

SCIENTIFIC SECTION

THE ALKALOIDS OF BOCCONIA FRUTESCENS L.

BY EMERSON R. MILLER.

The genus *Bocconia*, belonging in the *Papaveraceæ* or Poppy family, furnishes plants of much interest because of their beautiful foliage; they are, however, of especial interest to the plant chemist on account of their alkaloidal content.



Bocconia Frutescens, L.

Plants of the species *Bocconia frutescens* grow in Tropical America, the Caribbean Islands, Cuba, Mexico to Peru.

By Grisebach¹ they are described as suffruticose herbs with petiolate, oval oblong, sinuate pinnatifid leaves, the uppermost ones sometimes not divided. The leaves are large, particularly those of young plants, being six inches or more wide and twelve to eighteen inches long. The stems are from three to ten feet high with the flowers in pyramidal panicles, often a foot or more in length.

The beginning of chemical work on *Bocconia* may be said to have been made in 1881 by Ernesto Ochoa y Tapia² who examined the bark of *Bocconia frutescens* and reported indications of alkaloids, though no base was identified.

In 1884, Eijkman³ made a chemical study of the roots of *Bocconia cordata*, called by him *Macleya cordata*. He extracted sanguinarine and another

alkaloid which he called *macleiyne*, now thought to be identical with *protopine*.

In 1891 Rusby⁴ described several species of *Bocconia* growing in South America and published illustrations of *Bocconia cordata*, *Bocconia frutescens* and *Bocconia arborea*.

In 1892, J. M. Lasso de Vega⁵ reported upon the constituents of the bark of *Bocconia frutescens*. In addition to the more common constituents such as coloring matters, oil, resin and extractive he reported finding a glucoside and, apparently, two alkaloids, one yielding red crystalline salts and the other giving white salts. The former he called *bocconine*, but did not really identify any alkaloid.

¹ Flora of the "British West Indian Islands" (1864), 13.

² *Estudio sobre la Corteza del Bocconia frutescens* (1881).

³ *Rec. trav. chim.*, 3 (1884), 182.

⁴ *Bulletin of Pharmacy* (August 1891).

⁵ *Gaceta Medica de Mexico*, Tom, 28 (1892), 367-373.

According to Murrill and Schlotterbeck¹ bocconine is most probably identical with β -homochelidonine, which forms colorless salts. The red crystals were, no doubt, *sanguinarine* salts.

In 1895, J. A. Battandier,² using the bark of a large specimen of *Bocconia frutescens*, separated a mixture of alkaloids in which he identified *fumarine*, *bocconine*, a third alkaloid giving reactions very similar to those of *chelidonine* and lastly, much *chelerythrine*. *Fumarine* is now considered to be identical with *protopine*.

In 1898, Hopfgartner³ examined the stems and leaves of *Bocconia cordata* (called by him *Macleya cordata*) for alkaloids and separated *protopine* and β -*homochelidonine* but found no *sanguinarine*.

In 1900, Murrill and Schlotterbeck⁴ investigated *Bocconia cordata*, using mainly the root. They separated *protopine*, β -*homochelidonine*, *chelerythrine* and *sanguinarine*.

EXPERIMENTAL.

While connected with the Cuban Experiment Station the writer, through the kindness of the late Dean Charles Fuller Baker, was able to obtain a quantity of material from both the old and young plants of this species. The largest specimen observed was ten or twelve feet high with a decidedly woody stem three to four inches in diameter. The inner bark has a very acrid taste and varies in color from deep red to pale yellow.

An examination of the bark of the large plants showed that it is rich in alkaloids and also contains a considerable amount of a reddish brown resin.

Greater interest, however, attached to the leaves both because of their size and also because they had not been the subject of a chemical investigation.

The dried powdered leaves were extracted mainly by means of hot 95% alcohol, the alcohol in greater part distilled off and the residue mixed with acidulated water, the filtrate made alkaline with ammonia water and the precipitated alkaloids shaken out with ether. It was found that the mass of amorphous bases was readily soluble in ether, but soon separated from it in crystalline condition.

The ammoniacal liquid was shaken out by chloroform and the resulting bases repeatedly crystallized from alcohol and a mixture of alcohol and acetic ether.

From the crystalline mass there were separated, mechanically, long prismatic crystals which melted at 168–169° C. A small amount of this material was obtained and subjected to elementary analysis.

1.—0.1745 Gm. of material yielded 0.0964 Gm. of H₂O and 0.4352 Gm. of CO₂, corresponding to 6.13% H and 68.01% C.

2.—0.2023 Gm. of material gave 0.1182 Gm. of H₂O and 0.5036 Gm. of CO₂, corresponding to 6.49% H and 67.90% C.

3.—0.0990 Gm. of the platinic chloride double salt yielded by ignition 0.0161 Gm. metallic platinum, corresponding to 16.26% platinum.

¹ PROCEEDINGS A. PH. A., 48 (1900), 132.

² *Compt. rend.*, 120 (1895), 1276.

³ *Monatshefte für Chemie*, 19 (1898), 179.

⁴ PROCEEDINGS A. PH. A., 48 (1900), 128.

The formula $C_{21}H_{23}NO_5$ requires C = 68.292%; H = 6.23%.

The formula $(C_{21}H_{23}NO_5 \cdot HCl)_2PtCl_4$ requires Pt = 17.00%.

From these data it is concluded that the base in question is γ -*homochelidonine*.

A few crystals were also separated mechanically which began to soften at 155° C. and were completely melted at 159–160° C. Although no analytical data were obtained the melting point shows that these crystals consisted of β -*homochelidonine*.

By repeatedly converting the larger part of the total alkaloids into hydrochloride and fractionating, then converting into free base, followed by repeated fractional crystallization from alcohol or a mixture of alcohol and acetic ether there was obtained a base which was white in the free state and also formed white salts. The melting point of the free base was 206–207° C.

An elementary analysis of this base gave the following results:

0.1731 Gm. of substance yielded 0.0925 Gm. of H_2O and 0.4292 Gm. of CO_2 , corresponding to 5.93% H and 67.6% C. The formula $C_{20}H_{19}O_6N$ requires C = 67.98%; H = 5.38%.

These results show that the base in question is *protopine*.

Circumstances made it impossible to investigate these interesting alkaloids further, but the fact that there was present a considerable amount of a base which in the free state is white but which forms pale yellow salts is perhaps sufficient evidence to justify the conclusion that *chelerythrine* is also present.

SUMMARY.

The leaves of *Bocconia frutescens* L. contain at least four alkaloids. By elementary analysis and melting point determination two of these were identified as γ -*homochelidonine* and *protopine*, respectively.

A third one agrees in melting point with β -*homochelidonine*. Judging from the color (white) of the free base and the yellow color of its salts a fourth one is believed to be *chelerythrine*.

On account of the size of the leaves and their high alkaloidal content this plant is probably the best known source of *protopine*.

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AMMONIUM ACETYL SALICYLATE "AMMON-ASPIRIN"



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In order to produce a new chemical for the drug trade that would give simultaneously the physiological effects of commercial Aspirin and Aromatic Spirit of Ammonia, work was begun on the preparation of the ammonium salt of aspirin, namely, ammonium acetyl salicylate. Commercial aspirin, it should be recalled, is acetyl salicylate. This new chemical, will when taken internally in five-grain

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