of tellurium by means of the hydroxylamine precipitation it seems quite proper that I should continue it, notwithstanding the fact that Prof. Jannasch, of the University of Heidelberg, announced in the *Berichte* for October, 1898, that he is engaged in work on the same line.

THE ASSAY OF NUX VOMICA.[1]

BY EDWARD R. SQUIBB.

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IN the preparation of a paper on acetic acid as a substitute for ethyl alcohol in extracting the active principles of some officinal drugs, it became necessary to have a convenient and moderately accurate method of assaying nux vomica. The whole of this paper would interest very few members of the American Chemical Society, and such as it would interest may find it in the *American Journal of Pharmacy* for January, 1899. But the assay process that ends the paper may be far enough within the line of interest to this society to warrant the writer in offering it here.

The short and easy methods of Messrs. Dunstan and Short, given in the *British Pharm. Journ. and Trans.*, 3d Series, **13**, 665–1055, and **14**, 621, and given in the British Pharmacopœia, were found objectionable on some accounts, but chiefly because the results are too high. For example, a table is given on p. 1055, wherein from seven samples the percentage of total alkaloids ranged from 3.04 to 3.90 per cent. with an average of 3.29 per cent. This, in the writer's experience, is much too high, and there is a probability that the plus error may be due to weighing the chloroform extract as alkaloid. The most recent authority noticed is the new, 1898, British Pharmacopœia, but its method is liable to the same objection of weighing a chloroform extract as alkaloid. The U. S. Pharmacopœia of 1890 has an excellent method that avoids this source of error by titrating the alkaloids. This method[2] first makes a dry extract and then assays that for use in its standardized preparations.

Two grams of the dry extract are dissolved by shaking in a separator with twenty cc. of a previously-made mixture of two

[1] Read at the New York meeting of the American Chemical Society, December 28, 1898.

[2] U. S. Pharmacopœia (*1890*), pp. 152 *et seq.*

volumes of alcohol (ninety-one per cent.), one volume of ammonium hydroxide (ten per cent.), and one volume of water. Then twenty cc. of chloroform (ninety-nine per cent.) is added and the mixture is agitated during five minutes. The chloroform is then allowed to separate and is drawn off as far as possible by the stop-cock. This washing out is repeated with two further portions of chloroform of fifteen cc. each. The chloroform solutions are then collected in a beaker and exposed on a water-bath until the chloroform and ammonia are completely dissipated.

Then ten cc. of decinormal sulphuric acid is added, stirred, diluted with twenty cc. of hot water, and when solution is complete two cc. of brazilwood indicator is added. Centinormal potassium hydroxide is added until a permanent pinkish color is produced. The number of cubic centimeters of potassium hydroxide required is divided by 10, the number found is subtracted from 10, and the remainder is multiplied by 0.0364, and that product by 50, which will give the percentage of total alkaloids in the two grams of extract taken, it being assumed that strychnine and brucine are present in equal proportion, and the above factor being found by taking the mean of their respective molecular weights ($334 + 394 \div 2 = 364$).

This very well-designed method was found impracticable in the writer's hands, through difficulty in carrying out the details. The first obstruction encountered was the very nearly constant emulsifying of the chloroform and the consequent refusal of the liquids to separate on standing, and the difficulty and loss of time in managing an emulsion once formed. The U. S. Pharmacopœia directs the immiscible liquids to be "agitated," not shaken; yet if shaking be avoided and the agitation be ever so cautiously managed, some emulsion seems unavoidable, whilst a degree and kind of agitation that is short of shaking washes out the alkaloids imperfectly. Emulsions that did form were best managed by running them out into a capsule, driving off the chloroform on a water-bath, returning the dark liquid to the separator, and managing the next chloroform with greater care. But a better expedient was found in a recommendation of A. H. Allen and others, to use a mixture of equal volumes of chloroform (ninety-nine per cent.) and ether (ninety-six per cent.(. With this mixture, used in large quantity, vigorous shaking and

consequent effective washing may be employed with little emulsion, if any, at the last of the washings, the separations being very prompt and sharp, usually ready to draw off within half an hour after shaking. The clear chloroform and ether solutions are better managed if drawn off into and boiled off from a flask, as the dissolving, the heating up, and the titration are more easily done in a flask. The solution to be titrated is always of a full yellow color, from a bright pale yellow to a deep yellow, with a reddish tint by reflected light; a color in which the first increase of pinkish tint is difficult to detect, and the want of sharpness and decision in this end-reaction is the persisting difficulty with all methods of titration that were tried, but in comparing indicators brazilwood was found to be inferior to logwood. A decinormal potassium hydroxide is preferable to centinormal, as it does not dilute the solution of alkaloids so much, while in accuracy of reading it is far within the limit of error of the indicator.

Chiefly in consideration of these conditions the following method was reached and used:

A fair sample of nux vomica is drawn and an average dozen or so of the seed is so milled as to pass through a No. 9 sieve. Of this ten grams are weighed off and exhausted with ten per cent. acetic acid. This exhaustion is easily and conveniently done in a Soxhlet apparatus, but so large an amount of extractive is washed out by the warm acid, that the extract is very difficult to dry, and afterwards at once forms an emulsion that is difficult and tedious to manage. Cold percolation to complete exhaustion gives a much better result, and is not difficult to effect, provided the powder be moistened for packing with not more than ten cc. of the acetic acid, and be not packed too tightly.

The percolate is evaporated to dryness on a water-bath, in a large (twelve cm.) flat-bottomed capsule, so that the extract is in a thin layer, easy to dry and easy to dissolve. The weight gives the yield of extract.

If a fluid extract or tincture is to be assayed, it is measured, weighed, and dried in the same way.

A mixture is made of two volumes of alcohol (ninety-one per cent.), one volume of ammonium hydroxide (ten per cent.), and one volume of water, and of this, ten cc. are poured upon the dry

extract in the capsule. Then by patiently moving a stirrer over the smooth surface of the dry extract for a quarter of an hour or more, a smooth solution of the extract, easy to wash, is obtained. This is poured into a separator of 150 cc. capacity, and the capsule and stirrer are rinsed clean with ten cc. more of the alcohol and ammonia solution.

A mixture is made of equal volumes of chloroform (ninety-nine per cent.) and ether (ninety-six per cent.), and forty cc. of this is added to the liquid in the separator; the whole is shaken vigorously during five minutes, and then allowed to separate. In twenty to thirty minutes the separation will be complete to a sharp line, when the depth of the upper, dark stratum should be observed and measured. The chloroform-ether solution is then drawn off into a tared flask of about 100 cc. capacity, and the flask is immersed in a hot water-bath so that the chloroform-ether may be boiled off by the time another washing is ready. In the meantime forty cc. more of chloroform-ether have been added to the contents of the separator, and the shaking, separating, and drawing off into the flask repeated. This second washing may or may not be then followed by a third, managed in the same way, if required.

If after standing, to separate completely a second time, the dark liquid on top shall be found to have increased in depth, the indication is that emulsion has been formed to that extent, and that the chloroform forming that emulsion holds the proportion of alkaloids present in solution at the time that emulsion was formed, and as the chloroform cannot be washed out of an emulsion, so the alkaloids held by that chloroform cannot be washed out. Therefore, in the case of any considerable amount of emulsion after the chloroform-ether solution is drawn off into the flask, the dark liquid is drawn off into the flat capsule and warmed on a water-bath until all the chloroform-ether is driven off. The dark liquid is then returned to the separator and again washed as before. If a small amount of emulsion again forms, as very rarely occurs, the chloroform in it holds so very little alkaloid as to be within the limit of error of the method.

The tared flask will then contain the total chloroform extract, and the weight of this was long erroneously accepted as the weight of alkaloids.

Ten cc. of decinormal sulphuric acid are now carefully measured from a burette into the flask, which is rinsed round and warmed by immersion in a water-bath until the soluble alkaloids are dissolved, when the insoluble residue will show how much of this extract is not alkaloid.

Twenty cc. of hot water are added to the contents of the flask, and a definite quantity (ten drops) of logwood indicator. The color is then closely observed by transmitted light, and matched by a similar quantity of liquid in a similar flask. Decinormal potassium hydroxide is now dropped in from a burette until the color changes slightly to a pinkish tint or shade of the original yellow by transmitted light, and when this hardly perceptible change is now looked at by reflected light the pink tint is very distinct.

The number of cubic centimeters required subtracted from 10 (cubic centimeters of acid used) gives the number of cubic centimeters of acid saturated by alkaloids, and this number multiplied by the mean of the molecular weights of the two alkaloids ($0.0334 + 0.0394 \div 2 = 0.0364$), gives the amount of alkaloids obtained from ten grams of nux vomica, the strychnine and brucine being assumed to be present in equal proportions.

Then as 10 is to the product from 10, so is 100 to the percentage of the mixed alkaloids.

DETECTION OF CARAMEL IN SPIRITS AND VINEGAR.

BY C. A. CRAMPTON AND F. D. SIMONS.

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HAVING had frequent occasion to determine the question as to whether a sample of spirits was colored with artificial coloring-matter or owed its color to a long age in wooden packages, one of us has for a long time endeavored to obtain some reliable test by which the presence of caramel could be definitely proved. The principal methods given in the books are (1) the reducing action of caramel on Fehling's solution, and (2) the precipitation of the coloring-matter by paraldehyde. Neither of these methods has given satisfactory results in our hands. Spirits extract from oak wood, especially when charred, substances which have nearly, if not quite, as high a reducing power on Fehling's solution as caramel. The test with paralde-