[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Application of the Cleavage Type of Oxidation by Periodic Acid to Starch and Cellulose[1]

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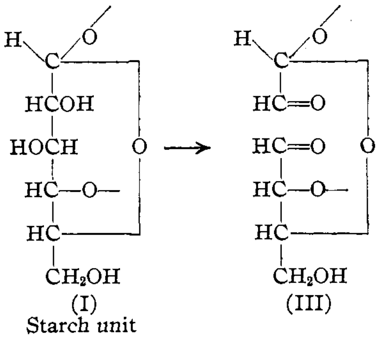
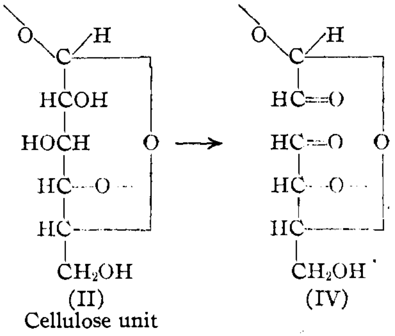
Starch and cellulose, if composed of molecules built predominantly of units having structures (I) and (II), respectively, as is now generally supposed, should be oxidized by periodic acid (Malaprade's reaction) in the manner that we have proved for the methylaldohexosides and the methylaldopentosides,[2] to produce substances of structures (III) and (IV), respectively, where the glycosidic linkage at carbon atom 1 is alpha for starch (I and III) and beta for cellulose (II and IV).





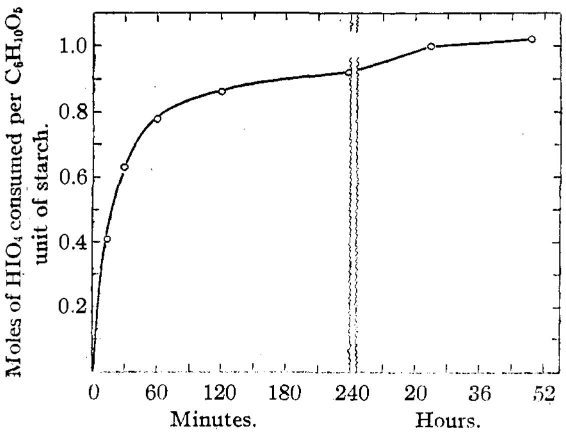


Fig. 1.—Oxidation of cornstarch by 0.533 *M* aqueous periodic acid solution at 21–22°.

Cornstarch is oxidized readily at ordinary temperature by aqueous periodic acid solution. The rate of consumption of the oxidant in the heterogeneous reaction is shown by the curve in Fig. 1. The quantity consumed at the end of twenty-four hours is closely one molecular equivalent, which is the theoretical amount required to oxidize (I) to (III). Since the consumption in excess of this amount proceeds at such a diminished rate, the principal reaction apparently is complete with the utilization of one mole. The yield of oxidized starch is quantitative. After oxidation the granules appear unchanged under the ordinary microscope, but with crossed nicols[3] oxidized starch shows a uniformly dark field in contrast to the characteristic cross of the corn starch granule. When a mixture of cornstarch and 0.533 *M* aqueous periodic acid solution at about 28° is observed with crossed nicols, the starch granules become invisible, as oxidation progresses, through spreading of the dark bands of the cross; some of the granules lose the cross within five minutes and in about twenty minutes none of them show it. The granules swell somewhat during oxidation and the refractive index becomes slightly lower than that of cornstarch. Oxidized starch is insoluble in cold water, but may be dissolved, without a gel stage, by prolonged heating (see Table I, note *c*). It shows no color with iodine; indeed, the color test for starch becomes negative after the consumption of about 0.8 mole of periodic acid. In aqueous solution it rotates[4] +9°, reduces Fehling's solution and forms an amorphous precipitate immediately with phenylhydrazine at 25°. Spontaneous evaporation of its solution yields a very clear transparent film, flexible but brittle, and unlike the cloudy residue obtained by drying a

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[2] Jackson and Hudson, THIS JOURNAL, **58**, 378 (1936); **59**, 994 (1937).

[3] We express our thanks to Dr. F. H. Goldman of this Institute for his coöperation in making the microscopic observations.

[4] All rotations in this article are specific rotations at 20° for sodium light.

layer of gelatinized cornstarch. The substance is hydrolyzed with some decomposition, as shown by the development of a brownish color and the separation of a small amount of dark floccules, by 0.1 *N* aqueous hydrochloric acid at 99–100°, the rotation changing during twenty hours to a levo value near the equilibrium rotation of −14.5° reported by Ruff[5] for *d*-erythrose, which should result from the hydrolysis of (III). While the presence of *d*-erythrose is thus suspected, it is emphasized that definite identification has not yet been established. Refluxing dry oxidized starch with 3% methyl alcoholic solution of hydrogen chloride yields a strongly levorotatory solution from which a non-reducing liquid may be recovered. Malt diastase appears to be inactive toward oxidized starch; it causes at 55° no change in the rotation of an aqueous solution of the substance.

TABLE I

OXIDATION OF STARCH AND CELLULOSE BY PERIODIC ACID AT 21–22°

Substance	Amount oxidized, g.	HIO_4 soln. in water Concn., *M*	HIO_4 soln. in water Vol., ml.	Oxidation time, hrs.	HIO_4 consumed, moles	Rotation[c] of product, $[\alpha]^{20}D$ in water
Starch[a,b]	1.728	0.533	50	24	1.00	+ 9°
Starch[a]	9.883	.542	150	210[d]	1.16	+ 5°
Cotton[e]	10.000	.533	154	430	1.22	−25°
Filter paper[f]	10.542	.271	320	37 days[g]	1.86	−29°

[a] Edible "Argo" cornstarch dried at 100° for twenty hours. [b] See Fig. 1. [c] Slightly opalescent solutions were prepared by heating on the steam-bath suspensions of 0.5 g. of the dry oxidation products in 20 ml. of distilled water; the amounts of the products dissolved were 99.6% from starch (+9°) in two hours, 92% from cotton in ten hours and 98% from filter paper in eight hours. None of these products separated upon cooling their solutions. (Addendum of Aug. 26: an aqueous 2% solution of oxidized starch, kept for several days at about 4°, has precipitated much of its solute as gelatinous aggregates, which redissolved at once on heating.) The rotation of the product from starch changed from +9 to +5° when its aqueous solution was heated on the steam-bath for seven hours; similar heating for twelve hours of the solutions from cotton and filter paper produced no appreciable change in rotation. [d] After the consumption of 1.02 moles of periodic acid (sixty-seven hours), the product was filtered off, washed free from iodic acid with cold water, dried at 50° and then mixed with 60 ml. of 0.542 *M* periodic acid soln. [e] Absorbent cotton, Grade A (Johnson and Johnson); moisture content, 5.1%. [f] Whatman's No. 2, cut into 5-mm. squares and dried at 100° for forty-five hours. [g] After the consumption of 0.96 mole of periodic acid (nine days), the product was filtered off, washed free from iodic acid with cold water, dried at 50° and then mixed with 120 ml. of 0.271 *M* HIO_4 soln. This operation was repeated after the consumption of an additional 0.45 mole during eleven days.

Cellulose also is oxidized by periodic acid but at a slower rate than starch. The data for cotton and filter paper in Table I show that the consumption of the oxidant may exceed considerably the theoretical amount, possibly due to some degradation of the product by prolonged contact with the acid medium. The cellulose shows a marked contraction during the oxidation reaction, which manifests itself by the squeezing of the solution from the cotton; measurement of a piece of filter paper before and after oxidation showed a shrinkage to 25% of the original area, 16 sq. cm. becoming 4 sq. cm. Oxidized cellulose, recovered in quantitative yield, is insoluble in cold water and slowly soluble in boiling water; it behaves like oxidized starch toward Fehling's solution, phenylhydrazine and iodine, and yields a similar film on evaporation of its aqueous solution. The sign of its rotation in water (−25° for oxidized cotton) is opposite to that of oxidized starch; this is presumably a consequence of the alpha-beta configuration of carbon atom 1 in the glucose units of the polysaccharides. Upon hydrolysis by 0.1 *N* aqueous hydrochloric acid at 99-100° the rotation decreases in twelve hours to a levo value near the equilibrium rotation of *d*-erythrose. In contrast to cellulose, oxidized cellulose is mostly soluble in hot 5% methyl alcholic solution of hydrogen chloride to yield a levorotatory solution.

The study of starch and cellulose along these lines is being continued, but we have no desire to reserve any part of the field.

Summary

Cornstarch is oxidized rapidly at ordinary temperature by an aqueous solution of periodic acid, apparently quantitatively, with the utilization of one mole of the oxidant per $C_6H_{10}O_5$ unit of starch. Filter paper and cotton cellulose have been oxidized similarly by this reagent, but the quantity of oxidant consumed was not as well defined as in the case of cornstarch, probably due to secondary reactions caused by the acidity of the medium during the much slower oxidation of the cellulose. Oxidized starch rotates +9° in water and oxidized cotton rotates −25° in the same solvent. Certain properties, which distinguish the oxidation products from starch and cellulose, are described.

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(5) Ruff, *Ber.*, **32**, 3672 (1899).