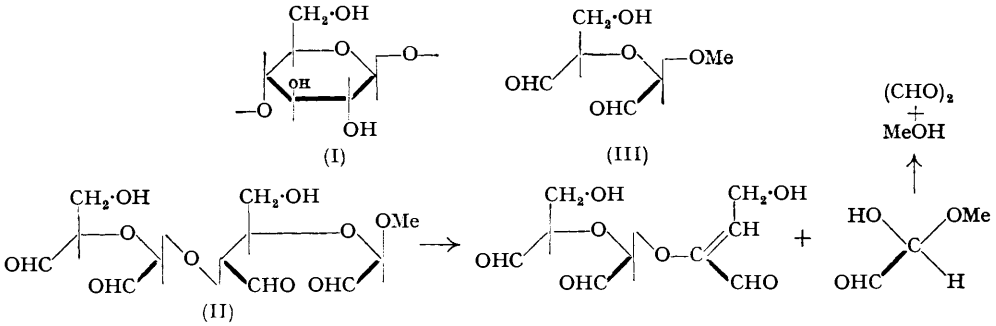
462. *The Degradation of Carbohydrates by Alkali. Part II.* Lactose.*

By W. M. Corbett and J. Kenner.

The decomposition by oxygen-free saturated lime-water at 25° of lactose into galactose and α- and β-*iso*saccharinic acids has been studied. Its mechanism is interpreted in terms of the behaviour of β-alkoxy-carbonyl compounds.

It was concluded in Part I * that analogy with α-alkoxy-ketones suffices to explain the reducing properties of many forms of oxycelluloses but not their sensitivity at the ordinary temperature to weak alkali. Now, in an anhydroglucose unit (I) of cellulose replacement of any of the alcohol groups by a carbonyl group leads to a structure which in relation to the adjoining anhydroglucose units of the chain can be regarded not only as an α- but also as a β-alkoxycarbonyl compound, and in this and subsequent papers we shall adduce evidence of the merits of the latter comparison. Although the behaviour of β-alkoxycarbonyl derivatives towards alkali has not been systematically studied, the formation of αβ-unsaturated carbonyl systems from β-hydroxy- and β-nitrosamino-carbonyl derivatives (Jones and Kenner, *J.*, 1933, 363, Adamson and Kenner, *J.*, 1934, 838), and the reversal of the Michael reaction (Ingold and Powell, *J.*, 1921, 1976) are familiar. Closer to our theme is the formation of tetraethyl propane-1 : 1 : 3 : 3-tetracarboxylate by interaction of chlorodimethyl ether with ethyl sodiomalonate (Simonsen, *J.*, 1908, **93**, 1777) and of crotononitrile by the action of ethylmagnesium iodide on β-methoxybutyronitrile (Bruylants and Mathus, *Bull. Acad. roy. Belg.*, 1926, **11**, 637), and Head has recorded the rapid formation of glyoxal by the action of cold dilute aqueous sodium carbonate on the periodate oxidation product (II) of β-methylcellobioside but not from that of β-methylglucoside (III) (*J. Textile Inst.*, 1947, **38**, 389) :


(I)

(III)

(II)

Owing to the indefinite character of the oxycelluloses we have in mind (to which we assign the generic term " carbonyl oxycelluloses ") we have first studied lactose from this point of view. Lactose was dissolved in oxygen-free saturated lime-water solution at 25° and at appropriate intervals the changes in alkalinity, optical rotatory power, and contents of mono- + di-saccharide, monosaccharide, and saccharinic acid were determined, the identity of the monosaccharides being established by paper chromatography. The results exhibited in the accompanying Table show a correspondence between the rate of decomposition of lactose and the rates of formation of monosaccharides and saccharinic acids.

The known relatively slow conversion of lactose (IV) into lactulose (V) (Montgomery and Hudson, *J. Amer. Chem. Soc.*, 1930, **52**, 2101) is followed by the rapid degradation of

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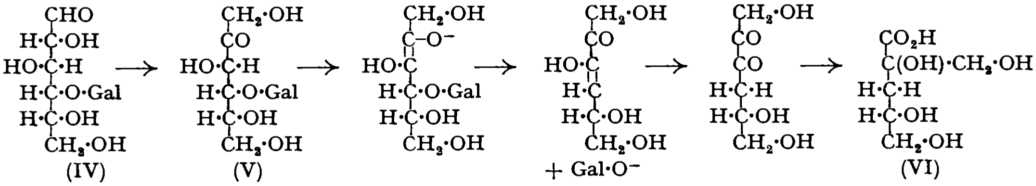
* Part I, preceding paper.

the latter into α- and β-*iso*saccharinic acids (VI) and galactose, the latter being in turn gradually disintegrated into acidic products :



(IV) (V) (VI)

(Gal = galactosyl)

Degradation of lactose by saturated lime-water at 25°.

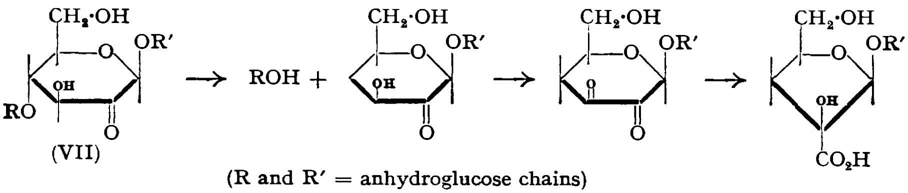
Time (hr.)	α_D	Lactose (10^{-4} mole)		De-comp. (%)	Monoses (10^{-4} mole)	Sac-charinic acids (10^{-4} mole)	Paper chromatography †					
		present	decompd.				Lact-ose	Lac-tulose	Gal-actose	Tag-atose	Sac. acids	Tal-ose
0·1	+0·20°	1·042	0	0	0	*	4	—	—	—	—	—
0·5	0·20	1·022	0·020	1·9	0·042	*	4	1	—	—	—	—
1	0·20	1·018	0·024	2·4	0·055	*	4	1	—	—	—	—
2	0·18	0·972	0·070	6·7	0·132	*	4	2	—	—	—	—
3	0·16	0·968	0·074	7·2	0·160	*	4	2	1	—	—	—
4	0·14	0·965	0·077	7·4	0·168	*	4	2	1	—	—	—
6	0·10	0·935	0·107	10·3	0·172	*	4	2	1	—	—	—
7	0·12	0·895	0·147	14·2	0·250	0·138	4	2	1	—	—	—
24	0·05	0·685	0·357	33·9	0·395	0·422	3	3	2	1	1	—
31	0·04	0·592	0·450	43·2	0·480	0·452	3	3	2	1	1	1
48	0·05	0·402	0·640	61·4	0·660	0·532	3	3	2	1	2	1
55	0·05	0·355	0·687	66·0	0·722	0·680	3	3	2	1	2	1
72	0·05	0·272	0·770	73·9	0·758	0·745	2	3	2	1	2	1
96	0·05	0·226	0·816	78·2	0·792	0·752	2	3	2	1	2	1
122	0·05	0·175	0·867	83·3	0·820	0·758	1	3	2	1	3	1
168	0·05	0·168	0·874	84·0	0·777	*	1	3	2	1	3	1
216	0·05	0·146	0·896	85·8	0·758	0·832	1	3	1	1	3	1

* Not determined. † Numerals denote relative intensity, 4 denoting the greatest intensity.

In later papers the general applicability of the above scheme will be illustrated.

The significance of the β-hydroxycarbonyl system for carbohydrate chemistry has been previously discussed by Wohl (*Z. angew. Chem.*, 1907, **20**, 1169) and Isbell (*J. Res. Nat. Bur. Stand.*, 1944, **32**, 45), and that of the β-alkoxycarbonyl system by Nicolet (*J. Amer. Chem. Soc.*, 1931, **53**, 4458) and, with particular reference to oxycelluloses, by Haskins and Hogsed (*J. Org. Chem.*, 1950, **15**, 1264). Much earlier Kiliani and his collaborators (*Ber.*, 1909, **42**, 2603, 3903, and earlier papers) had obtained *iso*saccharinic acid from lactose by the action of lime-water at and above room temperature. Further, it should be realised that acceptance of the mechanism here developed involves rejection of that put forward by Evans (*Chem. Reviews*, 1942, **31**, 537).

Meanwhile, it appears permissible to interpret the decomposition of carbonyl oxycelluloses along similar lines. Thus, in the case of a 2-carbonyl group in an anhydroglucose unit (VII) of the cellulose chain we have :



(VII)

(R and R′ = anhydroglucose chains)

Experimental

Determination of the Degradation Products.—A solution (100 ml.) of " AnalaR " lactose (0·8675 g.) in saturated oxygen-free lime-water (0·0386N) was kept at 25°. At intervals

5-ml. portions, again freed from oxygen by a stream of oxygen-free nitrogen, were titrated against 0·02N-sulphuric acid (bromothymol-blue), and diluted to 20 ml. The optical rotatory power was observed and an indication of the sugars present was obtained by paper chromatographic analysis. The saccharinic acid content of this solution (1 ml.) was determined by the lactonisation method of Bamford, Bamford, and Collins (*Proc. Roy. Soc.*, 1950, *A*, **204**, 85).

For determination of the saccharides the solution (2 ml.) was diluted to 25 ml. and the adsorbate on a charcoal–Celite column (0·8 × 1·0 cm.) from an aliquot portion (1 ml.) of this diluted solution was eluted with water (15 ml.), the monose content of the eluate being determined by Hagedorn and Jensen's micro-method (*Biochem. Z.*, 1923, **135**, 46). The difference in reducing power of the solution before and after adsorption on the charcoal column was due to the disaccharides only.

The results recorded in the table are calculated for the solution used for the observation of α_D; although a complex mixture of carbohydrates may arise in solution, *e.g.*, by epimerisation, the total monosaccharides are quoted as galactose and the total disaccharides as lactose rather than as individual components.

Isolation of the Degradation Products. Lactose (8·599 g.) was dissolved in saturated oxygen-free lime-water (1 l.) and kept at 25° for 10 days, after which the solution was neutralised with oxalic acid. The filtered solution was concentrated to 50 ml. at 45° under reduced pressure. Calcium α-*iso*saccharinate (1·635 g.) slowly crystallised. The brucine salt (m. p. 159—161°) was prepared by the standard method (Found: N, 5·1. Calc. for $C_{29}H_{38}O_{10}N_2$: N, 4·9%). Nef (*Annalen*, 1910, **376**, 52) gives m. p. 164°. The mother-liquors were concentrated to a syrup which slowly crystallised, to give galactose (0·676 g.), $[\alpha]_D^{23}$ (equil.) +76·5° (*c*, 0·890 in H_2O) [osazone, m. p. 194·5—196° (decomp.); Fischer (*Ber.*, 1887, **20**, 3390) gives m. p. 196—197°]. From a portion of the residual syrup (0·429 g.) was isolated the brucine salt of β-*iso*saccharinic acid (0·144 g.), m. p. 185—209° (decomp.) (Found : N, 5·3%). Nef (*loc. cit.*) gives m. p. 200—210° (decomp.).

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