hydroxymercuri-1-naphthoic acid, its sodium salt, sodium 3-nitro-8-hydroxymercuri-1-naphthoate, sodium 8-mercuri*bis*-3-nitro-1-naphthoate and anhydro-4-nitro-8-hydroxymercuri-1-naphthoic acid.

3. Other compounds were prepared, as follows: 3-nitro-1-naphthoic acid, its ethyl ester, its amide, 3-amino-1-naphthoic acid, its acetyl derivative, 6-nitro-1-naphthoic acid, its ethyl ester, its amide, 5-nitro-1-naphthamide.
4. Satisfactory preparative methods were developed for 3-nitro-1-naphthoic acid and 4-nitro-1-naphthoic acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

CALYCANTHINE. I. THE ISOLATION OF CALYCANTHINE FROM MERATIA PRAECOX

BY RICHARD H. F. MANSKE[1]

RECEIVED JANUARY 17, 1929 PUBLISHED JUNE 5, 1929

The first chemical investigation of the alkaloid, calycanthine, was made by Gordin.[2] He obtained it from *Calycanthus glaucus, Willd.*, and described a convenient procedure for its isolation. In later papers by the same author[3] we are informed that a second lot of seeds, presumably identical with the first, yielded only an isomeric base, namely, isocalycanthine.

Recently a contribution by Späth and Stroh[4] elucidated some obscure points in Gordin's work and established the empirical formula $C_{22}H_{28}N_4$, although the present author is of the belief that $C_{22}H_{26}N_4$ is not entirely excluded.

It was decided to subject the alkaloid to a more rigorous examination and, if possible, to elucidate the relation between calycanthine and isocalycanthine, if indeed the latter has an existence. It may be mentioned that botanists do not appear to be in complete accord in regard to the nomenclature of the various species of *Calycanthus*, but it may be taken for granted that *Calycanthus floridus L.*, and *Calycanthus fertilis, Walt.* (*C. glaucus, Willd.*) are two distinct species. From the former the author has isolated about 1.2% of an alkaloid which appears to be identical in all respects with Gordin's calycanthine and also with the base examined by Späth and Stroh.[4] No evidence of the presence of isocalycanthine has been forthcoming although other bases appear to be present in small amounts. The possibility is not excluded that Gordin's second lot of seeds in reality consisted of *C. fertilis*, whereas the first was *C. floridus*. When the former seeds become available an attempt will be made to determine this point.

[1] Holder of the Eli Lilly Company Research Fellowship at Yale University, 1927–1928–1929.

[2] Gordin, THIS JOURNAL, **27**, 144, 1418 (1905).

[3] Gordin, *ibid.*, **31**, 1305 (1909); **33**, 1626 (1911).

[4] Späth and Stroh, *Ber.*, **58**, 2131 (1925).

The author was impressed by the fact that so far calycanthine had been found only in plants native to America. Such would be a unique fact, since all other alkaloids found in American plants have been found elsewhere. The natural order *Calycanthaceae* embraces only two well-defined American and a few Asiatic species, and it was thought that an examination of Asiatic species might reveal the presence of calycanthine or a closely related alkaloid. Actually, it was found that *Meratia praecox, Rehd. and Wils.*, contained more than 2.5% of calycanthine, identical in all respects with the alkaloid from *C. floridus*. In addition, two other bases were found in minute amount.

The following description was kindly furnished by Mr. John Murray of the Marsh Botanical Garden, Yale University.

Meratia praecox, Rehd. and Wils. (order *Calycanthaceae*). Meratia species are often united with *Calycanthus*, but differ in their scaly winter-buds, the yellow flowers appearing long before the leaves on short scaly stalks from axillary buds on branches of the previous year, and in the 5 or 6 stamens. *M. praecox* is a deciduous shrub growing to a height of 3 meters. The leaves are elliptic-ovate to ovate-lanceolate, 7–15 cm. long, acuminate, bright green and lustrous above, and glabrous beneath. The flowers are about 2.5 cm. broad, very fragrant, the outer sepals yellow, the inner striped purplish-brown; fruit ellipsoid, about 4 cm. long, inclosing several dark brown seeds with a very tough and hard epicarp. Cultivated in China and Japan as an ornamental shrub, and introduced to America in 1766.

Experimental

In a preliminary extraction 50 g. of seeds was ground to a coarse powder and extracted in a Soxhlet extractor with the solvents in the order named.

Solvent	Petroleum ether	Chloroform	Methanol (abs.)	
% of extract	22.7	0.9	18.8	Total, 52.4
Alkaloid isolated	2.6			

The methanol extract was acidified with dilute hydrochloric acid, largely diluted with water, the solution basified and the precipitated alkaloid thoroughly washed with water. The portion soluble in acetone weighed 1.3 g. The petroleum ether and the chloroform extracts contained a further small amount of base.

For the purpose of obtaining the alkaloid in quantity, four kilos of seeds, ground as finely as practicable, was extracted completely with a mixture of 2 volumes of chloroform and 8 volumes of petroleum ether (40–60°). This removed all of the fat, sterols, waxes and a trace of alkaloid.[5] The residue was freed of solvent and extracted in a

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[5] The examination of the fat has yielded thus far a large amount of unsaponifiable matter, together with an unsaturated acid, presumably oleic, which on hydrogenation yielded stearic acid. It is hoped that the result of a further investigation of this extract, together with that from *C. floridus*, will form the subject of an early communication.

continuous apparatus with absolute methanol. The extract consisted of a dark colored sirupy mass, which was almost completely soluble, but for a small amount of amorphous and gelatinous material, in water made just acid with hydrochloric acid. Filtration offered some difficulty, but treatment of the warm solution with norite tended to coagulate some of the colloidal material and filtration through a layer of norite in a large funnel became possible. The dark brown though clear solution was cautiously basified, and by seeding and scraping the walls of the vessel the crude base was obtained crystalline at once. After a short time it was filtered off, washed with much water and dried. Two recrystallizations from acetone, by the cautious addition of water, yielded 70 g. of pure alkaloid, melting alone or admixed with a specimen from *C. floridus*, at 219–220°.[6] A specimen dehydrated by means of potassium carbonate in chloroform melted sharply at 245°. Admixture with a specimen similarly prepared from *C. floridus* did not depress the melting point. Comparison of crystals of the alkaloid from the two sources under the petrographic microscope failed to show any differences.

Examination of the Aqueous Filtrate from the Base.—A small portion of the aqueous alkaline filtrate was acidified with acetic acid, extracted several times with ether, to remove coloring matter, the ether removed by warming, the solution treated with phenylhydrazine and heated on a steam-bath for a short time. The voluminous crystalline precipitate of an osazone was filtered off and washed first with water and then with acetone. It was recrystallized from 95% alcohol and then consisted of the characteristic crystals of glucosazone, which alone or admixed with a genuine specimen melted at 207–208°.

Isolation of Two Other Bases.—Repeated attempts to isolate other bases by extracting the aqueous solution with immiscible solvents resulted in such a concentration of impurities that only tarry products could be obtained. The following abortive attempt to obtain crystalline water-soluble products resulted in isolating minute amounts of two other alkaloids.

The remaining basic filtrate was treated with a stream of carbon dioxide until neutral and allowed to stand for four weeks. The clear, supernatant liquid was decanted from some residue which had separated and evaporated to a thick sirup under reduced pressure. The latter was extracted once with a liter of 95% alcohol and the solution evaporated. The residue was dissolved in water and sugars were removed by fermentation with yeast. The filtered solution was clarified with basic lead acetate, excess lead was removed by a stream of hydrogen sulfide and the filtrate evaporated to a thick sirup *in vacuo*. The residue was taken up in 95% alcohol, the solution evaporated to dryness and extracted with absolute methanol. This extract was evaporated to a sirup and poured into a large volume of acetone. The acetone solution was evaporated to a thick sirup and extracted repeatedly with boiling ether. The combined ether extracts on being evaporated yielded about 0.5 g. of colorless prismatic crystals, which after one recrystallization from acetone melted at 197–198° with a slight darkening.

This base, which will be designated α-alkaloid, is sparingly soluble in ether, acetone or water, but readily soluble in dilute acids. The absence of phenolic hydroxyl groups is proved by the insolubility in alkali. A test for nitrogen was strongly positive. With Ehrlich's reagent it gives a beautiful red color, and on heating in a glass tube to a high temperature the odor of indoles becomes apparent.

The mother liquor from the α-alkaloid, from which no more of this base could be obtained, was converted to the hydrochloride and evaporated to a thick sirup. This was extracted several times with boiling chloroform and the extract evaporated. The residue was triturated with a little acetone and then readily crystallized to a magma of microscopic needles. This was filtered off, washed with acetone and recrystallized by

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[6] Melting points are corrected.

adding acetone to a concentrated alcoholic solution. As thus obtained the hydrochloride melts at 219–220°. Calycanthine hydrochloride melts at 217°, but a mixture of the two began to sinter at 205° and melted completely at 208°. The free base, which will be designated β-alkaloid, was only obtained as a colorless oil, readily soluble in ether. Seeding with α-alkaloid did not induce crystallization. This base also gives a red color with Ehrlich's reagent.

Isolation of Xylose from the Epicarp of the Seeds.—The residue after thorough extraction consisted of the inner fleshy portion of the seed together with the still tough and dark brown epicarp in large flat pieces. By virtue of a difference in density, the two parts could be easily separated by a process of flotation with water, the epicarp sinking. When most of the fleshy portions had been removed by this means, the residue of hulls was hydrolyzed with 2% boiling sulfuric acid for three hours, neutralized with calcium carbonate, filtered, the solution evaporated to a thick sirup *in vacuo* and the latter extracted once with a large volume of absolute methanol. The extract, on evaporation, yielded about 6% of almost colorless crystals which, after two recrystallizations, melted at 150° alone or admixed with a genuine specimen of *l*-xylose. It may here be mentioned that the epicarp from *C. floridus* under similar treatment yielded the same sugar in approximately the same amount.

Summary

1. The alkaloid, calycanthine, has been isolated from *Meratia praecox, Rehd. and Wils.*, a shrub native to Asia. Its identity with the alkaloid from *Calycanthus floridus, L.*, has been established.
2. Two other alkaloids were isolated in small amounts, but the investigation of these is delayed until more material is available.
3. The existence of glucose, or a sugar which gives glycosazone, in the seeds has been shown.
4. Xylose was isolated from the epicarp of the seeds by hydrolysis with dilute sulfuric acid.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

CHARACTERISTICS OF THE NON-EXPLOSIVE OXIDATION OF PROPANE AND THE BUTANES[1]

BY ROBERT N. PEASE[2]

RECEIVED JANUARY 21, 1929 PUBLISHED JUNE 5, 1929

The reactions between hydrocarbon vapors and oxygen are of interest for a number of different reasons. Information as to their nature is of

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[1] This paper contains results obtained in an investigation on "Catalytic Methods Applied to Petroleum Hydrocarbons" listed as Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor of Princeton University is Director of Project No. 7.

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