but was identified by transformation into the acid barium salt which crystallized in the warty aggregates already described, and by the preparation and analysis of the acid aniline salt.

ANILINE SALT.—Like Palmer, we found it difficult to prepare a homogeneous amide of *m*-sulfocinnamic acid, but one of us[5] had already pointed out that it is frequently more convenient to characterize sulfonic acids by their salts with organic bases. This proved to be the case here. A solution of the crude acid in 5 times its weight of water was mixed with its own weight of aniline sulfate in suspension. The mixture solidified at once. It was warmed until solution was complete and then cooled. The product obtained was dried and crystallized 4 times from a mixture of alcohol and ether, from which it separated in lustrous needles melting at 238° with evolution of gas.

*Analyses:* Subs., 0.4123: 15.2 cc. N, (20°, 744 mm.). Subs., 0.1603, 0.1574: $BaSO_4$, 0.1174, 0.1153. Calc. for $C_{15}H_{15}O_5NS$: N, 4.36; S, 9.97. Found: N, 4.28; S, 10.00, 10.06.

The identity of this compound with the acid aniline salt of the acid formed by sulfonating cinnamic acid was established by preparing the salt from that source for comparison. It was found to contain 4.26% of nitrogen and melted at 238°. A mixture of the 2 samples melted at the same temperature.

A *p*-toluidine salt of the acid made by sulfonation was also prepared. It was more difficult to purify and was not analyzed. It melted at 229–230° with gas evolution.

## Summary.

1. The secondary product formed in the sulfonation of cinnamic acid is *m*-sulfocinnamic acid. It is identical with that already obtained from *m*-sulfobenzaldehyde by the Perkin synthesis.

2. The *ortho* acid is therefore still unknown. Attempts are in progress to prepare it, and to make a comparative study of the three.

3. Another case has been found which illustrates the convenience of characterizing sulfonic acids by their salts with organic bases.

CAMBRIDGE 39, MASSACHUSETTS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW YORK STATE HOSPITALS.]

# IDENTIFICATION OF ALKALOIDS UNDER THE MICROSCOPE FROM THE FORM OF THEIR PICRATE CRYSTALS.

BY BURT E. NELSON AND HELEN A. LEONARD.

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No satisfactory systematic scheme for the qualitative identification of all the common vegetable alkaloids is known, and while certain partial schemes serve fairly well for particular groups, they frequently do so only in the known absence of others. Moreover, many of these schemes and in fact the classical methods for identifying organic compounds generally, are quite frequently inapplicable because of the small amount of material available, particularly in the analyses of certain medicines and in forensic cases. The well-known color reactions, often interpreted largely by a

process of exclusion, while applicable to small portions of residues, have the disadvantage of destroying the material for further tests.

Micro-chemical and micro-crystallographic methods (the latter including determinations of refractive indices) have here the distinct advantages of utilizing only a small amount of material, and often of leaving the alkaloid in a combination suitable directly for melting-point determinations and from which it may be again obtained in free form for color reactions, pharmacological tests, etc.

Among the compounds utilized most frequently for micro-chemical identification of alkaloids the picrates have long been popular, although in many instances the picrolonates serve better. Other commonly used double compounds are those with gold and platinum chlorides, iodopotassic, iodomercuric, bismuthic and cadmic iodides, etc.

In using these compounds we have felt the need of a convenient reference chart for quickly classifying into crystal groups and arriving at the probable base or bases present from the form or "habit" of the crystals, or at any rate for determining the base to be probably one of a few, before proceeding to further crystallographic or chemical tests for the final identification. For this preliminary comparison it is obviously necessary to use the same derivative of the alkaloids, and for our own use the picrates were chosen because they can as a rule be conveniently precipitated directly from many mixtures and because their forms are usually quite diverse and characteristic. For the further confirmatory tests, however, they are less suitable than the common acid salts and some double compounds, because their high refractive indices preclude the possibility of determining these values by the immersion method with any of the liquids now used.

The figures in the accompanying chart, however, have to do only with the form or habit of the crystals, and this we have found to be constant after following the procedure given below. Thus far we have not found that the presence of another alkaloid offers serious interference. The chart has, in fact, in many cases been useful even without subsequent confirmatory optical tests, although naturally these should be made.

All of the alkaloids studied met the pharmacopeial requirements. Aconitine was of the amorphous active variety. Caffein and theobromine among the purin bodies, and free picric acid, are included for comparison, in the drawings.

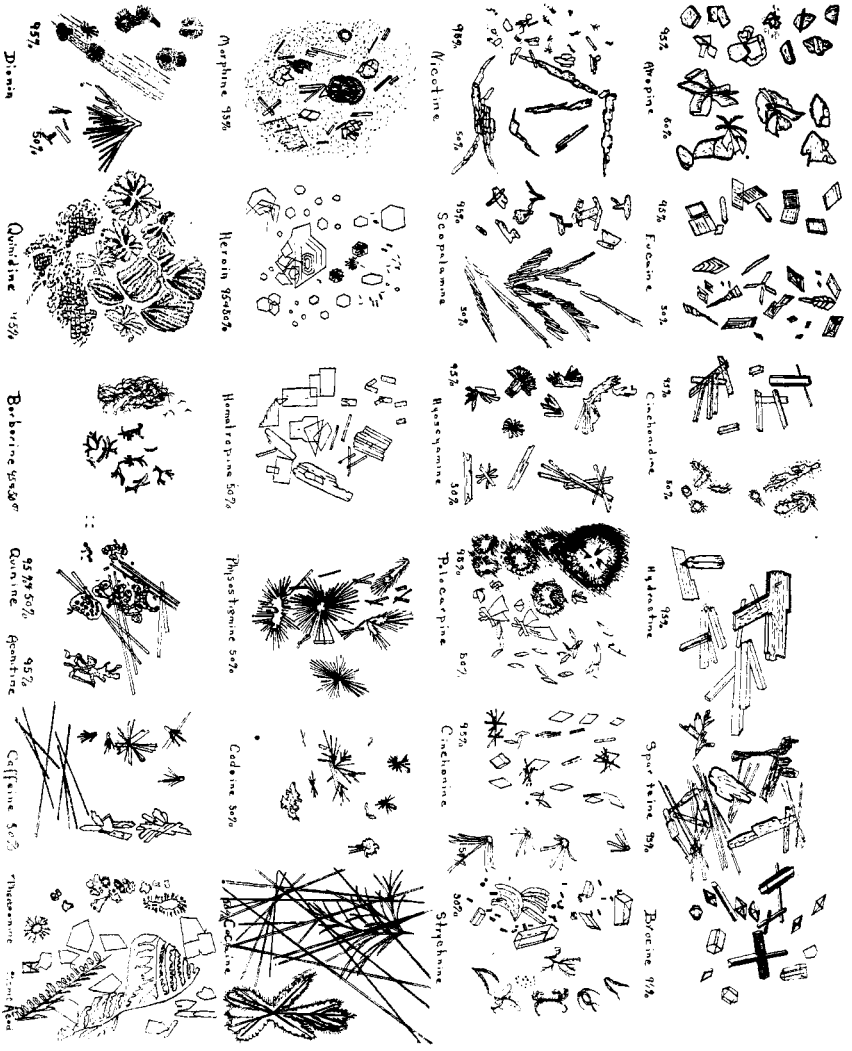
In using the form or habit of the picrate crystals for this preliminary identification, it must not be forgotten that except when obtained under identical physical conditions form is not a fixed and unchanging physical property. Among the conditions influencing the form may be mentioned temperature, concentration and purity of the solution crystallized, and the rate of crystallization. Even the presence of traces of grease on the micro-

scope slides will often affect the result. Where crystallization occurs from too dilute a solution or over too large a cell area, "starved" or skeleton crystals are apt to form in feathery or fern-like dendritic masses.

For the above reasons uniform methods of procedure must be followed, and after the first examination it is well to repeat the crystallization and to compare with a known standard similarly treated to insure constant results.

## Method.

The aqueous solution (fairly concentrated in a few cases) of the separated alkaloid, slightly acidified with hydrochloric acid, is precipitated in a



small test-tube with a slight excess of saturated solution of picric acid and the precipitate deposited and slightly washed in a centrifuge. The picrates are now dissolved in a corked test-tube in the smallest practical volume of warm 95% alcohol, the tube being held in a warm water-bath. The solution is next allowed to cool somewhat slowly with the bath, when crystals will usually form. Further strong cooling will increase the yield. The crystals are now deposited firmly in the centrifuge and the supernatant fluid decanted as completely as possible into a second small test-tube. By means of a curved, pointed glass rod the crystals are now transferred, together with any adherent mother liquor to a paraffin-ringed cell on a glass microscope slide. This cell is conveniently made by touching the warmed smooth-cut end of a thin metal tube, first to a solid block of paraffin and then squarely against the glass. An equal volume of water is next added to the remaining alcoholic solution in the second tube, previously concentrated if necessary, so that on adding to the remaining crystals in the first tube the former are again dissolved completely only on warming, and a second lot of crystals obtained as above with this 50% alcoholic solution. The whole operation will not, as a rule, require more than 10 or 15 minutes.

In this manner we obtain 2 separate cells of crystals, from one or both of which characteristic forms will usually be obtained. These are to be compared with the figures and the known sample similarly treated.

Direct addition of the reagent to an acidified drop of solution on the microscope slide has not furnished as reliable results with us.

For this tentative identification of the crystals thus formed only an ordinary microscope is, of course, required, but for optical crystallographic measurements, which are nearly as applicable to powder fragments as to entire crystals, a good petrographic or chemical microscope is essential. As the present article does not consider the methods of optical crystallography or chemical microscopy, the beginner is referred to standard texts,[1] although we hope to present the crystallographic data later.

In the mean time this preliminary but tentative identification by means of the chart will, we trust, be convenient.

[1] Parker, "Some Microchemical tests for Alkaloids," J. B. Lippincott Co. Chamot, "Elementary Chemical Microscopy," John Wiley and Sons Co. Luquer, "Minerals in Rock Sections," John Wiley and Sons Co. McCoughey and Fry, "The Microscopic Determination of Soil Forming Minerals," *Bull.*, **91**, U. S. Dept. Agriculture. Wherry, "The Application of Optical Methods of Identification to Alkaloids and Other Organic Compounds," *Bull.*, **679**, U. S. Dept. Agriculture. Groth, "Elemente der physikalischen und chemischen Krystallographie," R. Oldenbourg, Berlin. Wright, The Petrographic Microscope in Analysis, THIS JOURNAL, **38**, 1647 (1916). Wormley, "Microchemistry of Poisons," J. B. Lippincott Co. Behrens, "Anleitung zur mikrochemischen Analyse," Wherry and Yanovsky, The Identification of The Cinchona Alkaloids by Optical-Crystallographic Methods, THIS JOURNAL, **40**, 1063 (1918).

## Summary.

We believe that the more commonly occurring vegetable alkaloids may be tentatively identified under the microscope by the form or habit of their picrate crystals prepared under standard conditions. We hope to consider the optical properties of other of their compounds later.

BINGHAMTON, NEW YORK.

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[COMMUNICATION NO. 131 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY.]

# THE DRYING AND SWELLING OF GELATIN. PRELIMINARY NOTE.[1]

BY S. E. SHEPPARD AND F. A. ELLIOTT.

Received October 27, 1921.

The following notes, or more accurately notes and queries, are concerned principally with the influence of the earlier phases of a dehydration-hydration cycle in gelatin jellies on later phases of the cycle. The view that the influence of the history of a gelatin gel on its swelling after drying is explicable in terms of an internal supermolecular structure has been recently clearly expressed by L. Meunier. In a review of recent work "On the Properties of Gelatin"[2] he states "We have already mentioned that according to Hardy's conception, the solid phase of a gelatin jelly has a structure related to its concentration; the cells of the lattice would be open in the case of the less concentrated jellies, and closed in the case of the more concentrated. Admitting this hypothesis, it may be conceived that the absorbing power for water of thin sheets of gelatin will be in relation to the concentrations of the solutions from which they are prepared. If we prepare from the same gelatin two solutions, one at 6%, the other at 20%, and coat thin sheets of gelatin from these on glass, dry at low temperature, the leaves prepared from the diluted solution will absorb more water and will swell more, for equal weight [of gelatin] and time, than the sheets prepared from the concentrated solution."

Similar experiments are recorded by H. R. Procter[3] and by W. D. Bancroft[4] and have been confirmed in this Laboratory. There remains the question as to whether they are due to internal structure, as suggested, or whether a more obvious cause exists.

## The Drying of Gelatin Jellies.

Gelatin jellies, of given definite geometrical shape and water content, might be supposed to dry in such a way that the shape would remain un-

[1] Paper read at the Spring Meeting of the American Chemical Society, Rochester, N. Y., April, 1921.

[2] Meunier, *Chimie et industrie*, **5**, (T.) 220 (1921).

[3] Procter, *J. Chem. Soc.*, **105**, 313 (1914).

[4] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., **1921**, p. 251.