

THE TECHNICAL ANALYSIS OF LICORICE PASTES.

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WHEN I was first confronted with the analysis of licorice products, I had to select a method, which, giving the necessary data required by the trade, could easily be carried out in a reasonably short time.

The literature on that subject was found to be rather meager and only fragments could be found here and there. More comprehensive was the article on the subject of licorice found in Hager's *Pharmaceutische Praxis*, and for the determination of some constituents the method therein described was at first carried out with a few minor modifications; instead of taking 10 grams of substance as prescribed only 2 grams were used. The first amount required too large quantities of ammonia and alcohol on one hand and absolute alcohol on the other hand to get a colorless filtrate, besides requiring too much time, extra large filters and weighing-bottles. It soon developed, however, that the above method gave too high results in glycyrrhizin, which results were out of question, in case glucose had been added to the paste, as the following figures will show:

	Glycyrzhizin. Per cent.
1. Paste with no glucose added	22.25
2. Same paste with 15 per cent. glucose added.....	29.61
3. " " " 20 " " " "	34.12

Instead of going down on glycyrrhizin as it should be through the addition of the glucose, the values for that substance rose with the amount of glucose added. It was examined for that substance as glucose might have been thrown down together with the glycyrrhizin and was not entirely removed during washing, by precipitating the glycyrrhizin with basic lead acetate but only about 2 per cent. of glucose were found in No. 2, not explaining the rise in glycyrrhizin. I concluded therefore that that rise was due to the presence of a substance or substances formed from the glucose by the ammonia, especially while concentrating the run-off from the first operation, which substances were absolutely insoluble in absolute alcohol and could not be washed out by the same. After several experiments along those lines the following mode of operation was adopted and found to work satisfactorily.

To 2 grams of the extract to be examined add 5 cc. water, place on a warm plate, and by means of a glass rod make up to a perfectly even mass. Add little by little, while stirring, 20 cc. of 96 per cent. alcohol and allow to settle. Filter through a weighed filter and wash with a mixture of 1 part water and 4 parts alcohol of above strength until run-off is colorless, which takes about 100 cc. of wash liquor. Keep the top of the filter wet, as it easily dries out and is then washed with difficulty. The filter, with contents, is dried at 105° C. for three hours and weighed. It gives the gummy matter, starch, etc., contained in the extract. The filtrate is either distilled off or evaporated. Take a large beaker for evaporating, or else liquor creeps up to the edges incurring losses. When nearly evaporated transfer to a small beaker, evaporate further to a thick sirup, making about 1 or 1.5 cc. It is then dissolved in 2 cc. glacial acetic acid, and 30 cc. absolute alcohol are added with constant stirring. Too violent stirring produces a lumpy mass, which is difficult to wash out. The solution is allowed to settle. Filter through a weighed filter, wash with absolute alcohol until no acid reaction, dry at 105° C. for three hours, and weigh. The figure obtained is not pure glycyrrhic acid, but rather a salt. To get the acid sufficiently accurate, an aliquot part is incinerated, using blast heat at the end, and deducting 0.7 of the percentage of ash from the percentage of the salt found. The ash consists mainly of calcium oxide, but contains also very small amounts of alumina and magnesia.

The glycyrrhizin salt as prepared by my method represents a light yellow amorphous powder, soluble in glacial acetic acid, cold and hot water, and dilute alcohol. It has a very sweet taste. (The pure glycyrrhic acid is according to Haberman¹ a tribasic acid and forms acid and normal salts. It dissolves in the same reagents as the salt above described, but only in hot water, while making a jelly with cold water.)

The filtrate from the glycyrrhizin is distilled off, diluted and evaporated, and this repeated until the acetic acid is driven off. The residue is dried at 105° C. for three hours and weighed. This amount represents the so-called extractive matters, containing the saccharine matter that the root contained originally or which had been added subsequently to the paste; they contain also some tannin, resin, etc.

¹ *Ann. Chem.* (Liebig), 197, 105.

Ash, in the paste, is determined by incinerating 2 grams in a platinum dish. For total solids, about 5 grams are dissolved in hot water and made up to 500 cc. after cooling the liquor. It is well shaken and 50 cc. are evaporated, dried at 105° C. for three hours, and weighed.

For solids soluble in cold water, 50 cc. of the clear filtrate are evaporated, dried, and weighed. For evaporation, flat bottomed, so-called crystallizing glasses have been found to be very convenient.

The difference between "total solids" and "soluble solids" represents the residue insoluble in cold water.

The moisture is taken as the amount obtained by subtracting the "total solids" from 100.

Reducing substances are determined as usual after precipitating with basic lead acetate and titrating the filtrate, freed from lead, with standardized Fehling's solution.

Following are the results obtained by the above method from different samples of licorice extract:

	1. Per cent.	2. Per cent.	3. Per cent.	4. Per cent.
Moisture	24.18	25.14	19.58	23.99
Residue insoluble in cold water.	3.95	6.79	14.35	2.54
" " " mixture of				
1 water and 4 alcohol	27.27	25.20	36.58	24.65
Glycyrrhizin	22.78	21.97	18.51	19.90
Extractive matter	25.02	25.05	26.02	28.91
Ash	6.25	6.02	5.60	5.59
Reducing matters as glucose.....	9.76

Sample No. 1 was one of Scudder's brands.

Sample No. 4 gave, by the method described in Hager's *Pharmaceutische Praxis* for glycyrrhizin, 28.57 per cent.

An analysis of fresh and spent licorice root gave the following results:

	Fresh. Per cent.	Spent. Per cent.
Moisture	8.40	10.00
Total solids	33.18	10.86
Cold solubles	29.65
Gummy matter, starch, etc	8.07	3.56
Glycyrrhizin	11.21	2.25
Extractive matters.....	14.77	5.60
Ash	2.68	0.55
Reducing matters.....	0.52