanning between pH 5 and pH 2, the solutions of the myrobalan extract and those of the component acids, have their pH values automatically adjusted to the optimum conditions for tanning purposes. It is also interesting to note that the pH of the myrobalan tannic acids at the first stage and even the second stage of neutralisation correspond to the isoelectric point of the other form of collagen, although Britton (*Hydrogen Ions,* p. 441) does not accept the explanation regarding the second form of collagen.

SUMMARY.

The first dissociation constants of chebulinic, ellagic and ellagitannic acids have been determined by the potentiometric method and it has been shown that ellagitannic acid from myrobalans is nearly as strong as gallic acid.

The significance of the pH of the various solutions of myrobalan tannic acids from the point of view of tanning has been pointed out.

The various tannic acids have been electrometrically titrated by the differential method and the equivalents and the polybasic nature of these acids have been confirmed.

All the tannic acids showed prominent spurious peaks in the differential titration curves for which no adequate reason could be assigned. Importance was given to those equivalents which were confirmed by the appearance of subsidiary peaks which were multiples of the main peak.

The quarter basic nature of chebulinic acid and the value of the equivalent have been found to be in accordance with the original digalloyl structure of this acid given by Freudenberg and Fick with, however, six molecules of water of crystallisation.

Ellagic acid was titrated to the second stage of neutralisation. The equivalent was found to be in agreement with the original formula suggested by Schiff.

The electrometric titration of ellagitannic acid shows the first stage of neutralisation corresponding to the formula $C_{26}H_{28}O_{19}$ (Nierenstein) and the last stage being shown when the value of the equivalent is 1/5 of the first, these results being in agreement with the fact that there are four hydroxyl groups and one carboxyl group in the acid, the intermediate stages of neutralisation being also indicated by subsidiary peaks.

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