tent, when the double cyanide is mixed with potassium hydroxide in solution, for the gold-dissolving power of a double cyanide solution is considerably increased by addition of caustic alkali, the increment of solvent power decreasing for successive equal additions of alkali.

Several other reactions have been suggested as taking place between some of the substances investigated, but no experimental verification has been found for those investigated: for instance, the equation $K_2ZnCy_4 + 2KOH = Zn(OH)_2 + 4KCy$ is contrary to all observed facts.

THE ALKALOIDS OF ADLUMIA CIRRHOSA.

By J. O. Schlotterbeck and H. C. Watkins.

Received March 31, 1903.

[SECOND PAPER.]

In a previous paper,[1] "Adlumia Cirrhosa, a New Protopine-bearing Plant," the preliminary experiments upon the root of the first year's plant of this biennial were reported. Of the dried root only about 100 grams were available and it was treated as follows: It was first moistened with dilute ammonia water for the purpose of liberating the alkaloids from their combinations with acids. To avoid any possible change in the nature of the constituents, the powder was dried at room temperature by spreading out in thin layers in a room in which there was good circulation of air. The drug was now exhausted with chloroform in a Soxhlet apparatus since most free alkaloids are easily soluble in this solvent. The chloroform was recovered from the solution by distillation and the stiff, waxy residue then repeatedly digested with hot, very dilute acetic acid until all alkaloidal matter had been extracted. The combined acid aqueous extracts were concentrated, cooled, filtered and precipitated with ammonia water, being careful to avoid a great excess. The curdy precipitate was thoroughly washed on a filter, redissolved in dilute acetic acid, placed in a separator, made alkaline with ammonia and shaken out with ether. Solution of the alkaloid was almost instantaneous but only temporary. The ethereal liquid was passed through a tuft of cotton into a wide-mouthed flask and set aside. In a very short time

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[1] *Am. Chem. J.*, **24**, 249.

crystals began to separate and in the course of two hours most of the alkaloid had crystallized out. This alkaloid upon purification was found to be protopine, and at the time it was thought that this was the only alkaloid present in the root.

Wishing to continue the chemical study of this interesting and widely known plant, an endeavor was made to secure it in large quantities. Although it is claimed that it grows wild in wet woods from New England to Michigan and eastern Kansas southward, it was impossible to obtain the plant from botanic druggists, and collectors could not be found to gather it. It was then decided to grow it ourselves. The small, shiny black seeds were obtained without difficulty from seedsmen and sowed as directed, in spring. Not a single seed germinated that year. Not desiring to postpone the work for a year, growing plants were solicited from the citizens of Ann Arbor who grow it quite generally about porches and doorsteps. About 150 of the first year's plants and sufficient of the second year's vine to make about 15 pounds when dry were kindly donated. The growing plants were transplanted to the experimental garden and the following year's crop reserved for further study. It has since been learned that the seeds are very slow in germinating and must be sown in a cool, moist soil.

Self-sown seeds do not germinate as a rule until June of the following year.

In the present study the entire plant of the second year's growth was employed, no attempt being made to separate root from stem or leaves. The finely ground drug was treated exactly as outlined above. About 30 grams of a dirty gray mass of alkaloids was obtained and after redissolving in dilute acetic acid, making alkaline with ammonia water and shaking out with ether, several different forms of crystals separated. They were isolated as far as possible mechanically, and each one purified by many recrystallizations. Five distinct alkaloids were isolated by fractional crystallization as follows:

ALKALOID I, PROTOPINE.

The identity of this alkaloid was established in the preliminary examination which has been reported. It has the composition $C_{20}H_{19}NO_5$ and melts at 204°-205° C.

ALKALOID II, β-HOMOCHELIDONINE.

This alkaloid crystallized in rather characteristic form, *viz.*, in beautiful clusters or rosettes of boat-shaped crystals with truncated ends. When purified, the crystals melted at 159° C. Sulphuric acid gives at once a rose-pink color which is intensified when the vapor of nitric acid is blown over it. Erdman's reagent colors it yellowish, then passing into beautiful violet.

Combustions gave the following results:

	Calculated for $C_{21}H_{23}NO_5$.	Found. I.	Found. II.
Carbon	68.27	68.66	68.6
Hydrogen	6.24	6.2	6.9
Nitrogen	3.8	3.8	3.76

ALKALOID III, ADLUMINE.

This alkaloid constituted the principal portion of the entire or total alkaloid. After purification it melted at 188° C. It crystallizes easily and in beautiful large crystals. A mixture of chloroform and alcohol constitutes the best crystallizing medium, from which large colorless, orthorhombic crystals can be obtained.

The following color tests were obtained:

Sulphuric acid	Lemon-yellow.
Erdmann's reagent	Olive-green to brown, then wine-red.
Nitric acid	Lemon-yellow to orange.
Marquis' reagent	Light yellow, changing to lavender.

A weighed quantity of desiccator-dried material lost no weight upon heating for several hours at 100° C. It therefore contains no water of crystallization. The material at hand permitted the following combustions for composition:

	Calculated for $C_{39}H_{39}NO_{12}$.	Calculated for $C_{39}H_{41}NO_{12}$.	Found. I.	Found. II.	Found. III.
Carbon	65.62	65.45	65.95	65.77	65.45
Hydrogen	5.46	5.74	5.75	5.64	5.59
Nitrogen	1.97	1.96	2.08	2.18	2.02
Oxygen	26.95	26.85	26.22	26.41	26.94

From the above results alone it is impossible to determine, with certainty, whether the formula is $C_{39}H_{39}NO_{12}$ or $C_{39}H_{41}NO_{12}$, the difference of two atoms of hydrogen being difficult to adjust because of the size of the molecule.

Platinum chloride does not precipitate the alkaloid from its solution. Gold chloride throws down a copious yellow, amorphous precipitate, which can be crystallized by redissolving in hot water and allowing to cool. The crystals of the gold salt are deep orange-red in color, and contain no water of crystallization. During crystallization, a part of the gold is reduced. Incineration of the gold salt did not furnish concordant results, as we were probably dealing with a mixture of reduced gold and gold salt. This reaction will be studied further when more material is available.

Determination of Methoxyls.—Of the pure alkaloid, 0.100 gram was treated according to the Zeissel method for the determination of methoxyls. An abundant precipitate of AgI was formed in the flask containing the $AgNO_3$ solution. This was transferred to a Gooch crucible thoroughly washed, dried and weighed. The weight of AgI (0.847 gram) is equivalent to 8.68 per cent. methoxyl calculated from the formula having the higher hydrogen content. This is exactly equal to two methoxyl groups.

Determination of Hydroxyls.—A small amount of the pure alkaloid was heated with acetic anhydride on the steam-bath for several hours and the solution then evaporated to dryness. The amber-colored residue was taken up with a little chloroform, alcohol added and set aside. Colorless crystals, which melted at 177° C. when purified, separated quite rapidly.

Of this compound, 0.1412 gram was saponified by boiling with freshly prepared $Mg(OH)_2$ under a reflux condenser for two hours. Upon cooling, the liquid was filtered, the precipitate thoroughly washed, all the washings combined and concentrated and the magnesia determined as $Mg_2P_2O_7$. The weight obtained was 0.0202 $Mg_2P_2O_7$ which is equivalent to 5.54 per cent. of the acetic radical. Theory requires 5.68 per cent. for one acetyl group based on the formula with higher molecular weight.

The compound is then written $C_{37}H_{34}(OH)(OCH_3)_2NO_9$.

Finally, this alkaloid, which we have named adlumine because it seems not to have been known before, rotates the plane of polarized light $(\alpha)_D = +39.88$.

ALKALOID IV, ADLUMIDINE.

This alkaloid crystallizes in small, almost colorless, square plates melting at 234° C. When perfectly pure it is colorless, but it is extremely difficult to remove the last traces of the yellow color which adheres to it. It appears to be also a new alkaloid and we have therefore named it adlumidine.

The quantity available was too small to permit of more than the following combustions:

	Calculated for $C_{30}H_{29}NO_9$.	Found. I.	II.	III.
Carbon	65.6	65.69	....	65.45
Hydrogen	5.3	5.6	5.1	5.2
Nitrogen	2.54	2.6	....	2.63
Oxygen	26.5	26.11	....	26.72

The color reactions are striking.

Sulphuric acid	Bright red, changing to olive-brown, then pink.
Erdmann's reagent	Brick-red, changing to shades of green, to brown.
Nitric acid	Orange to light yellow.
Marquis' reagent	Bright red to dark brown, then purple-violet.

ALKALOID V, UNNAMED.

This alkaloid was found in such small quantity that only the melting-point 176°-177° C. and the color reactions could be determined.

Sulphuric acid	Light yellow.
Erdmann's reagent	Dirty olive, brown, wine-red.
Nitric acid	Light yellow.
Marquis' reagent	No color.

ORGANIC ACIDS.

The dregs left after removing the alkaloids with chloroform were percolated with boiling water and the percolate concentrated to a small volume. Upon cooling, a crystalline sediment accumulated in the bottom of the dish. This dark-colored deposit was collected on a Büchner filter and thoroughly washed with cold water. There was left a grayish granular mass of salts of ammonia and calcium. This mass was dissolved in hot water with the aid of a little acetic acid, and then precipitated with a solution of lead subacetate. This precipitate was collected and rapidly washed with cold water by the aid of suction, then suspended in water and decomposed with hydrogen sulphide, the lead sulphide removed by filtration and the filtrate evaporated to dryness. This was boiled with alcohol and filtered. From the filtrate, a white precipitate separated, on cooling, which was found to contain calcium. Calcium tartrate was suspected. It was dissolved in acetic acid and treated with ammoniacal silver nitrate solution from which it deposited silver in the form of a mirror upon boiling. The free acid was precipitated by calcium hydroxide in the cold (distinction from citric acid).

The residue left after treating with boiling alcohol was tested with ammoniacal silver nitrate solution but it did not precipitate silver and was not precipitated by calcium hydroxide in the cold, though it was precipitated on heating.

The free acid was crystallized later and the rhombic prisms of citric acid identified.

SUMMARY.

Adlumia cirrhosa contains at least five distinct alkaloids as follows:

(1) Protopine, $C_{20}H_{19}NO_5$, melting-point 204°-205° C.

(2) β-Homochelidonine, $C_{21}H_{23}NO_5$, melting-point 159° C.

(3) Adlumine, $C_{39}H_{39}NO_{12}$ or $C_{39}H_{41}NO_{12}$, melting-point 187°-188° C.

(4) Adlumidine, $C_{30}H_{29}NO_9$, melting-point 234° C.

(5) Unnamed, melting-point 176°-177° C.

Also tartaric and citric acids.

The investigation is being continued.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 78].

3-NITROPHTHALYL CHLORIDE AND ITS ACTION WITH AMMONIA AND WITH AROMATIC AMINES.

BY VICTOR JOHN CHAMBERS.

Received April 6, 1903.

THE action of phosphorus pentachloride upon 3-nitrophthalic acid has been tried before, but the product isolated from the reaction mass has not been the acid chloride. Boroschek[1] obtained the anhydride of 3-nitrophthalic acid and also the anhydride of 3-chlorphthalic acid. Levi[2] obtained only the anhydride of 3-nitrophthalic acid.

By using the process described in the experimental part, the author was able to obtain the acid chloride in the form of colorless, transparent, well-defined crystals melting at 76°-77° corr.

Phthalyl chloride, as is well known, has been assigned both a

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[1] Inaug. Dissertation, 1901.

[2] Inaug. Dissertation, 1891.