hydro structures occur[14-17] and we suggest that the polymerization of 1,6-anhydroglucose probably proceeds in part *via* some intermediate related structurally to 1,2-anhydroglucopyranose. One cannot but be impressed by the variety of compounds produced by these similar reactions under various experimental conditions, but the system is so complex that there seems little value in speculating on the effect of experimental factors on the course of the reaction.

It is perhaps surprising that levoglucosan polymerizes at all since it contains a fused five- and six-membered ring. A bicyclic lactone of a similar 3:2:1 system does not polymerize and the driving force for the polymerization of the corresponding lactam is apparently supplied by the conversion of a non-planar amide linkage in the monomer into a planar one in the polymer in which more nitrogen–carbonyl interaction was possible.[18] Levoglucosan, however, is not in the preferred conformation for glycosidic structures.[19] By opening the 1,6-oxide ring, the more favorable ring conformation is permitted and this transformation to a lower energy state probably assists the polymerization.

**Acknowledgment.**—The authors wish to acknowledge with gratitude the active interest and assistance of the Director of Portuguese Forest Service, Eng. J. Mendes Frazão to J. daS. C. and the valuable financial support of the Calouste Gulbenkian Foundation. Some exploratory experiments related to this research were carried out by Mr. Edwin J. Quinn and supported by the United States Army, Office of Ordnance Research.

(14) C. M. McCloskey and G. H. Coleman, *J. Org. Chem.*, **10**, 184 (1945).
(15) M. P. Bardolph and G. H. Coleman, *ibid.*, **15**, 169 (1950).
(16) A. Dyberman and B. Lindberg, *Acta Chem. Scand.*, **4**, 878 (1958).
(17) R. U. Lemieux and C. Brice, *Can. J. Chem.*, **30**, 295 (1952).
(18) H. K. Hall, Jr., THIS JOURNAL, **80**, 6412 (1958).
(19) R. E. Reeves, *ibid.*, **71**, 2116 (1949).

SYRACUSE, N. Y.

---

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

# Alkaline Degradation of Periodate-oxidized Xylan and Dextran[1]

BY ROY L. WHISTLER, P. K. CHANG AND G. N. RICHARDS

RECEIVED JANUARY 12, 1959

Xylan from corn cobs is oxidized with sodium metaperiodate and then treated with dilute sodium hydroxide solution at room temperature. The major products are acidic, with glycolic and lactic acids predominating. Similarly, oxidized dextran from *Leuconostoc mesenteroides*, when treated with alkali in the same way, also yielded glycolic and lactic acids predominantly. It is concluded that both oxidized polysaccharides undergo alkaline degradation mainly by β-alkoxycarbonyl elimination, but that alternative modes of degradation also occur, which yield glycolic but not lactic acid.

Recent work on the alkaline degradation of model compounds[2] and on periodate oxidized cellulose[3] and starch[4] has shown that both of the oxidized 1→4-linked glucans degrade in alkali predominantly by β-alkoxycarbonyl elimination at the C5 position of the original D-glucose unit. Since other periodate-oxidized polysaccharides also contain the β-alkoxycarbonyl grouping, this type of degradation should be general.

Xylan from corn cobs,[5] which is essentially linear and 1→4-linked, is partially oxidized with sodium metaperiodate and the product treated with oxygen-free dilute sodium hydroxide at room temperature. Acidic and neutral products are separated by ion exchange resins and the former are further resolved by paper chromatography. Glycolic and lactic acids are identified as the acidic products, together with formic acid and a resinous acidic product similar to that obtained from periodate oxystarch.[4] The results of semi-quantitative analyses are expressed in Table I.

It is concluded that the predominant course of alkaline degradation of periodate oxyxylan is analogous to that proposed for the corresponding oxystarch[4] and may be expressed as shown (I → IV + V). In accordance with arguments already expressed[2,4] it is assumed that the intermediate III will react readily as shown, while the intermediate II will rearrange to lactic acid so long as the group R represents another oxidized unit. The excess of glycolic over lactic acid and the low yields of both suggest that competing reactions also occur and probably result from alternative modes of degradation of the original oxyxylan, analogous to those discussed earlier.[4]

TABLE I

PRODUCTS ISOLATED FROM DEGRADATION WITH 1 *N* SODIUM HYDROXIDE SOLUTION

Except for the first line, yields are expressed in equivalents per mole of oxidized D-glucose unit.

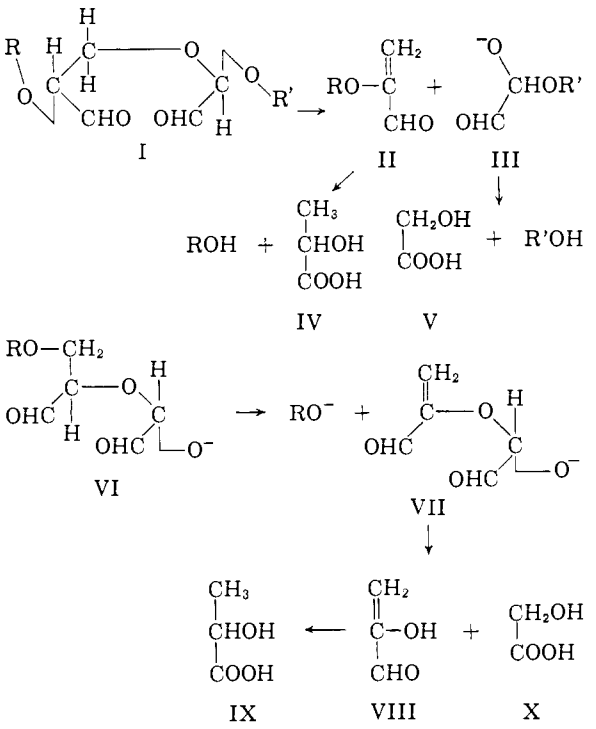
| | Oxyxylan | Oxydextran |
|---|---|---|
| Neutral products | 18% | 18% |
| Total acids | 1.15 | 0.91 |
| Volatile acids | 0.13 | .08 |
| Formic acid | .08 | .06 |
| Glycolic acid | .62 | .51 |
| Lactic acid | .32 | .25 |

A dextran, which is mainly a linear, 1→6-linked glucan, is also oxidized with periodate and the product treated with dilute sodium hydroxide at room temperature. The acidic products again consist mainly of glycolic and lactic acids together

(1) Journal Paper No. 1362 of the Purdue University Agricultural Experiment Station, Lafayette, Ind.
(2) D. O'Meara and G. N. Richards, *J. Chem. Soc.*, 1204 (1958); *Chemistry & Industry*, 41 (1958).
(3) D. O'Meara and G. N. Richards, in press.
(4) R. L. Whistler, P. K. Chang and G. N. Richards, THIS JOURNAL, **81**, 3133(1959).
(5) R. L. Whistler, J. Bachrach and D. R. Bowman, *Arch. Biochem.*, **19**, 25 (1948).

with formic acid and the same type of resinous acidic material as was obtained from both oxystarch and oxyxylan. The results of semi-quantitative analyses are expressed in Table I.

The predominant cause of alkaline degradation may therefore be expressed as shown (VI → IX + X) for the completely oxidized polymer, in which VII is similar to $RO^-$. Alkaline degradation of the intermediate VII, which is the anion of a glyoxal hemiacetal, should proceed as shown to yield glyoxal and the intermediate VIII, the former rapidly yielding glycolic acid and the latter yielding lactic acid. The presence of 1→3-links in the original dextran results in unoxidized D-glucose units which are partly liberated as D-glucose during the alkaline degradation and which may also cause the stabilization of substituted intermediates similar to VII.



Competing reactions are again evident, since the yield of glycolic acid is greater than that of lactic acid and both are less than the theoretical. The predominance of glycolic acid in the products of alkaline degradation of each of the periodate oxidized polysaccharides so far examined[3,4] strongly suggests the occurrence, in addition to the β-alkoxycarbonyl elimination, of a reaction producing glycolic acid, but not the second major product (lactic acid). The ketene acetal hydrolysis mechanism proposed by Pacsu[6] is in accordance with these requirements, but at present lacks further experimental support.

Formic acid also results from the alkaline degradation of each of the periodate-oxidized polysaccharides so far examined and evidently arises from complex fragmentation reactions whose mechanism is as yet unknown.

(6) E. Pacsu, *Textile Res. J.*, **15**, 354 (1945); *Fortschr. Chem. Org. Naturstoffe*, **5**, 128 (1948).

## Experimental

These various solvents and sprays were used for paper chromatography with Whatman No. 1 paper at 25°. Solvent A, ethyl acetate–acetic acid–water (10:1.3:1.0, v./v.); solvent B, ethyl acetate–pyridine–water (40:11:6, v./v.). Sprays, A, brom thymol blue indicator[7]; B, hydroxylamine–ferric chloride[8]; C, ammoniacal silver nitrate.[9] $R_g$ = rate of movement relative to D-glucose; $R_x$ = rate of movement relative to D-xylose; $R_l$ = rate of movement relative to lactic acid.

**Preparation of Periodate-oxidized Xylan and Dextran.**—Thirty grams of air-dried reprecipitated corn cob xylan[5] was made into a paste with water and stirred at room temperature with a solution of 73 g. of sodium metaperiodate in 600 ml. of water.[10] After the oxidation reached 70% of completion it was stopped by addition of 5 ml. of ethylene glycol. The oxyxylan was completely dissolved at this stage. The product was recovered by lyophilization after dialysis in running water until free from iodate ion. Thirty grams of purified dextran from *L. mesenteroides* (NRRL B-512) was oxidized with a solution of 118 g. of sodium metaperiodate in the same way as for xylan except that the uptake of periodate was 2.0 moles per mole of D-glucose unit when the reaction was stopped by the addition of ethylene glycol. The product also was recovered by lyophilization after dialysis. The moisture content of these lyophilized samples was less than 0.1%.

**Alkaline Degradation of the Oxidized Polysaccharides.**—The rate of degradation in 1 *N* sodium hydroxide at 25° was measured as described for oxystarch.[4] In further large-scale experiments a 7.00-g. sample of the relevant oxypolysaccharide was dispersed in 5 ml. of water and 175 ml. of oxygen-free 1 *N* sodium hydroxide was added at room temperature. In each case, the solution temperature rose to 30–35° within a few minutes. After 30 minutes, the solutions were passed through a column of Amberlite[11] resin IR-120 (H).

**Isolation and Preliminary Examination of Degradation Products.**—The procedure for the isolation of neutral and acidic degradation products was the same as that described for the 1 *N* sodium hydroxide treatments of oxystarch,[4] the acidic products being obtained as an aqueous solution of their barium salts.

**Neutral Fractions.**—Neutral degradation products had generally the same appearance as those obtained from alkaline degradation of periodate-oxidized starch. Their solutions foamed readily and yielded glassy solids on evaporation. Paper chromatographs prepared by the use of solvent B, and ammoniacal silver nitrate spray, showed extensive streaking for both oxystarch and oxyxylan, but with oxyxylan the major components had $R_x$ 1.00 with components also of $R_x$ 0.59, 1.43 and 1.86, while oxydextran gave a prominent elongated zone of $R_g$ about 2.4, with components also of $R_g$ 1.00, 1.20, 1.65 and 3.0.

**Acidic Fractions.**—Samples of barium salt solutions were treated with Amberlite resin IR-120 (H) and then chromatographed with solvent A and some papers sprayed with brom thymol blue while others were sprayed with ammoniacal silver nitrate. The products from oxyxylan gave major acidic components of $R_l$ 0, 0.76 and 1.00 with a trace acidic component of $R_l$ 0.16. The products from oxydextran also gave major acidic components of $R_l$ 0.76 and 1.00 with smaller amounts of acidic components of $R_l$ 0.14 and 0.25. Authentic glycolic acid showed $R_l$ 0.76.

**Identification of Major Acidic Products.**—Portions of the solutions of barium salts from both oxidized polysaccharides were stirred with excess Amberlite resin IR-120 (H) at room temperature for 30 minutes, and the supernatant liquid was transferred uniformly without heating to 46 × 56 cm. sheets of Whatman 3 MM paper which had been washed with water and dried. Approximately 5 milligram equivalents of acid was applied to each paper which was then irrigated with solvent A for 6 hours. Guide strips were sprayed with brom thymol blue, and the relevant zones

(7) F. Cramer, "Paper Chromatography," The Macmillan Co., London, 1952, p. 85.

(8) M. Abdel-Akher and F. Smith, THIS JOURNAL, **73**, 5859 (1951).

(9) S. M. Partridge, *Biochem. J.*, **42**, 238 (1948).

(10) S. K. Chanda, E. L. Hirst, J. K. N. Jones and E. C. V. Percival, *J. Chem. Soc.*, 1289 (1950).

(11) Product of Rohm and Haas. Co., Washington Square, Philadelphia 5, Penna.

were eluted with water. Glycolic and lactic acids were obtained from both oxyxylan and oxydextran and identified as the 4-bromophenacyl ester in each case, m.p. and mixed m.p. 138–139° and 107–109°, respectively.

**Quantitative Determinations of the Major Degradation Products. Neutral Fraction.**—The neutral fractions of the degraded oxypolysaccharides were weighed directly after evaporation of the solutions resulting from deionization with Amberlite ion exchange resins, IR-120 (H) and IRA-401 (carbonate).

**Total acidity and volatile acids** were determined by the same methods as described for oxystarch.[4]

**Major Non-volatile Acids.**—Glycolic and lactic acids were first separated by the quantitative paper chromatographic method described for periodate oxystarch.[4] Calkins' method[12] was used to determine glycolic acid samples and a correction factor for recovery from paper chromatography applied as described earlier.[4] For the lactic acid eluate, the method described by Hullin and Noble[13] was used. Calibration of the recovery of authentic lactic acid from this procedure showed a considerable dependence of recovery on the loading of the paper. With loading of lactic acid comparable to that present in the mixtures, a recovery of 80% was obtained and this correction has been applied to the results in Table I, but as suggested in earlier work[4] these acid yields are approximate and may be subject to errors of the order ±10%. The higher recovery of lactic acid than of glycolic acid from the paper chromatogram in the calibration experiments is probably due to the fact that a wide band (10—15 cm.) of paper was eluted to include dimers and trimers of lactic acid, whereas a band of minimal width was cut for glycolic acid in order to exclude trace products of similar $R_1$ values.

(12) V. P. Calkins, *Anal. Chem.*, **15**, 762 (1943).

(13) R. P. Hullin and R. L. Noble, *Biochem. J.*, **55**, 289 (1953).

LAFAYETTE, IND.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

# The Structure of Photoisopyrocalciferol and Photopyrocalciferol[1—3]

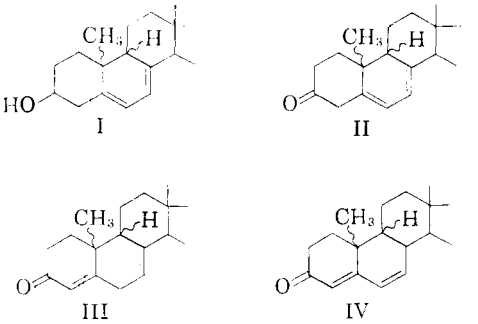
BY WILLIAM G. DAUBEN AND GERHARD J. FONKEN

RECEIVED DECEMBER 2, 1958

Windaus and Dimroth have reported the formation of "photo" compounds VIII and IX by the irradiation of the pyrocalciferols Ic and Id with ultraviolet light. On the basis of limited evidence structures XII and XIII were suggested. The present results add evidence in favor of structure XIII, a valence tautomer of Ic and Id; VIII possesses five rings, a nuclear disubstituted double bond and a $\Delta^{22}$-unsaturated link in the sidechain. Oxidation of VIII yields the non-conjugated, unsaturated ketone X and ozonization of VIII gives a $C_{22}$-triacid XVI which is converted readily to a cyclic anhydride-acid XVII. Compound VIII upon hydrogenation is transformed into a 22-dihydro (XIV) and a tetrahydro derivative XV. Both XIV and XV are stable to acid; XV upon mild oxidation gives the saturated ketone XXI and upon vigorous oxidation the *seco*-diacid XXII. Perbenzoic acid oxidation of XV yields lactone XXIII which upon saponification and oxidation gives the same *seco*-diacid. Treatment of ketone X with base yields dienone IV. A similar series of transformations are found with IX. The chemistry of Ic and Id and of various valence tautomers are discussed. The mechanism of the transformation is considered.

In the course of their classical work on the mechanism of formation of vitamin $D_2$ from ergosterol, Windaus and his collaborators[4] prepared the four 5,7-dienes (Ia-d), isomeric at $C_9$ and $C_{10}$. Recently, the stereochemistry of the four isomers has been shown[5] to be 9α-H,10β-$CH_3$ in ergosterol (Ia), 9 β-H,10α-$CH_3$ in lumisterol (Ib), 9β-H,10β-$CH_3$ in isopyrocalciferol (Ic) and 9 α-H, 10α-$CH_3$ in pyrocalciferol (Id).[6] It is seen that the first two compounds are 9,10-*anti* isomers while the last two compounds are 9,10-*syn* isomers.

The change from *anti* to *syn* in the backbone stereochemistry reflects itself in many of the reactions shown by these two series of compounds. For example, in the *anti* series when the alcoholic group is oxidized under Oppenauer conditions, a 4,7,22-triene-3-one (IIIa or b) is obtained directly.[7] In the




a, 9α-H,10β-$CH_3$; b, 9β-H,10α-$CH_3$
c, 9β-H,10β-$CH_3$; d, 9α-H,10α-$CH_3$

*syn* series, similar oxidation yields the unrearranged 5,7,22-triene-3-one (IIc or d) which must be treated with base to be transformed into the isomeric 4,7,22-triene-3-one (IIIc or d). In the *anti* series, when the alcohol (Ia or b) is hydrogenated under neutral or slightly acid conditions, only a tetrahydro product ($\Delta^{8,14}$) is obtained,[8] but under strongly acid conditions a hexahydro product is formed.[9] With the *syn* series, it has been reported

(1) Presented at the 15th National Organic Chemistry Symposium of the American Chemical Society, Rochester, N. Y., June 17–20, 1957.

(2) This work was supported, in part, by Grant A-709 (C5)-Bio (5) of the U. S. Public Health Service, National Institutes of Health, Department of Health, Education and Welfare.

(3) A preliminary communication of these results appeared in THIS JOURNAL, **79**, 2972 (1957).

(4) For a summary of this work, see L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 3rd edition, 1949, p. 167.

(5) J. Castells, E. R. H. Jones and R. W. J. Williams, *Proc. Chem. Soc.*, 7 (1958); *J. Chem. Soc.*, **1159** (1959).

(6) Jones and his co-workers[5] recently suggested that isopyrocalciferol be called 9β-ergosterol and pyrocalciferol be called 9α-lumisterol. In the present discussion, the older trivial names will be used since all previous work has been based upon this nomenclature system.

(7) R. V. Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937); I. M. Heilbron, T. Kennedy, F. S. Spring and G. Swain, *J. Chem. Soc.*, 869 (1938).

(8) F. Reindel, E. Walter and H. Rauch, *Ann.*, **452**, 34 (1927); F. Reindel and E. Walter, *ibid.*, **460**, 212 (1928); M. C. Hart, J. H. Speer and F. W. Heyl, THIS JOURNAL, **52**, 2016 (1930).

(9) G. Ahrens, E. Fernholz and W. Stoll, *Ann.*, **500**, 109 (1933); I. M. Heilbron, G. L. Moffet and F. S. Spring, *J. Chem. Soc.*, 411 (1937).