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Interaction of D-Glucono-1,5-Lactone with Water

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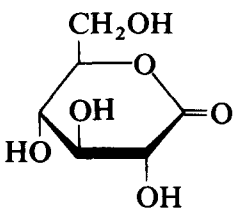
ABSTRACT

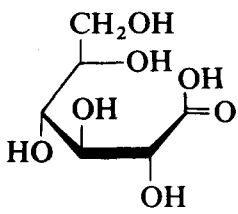
Some studies of the interconversion of D-*glucono-1,5-lactone,* D-*gluconic acid and* D-*glucono-1,4-lactone have been undertaken. High-performance liquid chromatography on reversed-phase supports was successfully used to resolve these components in water solution. There are no interactions between the 1,5-lactone and gluconic acid manifested as optical rotation effects. The course of hydrolysis of* D-*glucono-1,5-lactone, as measured by optical rotation is corroborated by the hplc data. The 1,4-lactone is predictably more stable than the 1,5-lactone and rate constants for the hydrolysis of the 1,5-lactone, and the lactonisation of* D-*gluconic acid were determined in* D-*gluconic acid solution which had a constant pH of 2·4. At 20°C the rate constants were found to be* $1{\cdot}730 \times 10^{-4}\ s^{-1}$ *and* $3{\cdot}807 \times 10^{-5}\ s^{-1}$*, respectively. The specific rotation of* D-*gluconic acid was affected by the presence of inorganic ions; its value in the absence of interfering ions was determined to be* $-5{\cdot}11°$ *(*c*, 4·5, 20°C, water).*

INTRODUCTION

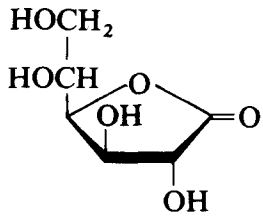
D-glucono-1,5-lactone is an internal ester, which interacts with water forming D-gluconic acid; D-glucono-1,4-lactone is also formed in the reaction.



D-glucono-1,5-lactone

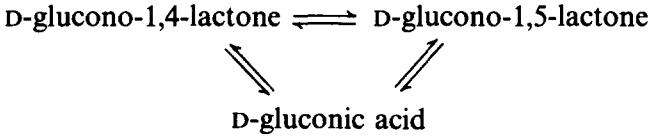


D-gluconic acid



D-glucono-1,4-lactone

An equilibrium mixture of D-gluconic acid, D-glucono-1,4-lactone and D-glucono-1,5-lactone results after sufficient time, the equilibrium proportions of the constituents varying with temperature, pH and concentration of solvent (Isbell & Frush, 1963). A model for this system in water has been assumed (Sawyer & Bagger, 1959) and, depending on the pH of reaction, direct lactone interconversion is reported to occur (Jermyn, 1960; Takahashi & Mitsumoto, 1963).



The gluconolactone–gluconic acid system has been studied in detail by several methods, including optical rotation (Levene & Simms, 1926; Sawyer & Bagger, 1959; Mitchell & Dike, 1970), colorimetric analysis (Jermyn, 1960), paper chromatography (Takahashi & Mitsumoto, 1963) and infrared spectroscopy in deuterium oxide (Shimahara & Takahashi, 1970). These methods were not entirely satisfactory for the study of this system in water, however, either because they failed to distinguish between the 1,4- and 1,5-lactones in solution (optical rotation and colorimetric analysis), or because water was not the solvent when these lactones were distinguished. A new procedure, that of high-performance liquid chromatography on reversed-phase supports, is here used to distinguish D-glucono-1,4-lactone from D-glucono-1,5-lactone and both lactones from D-gluconic acid. This method was a rapid, non-destructive, quantitative assay of these components in water solution, and is now described.

MATERIALS AND METHODS

Materials

D-Glucono-1,5-lactone was obtained from Fluorochem Ltd., Glossop. D-glucono-1,4-lactone was prepared from D-glucono-1,5-lactone as previously described (Isbell & Frush, 1963) (except that no mineral acid was added to the acetic acid); it had a melting point of 132° to 135°C. D-gluconic acid was

prepared by ion-exchange of sodium-D-gluconate solution. Sodium-D-gluconate (Fluorochem Ltd.) was dissolved in water to known concentration and added to an equal volume of Amberlite IR120 cation exchange resin in the hydrogen form (analytical grade, Rohm & Haas Ltd., Jarrow). The resin had previously been regenerated using hydrochloric acid and was dried free of surface water by Büchner filtration. The solution of sodium-D-gluconate was stirred with the resin for 20 s and the supernatant filtered (8 μm, Anderman & Co., Kingston-upon-Thames) to give a solution of D-gluconic acid. Distilled, or degassed ultra pure Milli Q water (Waters Associates Ltd., Harrow) was used for solution preparation.

General methods

All solutions were maintained at, and all measurements were made at, 20°C $\pm$ 1°C. D-Glucono-1,4- and -1,5-lactones, and sodium-D-gluconate used for solution preparation were weighed to the fourth decimal place.

Conductivity and pH

Solution conductivity was measured using a Phillips conductivity meter PW 9505 (Pye Unicam Ltd., Cambridge), pre-set before any series of measurements using standard solutions of potassium chloride.

Solution pH was measured using a pH meter (Pye Unicam PW 9409) pre-set before any series of measurements using two buffers (pH 4·00 and pH 7·00; BDH Chemicals Ltd., Poole).

Optical rotation

Optical rotation of solutions was measured using a digital read-out polarimeter (Optical Activity Ltd., Huntingdon; polarimeter type AA-10) at 589 nm. Unless otherwise stated a 2 dm steel jacketed thermostatted polarimeter tube was used, introducing solution by a syringe fitted with an in-line filter (8·0 μm, Anderman & Co. Ltd.) as required. Temperature was controlled using a thermocirculator (Churchill Ltd., Uxbridge). A non-jacketed 1 dm polarimeter cell was otherwise used. Readings were taken when the polarimeter had stabilised (about 30 s after solution introduction).

High-performance liquid chromatography

Analysis of solutions by high-performance liquid chromatography (hplc) was done using a Waters pump, U6K injector with an R401 differential refractometer as the detector (Waters Associates Ltd., Harrow).

Reversed-phase columns (Dextropak, Waters Associates Ltd., and Whatman Partisil PXS 10/25 ODS-2, Whatman Ltd., Maidstone) were used

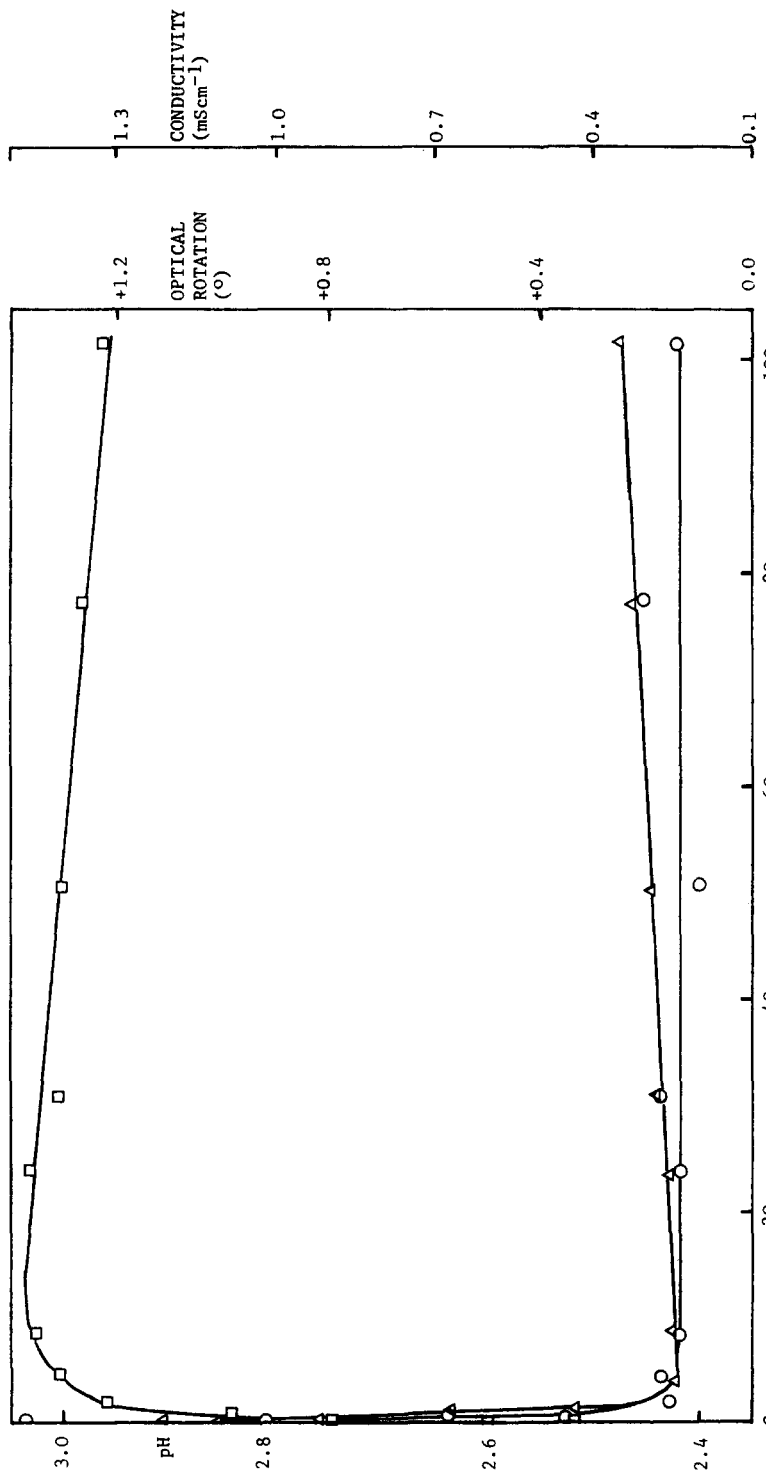


Fig. 1. Hydrolysis of D-glucono-1,5-lactone (1·78% w/v) at 20°C in water solution, no buffer. ○, pH; △, optical rotation (1 dm cell); □, conductivity with time.

to make chromatographic separation with water as the mobile phase. The column was pre-conditioned before use with tetrahydrofuran (not stabilised, hplc grade, Fisons Ltd., Loughborough; 100 to 150 cm^3 at 0·3 cm^3 min^{-1}) followed by water (0·3 cm^3 min^{-1} for about 20 h).

Calibration of lactone concentration by peak height was used in the study of D-glucono-1,5-lactone hydrolysis, comparing hplc analysis with optical rotation data. For this study, the standard lactone solutions were run immediately before the hydrolysing lactone to minimise machine error.

RESULTS AND DISCUSSION

The hydrolysis of D-glucono-1,5-lactone was monitored in several ways (Fig. 1). After the initial rapid hydrolysis, there was an increase in optical rotation

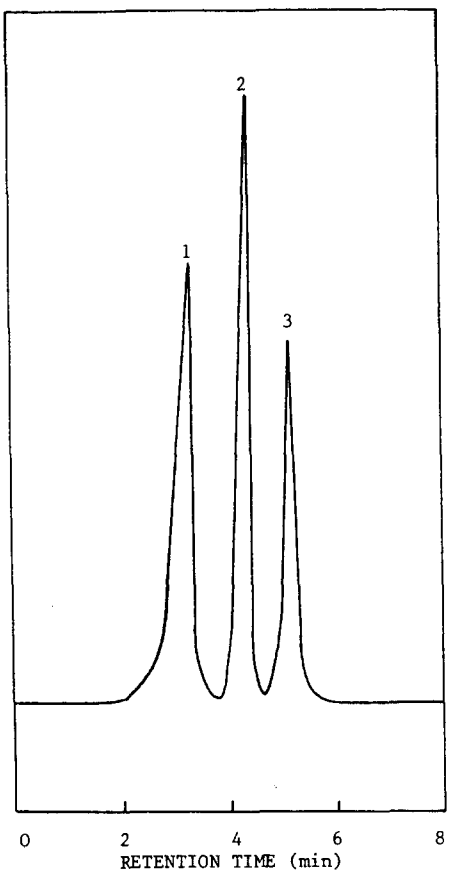


Fig. 2. Hplc analysis of (1) D-gluconic acid, (2) D-glucono-1,5-lactone, and (3) D-glucono-1,4-lactone. (Column: Dextropak; temperature: 20°C; eluent: water; flow rate: 0·7 cm^3 min^{-1}; sample: 5 μl of about 5·0% w/v total carbohydrate; detector: Waters R401 differential refractometer.)

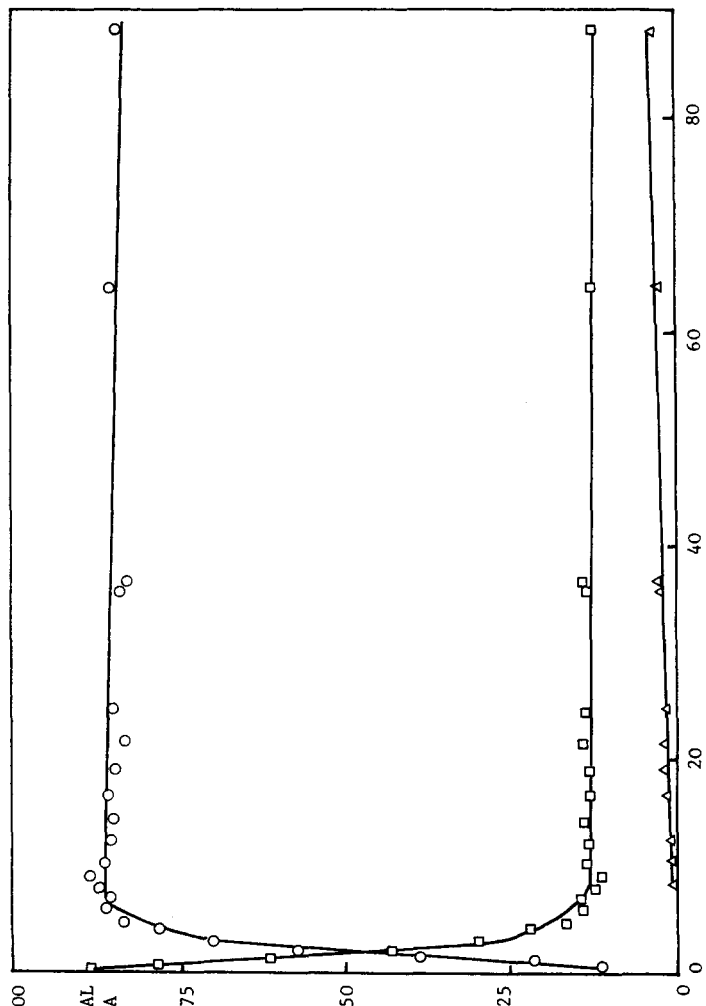


Fig. 3. Hydrolysis of D-glucono-1,5-lactone (1·78% w/v) at 20°C in water solution, no buffer, followed by hplc (Dextropak). ○, D-gluconic acid; △, D-glucono-1,4-lactone; □, D-glucono-1,5-lactone.

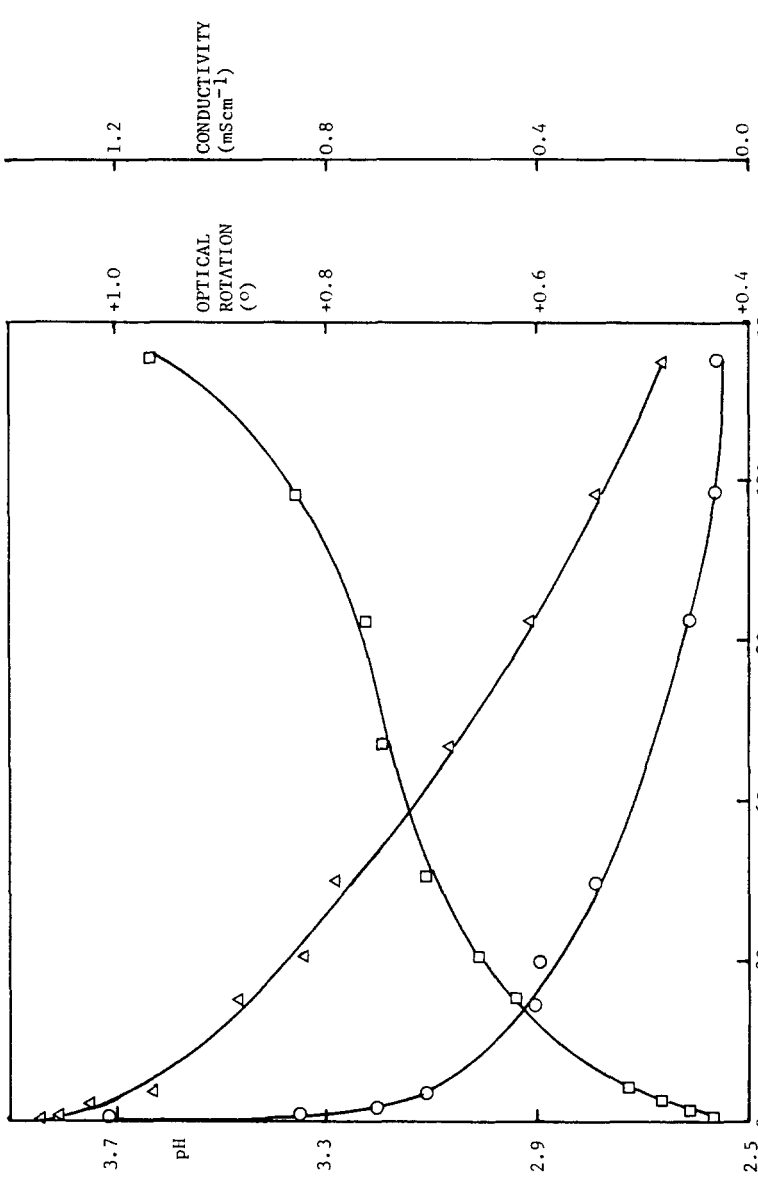


Fig. 4. Hydrolysis of D-glucono-1,4-lactone (1·78% w/v) at 20°C in water solution, no buffer. ○, pH; △, optical rotation (1 dm cell; □, conductivity.

and a decrease in conductivity, indicating the formation of lactone from D-gluconic acid. The components of this system were successfully resolved by high-performance liquid chromatography (hplc) (Fig. 2). The noted increase in optical rotation corresponded with an increase in the concentration of D-glucono-1,4-lactone in solution (Fig. 3).

In comparison with the 1,5-lactone, D-glucono-1,4-lactone hydrolysed slowly (Figs 4 and 5). The slow formation of D-glucono-1,5-lactone was

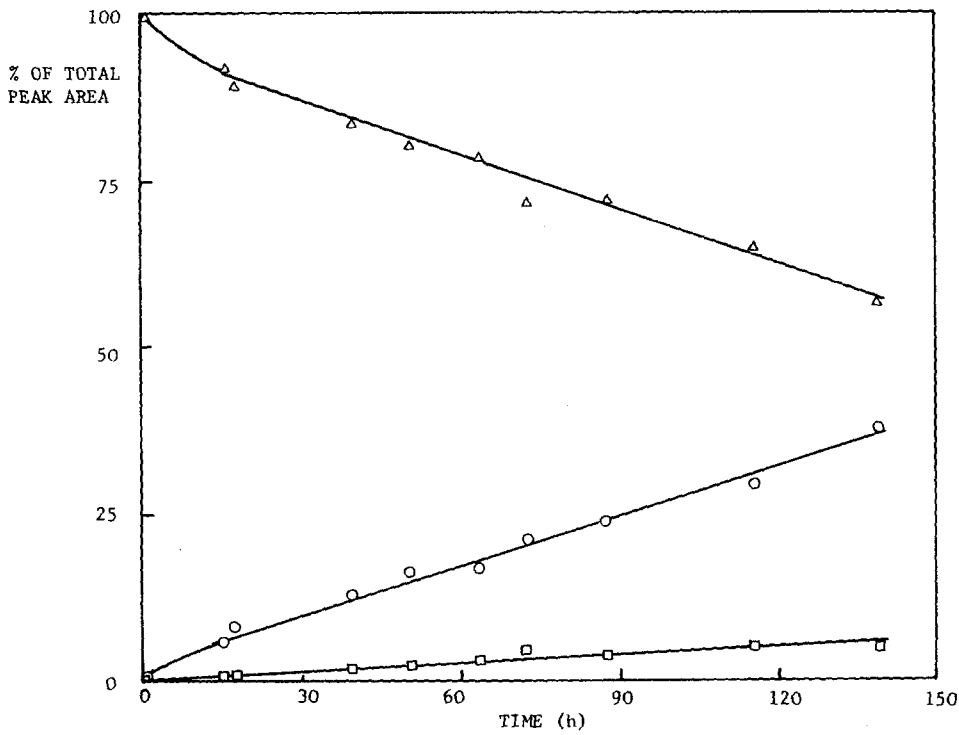


Fig. 5. Hydrolysis of D-glucono-1,4-lactone (1·78% w/v) at 20°C in water solution, no buffer, followed by hplc (Dextropak). ○, D-gluconic acid; △, D-glucono-1,4-lactone; □, D-glucono-1,5-lactone.

observed in this reaction. In general, aldono-1,4-lactones are more stable than the 1,5-lactones. This greater stability has been attributed to the well-established fact that an exo double bond stabilises a five-membered ring and destabilises a six-membered ring (Brown *et al.*, 1954).

The lactonisation of D-gluconic acid was characterised by a rapid increase in optical rotation (Fig. 6) corresponding to the formation of D-glucono-1,5-lactone (Fig. 7). A low level of D-glucono-1,4-lactone was detected by hplc in this reaction.

A correspondence between hplc data and data from optical rotation, pH

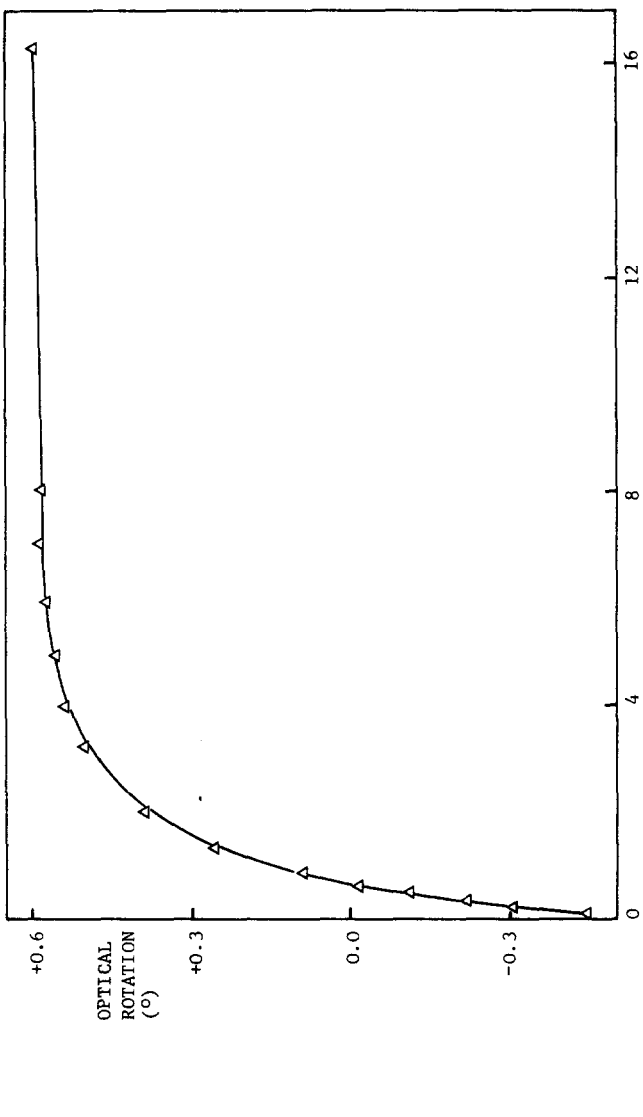


Fig. 6. Lactonisation of D-gluconic acid (4·5% w/v) at 20°C in water solution, no buffer, followed polarimetrically (2 dm cell).

and conductivity measurements was generally observed for these hydrolysis and lactonisation reactions. Upon close inspection of the hydrolysis of D-glucono-1,5-lactone, however, a slight difference in the rate of hydrolysis was observed, depending on whether optical rotation or hplc data were used to follow the reaction. By calibrating acid and lactones by optical rotation (Fig. 8), the optical rotation of samples measured by hplc could be calculated, assuming the rotations of acid and lactone are additive. These calculated

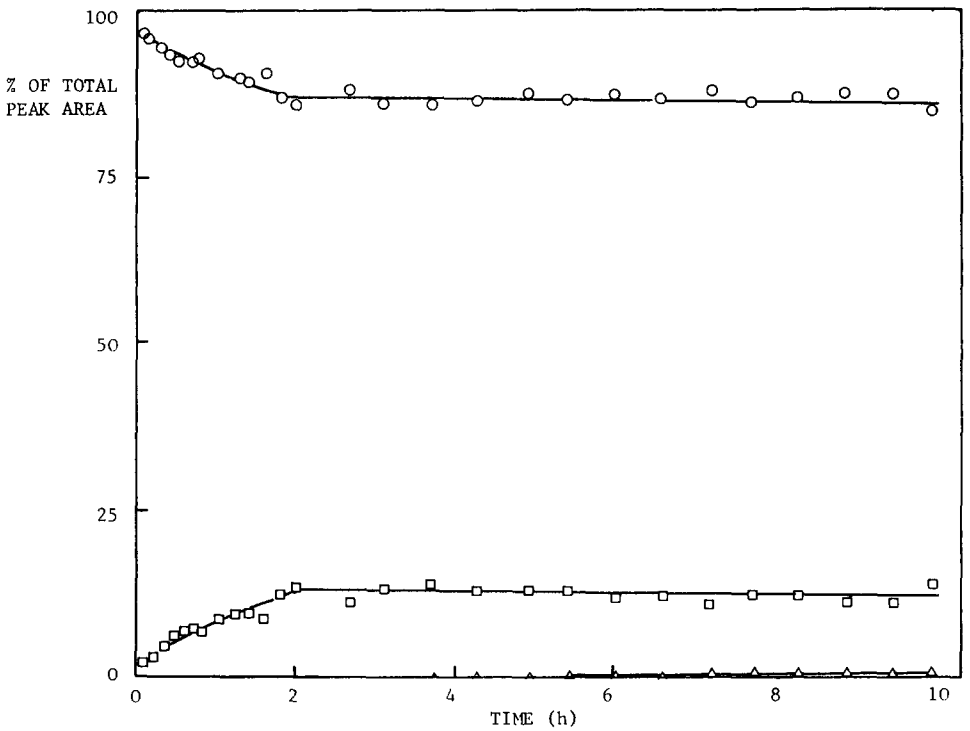


Fig. 7. Lactonisation of D-gluconic acid (4·5% w/v) at 20°C in water solution, no buffer, followed by hplc (Dextropak). ○, D-gluconic acid; △, D-glucono-1,4-lactone; □, D-glucono-1,5-lactone.

optical rotation values differed from the values found polarimetrically (Fig. 9). Closer agreement, however, was found using Partisil ODS-2 for the hplc column instead of Dextropak. Was the true rate of hydrolysis represented by hplc data, optical rotation data, or neither? One possibility was that D-gluconic acid affected the optical rotation of D-glucono-1,5-lactone such that the optical rotation of a solution of acid + lactone was not equal to the sum of their separate rotations. This hypothesis was tested by dissolving D-glucono-1,5-lactone in D-gluconic acid solution at different concentrations and measuring the optical rotation. For the concentrations of acid and

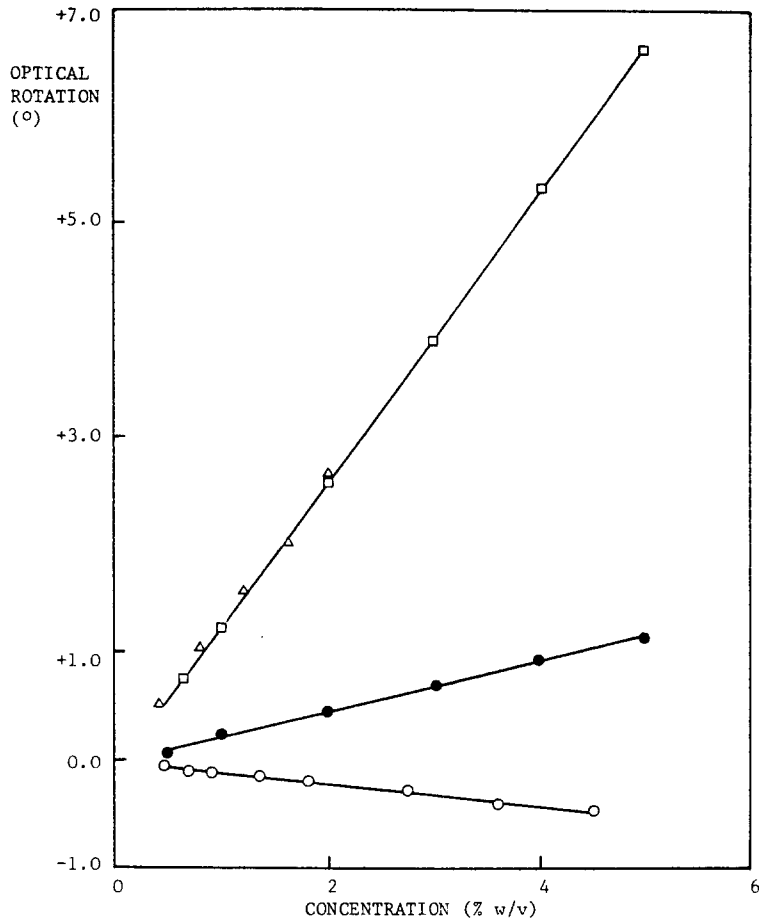


Fig. 8. Relation of optical rotation (2 dm cell) at 20°C to the concentration of D-gluconic acid (○), sodium D-gluconate (●), D-glucono-1,4-lactone (△), and D-glucono-1,5-lactone (□).

TABLE 1

Optical Rotation of D-Glucono-1,5-Lactone and D-Gluconic Acid, Separately and Combined

Solution	*Initial optical rotation*	
	Measured polarimetrically (20°C, 2 dm cell)	*Calculated by addition*
D-glucono-1,5-lactone (1·0% w/v)	+1·32°	
D-glucono-1,5-lactone (2·0% w/v)	+2·66°	
D-gluconic acid (2·7% w/v) (solution A)	−0·27°	
D-gluconic acid (4·5% w/v) (solution B)	−0·46°	
D-glucono-1,5-lactone (1·0% w/v) dissolved in A	+1·07°	+1·05°
D-glucono-1,5-lactone (1·0% w/v) dissolved in B	+0·88°	+0·86°
D-glucono-1,5-lactone (2·0% w/v) dissolved in A	+2·39°	+2·39°
D-glucono-1,5-lactone (2·0% w/v) dissolved in B	+2·20°	+2·20°

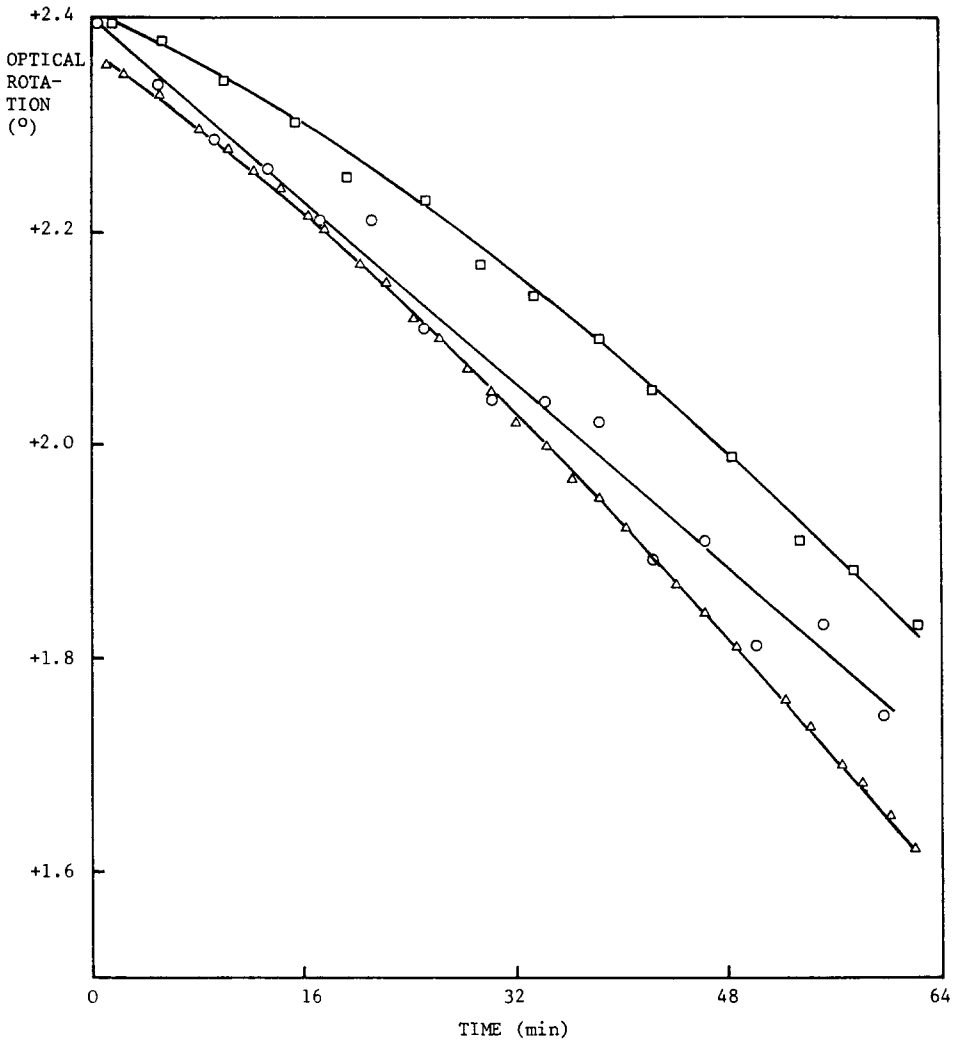


Fig. 9. Hydrolysis of D-glucono-1,5-lactone (1·78% w/v) at 20°C in water solution, no buffer. Optical rotation measured polarimetrically (2 dm cell (△)) and estimated from hplc data using Dextropak (□) and Partisil ODS-2 (○).

lactone examined, the rotation of a mixture was equal to the sum of the rotations of the components (Table 1). Optical rotation was therefore a true measure of the hydrolysis of this lactone.

Inorganic ions did, however, affect the optical rotation of D-gluconic acid (Fig. 10). Sodium sulphate increased, and sodium chloride decreased, the initial (zero time) rotation of D-gluconic acid, respectively. Conventionally, D-gluconic acid had been analytically prepared by acidifying sodium-D-gluconate solution with hydrochloric acid or sulphuric acid (Sawyer & Bagger, 1959). Using the latter technique the specific rotation of D-gluconic

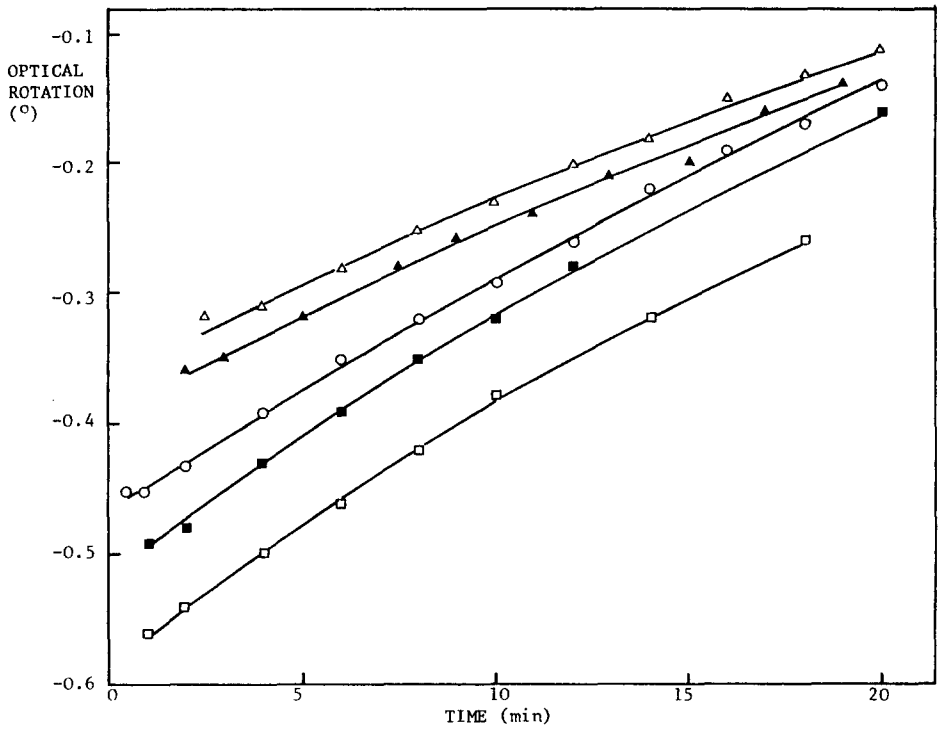


Fig. 10. Effect of inorganic ions on the optical rotation (2 dm cell) of D-gluconic acid (4·5% w/v) at 20°C. ○, No added salt; △, 1·63% w/v Na_2SO_4; ▲, 3·26% w/v Na_2SO_4; ■, 4·50% w/v NaCl; □, 9·00% w/v NaCl.

acid was found to be +5·40° (25°C, 0·05 to 0·10 mol dm^{-3} solution). This value was considerably higher than that determined in this study ($[\alpha]_D^{20} = -5{\cdot}11°$, *c*, 4·5, water).

The presence of sodium sulphate with D-gluconic acid may therefore have caused the higher rotation reported in the literature. In the present study, D-gluconic acid was made by cationic exchange of sodium-D-gluconate solution using ion-exchange resin in the hydrogen form; there were no interfering ionic effects.

Since the optical rotation of a solution of D-glucono-1,5-lactone in D-gluconic acid is equal to their combined rotations, the rate constants for the lactonisation and hydrolysis reactions were calculated using the following equation:

$$-\ln\frac{x_e - x}{t} = k_1 + k_{-1} \qquad (1)$$

x_e = equilibrium concentration of D-glucono-1,5-lactone (mol dm^{-3})
x = concentration of D-glucono-1,5-lactone (mol dm^{-3}) at time t
k_1 = rate constant for the lactonisation reaction
k_{-1} = rate constant for the hydrolysis reaction.

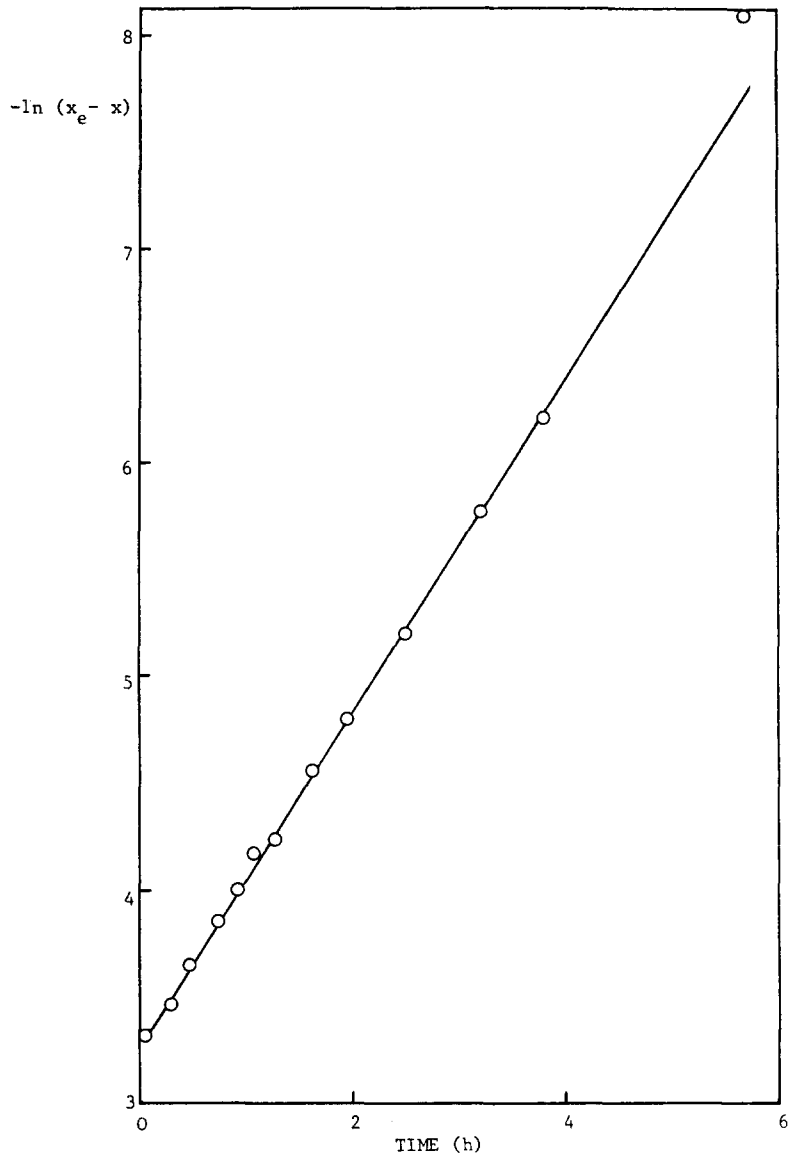


Fig. 11. Lactonisation of D-gluconic acid (4·5% w/v) at 20°C in water solution, no buffer. The slope of the line represents the sum of the rate constants for the lactonisation reaction and the hydrolysis of D-glucono-1,5-lactone. x_e and x represent the equilibrium concentration and the concentration at any time, respectively, for D-glucono-1,5-lactone.

Values for x_e and x were obtained from Fig. 6 (a constant pH of 2·4 pertained throughout reaction) and were used to construct the rate plot (Fig. 11). The slope of this plot is equal to $k_1 + k_{-1}$. This ratio of the concentration of the two components at equilibrium is equal to the ratio of the two rate constants:

$$\frac{k_1}{k_{-1}} = \frac{x_e}{a - x_e} \tag{2}$$

where a is the initial concentration of D-gluconic acid (mol dm^{-3}). The values of k_1 and k_{-1} can then be obtained by solving the two simultaneous equations (1) and (2). They were determined to be:

$$k_1 = 3{\cdot}807 \times 10^{-5}\, s^{-1}$$
$$k_{-1} = 1{\cdot}730 \times 10^{-4}\, s^{-1}$$

In this study of the D-gluconolactone-D-gluconic acid system a novel hplc method was used successfully to distinguish D-glucono-1,4-lactone, D-glucono-1,5-lactone and D-gluconic acid in water solution. This gave similar results to those obtained by optical rotation measurement of a 1,5-lactone solution undergoing hydrolysis and is therefore believed to be superior to alternative methods previously described (Jermyn, 1960; Takahashi & Mitsumoto, 1963; Shimahara & Takahashi, 1970. It has usually been assumed (Sawyer & Bagger, 1959; Mitchell & Duke, 1970) that a solution containing both D-glucono-1,5-lactone and D-gluconic acid has an optical rotation equal to the sum of their separate rotations; this assumption was shown to be justified for the concentrations tested here. Interactions between inorganic ions and D-gluconic acid affect its specific rotation. These interactions were probably responsible for the specific rotation of D-gluconic acid, determined in salt solution (Sawyer & Bagger, 1959), which differed appreciably from that determined here, in the absence of inorganic ions. Since the optical rotation of D-glucono-1,5-lactone solution at initial stages of hydrolysis was shown to be equal to the sum of the separate rotations of 1,5-lactone and D-gluconic acid formed, rate constants for both the hydrolysis and lactonisation reactions were determinable. This is the first reported method of obtaining these constants from a solution of D-gluconic acid and D-glucono-1,5-lactone containing no added buffer ions and at constant pH.

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