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Action of Neutral Sulphite Solution on Carbohydrates at High Temperatures. Part I. A Sulphocarboxylic Acid Derived from Xylose

SVEN YLLNER

Department of Wood Chemistry, Swedish Forest Products Research Laboratory, Stockholm, Sweden

When heated in neutral sulphite solution at 135°C xylose is rapidly degraded. From the reaction products an acid was isolated, which was shown to have the structure of α,δ-dihydroxy-γ-sulphovaleric acid. It was degraded to the lactone of β-sulpho-γ-hydroxybutyric acid, which was synthesised by the addition of sulphite to the lactone of γ-hydroxy*iso*crotonic acid.

In account of its technical importance, considerable interest has been devoted to the decomposition of carbohydrates in sulphite solutions at high temperatures. Thus Hägglund and Johnson [1] found that aldoses in acid sulphite solutions are oxidised to the corresponding aldonic acids, and in similar experiments on holocellulose Heiwinkel [2] and Adler [3] showed that a considerable part of the decomposition of carbohydrates must be attributed to the formation of sulphonic acids, which, on account of their stability to alkali, can be distinguished from the well-known aldehyde-bisulphite addition compounds. In continuing the early work of Marusawa *et al.*[4] concerning the action of bisulphite on glucose, Matsui [5] obtained a sulphonic acid, which he suggested was "levoglucosan-6-sulphonic acid".

A sulphonic acid of quite different type was isolated by Hägglund, Johnson and Urban [6] after heating glucose in sodium sulphite-bisulphite solution of pH 6. This acid contained one carboxyl, one carbonyl and one sulphonic acid group. From the reaction product Adler [3] isolated another sulphocarboxylic acid, which lacked the carbonyl function. Moreover, both acids, with the compositions $C_6H_9O_5(SO_3H)$ and $C_6H_{11}O_5(SO_3H)$, respectively, were proved to contain a terminal glycol grouping. The complete structure of these two acids remained unknown.

Recently, the production of wood pulp using the neutral sulphite process has steadily increased. Thus the decomposition of carbohydrates in neutral

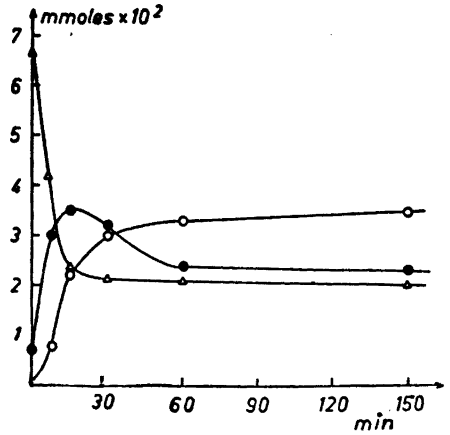


Fig. 1. The reaction of xylose in neutral sulphite solution at 135° C (using for titration 4 ml of the diluted reaction solution).

○ *"Total SO_2" consumed.*
● *"Loosely bound SO_2".*
△ *Reduction capacity calc. for xylose.*

sulphite solution is of current interest, and some additional facts pertaining to this subject have now been uncovered. As even glucose gives rise to rather complicated products, the problem has been somewhat simplified by using xylose as starting material. The present communication deals with the isolation and structural elucidation of α,δ-dihydroxy-γ-sulphovaleric acid, which is formed by heating xylose in neutral sulphite solution. Further work is in progress with the purpose of elucidating the mechanism of the formation of this acid.

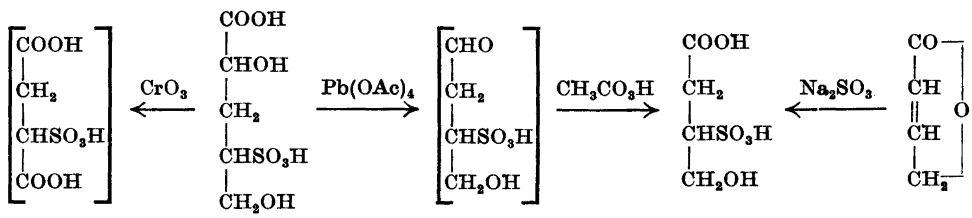
The course of the reaction at 135° C of xylose, dissolved in a solution of sodium sulphite and bisulphite in equimolecular amounts, was followed titrimetrically. The titrimetric method was essentially the same as used by Hägglund, Johnson and Urban [6] in the case of glucose, and the results are shown in Fig. 1.

The reduction capacity, calculated for xylose, decreased rapidly to an almost constant value corresponding to the decomposition of about 70 % of the initial quantity of xylose. Simultaneously "total SO_2" was consumed equivalent to the formation of sulphonic acid in a maximum yield of about 50 % calculated on xylose. The percentage of "loosely bound SO_2" was low at the start of the reaction, but rapidly increased to a maximum after 15 minutes. After one hour further heating produced only insignificant changes in the reduction capacity, "total SO_2" and "loosely bound SO_2". As was also reported by Hägglund, Johnson and Urban [6] in the case of glucose, no appreciable formation of sulphate (in the present investigation determined according to Samuelson and Ögren [7]) was found. The specific rotation calculated on the xylose content in the starting solution was +7.4°, but after 15 minutes at 135° C the reaction mixture no longer showed any optical activity. The pH (determined at room temperature) remained almost constant (6.5) during the cook.

From the reaction solution, after one hour at 135°, were isolated crude, optically inactive barium salts of organic acids containing sulphur and with a Ba to S ratio of 0.93—0.97. For a pure sulphocarboxylic acid this ratio is 1.

Calculated as such the yield of crude barium salt was almost 50 %. Coloured impurities were removed by passing an aqueous solution of the crude product through a carbon column. Although the barium salts thus purified, were almost homogeneous chromatographically (and gave the same analysis as the barium salt described below) they showed no tendency to crystallise. They were therefore converted into the brucine salts, which by crystallisation gave two compounds, one of which was obtained in about 50 % yield. This brucine salt, which could also be obtained directly from the crude barium salts in about 25 % yield, calculated on xylose, was converted back into the barium salt, which now crystallised readily. The pure barium salt was optically inactive.

According to the Ba to S ratio the molecule obviously contained one carboxyl and one sulphonic acid group. The free acid showed no tendency to lactonise in aqueous solution and the titration curve showed that the carboxyl group is strongly acidic. On the assumption of a C_5 unit, and since the substance showed no reducing properties, the remainder of the oxygen could probably be assigned to two hydroxyl groups. The substance thus seemed to be a dihydroxysulphovaleric acid, and closely related to the non-reducing "glucosesulphonic acid" isolated by Adler [3]. Unlike the latter acid it was not oxidised by periodic acid, and thus contains no glycol grouping. On the other hand it consumed one mole of lead tetraacetate with the libration of one mole of carbon dioxide indicating an α-hydroxycarboxylic acid grouping. Strong evidence for the second hydroxyl group being situated in terminal position



Scheme 1.

was obtained by oxidising the acid with dichromate. The consumption of dichromate was practically equal to that calculated (2.67 moles of CrO_3 per mole of sulphonic acid) for the formation of a sulphosuccinic acid (Scheme 1, Table 1).

The formulation of the acid as α,δ-dihydroxy-γ-sulphovaleric acid was supported by the following evidence: The product from the oxidation with lead tetraacetate (a sulphoaldehyde, not isolated) was oxidised with peracetic

Table 1. Oxidation of the sulphocarboxylic acid with dichromate.

Minutes	15	60	120	180	330	1 320
Moles of CrO_3 per mole of acid	1.19	1.81	2.16	2.36	2.60	2.76

acid to β-sulpho-γ-hydroxybutyric acid, which was isolated as the pyridinium salt of the corresponding lactone, the identity of which was shown by analysis and mixed melting point with an authentic sample of β-sulpho-γ-butyrolactone.

This was synthesised by the addition of sulphite to the lactone of γ-hydroxy*iso*crotonic acid, since, according to Schenck and Danishefsky [8], the addition of bisulphite to α,β-unsaturated carboxylic acids directs the sulphonic acid group to the β-position. The free β-sulpho-γ-hydroxybutyric acid lactonised spontaneously and the pyridinium salt of the lactone melted without decomposition and was suitable for the identification mentioned above. The sodium salt melted (with decomposition) about 30° lower than reported for the sodium salt of α-sulpho-γ-butyrolactone [9].

α,δ-Dihydroxy-γ-sulphovaleric acid contains two asymmetric carbon atoms. It therefore seems probable, that the crystalline brucine salt examined (rods), since it gave rise to an optically inactive barium salt, represents one of the two possible DL-forms of the acid. Further work will be done to elucidate the structure of the second brucine salt (needles), which may be derived from the other DL-form of this acid.

EXPERIMENTAL

Course of the reaction of xylose in sodium sulphite-bisulphite solution. Xylose (2.50 g), sodium pyrosulphite (3.7 g) and sodium sulphite hepta hydrate (9.8 g) were dissolved in water, and the solution made up to 100 ml. Samples (10 ml) of this solution were heated in sealed glass tubes in an oil bath at 135° C. When cooled each sample was diluted to 100 ml.

"Free SO_2" was determined by iodine titration of an acidified (pH 2) sample of this solution, and "total SO_2" by iodine titration of a sample buffered with calcium carbonate. "Loosely bound SO_2" was calculated as the difference between "total SO_2" and "free SO_2". The reduction capacity was determined according to Bertrand. The results are shown in Fig. 1.

Fractionation of the reaction products as barium salts. Xylose (5 g), sodium pyrosulphite (7.4 g), and sodium sulphite hepta hydrate (19.6 g) were dissolved in water (100 ml total volume) and the solution was heated in sealed glass tubes for one hour. The faintly yellow reaction mixture was passed through a column of Amberlite IR-120 (300 ml) in the H^+-state. Nitrogen was bubbled through the sodium free solution to remove most of the sulphur dioxide. Saturated barium hydroxide solution was then added until pH 7.5 was reached. Barium sulphate and sulphite were removed by filtration, and the solution, which had turned red, was evaporated *in vacuo* to 30 ml.

To the vigorously stirred solution ethanol (10 ml) was added dropwise, a syrupy precipitate being formed (fraction 1). The clear solution was decanted, another portion of ethanol (4 ml) was added giving a further, somewhat larger syrupy precipitate (fraction 2). Additional ethanol (20 ml) gave rise to only a small precipitate (fraction 3). The solution, containing more than 50 % ethanol, was evaporated *in vacuo* to 10 ml and further precipitation was effected by addition of this solution to ethanol (60 ml). The precipitate was washed with abs. ethanol and ether and dried (fraction 4). The syrupy fractions 1—3 were each dissolved in water (10 ml), precipitated in ethanol (60 ml), washed with ethanol-ether and dried. Amounts and compositions of the fractions 1—4 are shown in Table 2.

Chromatographic examination of the fractions. Samples (200 mg) of the fractions 1—4 were dissolved in water, and the solutions passed through columns of IR-120 in the NH_4^+-state. The ammonium salts were chromatographed on Whatman No. 1 filter paper with a solvent system of ethanol:water (4:1) using the descending technique. The chromatograms were sprayed, according to van Duuren [10], with 4 % formaldehyde and dried at 60° C in order to convert the ammonia to urotropine. The free acids were then detected by spraying with a solution containing starch, potassium iodide and iodate [10]. Fractions 1—3 were found to be very similar giving a few weak spots and one strong spot ($R_F = 0.20$),

Table 2. The crude barium salt fractions.

Fraction. No	g	% Ba	% S	Ba/S molar ratio
1	1.80	37.7	9.09	0.97
2	2.80	36.6	9.04	0.95
3	0.88	36.8	9.23	0.93
4	2.86	32.3	9.52	0.79

which obviously contained the main part of the acids. Fraction 4 on the other hand gave four almost equally strong spots with R_F-values of 0.20, 0.26, 0.30, and 0.36, and a somewhat weaker spot with R_F = 0.40. The identity of the latter four of these, which also appeared as very weak spots in the fractions 1—3 has yet not been established.

By using silver nitrate and sodium hydroxide as spray reagent according to Trevelyan *et al.*[11] no spots were obtained with R_F = 0.20, and only some of the substances in fraction 4 showed reducing properties.

Purification of the crude barium salt. Fractions 1—3 were strongly discoloured, but the impurities could be removed by filtering a water solution of the crude product through a carbon column (Carbo animalis:Celite, 1:1). The barium salt solution thus purified, was evaporated to a small volume and precipitated by pouring into ethanol. (Found: Ba 38.5; S 9.23; C 17.3; H 2.45. Calc. for $C_5H_8O_7SBa$: Ba 39.3; S 9.17; C 17.2; H 2.31.).

The purified amorphous barium salts (490 mg) were dissolved in water and the solution passed through a column (5 ml) of Amberlite IR-120 in the H^+-state. The acids were neutralised by brucine and the solution then evaporated to a small volume. By addition of acetone a rapid crystallisation was achieved. The crystals were quite uniform in the shape of rods, more or less collected in bundles. Yield 0.46 g.

The mother liquor gave a new fraction containing chiefly crystals of the same shape but also a few bundles of long needles. Yield 0.35 g. The two fractions were combined and recrystallised from water-acetone, the product being rods only. (Found: S 3.33; OCH_3 12.1. Calc. for $(C_{23}H_{26}O_4N_2)_2C_5H_{10}O_7S$: S 3.20; OCH_3 12.4).

Additional brucine salt (0.34 g), mainly the needle-like modification, was obtained from the mother liquor.

The brucine salt with rod-like crystals was converted into the barium salt which crystallised readily from a concentrated water solution in the form of short rods and was recrystallised from water-ethanol. (Found: Ba 37.2; S 8.58; C 16.4; H 2.33; H_2O 5.15. Calc. for $C_5H_8O_7SBa$, H_2O: Ba 37.4; S 8.73; C 16.4; H 2.74; H_2O 4.91.)

Oxidation of the sulphonic acid with dichromate. Crystalline barium salt (310 mg) was dissolved in water (25 ml) and a solution (50 ml) of sulphuric acid (5 ml) and potassium dichromate (0.88 g) was added. The reaction mixture was made up to 100 ml, and two samples (5 ml) were immediately taken at room temperature, when the oxidation was slow, and added to a mixture of potassium iodide and sulphuric acid. The liberated iodine was titrated with 0.05 N thiosulphate. After the starting concentration had been determined, the sealed reaction flask was placed in a boiling water bath. The reaction mixture was cooled to room temperature each time samples were taken, and these were titrated as mentioned. Results in Table 1.

Oxidation of the sulphonic acid with lead tetraacetate. a) *Course of the reaction.* The following solutions were made:

A. Crystalline barium salt (70.8 mg) was dissolved in water and the solution made up to 50 ml.

B. A saturated solution (15 ml) of lead tetraacetate in acetic acid was diluted with acetic acid to 100 ml.

C. Potassium iodide (10 g) and sodium acetate (50 g) were dissolved in water. and the solution made up to 100 ml.

Five ml of A were rapidly mixed with 5 ml of B. At the end of the reaction time 5 ml of C were added and the liberated iodine titrated with 0.01 N thiosulphate. In the blank, 5 ml of water were used instead of A. When the reaction time exceeded 20 minutes lead dioxide was precipitated, and correct titration figures could then not be obtained. Results in Fig. 2.

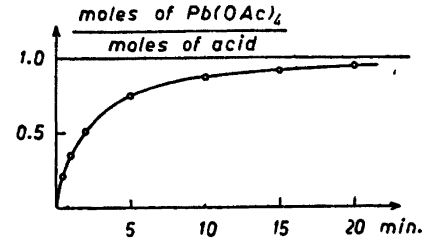


Fig. 2. Oxidation of the sulphocarboxylic acid with lead tetraacetate.

b) *Formation of carbon dioxide.* A test-tube (50 ml) fitted with a side tube and containing a saturated solution of lead tetraacetate in acetic acid (20 ml) was sealed with a rubber stopper fitted with a small separatory funnel and a capillary inlet tube reaching almost to the bottom of the test-tube. For 30 minutes a gentle stream of CO_2-free nitrogen was bubbled through the solution and was afterwards passed firstly through a tube containing $Mg(ClO_4)_2$ and kept at $-20°$ C and secondly through an absorption tube containing NaOH-asbestos. During this time the weight of the absorption tube was constant. The stream of nitrogen was cut off, a solution of the barium salt (209.6 mg) in water (5 ml) was added through the separatory funnel, which was washed out with a few millilitres of water and immediately closed. The stream of nitrogen was again passed through the apparatus, and the reaction tube warmed to 50° C. The absorption tube reached constant weight after about one hour. (Found: 25.0 mg of CO_2. Calc. for $C_5H_8O_7SBa$, H_2O: 25.1 mg of CO_2.)

c) *Degradation to β-sulpho-γ-hydroxybutyric acid.* The barium salt of the sulphonic acid (0.55 g) was dissolved in water and passed through a column (8 ml) of Amberlite IR-120 in the H^+-state. The solution of the free acid was diluted to 50 ml, and added to a saturated solution of lead tetraacetate in glacial acetic acid (50 ml). After 1 hour the reaction mixture was diluted with water (100 ml) in order to destroy excess lead tetraacetate. After filtration, a solution (2.0 ml) of peracetic acid [12] (equal volumes of H_2O_2 (30 %) and acetic anhydride, three days at room temperature) was added, and the reaction mixture kept at 75° C for 90 minutes. After cooling, excess H_2O_2 and CH_3CO_3H was destroyed by shaking the reaction mixture together with 1 g of Pd-asbestos (25 % Pd) overnight. The mixture was filtered, treated with H_2S and filtered again. The solution was evaporated *in vacuo* to 2.5 ml, kept at room temperature for three days for completion of lactonisation, neutralised with pyridine and evaporated to a syrup. This was dissolved in ethanol, some insoluble material was filtered off, and the solution again concentrated to a syrup. This was repeated once. The residual syrup was dissolved in 3 ml of ethanol, and a few drops of ether were added. A rapid crystallisation of the pyridinium salt of β-sulpho-γ-butyrolactone occurred. Recrystallisation from ethanol-ether yielded 0.21 g of optically inactive material. M. p. 160—161 °C. (Found: N 5.49; S 12.8; Calc. for $C_9H_{11}O_5NS$: N 5.72; S 13.1). No m. p. depression with an authentic sample of the pyridinium salt of β-sulpho-γ-butyrolactone was observed.

Synthesis of β-sulpho-γ-butyrolactone. γ-Hydroxy*iso*crotonic acid lactone (0.5 g), prepared according to Glattfeld *et al.*[13], was dissolved in a solution of sodium sulphite hepta hydrate (1.5 g) in water (3 ml). Sulphite was rapidly consumed, and the temperature rose to about 50° C. Next day the solution was passed through a column of Amberlite IR-120 in the H^+-state. The eluate was evaporated to 2 ml and kept at room temperature for three days. The acid was neutralised with pyridine (0.5 ml) and the solution evaporated to a syrup. When this was diluted with ethanol a rapid crystallisation of the pyridinium salt of β-sulpho-γ-butyrolactone occurred. Recrystallisation from ethanol-ether yielded prismatic plates, 1.05 g. M. p. 160—161 °C. (Found: N 5.55; S 13.2. Calc. for $C_9H_{11}O_5NS$: N 5.72; S 13.1.)

The sodium salt melted at 210-215° C (decomp.).

When chromatographed on Whatman No. 1 filter paper using the solvent system ethanol:conc. NH_3:water (20:1:4) and developing according to van Duuren [10] the acid gave two spots with R_F-values 0.28 and 0.41, respectively, the latter probably corresponding to the lactone and the former to the free sulphocarboxylic acid.

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