MINISTRY OF AGRICULTURE, EGYPT.

TECHNICAL AND SCIENTIFIC SERVICE.

Bulletin No. 3.

(CHEMICAL SECTION.)

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ALKALOIDS OF SOME EGYPTIAN SOLANACEÆ,

BY

FRANK HUGHES, F.C.S.,

CHEMIST TO THE MINISTRY OF AGRICULTURE.

Bulletin for printing on January 15, 1916.

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NOTE ON THE ALKALOIDS OF SOME EGYPTIAN SOLANACEÆ,

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The large and widely distributed natural order of the *Solanaceæ* includes, as is well known, many most important food-plants ; one needs only mention the Potato, Tomato, and Egg Plant. In addition to these, however, we find that some of the closely related species are among the most poisonous plants known, and even some of the food-plants themselves sometimes contain poisonous substances in those portions of the plant which are not generally used as food.

The genus *Solanum* contains several poisonous plants, but it is in the genera *Atropa*, *Datura*, *Hyoscyamus*, and *Scopolia* that we find the plants which are of the greatest importance in medicine. It is true that some other genera contain alkaloidal substances, but they have not such marked properties as those of the plants above mentioned and find but little application as drugs.

The well known drug belladonna is obtained as an extract from the plant *Atropa belladonna*. The alkaloid in this case is almost pure hyoscyamine, with sometimes a small amount of atropine. It may here be pointed out that these two substances have the same chemical composition and appear to be isomeric. Hyoscyamine can readily be converted into atropine, though the reverse process is not at present possible. Hyoscyamine is optically active, rotating the plane of polarization to the left, while atropine is optically inactive. The constitution of these bodies has been carefully studied and in some cases their synthesis has been effected. The two alkaloids above mentioned, together with a third, scopolamine, form a distinct class. Their properties are in many ways similar. They all possess a strong mydriatic action, *i.e.* even in dilute solution they possess the property, when applied to the eye, of causing the dilatation of the pupil. This effect occurs a few minutes after the application and remains for a

period depending on the quantity of alkaloid employed. As illustrating the powerful nature of these alkaloids it may be mentioned that $\frac{1}{4000}$ grain of hyoscyamine is capable of causing dilatation of the iris in the rabbit. This property is frequently employed for the detection of traces of these alkaloids.

Among plants of this order which are to be met with in Egypt various species of *Datura* and the common henbane are the most important. Many of the cultivated species of *Datura* contain alkaloids, but only *D. stramonium* is used as a material for the preparation of drugs. Egyptian henbane, on the other hand, contains a large amount of alkaloid and is a most useful material for the preparation of pharmaceutical extracts or of pure alkaloid. This plant, which is to be found in almost all parts of the country, both on cultivated land and also in the desert, contains quite a large proportion of the active substance. The leaves, stem and seeds all contain hyoscyamine, while even the oil expressed from the seeds is stated by some to contain traces of alkaloid. The oil of *Hyoscyamus* is officinal in many continental pharmacopœias, but not in the British.

It is a noteworthy fact that *H. muticus* grown in Egypt contains far more alkaloid than the same species grown in India. Dunstan and Brown,* who some years ago examined the plants from both countries, pointed this out in the "Journal of the Chemical Society" and showed the great value of the Egyptian plant. Curiously enough, however, no notice seems to have been taken of these reports, and British manufacturers of drugs continued to use the English and continental henbane (*H. niger* and *H. albus*), which plants contain a very much smaller proportion of alkaloid.

Henry, in "The Plant Alkaloids," gives a table showing the amounts of alkaloid found in the various plants. As might be expected, the amount of alkaloid found varies considerably even in the same species; this variation may be partly due to climatic conditions or to soil, but is also in great measure dependent on the fact that the plants examined have not all been collected at the same stage in their growth. That this is a matter of great importance is well shown by a table quoted by Winter Blyth in his work on poisons. From this it would appear that the English and continental species of *Hyoscyamus* contain

* J.C.S., 1899, LXXV, 71; 1901, LXXIX, 72.

the largest proportion of alkaloid at or just before the time of flowering. When the fruit is ripened and the plant commences to dry, the whole plant shows a much smaller proportion of active substance. This seems also to be the case with the Egyptian plant. Dunstan gives the alkaloidal content of the leaves as reaching 1·4 per cent, but I have found as much as two per cent in the dry matter of the green leaves collected at the time of flowering. There are, however, difficulties in dealing with the fresh plant at this stage of its growth owing to the large water content. The plant, when growing in well watered soil, may at the time of flowering contain as much as ninety-five per cent of water. This makes the process of drying difficult and tedious. Artificial drying at this stage is impossible, as the plant becomes converted into a mere pulp. Besides this, to heat the plant while it contains a large quantity of water would be fatal, as the whole of the alkaloid would be destroyed. The plant must be dried slowly in the sun, with frequent turning until the moisture is reduced to at most twenty per cent; after this stage is reached a gentle heat may be applied and the plant thoroughly dried, so that it may be readily ground.

An attempt was made to obtain the alkaloid by expressing the juice from the fresh plant. The presence of the alkaloid could readily be detected in the fresh juice and a quantity of a litre or so was evaporated in a partial vacuum (100 mm. Hg.); no trace of alkaloid could be detected in the concentrated liquor. The whole of the alkaloid appeared to have been hydrolysed and converted into tropic acid, a substance of no value.

The usual method of obtaining the alkaloid from these plants is to extract the dry and finely ground material with cold alcohol. If this is done by percolation a great quantity of alcohol is necessary, and it is therefore better to adopt some method of continuous extraction. The only obstacle to the employment of the extraction method is that the process must be carried out at reduced pressure. If this is done, the alcohol will boil at a temperature of about 50° C. To obtain such a reduction in the boiling point it is necessary that the pressure in the apparatus should not exceed 200 millimetres of mercury. It is of interest to note that in the course of extraction a considerable amount of potassium chloride is dissolved out by the alcohol, and unless this is occasionally removed from the boiler serious " bumping "

may occur. When extraction is complete the alcoholic solution is evaporated to pasty consistency and repeatedly extracted with dilute acid and finally water. The aqueous extracts are separated by filtration from any tarry matters and are then extracted while still acid with chloroform and ether until no more colouring matter is removed. The liquor is then made slightly alkaline with ammonia and again repeatedly extracted with chloroform until the extracts show only traces of alkaloid. For the purpose of testing the extracts for the alkaloid Mayer's solution will be found convenient. The chloroform solution is now dried with calcium chloride, and if necessary filtered and evaporated to dryness, preferably under reduced pressure, though now that water is absent this is of much less consequence than in the other stages of the extraction process. When most of the chloroform is evaporated the liquid becomes very viscous, and if left to cool frequently crystallizes in very characteristic spherical tufts of exceedingly fine needles. Before purification the crude alkaloid is generally of a brownish colour, and when prepared in quantity the crystalline mass obtained strongly resembles the mineral crocidolite in appearance. In order to obtain the alkaloid in a pure state it is necessary to recrystallize it a time or two from a mixture of benzene and petroleum spirit. In the latter of these liquids it is quite insoluble, so that a suitable mixture can be readily obtained. When pure, hyoscyamine forms fine white needles having a melting point at 108° C.

Hyoscyamine forms a well crystallized salt with gold chloride, which when pure melts at 162° C.* When crystallized from dilute hydrochloric acid it forms brilliant golden yellow plates. The picrate is also a finely crystalline salt but slightly soluble in cold water. It is of a brilliant canary yellow colour, and when pure melts at 167° C. These two salts are both well characterized and serve for the identification and purification of the alkaloid.

Associated with the alkaloid in henbane there appears to be some very strongly smelling body which in small quantity reminds one of oil of winter green (methyl salicylate), though when much is present the odour more resembles that of nicotine.

* It may be pointed out here that this melting point agrees with that given by Henry, but it is several degrees higher than that recorded by Dunstan and others. It would appear that their figures are some degrees too low. When pure the melting point is fairly sharp.

The actual amount of alkaloid contained in the Egyptian *H. muticus* appears to vary considerably. If the plant is collected after the ripening of the seed, the alkaloid may not exceed 0·6 per cent of the dry material. On the other hand, if the plant is pulled about the time of flowering, as much as one and a half to two per cent may be present. As above mentioned, great care is necessary in drying material of this nature or loss of alkaloid will result.

Datura contains much less alkaloid; usually less than 0·6 per cent, so that it is a less suitable material for the preparation of the alkaloid. There is, however, a special demand for carefully dried leaves and these command a good price.

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