heated. The anthranil first dissolved and then the quinazolone separated from the hot solution in colorless, silky needles, soluble in alcohol, and melting at 278° (cor.).

Found: N, 18.22. Calculated for $C_{12}H_{13}O_2N_3$: N, 18.18.

6-Acetamino-2-methyl-3-ethyl-4-quinazolone was prepared similarly, using ethylamine instead of methylamine. When the anthranil and ethylamine were heated together (the latter being used in aqueous solution), a clear solution was obtained, from which nothing separated on further heating or on cooling. A small amount of potassium hydroxide was added, the solution again boiled, and on long standing the quinazolone finely separated in long, colorless, silky needles which, after recrystallization from water, melted at 229° (cor.).

Found: N, 17.43. Calculated for $C_{13}H_{15}O_2N_3$: N, 17.14.

The crystals are highly refracting, and dissolve in hot water or in alcohol.

*6-Acetamino-2-methyl-3-*n*-propyl-4-quinazolone*, from the anthranil and *n*-propylamine, crystallizes from water in long, colorless, silky needles, melting at 181° (cor.).

Found: N, 16.45. Calculated for $C_{14}H_{17}O_2N_3$: N, 16.22.

6-Acetamino-2-methyl-3-phenyl-4-quinazolone.—The anthranil and pure aniline were heated together at 110°, and the product purified by repeated crystallization from dilute alcohol. It forms brownish plates, melting at 255° (cor.), very difficultly soluble in boiling water, readily in hot alcohol.

Found: N, 14.43. Calculated for $C_{17}H_{15}O_2N_3$: N, 14.33.

6-Acetamino-2-methyl-3-amino-4-quinazolone.—The anthranil was added to a dilute aqueous hydrazine hydrate solution and the mixture heated to boiling. The anthranil dissolved and, on cooling, the quinazolone crystallized out in rosettes of colorless, silky needles, which were washed with water and recrystallized from it, when they melted at 262–3° (cor.). The crystals are soluble in hot water or in alcohol.

Found: N, 24.29. Calculated for $C_{11}H_{12}O_2N_4$: N, 24.14.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, June, 1910.

ETHYL TANNATE.

BY R. J. MANNING.

Received June, 1910.

Of the naturally occurring tannins gallotannic acid, obtained from gallnuts and many other sources, is the most important and best known. Strecker[1] claims that gallotannic acid is a glucoside of gallic acid as it yielded gallic acid and glucose on hydrolysis. Schiff[2] synthesized di-

---

[1] *Ann.*, 90, 340.

[2] *Ibid.*, 170, 49.

gallic acid from gallic acid by means of phosphorus oxychloride and claims that digallic acid and gallotannic acid are isomers. If this were so, gallotannic acid would have a formula $C_{14}H_{10}O_9$ and on hydrolysis would yield no glucose. On account of the difficulty in purifying the tannin, determinations of its composition vary with different experimenters. I have prepared a crystalline ester and through it have obtained satisfactory analyses giving the composition of gallotannic acid and considerable information about it.

Description of the Gallotannic Acid Used.

The material used in these experiments was obtained through Lyman Bros., Toronto, from the German firm of Schering, and came in the form of light whitish brown flakes; extracted with ether in a Soxhlet, all dissolved, leaving a slight brown stain on the shell, soluble in boiling water. It was purified by the method described by Walden:[1] 100 grams of the commercial tannin were dissolved in 250 grams of amyl alcohol (which must contain a little water) and 350 grams of ether were added; no precipitate appeared. The tannin was then thrown down by gasoline, filtered and dried in a vacuum desiccator over sulphuric acid. So purified, it formed a whitish, rather heavy powder.

The crude sample of tannin contained a trace of gallic acid detected by the potassium cyanide method;[2] the purified product was free from this if excess of gasoline were not added during purification, and in every respect, except solubility, behaved like gallotannic acid as described in Allen's "Commercial Organic Analysis."[3]

Hydrolysis.—A dilute aqueous solution, after boiling for half an hour, reduced Fehling's solution (glucose) and gave a distinct red with potassium cyanide (Young's test for gallic acid); the same result is obtained by boiling for a moment with dilute hydrochloric acid. After long boiling with calcium carbonate while a current of air passed through the solution, the blue coloration changing to red with acids (which is characteristic of gallic acid) was observed.

Behavior with Reagents.—*Arsenic acid* in 5 per cent. alcoholic solution, warmed with its own volume of a 10 per cent. solution of the tannin, solidified to an insoluble jelly, which on standing in the air dried up to a garnet colored mass. *Ammonium molybdate* and *potassium ferricyanide*, reddish colorations; *lime water*, white precipitate quickly turning blue; *ferric chloride*, blue-black precipitate, soluble in much water; *lead acetate or nitrate*, white precipitate in not too dilute solutions; *silver nitrate*, silver mirror on warming; *copper sulphate*, greenish blue gelatinous precipitate turning black on warming; *potassium permanganate* in alkaline

---

[1] *Ber.*, 31, 3167 (1898).

[2] S. Young, *Chem. News*, 48, 31.

[3] Vol. III, Part I, pages 35-38 (1900).

solution, red-brown precipitate, dissolving on warming to a yellow-brown solution which becomes wine-red in the air; dilute *sulphuric acid* and dilute *hydrochloric acid*, and *concentrated salt* solutions form precipitates in moderately concentrated solutions of the tannin, which dissolve again on adding water.

Solubility.—My preparation was soluble in water, glycerol, ethyl acetate, and acetone; slightly soluble in anhydrous amyl alcohol, ether or ethyl alcohol; very slightly soluble in carbon disulphide, benzene and gasoline. It is quite insoluble in chloroform (the gallotannic acid and chloroform were shaken together and filtered, but the filtrate gave no coloration whatever with ferric chloride).

Allen[1] says that gallotannic acid is soluble in six parts of cold water; my preparation was much more soluble. In an experiment in which the tannin and water were shaken together in a thermostat at 0°, many successive portions of tannin kept dissolving until the liquid was a thick sirup, and further addition of the solid balled together and dissolved with extreme slowness. In the end the perfectly clear brownish sirup contained less than one and a half grams of water to one of tannin. At 32° the saturated sirup was still thicker, and contained more than two grams of tannin to one of water.

The solubility of tannin in ether, amyl alcohol, and ethyl acetate, is greatly increased by the addition of a trace of water, as shown by the following data:

One gram of	Dissolved at 15°.
Ethyl acetate (Kahlbaum)	0.2 g. tannin
" " with 5 per cent. water by volume	2.5 " "
Amyl alcohol normal (Kahlbaum)	0.1 " "
" " with 5 per cent. water by volume	0.84 " "

The solubility of mannose, glucose, galactose, cane sugar and of the glucosides, saponin, salicin, and amygdalin in amyl alcohol, acetone, and in ethyl acetate, is also much increased by the addition of a trace of water but not so markedly as in the case of tannin. The solubility of the alkaloids, strychnine and brucine, in ethyl acetate and in acetone, on the other hand, is not markedly increased by the addition of water.

In these solubility determinations the method of analysis for gallotannic acid was that described by F. Jean,[2] involving titration with iodine in alkaline solution.

Analysis of Gallotannic Acid.

To insure perfect dryness the tannin was heated in a hot air bath at 110° for two hours.

(*a*) The elementary analysis gave the following results:

---

[1] *Commercial Organic Analysis*, 3rd Ed., Vol. III, Part I, page 34.

[2] *Chem. Centr.*, 1900, I, 1107.

Calculated for $C_{41}H_{32}O_{26}$: C, 52.35; H, 3.40.
Found: C, 52.4, 52.25; H, 3.45, 3.49.

(*b*) To estimate the glucose in tannin, the following procedure was adopted: 0.2 to 0.5 gram of the tannin was boiled with 200 cc. water and 25 cc. of 10 per cent. hydrochloric acid for an hour. As gallic acid has a marked reducing action on Fehling's solution, it was removed by extraction with ether, and as glucose itself is somewhat soluble in water-saturated ether, the extraction was carried on quantitatively and a correction applied as follows:

From 0.1 to 0.25 gram glucose was mixed with 0.5 to 1.2 grams ethyl gallate and the mixture dissolved in 200 cc. water and 25 cc. of 10 per cent. hydrochloric acid. After boiling the solution for an hour, it was made up to 100 cc. and extracted six times by shaking up for ten minutes each time with 50 cc. of ether. After the sixth extraction, all the gallic acid formed by the hydrolysis of the ether except a slight trace had been removed. The following percentages of the original glucose were found by analysis in the aqueous layer:

Glucose	78.9	79.0	78.8	78.6 per cent.

Hence the boiled solution of tannin was extracted six times with ether, the free hydrochloric acid neutralized with sodium carbonate, the glucose estimated and the results multiplied by 100/79.

The analysis gave glucose: 19.0, 18.79 per cent. Calculated on the assumption that one formula weight of the tannin on hydrolysis gives one formula weight of glucose: 19.1 per cent.

(*c*) Formula weight determinations from the boiling point of solutions:

Water as solvent	813	843	922	1025	1500
Acetone as solvent	1672	2023	1500	1450	....
Water as solvent (from freezing point)	1957	1942	1769	1956	1972

Calculated for $C_{41}H_{32}O_{26}$: 940

Preparation of the Ethyl Ester of Gallotannic Acid.

50 grams of the tannin were dissolved in 250 cc. of Kahlbaum's 99.8 per cent. ethyl alcohol. After introducing the light brown solution into a 500 cc. flat-bottomed flask, hydrogen chloride gas, dried by passing through 18 inches of pumice stone moistened with sulphuric acid, was bubbled through for at least two and a half hours. During the operation the temperature of the liquid rose to about 60°. By cooling the solution during the passage of the gas through it, the yield was diminished, while applying heat to the flask did not noticeably increase the amount of the ester formed.

The dark brown sirup left after the passage of the hydrogen chloride gas was evaporated in a large porcelain evaporating dish until quite thick, and Kahlbaum's lime-free barium carbonate added in excess. The sticky mass was extracted three times with anhydrous ether, the resulting greenish brown ethereal liquid allowed to evaporate, and the residue heated for some hours in a water bath. A dark greenish brown powder remained.

The crude ethyl tannate so obtained was purified by extraction with chloroform in a Soxhlet for two days. This leaves behind the coloring matter and unaltered tannin but dissolves any ethyl gallate as well as the ethyl tannate; hence the necessity of using tannin as free as possible from gallic acid. During the extraction the ethyl tannate separated out of the chloroform in the form of pale yellow spherical nodules of about 2 mm. in diameter. The yield was about 40 per cent. of the tannin used.

In the hope of obtaining a better yield, 50 cc. of benzene[1] were added to the dark brown solution through which the hydrochloric acid gas had been passed, the whole well shaken and the benzene distilled off. After three successive treatments with benzene, the liquid left in the distilling flask was evaporated and treated with barium carbonate and ether as before. This method gave no better yield and was therefore not used again.

Description of the Ethyl Tannate.

On splitting open these nodules, they were seen to consist of a mass of light yellow shining crystals radiating from a common center. Their melting point was 157° (ethyl gallate melts at 141°).[2] They were readily soluble in ether, alcohol and water; slightly soluble in chloroform; insoluble in gasoline and in carbon bisulphide. Their aqueous solution resembled a solution of tannin in its reactions with ammonium molybdate, lead nitrate or acetate, silver nitrate, copper sulphate, and potassium permanganate. With potassium cyanide the aqueous solution of ethyl tannate always gave a slight red color indicating the presence of traces of gallic acid or its ester.

Analysis of the Nodules.

(*a*) *Elementary Analysis.*—The substance was mixed with a little carefully dried red lead and ignited in a porcelain boat.

The analysis gave:	C, 52.3	52.4	52.35;	H, 5.25	5.11	5.25
Calculated for $C_{51}H_{62}O_3$:	52.30			5.30		

(*b*) *Loss of Water on Heating.*—To estimate the percentage of water, the nodules were heated in an air bath to 125–135° for two hours. On first heating they became rather sticky, but did not melt completely, and on continued heating became drier again but showed a tendency to turn brown and to sublime. Hence care had to be taken not to allow the temperature to rise over 135°.

The analysis gave: 7.6, 7.5, 7.8 water; calculated for $C_{51}H_{52}O_{26}.5H_2O$: 7.69 per cent.

---

[1] *J. Chem. Soc.*, **88**, 852 (1905).

[2] Etti, *Ber.*, **11**, 1882.

(*c*) *Ethoxyl Determination.*—The method used was that of Zeisel as described in Meyer and Tingle's "Estimation of Organic Radicles," pp. 34–48. In some of my determinations the precipitate of silver iodide was brownish instead of yellow. The results with these colored precipitates varied widely, being too large, and hence were rejected. It was found afterward, however, that if the brown silver iodide precipitates in these high results were boiled for five minutes with 100 cc. of 15 per cent. nitric acid, filtered and weighed, the precipitates regained their normal color and the new results agreed with those not rejected. This treatment with nitric acid does not perceptibly affect the pure silver iodide.

OC_2H_5 found: 19.24, 19.32, 19.39, 19.55, 19.55 per cent.; calculated for $C_{41}H_{27}O_{21}(OC_2H_5)_5.5H_2O$[1]: 19.23 per cent.

(*d*) *Hydrolysis of the Ester and Estimation of the Glucose.*—2 grams of the ester were boiled with 100 cc. water for two hours with a return condenser and then 25 cc. distilled off. This distillate gave no trace of alcohol when tested by the iodoform method.[1] If, however, previous to the distillation, 10 cc. of dilute hydrochloric acid or of dilute caustic potash were added to the distilling flask, the distillate then gave, especially in the latter case, a distinct deposit of iodoform.

The freshly prepared solution of ethyl tannate reduced Fehling's solution slightly; but the solution which had been boiled with acid or with caustic potash reduced Fehling's solution readily and gave a marked potassium cyanide test for gallic acid. The products of the hydrolysis are therefore ethyl alcohol, glucose, and gallic acid.

The glucose was estimated by the same method as was used for the estimation of glucose in the gallotannic acid and the same correction was applied.

The analysis gave: 15.37, 15.42, 15.51, 15.13 per cent. glucose. Calculated on the assumption that one formula weight ($C_{51}H_{62}O_{31}$) of the ester on hydrolysis gives one formula weight of glucose: 15.38 per cent.

(*e*) *Estimation of the Gallic Acid.*—0.2 to 0.3 gram of the ethyl tannate was hydrolyzed by boiling with dilute hydrochloric acid as in the estimation of the glucose. The boiled solution was then diluted to 250 cc. and the gallic acid estimated by the iodine titration method of Jean.[2]

Gallic acid found: 72.56, 72.66, 72.8. Calculated on the assumption that one formula weight ($C_{51}H_{62}O_{31}$) of the ester on hydrolysis gives five formula weights of gallic acid: 72.64 per cent.

(*f*) *Formula-weight Determinations from Boiling Point of Solutions.*—

Acetone as solvent: 255, 280, 257.
Ethyl acetate as solvent: 362, 275, 300.
Chloroform as solvent: 1335, 1000, 1200, 1467.
Water as solvent (from freezing point): 301, 309.
Calculated for $C_{51}H_{62}O_{31}$: 1170

---

[1] *Z. anal. Chem.*, **9**, 492.

[2] *Chem. Centr.*, **1900**, I, 1107.

Comparing these results, it is seen that those given by the chloroform solution are several times greater than those given by the other solutions. The lower numbers might be explained by assuming that in all the solvents but chloroform there is a dissociation into anhydrous ester and water. To test this, 0.5 to 1.0 gram of the ester was dissolved in 50 cc. acetone and the solution dehydrated carefully by introducing 10 grams anhydrous calcium chloride. After filtering and washing the calcium chloride carefully with acetone, the filtrate was diluted up to 100 cc. and its boiling point determined, giving the following results:

Formula weight found: 950, 1050. Calculated for $C_{51}H_{52}O_{26}$: 1080.

Moreover, on evaporating this solution to dryness, an amorphous, dark brown, sticky mass was left, instead of the crystalline substance before obtained.

A Higher Hydrate of the Ester of Gallotannic Acid.

On the evaporation of solutions of ethyl tannate in ether, chloroform, alcohol, acetone, and ethyl acetate, only minute crystals were obtained. To get large crystals, a cold (15°) saturated aqueous solution of ethyl tannate, obtained without heat, was allowed to evaporate in a round-bottomed evaporating dish by being placed in the sunlight. Even at that temperature a partial decomposition of the ester into ethyl gallate and glucose took place. The ethyl gallate, being less soluble, crystallized out first as a top ring of pale yellow, steep rhombic crystals around the sides of the evaporating dish. At the bottom of the vessel, on almost complete evaporation, were found large, light brown crystals, many between one and two centimeters in length, with a sticky fluid containing the glucose.

An aqueous solution of these crystals behaved like a solution of the lower hydrate of ethyl tannate. They melted at 132°[1] and effloresced readily over sulphuric acid and slowly in the air. They lost their water of crystallization on being heated at 125–135° like the lower hydrate.

Analysis gave: 20.5, 20.7, 21.0 per cent. water. Calculated for $C_{51}H_{52}O_{26}.15H_2O$: 20 per cent.

Synthesis of Ethyl Tannate from Ethyl Gallate and Glucose.

20 grams ethyl gallate prepared according to Schiff's method[2] were ground up with 5–6 grams glucose and mixed to a thin paste with phosphorus oxychloride. After heating this paste in a water bath for two hours, during which time great quantities of hydrochloric acid were given off, a dark sticky mass remained. This was further dried by heating at 120° for a couple of hours, extracted with anhydrous ether, the ether solution evaporated, and the residue again extracted with chloroform in a Soxhlet for twenty-four hours. At the end of that period a light

---

[1] Hydrated ethyl gallate melts at 90°.

[2] Schiff, *Ann. Chem.*, **163**, 215; **170**, 72.

colored mass had settled out of the chloroform. By the fractional crystallization of its aqueous solution as previously described, the higher hydrate of the ethyl ester of gallotannic acid was obtained. This gave all the reagent tests for tannin, for glucose, and ethoxyl groups. It melted at 132°. The maximum yield I obtained was only about 5% of the theoretical.

Summary.

1. Two crystalline derivatives of tannin have been obtained. They are ethyl esters of gallotannic acid differing in the amount of water of crystallization. The previous analyses of gallotannic acid varied because crystalline derivatives were not known and therefore pure material was very difficult to obtain.

2. These esters were synthesized from alcohol and gallotannic acid and one of them was also synthesized from ethyl gallate and glucose.

3. Various analyses show that the formulas for these esters are $C_{41}H_{27}O_{21}(OC_2H_5)_5.5H_2O$ and $C_{41}H_{27}O_{21}(OC_2H_5)_5.15H_2O$, and that they are glucosides of gallic acid in which one formula weight of glucose and five formula weights of gallic acid are represented in one formula weight of the ester. This gives the formula $C_{41}H_{32}O_{26}$ for gallotannic acid.

4. Dissociation of the hydrated ester into water and anhydrous ester would account for the low formula-weight determinations in acetone, etc.

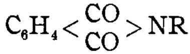
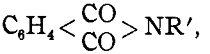
This work was done under the direction of Professor W. Lash Miller.

UNIVERSITY OF TORONTO.

ACTION OF AMINES ON PHTHALIC ACID. VII.[1]

BY J. BISHOP TINGLE AND S. J. BATES.

Received August 4, 1910.

The work described in the earlier papers by the senior author and his colleagues has shown that the phthalamidic acids combine with amines to form salts, $RNHCOC_6H_4CO_2NH_3R'$. Secondary or tertiary amines, if they are not too negative, convert these salts into imides,  $C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CO}NR$ or  $C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CO}NR'$, whereas primary amines give rise to one or more of the following products: the amidic acid $R'NHCOC_6H_4CO_2H$, the amides $RNHCOC_6H_4CONHR$ or $C_6H_4(CONHR')_2$, and the imides formulated above. In the case of the secondary phthalamidic acids, $RNR'COC_6H_4CO_2H$, where R and R′ may represent similar or dissimilar groups, the amine $R''NH_2$ behaves somewhat differently; it may cause hydrolysis of the original amidic acid to phthalic acid, or

---

[1] The previous papers bearing on this subject have appeared as follows: Bishop Tingle and Cram, *Am. Chem. J.*, **37**, 596 (1907); Bishop Tingle and Lovelace, *Ibid.*, **38**, 642 (1907); Bishop Tingle and Rolker, THIS JOURNAL, **30**, 1882 (1908); Bishop Tingle and Brenton, *Ibid.*, **31**, 1157 (1909); Bishop Tingle and Bates, *Ibid.*, **31**, 1233 (1909); Bishop Tingle and Brenton, *Ibid.*, **32**, 113 (1910).