quite a number patented for bringing this about. The principal substances employed in the lumping process are glue, tar, molasses, asphalt, etc.

Working along these lines, the writer decided upon the idea of using carbon—or coking these fine materials with bituminous coal. The coal in coking thoroughly incorporates the fine materials, acting as a fairly good carrier, being porous, takes the materials down to the zone of reduction and much of it still further to the tuyeres, carries more than enough carbon for reduction, carries no foreign materials into the furnace, and besides it is cheap. Samples have been made carrying 12½, 25 and 50 per cent. by weight of these materials. The 25 per cent. one, the mean shows, by analysis, to run:

	Port Henry. Per cent.	Buffalo. Per cent.
Iron	14.07	16.51
Lime	2.35	2.11
Magnesium	0.30	0.70
Alumina	2.00	2.30
Fixed carbon	61.28	65.25
Volatile matter	10.56	6.86

These tests were conducted in a clay crucible. The process can be carried on very nicely in a bee-hive oven. A small battery of these can be installed very reasonably and made to pay at a plant running four or more stacks. Any sized plant can be made to pay handsomely where the by-product ovens are used as they are at many plants to-day—and more are installing them. This plan is also applicable at any plant where the coke is made at or near the furnace.

I wish to acknowledge my indebtedness to Mr. L. D. Fraunfelder, chemist and assistant superintendent at Port Henry, N. Y., for his cooperation and analyses.

ON THE CRYSTALLINE ALKALOID OF CALYCANTHUS GLAUCUS.

By H. M. Gordin.

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Calycanthus glaucus (Willd.) is a shrub growing in Georgia, Notrh Carolina and Tennessee, where it is known as sweet-scented shrub, Carolina allspice or bubby. The seeds (achenes) of the plant are poisonous and have been known to kill cattle that happened to eat them. They were examined for the first time by Dr. G. R. Eccles,[1] who found the seeds to contain about 39 per cent. of fixed oil and a crystalline alkaloid, which he named calycanthine,[2] and of which he described several characteristic color reactions. Later Dr. H. W. Wiley[3] also worked upon the same subject, examining both the oil and the alkaloid. He found in the seeds about 47 per cent. fixed oil, of which he determined the specific gravity, the iodine absorption and the refractive index. The absence of volatile acids from the oil was also established. Besides the oil and the alkaloid of the kernel of the seeds Dr. Wiley also examined the alkaloid present in the hulls and the very small amount of alkaloid dissolved in the oil when the latter is extracted from the seeds by petroleum ether. He also showed that the seeds are very rich in albuminoids and sugar, but very poor in starch.

As considerable time has elapsed since the work of these chemists I undertook the investigation of the subject, intending to examine the alkaloid, the oil and the other constituents of the seeds. In the present paper I wish to report upon the results which I have so far obtained in the examination of calycanthine, hoping to supplement the work by more results in the near future.

As a complete description of *Calycanthus glaucus* is given in the above-mentioned articles of Dr. Eccles and Dr. Wiley, I shall refer to these articles for the botanical description of the plant and pass directly to the chemical investigation of the subject.

The first step in the preparation of calycanthine was to establish, by assay, the amount of alkaloid present in the seeds, and then find, by experiment, the best method which would give results approximating those of the assay. The assay was carried out by means of Prollius' fluid in the usual way and showed the presence of about 2 per cent. of alkaloid in the deoleated seeds. It was found that cold alcohol extracted only about 29 per cent. of the alkaloid, whereas hot alcohol extracted about 75 per cent. It is possible that acidulated solvents or ammoniacal chloroform or ether would give a larger yield, but as it was deemed de-

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[1] *Proc. Am. Pharm. Assoc.*, 1888, pp. 84 and 382.

[2] The alkaloid calycanthine, which is the subject of this paper, should not be confounded with the calycanthin obtained by Th. Hermann from *Calycanthus floridus*. Hermann's calycanthin is a glucoside, free from nitrogen, easily soluble in water with strong fluorescence and has the formula $C_{25}H_{23}O_{11}$ (*Jsb. d. Chem.*, 1868, p. 806).

[3] *Am. Chem. J.*, 1889, p. 557.

sirable to avoid the use of acids or alkalies with an alkaloid of unknown stability, it was decided to use hot alcohol for extraction. The method I have used then is as follows:

The seeds are ground up very coarsely and then extracted completely with petroleum ether or benzene. All the fixed oil is thus taken out, leaving the alkaloid. The deoleated seeds are dried at ordinary temperature until the color of the benzene or petroleum ether disappears. The drug is then again ground, but this time to a fine powder, which is exhausted with hot alcohol. From the alcoholic tincture the alcohol is distilled off completely and the thick residue extracted with water, slightly acidulated with sulphuric acid. A brown flocculent residue remains, consisting probably of the acids with which calycanthine is combined in the drug, mixed with calcium sulphate and colored by resinous matter. The alkaloid goes into solution as a sulphate.

The solution is filtered and the alkaloid precipitated from the clear filtrate by an excess of potassium hydroxide. A flocculent precipitate is formed at first, which, on standing over night, becomes crystalline and heavy, and settles to the bottom of the vessel. The impure calycanthine is collected on a filter, washed with water and dried at about 40° to 50°.

To see whether any alkaloid remains in the alkaline mother-liquor a portion of it was shaken out repeatedly with ether and the ether removed by distillation. Only a trace of alkaloid remained. Into another portion of the mother-liquor an excess of carbon dioxide was passed and the liquid again shaken out repeatedly with ether. On distilling off the ether again only a trace of alkaloid remained, showing the absence of alkali-soluble alkaloid in any appreciable quantity. Whether the seeds contain an alkaloid that is easily soluble in water, but insoluble in ether, I shall try to determine later.

The crude calycanthine, obtained as described above, was dissolved in ten times its amount of acetone, the solution filtered off from insoluble mineral matter (found to be mostly calcium carbonate formed from the calcium salts of the drug and the potassium carbonate present in the potassium hydroxide) and then mixed with a slight excess of strong sulphuric acid, previously diluted with five times its amount of alcohol. The sulphate of calycanthine, which is almost completely insoluble in acetone,[1] soon

[1] Calycanthine sulphate is so insoluble in acetone that on removal of the acetone and taking up with water no precipitate is obtained with Mayer's reagent.

settles in the form of fine, small needles. The sulphate is collected on a filter, washed with acetone and dried at 40° to 50°. The dry sulphate is dissolved in water and the alkaloid precipitated with potassium hydroxide. After the alkaloid settles it is collected, washed with water and dried at about 80°. The alkaloid is now almost perfectly white and has a crystalline appearance.

For further purification the alkaloid is dissolved in about twenty-five times its amount of boiling alcohol and to the solution is added an excess of sulphuric acid, previously diluted with five times the amount of alcohol. The calycanthine sulphate soon commences to crystallize in beautiful snow-white silky needles, which are very difficultly soluble in cold alcohol. After setting the liquid aside for two days the sulphate is collected, washed with alcohol and dried at about 80°. The sulphate is again dissolved in water and the alkaloid precipitated with potassium hydroxide. After washing and drying, the alkaloid is dissolved in ten times the amount of acetone and to the solution is added an amount of water equal to half the amount of acetone taken. In a few minutes the alkaloid commences to crystallize in brilliant, orthorhombic bipyramids, having pinacoid form. On standing over night, about 85 per cent. of calycanthine taken crystallizes out. The last operation is repeated several times until the melting-point remains constant.

Thus obtained calycanthine forms small, snow-white crystals of the above-mentioned form, containing 0.5 molecule of water of crystallization. By slow crystallization from hot alcohol the alkaloid can be obtained in large, hard crystals of the same form.[1]

On prolonged exposure to the atmosphere calycanthine assumes a yellowish tint without losing its water of crystallization. It melts between 216° to 218°, and if the tube in which the melting-point is determined is not too narrow, a slight effervescence can be noticed at this temperature. The water of crystallization is completely removed on drying the alkaloid three or four hours at 120°. Anhydrous, it melts sharply at 243° to 244°.

From the solution of its salts calycanthine is precipitated by alkalies, alkaline carbonates and ammonia, at first in a flocculent condition, but on standing a few hours the alkaloid becomes crystalline and heavy.

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[1] The exact crystallographic measurements and the optical rotation of calycanthine and of some of the more important of its salts will be given later.

Calycanthine has a bitter taste and a slightly alkaline reaction towards litmus. It is so little soluble in water that Mayer's reagent, in the presence of acid, gives only a slight turbidity. It is slowly, but completely, soluble in ether or chloroform and difficultly soluble in benzene. The best solvents for calycanthine I have so far found to be acetone and pyridine.[1] The alkaloid forms beautiful, crystalline salts with all acids so far tried. It is a monoacid, weak base. It forms a neutral and an acid sulphate, of which the former becomes yellow on exposure to the air, whereas the latter does not change color. The sulphates and hydrochloride are extremely easily soluble in water, but almost insoluble in acetone. In alcohol the sulphates are very difficultly soluble. The hydrochloride requires about 15 parts of alcohol for solution. The nitrate, hydriodide and oxalate are difficultly soluble in cold water or alcohol. The acetate is extremely easily soluble in water, alcohol or acetone, but cannot be obtained in a stable condition, as on exposure to air it continually loses acetic acid, which can be noticed by the odor.

The aqueous solutions of the neutral sulphate and the hydrochloride are strongly acid to litmus paper, showing the alkaloid to be only weakly basic. Both the hydrochloride and the hydrobromide contain 1 molecule of water of crystallization, but the hydrobromide is comparatively stable in the air, efflorescing only slightly upon exposure to the air and losing its water of crystallization only slowly in the vacuum desiccator over sulphuric acid, whereas the hydrochloride commences to lose its water of crystallization immediately on exposure to the air, and in the desiccator the loss is much quicker than in the case of the hydrobromide. If a crystal of the hydrochloride or of the hydrobromide be put on a watch-glass in a desiccator containing sulphuric acid, the crystal very soon falls to a fine powder, either spontaneously or upon the slightest touch. Most of the salts, except the acetate, can be obtained almost quantitatively by treating an acetone solution of calycanthine with the corresponding acid previously diluted with alcohol or acetone. Both the crystalline and the anhydrous salts of hydrochloric and hydrobromic acids have nearly the same melting-points for both acids.

Calycanthine also forms a chlorplatinate and a chloraurate. The chlorplatinate crystallizes easily from hot water in long,

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[1] The exact solubilities of the alkaloid and its salts will be given later.

orange-red aggregates. The chloraurate forms brown, microscopic needles, possessing strong pleochroism (yellow and orange).

The chloraurate is easily decomposed by cold water in the absence of hydrochloric acid or by hot water even in the presence of this acid, forming a deep violet colored solution from which gold is deposited on standing. It cannot be recrystallized from any solvent I have so far tried. It is very easily soluble in alcohol, but on slowly evaporating the alcohol the salt is partly decomposed. It is insoluble in ether. When calycanthine chloraurate is dissolved in alcohol in the presence or absence of hydrochloric acid, and ether added to the solution, beautiful long, silky needles soon commence to crystallize, but upon examination these needles were found to be not the gold salt, but simply calycanthine hydrochloride. This was shown by the fact that the needles were perfectly white, extremely easily soluble in water and left no residue upon calcination. The gold salt is possibly a mixture of several salts of different compositions and not a definite compound. It has no definite melting-point and continually, though slowly, loses weight on drying at 110°. Conditions under which a gold salt of definite composition is obtained I have so far been unable to ascertain.

All the salts of calycanthine so far examined lose some acid upon recrystallization from water or alcohol. It is therefore necessary to carry out their recrystallization in the presence of a slight excess of the corresponding acid.

With the volatile halogen acids it is not necessary to wash away every trace of free acid from the corresponding salts because these acids will be removed upon drying the substance in the air or in the desiccator over lime. But in the case of the nitrate the free nitric acid must be completely removed from the salt as otherwise the latter becomes dark green upon drying.

As shown by the following analytical data the formula of anhydrous calycanthine is $C_{11}H_{14}N_2$, hence calycanthine is one of the very few alkaloids that are crystalline at ordinary temperature and contain no oxygen.

EXPERIMENTAL.

ANALYSIS OF ANHYDROUS CALYCANTHINE, $C_{11}H_{14}N_2$.

For analysis the alkaloid was dried at 120°. It then melted at 243°-244° and did not resolidify on cooling for quite a while.

1. 0.1655 gram substance gave 0.46255 gram CO_2 and 0.1226 gram H_2O.

2. 0.1668 gram substance gave 0.46418 gram CO_2 and 0.12185 gram H_2O.

3. 0.14142 gram substance gave 0.39129 gram CO_2 and 0.10015 gram H_2O.

4. 0.20178 gram substance gave 0.56302 gram CO_2 and 0.14412 gram H_2O.

5. 0.16537 gram substance gave 23.4 cc. N($t = 21°$, $b = 744$).

6. 0.16745 gram substance gave 23.8 cc. N($t = 23°$, $b = 749$).

Calculated for $C_{11}H_{14}N_2$: C, 75.77; H, 8.12; N, 16.12.

	Found.					
	1.	2.	3.	4.	5.	6.
C	76.21	75.89	75.46	76.10	......	......
H	8.30	8.19	7.94	8.01	......	......
N	......	......	......	......	15.76	15.78

ESTIMATION OF WATER OF CRYSTALLIZATION.

Dried in the air at ordinary temperature calycanthine melted at 216°-218°.

0.36915 gram substance lost on heating to 120° to constant weight 0.0184 gram.

1.3373 grams substance lost on heating to 120° to constant weight 0.0660 gram.

Calculated for $C_{11}H_{14}N_2.\frac{1}{2}H_2O$: 4.92 per cent. H_2O; found: 4.98 and 4.93 per cent. H_2O.

Calycanthine Hydrochloride, $C_{11}H_{14}N_2.HCl.H_2O$.—Two grams of the alkaloid were dissolved in acetone (20 cc.) and the solution mixed with an excess of strong hydrochloric acid (31 per cent.) previously diluted with twice its amount of alcohol. Almost immediately crystallization begins and on standing over night most of the hydrochloride crystallizes out. After washing with acetone and drying at ordinary temperature the salt was dissolved in about fifteen times its weight of boiling alcohol containing a few drops of hydrochloric acid and the solution set aside in a desiccator filled with quicklime. The hydrochloride soon commences to crystallize in large, heavy, rectangular plates containing 1 molecule of water of crystallization. An estimation of the water of crystallization after washing with alcohol acidulated with hydrochloric acid and drying at ordinary temperature showed that the salt loses its water of crystallization even on exposure to the air. 0.2832 gram of air-dried substance kept in desiccator over sulphuric acid till the weight was constant (12 days) lost 0.200 gram.

Calculated for $C_{11}H_{14}N_2.HCl.H_2O$: 7.88 per cent. H_2O; found: 7.06 per cent. H_2O.

For the estimation of chlorine the salt was dried to constant weight over quicklime.

0.25605 gram substance gave 0.1756 gram AgCl.

0.3346 gram substance gave 0.2307 gram AgCl.

Calculated for $C_{11}H_{14}N_2.HCl$: 16.83 per cent. Cl; found: 16.96 and 17.04 per cent. Cl.

The hydrochloride after drying in the air melts at 212°-213° to a black liquid.

The anhydrous salt melts at 216°-217°.

A solution of the hydrochloride in alcohol or water assumes a yellowish color on standing.

Calycanthine Hydrobromide.—Made exactly like the hydrochloride, only substituting hydrobromic for hydrochloric acid, and has the same crystalline form.

Dried in the air the salt contains 1 molecule of water of crystallization and melts at 213°-214°.

0.28635 gram substance lost on drying over quicklime 0.0185 gram.

Calculated for $C_{11}H_{14}N_2.HBr.H_2O$: 6.59 per cent. H_2O; found: 6.46 per cent. H_2O.

For an estimation of bromine the salt was dried to constant weight over quicklime. It then melted at 216°-217° (same as the anhydrous hydrochloride).

0.26785 gram substance gave 0.1976 gram AgBr.

0.2309 gram substance gave 0.1700 gram AgBr.

Calculated for $C_{11}H_{14}N_2.HBr$: 31.33 per cent. Br; found: 31.39 and 31.33 per cent. Br.

A solution of the hydrobromide like that of the hydrochloride becomes yellow on standing.

Calycanthine Hydriodide.—Three grams of calycanthine were dissolved in about 30 cc. dilute sulphuric acid and an excess of a strong solution of potassium iodide added to the solution. A heavy curdy precipitate was formed which, when dissolved in hot alcohol containing some hydriodic acid, soon crystallized out in beautiful snow-white, silky needles. The hydriodide is difficultly soluble in cold water or cold alcohol but very easily soluble in hot water or hot alcohol. It seems to contain no water of crystallization as its weight becomes constant after standing only twelve hours in desiccator, over sulphuric acid. It melts at 221°-222° and assumes a yellowish tint on exposure to light.

0.3093 gram of substance gave 0.2410 per cent.AgI.

0.26325 gram of substance gave 0.2047 per cent. AgI.

Calculated for $C_{11}H_{14}N_2.HI$: 41.99 per cent. I; found: 42.10 and 42.01 per cent. I.

Calycanthine Chlorplatinate, $(C_{11}H_{14}N_2.HCl)_2.PtCl_4.H_2O$.—Two grams of calycanthine hydrochloride were dissolved in 500 cc. hot water acidulated with hydrochloric acid and a slight excess of chlorplatinic acid dissolved in a little hot water added to the hot solution. On slowly cooling the liquid, beautiful, long, thick aggregates of orange-red color separated. Dried in the air at ordinary temperature, the crystals contain 1 molecule of water of crystallization and are strongly double-refracting. The chlorplatinate commences to change color at 222° and at 237° melts with decomposition. On drying at 110° for about four hours the water of crystallization is removed. The anhydrous salt is very hygroscopic.

0.35625 gram of substance lost at 110° 0.00835 gram.

0.93113 gram of substance lost at 110° 0.02095 gram.

0.1819 gram of substance gave 0.0452 gram Pt.

0.29835 gram of substance gave 0.07435 gram Pt.

0.2463 gram of substance gave 0.27115 gram AgCl.

0.23555 gram of substance gave 0.2596 gram AgCl.

Calculated for $(C_{11}H_{14}N_2HCl)_2Pt.Cl_4.H_2O$: 2.32 per cent. H_2O; 25.12 per cent. Pt; 27.41 per cent. Cl. Found: 2.34 and 2.25 per cent. H_2O; 24.85 and 24.92 per cent. Pt; 27.22 and 27.20 per cent. Cl.

Of the several other salts which I have made, the sulphate, oxalate, nitrate and picrate crystallize in very pretty forms. The results of their examination I hope to report in my next paper.

A chloraurate was also made but concordant results could not be obtained in its analysis, owing undoubtedly to the indefinite composition of this double salt. I shall try to find conditions under which a definite gold salt can be obtained.

An acetate was made as follows: 3 grams calycanthine were dissolved in 30 cc. of acetone and then mixed with 2 grams of glacial acetic acid previously diluted with 4 cc. acetone. The solution was concentrated on a water-bath to about 10 cc., cooled and 30 cc. ether poured on the surface of the liquid. Very soon snow-white small plates commence to crystallize out. After standing over night the acetate was collected on a filter, washed with ether and dried in the air at ordinary temperature.

The acetate is extremely easily soluble in water, alcohol, and, unlike most of other salts of calycanthine, also in acetone, but almost insoluble in ether. On exposure to the light it becomes yellowish. It smells of acetic acid, which it continually gives off and has no definite melting-point, beginning to melt at 200° and becoming liquid only at 222°. This behavior of the salt indicating indefiniteness of composition, an analysis was not made.

Following is a list of color reactions which can be used for the identification of calycanthine:

1. If to a trace of calycanthine dissolved in very dilute hydrochloric acid a drop or two of a 5 per cent. gold chloride solution be added and the liquid made alkaline with sodium carbonate, a beautiful purple color is immediately produced, showing that the gold salt is quickly reduced. The value of this reaction consists in the promptness and extreme delicacy with which it occurs. While many alkaloids reduce gold salts in alkaline solution, I do not know of any other alkaloid that causes the reduction so quickly and in such extreme dilution. The reaction with calycanthine takes place with one part of calycanthine in a million parts of water.

2. Bromine water is first decolorized by a solution of calycanthine hydrochloride. If excess is added, a yellowish, flocculent precipitate is formed. If the addition of bromine water be stopped with the first appearance of a precipitate and the liquid filtered, a clear, colorless liquid is obtained which has a bluish fluorescence. If potassium hydroxide is added to this filtrate, a bulky, white precipitate is formed, which is insoluble in water and becomes gray when dried in the air.

3. Mayer's reagent gives a white, flocculent precipitate. Wagner's reagent gives a resinous precipitate. Tannic acid gives no precipitate either in neutral or acid solution. Marmé's reagent gives beautiful snow-white needles.

4. When Mandelin's reagent is put into a porcelain dish and a trace of calycanthine thrown upon the liquid, a magnificent blood-

red color is produced. After a few minutes the margin of the liquid assumes a green tint.

5. Potassium ferricyanide gives a white precipitate in concentrated solutions of calycanthine salts, but the precipitate dissolves when more water is added.

6. Potassium ferrocyanide behaves like the ferricyanide, but on heating the dilute solution of calycanthine hydrochloride to which some potassium ferrocyanide has been added, the clear liquid becomes turbid and assumes a greenish tint. After a few minutes a slimy precipitate separates out which is very difficultly soluble in water or alcohol.

7. On adding to a dilute solution of calycanthine hydrochloride a few drops of ferric chloride and then some potassium ferricyanide, Prussian blue is formed in a few minutes from the reduction of the ferri- to the ferro-salt.

8. Sulphuric acid colors calycanthine slightly yellow. If a few crystals of sugar be added to the mixture of the alkaloid with sulphuric acid, a beautiful pink color is produced.

9. Mercuric chloride gives a precipitate difficultly soluble in cold water, quite soluble in hot water, from which long, white needles separate out on cooling.

10. When calycanthine is heated to boiling for one hour with dilute hydrochloric acid the liquid soon becomes yellow, but has no odor. If the acid liquid is set aside, it becomes darker and darker. After ten days it becomes very dark red, but still has no odor. From this dark solution potassium hydroxide precipitates a yellow, flocculent precipitate insoluble in water or alkalies, extremely easily soluble in dilute acids and alcohol. The yellow substance emits a very agreeable odor when warmed with potassium hydroxide. Its solutions in acids has no odor.

11. Nitric acid brought in contact with calycanthine gives a beautiful green color.

12. Froehde's reagent colors calycanthine yellow at first, but the color becomes darker and darker on standing, until after about an hour it is almost red.

13. Picric acid gives beautiful, slender needles difficultly soluble in cold water, easily soluble in hot water.

14. Sulphuric acid and potassium dichromate gives a rose-red color.

Of the reactions here enumerated, those with nitric acid, sulphuric acid and sugar, sulphuric acid and dichromate were already observed by Eccles.

In order to test the physiological activity of calycanthine a few grams of the hydrochloride were sent to Dr. Cushny for experiments upon animals. The following is a preliminary report, which Dr. Cushny kindly sent me:

"Calycanthine hydrochloride was injected into the anterior lymph sac of a number of frogs of about 35 grams in weight. Smaller doses than 5 mg. had no definite effect; 5 mg. caused some clumsiness in movement without further change at first, but after twelve to twenty-four hours there was generally a very slight increase in the reflex irritability. The impairment of movement proved to be due to partial paralysis of the terminations of the motor nerve ends. Ten mg. induced more marked depression of the nerve ends, and after some hours this was accompanied by great increase in reflex irritability, the spinal cord appearing to be in the same condition as in strychnine poisoning, though the spasms were shorter, owing to the imperfect conduction of the impulses through the nerve ends. Fifteen mg. induced the same symptoms, but generally proved fatal to frogs of this size after one or two days.

"The drug was injected into mammals—cats and rabbits—hypodermically. Five mg. per kilogram had no distinct effect; 20 mg. per kilogram induced, after thirty to forty minutes, violent tetanic spasms, resembling those following strychnine.

"In several experiments the effect on the circulation was examined by means of the mercury manometer, when it was found that intravenous injection of 5 to 10 mg. per kilogram was followed by a marked fall in blood-pressure, with a very slow pulse and large oscillations. Atropine injection had no effect on these phenomena, so they must be ascribed to direct action on the heart. Similar changes in the heart-beat were found to follow the injection of calycanthine in the frog and turtle.

"In mammals, calycanthine seems to act as a stimulant to the spinal cord and as a depressant to the heart. In frogs it has, in addition, a weak, curare-like action on the terminations of the motor nerves. The symptoms are so similar to those described in cattle from poisoning with calycanthus that there can be no doubt that the alkaloid is the chief poisonous constituent."

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