

## THE ANALYTICAL AND MICROSCOPICAL EXAMINATION OF COMPOUND LIQUORICE POWDER.

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*(Read at the Meeting, April 5, 1911.)*

COMPOUND liquorice powder, prepared in accordance with the directions of the British Pharmacopœia, contains :

					Per Cent.
Senna, in fine powder	...	...	...	...	16·7
Liquorice root, in fine powder	...	...	...	...	16·7
Fennel fruit, in fine powder	...	...	...	...	8·3
Sublimed sulphur	...	...	...	...	8·3
Refined sugar, in powder	...	...	...	...	50·0
					100·0

## EXAMINATION OF COMPOUND LIQUORICE POWDER

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We understand that it is customary on the manufacturing scale to grind the whole ingredients into powder together, gradually sifting and returning the gruffs to the mill until they are reduced to a very low bulk, usually a few pounds. These are set aside and added to a succeeding batch, which is then treated in the same manner. By this process the correct ratio of the various ingredients is slightly altered, as the sulphur and sugar yield no gruffs, while the senna, liquorice, and fennel yield gruffs in varying quantities.

During the last three years we have examined over 100 samples of compound liquorice powder, the majority of which were submitted by the Inspectors under the Sale of Food and Drugs Acts. We have been much impressed with the great diversity in appearance of the samples, and several instances of careless manufacture have come under our notice. In several samples the sulphur was present to the extent of 16 per cent.—that is, nearly double the quantity prescribed by the British Pharmacopœia—whilst in other samples the sulphur was entirely omitted. Again, in our microscopical examination of several samples, the liquorice root was so predominant that the senna and fennel were identified with difficulty, and might justly be described as traces.

Many instances of gross adulteration with ground olive stones and ground almond shells have also come under our notice. These adulterants, we understand, find their way into compound liquorice powder through using foreign ground liquorice root, which is subject to these adulterations.

Upon referring to the literature on the subject, we find that the following standards have been suggested :

1. The Local Government Board (Ireland) : Ash, 4·5 per cent.
2. J. C. McWalter (*Pharm. J.*, 1902, **69**, 89) : Moisture should be from 4 to 6 per cent. ; ash, not above 5 per cent. ; soluble ash, not exceeding 3 per cent. Not less than 4 per cent. should be dissolved in 70 per cent. alcohol.
3. C. G. Moor ("Suggested Standards for Food and Drugs," p. 179) : Water should not exceed 6 per cent. ; ash should be about 4 to 5 per cent. ; soluble ash about 2·5 per cent.
4. H. W. Gadd (*Year-Book of Pharmacy*, 1901, p. 390) gives the following results of analysis of three samples of compound liquorice powder :

	Moisture per Cent.	Ash per Cent.	Soluble Ash per Cent.	Extractive in Tincture per Cent.*
A	6·35	4·5	2·80	4·83
B	5·40	4·5	3·15	3·73
C	4·15	4·8	2·68	4·47

5. J. F. Liverseege (*Year-Book of Pharmacy*, 1906, p. 269) : The amount of ash found in twenty-one samples was 3·8 to 6·4 per cent. This author suggests a method

\* The tincture was prepared by macerating 5 grms. of the powder in 70 c.c. of 70 per cent. alcohol.

of analysis by extracting the powder first with strong alcohol ; then with carbon bisulphide, to obtain the sulphur ; and finally with water, to obtain the sugar.

The amount of moisture in the samples examined by us varied from 3·7 to 4·2 per cent.

The following table shows the amount of ash found in commercial samples :

	Maximum.	Minimum.	Average.
Total ash ... ..	6·78	4·36	5·35
Insoluble ash ... ..	3·98	1·62	2·54
Soluble ash ... ..	3·20	2·48	2·80

Several samples not included in the above table contained abnormal proportions of total ash, even amounting to 8·5 per cent. In all these samples the ash insoluble in hydrochloric acid (sand) was excessive, amounting to nearly 4 per cent. In our opinion these samples were prepared from inferior or improperly cleaned drugs.

The disturbing action of the sulphur on the total and insoluble ash, due to the combination of the sulphur with the mineral constituents of senna, liquorice, and fennel, was pointed out by one of us in a previous paper (*Pharm. J.*, 1905, **74**, 363).

The presence of sulphur in the preparation not only causes an increase of total ash over the actual amount of mineral matter present in the several ingredients, but it also converts some of the insoluble into soluble ash.

The following table will illustrate this point :

	Compound Liquorice Powder. B. P.	Compound Liquorice Powder without Sulphur + 8 per Cent. Extra Sugar.
Total ash ... ..	4·66	3·75
Insoluble ash ... ..	1·68	2·76
Soluble ash ... ..	2·98	0·99

These two samples were prepared from the same ingredients.

Thus it will be seen that the percentage of soluble ash is of no value in detecting exhausted drugs in compound liquorice powder ; even if exhausted drugs had been employed, the percentage of soluble ash would still be raised, due to the conversion of the insoluble carbonate into soluble sulphides and sulphates. Again, the amount of extractive matter yielded to 70 per cent. alcohol, as suggested by some observers, is of little value for detecting the presence of exhausted ingredients, as the whole of the sugar is soluble in 70 per cent. alcohol ; thus the alcoholic extract would contain a large amount of sugar, together with a smaller amount of extractive matter from the drugs, and a slight variation in the proportion of sugar would vitiate the results. Sugar is soluble even in 95 per cent. alcohol.

The determination of the sulphur presents no special difficulty. The following

is the method employed by us : One grm. of the powder is treated with 15 to 20 c.c. of concentrated nitric acid and heated ; and if the sulphur fuses, a small quantity of bromine is added. When oxidation is complete, hydrochloric acid is added, and evaporated to remove excess of nitric acid, diluted with water, and filtered from any siliceous matter, and finally precipitated as barium sulphate. The amount of sulphur actually present, either as sulphates or organic sulphur, in the senna, liquorice, and fennel, is very small, and may be neglected. The determination of the sulphur by means of carbon bisulphide cannot, in our experience, be relied on, as commercial samples of sublimed sulphur are not always completely soluble in this reagent.

Before entering upon the consideration of the adulteration of compound liquorice powder with foreign vegetable powders, it is necessary that we should be thoroughly acquainted with the microscopic characters of those ingredients of which it is composed. The media employed by us in the routine microscopical examination of compound liquorice powder are water, glycerine, and a strong solution of chloral hydrate (50 grms. in 20 c.c. of water). Iodine water is also used for the better observation of the starch granules.

The histology of the senna leaf presents many characters by which it can be easily identified, even in such a complex mixture as compound liquorice powder. It has an iso-bilateral structure—that is, there is palisade tissue on both the upper and under surfaces—and between the two palisade tissues there is a layer of spongy parenchyma. It has peculiar hairs scattered over both the lower and upper surfaces. These hairs are one-celled and conical, they may be straight or curved, and are usually slightly contracted at the base. They are thick-walled and have a warty appearance. The stomata are surrounded by two large cells, which are parallel to the ostiole or opening of the stomata, and as a rule one of these cells is much larger than the other. The epidermal tissue is further characterised by the scars of fallen hairs and the peculiar radiating arrangement of the cells surrounding the base of the hair. Besides the foregoing, elements derived from the bundles of the midrib and veins possess certain characteristics. Thus, in a longitudinal section of a leaf bundle, wood vessels are followed by pericyclic fibres, and outside these comes a single layer of parenchymatous cells containing prismatic crystals of calcium oxalate. Though the presence of these crystal cells is not strictly diagnostic, a strip of the senna leaf bundle can always be recognised in a microscopic preparation of powdered senna by the sequence of the elements—namely, wood vessels, pericyclic fibres, and a single row of cells containing prismatic crystals.

The British Pharmacopœia describes liquorice root as the peeled root and peeled subterranean stem of *Glycyrrhiza glabra*. It is this decorticated portion that should be used in the manufacture of galenical preparations. It contains about 30 per cent. of starch, and the predominating feature of powdered liquorice root, when examined microscopically, is the abundance of starch granules. These granules vary both in outline and size, and present no distinct hilum or markings. They vary in outline from circular to elongated ellipses, but the majority are circular or elliptical. In size they vary from mere dots to even  $20\mu$ , and they average about  $10\mu$ . Some of the granules have even slight protuberances resembling budding yeast cells. Liquorice

root is further characterised by groups of thick-walled yellowish fibres and large thick-walled yellow-pitted vessels. The yellow colouring matter of liquorice root is almost entirely situated in the fibres and vessels. The best fibres of liquorice root are accompanied by regular rows of cells containing single prismatic crystals of calcium oxalate.

Fennel is the dried ripe fruit of *Feniculum capillaceum* (N.O. Umbelliferae), and consists of two readily separated mericarps. Each mericarp has five primary ridges, and in a transverse section shows six large vittæ, or oil canals. In the powder, fragments of the vittæ are easily recognised by their dark brown colour. Powdered fennel may be identified by the presence of large parenchymatous cells with spiral or reticulate thickening. The cells of the endosperm are polygonal in shape and have rather thick walls, and contains aleurone grains, oil globules, etc. Starch is absent. Groups of narrow elongated cells, arranged parallel to one another, are also seen in the powder; they are derived from the inner epidermis of the fruit. The fragments of vessels, sclerenchymatous fibres and tracheids, are derived from the fibro-vascular bundles of the fruit, and from the carpophore and pedicel of the fruit.

Mention was made earlier that some of the adulterants we had met with consisted of ground olive stones and ground almond shells. Fig. IV. is a characteristic example of compound liquorice powder adulterated with ground olive stones. The elements of senna, liquorice, and fennel are shown, and in addition will be observed peculiar sclerenchymatous cells which are foreign to any of the constituents of compound liquorice powder, and characteristic of such things as olive stones, date stones, and almond shells.

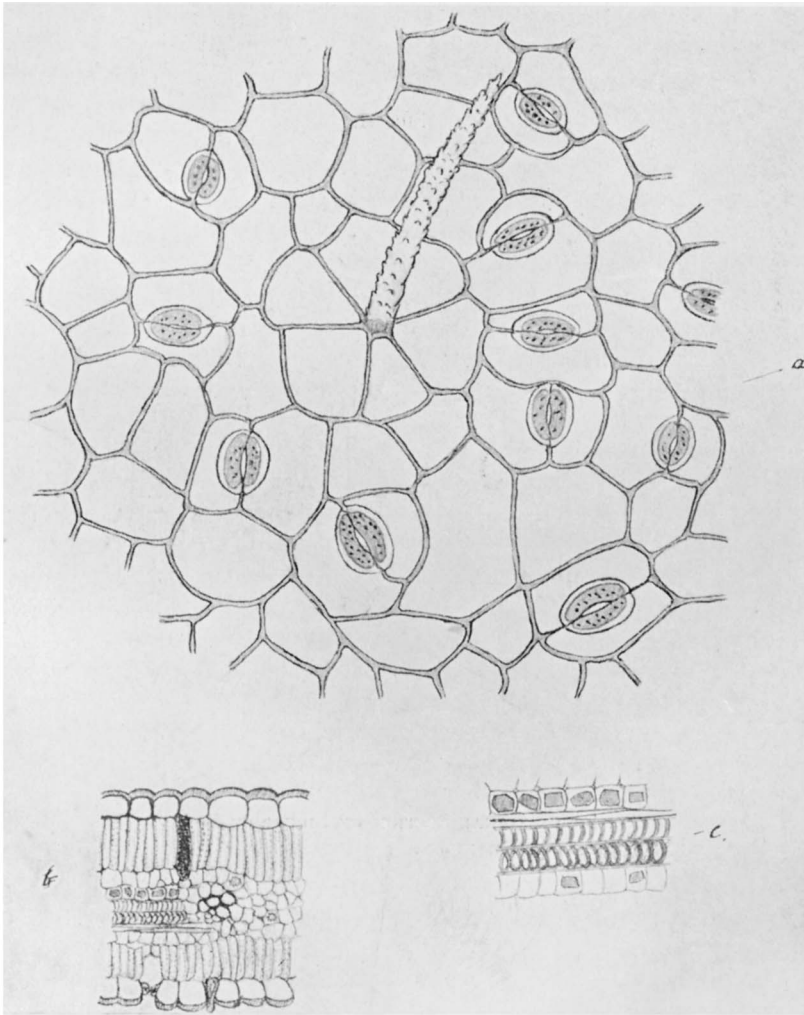
#### DISCUSSION.

Mr. C. A. HILL said that the ash of powdered Alexandrian senna was higher by 1 or  $1\frac{1}{2}$  per cent. than that of Tinnevely senna. In a sample of compound liquorice powder which he had examined for a special purpose, the ash, calculated from the ash contents of the several constituents, worked out at 3.79 per cent., while the compound powder yielded 4.25 per cent. of ash. The question of purity or genuineness was only likely to arise with the cheapest qualities of compound liquorice powder, which would certainly be made with Tinnevely senna.

Mr. F. W. RICHARDSON said that he had not found the proportion of ash to be of any great assistance, but it was very useful to examine microscopically the fibre obtained after treatment with dilute acid and alkali. This fibre generally amounted to about 16 per cent. The proportion of matter soluble in water, apart from the sugar, was usually about 12 per cent., and a determination of the total soluble matter, which with the sugar should amount to about 62 per cent., was also very useful. It might be mentioned that the proportion of sulphur even in genuine samples was liable to considerable variation, since the powder was sometimes comparatively coarse, and separation of the ingredients occurred.



FIG. I.



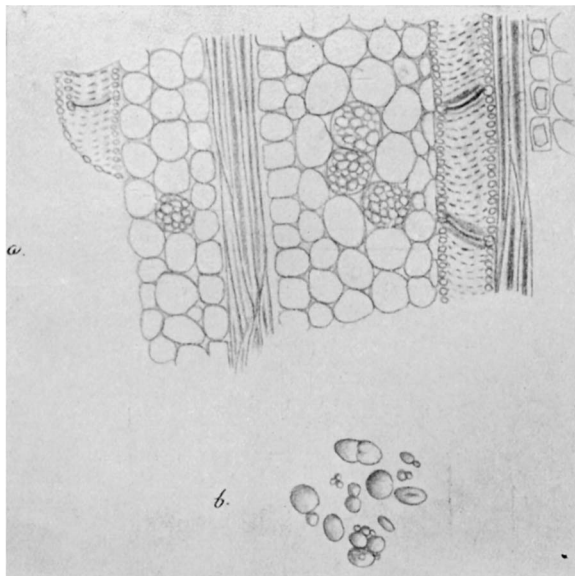
*a*, EPIDERMIS OF SENNA LEAF.

*b*, TRANSVERSE SECTION OF SENNA LEAF.

*c*, LONGITUDINAL SECTION OF MIDRIB.

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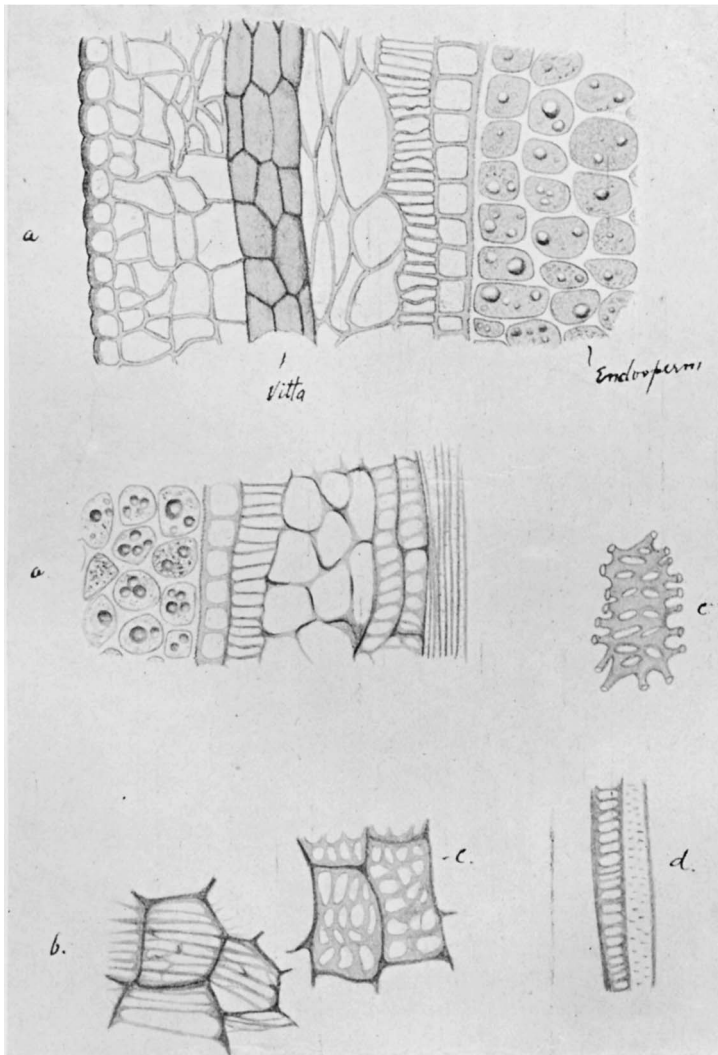
**FIG. II.**



*a*, LONGITUDINAL SECTION OF LIQUORICE ROOT.  
*b*, STARCH GRANULES.



FIG. III.

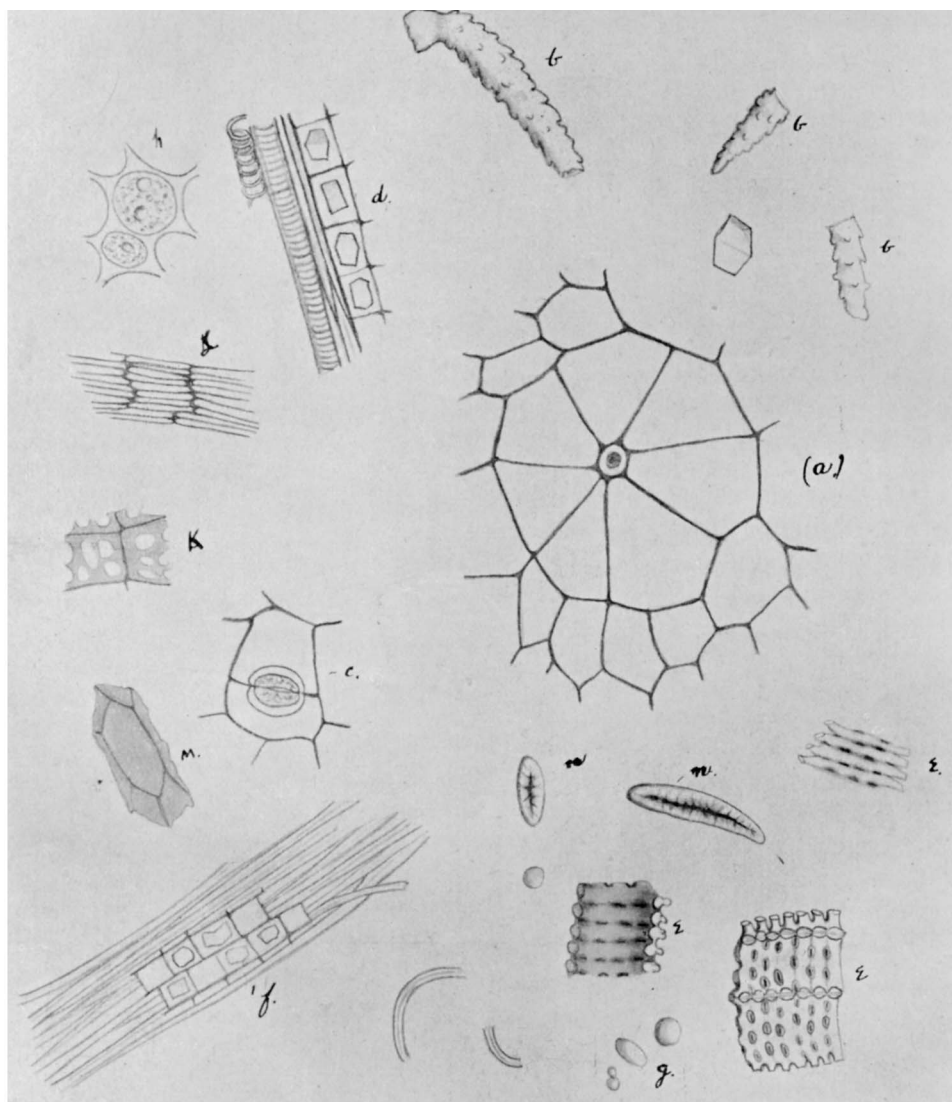


*a*, LONGITUDINAL SECTION OF FENNEL.  
*b*, INNER EPIDERMIS OF PERICARP.

*c* THICKENED CELLS OF MESOCARP.  
*d*. PORTIONS OF PEDICEL OF FRUIT.



FIG IV



- a*, EPIDERMIS OF SENNA LEAF.  
*b*, HAIRS AND FRAGMENTS OF HAIRS OF SENNA.  
*c*, PORTION OF EPIDERMIS WITH STOMA.  
*d*, FRAGMENT OF FIBRO-VASCULAR BUNDLE OF SENNA.  
*e*, PORTIONS OF VESSELS OF LIQUORICE ROOT.  
*f*, SCLERENCHYMATOUS FIBRES OF LIQUORICE ROOT.

- g*, STARCH GRANULES OF LIQUORICE ROOT.  
*h*, ENDOSPERM OF FENNEL FRUIT.  
*i*, CELLS OF MESOCARP OF FENNEL.  
*l*, INNER EPIDERMIS OF PERICARP OF FENNEL.  
*m*, PORTION OF VITTA, OR OIL CANAL.  
*n*, ISOLATED STONE CELLS FOREIGN TO LIQUORICE POWDER.