

ANALYSES OF BLACK AND WHITE MUSTARD.

By CHARLES H. PIESSE AND LIONEL STANSELL.

THE seeds of black and white mustard, *Sinapis nigra* and *S. alba*, when crushed and sifted constitute the mustard farina of commerce; both species are cultivated in this country, a considerable quantity, however, being imported from abroad. In the manufacture, the seeds of both variety in suitable proportions are crushed between rollers, then pounded and sifted. The residue in the sieve is called dressings; what passes through is farina or flour of mustard. This is re-sifted, yielding three qualities: (a) superfine, (b) fine, and (c) seconds. The seeds are tough and difficult to powder: the best method on a small scale is to pulverise them in an ordinary mortar with a large cast iron pestle.

The farina of black and white mustard differs but little in appearance, the brown being, however, slightly darker. In the unground state the seeds of white mustard are of a yellowish straw colour, those of brown a dark brownish purple.

A. 1 gram white seeds, Yorkshire, contain 170 seeds.

B. 1 „ „ „ Cambridge, „ 172 „

C. 1 „ brown „ Cambridge, „ 944 „

100 seeds of A weigh $\cdot 5882$ grm., B $\cdot 5814$ grm., C $0\cdot 1059$ grm.

Methods of Analysis Employed.—The Sulphur was estimated by oxidation with concentrated nitric acid, and subsequent precipitation with barium chloride.

For the determination of *Nitrogen* the soda-lime method was employed, the evolved ammonia being passed into standard acid. Mustard contains so large a proportion of fat, that during the combustion the amount of tar produced considerably interferes with the subsequent titration. It was therefore found necessary to exhaust a weighed quantity of the crushed mustard seeds (previously dried) with petroleum ether, to collect the exhausted mustard on a weighed filter and to dry it, then after re-weighing to calculate the ratio between the original mustard and that free from fat and moisture. A weighed quantity of

this exhausted mustard was then used for the estimation of the nitrogen. By this expedient the production of tar during the combustion was almost entirely prevented. The amount of nitrogen, after subtracting that contained in the potassium myronate*, in the case of black mustard, is multiplied by 6.25 to obtain the albuminoid substances.

Substances Soluble in Water (Myrosin and Albumin).—The amount of myrosin and soluble albumin appears not to differ in either variety. About two grammes of substance well digested for twelve hours with cold water, the fluid then filtered into a quarter litre flask, and the seeds washed thoroughly with cold, warm, and finally boiling water. Of the filtrate, 50 c.c. were evaporated to obtain the total soluble matter; 100 c.c. were boiled, and the coagulated albumin collected on a weighed filter.

Fat and Cellulose.—(a) About 2 grams of finely pulverised seed well dried; (b) extracted with petroleum ether, the insoluble matters collected on a weighed filter, dried and weighed; (c) boiled successively with very dilute hydrochloric acid, caustic soda, and hydrochloric acid, being washed with boiling water each time, finally with alcohol, dried, and weighed as cellulose.

Estimation of the Volatile Oil.—The distinguishing characteristic of brown mustard is the occurrence in it of potassium myronate, which, in presence of water, is acted upon by a peculiar ferment—myrosin, contained in the seed, whereby it is decomposed, yielding potassium, hydrogen sulphate, glucose, and allyl iso-thiocyanate, the pungent oil of mustard:— $\text{K, C}_{10}\text{H}_{18}\text{NS}_2\text{O}_{10} = \text{KHSO}_4 + \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_3\text{H}_5\text{CS, N}$. 100 parts potassium myronate yield 23.855 volatile oil.

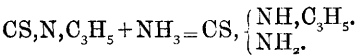
It is remarkable that the yield of volatile oil is greater when the brown mustard is mixed with some of the white. The results of many experiments have led to the following process:—

About 25 grams of the crushed brown seeds are mixed with about a quarter of their weight of white seeds (also crushed), in a 500 c.c. flask, 300 c.c. cold water added and allowed to stand for five or six hours. The highest yield of oil is obtained by standing for this length of time, and sensibly diminishes after six hours, gradually decomposing in contact with the myrosin; the yield after the lapse of 48 hours will reach only about two-thirds of that originally present, while after a week not one-third of the whole will be obtained. We have found after numerous trials that not less than three hours nor more than six should be allowed to elapse between the addition of the water to the mustard and its distillation, the rule finally adopted being to allow the mixture to stand for five hours. The flask is then to be connected with a small Liebig's condenser, and the liquid distilled until no more oily drops are seen to come over. The distillate is received in a small flask (150 c.c.), containing 30 c.c. ammonia sp. gr. 0.88. When the distillation is judged complete, the flask is disconnected and, after removing from the flame, shaken. If the steam possesses the sharp pungent odour of mustard oil, the contents are further distilled. This test is very sensitive. When the boiling proceeds rapidly, after 50 c.c. have come over, it will almost invariably be found that the mustard is entirely deprived of volatile oil. The distillation finished, the condenser is well rinsed out with cold distilled water into the receiver (this is necessary), the flask corked and put aside until the oily drops have quite disappeared, being occasionally shaken for this purpose; at least 24 hours are usually requisite. When the change is complete the flask is covered with a porcelain crucible lid,

* Potassium myronate contains 3.37 per cent. of nitrogen.

and boiled for a few minutes to expel the ammonia, transferred to a weighed platinum basin, and evaporated to dryness on the water-bath, subsequently dried in the water oven, and weighed. The amount of thio-sinamine thus obtained is multiplied by $\cdot 85344$: the product is the quantity of allyl iso-thiocyanate contained in the mustard operated upon. If the factor $3\cdot 5775$ be used, the amount of potassium myronate is ascertained.

Thio-sinamine is formed by the union of one molecule of ammonia with one molecule mustard oil.



ANALYSES OF WHITE MUSTARD.

	Mustard Whole Seeds.		Mustard Farina.		
	Yorkshire.	Cambridge.	Superfine.	Fine.	Seconds.
Moisture	9.32	8.00	30	5.78	6.06
Fat	25.56	27.51	37.18	35.74	32.55
Cellulose.....	10.52	8.87	3.90	4.15	9.34
Sulphur	0.99	0.93	1.33	1.22	1.26
Nitrogen.....	4.54	4.49	5.05	4.89	4.25
Albuminoids	28.37	28.06	31.56	30.56	26.56
Myrosin and Albumin	5.24	4.58	7.32	6.67	6.11
Soluble Matter	27.38	26.29	36.31	36.60	33.90
Volatile Oil	0.06	0.08	0.03	0.04	0.03
Ash	4.57	4.70	4.22	4.31	4.30
„ Soluble	0.55	0.75	0.44	0.55	0.33

ANALYSES OF BROWN MUSTARD.

	Mustard Whole Seeds.	Mustard Farina.		
	Cambridge.	Superfine.	Fine.	Seconds.
Moisture	8.52	4.35	4.52	5.63
Fat	25.54	36.96	38.02	36.19
Cellulose	9.01	3.09	2.06	3.26
Sulphur	1.28	1.50	1.48	1.30
Nitrogen	4.38	4.94	5.01	4.31
Albuminoids	26.50	29.81	30.25	26.06
Myrosin and Albumin	5.24	6.46	6.78	6.14
Soluble Matter	24.22	31.64	32.78	31.41
Volatile Oil.....	0.473	1.437	1.500	1.381
Potassium Myronate.....	1.692	5.141	5.366	4.940
Ash	4.98	5.04	4.84	4.91
„ Soluble.....	1.11	1.01	0.98	0.77

In the process of manufacture, the sifting chiefly removes the husk, and dries the farina, the other constituents being, as it were, concentrated. This is well seen in the amount of volatile oil in brown mustard. Again, the fat, which averages about 25 per cent. in the seeds, reaches 37 per cent. in the farina; the sulphur is increased nearly one-half of one per cent., and so on with the other constituents; while the cellulose falls about two-thirds and the moisture about one-half.

The white seeds differ in composition from the brown, chiefly in not yielding volatile mustard oil, in the fact that the sulphur is lower, and the soluble matters higher in the former than in the latter.

The results of over 40 experiments upon the amount of volatile oil present in brown mustard are here shown, a few of the separate determinations being given :—

							Volatile Oil per cent.
<i>Whole Mustard Seeds</i>	0·486	0·465	0·468	...	Average 0·473
<i>Brown Farina, Superfine</i>		1·439	1·436	...	do. 1·437
<i>Do. do. Fine</i>	1·51	1·49	1·50	...	do. 1·500
<i>Do. do. Seconds</i>	1·358	1·418	1·367	...	do. 1·381

Characteristic Tests.—I. The aqueous extract of white mustard yields with solution of ferric chloride a deep blood-red colouration ; this reaction is so slight as to be scarcely apparent with a similar extract of black mustard.

II. The aqueous extract of white mustard acquires in a few hours a powerful odour of sulphuretted hydrogen : that of the black mustard smells only of the pungent mustard oil.

ANALYSES OF ASH OF MUSTARD SEED.

	White Seeds.		Brown Seeds.
	Yorkshire.	Cambridge.	Cambridge.
Potash	21·29	18·88	21·41
Soda	0·18	0·21	0·35
Lime	13·46	9·34	13·57
Magnesia	8·17	10·49	10·04
Iron Oxide	1·18	1·03	1·06
Sulphuric Acid	7·06	7·16	5·56
Chlorine	0·11	0·12	0·15
Phosphoric Acid.....	32·74	35·00	37·20
Silica.....	1·00	1·12	1·41
Sand	1·82	1·95	1·38
Charcoal	12·82	15·14	7·57
	99·85	100·48	99·70

When the charcoal and sand are deducted, the following is the percentage composition of the ash. An analysis made in 1850 by Way and Ogston of White Mustard is appended :—

	White Seeds. Yorkshire.	White Seeds. Cambridge.	White. Wag & Ogston. 1850.	Brown Seeds. Cambridge.
Potash	24·98	22·64	25·78	23·59
Soda	0·21	0·25	0·33	0·38
Lime	15·79	11·19	19·10	14·95
Magnesia	9·58	12·58	5·90	11·06
Iron Oxide	1·38	1·23	0·39	1·16
Sulphuric Acid	8·28	8·58	2·19	6·12
Chlorine	0·12	0·14	trace.	0·16
Phosphoric Acid.....	38·48	41·97	44·97	40·99
Silica	1·17	1·34	1·31	1·55
	99·93	99·92	99·97	99·96

The ash for analysis was obtained by careful incineration at a heat below visible redness.

It will be noticed that the ash consists mainly of potassium, calcium and magnesium phosphate, with a very minute proportion of chlorine; and that no carbonates are present. Practically no difference exists between the ashes of the two varieties, so that no analytical indications can be obtained from the mere examination of that constituent.

We append a few reactions of thio-sinamine likely to prove of interest:—

I. Thio-sinamine dried at 100° is an oily substance, which solidifies when cold after some time. It dissolves readily in hot water, and crystallises therefrom in beautiful tufts of crystals (monoclinic).

II. Treated with nitric acid, it is partially oxidized, though even boiling with the concentrated acid for half-an-hour failed to effect complete decomposition, as evidenced by the percentage of sulphuric acid obtained by precipitating the liquid with barium chloride.

III. Silver nitrate added to an aqueous solution of thio-sinamine gives a white curdy precipitate, which redissolves less and less perfectly until the silver salt is in excess, when the precipitate remains permanent.

IV. Mercuric chloride gives a reaction precisely similar to silver nitrate.

V. Platinic chloride gives an abundant curdy orange-yellow coloured precipitate, which does not redissolve in the excess of thio-sinamine, nor in cold water. In hot water it dissolves after first melting and floating to the surface, and on cooling separates as an opaque mass of the consistence of balsam tolu, in which condition it remains. This salt, as well as the two before mentioned, is readily soluble in alcohol.

VI. Mayer's reagent ($\text{HgI}_2 + \text{KI}$) yields a dirty white coloured precipitate, which coheres in a few hours to form a number of oily drops. This change occurs at once on heating. The precipitate is only slightly soluble in either hot or cold water.

VII. Nessler's solution gives an insoluble yellow precipitate.

VIII. Picric acid only affords a precipitate in strong solutions.

For kindly placing at our disposal the various samples of mustard seeds and farinas, we are indebted to Messrs. Keen, Robinson, Bellville & Co., to whom we return our best thanks.
