

Educational (191/) Department.

ORDINARY MS.

G.O., No. 152

DATED 15-3-11

[Despatch Abstract.]

State Technical Scholarship

Receiving letter from the Government of India forwarding for the information of the Government of Madras the 8 diaries in original of certain state technical scholars.

BACK PAPERS.

G.O.	No.	Department.	Date.	G.O.	No.	Department.	Date.

FURTHER PAPERS.

G.O.	No.	Department.	Date.	G.O.	No.	Department.	Date.

[E. & L.]
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EDUCATIONAL DEPARTMENT.

CURRENT FILE.

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PAPERS PUT UP WITH CURRENT No. _____

Papers of the department to which the current belongs.

Number.	Date.	Original (=O.) or spare copy (=S. C.)	Remarks. (In this column such of the papers as have been removed for copying, printing, etc., should be marked with a cross.)	Initials of Referencer with date in token of return to Reference department.

Papers of other departments.

Department.	Number.	Date.	Original (=O.) or spare copy (=S. C.)	Despatcher to note the return of the papers to the departments concerned.



Sl. No. 473
Regd 3. 3. 4

No. 284

Government of India,
DEPARTMENT OF EDUCATION.
(Education) XIX

From

H. Sharp, Esq.,

Joint Secretary to the Government of India,

To

The Secretary to the Government of Madras,

Education Department.

Calcutta, the 25 February 1911.

Sir,

I am directed to forward, for the information of the
Government of Madras, the diaries (in original) of the
State technical scholars noted on the margin.

Messrs Panikar, Nair and Menon.

450
6-8-09

426
1-6-08 B

402
8-7-09 C



I have the honour to be,

Sir,

Your most obedient servant,

[Signature]

Joint Secretary to the Government of India.

✓ ✓
Extract from a letter of 14th June 1910

From the Vice-Chancellor
The University,
14th June 1910

Dear Professor Arnold

In accordance with the
instructions I have received, I beg to
report on the two following Indian
State Scholars who are studying here

M. A. R. Paniker

* *

Mr Paniker is still pursuing research
work in the Laboratory of our Leather
Industries Dept, and his conduct, industry
& progress are in every respect very
satisfactory

* * *

Believe me
Faithfully
(Sd) Natha

Professor Arnold
India Office S.W.

Copy II

Research carried out
in the Leather Industries Dept
during the Session 1909-10

by

W. R. Parker

Govt of India Scholar

Submitted to the Educational
Adviser for Approval.

have analysed the
at, as could be seen

4

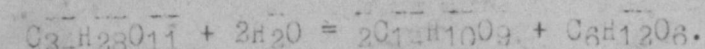
6

Investigation of the Acidity of Gallotannic Acid with
a view to throw some light on its chemical Constitution.

I. Historical Outline.

In spite of the large amount of experimental data, more or less conflicting and unconfirmed which have accumulated on the subject of late, the chemical constitution of gallotannic acid is still an unsettled problem.

The first serious attempt to study its constitution might safely be attributed to Strecker who in 1852 suggested the glucoside character. He found 23% glucose formed by the action of acids, alkalies or ferments. Blasiwetz (1837) maintained the view that it is a gumide or compound of dextrin which is finally converted into glucose by the hydrolytic action of acids. On the basis of a yield of 23% glucose, Schiff suggested the formula $C_{31}H_{28}O_{11}$ for the glucoside. The decomposition was supposed to take place as follows:



Utz (1905) boiled gallotannic acid with 25% HCl and isolated glucose which became finally converted into Levulinic acid and Furfurel.

More recent work on the subject seems to show that glucose is present in an uncombined form in the tanning material which speaks against its glucoside nature.

Feist (Chem. Ztg. 1903. 918) seems however to have observed that a glucoside of gallotannic acid could be extracted from Turkish Galls by the use of organic solvents while by aqueous extraction gallotannic acid is obtained in a free state. He therefore maintains that the tannin of galls is in reality a glucoside which owing to its unstable nature is split up by water into free gallotannic acid and glucoside.

It is enough for our purposes, to know that the commercial product prepared in a pure state is free from any Carbohydrate as impurity (Compare Nierenstein Chem. Ztg. 1909. No. 15)

Various investigators from the time of Berzelius have analysed the compound and the results are not satisfactorily concordant, as could be seen from the following table:

	C	H
Berzelius	51.5	3.8
Pelouze	51.5	4.1
Mulder	52.8	3.9
Bijlert	51.3	3.7
Strecker	52.4	3.5
Gautier	51.2	3.3
Frimole	52.1	3.5
Dekker	52.3	3.9
Walden	(52.27 to 52.85)	(3.78 to 4.33)
Inlijn	54.13	3.22

The nearest empirical formula which satisfies the majority of observations is $C_{14}H_{10}O_5$ and is generally accepted.

The colloidal character of the substance in aqueous solution prevents the determination of molecular weight being carried out by any of the ordinary osmotic methods. Walden and Ssabanjew have both shown that in glacial acetic acid and Phenol, it has the normal molecular weight (322), while in water the value varies with the degree of polymerisation.

Medium	Mol. Wt.	Sample used	Investigator
Water	1350	Sandcharit	Walden
"	1500	"	"
"	1580	"	"
"	783	Merck	"
"	753	"	"
"	1322	"	Ssabanjew (Jour. d. Russ. Physik Chem. Ges. 1891. 8)
Phenol	about 320		Patterno
Glacial Acetic Acid	"		"
(Zeit. f. phys. Chem. 4)			

A solution of potassium acetate in absolute alcohol gives a precipitate with a similar solution of gallotannic acid (in absolute alcohol). This precipitate has, in many analogous cases, been shown by A.G. Perkin to be either the potassium salts of the acid or an oxonium salt. An investigator

-2-

of this precipitate might, in case such a typical reaction takes place, give us some idea as to the correct molecular weight of the compound.

(This point, the operator intends to take up at an early opportunity)

The discovery of the optical activity of tannin has hitherto been claimed by Flawitsky (Jour. d. Russ. Chem. Ges. 22. 362. 1890) but it is worth while noting that Rosenheim (Ber. 42. 2452. (1909) attributes it to Van Tieghem (1867) (See Ann. des Sciences Nat. V.3 210. (1867) and still more recently Von Liepmann (Ber. 42. 4678) points out that the same property has likewise been previously described by Scheibler (Ztschr. f. Zucker industrie 13. 33. 1866)

Anyhow, it was not till Guntner (Cent. blatt 1896, 1. 189) rediscovered it in 1895, that more serious attention was drawn to the subject. Later on, the work was confirmed by Schiff (Chem. Zeit. 1895. 1330., 1896. 865) and also by Walden (B. 1897. 30. 3151)

For a considerably long time, this optical activity was supposed by many investigators (and especially by Flawitsky) to be due to the presence of carbohydrates as an impurity, but a careful investigation of the subject by Schiff and at a later date by Dekker has shown that, by hydrolysing the compound with dilute HCl under conditions when glucose or any other dextro-rotatory sugar could not possibly be converted into inactive compounds, optical activity diminishes gradually through the formation of inactive gallic acid. (Compare also the work of Nierenstein Chem. Ztg. 1902. 15)

It may then be accepted as proved that the optical activity must be due to some other component of gallotannic acid.

In support of this view the following experimental evidences may be cited:-

- a. Diminution in rotatory power when hydrolysed with HCl.
- b. The optical activity of derivatives like the acetyl and benzoyl compounds and the salts with alkaloids like quinine, all of which could be prepared in a pure state. (Rosenheim and Schidrowitz, J.C.S. 73. 878)
- c. Activity of condensation products of gallotannic acid with formaldehyde, e.g. Tannoform.

Dealing as we are with a substance of a pronounced colloidal character

the great difficulty which we have always to face is the method and extent of purification to which it is possible for us to subject the substance. Even the purest sample available in the market contains gallic acid as an impurity which is revealed by the Potassium cyanide test (See Young's reaction Chem. News 1883, 48. 31). Resinous matter, nitrogenous substances of varying composition, zinc salts and other mineral matter, all of which exert a marked influence on the specific rotatory power of the pure tannin have been shown to accompany gallic acid as impurities in any commercial sample of pure gallotannic acid.

Many investigators have attempted to utilise different methods of purification, a few of which might be worth mentioning.

Walden (B. 30. (1897) 3151) purifies it by

(1) Dialysis

- a. of a concentrated alcoholic solution of the substance through a porous cylinder in the dark, using 90% alcohol as the outer solution.
- b. of the same solution through parchment.

Stiasny and Neuner have shown that this method is not of great value, as the process of diffusion is always accompanied by a decomposition of gallotannin to gallic acid. It is therefore difficult by this means to get it entirely free from gallic acid.

(2) By shaking the aqueous solution with ether.

I have however found it extremely difficult to remove the last traces of Gallic acid, even after repeatedly shaking the solution for over 36 times with ether, the ethereal layer invariably gives gallic acid reaction with KCN solution.

(3) By dissolving in Ethyl Acetate (20 grms in 60 cc) and precipitating the filtrate solution by means of Benzene (30 cc) when an oily substance separates.

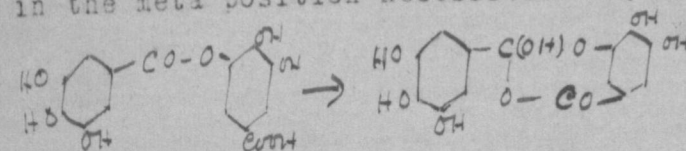
(4) Strecker's method of precipitating Tannins by means of Lead Acetate. The excess of lead is removed by H_2S and the residue obtained from the mother liquor on evaporation is extracted with acetic ether and evaporated at the ordinary temperature.

Procter and Nierenstein have shown that this method of purification leads to an alteration in the nature of the substance under treatment which is but a confirmation of the early observation of Schiff on the same subject.

Other methods are also in use of which mention is made later on (See p.

Through the examination of the optical activity of the substance, Walden comes to the conclusion that gallotannin is not an individual substance but a possible mixture of different chemical individuals. This supposition is mainly based on the fact that different fractions show different rotatory powers. (Loc. cit.) The same opinion was held by Kunz-Krause as a result of capillary analysis. The work of Walden was later on repeated by Rosenheim (Loc. cit.) who obtained a homogeneous substance of constant rotatory power $(\alpha_D) = +75^\circ$ approximately. They also prepared several derivatives of it such as the Acetyl Compound and the Quinine Salt, both from the purified and commercial samples which showed for the same derivative a constant rotation value in both cases.

It is an interesting point to recall that the same authors when they studied the influences modifying the specific rotatory power of gallotannic acid, observed the immediate total inactivity produced by the addition of five or six drops of ammonia to a 1% solution of gallotannic acid $(\alpha_D)_{15^\circ} = +75.2^\circ$. Caustic alkalies made the solution so dark that the measurement was rendered impossible. This point is very suggestive and one which might lead to far-reaching results in case the Potassium Compound proves to be optically inactive. Special precautions are no doubt necessary to exclude the presence of air from the preparation and examination of the substance. It is easy to imagine such a body as gallotannic acid to have the chemical configuration of a lactone type giving rise to an asymmetric Carbon in the molecule, which in solution might lead to a dynamic equilibrium of the two possible tautomeric forms. On the addition of an alkali the formation of the salt leads to the opening up of the lactone ring. The equilibrium being thus disturbed, the asymmetric carbon atom vanishes, followed by the disappearance of optical activity. This hypothesis might be set aside by the contention that the type of lactone compound in the meta position necessitated by our formula



has no analogy, the usually existing ones being invariably in the ortho position

(I intend to investigate this matter at an early date)

It would equally be worth while studying the optical activity of the Sodium salt of Acetyl Tannin which according to Nierenstein is soluble in

Sodium Carbonate.

The evidences on which different investigators have based their conception of the structure of gallotannin might be summarised under the following heads:-

1. The decomposition into gallic acid is almost quantitative.

Wetherill obtained 87.4% of gallic acid and later on Pottevin secured a yield of 95%.

2. The formation of penta methyl, penta acetyl or benzoyl derivatives indicate the presence of five hydroxyl groups in the substance.

According to Dekker's observation a hexa methyl derivative is obtainable but as his work is still unconfirmed we cannot judge the accuracy of his statement.

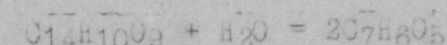
3. Bottinger's Researches (1834) on benzoyl derivatives seem to indicate the absence of a Carboxyl group and the possibility of the presence of a Carbonyl group only.

4. Formation of Ellagic Acid on Oxidation.

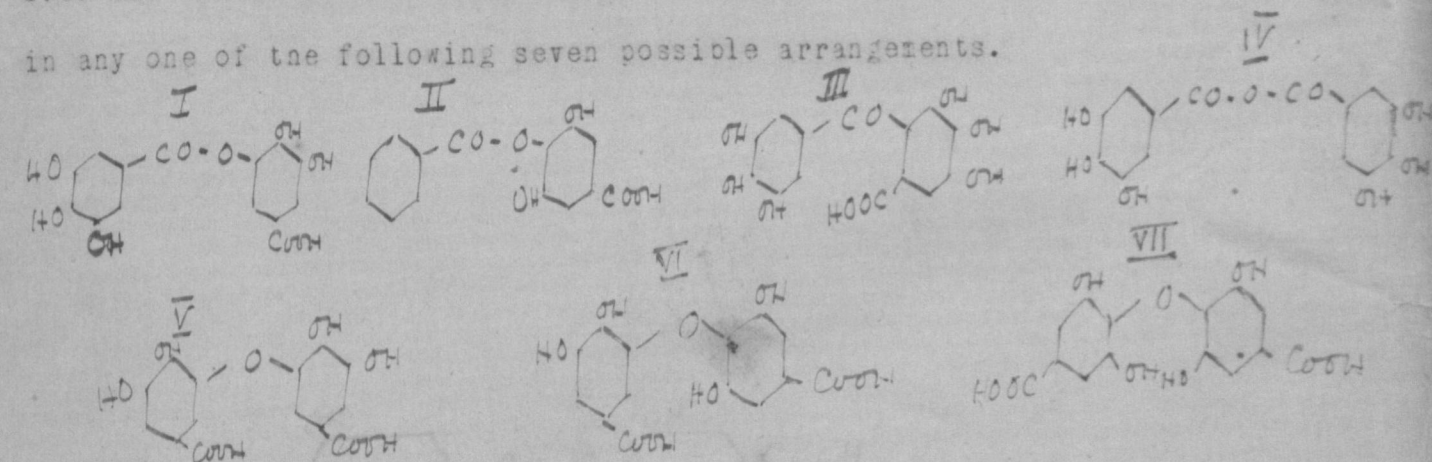
5. Reduction to Diphenyl methane by distillation over zinc dust (Nierengst 1905)

6. Existence of Optical Activity and the consequent necessity to assume the presence of an asymmetric carbon atom on the basis of the Van't Hoff-De Bel hypothesis.

If we accept the molecular weight (normal 322) found in a solution of phenol or acetic acid as our basis, then the following equation holds good:

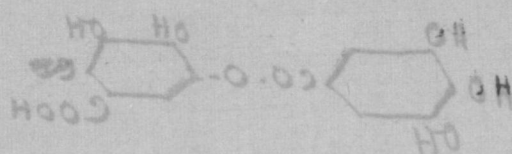


i.e. the substance must have a digallic acid formula capable of being tabulated in any one of the following seven possible arrangements.



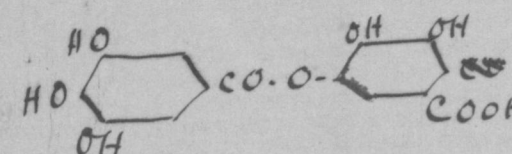
Formulae 5, 6 or 7 being of the ethereal type with no experimental proofs to admit either of them as a possible configuration, may safely be left out of account.

None of the rest of the four types are however able to explain



optical activity.

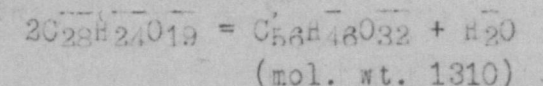
Formula 1.



was originally proposed by Schiff (Ann. d. Chem. 163 and 170) and still holds the ground in the absence of any other which would explain the formation of primary and secondary products from gallotannic acid so satisfactorily. The absence of an asymmetric carbon atom to explain the optical activity weakens the structure very much and it is therefore accepted with some reserve.

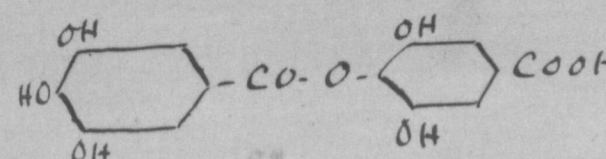
It is also conceivable that the required asymmetry might be brought about by polymerisation. The abnormal molecular weight found in aqueous solution might support this suggestion. On such an assumption we should expect to get the absence of optical phenomenon in acetic acid solution which has been shown to give the normal value of molecular weight. Schiff himself has, however shown that optical activity is exhibited by acetic acid solution, though to a less extent than by the aqueous. Theory therefore demands asymmetry in the simple molecule itself.

In 1898, Hermann Kunz-Krause (Pharmaceutischen Centralhalle) brought forward a curious suggestion based on a consideration of the molecular weight found by Ssabanefew in aqueous solutions (1322) to regard it as an anhydro compound of Cnebulinic acid (w. Adoloni Arch. d. Pharm. 230 (1892) 334), $(C_{28}H_{24}O_{19})$ a dextro-rotatory acid $[(\alpha_D) \text{ in alconolic solution} = +63.94]$ isolated from myrobalans and whose constitution and character have never yet been determined.

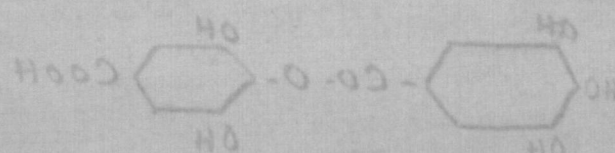


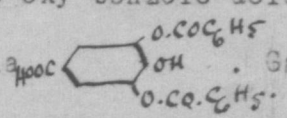
This seems to be quite a hypothetical assumption of no great significance. Any formula based on the molecular weight value obtained from aqueous solution is untenable as we know that the normal molecular weight value of 324 has been established in phenolic and acetic acid solutions.

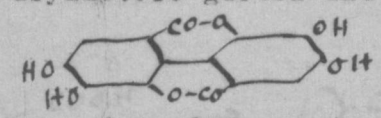
Formula II



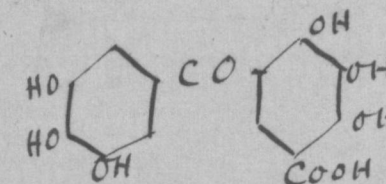
was proposed by Vournasos in 1903, as a result of an investigation of the pentabenzoyl derivative which by the action of alcohol and H_2SO_4 yielded a mixture



of tri and di benzoyl derivatives. The latter on reduction with sodium amalgam in ethereal solution at a low temperature gave p-Oxy benzoic acid, thus showing that the dibenzoyl compound must have the formula . Gallotan was on this account supposed by the author to possess the above configuration. The

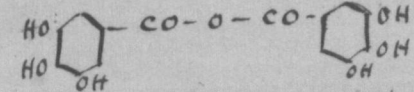
absence of an asymmetric carbon and the difficulty to explain the formation of Ellagic acid  whose structure has been established beyond doubt are a few of the objections which we have to raise against this formula.

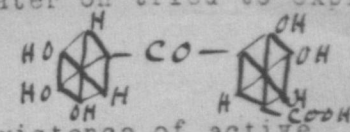
Formula III

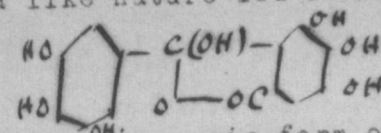


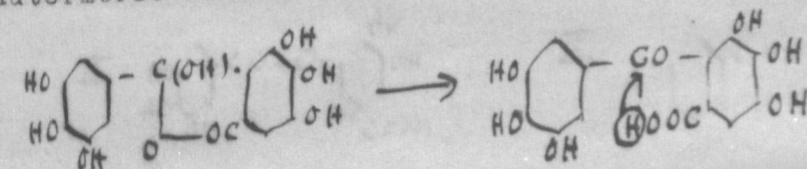
or Gallyl gallic acid was suggested by Etli in 1889, after a series of experiments on the Tannins of Oakbark.

A close examination of this formula reveals its untenable nature to a great extent. It demands a hexa acetyl derivative which is contrary to experimental evidence. It cannot further tell us anything of the mechanism of ellagic decomposition. As far as we know, no oxime or hydrazone which a ketonic substance must be expected to produce has yet been obtained from gallotannic acid. Its only recommendation seems to be the easy explanation of the formation of Rufigallic acid which the other formulae cannot very well explain without assuming a primary decomposition into gallic acid and subsequent condensation. Here again the question of optical activity is left out of account.

Formula IV  is an anhydride of gallic acid and all the objections which hold good in the previous cases have to be encountered. Hence it has been discarded.

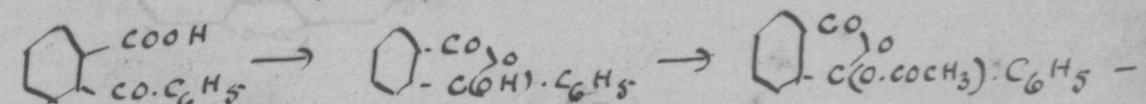
In spite of the difficulty to explain optical activity, Schiff's original formula has maintained its ground. Schiff himself later on tried to explain this on the Claus's unproved theory of benzene ring.  which as Dekker rightly points out would entail the existence of active

modifications of a similar body like the inactive Bromgallic acid. Considerations of a like nature led Dekker (B. 39. 2497) to put forward the following formula  which if more carefully examined is nothing other than a tautomeric form of Etli's formula mentioned above.

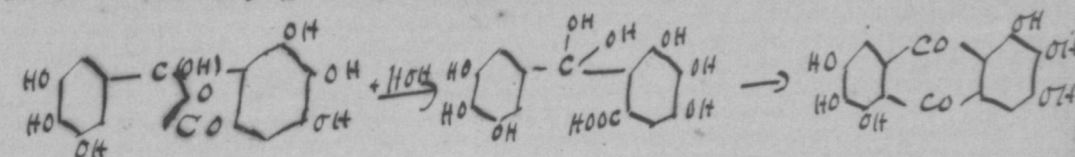


-12- 14

In place of a hepta acetyl derivative which the formula demands Dekker contends to have isolated a hexa derivative, while endeavouring to explain the difficulty of acetylating the OH attached to the CO group, by the protective action of the adjoining radicals. The whole formula is open to doubt. In this connection it is perhaps significant to allude to a statement by Nierenstein that O benzoyl benzoic acid yields an acetyl compound.



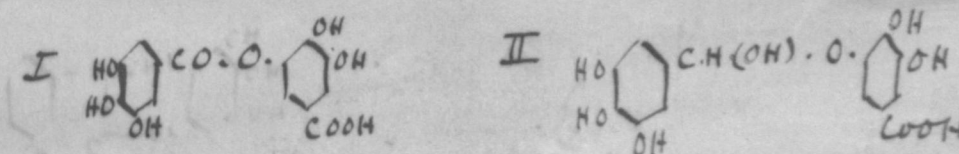
which shows that even a pseudo carboxyl group having the same situation as in Dekker's formula is capable of acetylation. There is no reason then to suppose that a hepta derivative if it exists, is difficult to be found. Dekker's configuration therefore seems to be very doubtful. In other ways the formula is not incapable of explaining the formation of decomposition products. It must however be observed that the formation of allagic acid has to be accounted for on the basis of a primary gallic decomposition while that of rufigallic acid is direct.



Contrary to this deduction

Nierenstein seems to have obtained more allagic than rufigallic acid by the oxidation of acetyl tannin and more rufigallic than allagic acid by oxidising gallic acid. As a derivative of gallic anhydride, one should expect the character of a colouring matter in the substance, which is however not the case.

After establishing the incomplete nature of a single formula to explain all experimental facts we come back to the discussion of the views previously held by Walden, Kunz-Krause and others who held gallotannin as a mixture and not as an individual substance. Following this view, Nierenstein upholds the theory that ordinary gallotannic acid is a mixture of Schiff's digallic acid I and another substance which differs from the former only by two atoms of hydrogen and known as "Leukotannin", to the latter of which he ascribes the optical activity. (B. 40 (1907) 916) The evidence is based on the precipitation of acetyl tannin in alcoholic solution by means of ether, the ethereal solution yielding a product on concentration which is capable of being further acetylated to a hexa acetyl compound. This compound yields on oxidation, traces of



gallic aldehyde which fact is adduced in support of the Leuco compound. Recently he claims (B. 43 (1910) 628) to have isolated the racemic Leuco tannin and resolved it further into its enantiomorphs by means of the strychnine salt.

I had occasion to repeat the former part of Nierenstein's work but failed to isolate the two acetyl compounds with the melting points (A = 203° - 206°) (B. = 166°). I could not push on with the work and estimate the acetyl value and try further to confirm his observations, but intend doing so at the first opportunity.

As has previously been stated, the same supposition has been held by Walden, Aweng and Krunz-Krause, and a confirmation of this recent communication on the subject would be a valuable contribution towards the solution of the subject under review.

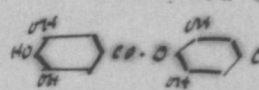
A good deal of attention has also been paid to the synthetic study of the substance with the ultimate object of clearing up the doubts on constitution.

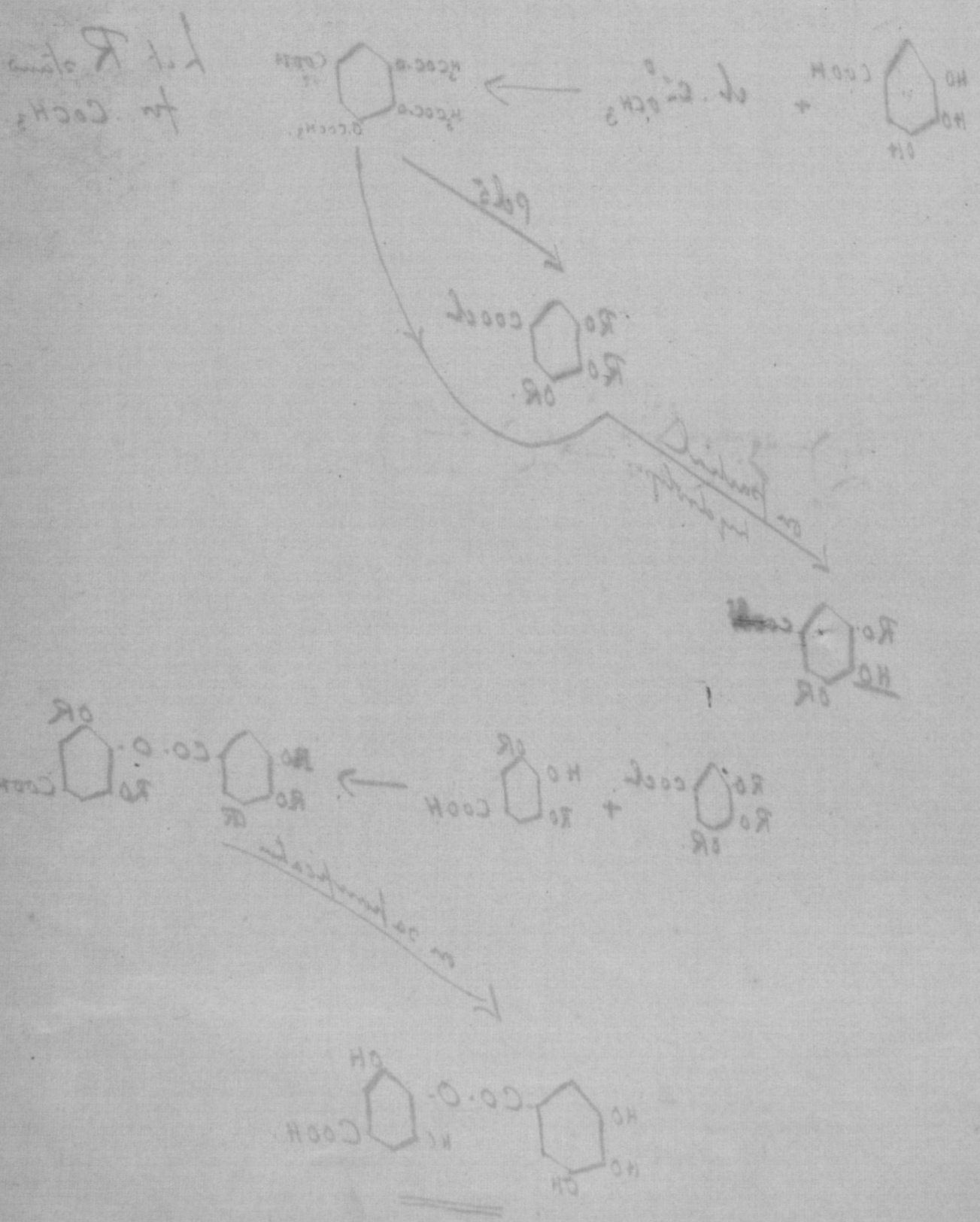
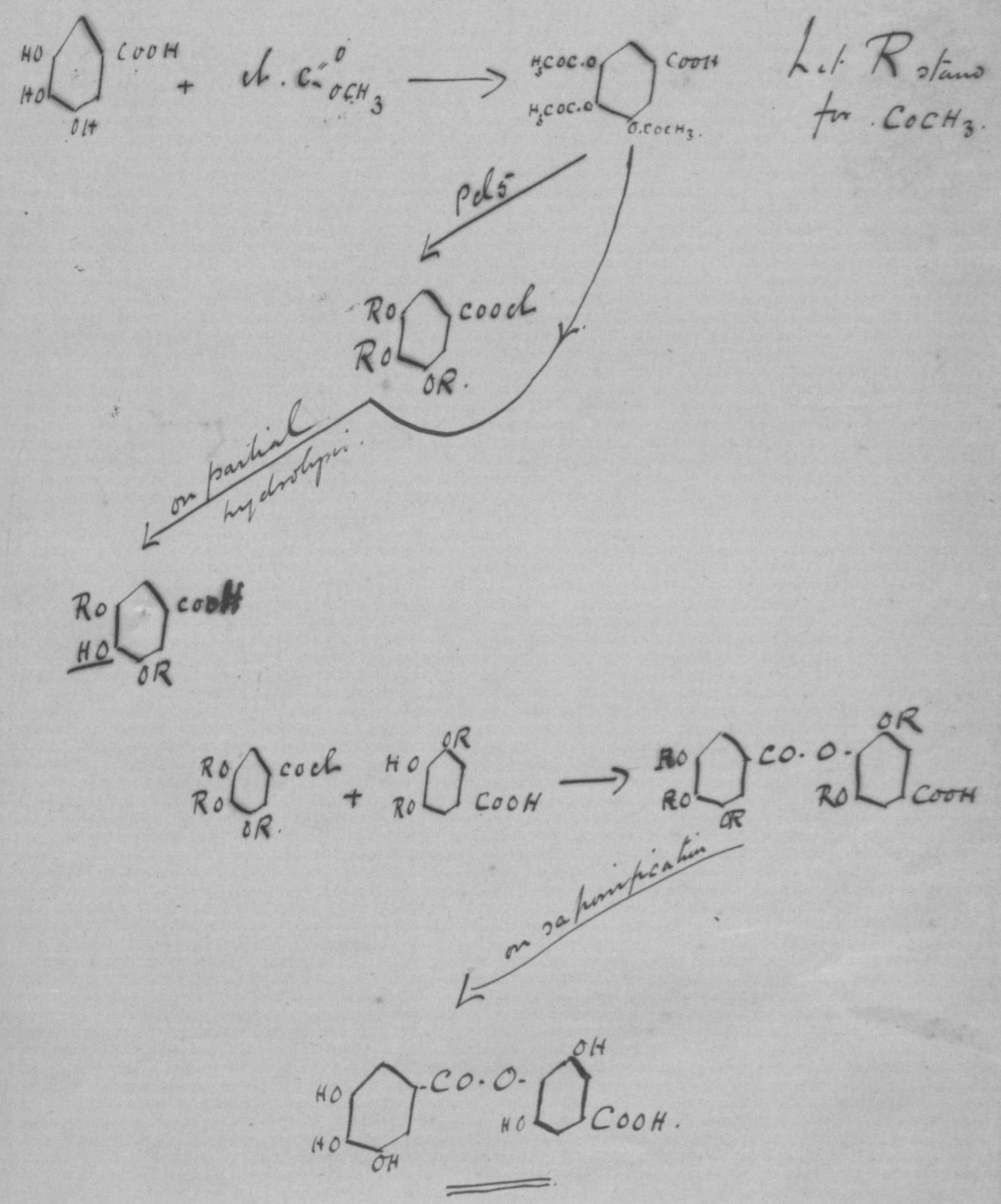
The first work of this nature was done by Löwe in 1869 when he treated barium gallate with silver nitrate. He also believed that by treating gallic acid with As_2O_5 , a digallic synthesis was effected. In 1871 Schiff tried the action of $POCl_3$ on dry gallic acid by heating the mixed paste first to 100° and finally to 120°. He also repeated Löwe's observations on the action of As_2O_5 on gallic acid.

Löwe's condensation with As_2O_5 was later on shown by Freda to be open to doubt as on a complete removal of arsenic, gallic acid is reformed. Schiff's $POCl_3$ condensation met with the same fate at the hands of Vournasos who found the product to contain large quantities of Phosphorus. Later on, Schiff's synthetic digallic acid was shown by Walden to be different from natural gallotannic acid in many of the leading properties which distinguish one chemical individual from another.

Another equally unsuccessful attempt was made by Hunt (Chem. News (52) 49) who digests potassium gallate with bromo proto catechuic acid in alcohol on the water bath for five hours. The result was subsequently challenged by Schiff

and the work has not yet been confirmed.

In 1908 E. Fischer (B. 41. 2385) attempted a synthesis of digallic acid of the type pictured by Vournasos.  As the author himself is not satisfied with the validity of his result we cannot speak much about it till more confirmatory work is done on the subject. The reactions involved in the synthesis may nowever be recapitulated as follows:



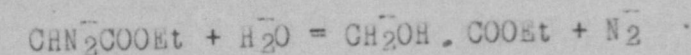
Introductory.

It is noticeable that a good deal of doubt still exists as to the exact configuration of gallotannic acid and as stated above many investigators have suggested that a free carboxyl group in the molecule is of doubtful existence.

Walden (B. 31, 3170) conducted a series of experiments on the electric conductivity of gallotannic acid. The value of the affinity constant ($K = \frac{[H^+][A^-]}{[HA]}$) was found to be so small that he attributed it to impurities present. He therefore comes to the conclusion that tannic acid possesses no carboxyl group in the free state.

The object of the following experiments is mainly to determine the hydron concentration of pure tannic acid in comparison with the weak organic acids of a similar nature. For this purpose the catalytic influence of hydrons on the rate of decomposition of Diazo acetic ester has been taken advantage of.

The chemical kinetics of Diazo acetic ester ($CHN_2COOC_2H_5$) has been extensively investigated by Fraenkel (Zeit. f. phys. chem. 60. 202/3) who has successfully applied it to study the strength of a series of organic and inorganic acids with varying hydron concentrations. In fact the method is more convenient to manipulate with greater accuracy than either the Inversion method or the hydrolysis of ethyl acetate method. The method under review is based on the catalytic influence of Hions on the velocity of the reaction.



Pure water has practically no action on the ester and the reaction is capable of indicating a Hion concentration varying from 0.00008 mols. per litre to 0.0025 mols. per litre at 25° without any difficulty in manipulation. In the one case, half the amount of ester used is decomposed in about 4 1/2 hrs. while in the other in about 9 minutes. Spitalsky (Zeit. f. Anorg. Chem. 54. 285) applied the same method to study the equilibrium condition of chromate and chromic acid in aqueous solutions and Bror Holmburg. (Zeit. f. phys. Chem. 82. 723) for the study of amphoteric electrolytes like Ortho-Amino benzoic acid; glutaminic acid, etc. In all cases the method has shown reliable and concordant results sufficient to justify its application to study the extent of acidity of gallotannic acid or bodies of an allied nature.

As the method affords such an easy and accurate means of determining

hydron concentration it would be well adapted for the determination of acidity in tan liquors. Accuracy could thus be combined with manipulative ease, if the yard liquors could be tested in different stages by means of the Procter lime-water method or any other standard method which could easily be graduated against diazo acetic acid. There seems to be a great possibility in this direction.

Descriptive

1. Preparation of hydrochloride of Glycocoll Ester.

The first step in the preparation of diazo acetic ester for the purposes of the experiment is the preparation of in the pure state. Two methods were followed and the yield and purity compared with the ease in preparation.

Method 1 (Klages B. 1903 36. 1508) is based on the preparation and subsequent hydrolysis of methylene amino aceto nitrile ($\text{CH}_2\text{NCH}_2\text{CN}$).

250 cc of (40%) formaldehyde are mixed with 90 grms of finely powdered pure ammonium chloride in a big churn jar fitted with a stirrer worked by means of a water turbine. The jar is cooled in a freezing mixture of salt and ice and when the temperature falls to 5° a concentrated solution of KCN (110 grms dissolved in 200 cc water) is slowly dropped into it from a funnel. The mixture is kept stirred all the time and the temperature is under no circumstances to be allowed to rise over 10° . Ammonium chloride gradually passes into solution and when about half the Cyanide solution is added, the whole of the suspended particles are dissolved. 63cc of glacial acetic acid are now added to the contents of the jar from another separating funnel at the same rate as the rest of the Cyanide solution. The temperature now rises from 10° to 15° but should always be kept below 15° . The stirring is to be continued for at least an hour after the addition of the Cyanide solution and acetic acid. A white granular precipitate of the nitrile begins to separate out. The contents of the jar are left standing over-night and the next day the precipitate is filtered, washed and dried. The mother liquor on standing generally gives a second crop. The yield of the nitrile is about 88 grms. It is further purified by crystallisation from alcohol. (MP 129°) and dried thoroughly in a vacuum desiccator.

The above yield of the nitrile is boiled for an hour on the reflex

condenser with 500 cc absolute alcohol previously saturated in the cold with dry HCl gas. Ammonium chloride is formed on hydrolysis and the hydrochloride of glycocoll ester goes into solution. The product of hydrolysis is filtered hot and the ester hydrochloride crystallizes out in needles from the filtrate on cooling. The yield is further increased by concentrating the mother liquor.

For further purification, absolute alcohol saturated with HCl gas is used. The yield in the present case had to be ^{re}crystallized twice before the melting point was sharp and at 144°. Final yield 52 grms.

Before utilising it for the preparation of the diazo ester it was dried in the thermostat between 90° and 100° for 48 hours to get rid of the free HCl.

Method II (Hantzsch and Silberrad B. 33. 70)

50 grms of $\text{CH}_2\text{Cl.COOH}$ are dissolved in 25cc water and the solution added in stages to 300cc of 24% Ammonia (Sp. Gr. 0.913 at 15°) kept in a large porcelain basin and stirred well during the addition. The solution is left in a cool place at 15° for 24 hours and then quickly evaporated on a ring burner to get rid of the excess of NH_3 . When the smell of NH_3 is no longer perceptible, 100cc of conc. HCl (Sp. Gr. 1.19) are added and the liquid evaporated down further till it turns yellow. The flame is then removed and the solution allowed to cool with constant stirring, to granulate the crystals which separate out. The white granules of the precipitate are filtered off and dried for 12 hours at a temperature of 115° in a bath surrounded by CaCl_2 . It is next finely powdered and dried again for 6 hours. The above substance which is but a mixture of the glycocoll salt and ammonium chloride, is next treated with 200 cc absolute alcohol and gradually heated on the water bath, while a stream of dry HCl gas is passed in. After about two hours the contents of the flask are filtered hot and the ester hydrochloride crystallises out of the filtrate on cooling for at least 12 hours. It is further purified from absolute alcohol till the MP remains sharp and at 144°. The pure ester is then dried at 100° for 48 hours to get rid of all free HCl. Yield 35 grms.

This method was more tedious to manipulate than the former one which required less time and gave further a better yield.

2. Preparation of Diazo Acetic ester.

Curtius (Jour. f. prakt. chem. 38. 396) and Ernst Müller (Dessertation Heidelberg 1904)., Silberrad (Trans. Chem. Soc. 1902. 600)

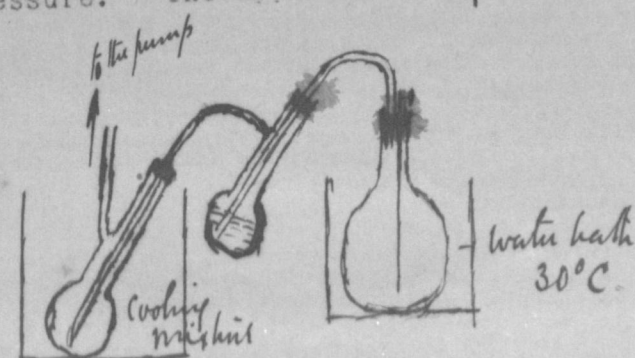
A detailed description of this method is further given by Fraenkel (Zeit. f. physik. Chem. 40. 202).

Following is a summary of the method.

50 grms. of pure hydrochloride of glycoll ester are dissolved in water just sufficient to hold it in solution and kept in a separating funnel (capacity 1/2 litre). When the temperature falls below 5° a concentrated aqueous solution of 25 grms NaNO_2 is added to it and well shaken. A few drops of 10% H_2SO_4 are next added and the solution soon becomes turbid owing to the separation of the diazo compound and the temperature simultaneously rises to about 7° . The mixture is immediately shaken up with 25 cc ether and the aqueous layer carefully drawn off into a flask standing in ice. The ethereal layer is filtered through a small funnel into a smaller separating funnel. When the aqueous portion falls below 5° in temperature, it is returned to the separating funnel, again acidified with a few more drops of H_2SO_4 and shaken out with a fresh quantity of ether. These operations are repeated till no more turbidity is observed on acidification and the ethereal layer remains green in colour owing to the liberation of N_2O_3 . On a further addition of 15 grms NaNO_2 to the aqueous layer and repeating the process of extraction, the yield of the ester can be increased.

The ethereal solution of the ester is next shaken with small quantities of a weak solution of Na_2CO_3 till the aqueous layer turns red. The ether solution is then carefully separated from the aqueous alkaline layer and washed three times with pure water (free from CO_2) using very small quantities to avoid loss of ester by solution. It is finally dried over fused CaCl_2 (granulated CaCl_2 absorbs the ester much more than fused and should therefore be avoided)

The major portion of the ether is next distilled off in vacuum at the ordinary temperature and the residue subjected to a distillation in steam under diminished pressure. The apparatus used for the purpose is shown below.



Before distillation a few grms of pure Ba. (OH)_2 8 Aq. (Crystals) are added to the ester, as in an alkaline medium, the distillation is quite safe without any fear of an explosion taking place. At a pressure of about 20 mm the ester mixes with water vapour and distils over at a temperature of 30° . Under no circumstances should the temperature be allowed to rise over 35° . To avoid loss of ester through the pump, the receiver is cooled to about -10° by a strong mixture of ice and CaCl_2 . The distillation is generally completed on an average from 60 to 90 minutes, when the yellow colour of the solution in the distilling flask changes to reddish brown.

The distillate is poured into a drop funnel and carefully separated from the upper aqueous layer and dissolved in pure ether.

The ether used throughout the preparation is purified from ordinary methylated ether standing for a fortnight over solid KOH, by denhydrating first with CaCl_2 and then over Sodium wire and finally kept over Sodium wire after distillation. It should then be freshly distilled immediately every time before use.

The ethereal solution of the ester is next carefully denhydrated over fused CaCl_2 for at least three days.

The ether is finally evaporated in vacuo and the residue distilled over freshly burned CaO under diminished pressure.

Under a pressure of 10 to 15 m.m. of Mercury the ester distils over at a temperature of 45 to 50° and is collected in a vacuum tube kept cooled in ice.

Yield about 20 to 25 grms on the average.

All apparatus used in the experiments is cleaned repeatedly with acid, washed and steamed for $1/4$ of an hour immediately before use.

If kept in a cool place well corked and standing over cold water in the dark, the ester is found to keep for at least a month without decomposition. The purity of the ester is tested from time to time by performing blank experiments with water alone and if any appreciable amount of nitrogen is found to be evolved it is redistilled over freshly burnt quicklime as stated above and again tested for purity. Sometimes this distillation alone would not be sufficient and in such cases it has to be purified with Ba (OH)_2 8 Aq. by distillation in

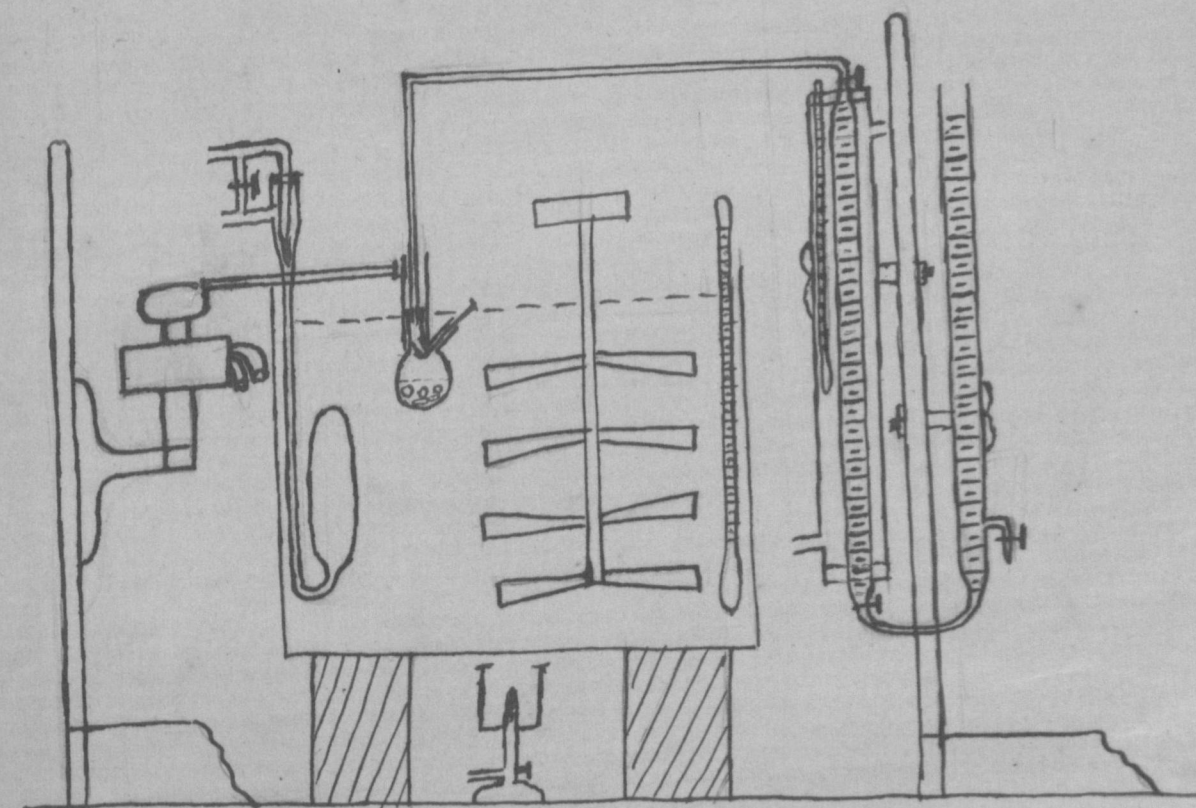
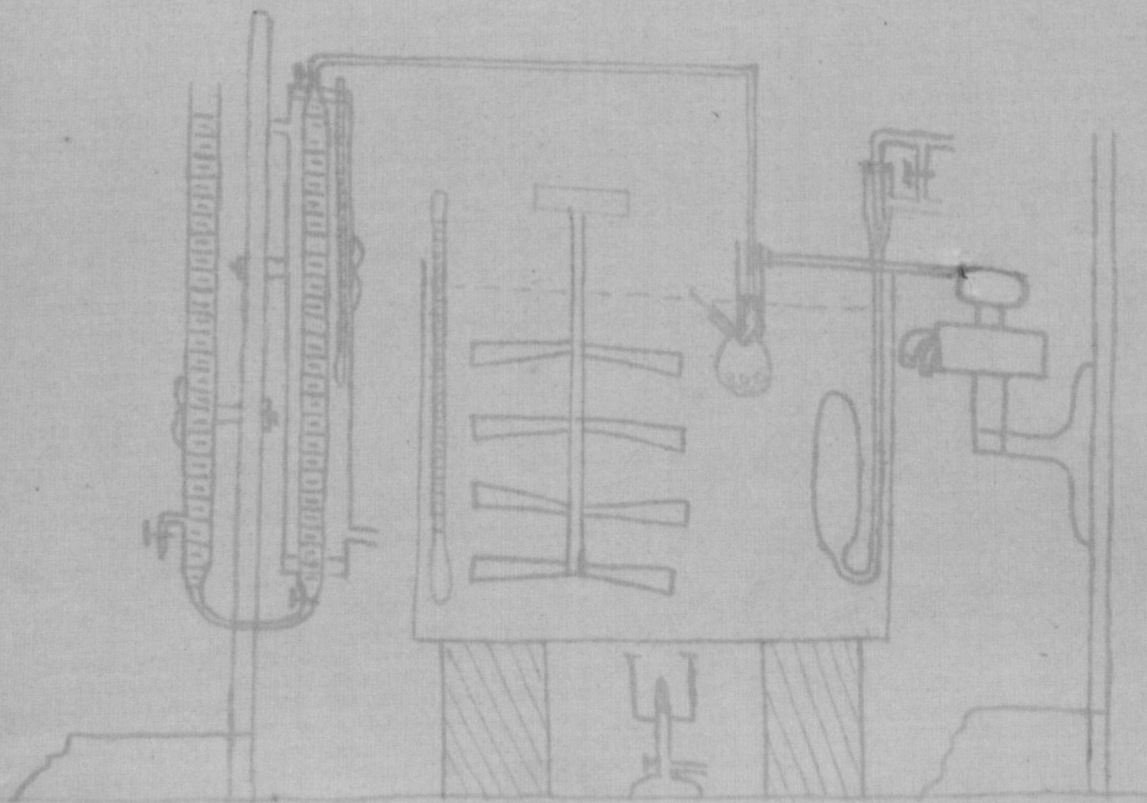
steam and further over burnt lime as described above.

Each experiment carried out with acids as conducted below affords a direct test for the purity of the preparation by comparing the volume of nitrogen evolved at the end of the reaction with that calculated from the weight of the ester used.

3. Apparatus and Modus Operandi

To study the reaction under consideration the following apparatus was used as originally suggested by Walton for the study of the reaction between H_2O_2 and Iodine (Zeit. f. physik. Chem. 47. 185) and supplied by Messrs. Desaga & Co. Heidelberg.

In the place of the more costly Ostwald thermostat, a copper bath with a glass front (18 inches by 12 inches) was fitted with a toluol thermoregulator and a micro-burner. An ordinary nitrometer graduated to 0.2cc and fitted with a water jacket was used for collecting the nitrogen evolved from the reaction flask.



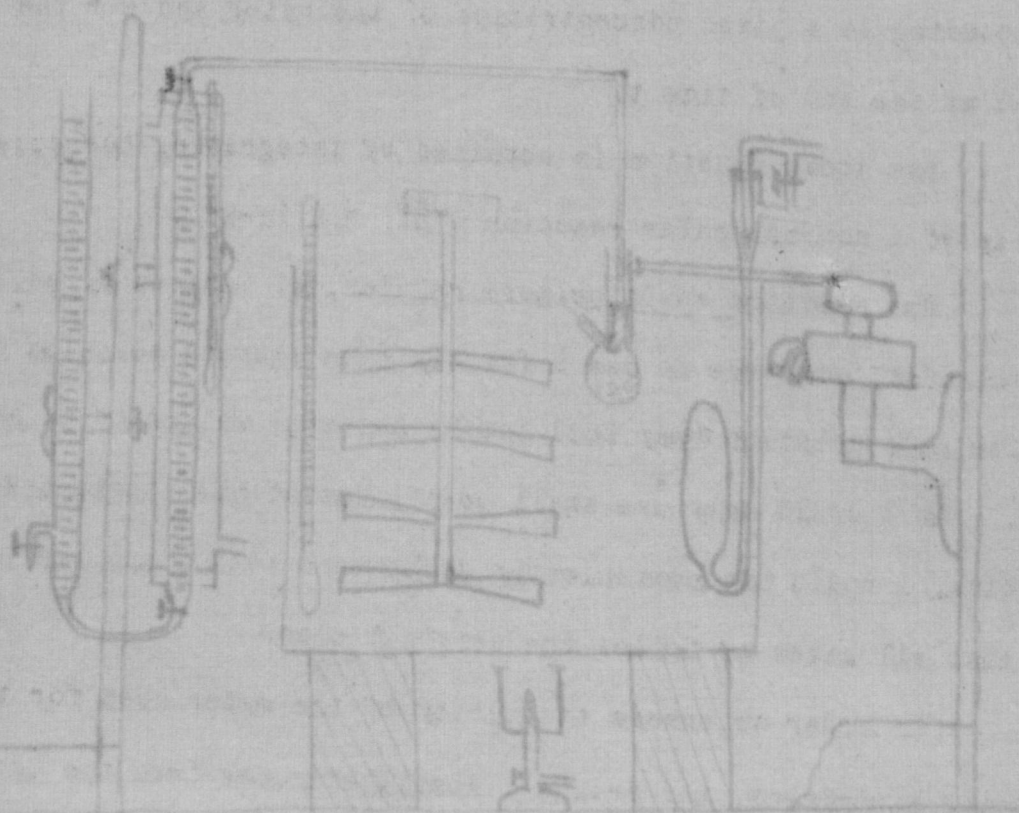
20cc of the solution containing the substance under examination were pipetted into the Walton flask and 0.2cc of the ester weighed into the small tube which was then made to rest in the neck of the flask on the tip of the glass rod which serves as a support. The flask was then closed by a tight fitting rubber stopper carrying the capillary tube which connects it to the nitrometer. When the flask had stood about ten minutes in the thermostat, the capillary tube was connected to the nitro-

meter by a piece of rubber tubing and tightly fixed by copper wire. The level of water in the nitrometer should previously be adjusted with care and any correction required for a change of pressure brought about by the connection of the apparatus should also be allowed for. All the experiments were performed at a temperature of the thermostat varying from 25° to 25.5°. At the commencement of the experiment, the time was carefully noted when the tube containing the ester was allowed to drop into the solution and the shaking started simultaneously. When the reaction had proceeded for a time (usually from 10 to 15 minutes) and the solutions were thoroughly mixed, the volume of nitrogen evolved was noted at fixed intervals and the temperature of water in the nitrometer jacket observed at the same time. Readings of the barometer were taken both at the commencement and end of the reaction. The volume of nitrogen generated within a given interval of time was reduced to normal conditions of temperature and pressure and the velocity of the reaction calculated from the formula $K = \frac{1}{4.343t} \cdot \log \frac{a}{a-x}$, where a = the total volume of nitrogen corresponding to a given concentration of the ester and x = the volume of nitrogen evolved at the end of time t .

The above equation is obtained by integrating the equation for the velocity of a monomolecular reaction $-\frac{dx}{dt} = K(a-x)$.

The reaction would be more regular, if instead of adding the ester to the acid solution, one were to use a freshly made aqueous solution of the ester and drop the acid solution (say 2cc) into a definite volume of it kept in the reaction Jena flask. As I could only use small quantities of the substances for the experiments at a time, I could not conveniently adopt this method and was therefore obliged in almost all cases to follow the original plan.

In order to ensure the purity of the water used for the purposes of the following experiment, the ordinary distilled water from the laboratory was redistilled usually two to three times through jena glass and stored away in a flask. It was further freed from carbonic acid by aspirating through it air which was drawn through concentrated sulphuric acid, a series of U tubes containing fused calcium chloride and soda lime and finally filtered through cotton wool packed in a long tube. Blank experiments with such water have given very satisfactory results, only such experiments were recorded as fitted in within the period when the ester had remained pure.



All chemicals used in the experiments have been tested for purity and where necessary repeatedly crystallized out of water (as purified above). Where it has been necessary to use alcohol, it was rendered absolute by leaving over pure lime for more than a month and finally distilled over calcium (See L. W. Winkler's B., 38. (1905) 3812).

The velocity constant was found to be affected by the alkalinity of the glass, where weak acids were used as catalysts, owing to the neutralisation of part of the acid by the alkali from glass and the subsequent reduction of Hion concentration.

Fraenkel used platinum flask in his experiments and Spitalsky found paraffinised glass as good as platinum or even better.

Towards the latter part of my experiments, I substituted silica for glass and the results were found to be more regular and much more reliable than with the glass apparatus.

The stock of ester which the glass flask had certified as pure was condemned by the silica flask, and on such occasions, the ester had to be purified by redistillation.

Methods of Purification employed.

Sample used:: - Kanlbaum's Extra pure Tannic Acid.

Method I

50 grms of the above substance were dissolved in 500cc water and salted out by means of a saturated solution of pure sodium chloride. The precipitate was repeatedly washed on the filter with the salt solution and again dissolved in a small quantity of water and salted out. This salting out process was repeated over half a dozen times and the product finally dried in vacuum oven for four hours. The dried mass was then extracted with freshly distilled methyl acetate filtered and the filtrate evaporated in vacuo at the laboratory temperature and dried thoroughly free from all traces of the solvent.

It was later on observed that the sample so obtained was by no means free from traces of gallic acid which are invariably brought down with the precipitate during the salting out operations.

Method II.

Rosenheim and Schidrowitz (Loc. cit)

50 grms Kahlbaum's Tannin were dissolved in a small quantity of pure acetone. On the addition of pure ether, a white amorphous precipitate was formed which soon settled down as black resinous matter. On the addition of a small quantity of water to the filtrate, two layers were formed. The heavier syrupy layer was separated and repeatedly shaken out with pure ether till the ethereal layer remained colourless. On the addition of more water, three layers were formed and the lowest layer containing the least amount of gallic acid was removed and again shaken out with the ether several times till the ethereal layer gave out a faint test with KCN. The emulsion was allowed to separate (usually from 24 to 48 hours) and the lower layer evaporated on the water bath, dried in vacuo for four hours and desiccated over sulphuric acid in a vacuum dryer protected from light. Yield about 25 grms.

The above purification was repeated several times and the resulting substance tested for acidity and optical activity in successive stages of purification.

This method, depending as it does on the phenomenon of distribution of a substance between two solvents, is by no means a perfect one. The small amount of Gallic acid which is always left behind in the purified sample introduces a greater variation in the degree of acidity than in the values obtained for the specific rotatory power of the substance.

Method III.

Neutralisation by means of Sodium bicarbonate and extraction with Ethyl acetate.

The commercial product was first purified from all resinous and colouring matter by repeatedly shaking out the acetone solution with ether (See Method II) and the residue dried as before. The product so obtained was dissolved in a small quantity of water. To avoid the presence of any normal carbonate, a current of CO_2 was passed through a saturated solution of Sodium bicarbonate for about 20 minutes. The aqueous solution of the Tannin was similarly freed from oxygen and neutralized with a bicarbonate solution.

23
26

-24-

(1) Till faintly alkaline to litmus.

The solution was then shaken out three times with freshly distilled ethyl acetate. The extract so obtained was washed with small quantities of water till free from traces of alkali, and concentrated in vacuum at the ordinary temperature and precipitated by means of pure dry benzene. The white precipitate so obtained was boiled with benzene to remove traces of the ester, filtered and finally dried in the vacuum oven for four hours.

The optical activity and acidity of the product were then tested.

The above purification was again repeated using more of the bicarbonate solution.

(2) till the liquid was more alkaline than in the previous case.

The product so obtained was tested both for acidity and optical activity.

Repeating the process of purification for a third time, the aqueous solution of the substance

(3) was finally precipitated with the bicarbonate solution and extracted as before.

The product was again examined as in the two previous cases.

The mother liquor obtained after precipitation with the bicarbonate solution

(4) was partly neutralized with hydrochloric acid

and extracted with ethyl acetate, washed, concentrated and finally precipitated with benzene. In the place of a white amorphous precipitate obtained in the last case, a dark viscous mass was thrown down which when dried was greyish white in colour.

The acidity and optical activity of this product were also noted.

Owing to the insolubility of sodium gallate and other allied salts in ethyl acetate, this method is an excellent means of purifying gallotannic acid.

The products so obtained are invariably free from even traces of sodium.

The white amorphous precipitate by the above salting out process was dissolved in absolute alcohol and precipitated with an absolute alcoholic solution of potassium acetate, filtered and the precipitate thoroughly washed with absolute alcohol. The product so obtained was next treated with pure ethyl acetate to

remove traces of any free gallotannic acid filtered and dried.

This substance which seems to be of the nature of a potassium salt, as has already been referred to in the historical outline, is now under investigation. If the same substance be dissolved in water and saturated with CO_2 for about 30 minutes we can extract the liberated gallotannic acid by means of acetic ether. The product so obtained is also under immediate investigation.

Experimental.

I. Glass Apparatus.

Preliminary Experiments.

Blank Test No 1

20cc water + 1.0cc ester.

Time	Volume of nitrogen generated.
21 hours 50 mins.	2 cc
44 " 20 "	8.4 "
72 " 0 "	11.8 "

The purity of the ester and water being thus tested, the following experiments were taken in order.

Experiment No 1.

Catalyser:

Pyrogallol

(0.0001597 Mol)

Concentration of ester 0.2258 gr in 20.2cc

No evolution of Nitrogen even after 17 hours.

Experiment No 2.

Catalyser:

Phenol

(0.0001597 Mol)

Concentration of ester 0.2330 gr in 20.2cc

No evolution of nitrogen even after 17 hours.

Experiment No 3.

Catalyser

Phenol

(0.002 Mol.)

Concentration of ester 0.2292 gr in 20.2cc

No evolution of nitrogen even after 18 hours.

Experiment No 4.

Catalyser

Boric Acid

(0.002 Mols)

Concentration of ester 0.2136 gr in 20.2cc

No evolution of nitrogen even after 18 hours.

Blank Test No 2.

20cc water + 0.2cc ester.

0.7cc nitrogen evolved at the end of 17 hours.

Experiment 3.

Catalyser

Gallic Acid

(0.0001597 mol)

Concentration of ester 0.2253 gr in 20.2cc.

Mean temperature

7°

Aqueous tension

7.5mm.

mean barometer 751.5 mm

of nitrometer jacket

at 7°

(x_1 represents the reduced value of x)

$a = 44.33$ cc.

t. (minutes)	x.	x_1	$a - x_1$	k.
20	10.95 cc	10.45 cc	33.88	0.01344
30	15.40 "	14.70 "	29.63	0.01343
40	19.20 "	18.33 "	26.00	0.01334
50	22.50 "	21.48 "	22.85	0.01325
70	28.25 "	28.96 "	17.37	0.01338
100	33.10 "	31.59 "	12.74	0.01247
130	38.75 "	36.08 "	8.25	0.01205
1225	44.90 "	42.88 "	-	-

Mean value of k 0.01337

Experiment 3.

Catalyser

Protocatechuic Acid

(0.0001597 mol)

Concentration of ester 0.2023 gr in 20.2 cc

Mean temp. nitrometer 8°

Aqueous tension 8° = 8.1mm

Mean barometer 757 mm

$a = 39.81$ cc

t (minutes)	x	x_1	$a - x_1$	k
20	8.05 cc	7.71 cc	32.10	0.01075
30	11.35 "	11.35 "	28.46	0.01119
40	15.15 "	14.51 "	25.30	0.01133
50	20.45 "	19.58 "	20.23	0.01128
90	26.25 "	25.13 "	14.68	0.01108
150	32.85 "	31.45 "	8.36	0.01040
1080	40.85 "	39.11 "	0.70	-

Mean value of k = 0.01122

Experiment 7.

Catalyser

β -Resorcylic Acid

(0.0001537 mol)

Concentration of ester 0.2123 gr in 20.2 cc

Mean temp. nitrometer 9.5° Aqueous tension 9 mm

Barometer 753 mm.

$a = 41.81$ cc.

t. (minutes)	x.	x_1	$a - x_1$	k
20	29.1 cc	27.53 cc	14.28	0.05371
30	35.2 "	33.80 "	8.51	0.05306
40	38.5 "	36.42 "	5.39	0.05121
50	41.7 "	39.45 "	2.36	0.04791
60	42.9 "	40.53 "	1.23	0.04403
55	43.1 "	40.77 "	1.04	-

Mean value of k = 0.04999.

Experiment 8.

Catalyser

Salicylic Acid

(0.0001597 mol)

Concentration of ester 0.21 gr in 20.2 cc.

Nitrometer Temp. 10°

Aqueous tension 9.2 mm

Barometer 754 mm

$a = 41.23$ cc.

t. (minutes)	x	x_1	$a - x_1$	k
15	30.1 cc	28.43 cc	12.80	0.07803
20	34.8 "	32.72 "	8.54	0.07873
30	39.1 "	36.97 "	4.29	0.07545
40	40.8 "	38.53 "	2.68	0.06833
55	41.8 "	39.53 "	1.73	0.05757

Mean value of k = 0.07510

Experiment 9.

Test Experiment with Gallotannic Acid.

(Commercial sample directly neutralized with Sodium bicarbonate and extracted with acetic ether)

Concentration

0.02718 gr or

0.00003435 mol. (based on mol. wt. 322) or

0.00002055 mol. (after Scharanejew mol. wt 1322)

Concentration of ester 0.2 cc in 20.2cc

t.(minutes)	x
10	0.25 cc
20	0.30 "
50	0.40 "
80	0.50 "
240	1.20 "
1200	2.30 "
2520	3.20 "
3180	4.20 "
5520	6.00 "

Experiment 10.

Catalyser

Gallotannic acid.

0.322 gr or

Method I (See page 19)

0.001001 mols (normal) or

0.0002433 mols. (Ssabanjew)

Concentration of ester 0.2032 gr in 20.2 cc

Mean temp. nitrometer 10°

Aqueous tension 9.2 mm

Mean barometer 748.8 mm

a = 39.93 cc

t. (minutes)	x	x ₁	a - x ₁	k
10	1.3 cc	1.22 cc	38.71	0.003103
15	1.8 "	1.89 "	38.04	0.002985
20	2.4 "	2.25 "	37.68	0.002900
25	3.0 "	2.82 "	37.11	0.002823
40	4.4 "	4.13 "	35.80	0.002723
50	5.4 "	5.07 "	34.86	0.002713
60	6.4 "	6.01 "	33.92	0.002719
155	14.0 "	13.14 "	26.79	0.002676

Mean value of k 0.00282.

As the rate of decomposition of the ester is directly proportional to the concentration of Hions in solution, the specific influence of the Hion must be a constant factor. In other words k/C_H is a constant quantity. The value of this constant has been determined by Fraenkel (Loc. cit) For aqueous solution $k/C_H = 38.5$.

For the above experiment,

C_H (calculated from the above equation) = 7.8×10^{-2}

Experiment 11.

Experiment 10 repeated

Concentration of ester 0.2040 gr in 20.2 cc.

Mean temp. nitrometer 19° Aqueous tension 3.6 mm Mean barometer 756.25 mm

a = 40.08 cc.

t. (minutes)	x	$\bar{x}$	a - x ₁	k
10	1.2 cc	1.14 cc	38.94	0.002886
15	1.8 "	1.71 "	38.37	0.002907
20	2.4 "	2.29 "	37.79	0.002912
30	3.6 "	3.43 "	36.65	0.002976
40	4.8 "	4.38 "	35.70	0.002893
50	5.8 "	5.33 "	34.75	0.002864
60	6.8 "	6.39 "	33.79	0.002846
80	8.4 "	8.00 "	32.08	0.002783
100	10.2 "	9.62 "	30.46	0.002712

Mean value of k = 0.002866

$C_H = 7.4 \times 10^{-5}$

11.

Silica Apparatus.

Blank Test 3.

20cc water + 0.2cc ester.

In 18 hours, 15.4cc of nitrogen were generated.

Blank Test 4.

The same test repeated in the glass apparatus

In 18 hours, 4.6cc of nitrogen were generated.

Consequently the ester was purified by distillation.

Blank Test 5

20 cc water + 0.2cc ester.

0.6cc nitrogen evolved in 21 hours.

Experiment 12.

Catalyser

Pyrogallol

(0.001 mol)

Concentration of ester 0.2018 gr. in 20.2 cc.

Mean temp. Nitrometer 11°

Aqueous tension 9.9 mm

Barometer 759.5 mm

$a = 39.85$ cc.

t (minutes)	x	x ₁	a-x ₁	x
300	1.0 cc	0.95 cc	38.70	0.000030
420	1.4 "	1.33 "	38.52	0.000013
600	2.2 "	2.03 "	37.82	0.000030
1440	4.1 "	3.83 "	36.02	0.000071

Mean value of k 0.0000810

Experiment 13.

Experiment 10 repeated. with the Silica flask.

Catalyser

Gallotannic acid

0.322 gr or

0.0002436 mols (Sasagane)

Concentration of ester 0.1936 gr in 20.2 cc.

Mean temp. nitrometer 11°

Aqueous tension 9.3 mm Barometer 755.7 mm

a = 33.04 cc.

t. (minutes)	x.	x ₁	a-x ₁	k
20	1.9 cc	1.79 cc	33.25	0.003213
25	2.6 "	2.45 "	35.59	0.003329
30	3.2 "	3.02 "	35.02	0.003297
40	3.8 "	3.58 "	34.46	0.003267
50	5.0 "	4.72 "	33.32	0.003312
60	7.3 "	6.89 "	31.15	0.003330
100	9.5 "	8.98 "	29.06	0.003357
130	11.5 "	10.85 "	27.19	0.003353

Mean value of k 0.003277

C = 3.5 x 10⁻⁵

Experiment 14.

Catalyser

Gallotannic Acid

(Sample same as in Experiment 9. p. 26)

0.322 gr or

0.0002436 mols (Sasagane)

Concentration of ester 0.1830 gr in 20.2 cc

Mean Temp. nitrometer 11°

Aqueous tension 9.3 mm

Barometer 760 mm

a = 33.94 cc

t. (minutes)	x	x ₁	a-x ₁	k
30	0.6 cc	0.57 cc	33.37	0.0005172
45	0.9 "	0.85 "	33.09	0.0005171
135	2.5 "	2.37 "	34.57	0.0004912
195	3.8 "	3.61 "	33.33	0.0005274
1030	19.0 "	18.02 "	18.92	0.0008135
1170	20.3 "	19.54 "	17.40	0.0008435

Mean value of k = 0.0005527

C = 1.4 x 10⁻⁵

21. 33 36
(Experiment 14 is not reliable as the sample was later on found to be contaminated with traces of sodium.)

Experiment 15.

Catalyser

Gallotannic acid

0.322 gr or

0.0002438 mol (Ssabanjeu)

Sample II (See page 20 Rosenheim and Schidrowitz)

First Purification.

Concentration of ester 0.2038 gr in 20.2 cc.

Mean Temp. nitrometer 11°

Aqueous tension 9.9 mm

Barometer 750.5 mm

a = 40.01 cc

t. (minutes)	x.	x1	a-x1	k
25	3.9 cc	3.85 cc	36.16	0.003823
35	6.0 "	5.82 "	34.19	0.004325
50	8.7 "	8.15 "	31.86	0.004553
80	10.0 "	9.87 "	30.14	0.004443
75	12.4 "	11.62 "	28.39	0.004574
90	14.5 "	13.58 "	26.43	0.004307
100	15.8 "	14.80 "	25.21	0.004319
210	23.8 "	25.10 "	14.91	0.003734
240	29.0 "	27.17 "	12.84	0.004733
300	32.4 "	30.33 "	9.68	0.004740
1140	41.2 "	36.53 "	4.48	

Mean value of k = 0.004417

$C_H = 11.47 \times 10^{-5}$

Experiment 13.

Catalyser

Gallicotannic acid

0.33332 gr or

0.0002559 mol (Gsatansien)

Sample II (See page 20 (Kosenneln and Schifrowitz))

Second Purification.

Concentration of ester 0.2123 gr in 20.2 cc.

Main temp. nitrometer 11°

Aqueous tension 9.9 mm

Barometer 757.2 mm.

a = 41.72 cc.

t (minutes)	x	x ₁	a-x ₁	k
20	1.8 cc	1.70 cc	40.02	0.002080
25	2.4 "	2.27 "	39.45	0.002238
30	2.9 "	2.74 "	38.98	0.002334
35	3.5 "	3.31 "	38.41	0.002332
50	4.9 "	4.53 "	37.09	0.002352
60	5.9 "	5.53 "	36.14	0.002393
70	6.9 "	6.52 "	35.20	0.002422
85	8.3 "	7.88 "	33.87	0.002452
90	8.8 "	8.32 "	33.40	0.002471
100	9.7 "	9.17 "	32.55	0.002482
120	11.3 "	10.93 "	30.78	0.002540
135	24.5 "	23.15 "	18.58	0.002845

Mean value of k = 0.002393.

$C = 3.2 \times 10^{-5}$

Blank Test 8.

20 cc water + 0.2 cc ester.

0.3 cc nitrogen evolved after 21 hours.

Experiment 17.

Catalyser

Gallotannic acid

0.32888 gr or

0.0002438 mol (Ssabanejew)

Sample II (See page 20)

Third Purification.

Concentration of ester 0.2103 gr in 20.2 cc.

Mean temp. nitrometer 11°

Aqueous tension 9.9 mm

Barometer 762 mm.

a = 41.39 cc

t. (minutes)	x.	$\bar{x}_1$	a - $\bar{x}_1$	k.
15	1.3 cc	1.24 cc	40.15	0.002028
20	1.7 "	1.32 "	39.77	0.001993
25	2.1 "	2.00 "	39.39	0.001981
30	2.6 "	2.47 "	38.92	0.002046
35	3.0 "	2.85 "	38.54	0.002038
50	4.1 "	3.90 "	37.49	0.001979
60	4.7 "	4.47 "	36.92	0.001905
70	5.5 "	5.23 "	36.16	0.001930
75	5.8 "	5.52 "	35.87	0.001908
85	6.5 "	6.18 "	35.21	0.001902
90	6.9 "	6.53 "	34.83	0.001917
100	7.5 "	7.13 "	34.26	0.002012
210	15.5 "	14.74 "	26.65	0.002033
240	13.4 "	15.30 "	26.79	0.001971
315	20.3 "	19.31 "	22.08	0.001996

Mean value of k = 0.001930

$C_H = 5.1 \times 10^{-5}$

Experiment 18

Catalyser

Gallicannic acid

0.33472 gr or

0.0002532 mol. (Ssapanejew)

Sample III (See page 20)

Purified with NaHCO_3 and extracted with CH_2COOEt .

First Purification.

Concentration of ester 0.2111 gr in 20.2 cc.

Mean Temp. nitrometer 11°

Aqueous tension 9.9 mm

Barometer 740.7 mm

$a = 41.48$ cc.

t. (minutes)	x	x_1	$a - x_1$	k
20	3.2 cc	2.98 cc	38.52	0.003702
30	3.8 "	3.51 "	37.97	0.002940
40	4.3 "	3.98 "	37.5	0.002522
50	4.9 "	4.53 "	36.95	0.002318
60	5.5 "	5.08 "	36.40	0.002177
70	6.0 "	5.55 "	35.93	0.002052
85	6.8 "	6.29 "	35.19	0.001935
98	7.4 "	6.84 "	34.64	0.001877
100	7.7 "	7.12 "	34.36	0.001883
110	8.2 "	7.58 "	33.9	0.001834
120	8.8 "	8.13 "	33.35	0.001818
180	12.3 "	11.37 "	30.11	0.001725

Mean value of $k = 0.002233$

$C_H = 5.8 \times 10^{-5}$

Experiment 19

Catalyser

Gallotannic acid

0.30128 gr. or

0.0002279 mol (Ssabarajew)

Sample III (See page 20)

Second Purification.

Concentration of ester 0.2079 gr in 20.2 cc.

Mean barometer 762.5 mm.

a = 40.85 cc.

t (minutes)	x	temp.	$\bar{x}_1$	$a - \bar{x}_1$	k
20	1.7 cc	12°	1.61 cc	39.24	0.002011
32	2.4 "	"	2.27 "	38.58	0.001787
45	3.0 "	"	2.84 "	38.01	0.001602
56	3.4 "	"	3.22 "	37.63	0.001486
68	4.0 "	"	3.79 "	37.06	0.001475
70	4.2 "	"	3.98 "	36.87	0.001465
81.5	4.8 "	"	4.55 "	36.30	0.001449
90	5.1 "	"	4.83 "	36.02	0.001398
100	5.6 "	"	5.31 "	35.54	0.001393
110.5	6.2 "	"	5.88 "	34.97	0.001407
120	6.6 "	"	6.26 "	34.59	0.001386
130	7.0 "	"	6.63 "	34.22	0.001362
150	7.9 "	"	7.49 "	33.36	0.001350
165	8.6 "	"	8.15 "	32.70	0.001341
180	9.4 "	11.5°	8.93 "	31.92	0.001370
330	16.1 "	12°	15.26 "	25.59	0.001417
360	17.6 "	"	16.68 "	24.17	0.001458
376	18.2 "	"	17.25 "	23.60	0.001459

Mean value of k = 0.001478

$C_H = 3.8 \times 10^{-5}$

Experiment 20

Catalyser

Gallotannic acid

0.31592 gr. or

0.0002390 mol (Ssaoaneje)

Method III (See page 20)

Third purification.

Concentration of ester 0.2034 gr in 20.2 cc.

Mean barometer 764.7 mm.

 $a = 33.97$ mm.

t. (mins)	temp	x	$\bar{x}$	$a - \bar{x}$	k
15	13°	0.7 cc	0.33 cc	33.31	0.001104
20	"	0.9 "	0.35 "	33.12	0.001070
21	"	1.0 "	0.35 "	33.02	0.001141
30	13.5	1.4 "	1.32 "	33.35	0.001114
40	"	1.8 "	1.70 "	33.27	0.001034
46.5	"	2.2 "	2.03 "	37.83	0.001147
55	"	2.5 "	2.33 "	37.61	0.001105
60	13.0	2.8 "	2.65 "	37.32	0.001142
68	"	3.1 "	2.93 "	37.04	0.001152
70	"	3.3 "	3.12 "	36.85	0.001130
80	"	3.8 "	3.60 "	36.37	0.001173
90	"	4.0 "	3.79 "	36.18	0.001108
100	13.5	4.5 "	4.25 "	35.72	0.001149
110	13.0	4.8 "	4.54 "	35.43	0.001095
120	"	5.2 "	4.92 "	35.05	0.001095
132	"	5.8 "	5.49 "	34.48	0.001119
240	"	9.6 "	9.09 "	30.88	0.001075
385	"	15.0 "	14.20 "	25.77	0.001140

Mean value of $k = 0.001121$

$$C_H = 2.9 \times 10^{-5}$$

Experiment 21

Catalyser

Gallotannic acid

0.32408 gr or

0.0002451 mol
(ssabaneje)

Method III (See page 21)

4

(Sample extracted from the mother liquor after partial acidification)

Concentration of ester 0.2012. gr. in 20.2 cc.

Mean barometer 747.6 mm.

a = 39.53 cc.

t (mins)	temp	x	$\bar{x}$	a - $\bar{x}$	K
10	13.75	1.0 cc	0.92 cc	38.61	0.002335
15	"	1.4 "	1.29 "	38.24	0.002219
20	"	1.8 "	1.66 "	37.87	0.002150
25	"	2.25 "	2.07 "	37.46	0.002155
30	"	2.70 "	2.49 "	37.04	0.002137
40	13.5	3.5 "	3.23 "	36.30	0.002134
45	"	4.0 "	3.69 "	35.84	0.002133
55	"	4.7 "	4.34 "	35.19	0.002118
60	"	5.1 "	4.71 "	34.82	0.002116
65	"	5.6 "	5.17 "	34.36	0.002125
70	"	5.9 "	5.44 "	34.09	0.002117
80	"	6.5 "	6.00 "	33.53	0.002059
85	"	6.7 "	6.18 "	33.35	0.002049
90	"	7.2 "	6.64 "	32.89	0.002041
105	"	8.2 "	7.56 "	31.97	0.002010
120	"	9.25 "	8.53 "	31.00	0.002025
135	"	10.05 "	9.27 "	30.26	0.002035
150	"	11.65 "	10.75 "	28.78	0.002117
165	"	12.7 "	11.72 "	27.81	0.002132
180	13.75	13.6 "	12.54 "	26.99	0.002121
197	"	14.75 "	13.60 "	25.93	0.002141
210	13.5	15.5 "	14.30 "	25.23	0.002139
225	"	16.45 "	15.18 "	24.35	0.002144

Experiment 21 (cont)

t. (mins)	temp.	x	$\bar{x}_1$	a-x $\bar{x}_1$	k
240	13.75	17.25 cc	15.90 cc	23.63	0.002144
255	"	18.0	16.59	22.94	0.002134
285	13.5	19.6	18.08	21.45	0.002145
300	"	20.3	18.73	20.80	0.002133
315	"	21.2	19.55	19.96	0.002163
330	"	22.05	20.34	19.19	0.002190
360	"	23.7	21.88	17.67	0.002237
420	"	23.45	24.40	15.13	0.002337
443.5	"	27.4	25.23	14.25	0.002301

Mean value of k = 0.002143

$C_H = 5.6 \times 10^{-5}$

Experiment 22

Catalyser

Boric acid

0.0003671 mol in 22cc

20cc of ester solution + 2cc of boric acid solution .

Concentration of ester 0.20352 gr in 22cc .

Mean temp. Nitrometer 11.5° Aqueous tension 10.2mm barometer 752.1 mm
a = 40.0 cc.

t (mins)	x	$\bar{x}_1$	a-x $\bar{x}_1$	k
120	0.3cc	0.23 cc	39.72	0.000053
300	0.7"	0.63 "	39.34	0.000054
1115	2.9"	2.72 "	37.28	0.000033
1140	3.0"	2.81 "	37.19	0.000034
1200	3.2"	3.0 "	37.0	0.000035
1380	4.15"	3.83 "	36.11	0.000074
1440	4.50"	4.22 "	35.78	0.000077

Mean value of k = 0.000065

Analysis of experiments with Gallic Tannic Acid.

Publication		Concentration	Value of K	Concentration of Hydroxide	Specific rotating power [α] _D ²⁰	Remarks
Method	Order					
Method I	—	0.3229 ^g in 20.2 cc	328 x 10 ⁻⁵	8.5 x 10 ⁻⁵	—	Back in Gallic Acid
" II	Sample 1/1	0.322 ..	442 x ..	11.5 x ..	73.29°	..
	.. 2 nd	0.33832 ..	240 x ..	6.2 x ..	72.12°	With Catechu Gallic acid.
	.. 3 rd	0.32885 ..	198 x ..	5.1 x ..	72.37°	
	.. 4 th	0.3244 ..	231 x ..	6.0 x ..	70.90°	..
Method III	.. 1 st	0.33472 ..	224 x ..	5.8 x ..	56.76°	Experiments with Gallic Acid
	.. 2 nd	0.30128 ..	148 x ..	3.8 x ..	64.72°	..
	.. 3 rd	0.31592 ..	112 x ..	2.9 x ..	69.60°	..
Sample extracted from the mother liquor in Method III		0.32408 ..	214 x ..	5.6 x ..	65.10°	..

Experiment 23.

Catalyser

Gallotannic acid

0.3244 gr or

0.0002505 mol (Sasabanejew)

Method II (See page 20)

Fourth Purification.

Concentration of ester 0.2050 gr in 20.2cc.

Mean barometer 748.3 mm.

a = 40.28 cc.

t (mins)	temp	x cc.	x1 cc	a-x1	k
30	14°	2.805	2.41	37.87	0.002052
40	13.5	3.80	3.33	36.95	0.002158
50	"	4.80	4.23	36.03	0.002233
60	"	5.80	5.09	35.19	0.002252
70	"	6.40	5.91	34.37	0.002267
80	"	7.80	6.74	33.54	0.002282
90	"	8.20	7.57	32.71	0.002313
100	"	9.10	8.40	31.88	0.002329
110	"	9.90	9.14	31.14	0.002340
120	"	10.805	9.79	30.49	0.002321
130	"	11.40	10.52	29.76	0.002328
140	"	12.20	11.23	29.02	0.002342
150	"	12.85	11.88	28.42	0.002325
160	"	13.80	12.58	27.72	0.002336
170	"	14.30	13.20	27.08	0.002336
180	"	15.00	13.84	26.44	0.002332
225	"	18.00	16.82	23.46	0.002385
250	"	19.50	18.00	22.28	0.002369
265	"	20.40	18.38	21.90	0.002377
280	13.0°	21.20	19.88	20.42	0.002391
300	"	22.30	20.68	19.60	0.002398
330	"	23.85	21.93	18.35	0.002383
360	"	25.05	23.23	17.05	0.002358

Mean value of k = 231×10^{-5}

$C_H = 3 \times 10^{-5}$

40 43 46
SUMMARY.

1 Conditions which govern the progress of the reaction.

It is evident from the above experiments that glass has a very marked influence on the rate of decomposition of the ester. In all cases where the apparatus has been used, the value of k diminishes as the reaction proceeds. This is no doubt due to the alkalinity of the glass which tends to decrease the concentration of H ions in solution. With stronger acids this influence is so easily felt as in the case of the weaker organic acids with which we are here directly concerned. Spitalsky had no doubt got over this difficulty by coating the interior of the flask with paraffin but as he pipettes his acid directly into the reaction flask, he could dispense with the use of the drop-tube which owing to manipulative difficulties we have been obliged to use in the present case. The presence of the drop-tube inside the flask injured the paraffin coat during the shaking of the apparatus. This led us to try a Silica flask in the place of the more costly platinum and the results obtained have been very satisfactory. The drop-tube and the beads introduced into the flask to give an efficient mixing of the reacting solutions are likewise made of Silica so that in no case is the solution in contact with glass while the reaction is in progress.

The influence of the alkalinity of glass on the reaction is particularly noticeable in the case of phenol, pyrogallol and boric acid, all of which are so feebly dissociated in solution that the concentration of H ions produced is not sufficient to give a measurable velocity of the reaction. When the reaction is allowed to take place in the Silica flask, we see at least a qualitative indication of the feeble acidity of these substances, although the constants obtained are owing to the slowness of the reaction rough at first. In the case of the glass apparatus, even this indication is absolutely obscured by its alkalinity. It is unnecessary to point out that the constants obtained for gallic, protocatechuic, o resorcylic and p resorcylic acids are all in the same order, as found by the electric conductivity method, thus showing the influence of constitution on chemical affinity.

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40

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SUMMARY.

1 Conditions which govern the progress of the reaction.

It is evident from the above experiments that glass has a pernicious influence on the rate of decomposition of the ester. In all cases where the apparatus has been used, the value of k diminishes as the reaction proceeds. This is no doubt due to the alkalinity of the glass which tends to decrease the concentration of Hions in solution. With stronger acids this influence is not so easily felt as in the case of the weaker organic acids with which we are here directly concerned. Spitalsky had no doubt got over this difficulty by coating the interior of the flask with paraffin but as he pipettes his acid directly into the reaction flask, he could dispense with the use of the apparatus which owing to manipulative difficulties we have been obliged to use in the present case. The presence of the drop-tube inside the flask injures the paraffin coat during the shaking of the apparatus. This led us to try a Silica flask in the place of the more costly platinum and the results obtained have been very satisfactory. The drop-tube and the beads introduced into the flask to give an efficient mixing of the reacting solutions are likewise made of Silica so that in no case is the solution in contact with glass while the reaction is in progress.

The influence of the alkalinity of glass on the reaction is particularly noticeable in the case of phenol, pyrogallol and boric acid, all of which are so feebly dissociated in solution that the concentration of Hions produced is not sufficient to give a measurable velocity of the reaction. When the reaction is allowed to take place in the Silica flask, we see at least a qualitative indication of the feeble acidity of these substances, although the constants obtained are owing to the slowness of the reaction rough and approximate. In the case of the glass apparatus, even this indication is absolutely removed by its alkalinity. It is unnecessary to point out that the magnitude of the constants obtained for gallic, protocatechuic, o resorcylic and salicylic acids are all in the same order, as found by the electric conductivity method, showing the influence of constitution on chemical affinity.

ments have not been repeated in the Silica flask and concentrations, I have not gone into any of their quantitative

The temperature coefficient of the reaction, judging drawn from similar catalytic reactions, is by no means negligible of 0.25° to 0.5° which the thermostat had shown during the course experiments is perhaps sufficient in the majority of cases to account for the deviation which k exhibits from its mean value.

The rate of evolution of nitrogen as measured by the nitrometer readings is considerably influenced by the character of the solution. When it is of a colloidal character as with gallotannic acid solution a considerable amount of the gas is retained on the surface of the solution in the reaction flask, which consequently escapes measurement and leads to a lower observed rate of the reaction.

2. A comparative review of the different methods of purification of gallotannic acid.

a. Method I (Precipitation by means of NaCl) is not sufficient to get rid of all gallic acid from the commercial sample. A sample which was washed out 24 times still gave after extraction with ethyl acetate or alcohol, a positive gallic acid reaction with KCN . This fact is clearly shown by the high values obtained for k and C_H .

b. Method II (Unequal distribution of gallic and gallotannic acid between ether and acetone) is a tedious one and we can never, even from theoretical considerations, get a sample completely free from gallic acid. It can be seen from the tables that as the purification proceeds the velocity constant k and consequently the Hion concentration both diminish and approximate to a constant value.

c. Method III (Insolubility of sodium gallate in acetic ether) is by far the best means which have been employed for the complete separation of gallic acid impurity from gallotannin. Unlike Method II, even the first fraction is so thoroughly free from gallic acid that we might with sufficient justification state that the Hion concentration 5.8×10^{-5} (See table) is outside the influence of gallic acid.

3 Affinity constant and optical activity.

No proportionality seems to exist between the specific rotation of the substance and its velocity constant. This relationship seems very much on the method of purification employed.

Purification by Method II, based on the work of Rosenheim and Schidrowitz gives a substance with constant values for k and a_D and judge it would seem to indicate that gallotannic acid is an acid of constant k power and of definite acidity. When we ~~are to~~ proceed to purify the substance according to Method III, a perceptible increase in the value of a_D manifests itself as the value of k drops down with the order of purification. This naturally indicates a partial differentiation of the proximate constituents. This method has already been stated to yield a product free from gallic acid. The fact that we are able to extract a substance after neutralisation with sodium bicarbonate shows that the purified product (Sample 3) must be either lactone or an acid more freely dissociated in aqueous solution than carbonic acid. As could be gathered from the figures given in the table, the value of k in this case does not come up to the amount shown by any of the purified samples under Method II. Further, the acidity of the products in this case approximates to a minimum value. Moreover, by extracting the neutralised product from mother liquor according to Method III₄, we get a body which gives a velocity constant with almost the double value obtained in the case of the third sample (Method III). If these be two different chemical individuals, then naturally the one must be twice as strong as the other in its chemical affinity. These facts do not permit us to conclude that we are here dealing with a homogeneous substance.

To compare the degree of dissociation of gallotannic acid with that of any other weak organic acid like gallic, we should naturally have some idea of the molecular weight of the substance in aqueous solution. According to Ssabanejew, gallotannic acid has a molecular weight 1322 in water but we know well enough that this number has no molecular significance in as much as the ordinary osmotic methods cannot be used for the determination of the molecular weight of substances in a colloidal solution.

Working with ~~the~~ precipitate with potassium acetate referred to on of which mention is made below, the following analytical figures which when calculated seems to agree with the monomolecular form

$C_{14}H_9O_5K$ for the potassium salt.

0.4383 gr of the substance yielded on ignition with H_2SO_4 , 0.10

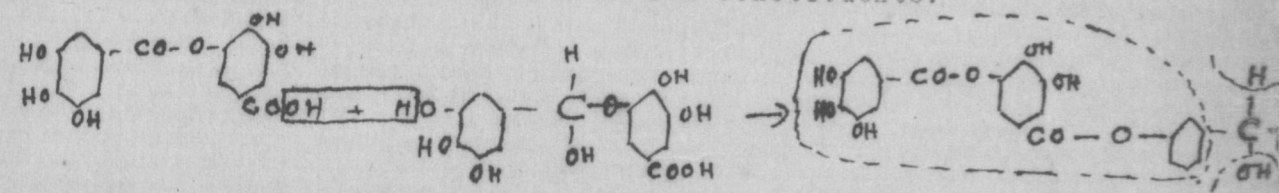
$C_{14}H_9O_5K$

K_2SO_4	calculated	0.1059 gr
	found	0.1032 "

Although it may be too premature to draw definite conclusions from the work done on the subject, it may be mentioned that the results seem to indicate that gallotannin as purified according to Method III is not a single substance but a probable mixture of at least two substances which seem to be of an identical character but for the different degrees of acidity. It is impossible to say at present whether it is caused by a tautomeric or any other change. A point of great interest in this connection has been noted in the potassium compound formed by precipitating the third sample under the same conditions in an alcoholic medium with potassium acetate is optically inactive, $\alpha_D = 39.6^\circ$ of the original sample. If this optical extinction be due to a form of tautomeric change, the free acid liberated from the potassium salt on acidification should be racemic and hence optically inactive, which is actually found to be the case. Imagination cannot picture the possibility of a phenomenon occurring with Nierenstein's leucotannin, the potassium salt of which should under no circumstances show indifference to polarised light. Still the view advanced by Kunz-Krause, Walden, Aweng and finally worked out recently in its detailed form by Nierenstein is in its skeleton supported by the results of the above experiments. It is not possible for us to connect which of the limiting values of k must be attributed to Nierenstein's leuco acid and which to his leuco compound, as his work has not been for the products isolated by him.

44. 47
their separation we remove more and more of the constituent which possesses the greater acidity or in some way facilitate the formation of a less active substance from an inactive acid with a higher dissociation factor.

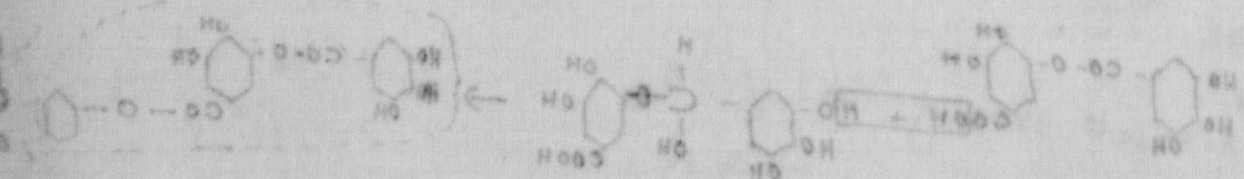
2nd. This hypothesis would depend on a supposition that, owing to methods employed in purification, a condensation takes place between the constituents which Nierenstein speaks of. By the condensation of the carboxylic and phenolic Hydroxyls in the digallic acid and leuco tannin we get an increase in weight of one of the groups attached to the asymmetric carbon atom which could possibly account for the observed increase in optical activity. By the formation of a lactone of this type it is evident that the acidity of the product would be less than the sum of its constituents.



It is impossible for us at present to test the comparative merits of the two above mentioned hypotheses.

The foregoing experiments do not give us a thorough insight into the chemical constitution of gallotannic acid but contrary to the theory upheld by Walden, Dekker and others regarding the possible non-existence of the free carboxyl group in the molecule, experiments show that the acidity is not due to any accident but should be attributed to the constituents of the substance itself. In other words, gallotannic acid possesses a free carboxyl group and seems to be a mixture of two or more chemical individuals possibly of an amphoteric character.

NOTES.



E. & L. 73

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see pages 2 to 47 current file.

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