its reducing effect upon the permanganate, the solution was filtered as above and in the clear filtrate the titration was carried to completion. The results were 10.02, 10.16, and 10.70 per cent. ferrous oxide. Inasmuch as the smallest of these three charges of pyrite was several times greater than what may be considered an unusually high amount for an igneous rock, it is very evident that for all practical purposes the influence of pyrite on the ferrous iron estimation by the Cooke method is negligible. At the same time, it is to be borne in mind that with increased content, either of ferric iron or of pyrite, an increased amount of pyrite will be attacked and that the extent of this attack is undoubtedly influenced by the degree of fineness of the pyrite powder.

All users of the method have noticed the rapid disappearance in hydrofluoric solutions, when titrating ferrous iron, of the pink color produced by an excess of permanganate. If much ferrous iron be present, many cubic centimeters of permanganate can be added without causing more than a transitory pink coloration. The solution takes on, however, in ever-increasing intensity, the red-brown color characteristic of manganic salts. It seems that manganous fluoride in acid solution is very susceptible to oxidation by permanganate, for the above-mentioned changes take place when permanganate is added to sulphuric and hydrofluoric acids containing some manganous sulphate.

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ON THE DIGESTION AND ASSIMILATION OF PENTOSES AND FURFUROIDS.

BY C. F. CROSS, E. J. BEVAN, AND J. S. REMINGTON.

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THE furfural-yielding constituents of plant tissues continue to be designated by the majority of observers as pentosans. It is probable, however, that the group of natural products thus constituted are of more varied characteristics.

It must be noted first that we have no specialized form of pentosane comparable with starch and that the substances described as such are products isolated by chemical processes in the laboratory and devoid of the well-marked individuality and properties of the hexose-anhydride. We are not aware of any evidence upon which the individuality of the best known of the reputed pentosanes, *viz.*, "Holzgummi," has been finally established.[1] Generally this group of substances is investigated in terms of furfural, obtained by boiling with condensing acids ; and the relation of this aldehyde to the pentoses is indirect and of course not exclusive. Several of the now well-known oxidized derivatives of the hexose-carbohydrates are similarly condensed to furfural ; of these we can call to mind: (*a*) Glycuronic acid ; (*b*) the osones or ketoaldoses obtained by Fischer from the osazones and more recently and directly by ourselves by the action of hydrogen peroxide on the hexoses ;[2] (*c*) a number of imperfectly defined products of oxidation of the hexoses and their polyanhydrides obtained both by laboratory and natural processes.[3]

Lastly it must be noted that investigation has failed to identify the pentoses as such occurring in the plant and the conclusion generally accepted at this date with regard to their formation is that they are not direct products of the assimilation process but originate from hexoses by processes of oxidation or internal change.[4]

Complementary confirmation of the exceptional physiological relationships of the pentoses is also supplied by the facts (1) that they are entirely resistant to alcoholic fermentation (yeast) and (2) are not assimilated by animal digestion.

From this brief résumé of the present state of our knowledge we draw the following conclusions: (*a*) That the group of furfural-yielding constituents of plants may comprise in addition to petosans, oxy-hexoses (respectively anhydride) representing intermediate terms of a complex hexosan-pentosan series ; and in view of this probability we prefer as a group designation the term furfuroid, and (*b*) that such oxyhexoses may yield to yeast fermentation and to animal assimilation.

Since these furfuroids are constituents of cellular tissues the question of alcoholic fermentation can only be studied by way of the products of acid hydrolysis. In so far as these products are pentoses they resist fermentation. This has been finally

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[1] "Kohlenhydrate," II, p. 202, Tollens.

[2] *J. Chem. Soc.*, 73, 463 (1898); Morrell Crafts : *Ibid.*, 75, 786 (1899).

[3] *Ber. d. chem. Ges.*, 27, 1061 : Krüger an Tollens : *Ztschr. angew. Chem.*, 1896, Heft 2.

[4] "Kohlenhydrate," II, p. 60.

established by the very careful investigation of Tollens;[1] at the same time we and other observers have studied cases of yeast fermentation in which there has been a considerable disappearance of the furfuroids from solutions in which they exist in a more or less fully hydrolyzed form.

In his investigation of this result Tollens arrives at the conclusion that the disappearance of the furfuroids is accompanied by the appearance of acid products; also that this effect is not inconsistent with the view that the products reacting in this way are pentoses.[2] Still the question is by no means finally elucidated and the incompleteness of the present solutions of the problem involved should be recognized.

In regard to the problem of animal digestion and assimilation we have to notice the results of investigation from two points of view. The pentoses proper have been investigated by Ebstein[3] who found that xylose is not assimilated, being voided in unchanged form in the urine and Salkowski[4] whose observations on arabinose led to the following conclusions: "Von dem jeden Thiere eingegebenen 10 g. Arabinose wurde etwa 1/5 unverändert durch den Harn ausgeschieden: das Blut enthält wenig, die Muskeln reichlich Arabinose. In der Leber fand sich gewöhnliches Glykogen und nicht, wie gehofft ein Pentosan. Die Resorption der Arabinose erfolgt schnell u. vollstandig."[5]

On the other hand the furfuroids of fodder plants have been investigated by a number of observers who have variously estimated the proportion digested at from 40–90 per cent. These numbers represent for the most part the percentage ratio of the furfuroids disappearing in the digestive process, but they do not attempt to deal with the further question of assimilation. This more elaborate problem has recently been solved in a typical case by O. Kellner and A. Kohler.[6] Oxen were fed upon a rye straw which had been previously extracted by boiling with alkaline lye—the product containing:

78.6 per cent. Rohfaser with
31.1 per cent. Furfurol gebende substanz.

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[1] Stone and Tollens: *Ann. Chem.* (Liebig), 249, 257; Tollens: *J. Fed. Inst. Brewing*, 1898, 451.

[2] Tollens: *Ibid.*

[3] *Archiv. Pathol. Anat.*, **129**, 401.

[4] *Central bl. Med. Wiss.*, 1893, No. 11.

[5] *Ber. d. chem. Ges.*, 1893, 896.

[6] Landw. Vers. Stat., 1900, 53, 1, 474.

This product was added to the "Grundfutter" specially designed "zur Deckung des Mindestbedarfes des Thiers". The following results were obtained: Of the total product 95.8 per cent. was digested, and of the total available energy, 63.1 per cent. contributed to the formation of flesh and fat. The "furfuralgebende Substanz" contributed its proportion to the result and generally the cellulosic substance thus prepared has approximately the same feeding characteristics and value as starch.

But we find no records of investigations in which the furfuroids have been previously isolated by processes of acid hydrolysis. In absence of such results the proportions determined above are open to the objection that they are complicated by the unknown factor of digestive hydrolysis. To further elucidate the problem, therefore, we have carried out feeding experiments with the complex of products obtained from brewers' grains by digestion with dilute sulphuric acid (1 per cent. H_2SO_4) in an autoclave at a temperature of 130°. Under these conditions the furfuroids are selectively attacked and constitute 80–90 per cent. of the total soluble extract. The products in this form we have previously investigated and have found to be fully hydrolyzed from the numbers for cupric reduction; *viz.*, 110–120 (dextrose = 100) and yields of osazones.[1]

The acid extract is neutralized ($CaCO_3$), filtered and evaporated. On distillation with hydrochloric acid of 1.06 sp. gr., the extract yielded 39.5 per cent. furfural calculated to the total dry weight. To convert the product into a form in which it could be easily administered to the animal (rabbit) as a foodstuff, it was mixed with a strong solution of gelatin at 20° C. and then with sufficient bread to give, when cold, a solid granular product. With this artificial food was associated a due proportion of fresh vegetable food; *viz.*, carrot and cabbage. The experiments were conducted with the usual precautions, in parallel series, one animal receiving the diet as above, a second receiving this same diet less the artificial furfuroid constituent. The details of the experiment are published elsewhere and need not be reproduced here.[2]

[1] *J. Chem. Soc.*, 1897, 1001–1010.

[2] *J. Soc. Chem. Ind.*, 1900, April 30.

The results obtained established the following high proportion (per cent.) of digestion and assimilation of the total furfuroids of the mixed diet

96.4	98.4	97.3	96.4	94.5

which are certainly minimum numbers for the special group of furfuroids under investigation. No pentoses or other furfural-yielding products were present in the urine, which was examined from time to time.

It may be concluded from these results that the typical furfuroids of cereal tissues when fully hydrolyzed are digested and assimilated by the herbivera as completely as starch and its products of hydrolysis. In this respect they differ from the pentoses and their anhydrides.

In view of these results and the exceptional physiological history of this group of constituents of plant tissues, which is by no means fully elucidated, we consider the term "furfural gebende substance," or more shortly "furfuroid" is to be preferred as a general designation, reserving the term pentosan for its strict use; *i. e.*, as applied to a pentose-anhydride ($H.C_5H_{10}O_5—MH_2O$).

4 NEW COURT, LONDON, AND LANCASTER,
ENGLAND, May 10, 1900.

ESTIMATION OF PYRRHOTITE IN PYRITES ORE.

BY F. B. CARPENTER.

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SINCE the introduction of pyrites into the manufacture of sulphuric acid, industrial laboratories have been frequently called upon to make analyses of pyrites ores to determine their quality for manufacturing purposes. In order to determine the relative value of these ores it is not only necessary to determine their sulphur content, but it is also essential that an estimation be made of those sulphides, which are difficult to decompose in the furnace. Fairly satisfactory methods have been described for the determination of zinc, arsenic, copper, etc., but I have heretofore seen published no satisfactory methods for the estimation of pyrrhotite. It is well known by acid makers that it is difficult to get the sulphur from this material, especially in lump burners, and as it is contained in nearly all our domestic ores to