

ratio as regards ferrocyanide becomes  $6Zn = 5Cd$ , and the strength of the solution used would be 1 cc. = 0.00838 gram cadmium.

Our results in acid solutions are intermediate between these values and indicate a variation in the composition of the precipitate between the formulas of Hermann and of Wyruboff. They are confirmed by a statement by Mackay<sup>1</sup> that it requires about  $2\frac{1}{2}$  per cent. less potassium ferrocyanide to precipitate cadmium than is required by the formula  $CdK_2Fe(CN)_6$ , or in other words the cadmium standard is higher than would be obtained by calculation. They are again in direct contradiction to the statement by Furman that the cadmium standard can be obtained from the zinc standard by direct proportion assuming that  $2Zn = 2Cd$ .

In order to ascertain the composition of cadmium ferrocyanide under different conditions analyses of the precipitates must, of course, be made. This work has already been started and while no results have yet been obtained the marked difference in the physical properties of the precipitates seems to confirm the variation in composition.

COLUMBIA UNIVERSITY,  
June 27, 1900.

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[CONTRIBUTION FROM THE LABORATORY OF THE NORTH CAROLINA  
AGRICULTURAL EXPERIMENT STATION.]

## THE DIGESTIBILITY OF SOME NON-NITROGENOUS CON- STITUENTS OF CERTAIN FEEDING-STUFFS.<sup>2</sup>

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THE ether extract, protein, nitrogen-free extract, and crude fiber, which are determined in ordinary feeding-stuff analyses, are groups of compounds, and are composed of various substances with different properties and different coefficients of digestibility. The ether extract may contain (besides the true fats) waxes, cholesterin, phytosterin, lecithin, hydrocarbons, coloring-matters, etc. "Protein" includes amido compounds, acid amides, organic bases, ammonia, and nitrates, besides proteids of varied nature, one of which, nuclein, is entirely indiges-

<sup>1</sup> This Journal, 21, 940 (1899).

<sup>2</sup> This work was suggested to the author by Prof. W. A. Withers, Chemist of the Station. See Bulletin 172.

tible. The nitrogen-free extract may contain sugars, dextrin, gums, starches, pentosans, coloring-matters, organic acids, lignocellulose and cellulose, the two latter remaining in part in the crude fiber. The crude fiber contains cellulose, lignocellulose, etc. Considering the number of substances which may enter into the composition of the fodder-groups, and the variations which take place in the quantity present, it is not surprising that the digestibility of these groups differs greatly with different feeding-stuffs.

The digestibility of some of the proximate constituents of feeding-stuffs has been determined, or, more correctly, groups of proximate constituents, namely, the sugar group, the starch group, and the pentosan group. All three of these groups have not been determined on the same material. The work about to be described in this paper has given a basis for calculating the digestibility of certain proximate groups, which can be arranged in the following tentative order, according to their digestibility: Sugars, starches, pentosans, crude fiber, residual nitrogen-free extract, and pentosans in the crude fiber. The number of digestion experiments made is not large, but it is not believed that future experiments will materially modify the order above given. This Station expects to continue the work along this line.

The materials used in this work are from digestion experiments on sheep, one described in Bulletin 148 of this Station, six described in Bulletin 160, one not yet published. Excepting timothy hay No. 1, all figures are means of experiments with two sheep.

#### DIGESTIBILITY OF SUGARS.

W. H. Jordan, J. M. Bartlett, and L. H. Merrill, at the Maine Experiment Station,<sup>1</sup> found that the sucrose and reducing sugars in alsike clover, white clover, blue joint, orchard grass, red top, timothy, wild oat grass, witch grass, buttercup, and white weed were completely digested. E. F. Ladd, at the New York (Geneva) Experiment Station,<sup>2</sup> found the sucrose and reducing sugars to be completely digested in alfalfa hay, mixed hay, wheat bran, corn-meal, cottonseed-meal, linseed-meal, and oats; the

<sup>1</sup> Report 1888, 98.

<sup>2</sup> Report 1889, 149.

sucrose in turnips fed with mixed hay was digested only 78.7 per cent., the reducing sugars being completely digested. B. W. Kilgore and F. E. Emery, at the North Carolina Station,<sup>1</sup> found the reducing sugars completely digested in corn-fodder, crimson clover hay, cowpea vine hay, soja-bean silage, cottonseed, and cottonseed hulls. H. C. Sherman<sup>2</sup> found the glucose and sucrose (soluble carbohydrates) of wheat bran digested 96.7 per cent., the feces containing 0.7 per cent.

Twenty-three excrements from a number of digestion experiments made at this Station were tested for sugars in the usual way, after treating the solution with lead acetate. In twelve of them, traces of copper were reduced, corresponding to from 0.04 to 0.20 per cent. of sugars, with a mean of 0.09 per cent. This reduction is not believed to be caused by sugars, but by other reducing matters, as is plain from the following experiment: Excrement 1376, from corn silage, giving 0.15 per cent. apparent sugars; excrement 1377, from corn silage, 0.05 per cent. sugars; excrement 1411, from timothy hay, 0.20 per cent. sugars; and excrement 1437, from sorghum fodder, 0.14 per cent. sugars were taken. Fifty grams of each were digested with 500 cc. cold water, filtered, and washed with about 1000 cc. water. Basic lead acetate was added in excess, filtered, and the filtrate evaporated to about 25 cc. on a water-bath, organic matter separating. The lead was removed with sodium carbonate, filtered off, and the filtrate made up to 100 cc. Twenty-five cc., corresponding to 12.5 grams excrement, and about seventeen times as much as was used in the preliminary test, gave no trace of either sucrose or dextrose in any of the four excrements. The reducing substances probably separated during the evaporation. The traces of copper oxide were probably not due to reduction by sugars.

The twenty-three excrements were as follows: From crabgrass hay, crabgrass hay and pea-meal (2), crabgrass hay and corn bran (2), green rape (3), crabgrass hay and rice bran (2), cat-tail millet (2), sorghum fodder (2), crimson-clover hay, soja-bean silage, corn silage (4), timothy hay (2), corn fodder. In

<sup>1</sup> Technical Bulletin No. 4.

<sup>2</sup> This Journal, 19, 291.

the twelve materials and twenty-three experiments, sucrose and reducing sugars were completely digested.

Taking all the experiments into consideration, it is found that in thirty materials and forty-one experiments, reducing sugars are invariably digested completely, and in twenty-eight of the thirty materials, and thirty-nine of the forty-one experiments, sucrose is completely digested. The assertion that sugars are, as a rule, completely digested may be taken as established.

The determination of sugars is important with hays, and cottonseed-meal; less so in the case of the starchy foods. Hays contain a moderate amount of sugars; for example,<sup>1</sup> red clover (average of 21) contains 6.36 per cent., timothy hay (average of 21) 8.44 per cent., sorghum 21 per cent., corn fodder 3.9 per cent.; cottonseed-meal contains 9.22 and 7.94 per cent. raffinose, being 33.5 and 32.9 per cent. of the nitrogen-free extract, respectively. If the sugar in the hays is subtracted from the nitrogen-free extract, and then the digestibility of the latter is calculated, a considerable decrease is often found. The digestibility of nitrogen-free extract, containing sugars, is 71.8 in alfalfa hay; if sugar is subtracted, it is 68.5, a decrease of 4.6 per cent. With mixed hay, the decrease is from 55.5 to 40.4, a decrease of 27 per cent.; with timothy hay, from 60.3 to 53.5, or 11 per cent., and 56.2 to 51.1, or 9.1 per cent.; with green rape, from 93.8 to 92.5, or 1.4 per cent.; and with cottonseed-meal, from 61.5 to 42.5, the enormous decrease of 31 per cent. These figures may serve to emphasize the importance of determining sugars. The calculations and details of all these experiments are published in Bulletin No. 172 of this Station.

#### DIGESTIBILITY OF PENTOSANS.

The furfural produced by distillation of feeding-stuffs with hydrochloric acid comes, for the most part, from pentosans; *i. e.*, bodies which yield pentose sugars on hydrolysis. Other bodies than true pentosans are found in plants, which are decomposed with formation of furfural, such as the oxycelluloses and lignocelluloses. The latter are usually described as mixtures of cellulose and incrusting substance, or lignin.

The true pentosans are, presumably, dissolved by dilute acids

<sup>1</sup> E. F. Ladd: *Am. Chem. J.*, 10, 49.

and alkalis, and hence are contained in the nitrogen-free extract, but the oxycelluloses and lignocelluloses are partly attacked by these reagents also. The furfural from the crude fiber may be considered as originating from the latter bodies, to which the name pseudopentosans may be given.

W. E. Stone<sup>1</sup> determined the digestibility of total pentosans in a number of feeding-stuffs, titrating the furfural distillate with phenylhydrazine, and using Fehling's solution as an indicator. The per cent. of pentosans digested was found to be: in timothy hay, 48.0 and 49.5 per cent.; ditto early bloom, 60.4 and 54.6 per cent.; ditto late cut, 62.8 and 48.2 per cent.; *Danthonia spicata*, 68.6 per cent.; *Agrostis vulgaris*, 70 per cent.; *Calamagrostis canadensis* 90.4 per cent.; *Triticum repens*, 59.9 per cent.; Hungarian grass, 68.2 per cent.; *Trifolium hybridum*, 56.8 per cent.; corn fodder, northern, 76.6 per cent.; ditto southern corn, 69.6 per cent.; timothy hay and sugar-beets, 71.3 per cent.; timothy hay and rutabagas, 57.1 per cent.; timothy hay and wheat bran, 45.6 per cent.; timothy hay and gluten meal, 59.1 per cent.; *Agrostis vulgaris* and wheat bran, 54.1 per cent.; ditto and wheat middlings, 64.9 per cent. Excluding *Calamagrostis canadensis*, the average digestibility of the pentosans in the nineteen substances is 60.3 per cent., with a minimum of 45.6 and a maximum of 71.3 per cent.

J. B. Lindsay and E. B. Holland<sup>2</sup> have determined the digestibility of pentosans in the following materials: Hay of mixed grasses, (a) 63 per cent., (b) 62 per cent.; Buffalo gluten feed, 78 per cent.; new process linseed-meal, 89 per cent.; old process linseed-meal, 84 per cent.; corn cobs, 62 per cent.; dried brewer's grains, 55 per cent.; spring-wheat bran, 62 per cent.; winter-wheat bran, 64 per cent. The mean is 68.8 per cent.

H. C. Sherman<sup>3</sup> found the digestibility of pentosans in wheat bran to be 66.2 per cent.

Determination of the total pentosans and pentosans in the crude fiber (pseudopentosans) have been made in feeding-stuffs, wastes, and excrements from digestion experiments made at this Station. The method of determining pentosans used is, in

<sup>1</sup> *Agr. Science*, 7, 6.

<sup>2</sup> *Ibid.*, 8, 172.

<sup>3</sup> This Journal, 19, 308.

brief, as follows: Three grams of substance in a side-necked flask on a wire gauze are distilled with 100 cc. of hydrochloric acid of 1.06 specific gravity. When 30 cc. have distilled over, 30 cc. of the acid are run into the flask through a separatory funnel in such a manner as to wash down the particles on its sides. The distillation is continued in this manner until the volume of the distillate is 360 cc. A sufficient quantity of phloroglucinol to precipitate all the furfural, is added, the volume made up to 500 cc., the precipitate collected on a Gooch filter, washed with 100 cc. water, dried to constant weight at 100°, and weighed. The time required to dry the precipitate is from seven to nine hours. Commercial phloroglucinol is used, and is purified by dissolving it in hydrochloric acid of 1.06 specific gravity and allowing the diresorcinol to crystallize out.

In the case of crude fiber, three grams of material were treated, in the usual way for the determination of crude fiber using, however, 300 cc. of the acid and 300 cc. of the alkali. The fiber was then distilled with acid, as described above.

The composition of the feeding-stuffs is given in the table.

COMPOSITION OF FEEDING-STUFFS.

(Dry Matter.)

	Sugars.	Total pentosans.	Pentosans.	Pseudo- pentosans.	Residual N-free extract.
Timothy hay No. 1.....	8.33	24.86	19.71	5.15	16.88
Crabgrass hay No. 1.....	1.89	26.25	21.90	4.35	21.40
Crabgrass hay No. 2.....	2.20	24.71	19.85	4.85	24.09
Cowpea-meal.....	5.66	6.83	6.83	0	52.20
Corn bran.....	2.93	25.15	25.15	0	41.36
Green rape No. 1.....	8.41	10.57	9.57	1.00	29.81
Green rape No. 2.....	7.03	8.71	8.04	0.67	26.04
Rice bran.....	1.56	10.88	9.88	1.00	40.31
Cottonseed-meal.....	7.94	7.83	....	....	....

The pentosans in the crude fiber is, in timothy hay No. 1, 20.7 per cent. of the total pentosans; in timothy hay No. 2, 20.5 per cent.; in crabgrass hay No. 1, 18.4 per cent.; in crabgrass hay No. 2, 19.6 per cent.; in cowpea-meal and corn bran, none; in green rape No. 1, 9.5 per cent.; in green rape No. 2, 7.7 per cent., and in rice bran, 9.2 per cent. It is apparent that the crude fiber of hays contains a large percentage of the pentosans. The pentosans are distributed between the crude fiber and the nitrogen-free extract. The pentosans in the crude fiber

are not here regarded as true pentosans, but are called pseudopentosans; they are different from the pentosans in the nitrogen-free extract, although the line of separation between the two is an arbitrary one. The distribution and digestibility of the pentosans are given in the table. It is seen that from 0 to 21 per cent. of the pentosans are pseudopentosans, and that in four of the five cases the pseudopentosans are less digestible than the pentosans in the nitrogen-free extract. The digestibility of the total pentosans varies from 53 to 95 per cent.

DISTRIBUTION AND DIGESTIBILITY OF PENTOSANS.

	Of 100 parts pentosans		Digestibility of pentosans.		
	True	Pseudo.	Total	True	Pseudo.
Timothy hay No. 1.....	79.3	20.7	55.8	58.1	46.9
Timothy hay No. 2.....	79.5	20.5	55.9	57.0	52.0
Crabgrass hay No. 1.....	81.6	18.4	63.1	61.0	69.9
Crabgrass hay No. 2.....	80.4	19.6	....	....	....
Cowpea-meal <sup>1</sup> .....	100.0	0	76.1	76.1	....
Corn bran <sup>1</sup> .....	100.0	0	71.6	71.6	....
Green rape No. 1.....	90.5	9.5	94.6	95.7	84.6
Green rape No. 2.....	92.3	7.7	91.9	93.2	75.9
Rice bran <sup>1</sup> .....	90.8	9.2	53.5	57.3	....

DIGESTIBILITY OF NITROGEN-FREE EXTRACT.

The composition and digestibility of the nitrogen-free extract is given in the table below. The residual nitrogen-free extract is the total nitrogen-free extract less sugars and pentosans. It varies in quantity from 47 to 85 per cent. of the nitrogen-free extract.

COMPOSITION AND DIGESTIBILITY OF NITROGEN-FREE EXTRACT.

	In 100 parts			Sugars 100 per cent.	Digestibility.	
	Sugars.	Pentosans.	Residue.		Pento- sans.	Resi- due.
Timothy hay No. 1.....	14.9	35.2	49.9		58.1	50.1
Timothy hay No. 2.....	10.5	41.6	47.9		57.0	46.0
Crabgrass hay No. 1.....	4.2	48.4	47.4		61.0	32.7
Crabgrass hay No. 2.....	4.8	43.0	52.2		....	....
Cowpea-meal <sup>2</sup> .....	4.8	10.6	84.6		76.1	97.4
Corn bran <sup>2</sup> .....	4.2	36.2	59.6		71.6	86.1
Green rape No. 1.....	15.2	20.6	64.2		95.7	91.4
Green rape No. 2.....	19.8	18.9	61.3		93.2	86.5
Rice bran <sup>2</sup> .....	3.0	19.1	77.9		57.3	85.0

<sup>1</sup> Calculated from ration with crabgrass hay.

<sup>2</sup> Digestibility calculated from ration with crabgrass hay.

In the timothy hays, the crabgrass hay, and the green rape, the order of digestibility is: sugars, pentosans, residue. In the cowpea-meal, the corn bran, and the rice bran, the order is: sugars, residue, pentosans, but this residue consists most largely, if not entirely of starch, so that we may say that starch is more digestible than pentosans. The order of digestibility of the components of the nitrogen-free extract is, then,—sugars, starch, pentosans, and residue.

#### DIGESTIBILITY OF CRUDE FIBER.

Crude fiber contains from 0 to 21 per cent. of the total pentosans, sometimes as much as 42 per cent.<sup>1</sup> The table below exhibits the composition and digestibility of the crude fiber. In four of the five cases, the pseudopentosans are less digested than the residue, and the residue more so than the total crude fiber, although the difference is not great. The digestibility of the residual nitrogen-free extract has been placed in the table for purposes of comparison. With timothy hay, and crabgrass hay, it is less digestible than the residual crude fiber, in one case more, the other two less, digestible than the pseudopentosans. With the green rape, its digestibility is slightly greater than that of the residual crude fiber. With the starchy foods, its digestibility is greater, as a matter of course, since it consists for the most part of starch.

#### COMPOSITION AND DIGESTIBILITY OF CRUDE FIBER.

	In 100 parts		Digestibility.			Residual nitrogen-free extract.
	Pseudo-pentosans.	Resi- due.	Total.	Pseudo-pentosans.	Resi- due.	
Timothy hay No. 1 .....	9.2	90.8	52.3	46.9	53.3	50.1
Timothy hay No. 2 .....	14.4	85.6	53.8	52.0	54.1	46.0
Crabgrass hay No. 1 .....	13.0	87.0	67.3	69.9	67.0	32.7
Crabgrass hay No. 2 .....	13.4	86.6	....	62.5 <sup>2</sup>	....	....
Cowpea-meal <sup>3</sup> .....	0	100.0	39.2	....	39.2	97.4
Corn bran <sup>1</sup> .....	0	100.0	50.8	....	50.8	86.1
Green rape No. 1 .....	7.7	92.3	90.0	84.6	90.4	91.4
Green rape No. 2 .....	6.3	93.7	84.0	75.9	84.6	86.5
Rice bran <sup>1</sup> .....	8.3	91.6	19.1	....	19.1	85.0

While, therefore, the order in the series, sugar, starch, pentosans, and residual nitrogen-free extract, is subject to little doubt,

<sup>1</sup> J König: *Landw. Versuch. Stats.*, 48, 93.

<sup>2</sup> Calculated from ration with crabgrass hay.

<sup>3</sup> Calculated from ration with cowpea-meal.



and the order, residual crude fiber, pseudopentosans, is not doubtful, the combination of the two series is more doubtful. The approximate arrangement in the order of digestibility would be sugar, starch, pentosans, residual crude fiber, residual nitrogen-free extract, pseudopentosans, the position of residual crude fiber and pseudopentosans being subject to change.

It is seen that the residual nitrogen-free extract, in three hays at least, is less digestible than the residual crude fiber. Is this an actual or an apparent difference? It is assumed in digestion experiments that those fodder groups which are not digested pass through unchanged, an assumption that must be modified for the nitrogenous matters and the ether extract, since products of metabolism appear in the excrement which fall into these two groups. It is quite possible that crude fiber undergoes some change that renders it soluble in acids or alkalies.

Crude fiber may disappear :

- (1) By formation of soluble compounds and resorption ;
- (2) By decomposition to carbon dioxide and marsh gas ;
- (3) By decomposition with the formation of carbon dioxide and marsh gas, and soluble products which are resorbed ;
- (4) By decomposition with formation of products which are not resorbed, and are soluble in hot acids or alkalies, hence goes into the nitrogen-free extract.

Besides the sugars, starches, gums, etc., the nitrogen-free extract of hays is composed of the less resistant portions of the cell walls, partly made up of pentosans. Our digestion experiments seem to show that the older and more resistant cellular structures (crude fiber) are in many cases digested to a greater extent than the younger and less resistant. To avoid this difficulty, it has been assumed that the more resistant portions are converted by bacteria into gases and soluble products, which are resorbed. This may be part of the truth, but not all of it. We would naturally suppose the less resistant portions—in the nitrogen-free extract—to be attacked by the bacteria first, and the nitrogen-free extract ought to be digested more completely than the crude fiber. The explanation that seems probable is, that the crude fiber and undigested nitrogen-free extract, remaining several days in the intestines under very favorable conditions for the action of micro-organisms, are decomposed, with formation

of gases, of soluble products which are resorbed, and of insoluble products which pass into the excrement, and, being soluble in acids or alkalies, appear in the analysis as nitrogen-free extract. The digestibility of the nitrogen-free extract would appear less than it really is, and that of the crude fiber, greater.

#### ANALYSIS OF FEEDING-STUFFS.

This work has shown that if we take the sugars, starch, and pentosans from the nitrogen-free extract, the residue is sometimes more, sometimes less digestible than the crude fiber, and often the difference is not great. For this reason, in the analysis of feeding-stuffs, it is of more importance to determine sugar, starch, and pentosan, than to determine crude fiber.

E. Schulze<sup>1</sup> has proposed that, in addition to the determination of crude fiber, the non-nitrogenous matters insoluble in ether, alcohol, water, and diastase solution be determined. The residue would consist of the material of cell walls, insoluble proteids, and a portion of the ash. It is corrected for the ash and proteids. This method should not be used in digestion work, since insoluble nitrogen-free extract or crude fiber may have become soluble during its several days' stay in the animal. It may be used when a knowledge of the properties of a feeding-stuff is desired quickly.

#### SUMMARY.

1. Sugars are found in all feeding-stuffs, are completely digested, as a rule, and their determination is of especial importance in the case of hays and cottonseed-meal.

2. The average digestibility of pentosans in thirty-four samples is 64.2. The average for timothy hay (eight samples) is 53.9.

3. The constituents of the nitrogen-free extract may be arranged in the following order according to their digestibility: (1) sugars, (2) starch, (3) pentosans, (4) residue.

4. The pseudopentosans of crude fiber are less digestible than the residue. The residue is sometimes more, sometimes less digested than the residual nitrogen-free extract.

5. Crude fiber may be changed during digestion so as to appear as nitrogen-free extract in the excrement.

6. The determination of sugar, starch, and pentosans is more important than that of crude fiber.

May, 1900.

<sup>1</sup> *Landw. Versuch.-Stats.*, 49, 434.