

If filtrations have taken place during the latter part of the day the filters may be removed from the funnels and allowed to stand over night after which they are titrated as described.

The writer hopes that the simplicity and accuracy of the method may render it generally useful.

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A PRELIMINARY COMMUNICATION UPON RICININE.

BY THOMAS EVANS.

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TUSON¹ obtained a substance crystallizing in plates which he called ricinine, by extracting castor beans, the seed of the *Ricinus communis*, with boiling water, filtering, evaporating to a thick sirup and again extracting with boiling alcohol.

Tuson states that ricinine is soluble in water and alcohol and very little soluble in ether and benzene, and that when heated with solid potassium hydroxide ricinine evolves ammonia.

He describes, but gives no analyses of crystalline compounds obtained by the action of nitric acid, mercuric chloride, and platonic chloride.

No salts with acids, with the possible exception of the nitric acid salt, were obtained by Tuson.

A few years later Werner² claimed that the ricinine of Tuson contained no nitrogen and was the magnesium salt of an acid with the formula $C_{11}H_{20}O_{10}Mg_2 \cdot 2H_2O$. To this Tuson³ replied that Werner had evidently investigated an entirely different substance, as his ricinine contained 20.79 per cent. of nitrogen.

Schulze⁴ obtained a nitrogenous substance from the germinated seed of *Ricinus communis*, by extracting with alcohol, distilling this off, taking up the residue with water, treating with tannic acid and lead acetate, filtering, removing lead with hydrogen sulphide, and evaporating the filtrate to small bulk.

The impure product was purified by boiling the aqueous solution with animal charcoal and finally by crystallizing from absolute alcohol, from which it separated in small colorless prisms melting at 193° C.

¹ *J. Chem. Soc.*, 17, 195.

² *Jsb. d. Chem.*, 877 (1870).

³ *Ibid.*, 877 (1870).

⁴ *Ber. d. chem. Ges.*, 30, 2197.

Schulze says he is unable to identify this body with any known substance and calls it ricidine, assigning it the formula $C_{13}H_{15}N_3O_3$.

Pictet¹ gives ricinine the formula $C_{17}H_{18}N_4O_4$ but makes no reference to the original article from which this formula was obtained.

In the following investigation finely ground castor press cake, known as castor pomace, which was kindly furnished by The Brown Oil Co., of St. Louis, was used as a raw material. This was extracted by both Tuson's and Schulze's methods and in each case the same product was obtained, thus identifying the ricidine of Schulze with the ricinine of Tuson.

Tuson's method of extraction was found to be less satisfactory than that of Schulze, although the product so obtained was much lighter in color. It was found advantageous to modify Tuson's process, and use boiling toluene instead of alcohol to extract the residue from the evaporation of the aqueous extract. Upon sudden cooling of the toluene solution ricinine deposits on the sides and bottom of the containing vessel, in small, almost colorless prismatic crystals, which are frequently crossed and sometimes whetstone shaped, and which adhere tightly to the walls of the vessel.

The ricinine so obtained was purified by recrystallization from alcohol, from which it deposited in small plates frequently united to form rosettes. The melting-point was $193^{\circ}C$. and the analysis gave the following results, which agree very well with Schulze's figures :

	Calculated for $C_{12}H_{13}N_3O_3$.	Calculated for $C_{16}H_{18}N_4O_4$.	Calculated for $C_{16}H_{18}N_4O_4$.	Schulze.		Evans.
Carbon	58.30	58.54	58.18	58.20	58.44	58.20
Hydrogen	5.26	4.88	5.45	5.15	5.31	5.06
Nitrogen	17.00	17.07	16.97	17.11	17.15	

In order to render the extraction by Schulze's method more complete a brass extractor of the Soxhlet type was constructed ; this held about 900 grams of pomace and was surrounded by a brass jacket, forming an air space between the two, through which the alcohol vapor could ascend to the return condenser, thus keeping the alcohol hot in the extractor. Later on it was found advantageous to place an additional jacket of asbestos around the brass one.

¹ Les Alcaloides vegetaux. 2nd. ed.

The dark brown alcoholic extract was treated according to Schulze's directions, giving a dark brown aqueous solution of ricinine from which yellowish brown crystals deposited on standing for twelve hours or longer.

Further evaporation of the mother-liquor gave a small amount of the substance; it was found impracticable to further concentrate the second mother-liquor, but upon diluting it with water, precipitating with subacetate of lead, filtering, precipitating out the excess of lead with hydrogen sulphide, filtering and evaporating to small bulk, more crystals of ricinine were obtained. An attempt to remove the brown color of the solution with animal charcoal, either before or after treatment with subacetate of lead, proved unsuccessful.

The impure product was purified by boiling its aqueous solution with animal charcoal. So prepared the substance showed a melting-point of 193° uncorr., and was evidently the same as the product obtained by the aqueous extraction of the pomace, as both gave the reddish purple color obtained by Schulze¹ by dissolving a few crystals in concentrated nitric acid, evaporating to dryness on the water-bath, taking up with water and again evaporating, and finally adding a drop of ammonia water.

To make sure that the product obtained by the extracting of the castor pomace was the same as Tuson obtained by the extraction of the beans, a quantity of these were extracted by his process and yielded a crystalline substance melting at 193° and was evidently the same as the products already described.

While it was found that neither sample of ricinine gave precipitates with silver nitrate, mercuric nitrate, or mercuric chloride, both gave a feathery crystalline product on long standing of a mixture of cold concentrated solutions of ricinine and mercuric chloride.

The chlorplatinate described by Tuson seems to be due to the presence of some more highly nitrogenous body; this seems the more probable when we compare Tuson's percentage of nitrogen (20.79 per cent.) with that found by Schulze (17.11 per cent.).

The writer has obtained the chlorplatinate referred to, but in each case it was with a ricinine which was manifestly impure as

¹ *Ber. d. chem. Ges.*, 30, 2198.

it melted partially at 188° and was completely melted at 190° – 191° .

Further investigations of the double salt with mercuric chloride, the products obtained by the action of nitric acid and ammonia, are now in progress.

BROMINE DERIVATIVE.

When bromine or bromine water is added to a moderately concentrated solution of ricinine in water, the resultant red solution decolorizes very slowly, and upon heating on the water-bath to drive out the excess of bromine, long colorless radial needles separate, either immediately after the expulsion of the bromine or, if the solution be more dilute, upon evaporation.

The product was purified by repeated crystallization from alcohol, 95 per cent., and upon heating in a capillary tube darkened at 220° – 225° C. shrinking at the same time and melted at 229.5° – 230° under decomposition and evolution of gas. By moderately rapid heating the melting-point was found at 232° .

Qualitative tests showed the substance to contain both bromine and nitrogen. Upon boiling the aqueous solution with 10 per cent. silver nitrate there was a very slight darkening of the solution but no precipitation of silver bromide, thus showing the substance to be a bromide and not a salt of hydrobromic acid.

The same bromide was obtained upon treating a chloroform solution of ricinine with bromine in chloroform, as follows:

Two grams of ricinine were dissolved in about 200cc. of chloroform by boiling in a flask connected with a return condenser; to this solution 12 cc. of a solution of 10 cc. of bromine in 50 cc. chloroform was added. After about a minute a considerable precipitate formed and settled to the bottom of the flask. (Ricinine floats on chloroform and it seems probable that the precipitate consists of the hydrobromic acid salt of ricinine, along with some dibromricinine.)

After boiling for ten minutes copious fumes of hydrobromic acid were evolved from the top of the condenser; boiling was continued for some time after these fumes ceased to come off, in all about an hour. The precipitate formed at first did not appreciably increase or diminish during the boiling.

The flask and contents were allowed to stand over night, the precipitate filtered off, washed with chloroform, and the filtrate

evaporated to dryness on the water-bath, the heating being continued until the residue had lost nearly all of its yellow color. The weight of the residue, impure dibromricinine, equaled 2.06 grams, and the dried precipitate weighed 1.82 grams.

When the precipitate was dissolved in boiling alcohol and the solution allowed to cool, prismatic crystals were obtained melting at 192° uncorr., which were evidently unchanged ricinine, as they gave the characteristic reaction with nitric acid and ammonia, while the bromide gave no such reaction.

The weight of ricinine recovered was about 1 gram.

The residue from the evaporation of the chloroform filtrate gave beautiful, long, brittle needles, generally radiating in clusters from several points, and whose length was largely dependent upon the diameter of the beaker and the depth of the solution. These crystals gave the same melting-point, 230° C., as those obtained by brominating in aqueous solution, which would seem to indicate that ricinine was an acid amide or perhaps a diureide. It was at first thought that it might be a substituted uric acid, but the fact that the murexide test fails to give the characteristic color, when performed with potassium chlorate and hydrochloric acid, or with dilute nitric acid, makes this seem doubtful.

The analysis of the recrystallized bromide gave the following results:

Water of crystallization, none.

I. 0.3525 gram substance, dried at 120° , gave 0.5173 gram carbon dioxide, and 0.1084 gram water.

II. The substance was recrystallized from absolute alcohol and 0.2055 gram substance, dried at 120° , gave 0.3000 gram carbon dioxide, and 0.0561 gram water.

	Calculated for $C_{16}H_{14}Br_2N_4O_4$.	Calculated for $C_{16}H_{16}Br_2N_4O_4$.	I.	II.
Carbon	39.53	39.99	40.02	39.81
Hydrogen	2.88	3.27	3.41	3.03
Bromine	32.92	32.79	32.343	...
Nitrogen	11.52	11.42	12.28	11.97

The discrepancy between the results obtained and the theory is probably due to impurity in the form of ricinine. Lack of substance has prevented a more careful separation of the dibromide

from possible impurity; but with more substance more satisfactory results are expected.

The formula $C_{12}H_{13}N_3O_3$, proposed by Schulze does not suit the bromine derivative as well as the ones suggested above, as $C_{12}H_{12}BrN_3O_3$ calls for 24.54 per cent. of bromine and $C_{12}H_{11}Br_2N_3O_3$ for 39.50 per cent.

Ricinine dibromide is soluble in about 200 parts of 93 per cent. alcohol and in practically the same amount of water; it is rather less soluble in chloroform. From dilute solutions in alcohol or water it crystallizes in long needles, while from more concentrated solutions it is obtained as a mass of short, silky, white needles.

So far all attempts to make a bromide containing less bromine have proved unsuccessful, the same product being obtained with varying amounts of bromine.

Ricinine dibromide is soluble in hot, dilute, or concentrated hydrochloric acid and separates out unchanged on cooling. When treated with concentrated nitric acid and ammonia as described under ricinine, it gives no characteristic color.

Its aqueous solution appears to be neutral, and it was found impossible to prepare double salts with platinic or auric chloride.

OXIDATION OF RICININE.

Schulze states that upon oxidizing ricidine with potassium bichromate and sulphuric acid an odor of hydrocyanic acid was obtained, but does not mention other oxidation products.

Upon treatment of an alkaline solution of ricinine with potassium permanganate, the latter was almost immediately reduced, the reduction being accompanied with a faint odor of hydrocyanic acid. Upon filtering off the oxide of manganese a colorless solution was obtained, which became red with a yellow fluorescence upon acidifying with hydrochloric acid; when heated on the water-bath the solution became more intensely colored, and upon evaporation and subsequent cooling, beautiful, long, wavy, salmon-pink needles separated. These proved to be free from inorganic matter and were completely decolorized when their aqueous solution was boiled with animal charcoal.

The oxidation was carried out as follows:

One-half gram ricinine was dissolved in 20 cc. of boiling water

to which 5.5 cc. of approximately normal potassium hydroxide were added. After cooling to 17° C. a solution of potassium permanganate, containing 5.8 grams of the solid in 320 cc. of water, was slowly added until a further addition produced an evolution of a few bubbles of gas; in all 16 cc. of the permanganate were added.

The flask and contents were then allowed to stand for five hours; the oxide of manganese, which had settled, was filtered off after being washed by decantation. The filtrate and washings equaled 100 cc.

The colorless alkaline solution was heated on the water-bath, and made faintly acid with hydrochloric acid, when a few bubbles of carbon dioxide were evolved and the solution became red. Upon evaporation until crystals were deposited on the sides of the dish at the level of the liquid, and then allowing to stand, 0.27 gram of pink silky needles were obtained, melting, after previous blackening, at 269.5°. After repeated boiling of the aqueous solution with animal charcoal, the crystals were obtained snowy white; it was impossible to remove all of the color from the mother-liquor.

The purified substance melted at 279°—280°, becoming black several degrees below the melting-point.

The aqueous solution of the oxidation product is acid to litmus paper, and forms crystalline salts with alkalis as well as with silver nitrate. A test for the degree of acidity, using phenolphthalein as an indicator, gave the following results:

0.1079 gram acid dissolved in 50 cc. of water required 7.1 cc. standard alkali containing 0.001971 gram NaOH per cc., for neutralization; or 0.00805 gram Na, which equals 7.46 percent. Na.

The acid contains nitrogen, and on evaporation with nitric acid and moistening with ammonia, gave the reddish purple color characteristic of ricinine, but to a lesser degree,—hence the thought that this may be due to impurity in the form of unoxidized ricinine.

A second portion of 1 gram of ricinine was oxidized in the manner already described, made acid with hydrochloric acid, and concentrated until 6 grams of reddish needles, mixed with dark red prisms, were obtained; these were filtered off and boiled with benzene for several hours, when a reddish yellow solution

with a green fluorescence was obtained, the prismatic crystals being dissolved while the needle-like crystals appear to be quite insoluble. Upon evaporation of the benzene solutions red prismatic crystals were obtained which became colorless with ammonia, and on evaporation of the solution so obtained gave a colorless crystalline mass.

The difficulty in preparing even small amounts of ricinine has materially interfered with the process of the investigation. The writer is now germinating seed in the dark, and hopes to be able to contribute further in the near future.

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NOTES.

Retention of Moisture by Asbestos.—In the use of the Gooch crucible error may result from ignoring the fact that asbestos (some asbestos at any rate) retains moisture with great tenacity, so that after being dried at 100° C. to constant weight, the Gooch apparatus will suffer a further and notable loss of weight upon ignition over a Bunsen burner.

	Grams.
1. Dried one hour at 100° C., weighed.....	21.0452
Again dried one hour at 100° C., weighed.....	21.0450
Then ignited ten minutes, weighed.....	21.0441
2. Dried one hour at 100° C., weighed.....	21.0436
Then ignited five minutes, "	21.0429
3. Dried one hour at 100° C., "	21.0418
Again dried one hour at 100° C., weighed	21.0418
Then ignited five minutes, weighed	21.0409
4. Dried two hours at 100° C., "	20.7304
Then ignited one-fourth, weighed	20.7293
5. Dried three hours at 103° C., weighed.	20.8250
Then ignited one-fourth hour, weighed	20.8246
6. Not dried in air-bath.....
Ignited five minutes.....	21.0950
Then ignited again one hour	21.0944
7. Asbestos in larger quantity from a Hirsch funnel dried in a platinum crucible six hours at 90° – 100° C.	20.2828
Then ignited one hour	20.2811
8. Ignited in a platinum boat in porcelain combustion tube in current of oxygen, then dried three hours at 100° C	21.1742
Then ignited one hour.....	21.1726