ELECTROMETRIC TITRATION OF TANNIC ACIDS.

PART II. ELECTROMETRIC TITRATION OF GALLIC AND GALLOTANNIC ACIDS.

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GALLIC ACID.

Smith and Jones (*Amer. Chem. Jour.,* 1913, **50**, 39) calculated the dissociation constant K_1 of gallic acid from the conductivity measurements.

The values of the dissociation constant K_1 ($\times 10^4$) which were obtained at different dilutions (V) and temperatures (T) are given below:

(V)	Temperature (T)				
	0	26	35	50	65
64	0·32	0·38	0·39	0·42	0·42
128	0·33	0·38	0·39	0·42	0·42
512	0·38	0·43	0·44	0·49	0·41
1024	0·34	0·38	0·38	0·42	0·42
2048	0·34	0·38	0·38	0·39	0·37

Even at a dilution of 2048 litres the dissociation has not gone beyond the first stage. Thus the mean value of the first dissociation constant of gallic acid at 25° C. is 4.6×10^{-5}.

The object of the present investigation is to check the above value by potentiometric titration and also to obtain the value of the second dissociation constant K for the strongest of the OH groups in the gallic acid.
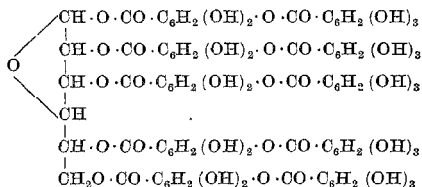
EXPERIMENTAL.

Pure gallic acid was prepared from the myrobalan tannic acid as follows:—

The purified myrobalani tannic acid was boiled with sulphuric acid for about 6–8 hours and extracted with ether (gallic acid being more soluble in ether than in water). The acid was crystallised thrice from boiling water and treated with animal charcoal when fine, lustrous, silky needles with one molecule of water of crystallisation were obtained; m.p. 239–240° with decomposition; m.p. methyl ester 192°.

The acid was titrated electrometrically using hydrogen and saturated calomel electrodes using the apparatus and method described in Part I.

The carboxyl group is neutralised on adding 12.45 c.c. of NaOH (0.0718 N) to 0.1696 grams of acid, corresponding to equivalent weight of 189.7 (calculated 188).

The first dissociation constant of gallic acid is calculated from the titration results which are given in the following table:—

Dissociation Constant K_1 of Gallic Acid. Temp. 28°.

Wt. taken = 0.1696 gm.   NaOH = 0.0718 N.   Mol. wt. = 188.
Dilution = 200 c.c. of 0.00451 Molal solution.

c.c. NaOH	E.M.F.	pH	H-ion concentration	Free acid $\times 10^4$	Undissociated acid $\times 10^4$	NaR $\times 10^4$	$K_1 \times 10^5$
3.2	0.47558	3.9	1.259×10^{-4}	33.09	31.83	11.33	4.47
5.2	0.49261	4.19	6.457×10^{-5}	25.76	25.12	18.2	4.67
6.5	0.50328	4.635	4.315×10^{-5}	21.10	20.67	22.59	4.72
8.3	0.51913	4.63	2.344×10^{-5}	14.71	14.48	28.61	4.63
9.49	0.53131	4.88	1.318×10^{-5}	10.53	10.40	32.54	(4.12)
							4.6

The first dissociation constant K_1 is 4.6×10^{-5}, which is in fair agreement with the value obtained by Smith by the conductivity data.

Second dissociation constant K_2 calculated from our results is 2.57×10^{-9}. This value is due to the dissociation of the *para*-hydroxy group.

Dissociation Constant K_2 of the Phenolic Group in Gallic Acid.

Wt. taken = 0.1696 gm.   NaOH = 0.0718 N.   Mol. wt. = 188.
Dilution = 200 c.c. of 0.00451 Molal solution.

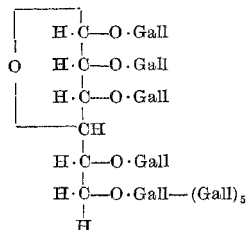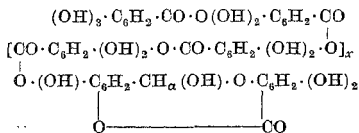| C.C. NaOH	E.M.F.	pH	H-ion concentration	$Na_2R \times 10^4$	NaHR $\times 10^4$	$K_2 \times 10^9$
13.5	0.70187	7.67	2.138×10^{-8}	6.45	38.05	(3.56)
15.5	0.73388	8.2	6.31×10^{-9}	13.45	31.65	2.68
18.0	0.75741	8.6	2.51×10^{-9}	21.6	23.5	2.25
22.0	0.79037	9.15	8.079×10^{-9}	35.36	9.74	2.50
23.0	0.80175	9.33	4.677×10^{-10}	38.65	6.45	2.85
						2.57

GALLOTANNIC ACID.

Gallotannic acid is amorphous and hygroscopic and hence different methods have been suggested for its purification including precipitation with sodium chloride or fractional precipitation with solvents. The most common impurity is gallic acid. Paniker and Stiasny (*J.C.S. Trans.*, 1911, **99**, 1821) claim to have obtained purest tannic acid free from even a trace of gallic acid by their method of purification. They dissolved tannic acid in a small quantity of water and neutralised it with sodium hydrogen carbonate and extracted with ethyl acetate. Ethyl acetate extract was washed with little water till free from alkali. Finally, after distilling off most of the solvent, it was precipitated with benzene.

The following structural formulæ of gallotannic acid have been suggested:—

$$\text{O} \begin{cases} \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_3 \\ \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_3 \\ \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_3 \\ \text{CH} \end{cases}$$

$$\begin{aligned} &\text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_3 \\ &\text{CH}_2\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_3 \end{aligned}$$

I.   Fischer.

$$\text{O} \begin{cases} \text{H} \cdot \text{C}\!-\!\text{O} \cdot \text{Gall} \\ \text{H} \cdot \text{C}\!-\!\text{O} \cdot \text{Gall} \\ \text{H} \cdot \text{C}\!-\!\text{O} \cdot \text{Gall} \\ \text{CH} \end{cases}$$

$$\begin{aligned} &\text{H} \cdot \text{C}\!-\!\text{O} \cdot \text{Gall} \\ &\text{H} \cdot \text{C}\!-\!\text{O} \cdot \text{Gall}\!-\!(\text{Gall})_5 \\ &\text{H} \end{aligned}$$

II.   Freudenberg.   Gall stands for $\text{CO} \cdot \text{C}_6\text{H}_2 (\text{OH})_3$

$$(\text{OH})_3 \cdot \text{C}_6\text{H}_2 \cdot \text{CO} \cdot \text{O} (\text{OH})_2 \cdot \text{C}_6\text{H}_2 \cdot \text{CO}$$

$$[\text{CO} \cdot \text{C}_6\text{H}_2 \cdot (\text{OH})_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 \cdot (\text{OH})_2 \cdot \text{O}]_x$$

$$\text{O} \cdot (\text{OH}) \cdot \text{C}_6\text{H}_2 \cdot \text{CH}_\alpha (\text{OH}) \cdot \text{O} \cdot \text{C}_6\text{H}_2 \cdot (\text{OH})_2$$

$$\text{O}\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\text{CO}$$

III.   Nierenstein.

Gallotannic acid, according to Nierenstein, is a polydigalloylleucodigallic acid anhydride, which sometimes occurs in the form of a

glucoside, the glucose being attached to the position marked *a* in formula III.

Different workers have found different values of specific rotation of gallotannic acid ranging from 64° to 75° according to the methods of purification employed by them. In the following table the methods of purification and the corresponding specific rotations are summarised. It will be seen from the table that specific rotation is no criterion of purity of the tannic acid.

Kahlbaum's Gallotannic Acid.

Reference	Method of purification	$[\alpha]_D$
Iljin (*Berichte*, 1909, **42**, 1731) ..	1. Walden's method	+ 67·8°
	2. Rosenheim and Schidrowitz's	+ 70·9°
	3. Precipitation with NaCl	+ 64·9°
	4. Precipitation with chloroform	+ 74·8°
Paniker and Stiasny (*J.C.S. Trans.*, 1911, **99**, 1821)	1. Precipitation with NaCl	..
	2. Rosenheim and Schidrowitz's method 1st ..	+ 73·29°
	2nd ..	+ 72·12°
	3rd ..	+ 72·37°
	4th ..	+ 72·37°
	3. (*a*) Neutralisation with $NaHCO_3$ and extraction with ethyl acetate	+ 56·76°
	(*b*) Made strongly alkaline and extracted with ethyl acetate	+ 64·72°
	(*c*) Precipitated by $NaHCO_3$ and then extracted with ethyl acetate ..	+ 69·6°
	(*d*) Filtrate from (*c*) acidified and then extracted	+ 65·1°
Freudenberg (*Berichte*, 1912, **45**, 919)	1. Neutralisation with alkali and extraction with ethyl acetate	+ 70·9°
	2. Potassium salt decomposed by H_2SO_4 and extracted	+ 70·77°
	3. Dissolved in water and dried in order to remove traces of solvent used in purifying	+ 68·48°
Authors	1. (*a*) Original tannic acid " Kahlbaum " A.R.	+ 62·7°
	(*b*) Paniker and Stiasny's method ..	+ 58·7°
	(*c*) Walden's method 1st fraction ..	+ 49·0°
	,, ,, 2nd fraction ..	+ 56·9°
	,, ,, last fraction ..	+ 60·6°
	2. Tannic acid (Baird and Tatlock)	
	(*a*) Original	+ 66·8°
	(*b*) Purified by Paniker and Stiasny's method	+ 75·6°
	3. Tannic acid (Riedel and Haen)	
	(*a*) Original	+ 67·0°
	(*b*) Paniker and Stiasny's method	+ 69·4°

Due to the amorphous and hygroscopic character of gallotannic acid and to the impurities, different workers have obtained varying molecular weights as shown in the following table given by Nierenstein (*Natural Organic Tannins*, 1934, p. 118) :—

Worker	Reference	Molecular weight	Solvent used
Paterno		340	glacial acetic acid
,,		2643—3700	Water
Sabanejeff	*Jour. Russ. Phys. Chem. Soc.*, 1890, **22**, 104.	1104	Water
,,	,, ,, ,,	1113—1322	Glacial acetic acid
Walden	*Berichte*, 1898, **31**, 3167.	1350—1560	Acetone (Schuchardt gallotannin)
,,	,, ,, ,,	753—763	,, Merck's
Krafft	*Berichte*, 1899, **32**, 1608	1587—1626	Water
Feist	*Chem. Zeitz.*, 1908, p. 918.	615	Acetone
Iljin	*Jour. prakt. Chemic.*, 1910, (2) **32**, 422.	1247—1637	,,
Feist	*Arch. d. Pharm.*, 1912, **250**, 668.	615—746	,,
,,	,, ,, ,,	521	,, (Aleppo gallotannin)
,,	,, ,, ,,	899	,, (Chinese gallotannin)
,,	,, ,, ,,	1045	,, ,, ,,
Navassarat	*Kolloid Zeitschr.*, 1913, **12**, 99.	714—2383	Water
,,	,, ,, ,,	774—852	Acetone
,,	,, ,, ,,	441—705	Glacial acetic acid

The divergent results obtained for the molecular weight of gallotannic acid, especially the very low values in acetone and acetic acid as solvent, cannot be easily accounted for, although the difficulty of obtaining a pure substance may be the reason for some of the marked discrepancies. L. F. Iljin (*Berichte,* 1909, **42**, 1731; 1914, **47**, 985) has shown from his experiments by fractional precipitation with solvents and with zinc acetate that, gallotannic acid is not a homogeneous substance. E. Fischer (*Berichte,* 1919, **52**, 828) supposes that gallotannic acid from Chinese galls contains not only a mixture of isomeric substances but also a mixture of substances having various empirical compositions. Freudenberg (*Die Chemie der naturlichen*

Gerbesoffe, 1920, p. 101, Berlin) points out that the formula for gallo-tannic acid may have at least a hundred variants and therefore suggests that in addition to Fischer's formula I, formula such as II may be also true, both formulæ being the corresponding limits of possibilities. Karrer, Salomon and Peyer (*Helv. Chim. Acta.*, 1923, **6**, 16) suggest that in Chinese gallotannin there are fractions which have 9 gallic acid residues connected to 1 mol. of glucose (nona-galloyl-glucose), and that it is probably a mixture of deka-, nona- and octa-galloyl-glucose. According to Nierenstein, gallotannic acid is polydi-galloylleucodigallic anhydride (formula III).

The remarkably strong acidity of the gallotannic acid is also worth noting. As there is no free carboxyl group in the acid, the acidity of gallotannic acid has been ascribed to the cumulative effect of the hydroxyl groups of the pyrogallol nuclei in the gallotannin molecule.

EXPERIMENTAL.

In our experiments we used Kahlbaum's A.R. gallotannic acid. It has original rotation $[a]_D = + 67.0°$. We purified it by two methods: (1) Paniker and Stiasny's, (2) Walden's.

Method 1—consists in neutralising tannic acid with sodium hydrogen carbonate and then extracting with ethyl acetate. Its original rotation $[a]_D = + 67·0°$ changed to $[a]_D = + 58·7°$.

Method 2.—5 grams of Kahlbaum's tannic acid were dissolved in 5 c.c. of 95% alcohol and to this, 100 c.c. of *iso*amyl alcohol were added. To the filtrate 70 c.c. of petroleum ether (b.p. 40–50°) were added and filtered from dirty grey flocky precipitate. This fraction was rejected and the acid was fractionally precipitated thrice (I, II and III) with 70 c.c. of petroleum ether. The precipitate was washed carefully to remove amyl alcohol adhering to it and dried at 100° C. for about an hour.

Yields from 5 gms.	I 2 gms.	II 1·2 gms.	III Fractions 1 gm.
$[a]_D^{25°}$	$+ 49·0°$	$+ 56·9°$	$+ 60·6°$

The tannic acid purified according to the method (1) was titrated electrometrically using polished tungsten wires in differential titrations. The results are given in the following table:—

Electrometric Differential Titration of Gallotannic Acid.

(1) Kahlbaum's sample purified by Paniker and Stiasny's method.

Wt. taken = 2·5052 gm.   NaOH = 0·112 N.

Polished Tungsten Wire Electrodes.

c.c. of NaOH	$\frac{dE}{dC}$	c.c. of NaOH	$\frac{dE}{dC}$	c.c. of NaOH	$\frac{dE}{dC}$
1·9	31·0	12·0	77·5	18·4	13·0
4·8	14·0	12·1	155·0	21·1	7·5
6·0	16·2	12·2	155·0	21·3	80·0
7·1	14·0	12·3	155·0	22·1	20·6
8·0	20·5	12·5	80·0	24·9	7·0
9·1	17·0	12·6	145·0	26·3	12·0
9·8	25·0	12·7	145·0	33·0	3·6
10·2	44·0	12·8	155·0	34·2	15·5
10·4	77·5	13·0	80·0	41·5	3·0
10·6	77·5	13·1	155·0	50·0	2·6
10·9	52·0	13·9	20·6	80·4	0·87
11·2	52·0	14·3	39·0	95·8	1·9
11·4	77·5	16·2	10·0	100·0	5·5
11·6	77·5	16·4	80·0	104·1	6·0
11·8	75·0	17·1	23·5	109·	4·7

The curve (Fig. 1) is plotted as c.c. of NaOH against dE/dC which shows three distinct peaks corresponding to equivalent weights, 1745, 1372, 1055 on addition of 12.75, 16.3 and 21.2 c.c. respectively.

Kahlbaum's gallotannic acid purified by Walden's method was titrated electrometrically using hydrogen and saturated calomel electrodes; the results of the titration are given in the following table:—

Potentiometric Titration of Gallotannic Acid.

(1) Kahlbaum's sample purified by Walden's method.

Wt. taken = 0·5722 gm.   NaOH = 0·0772 N.

Electrodes H_2 — Sat. calomel.

C.C. NaOH	Cell C.°	Calomel C.°	E.M F.	$\frac{dE}{dC}$	c.c. NaOH	Cell C.°	Calomel C.°	E.M.F.	$\frac{dE}{dC}$
0·0	25·9	27·0	·50329	..	6·91	26·5	27·6	·654	·0040
0·45	26·1	,,	·43531	..	7·6	,,	,,	·655	·0014
0·95	26·2	27·1	·46185	·05319	8·22	,,	,,	·660	·008
1·1	,,	,,	·47385	·080	9·07	,,	,,	·664	·0047
1·65	,,	27·2	·49235	·0336	10·30	26·6	27·7	·673	·0073
2·27	,,	27·4	·50939	·0274	11·30	,,	,,	·681	·008
2·83	,,	,,	·53041	·0375	12·45	,,	,,	·689	·007
3·15	26·3	27·5	·54983	·0583	13·78	,,	,,	·695	·0045
3·5	,,	,,	·56854	·0534	15·55	,,	,,	·703	·0045
3·62	,,	,,	·57607	·0627	17·3	,,	27·6	·714	·0062
3·83	26·4	,,	·58677	·0510	19·2	,,	,,	·720	·0031
4·00	,,	,,	·59783	·065	21·1	26·7	,,	·727	·0036
4·21	,,	27·6	·61167	·066	27·0	,,	,,	·738	·00194
4·54	26·5	,,	·62354	·035	30·0	,,	,,	·746	·0026
4·84	,,	,,	·62923	·0189	35·0	,,	,,	·759	·0026
5·3	,,	,,	·63103	·0009	42·0	,,	,,	·822	·009
5·6	,,	,,	·64429	·0398	44·0	,,	,,	·855	·0165
5·92	,,	,,	·648	·0131	45·0	,,	,,	·866	·0110
6·4	,,	,,	·652	·0083	46·0	,,	,,	·872	·006

The curves (Fig. 2) are plotted as c.c. of NaOH against E.M.F. and c.c. of NaOH against dE/dC.

The dE/dC curve shows six peaks corresponding to equivalent weights 1808, 1360, 937, 686, 452 and 172, on addition of 4.1, 5.54, 7.25, 10.8, 16.4 and 43 c.c. of alkali.

The dissociation constant of Kahlbaum's gallotannic acid purified by Walden's method is calculated from the above titration results and the values obtained are given in the following table:—

Dissociation Constant of Purified Gallotannic Acid.

Wt. taken = 0·5722 gm.   NaOH = 0·0772 N.   Mol. wt. = 1700.
Dilution = 250 c.c. of 0·001346 Molal solution.

c.c. NaOH	E.M.F.	pH	H-ion concentration	Free acid × 10^4	Undissociated acid × 10^4	NaR × 10^4	K × 10^5
3·15	0·5489	5·136	7·311 × 10^{-6}	3·69	3·62	9·61	(1·94)
3·5	0·5685	5·450	3·55 × 10^{-6}	2·62	2·585	10·66	(1·46)
3·62	0·5761	5·57	2·692 × 10^{-6}	2·25	2·22	11·03	1·34
3·83	0·5868	5·748	1·786 × 10^{-6}	1·61	1·58	11·65	1·32
4·00	0·5978	5·933	1·17 × 10^{-6}	1·09	1·078	12·16	1·32
4·21	0·6117	6·165	6·84 × 10^{-7}	0·456	0·449	12·78	(1·95)
						mean	1·32

In the case of Riedel and Haen's tannic acid it had originally an optical rotation $[\alpha]_D^{25} = 67.0°$. After purifying by Paniker and Stiasny's method its optical rotation changed to $[\alpha]_D^{25} = +69.4°$.

The results of differential titration with tungsten electrodes are given in the following table.

(2) Riedel and Haen's sample purified by Paniker and Stiasny's method.

Wt. taken = 2·3194 gm.   NaOH = 0·112 N.
Polished Tungsten Electrodes.

c.c. NaOH	$\frac{dE}{dC}$	c.c. NaOH	$\frac{dE}{dC}$	c.c. NaOH	$\frac{dE}{dC}$
1·3	−44·6	14·1	62·5	25·3	10·0
2·6	+17·0	14·3	67·5	26·2	12·8
4·3	10·0	14·5	65·0	27·1	12·1
5·7	7·5	14·8	43·0	28·5	8·0
7·6	6·0	15·3	27·0	28·8	31·0
9·2	6·6	15·7	30·0	29·3	18·0
10·1	9·0	16·0	41·6	30·1	11·9
11·0	10·5	16·3	40·0	30·5	21·0
11·6	22·5	16·8	23·0	31·1	24·0
12·0	33·75	19·1	7·0	32·1	9·5
12·3	45·0	21·1	7·75	33·1	9·7
12·8	29·0	22·4	10·0	33·9	12·0
13·6	19·5	24·1	8·4	..	..
13·9	45·0	..	..	..	..

The curve (Fig. 3) is plotted as c.c. of NaOH against dE/dC which shows four peaks corresponding to equivalent weights 1704, 1458, 1307 and 730 on addition of 12.15, 14.2, 15.8 and 28.6 c.c. of alkali.

Next, tannic acid from the firm Baird and Tatlock was used. It had an optical rotation $[a]_D^{2.5} = +66.8°$ at the beginning. On purifying by the Paniker and Stiasny's method it changed to $[a]_D^{2.5} = +75.6°$.

The results of the electrometric titration using Ag/AgCl-Hydrogen electrodes and employing the original tannic acid without any further purification, are given in the following table :—

(3) Baird and Tatlock's sample.

Wt. taken = 0·5182 gm.   NaOH = 0·146 N.

Electrodes Ag/AgCl — H_2 Electrodes.

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	0·674		5·5	0·830	−0·008	7·2	0·856	0·020
1·0	0·703	0·029	6·0	0·829	−0·002	7·6	0·858	0·005
1·5	0·726	0·046	6·2	0·836	+0·035	7·8	0·862	0·020
2·0	0·745	0·038	6·3	0·841	0·050	8·0	0·868	0·030
3·0	·795	·050	6·4	·843	·020	8·3	·869	·003
3·6	·811	·026	6·5	·844	·010	8·5	·870	·005
4·0	·823	·030	6·6	·846	·020	8·7	·871	·005
4·5	·832	·018	6·8	·848	·010	8·9	·860	−0·055
4·7	·834	·010	7·0	·852	·020	9·2	·865	+0·015
5·0	·834	·00						

The curve (Fig. 4) is plotted as c.c. of NaOH against dE/dC which shows six peaks corresponding to equivalent weights, 2838, 1420, 934, 568, 542 and 450, on adding 1.2, 2.5, 3.8, 6.2, 6.5 and 7.9 c.c. of the alkali.

DISCUSSION.

According to the penta-(m-digalloyl)-glucose formula suggested by Fischer, the acid should be mainly *penta*-basic ; because out of three hydroxyl groups in the molecule of gallic acid contained in the digalloyl group, only one, *viz.,* the *para*-hydroxy, is comparatively strong as has been shown experimentally in the case of gallic acid. As the acid is *penta*-basic, the differential titration curve should have 5 main peaks corresponding to the neutralisation of each of the free and
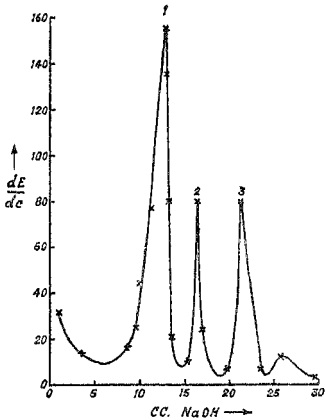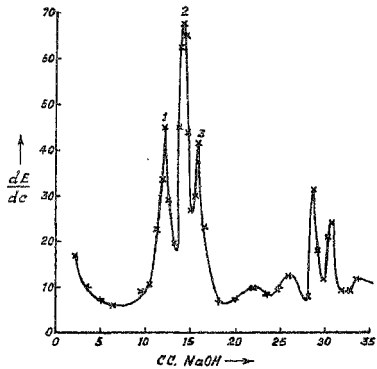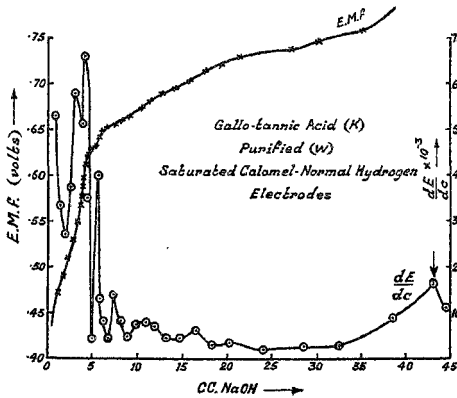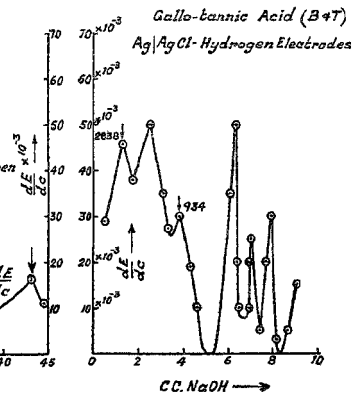
Fig. 1.

Fig. 3.

Fig. 2.

Fig. 4.

strongly acidic hydroxyl group in the five gallic acid residues of the digalloyl groups. In addition to these main peaks there should be also a number of minor peaks corresponding to the neutralisation of other hydroxyl groups contained inside the acid molecule. The molecular weight according to *penta*-digalloyl glucose formula is 1700, and the spacing of the five peaks should correspond to 340 as value of equivalent, which we have experimentally found and also reached half this value for the equivalent (172).

According to Nierenstein's formula for gallotannic acid, the molecular weight should be 1684 when $x = 3$. In all the titrations carried out, the values for the first peak agree within the experimental error of the measurements with both the formulæ and the variations found may be due to impurities. One cannot therefore decide between the two formulæ.

The following table gives the calculated values of the equivalent weights of the acid at different stages of neutralisation and those found experimentally:—

Theoretical		Observed			
Nierenstein's $x = 3$	Fischer's	Kahlbaum's gallotannic acid		R & H	B & T
		(P and S) fig. 1	(W) fig. 2	(P and S) fig. 3	fig. 4
1684	1700	1745	(1800)	1704	..
	1360	1372	1360	1307	1420
	1020	1055	938	..	934
	680	665	686	730	568
	340	..	359	..	450
	..	..	172	..	..

In the case of Kahlbaum's gallotannic acid purified by (1) Paniker and Stiasny's method, (2) Walden's method, the calculated values somewhat agree with the theoretical ones. In the table, the values given for Fig. 1 are obtained with tungsten electrode and those for Fig. 2 with hydrogen electrode. Some of the values in Fig. 2 are in closer agreement with the calculated values than some of those in Fig. 1 and *vice versa*. The last value 172 may be taken as due to the neutralisation of the hydroxyl group inside the molecule. The fluctuations in the value of the equivalent are due to the fact that the hydrogen electrode did not function satisfactorily. It is intended to investigate this subject further by using a glass electrode.

In the case of gallotannic acid obtained from Riedel and Haen and purified by Paniker and Stiasny's method, the first peak in the differential curve (Fig. 3) with tungsten electrodes correspond very closely to the calculated value according to the Fischer's formula. There is wide variation in the other values represented by the peaks in the curve, the electrode apparently not having attained equilibrium.

In the experiments on the electrometric titrations of gallotannic acid obtained from Baird and Tatlock, although the acid is impure, there is a fixed proportion in the values obtained for the peaks in the differential curve (Fig. 4), the first five peaks being equidistant at 1.25, 2.5, 3.8, 6.2 and 7.9 c.c. of 0.146 N alkali.

The dissociation constant of the purified gallotannic acid, calculated from the titration results with hydrogen electrode is 1.32×10^{-5}. The dissociation constant is rather high and cannot be accounted for, unless there is free carboxyl group in the acid. For pyrogallol, K_1 is of the order 10^{-10}. The assumption of free carboxyl group makes the Fischer's or Freudenberg's formula untenable. Nierenstein's formula can only hold good, if it is assumed that the anhydride linking, which is really a lactone, breaks up on adding alkali and contributes to the acidity of the compound, which appears to be the case.

We take this opportunity to thank Mr. C. T. Abichandani for his help in the electrometric titrations.

SUMMARY.

The first and the second dissociation constants (4.6×10^{-5}, 2.57×10^{-9}) of gallic acid have been determined, corresponding to the dissociation of the carboxyl and that of one of the phenolic groups which is stronger than the remaining two. The quarterbasic nature of this acid has been clearly shown although the dissociation constants for the other stages were not calculated.

In the case of gallotannic acid the first dissociation constant (1.32×10^{-5}) has been calculated, the equivalent found being in agreement with Nierenstein's formula when $x = 3$. The remarkably high value of the dissociation constant is obviously due to the acid obtained by the easy hydrolysis of the lactone, which is the distinctive feature of Nierenstein's formula "polydigalloylleucodigallic acid anhydride".

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