TABLE III.—PROXIMATE ANALYSIS CALCULATED FOR THE MATERIALS IN THEIR NATURAL MOIST CONDITION.

	Water.	Ash.	Protein (N × 6.25).	Woody fiber.	Cellulose.	Fats.	Starch.	Undetermined.	Ash, protein, fats, woody fiber, water, cellulose.	Starch by difference.
Broccoli	91.69	0.58	2.53	1.02	0.96	0.24	2.63	0.60	96.77	3.23
Brussels sprouts	89.27	0.56	2.84	1.12	1.05	0.07	4.29	0.80	94.91	5.09
Rice	80.93	0.06	0.13	0.02	0.09	0.01	16.87	0.89	82.24	17.76
Rhubarb	95.25	0.56	0.61	0.75	0.77	0.09	1.74	0.23	98.03	1.97
Macaroni	66.13	0.23	5.59	0.23	0.14	0.11	27.90	...	72.43	27.57
Lentils	66.04	0.70	8.82	0.45	0.82	0.19	20.53	2.45	77.02	22.98
Asparagus	93.04	0.70	2.08	0.64	1.18	0.09	2.10	0.17	97.73	2.27
Leeks	86.12	0.80	1.45	1.53	1.52	0.13	7.80	0.65	91.55	8.45
Oatmeal (water)	72.54	1.16	3.74	0.59	0.13	1.84	18.48	1.72	79.80	20.20
Oatmeal (milk)	64.74	1.55	4.39	0.40	0.84	2.10	25.96	0.02	74.02	25.98
Peas	62.18	0.67	9.40	2.21	2.53	0.70	23.16	...	77.69	22.31
Tapioca	80.62	0.09	0.58	0.03	0.04	0.03	16.65	3.55	79.80	20.20
Green artichokes	84.72	1.15	2.95	1.01	1.70	0.26	7.68	0.53	91.79	8.21
Petit pois	84.18	0.63	4.28	2.13	1.42	0.06	8.92	...	92.70	7.30
Baked beans	69.85	1.78	4.99	1.20	0.20	0.19	21.69	2.10	76.21	23.79

Clifton, Bristol, England.

INVESTIGATION OF THE BODIES CALLED FIBER AND CARBOHYDRATES IN FEEDING-STUFFS, WITH A TENTATIVE DETERMINATION OF THE COMPONENTS OF EACH.[1]

BY P. SCHWEITZER.

Received December 30, 1903.

THE results of a continuation and extension of the work of which a preliminary part was published in the Annual Report of the Missouri Agr. Expt. Station for 1898 are here presented. Ten substances—two of corn stalks, two of corn leaves, three of timothy hay, two of red clover, and one of blue grass—were selected for the purpose. The character and composition of these, as ascertained by the Official Agricultural Chemists' method, all determinations being in duplicate and made with great care under conditions as nearly alike for the same groups of bodies

[1] Read at the St. Louis meeting of the American Chemical Society. The larger part of the laboratory work was done by Mr. W. B. Cady.

in the different feeds as it was possible to maintain, are tabulated in Table I. The carbohydrates are, of course, given by difference and, for comparison's sake, the percentages also of the fibers by the chlorate and bromine methods. Both of these methods, described by Dr. Hugo Müller under Pflanzenfaser on pages 26 and 27 of the "Bericht über die Entwickelung der chemischen Industrie, 1877, by Dr. A. W. Hofmann," were modified, as necessity seemed to require, yet without, it is believed, seriously interfering with the quantitative production of a fairly pure fiber.

The percentages of fiber by the three methods are, as was expected, different and may be compared in Table II, which is calculated for water and ash-free material. The differences in the fibers affect, of course, also the carbohydrates and, while the official and chlorate methods yield results that, by averaging, come near one another, those by the bromine method are much higher for fiber and correspondingly lower for carbohydrates, through retaining the pectose bodies, shown in the published preliminary investigation to be present.

The percentages of ash in the fibers are quite large and are given, along with the nitrogen, as averages for each ten samples at the bottom of the table.

The Ultimate Composition of the fibers[1] obtained by the three methods is given in Table III, calculated for ash, nitrogen and water-free material; that of the portions dissolved by the Schweizer reagent and precipitated by hydrochloric acid is added for the sake of comparison. It will be seen that in no instance do we deal with chemically pure cellulose; the oxygen falls in twenty-nine of the thirty analyses below the requirements of the hydrogen to form water and it would, therefore, be plainly useless to construct any symbols for the fibers analyzed. The bodies recovered from their solution in the ammoniacal copper solution, likewise, differ slightly from one another, yet, on the whole, they are what G. Bumcke and R. Wolfenstein[2] call the lactone of the acid cellulose, the percentage composition of which is closely approached by the average of the three analyses given.

[1] The requisite quantity of fiber by each of the three methods was prepared by treating successively 2 grams of the material until about 6 grams of crude fiber was obtained. This, finely ground, furnished the material for this and the other work of the investigation.

[2] *Ber. d. chem. Ges.*, **32**, 4293.

If symbols for these compounds were to be offered, they might be as follows:

$C_{44}H_{70}O_{37}$ by O. A. C. method $C_{43}H_{68}O_{38}$ by chlorate method $C_{43}H_{68}O_{37}$ by bromine method	*Percentage Composition:* C = 43.64 H = 6.34 O = 50.02
$C_{36}H_{60}O_{31}$ B. & W.'s lactone.	C = 43.73 H = 6.07 O = 50.20

The Calorific Values of the different fibers, ascertained by the bomb-calorimeter with completely dried material, may be averaged for each of the three methods and compared with that for pure cellulose. The official method produces a product richer in carbon than the others caused, probably through retaining a greater quantity of encrusting material; the values, in calories per gram, are:

Fiber by O. A. C. method (average)	4408.
Fiber by chlorate method (average)	4249.
Fiber by bromine method (average)	4170.
Cellulose	4200.

Treatment of the Crude Fiber with the Schweizer Reagent.— The reagent itself was prepared in the following manner: 300 grams of chemically pure copper sulphate were dissolved in 6 liters of water, 30 grams of ammonium chloride added and the copper hydroxide precipitated by cautious additions of a dilute solution of sodium hydroxide to slight excess. The precipitate was then washed free from alkali by decantation and dissolved by strong ammonia so as to yield a fluid containing about 15 per cent. of the latter.

One-half gram of the water-free fiber was then digested for twenty-four hours in a closed flask of 200 cc. capacity with 100 cc. of the reagent with frequent shaking. Water was then added and the solution filtered through asbestos by means of the suction-pump and, after sufficient washing, the residue dried to constant weight at from 100° to 105° C. The filtrate, in turn, was acidulated with hydrochloric acid and set aside for twenty-four hours, when the liquid was carefully decanted off, and the precipitate finally washed on the filter and dried and weighed. The operations described were in all cases slow and difficult, especially so with the materials from Nos. 1411 and 1425, as the undissolved residues, as well as the re-precipitated cellulose materials, were all more or less gelatinized and required special precautions for

successful washing. The direct weighing of the two bodies, however, permitted now the estimation, by difference, of the amount of the fiber dissolved by this reagent, as well as the amount kept in solution after acidulation. All operations were conducted as nearly alike in manner, time and strength of solution used, as was possible, and the results may be taken as fairly accurate and comparable.

It is seen from Table IV that the action of the O. A. C. method on the fibers is not as powerful as that of the chlorine and bromine methods; for the average percentage of the fibers undissolved by the former is 14.07, while amounting to only 2.29 and 3.28 in the cases of the others. Corresponding to these effects, we find the hydrolyzed or inverted portions of the materials by the three methods to be 10.32, 14.14 and 24.96 per cent. of the original amounts operated upon.

Furfural Obtained from Feeds and Fibers.—Two grams of finely ground dry substance were brought into an Erlenmeyer flask of 300 cc. capacity, connected with a Liebig condenser and separatory funnel by a 2-hole rubber stopper, and 100 cc. of hydrochloric acid of specific gravity 1.06 were added. The flask was then heated on wire gauze so that about 30 cc. distilled over every fifteen minutes; with every such portion having passed over, 30 cc. of the acid were added so as to enter the flask at about the same rate as the distillate left it, keeping the contents of the flask throughout as near 70 cc. as possible. The flask was shaken from time to time to bring down the particles that would adhere to its sides.

The distillation was continued until a drop of the distillate on a slip of filtering paper, moistened with aniline acetate, gave no red coloration, yielding in the cases here described from 250 cc. to 350 cc. of furfural-containing liquid. The distillate was then neutralized with sodium carbonate, made slightly acid with acetic acid and brought up to 500 cc. with a salt solution of 208 grams of salt to the liter, and 10 cc. of phenyl hydrazine acetate added (10 grams of phenyl hydrazine, 7.5 grams of glacial acetic acid to 100 cc. of solution). The whole was then stirred for one-half hour with a rubber-tipped stirring rod when the hydrazone began to separate out in fine orange-red crystals; set aside for twenty-four hours, the precipitate was now collected in a Gooch

crucible on asbestos by aid of the suction-pump and washed with 100 cc. of water; the precipitate being slightly soluble, the same amount of wash-water was used in every instance. The hydrazone could be removed without difficulty from the sides of the beaker by means of the stirring rod, except in a few cases where it seemed to be gummy and had to be dissolved by alcohol; in these the alcoholic liquid was evaporated and the slight residue weighed separately. The suction-pump was run five minutes after washing the main precipitate so as to remove most of the water, when it was placed for three hours in a vacuum oven heated to 65° to 70°, while a current of dry air passed slowly over it. At the expiration of this time, crucible and contents were cooled and weighed, the contents dissolved with warm alcohol, the crucible dried and weighed again and the difference in weight taken as furfural hydrazone, from which, by multiplication with 0.538, the furfural itself was derived. The method, as tested with known weights of furfuramid, especially prepared for this purpose, gave sufficiently reliable and accurate results and was, on the whole, not excessively troublesome.[1]

From the values thus obtained the percentages, and weights in grams from so much of the fibers as are contained in 100 grams of the feeds, are found and from these again percentages and quantities of pentosan in the feeds are derived by multiplication with 1.84 and given in Table V.

The Determination of Sugar and Starch in the nine samples of feed (the material of No. 1426 had unfortunately given out) was made by washing out the sugar with cold water and inverting it, as also the residue, by the usual O. A. C. method and making the calculations from the weights of the reduced copper. The correction for starch was made by subtracting from the reduced copper, as found, the quantity of it reduced by the pentosan, *i. e.*, the pentosan which was readily invertible, not the portion remaining with the fiber and subsequently determined by treatment with stronger acid. The values are given in Table VI.

[1] The furfuramid, after recrystallization, was drained, pressed between filtering paper and carefully air-dried. One gram of it should yield 1.0746 grams of furfural. Experiment yielded in two trials, taking in each case 0.5 gram (0.3224 gram of furfural), 0.3012 gram and 0.2359 gram. A third and fourth determination, made with 2 grams of feed (No. 1416), to which had been added 2 grams of furfuramid (0.2149 gram furfural), yielded respectively 0.4140 gram and 0.4455 gram furfural or, subtracting that from the feed itself 0.1822 gram and 0.2137 gram. Considering the difficulty of obtaining perfectly dry and undecomposed furfuramid, the results are acceptable.

The Conclusions of the Investigation are tabulated in Table VII and will be readily understood. The contents of the feeds by the O. A. C. method in fiber and carbohydrates, the latter, of course, by difference, are placed at the head and, below, follow the true values for fiber with such individual carbohydrate components as could be determined by a combination of methods. The true value for fiber is the crude fiber less the furfural-yielding complex retained by it, calculated as pentosan. In this, then, a differentiation in the two groups of bodies occurring in crude fiber has been made, resulting in a more correct value for fiber as well as for carbohydrates. In the table, this pentosan is given separately as fibro-pentosan to indicate its origin.

As pectoses, are counted the substances remaining with the fiber by the bromine method and removable by treatment with acid and alkali, as shown in the paper published in the annual report previously referred to. The fiber values by the O. A. C. method subtracted from those of the bromine method furnished, consequently, the values of pectose which, on comparison, agree fairly well with those from similar material in 1898. These pectoses are now found to yield furfural as well as the fibers, for on subtracting one fiber from the other we subtract also, of course, the pentosan retained by it and, as the latter fiber yields a much larger amount of this than the former, the difference must be attributed to the pectose complex; it is indicated in the table as pecto-pentosan and made to serve, by difference again, to yield the pentosan derived, in part from sugar and starch, but in the main from the carbohydrates of unknown composition and character present.

A comparison of these three values is not without interest, averaging for the ten feeds as follows:

13.43 per cent. of pentosan from fiber;
26.23 per cent. of pentosan from pectose;
54.73 per cent. of pentosan from indefinite carbohydrates.

The need of additional investigation in certain definite directions is seen plainly.

TABLE I.—PERCENTAGE COMPOSITION OF FEEDS (O. A. C. METHOD) CALCULATED FOR WATER-FREE MATERIAL.

Mark.	No.	Water.	Albuminoid nitrogen.	Amido nitrogen.	Protein.	Ether extract.	Crude fiber.			Carbohydrates.	Ash.
							O. A. C. method	Chlorate method.	Bromine method.		
Corn stalks, just before blooming	1427	9.14	0.858	0.547	8.810	2.730	26.36	30.61	40.24	55.79	6.31
Corn stalks, seed in dough	1464	5.62	0.445	0.016	2.880	1.710	34.20	36.10	44.61	54.73	6.48
Corn blades, just before blooming	1426	7.82	2.690	0.500	19.940	4.570	20.57	24.05	35.35	45.50	9.42
Corn blades, seed in dough	1465	7.63	1.450	0.110	9.750	3.550	21.04	24.42	33.72	53.27	12.39
Timothy, just heading	1412	7.85	0.928	0.532	9.120	2.520	32.44	32.65	48.99	49.58	6.34
Timothy, coming into bloom	1416	7.95	1.130	0.080	7.560	3.280	34.66	35.82	47.03	46.62	7.88
Timothy, seed ripe	1463	7.59	0.666	0.016	4.260	2.220	36.31	33.48	43.00	52.55	4.66
Red clover, in bloom	1411	8.03	2.110	0.800	18.130	5.360	23.38	23.23	28.17	45.39	7.74
Red clover, seed ripe	1425	8.95	1.780	0.170	12.310	4.050	30.00	26.62	39.10	46.95	6.69
Blue grass, seed ripe	1413	7.54	1.090	0.110	7.500	2.950	33.99	32.73	46.74	47.97	7.59

TABLE II.—PERCENTAGES OF CRUDE FIBER AND CARBOHYDRATES, CALCULATED FOR ASH AND WATER-FREE MATERIAL.

	O. A. C. method.		Chlorate method.		Bromine method.	
No.	Fiber.	Carbohydrates.	Fiber.	Carbohydrates.	Fiber.	Carbohydrates.
1427	28.14	59.55	32.67	55.01	42.95	44.73
1464	36.57	58.52	38.60	56.49	47.70	47.39
1426	22.71	50.23	26.55	46.39	39.00	33.94
1465	24.02	60.80	27.87	56.94	38.49	46.33
1412	34.64	52.94	34.86	52.71	52.31	35.26
1416	37.62	50.61	38.88	49.35	51.05	37.18
1463	38.08	55.12	35.12	58.09	45.10	48.10
1411	25.34	49.20	25.18	49.36	30.53	44.01
1425	32.15	50.32	28.53	53.94	41.90	40.56
1413	36.78	51.91	35.42	55.44	50.58	40.28
	Average per cent. of ash and nitrogen in fibers.					
	0.705		1.328		0.839	

TABLE III.—ULTIMATE COMPOSITION OF THE CRUDE FIBERS BY THE THREE METHODS, CALCULATED FOR ASH, NITROGEN, AND WATER-FREE MATERIAL.

	O. A. C. method.			Chlorate method.			Bromine method.		
No.	Carbon.	Hydrogen.	Oxygen.	Carbon.	Hydrogen.	Oxygen.	Carbon.	Hydrogen.	Oxygen.
1427	44.35	6.50	49.15	44.95	6.32	48.73	44.43	6.40	49.17
1464	44.73	6.25	49.02	44.81	6.38	48.81	44.03	6.18	49.79
1426	44.48	6.39	49.13	42.90	6.31	50.79	44.55	6.62	48.83
1465	46.17	6.74	47.09	45.12	6.39	48.49	44.79	6.57	48.64
1412	44.22	6.57	49.21	44.72	6.38	48.90	44.14	6.22	49.64
1416	44.47	6.48	49.05	44.98	6.54	48.48	44.49	6.41	49.10
1463	44.98	6.39	48.63	44.83	6.43	48.74	44.06	6.48	49.46
1411	46.55	6.42	47.03	44.43	6.39	49.18	44.61	6.50	48.89
1425	47.06	6.54	46.40	45.05	6.45	48.50	44.99	6.48	48.53
1413	44.72	6.40	48.88	44.89	6.47	48.64	44.50	6.73	48.77
	Composition of that part of the fiber dissolved by and reprecipitated from the Schweizer reagent.								
	44.06	6.59	49.35	43.00	6.28	50.72	43.85	6.15	50.00

TABLE IV.—TREATMENT OF THE CRUDE FIBERS WITH AMMONIACAL COPPER SOLUTION. PERCENTAGES OF UNDISSOLVED FIBER AND OF CELLULOSE RECOVERED BY PRECIPITATION; ALSO, BY DIFFERENCE, THE PERCENTAGES OF DISSOLVED AND HYDROLYZED SUBSTANCE.

	O. A. C. method.				Chlorate method.				Bromine method.			
No.	Undissolved.	Dissolved.	Reprecipitated	Hydrolyzed.	Undissolved.	Dissolved.	Reprecipitated.	Hydrolyzed.	Undissolved.	Dissolved.	Reprecipitated.	Hydrolyzed.
1427	1.00	99.00	92.38	6.62	0.00	100.00	80.00	20.00	0.10	99.90	74.80	25.10
1464	5.62	94.38	78.18	16.20	1.60	98.40	88.80	9.60	1.09	98.91	78.40	20.51
1426	4.82	95.18	89.40	5.78	2.80	97.20	82.50	14.70	1.64	98.36	71.48	26.88
1465	3.90	96.10	80.00	16.10	1.92	98.08	87.00	11.08	3.40	96.60	67.27	29.33
1412	5.40	94.60	82.40	12.20	3.20	96.80	79.04	17.76	3.42	96.58	68.80	27.78
1416	12.50	87.50	78.80	8.70	3.56	96.44	86.00	10.44	5.62	94.38	71.40	22.98
1463	26.48	73.52	62.50	11.02	0.40	99.60	88.00	11.60	3.40	96.60	69.00	27.60
1411	34.58	65.42	57.20	8.22	3.20	96.80	80.00	16.80	4.60	95.40	74.10	21.30
1425	34.48	65.52	58.00	7.52	3.40	96.60	81.48	15.12	6.30	93.70	68.40	25.30
1413	11.90	88.10	77.20	10.90	2.80	97.20	82.90	14.30	3.20	96.80	74.00	22.80

TABLE V.—PER CENT. OF PENTOSANS IN DRY AND ASH-FREE MATERIAL, CALCULATED FROM FURFURAL; FACTOR 1.84.

	Per cent. of pentosan in feed and fiber.				Grams of pentosan in fiber from 100 grams of feed.		
		Fibers by					
No.	Feed.	O. A. C. method.	Chlorate method.	Bromine method.	O. A. C. method.	Chlorate method.	Bromine method.
1427	23.13	16.93	13.91	25.74	3.74	4.52	11.00
1464	27.25	14.94	16.80	24.14	5.43	6.41	11.47
1426	23.39	16.85	17.26	29.02	3.79	4.41	11.23
1465	25.10	15.11	19.45	30.54	3.53	5.20	11.27
1412	17.46	13.21	19.34	24.49	4.56	6.65	12.74
1416	23.15	13.01	16.71	23.64	4.87	6.41	12.01
1463	25.23	15.33	15.84	27.51	5.79	5.51	12.34
1411	14.06	11.94	9.81	16.87	3.00	2.44	5.11
1425	16.65	12.84	11.42	21.67	4.11	3.23	8.96
1413	23.90	13.28	19.83	26.64	4.86	6.93	13.38
Average,	21.93	14.04	16.04	25.03	4.37	5.17	10.95

TABLE VI.—PER CENT. OF SUGAR AND STARCH IN WATER AND ASH-FREE FEEDS.

Per cent. of		Starch and pentosans calculated as starch.
Sugar.	Starch.	
20.69	...	19.39
2.31	1.42	23.56
...	...	....
3.20	2.02	23.89
2.91	9.24	21.99
3.16	6.12	24.96
3.82	6.19	26.29
3.86	12.01	23.56
4.58	4.84	17.46
3.45	6.34	24.39

TABLE VII.—PER CENT. OF CRUDE FIBER AND CARBOHYDRATES IN THE WATER AND ASH-FREE FEEDS BY O. A. C. METHOD, AND OF SPECIAL CONSTITUENTS BY THE COMBINATION OF METHODS PURSUED IN THIS INVESTIGATION.

Number of sample	1427	1464	1426	1465	1412	1416	1463	1411	1425	1413
Crude fiber	28.14	36.57	22.71	24.02	34.64	37.62	38.08	25.34	32.15	36.78
Carbohydrates	59.55	58.52	50.23	60.80	52.94	50.61	55.12	49.20	50.32	51.91
Total,	87.69	95.09	72.94	84.82	87.58	88.23	93.20	74.54	82.47	88.69
Pure fiber	24.40	31.14	18.92	20.49	30.08	32.75	32.29	22.34	28.04	31.92
Fibro-pentosan	3.74	5.43	3.79	3.53	4.56	4.87	5.79	3.00	4.11	4.86
Pectose	7.55	5.09	8.85	6.73	9.49	6.29	0.47	3.08	4.90	5.28
Pecto-pentosan	7.26	6.04	7.44	7.74	8.18	7.14	6.55	2.11	4.85	8.52
Pentosan	12.13	15.78	12.16	13.83	4.72	11.14	12.89	8.95	7.65	10.52
Sugar	20.69	2.31		3.20	2.91	3.16	3.82	3.86	4.58	3.45
Starch	....	1.42	21.78	2.02	9.24	6.12	6.19	12.01	4.84	6.34
Indefinite carbohydrates	11.92	27.88		27.28	18.40	16.76	25.20	19.19	23.50	17.80
Total,	87.69	95.09	72.94	84.82	87.58	88.23	93.20	74.54	82.47	88.69