245. *Elimination Reactions of Esters. Part III.* Derivatives of Dibasic Polyhydroxy-acids.*

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The diacetate and the dimethanesulphonate of dimethyl (±)-ββ′-dihydroxyadipate undergo elimination with alkali and give *trans-trans*-muconic acid. Dimethyl mucate, with methanesulphonyl chloride and pyridine, undergoes esterification and elimination to give dimethyl *trans-trans*-αα′-dimethanesulphonyloxymuconate. Complicated changes occur on treatment of dimethyl 2 : 3 : 4 : 5-tetra-*O*-acetylmucate with dilute alkali; one product is αα′-dihydroxymuconic acid (αα′-diketoadipic acid).

Hydroxylation of *trans*-Δ^{β}-dihydromuconic acid with pertungstic acid results in a considerable amount of *cis*-addition, and gives the dilactone of (±)-ββ′-dihydroxyadipic acid. This, in cold alkaline solution, isomerises to the unsaturated lactonic acid, γ-carboxymethyl-Δ^{α}-butenolide. Mannosaccharodilactone, known to undergo a similar change under mild conditions (Heslop and F. Smith, *J.*, 1944, 577), on more vigorous treatment gives some αα′-dihydroxymuconic acid.

Only one ester group in the 2 : 5-dimethanesulphonate of mannosaccharodilactone is removed by reaction with sodium iodide and the product is probably γ-carboxymethylene-α-methanesulphonyloxy-Δ^{α}-butenolide; a stereoisomer is formed in a similar reaction with calcium carbonate.

The stereochemical results of these reactions can be explained by a mechanism of *trans*-elimination in all cases.

The elimination reactions described in Parts I and II (preceding papers) involved derivatives of mono- and di-hydroxy-monocarboxylic acids. In extending the investigation to dicarboxylic acids, some derivatives of ββ′-dihydroxyadipic acid were studied first, because they were expected to give a muconic acid, the various stereoisomers of which are now well known (Elvidge, Linstead, Sims, and Orkin, *J.*, 1950, 2235).

cis-Hydroxylation of methyl *trans*-Δ^{β}-dihydromuconate (I) with buffered aqueous permanganate at low temperature gave crystalline dimethyl (±)-ββ′-dihydroxyadipate (II), from which the diacetate and ditoluene-*p*-sulphonate (VIII) were prepared; with cold potassium hydroxide in aqueous dioxan both derivatives underwent a double elimination reaction and gave *trans-trans*-muconic acid (VII). In these reactions the probable occurrence of *trans*-elimination at each position in no way controls the stereochemistry of the resulting muconic acid, because two hydrogen atoms are available at each α-position, and free rotation is possible between all the carbon atoms in the saturated compounds. The formation of the *trans-trans*-acid is a consequence only of the fact that it is the most stable of the three isomers.

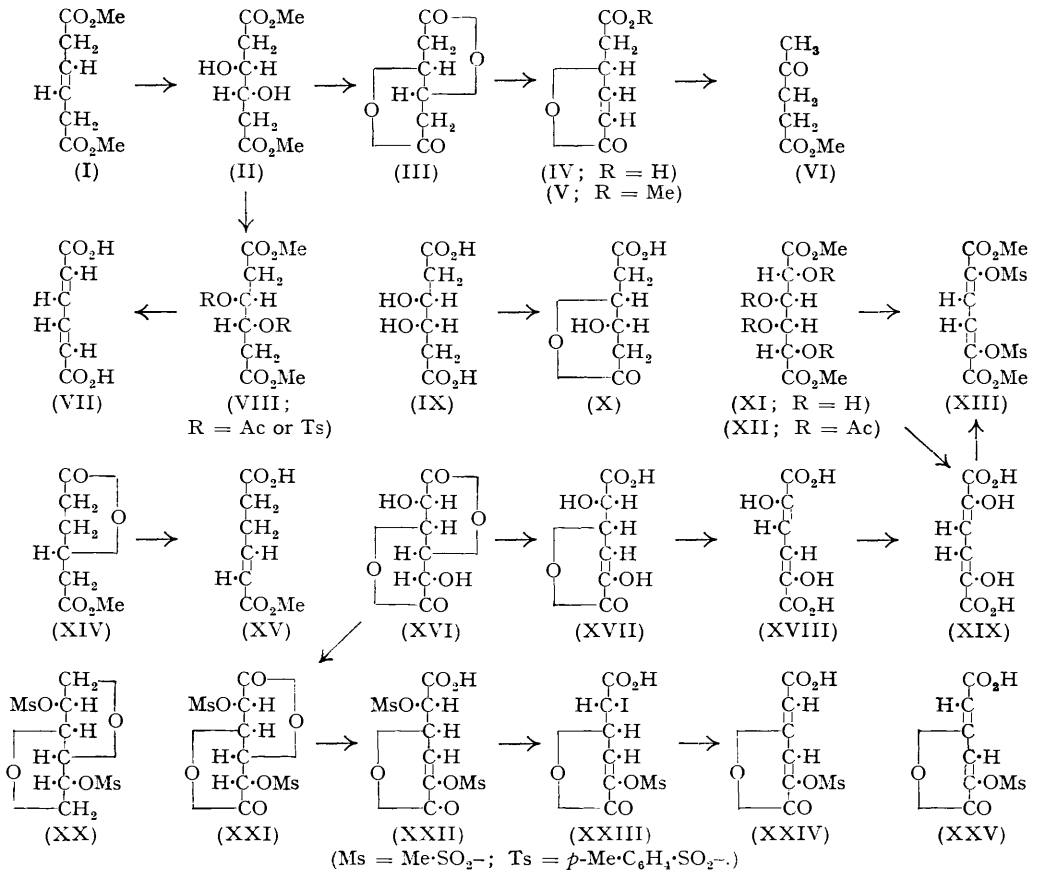
Attempts to prepare *meso*-ββ′-dihydroxyadipic acid (IX) by *trans*-hydroxylation of *trans*-Δ^{β}-dihydromuconic acid were unsuccessful. With pertungstic acid, a reagent which is stated (Mugdan and Young, *J.*, 1949, 2999) to bring about *trans*-addition, the product was a mixture of a mono- and a di-lactone, the latter being identical with the compound (III) previously isolated from the lactonisation products of *cis-cis*-muconic acid (Elvidge, Linstead, Orkin, Sims, Baer, and Pattison, *J.*, 1950, 2228; Elvidge, Linstead, Sims, and Orkin, *loc. cit.*). By analogy with the corresponding carbon-ring compounds (Barrett and Linstead, *J.*, 1935, 436) a *cis*-fusion of the two five membered rings is favoured, and the dilactone is therefore derived from the (±)-acid and not from the *meso*-form; † this is supported by the observation that the dilactone is obtained in almost quantitative yield by acid hydrolysis of the (±)-ester (II). The *meso*-acid, however, could form a monolactone (X), and it seems therefore, from the isolation of both products, that pertungstic acid has given both *cis*- and *trans*-hydroxylation. Reaction of *trans*-Δ^{β}-dihydromuconic

* Part II, preceding paper.

† Compare the ready formation of dilactones from mannosaccharic and glucosaccharic acids (*trans*-configuration of hydroxyls at $C_{(3)}$ and $C_{(4)}$), but not from mucic acid (*cis*-configuration).

acid with performic acid, a reagent which invariably results in *trans*-hydroxylation, gave only the monolactone (X); no dilactone could be detected.

Treatment of the methyl ester of (X) with toluene-*p*-sulphonyl chloride and pyridine gave γ-(methoxycarbonylmethyl)-Δ^{α}-butenolide (V); this reaction probably proceeds through the intermediate β-toluene-*p*-sulphonate, which is so unstable that it undergoes elimination of acid in the presence of pyridine. A similar reaction was shown by dimethyl mucate (XI), which on treatment with methanesulphonyl chloride and pyridine gave dimethyl *trans-trans*-αα′-dimethanesulphonyloxymuconate (XIII); the corresponding



ditoluene-*p*-sulphonate was obtained in the same way. Presumably the tetrasulphonates are initially formed, but are spontaneously decomposed by the pyridine. The configuration assigned to (XIII) is based on the assumption that *trans*-elimination occurs from both the β-positions; the presence of the highly conjugated muconic acid structure was confirmed by the absorption spectrum (maxima at 2720 and 2800 Å, ε 16,000 and 18,000). Unlike the α-sulphonyloxy-derivatives of crotonic and cinnamic acids, which were readily hydrolysed to the α-keto-acids (Part II, *loc. cit.*), the methanesulphonate (XIII) and the corresponding toluene-*p*-sulphonate were comparatively resistant; prolonged boiling with alkali, with a view to obtaining αα′-dihydroxymuconic acid (αα′-diketoadipic acid) gave only tars.

Kremann (*Monatsh.*, 1905, **26**, 783) found that hydrolysis of diethyl mucate and of tetra-*O*-acetylmucic acid with alcoholic alkali proceeded normally and gave a colourless solution, whereas diethyl tetra-*O*-acetylmucate gave a yellow solution and a brown precipitate which, although consisting largely of sodium mucate, contained an unidentified by-product. Simon and Guillaumin (*Compt. rend.*, 1924, **179**, 1324) reported, however,

that dimethyl tetra-*O*-acetylmucate (XII) on alkaline hydrolysis gave a quantitative yield of potassium mucate, though no experimental details were given. We found that this ester (XII), on brief treatment with an excess of warm aqueous-alcoholic alkali, gives a yellow solution having light-absorption consistent with the formation of αα′-dihydroxymuconic acid (XIX) (cf. Haworth, Hirst, and Jones, *J.*, 1938, 710; Wille, *Annalen*, 1939, **538**, 237). When the alkaline solution was kept for a short time the absorption spectrum altered, probably owing to further changes involving cyclisation to an α-pyrone, and ketonisation to αα′-diketoadipic acid; confirmation of the formation of the diketo-acid was provided by oxidation to succinic acid. Tetra-*O*-acetylmucic acid on similar treatment gave a colourless solution with no appreciable light-absorption, which shows that the activating effect of the free carboxyl groups is insufficient to cause elimination of acid. In Part I (*loc. cit.*) it was shown that elimination is favoured by the production of a highly conjugated product, and this probably accounts for the occurrence of elimination with (XII) and not with methyl αβ-diacetoxybutyrate (Part II, *loc. cit.*).

It has been pointed out (Elvidge, Linstead, *et al.*, *locc. cit.*) that the alkaline isomerisation of certain lactones to unsaturated acids is a special case of the elimination of a β-acyl group to form an αβ-double bond. Thus the lactone (XIV), which is an intramolecularly acylated β-hydroxy-ester, with sodium methoxide gives the αβ-unsaturated ester (XV). It was therefore of interest to examine the behaviour of the dilactone (III) towards alkali. The compound in aqueous solution showed no appreciable light absorption above 2200 Å, but in alkaline solution it showed end-absorption (ε 1200 at 2260 Å) which persisted, though with lower intensity (ε 400 at 2260 Å), when the solution was acidified. This behaviour suggested that isomerisation had occurred into the unsaturated lactonic acid (IV) (which also showed end-absorption of intensity greater in alkaline than in acid solution); and this was confirmed by isolation of (IV) after momentary treatment of the dilactone with 1 equivalent of cold dilute sodium hydroxide solution. A closely related compound, D-mannosaccharo-1 → 4 : 6 → 3-dilactone (XVI), has been shown by F. Smith and his associates to be very readily isomerised under mild conditions. Thus, with cold methanolic sodium methoxide it gives the enolic lactonic acid (XVII) (Heslop and Smith, *J.*, 1944, 577) whilst with diazomethane, or with silver oxide and methyl iodide, the corresponding methylated product is obtained (Haworth, Heslop, Salt, and Smith, *ibid.*, p. 217). The formation of (XVII) from (XVI) is exactly analogous to the conversion of the dilactone (III) into the lactonic acid (IV), and it is significant that the configuration of (XVI) is such that *trans*-elimination between $C_{(4)}$ and $C_{(5)}$ would give the necessary *cis*-configuration at the double bond in (XVII). We have now found that when mannosaccharodilactone is treated with an excess of sodium methoxide both lactone rings are opened to give an αα′-dihydroxymuconic acid, which, on the assumption that the second elimination also proceeds by a *trans*-mechanism, would be expected to have the *cis-cis*-configuration (XVIII). Since, however, the product is a di-enol, there is little doubt that under the basic conditions it would isomerise, through the diketo-form, into the more stable *trans-trans*-structure (XIX); its properties were, in fact, similar to those described by Wille (*loc. cit.*) for the αα′-dihydroxymuconic acid obtained by enolisation of αα′-diketoadipic acid, and its dimethyl ester, with methanesulphonyl chloride and pyridine, gave the dimethanesulphonate (XIII). The dilactone (III) might be expected to undergo a similar double elimination reaction with excess of alkali, but it has already been shown (Elvidge, Linstead, Orkin, Sims, Baer, and Pattison, *loc. cit.*) that the lactonic acid (IV) with hot aqueous sodium hydroxide gives lævulic acid, and not muconic acid; consequently it was not unexpected to find that methyl lævulate (VI) was obtained when the dilactone (III) was treated with an excess of hot methanolic sodium methoxide. The formation of keto-ester clearly involves a base-catalysed migration of the double bond in (IV), possibly after opening of the lactone ring, which evidently occurs much more readily than in (XVII).

Treatment of mannosaccharodilactone with methanesulphonyl chloride, toluene-*p*-sulphonyl chloride, or thionyl chloride under a variety of conditions gave only tars, but with methanesulphonic anhydride an almost quantitative yield of the crystalline 2 : 5-dimethanesulphonate (XXI) was obtained. This reacted with sodium iodide in boiling acetone, but only one sulphonyloxy-group was attacked. Since positions 2 and 5 in the

manno-configuration are identical, this result is at first sight very surprising, particularly since Wiggins and Wood (*J.*, 1951, 1180) have found that both ester groups in 2 : 5-dimethanesulphonyl 1 : 4-3 : 6-dianhydromannitol (XX) are reactive towards sodium iodide. In the present instance, however, a crystalline product, m. p. 155—156°, isolated in fair yield, had the properties and equivalent weight of an unsaturated monocarboxylic lactone; the absorption spectrum was similar to that of γ-carboxymethylene-Δ^{α}-butenolide (cf. Eisner, Elvidge, and Linstead, *J.*, 1951, 1501) and the compound is therefore formulated as γ-carboxymethylene-α-methanesulphonyloxy-Δ^{α}-butenolide (XXIV). If it be assumed that the initial reaction is an isomerisation of (XXI) to (XXII), the sulphonyloxy-group at $C_{(5)}$ would be expected, from analogy with (XIII), to be comparatively resistant. Under vigorous conditions (*e.g.*, at 120° under pressure) this remaining group was attacked by sodium iodide, lithium chloride, or potassium thiolacetate, but no recognisable products could be isolated.

When (XXI) was treated with calcium carbonate in boiling aqueous acetone it gave a compound, m. p. 144—145°, isomeric with (XXIV) and showing almost identical light-absorption, but the mixed melting point showed marked depression. The two products may be stereoisomers with regard to the exocyclic double bond; an initial replacement of the reactive methanesulphonyloxy-group by iodine, with inversion, to give (XXIII), followed by *trans*-elimination of hydrogen iodide, would clearly result in a *trans*-configuration (XXIV), whereas direct *trans*-elimination of methanesulphonic acid from (XXII) would give the *cis*-configuration (XXV).

Experimental

Dimethyl trans-Δ^{β}-*Dihydromuconate*.—Esterification (methanol–sulphuric acid) of *trans*-Δ^{β}-dihydromuconic acid (Ahmad, Sondheimer, Weedon, and Woods, *J.*, 1952, 4089) gave the dimethyl ester, b. p. 82°/0·2 mm., n_D^{21} 1·4490.

Dimethyl (±)-ββ′-*Dihydroxyadipate*.—To a vigorously stirred solution of *trans*-Δ^{β}-dihydromuconate (2·65 g.) in ethanol (100 c.c.), cooled to −40°, a solution of potassium permanganate (3·0 g.) and magnesium sulphate heptahydrate (3·0 g.) in water (100 c.c.) was added during 4 hours. The mixture was set aside at room temperature for 12 hours and then filtered, the manganese dioxide being thoroughly washed with water. The combined filtrate and washings were concentrated under reduced pressure and continuously extracted with ether. Evaporation of the dried (Na_2SO_4) extract gave a solid (0·9 g.) which on crystallisation from carbon tetrachloride afforded *dimethyl* (±)-ββ′-*dihydroxyadipate*, m. p. 76—77° (Found: C, 46·6; H, 7·1. $C_8H_{14}O_6$ requires C, 46·6; H, 6·9%). The *diacetate* (acetic anhydride–pyridine) formed needles (from carbon tetrachloride), m. p. 78°, b. p. 114—115°/0·001 mm. (Found: C, 49·7; H, 6·5. $C_{12}H_{18}O_8$ requires C, 49·6; H, 6·3%), and the *ditoluene*-p-*sulphonate* (toluene-*p*-sulphonyl chloride–pyridine at 0°), needles (from methanol), m. p. 142—143° (Found: C, 51·7; H, 5·5; S, 12·3. $C_{22}H_{26}O_{10}S_2$ requires C, 51·3; H, 5·1; S, 12·5%).

Action of Alkali on the (±)-*Diacetoxy- and Ditoluene*-p-*sulphonyloxy-adipates*.—(i) The diacetate (0·6 g.) was stirred at room temperature for 16 hours with potassium hydroxide (0·7 g.) in water (5 c.c.) and dioxan (13 c.c.); the excess of alkali was then neutralised with hydrochloric acid, and the dioxan was removed under reduced pressure with occasional addition of water. The solution was acidified with hydrochloric acid, concentrated (to 25 c.c.) at 40°/14 mm., and cooled. The precipitated solid (0·12 g.), m. p. 296—299°, was dissolved in aqueous sodium hydrogen carbonate; acidification of the filtered solution gave *trans-trans*-muconic acid, m. p. and mixed m. p. 300—301°.

(ii) The ditoluene-*p*-sulphonate (2·6 g.) was stirred for 12 hours with potassium hydroxide (3·4 g.) in water (25 c.c.) and dioxan (75 c.c.); the *trans-trans*-muconic acid (0·6 g.), isolated as above, had m. p. and mixed m. p. 301°.

γγ-*Dilactone of* (±)-ββ′-*Dihydroxyadipic Acid*.—A solution of dimethyl (±)-ββ′-dihydroxyadipate (30 mg.) in N-hydrochloric acid (5 c.c.) was slowly evaporated on the steam-bath (1 hour). The residue (20 mg.) solidified, and on crystallisation from ethyl acetate gave the dilactone, m. p. 127—128°, not depressed by a sample of similar m. p. prepared from *cis-cis*-muconic acid (Elvidge, Linstead, Orkin, *et al.*, *loc. cit.*).

Attempted trans-*Hydroxylation of* trans-Δ^{β}-*Dihydromuconic Acid*.—(i) Tungstic oxide (40 mg.) was dissolved in 30% hydrogen peroxide (35 c.c.) and water (50 c.c.); Δ^{β}-dihydromuconic acid (25·2 g.) in water (50 c.c.) was added, and the solution was stirred at 70° for 6 hours. Excess

of hydrogen peroxide was destroyed with sodium hydrogen sulphite (*ca.* 0·5 g.), and the solution acidified with 2N-hydrochloric acid and evaporated under reduced pressure. The residual dark syrup was extracted with acetone, and the extract dried ($MgSO_4$) and evaporated to a syrup (18 g.) which was dissolved in hot ethyl acetate (20 c.c.); from the cooled solution crystals (8·2 g.), m. p. 123—125°, were deposited. Recrystallisation from ethyl acetate afforded the γγ-dilactone, m. p. and mixed m. p. 127—128°, of (±)-ββ′-dihydroxyadipic acid. The original mother-liquors, after concentration, slowly deposited an acidic solid (4·3 g.), m. p. 53—62°. Recrystallisation from ethyl acetate gave hard nodules of *γ-carboxymethyl-β-hydroxybutanolide* (*γ-lactone* of *meso*-ββ′-dihydroxyadipic acid) (X), m. p. 91° (Found: C, 45·0; H, 5·2. $C_6H_8O_5$ requires C, 44·9; H, 5·1%).

(ii) [With P. Sims.] *trans*-Δ^{β}-Dihydromuconic acid (1 g.), formic acid (10 c.c.), and 30% hydrogen peroxide (0·9 c.c.) were kept together at 45° for an hour and then steam-distilled. The aqueous residue was evaporated under reduced pressure to a syrup, which slowly deposited a solid (0·6 g.). Recrystallisation from ethyl acetate gave the above monolactone, m. p. and mixed m. p. 91—92°.

γ-(Methoxycarbonylmethyl)-Δ^{α}*-butenolide.*—Treatment of γ-carboxymethyl-β-hydroxybutanolide (0·5 g.) with ethereal diazomethane furnished the viscous methyl ester (0·5 g.), b. p. 125°/0·0001 mm., which was dissolved in pyridine (1·5 c.c.), cooled to 0°, and treated with toluene-*p*-sulphonyl chloride (0·67 g.). After 60 hours at 0°, the mixture was diluted with ice-water (10 c.c.) and extracted with chloroform. The extracts were washed with 2N-sulphuric acid and with water, dried (Na_2SO_4), and distilled, to give a sulphur-free oil (0·3 g.), b. p. 82°/0·001 mm., n_D^{23} 1·4715. This failed to crystallise (Elvidge, Linstead, Orkin, *et al.*, *loc. cit.*, give m. p. 31°), but treatment of γ-carboxymethyl-Δ^{α}-butenolide with ethereal diazomethane, and distillation in the apparatus previously used, gave an identical product, b. p. 82°/0·001 mm., n_D^{23} 1·4718.

Dimethyl trans-trans-αα′*-Dimethanesulphonyloxymuconate.*—To dimethyl mucate (1·2 g.) suspended in pyridine (20 c.c.) at −5°, methanesulphonyl chloride (3·0 g.) in pyridine (10 c.c.) was added during ½ hour. The mixture was set aside at 0° for 20 hours, and diluted with ice-water (80 c.c.); the precipitate (1·3 g.) crystallised from di*iso*propyl ketone in colourless needles of *dimethyl* trans-trans-αα′*-dimethanesulphonyloxymuconate*, m. p. 204° (Found: C, 33·9; H, 4·3; S, 18·1. $C_{10}H_{14}O_{10}S_2$ requires C, 33·5; H, 3·9; S, 17·9%). Light absorption in dioxan: max. 2720, 2800 Å; ε 16,100, 18,300.

Dimethyl trans-trans-αα′*-Ditoluene-*p*-sulphonyloxymuconate.*—Similar treatment of dimethyl mucate (1·2 g.) in pyridine (20 c.c.) with toluene-*p*-sulphonyl chloride (4·1 g.) for 16 hours at 0° and 48 hours at room temperature gave plates (1·6 g.) (from chloroform–alcohol) of *dimethyl* trans-trans-αα′*-ditoluene-*p*-sulphonyloxymuconate*, m. p. 196° (Found: C, 51·4; H, 4·5; S, 12·2. $C_{22}H_{22}O_{10}S_2$ requires C, 51·7; H, 4·3; S, 12·5%).

Reactions of the Dilactone (III).—(a) *With aqueous sodium hydroxide.* (i) The dilactone (8 mg.) was dissolved in 0·05N-sodium hydroxide (10 c.c.). The solution gradually became bright yellow (5 minutes) and showed end light-absorption (ε 1200 at 2260 Å) which persisted (ε 400 at 2260 Å) in the colourless solution obtained when a portion was acidified with hydrochloric acid. When kept, the original alkaline solution became much paler, and after ½ hour was almost colourless, but there was little change in light-absorption (ε 1100 at 2260 Å; ε 400 after acidification). Similar colour changes occur with the γ-lactone of β-methylglucofururonoside (Owen, Peat, and Jones, *J.*, 1941, 339), which also contains two five-membered rings.

(ii) 1·00N-Sodium hydroxide (0·75 c.c.) was added to the dilactone (80 mg.) in water (2 c.c.). After 1 minute, 1·00N-hydrochloric acid (0·75 c.c.) was added, and the solution was evaporated to dryness at 0·2 mm. in a vacuum-desiccator over calcium chloride. The residue was triturated with ether (3 × 2 c.c.), which on evaporation gave a solid (30 mg.); recrystallisation from ethanol–benzene afforded γ-carboxymethyl-Δ^{α}-butenolide, m. p. and mixed m. p. 110°, which showed end light-absorption (at 2260 Å, ε 3100 in 0·05N-sodium hydroxide; ε 1400 after acidification).

(b) *With methanolic sodium methoxide.* The dilactone (2·3 g.) was kept with 0·2N-methanolic sodium methoxide (82 c.c.) at room temperature for 48 hours. Water (4 c.c.) was added, and the solution was neutralised with carbon dioxide, freed from methanol by evaporation, diluted with water (40 c.c.) and 2N-hydrochloric acid (12 c.c.), and continuously extracted with ether to give methyl lævulate (0·5 g.), b. p. 32°/0·0001 mm., n_D^{18} 1·4215 (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 140°).

Alkaline Hydrolysis of Dimethyl 2 : 3 : 4 : 5*-Tetra-*O*-acetylmucate.*—(i) To the ester (6 mg.)

(Simon and Guillaumin, *loc. cit.*) in ethanol (5 c.c.) at 60°, 2N-sodium hydroxide (0·1 c.c.) was added. The solution became bright yellow and cloudy. After 1 minute it was cooled and diluted to 10 c.c. with water, a clear yellow solution being obtained. This showed maximum light-absorption at 2650 and 3650 Å (ε 5000), changing on acidification (colourless solution) to 3230 Å (ε 5000). When the original alkaline solution was kept for an hour it became paler and showed maxima at 2930 and 3040 Å (ε *ca.* 1000), but the original acidified solution showed no change in appearance or absorption.

(ii) 2N-Sodium hydroxide (5 c.c.) was added to the ester (0·4 g.) in hot ethanol (20 c.c.). After 2 minutes, water (20 c.c.) was added and the clear yellow solution was cooled, acidified with 2N-sulphuric acid (10 c.c.), and concentrated under reduced pressure, with gradual addition of water, to remove all alcohol. More 2N-sulphuric acid (20 c.c.) was added, and the solution was heated to 70° and treated with 2% aqueous potassium permanganate until a pink colour persisted for 5 minutes. A trace of sodium sulphite was added to decolourise the filtered solution, which was then neutralised with sodium hydroxide, acidified with hydrochloric acid, and evaporated to dryness under reduced pressure. Extraction of the residue with boiling acetone gave an oil (0·1 g.) which partly crystallised and gave a strong fluorescein test with resorcinol and sulphuric acid; purification of the solid by sublimation and by recrystallisation from water gave succinic acid, m. p. 184°.

Mannosaccharo-1→4 : 6→3-dilactone.—Mannitol (60 g.) was heated at 60° with concentrated nitric acid (170 c.c.) and water (40 c.c.). After about 15 minutes the oxidation became vigorous and the solution was cooled in ice. It was then heated for 4 hours at 60° and for ½ hour at 85°, and evaporated under reduced pressure to a syrup, which was dissolved in ethanol (20 c.c.), and treated with ether (500 c.c.). The precipitate was recrystallised from 1 : 1 ethanol–ether (160 c.c.), and finally from ethanol, to give mannosaccharo-1→4 : 6→3-dilactone (12 g.), m. p. 187°, $[\alpha]_D^{22}$ +204° (*c*, 1·0 in water).

Reaction of Mannosaccharo-1→4 : 6→3-dilactone with Sodium Methoxide.—Sodium (4·6 g.) was dissolved in dry methanol (550 c.c.), the dilactone (4 g.) and glass beads were added, and the solution was refluxed under nitrogen for 6 hours. The orange precipitate (4·9 g.) was washed with ether and dissolved in water (100 c.c.). The solution was acidified with hydrochloric acid and evaporated at 40°/14 mm., under nitrogen, and the residue (dried by storage *in vacuo* over phosphoric oxide) extracted with dioxan (4 × 50 c.c.). The extracts, concentrated to 20 c.c., slowly deposited a solid (0·33 g.), m. p. 198—204°. Recrystallisation from dioxan afforded *trans-trans-αα′*-dihydroxymuconic acid, m. p. 242° (Wille, *loc. cit.*, gives m. p. 226—227° for the di-enol, and 234° for the diketo-acid). Treatment of a portion (0·1 g.) with boiling 1% methanolic hydrogen chloride gave the dimethyl ester (0·06 g.), m. p. 166° (from dioxan) (Wille, *loc. cit.*, gives m. p. 169—170°); light absorption in dioxan: max. 3230 Å, ε 14,800. With methanesulphonyl chloride and pyridine, this ester gave dimethyl αα′-dimethanesulphonyloxymuconate, m. p. 196—197°, not depressed on admixture with the compound, m. p. 204°, prepared from dimethyl mucate.

2 : 5-Dimethanesulphonyl Mannosaccharo-1→4 : 6→3-dilactone.—The mannosaccharodilactone (1·25 g.) was dissolved in methanesulphonic anhydride (5·0 g.) (Billeter, *Ber.*, 1905, **38**, 2018) by gentle warming; one drop of sulphuric acid was added and the solution was heated at 70° until it solidified (10 minutes). The product was cooled, water (40 c.c.) added, and the precipitated solid (2·4 g.), m. p. 176—179°, was washed with water and crystallised from ethyl formate in silky needles of *2 : 5-dimethanesulphonyl mannosaccharo-1→4 : 6→3-dilactone*, m. p. 200—201°, $[\alpha]_D^{20}$ +151° (*c*, 2 in dioxan) (Found: C, 29·3; H, 3·1; S, 19·4. $C_8H_{10}O_{10}S_2$ requires C, 29·1; H, 3·1; S, 19·4%).

Reactions of 2 : 5-Dimethanesulphonyl Mannosaccharo-1→4 : 6→3-dilactone.—(i) A solution of the dimethanesulphonate (6·6 g.) and sodium iodide dihydrate (15 g.) in acetone (200 c.c.) was refluxed, with occasional filtration, until 1 mol. (3·2 g.) of the sodium methanesulphonate–sodium iodide double salt had been precipitated (4 hours). The acetone was removed under reduced pressure, and the residue stirred with water (40 c.c.) and sufficient sodium thiosulphate to remove free iodine. Extraction with ether gave a solid, which on crystallisation from ethylene dichloride gave needles (3·8 g.) of *γ-carboxymethylene-α-methanesulphonyloxy-Δ$^{\alpha}$-butenolide*, m. p. 155—156° (Found: C, 36·1; H, 2·6; S, 13·6%; equiv. by rapid titration with 0·05N-baryta, 217. $C_7H_6O_7S$ requires C, 35·9; H, 2·6; S, 13·7%; equiv., 234). Light absorption in dioxan: max. 2510, 2690, 2800 Å; ε 10.500, 14,000, 16,800. With ethereal diazomethane it gave needles (from methanol) of *α-methanesulphonyloxy-γ-(methoxycarbonylmethylene)-Δ$^{\alpha}$-butenolide*, m. p. 111—112° (Found: C, 39·1; H, 3·4. $C_8H_8O_7S$ requires C, 38·7; H, 3·25%).

(ii) The dimethanesulphonate (5 g.), calcium carbonate (12 g.), water (5 c.c.), and acetone (150 c.c.) were refluxed for 24 hours; solid was then removed and washed with acetone (50 c.c.). The combined filtrate and washings were dried (Na_2SO_4) and evaporated under reduced pressure; the residue (2·5 g.), m. p. 138—140°, on recrystallisation from ethylene dichloride afforded an isomeric *γ-carboxymethylene-α-methanesulphonyloxy-*Δ^{α}*-butenolide*, m. p. 144—145° (Found: C, 36·1; H, 2·85; S, 13·6%; equiv., 212); light absorption in dioxan: max. 2510, 2690, 2800 Å; ε 9400, 14,500, 18,800. The m. p. was depressed to 137—139° on admixture with the isomer of m. p. 155—156°.

Light absorptions were determined in the spectrographic laboratory of this Department (Mrs. A. I. Boston).

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