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Note

Formation of cyclopentanedione by alkaline degradation of carbohydrates

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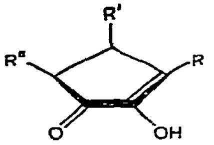
Treatment of carbohydrates with alkali usually gives a complex mixture of products, resulting both from rearrangements and fragmentations, which may be followed by various recombination reactions[1]. The best known reaction products are the saccharinic acids[1] and lower-molecular-weight carboxylic acids which are stable end-products of alkaline treatment of carbohydrates.

Carbocyclic compounds are not very well known among the dehydration products of carbohydrates. So far, only compounds **1**–**5** have been reported in the literature. Apart from reductic acid[2] (**1**), which is an acidic rather than an alkaline dehydration product of uronic acids, only 3-methyl-1,2-cyclopentanedione (**2**) has been known for some time. It is formed as a minor product during the destructive distillation of wood[3] and the digestion of spruce wood or D-galactose with sodium hydroxide[4]. Recently, it has been detected among the volatile compounds produced by the heating of D-glucose[5] and among the alkaline-degradation products of D-fructose[6]. In the latter case, three more cyclopentanediones (**3**, **4**, and **5**), in addition to **2**, have been reported[6]. 1,2-Cyclopentanedione (**6**) itself has so far not been reported as a decomposition product of carbohydrates. This Note reports the formation of **6** by alkaline degradation of a number of carbohydrates under mild conditions.



1 R = OH, R' = H, R'' = H
2 R = Me, R' = H, R'' = H
3 R = Me, R' = H, R'' = Me
4 R = H, R' = H, R'' = Et
5 R = Me, R' = Me, R'' = H
6 R = H, R' = H, R'' = H

EXPERIMENTAL AND RESULTS

The procedure for the detection and isolation of 1,2-cyclopentanedione, described here with maltose as starting material, was as follows: Maltose (61 mg) was treated with 2M potassium hydroxide (10 ml) for 20 h at room temperature under nitrogen. The reaction mixture was neutralized (pH 6.0–6.5) with 6M hydrochloric acid, saturated with ammonium sulfate, and extracted with ethyl acetate. T.l.c. of the extract (silica gel, 4:1, v/v, benzene–methanol) showed an intense, dark-blue spot (R_F 0.40) with diazotated benzidine as reagent for the enol group. The compound was isolated, in a yield of ~2%, by preparative t.l.c. with the same solvent system. It showed the same R_F value and color reaction as 1,2-cyclopentanedione (**6**) synthesized according to Hesse and Bücking[7] and Jaeger and Blumendal[8]. The structure was confirmed by i.r. spectrometry (ν_{max}^{KBr} 3210, 1960, 1690, and 1640 cm^{-1}); p.m.r. spectrometry (chloroform-*d*): δ 2.50 (4 H, m, 2 CH_2), 6.02 (1 H, broad s, OH), 6.56 (1 H, m, =CH–); and mass spectrometry: *m/e* 98 ($M^{+\cdot}$), 69 ($M^{+\cdot}-29$), 55 ($M^{+\cdot}-43$), 42 ($M^{+\cdot}-56$), 28 ($M^{+\cdot}-70$), and 18 ($M^{+\cdot}-80$). The compound exists in the enol form and readily decomposes upon exposure to air with browning, and it forms black spots when applied to the skin[9].

A number of carbohydrates were treated with alkali and tested by t.l.c. for the formation of 1,2-cyclopentandione as just described. The results (Table I) show that, with the exception of 2-deoxy-D-*erythro*-pentose, only reducing carbohydrates substituted at C-3 or C-4 give the title compound in significant amounts.

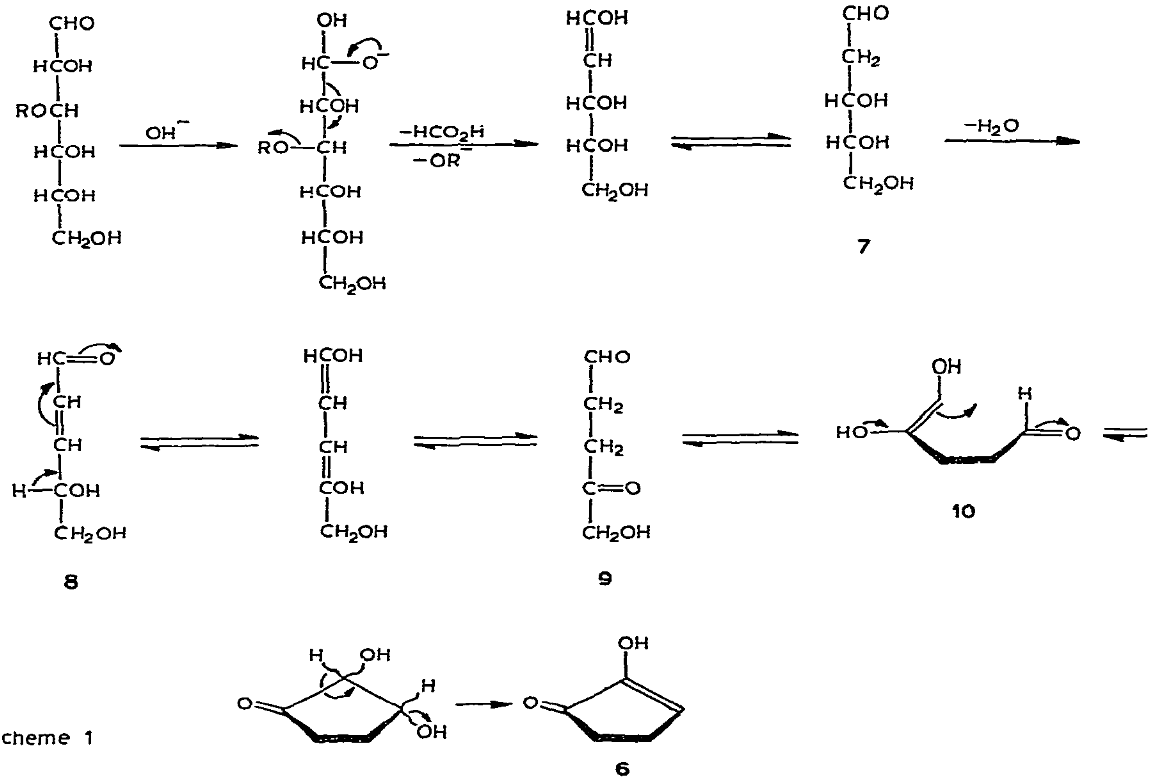
DISCUSSION

As in most alkaline degradations of carbohydrates, the reaction starts from the reducing group and eliminates the substituent at C-3 or C-4, respectively, and formic acid by splitting the bond between C-1 and C-2 . Therefore, high-molecular-weight polysaccharides (*e.g.* starch) having very few reducing groups do not generate enough cyclopentanedione to be detected, whereas degraded starches (dextrins) contain sufficient reducing groups to produce detectable amounts of **6**.

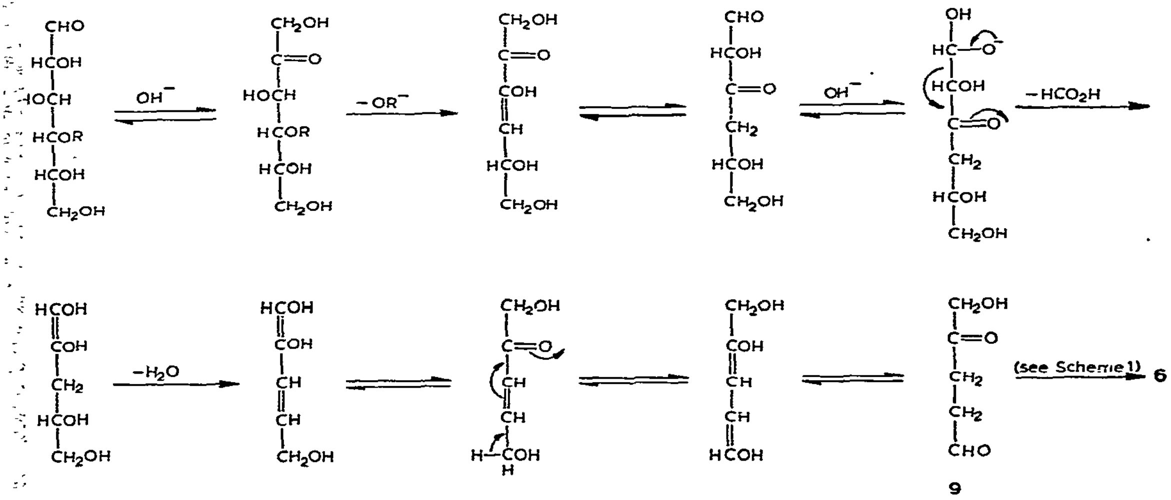
TABLE I

FORMATION OF 1,2-CYCLOPENTANEDIONE FROM VARIOUS CARBOHYDRATES

Carbohydrates	*Formation of 1,2-cyclopentanedione*
Maltose	+
Cellobiose	+
Lactose	+
Lactulose	+
3-*O*-Tosyl-D-glucose	+
Dextrin	+
2-Deoxy-D-*erythro*-pentose	+
D-Glucose	−
Melibiose	−
Sucrose	−
Starch	−
L-Arabinose	Traces
D-Fructose	Traces



Scheme 1



Scheme 2

A possible reaction mechanism for the formation of cyclopentanedione from C_3-substituted hexose derivatives is given in Scheme 1. The elimination of OR at the C-3 position and of formic acid gives 2-deoxy-D-*erythro*-pentose (**7**), and this reaction is indeed utilized for the preparation of this deoxy sugar[10,11]. Loss of water from **7** gives **8**, which is in equilibrium[12] with the tautomeric forms **9** and **10**. By an intramolecular aldol condensation and further loss of a molecule of water, 1,2-cyclopentanedione (**6**) is formed. The formation of **6** from **7** (Table I) lends support to this mechanism. A similar reaction scheme can be postulated for hexoses substituted at C-4 leading to **6** *via* the same intermediate **9** (Scheme 2). Small amounts of formic acid have been detected in alkaline digests of C-3- and C-4-substituted hexoses[13].

The formation of **6** as a possible artifact has to be considered when (1→3)- or (1→4)-linked oligosaccharides or carbohydrate derivatives (*e.g.* esters) are treated with alkali under mild conditions.

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