FAKE SAFFRON.*

BY ARNO VIEHOEVER AND J. F. CLEVENGER.

A most skilful attempt to change the appearance of a natural product other than saffron, so that it may appear to be that substance, has recently come to our attention. The material was imported from Spain. It resembled Crocus rather strikingly in appearance, as well as in flavor. Upon close inspection, however, it was quite evident that instead of the stigmas characteristic of Crocus, tubular florets characteristic of a member of the *Compositae* were present. This substitution was in fact complete, no stigmas of Crocus whatsoever being present. Considerable difficulty was experienced in identifying the product. Inasmuch as it appeared to be artificially colored and weighted, experiments were undertaken to determine the nature of the dye or dyes and of foreign substances, added to increase the weight.

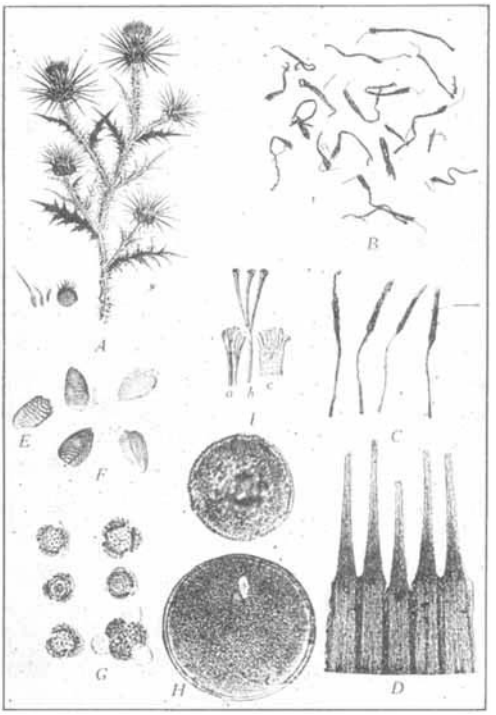

Plate 1.

A. *Onopordon sibthorpianum* Boiss and Heldr. (*O. macracanthum* Sibth. SM.) After Sibthorp, × 1/6.
B. Flowers of substitute as they appear in the drug, × 3/5.
C. Flowers of substitute soaked in water and straightened out, × 3/5, representing mainly the connectives.
D. Upper end of stamens of the flowers of the substitute, × 20.
E. Fruit found among the flowers of substitute, × 1 1/4.
F. Fruits from *Onopordon sibthorpianum*, × 1 1/4.
G. Pollen grains from flowers of substitute, × 125.
H. Pollen from flowers of *Crocus sativus* L., × 125.
I. *Crocus sativus*, showing:
   a. Upper part of stigma, slightly oversize.
   b. Style with stigmas, × 1/5.
   c. Papillose margin of stigma, × 25.
(After "National Standard Dispensatory.")

BOTANICAL EXAMINATION.

Identification of the material as derived from a species of *Onopordon* was based mainly on the structure of the flowers. No other parts of the vegetative plant were present. The flowers, with the general characteristics of the thistle, and apparently 3 cm. in length, showing the style distinctly longer than the corolla, and filaments with the anthers and connectives equal to or exceeding the corolla in length. The form of the connectives is important for the purpose of identification, *Onopordon* having the narrowest connectives of the different flowers used in the adulteration of saffron. The pollen grains (see illustration, Plate 1, G) were of the general shape of those reported for *Onopordon*, having a spiny exine with three distinct openings. The glandular hairs of the stigma, the

* Contribution from the Pharmacognosy Laboratory, Bureau of Chemistry, U. S. Department of Agriculture.

peculiar structure of the style and of the filament-base were also characteristic for *Onopordon*. In contrast to the flowers of *Onopordon*, saffron consists of branched styles with stigmas, Plate 1, *a*, *b*. These stigmas are characterized by a papillose margin, Plate 1, *c*. The pollen grains, observed in large numbers on the stigmas, are nearly spherical and have a smooth exine. They are about 75 to 150 microns in diameter, being approximately four times as large as the pollen grains of *Onopordon*.

Only one fruit was found in the material available to us. This fruit was compared with those of a species of *Onopordon* found in collections, and agreed most closely with that of *Onopordon sibthorpianum* Boiss and Heldr. This species is reported indigenous to Crete rather than to Spain, from where our material was shipped, and showed certain slight differences in the shape and structure of the fruit, being somewhat broader in outline and having less marked ridges. There is a possibility that the material was obtained from a species other than *sibthorpianum*. Unfortunately, no specimen of *sibthorpianum* could be found in the National Herbarium, nor did the fruits of certain species collected in Spain agree with the fruit found in our material. There is no question in our mind, however, that the product represents a species of *Onopordon* since the flowers in general, as well as the fruit, show the general type of that genera and are distinctly different from other genera, such as Cynara and Cnicus, reported to have been used as substitutes.

CHEMICAL DETERMINATION.

Identification of Artificial Color.—In order to ascertain whether the material was artificially colored, a portion of the flowers was placed in water, and from the concentrated solution a further dilution was prepared, resulting finally in a solution of 1–100,000. While, in the case of genuine Crocus, a distinct yellow color could be perceived, the solution obtained with the material was colorless. In fact, the tint produced with the substitute product in the more concentrated solutions was pinkish rather than yellow. The suspicion that artificial dye was added was further verified by the use of organic solvents.

STAINING TEST SAFFRON AND FAKE SAFFRON.[1]

Solvents used.	Genuine saffron (color).	Fake saffron (color).
Methyl alcohol	Yellow	Pink
Acetone	Lemon-yellow	Deep pink
Alcohol	Lemon-yellow	Salmon-pink
Dehydrated alcohol	Greenish yellow	Rose-pink
Ether	Yellow	Deep pink
Chloroform	Very slight yellow	Bright pink
Xylene	Colorless	Red
Benzene	Colorless	Deep pink
Carbon tetrachloride	Colorless	Pink
Carbon disulphide	Colorless	Red
H_2O	Yellow	Pinkish buff

As these data, ascertained by Ruth G. Capen, of this laboratory, showed the artificial dye added was distinctly different from crocetin, the glucoside of Crocus, further steps were taken to identify the coloring matter, which was found to be a mixture of Tartrazine (G. S. J. No. 94) and commercial Ponceau 2 R (G. S. J. No.

[1] 0.01 Gm. macerated in 5 Cc. of liquid.

55). The procedure used may be found in an article by Mathewson,[1] to whom we are indebted for the isolation and identification of the dyes.

Identification of Weighting Substances.—In order to ascertain whether the material was weighted, determinations were made of both the total and the acid-insoluble ash. The result was that while generally Crocus on the average contains only from 5 to 7 per cent total ash, over 30 per cent were found in the substitute material. The acid-insoluble ash was quite small, not exceeding 1 per cent.

Further experiments were carried on to identify the nature of the salt or salts present. We proceeded according to the method suggested by Nestler,[2] triturating about 20 flower parts in a mortar with a small amount of hot water, and evaporating the filtrate at room temperature on the object slide. Tetrahedral crystals of various sizes and characteristic shapes were found. (See Fig. I.) These crystals were identical with those obtained by evaporation at room temperature of a solution of borax and saltpeter. The crystals, though similar to saltpeter in general aspect, were found by Dr. E. T. Wherry, Crystallographer of the Bureau of Chemistry, to differ from that substance as well as from borax in crystallographic-optical properties. They therefore must represent a double salt of these two constituents, hitherto not described crystallographically in literature. In order to verify the presence of potassium nitrate and determine the approximate amount, a nitrogen determination was made in the Nitrogen Laboratory of this Bureau, resulting in 2 per cent total nitrogen, of which almost 1 per cent was in a water-soluble form. Calculated as potassium nitrate, this corresponds to 5.5 per cent. The presence of borax was shown by the well-known use of turmeric paper and the green flame of boric acid ester.

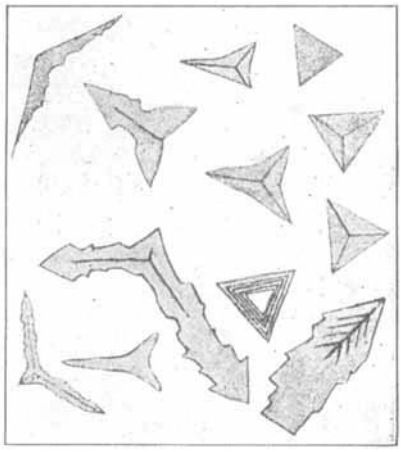

Fig. I.
Crystals of the double salt of potassium nitrate and borax. After Nestler.

Inasmuch as glycerin also had been found in adulterated samples of saffron, especially in those containing salt mixtures to which it had been added in order to prevent conspicuous crystallization, we tested for glycerin. In determining the presence of acreolin, a test of the distillation product of glycerin with the aldehyde reagent fuchsin sulphurous acid proved positive. When the material was overheated the characteristic odor of acreolin was also observed. We determined the glycerin quantitatively, according to the extraction method suggested by Cook,[3]

[1] Mathewson, W. E., Associate Chemist, Bureau of Chemistry, Department of Agriculture, "Separation and Identification of Food-Coloring Substances." *U. S. Dept. of Agric.*, Bull. No. 448, Feb. 15, 1917.

[2] Nestler, A., "Über Saffranverfälschungen," *Archiv für Chemie u. Mikroskopie*, 7, 70, 1914.

[3] Cook, F. C., "The Estimation of Glycerin in Meat Juices and Extracts," *Jour. Assoc. Official Agric. Chemists*, Vol. 1, No. 2, Aug. 1915, p. 279–281.

using further the methods recommended in *Bulletin* No. 107, Official and Provisional Methods of Analysis, Association of Official Agricultural Chemists, 1912, pp. 83–4. The amount found, after deducting the amount of color substance also obtained in the extraction of glycerin, was close to 4 per cent.

The odor of the drug suggested the addition of saffron oil and the crumpled appearance of the flowers indicated an intentional crinkling.

SUMMARY.

The product offered as saffron proved to be a substitute. This substitute was identified as a species of *Onopordon* closely related to *Onopordon sibthorpianum* Boiss and Heldr. The material was artificially dyed with a mixture of Tartrazine and commercial Ponceau 3 R. It was weighted with a salt mixture of at least 5 per cent potassium nitrate and borax. About 4 per cent glycerin was also found.

THE INFLUENCE OF INHIBITING FLOWERING ON THE FORMATION OF ALKALOIDS IN THE DATURAS.

BY A. F. SIEVERS.

It has always been a matter of conjecture as to what may be the rôle of alkaloids in plant metabolism. They have been considered as waste and as food products, the latter theory being somewhat strengthened by the fact that in many cases the seeds of alkaloid-containing plants contain a considerable percentage of alkaloids. Experiments have been made from time to time to determine the effect of the several elements in the soil on the formation of alkaloids, but the conclusions have been by no means concordant. The writer has shown that in belladonna the alkaloids occur in all parts of the plant but are present in the greatest concentration in the tender growing parts.[1] At an earlier date[2] it was shown that the average alkaloidal content of 59 belladonna plants was higher at the late fruiting stage when the berries were mostly ripe and the leaves small and sparse. It seemed logical to conclude that any interruption to the normal development processes of the growing plant would likely have a decided influence on the formation of such characteristic constituents as alkaloids, or greatly affect the translocation of such constituents. Since the seed of the Daturas contain a considerable quantity of alkaloids it was thought interesting to find out in what way the inhibition of seed formation, by removing the flower buds, would affect the alkaloidal content of such plants. It is the object of this paper to record the results of such an experiment, which, while probably not conclusive because it has not been carried on over a sufficiently wide range of conditions, gave such unexpected results that it should serve as a stimulus for further experiments along that line.

The experiment was made a number of years ago at Madison, Wis.,[3] and

[1] A. F. Sievers, "Distribution of Alkaloids in the Belladonna Plant," *Am. Journ. Pharm.*, Vol. 86, No. 3, p. 97, 1914.

[2] A. F. Sievers, "Individual Variation in the Alkaloidal Content of Belladonna Plants," *Jour. Agric. Res.*, Vol. 1, No. 2, pp. 129–146, 1913.

[3] The Pharmaceutical Experiment Station, University of Wisconsin, and the Office of Drug, Poisonous, and Oil Plant Investigations, Bureau of Plant Industry, U. S. Department of Agriculture coöperating. The writer wishes to acknowledge the assistance of Mr. G. A. Russell, the Department's representative at that time, who grew the plants, recorded the field observations, and furnished the material for assay.