The Structure of Daucic Acid †

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Daucic acid, a widely distributed sugar acid, has been shown to be 2,6-anhydro-3-deoxy-D-*xylo*-hept-2-enaric acid.

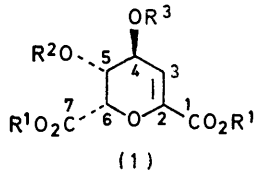
ANION-EXCHANGE chromatography of the nucleotide fraction of plant tissues frequently reveals acidic non-nucleotide contaminants.[1,2] Usually these have been detected by their characteristic u.v. absorption maxima. During a study on the free nucleotides of the root of carrot (*Daucus carota*),[3] a hitherto unreported contaminant, $\lambda_{max.}$ 240 nm, was observed to accompany the adenosine diphosphate fraction. This behaviour indicated the contaminant to be a strong or multibasic acid. A wider study showed the material, conveniently named daucic acid,[4] to be present in wheat (*Triticum sativum*), sugar beet (*Beta vulgaris*), sunflower (*Helianthus annuus*), and tobacco (*Nicotiana tabacum*). Thus it appears to be widespread across a range of plant families.

Bulk quantities of the acid were isolated from mature carrots by extraction of the pulped roots with hot water. After filtration, the acid, together with the nucleotide and polysaccharide material, was adsorbed on activated charcoal at pH 2. The charcoal was washed with water, and the acids desorbed with 0.2M-ammonium hydroxide. The solution was concentrated *in vacuo* and the ammonium salt of daucic acid was separated from high molecular weight material by gel filtration on Sephadex G 10 and G 50. Further purification was achieved by anion-exchange chromatography [5] and further adsorption on charcoal. The free acid was liberated by using the H^+ form of a cation-exchange resin. The resulting aqueous solution was evaporated and the residue recrystallised from ethyl acetate to give daucic acid (1; $R^1 = R^2 = R^3 = H$), m.p. 85—87° (0.0074% based on wet weight of carrot). The free acid could not be obtained analytically pure and was usually converted immediately into the dimethyl ester with diazomethane in methanol–ether.

Dimethyl daucate (1; R^1 = Me, $R^2 = R^3 = H$) had m.p. 130—131°, $[\alpha]_D^{24.5}$ −102°. Microanalysis and the mass spectrum indicated a molecular formula of $C_9H_{12}O_7$. The i.r. spectrum showed the presence of hydroxy ($\nu_{max.}$ 3 500 cm^{-1}) and saturated and unsaturated ester ($\nu_{max.}$ 1 740, 1 720, and 1 650 cm^{-1}) groups. The u.v. spectrum [$\lambda_{max.}$ (EtOH) 242 nm (ε 5 600)] agreed with that of the crude material and was consistent with an unsaturated ester assignment. The n.m.r. spectrum showed the presence of two methoxy-groups (singlets at τ 6.20 and 6.23), an olefinic proton (τ 3.96), and three protons α to oxygen (τ 5.34, 5.49, and 5.70, all multiplets). The coupling constants will be considered later.

The methylation procedure gave, in addition to dimethyl daucate, a mixture of dimethyl daucate monomethyl ethers (1; $R^1 = R^2$ = Me, $R^3 = H$) and (1; $R^1 = R^3$ = Me, $R^2 = H$), m.p. 114—115°, $[\alpha]_D$ −86°. These were chromatographically inseparable, but showed two additional methoxy-peaks (*ca.* 1.5 protons each) in the n.m.r. spectrum.

Acetylation of dimethyl daucate gave a diacetate (1; R^1 = Me, $R^2 = R^3$ = Ac), as an oil, and benzoylation gave a dibenzoate (1; R^1 = Me, $R^2 = R^3$ = Bz), m.p. 112°. The spectral data of these two compounds (see Experimental section) confirmed the assignments for dimethyl daucate. Coupling constants will be considered later.



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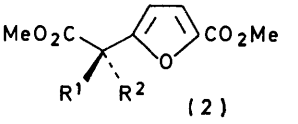

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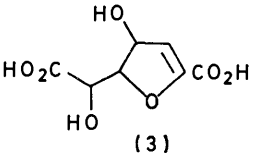

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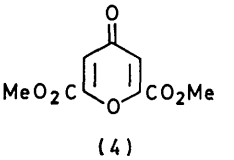

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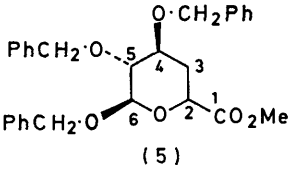

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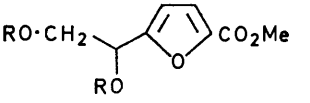


(6) R = H
(7) R = Ac

Treatment of the diester (1; R^1 = Me, $R^2 = R^3 = H$) with dry hydrogen chloride in anhydrous methanol gave the furan (2; R^1R^2 = H,OH), m.p. 134—135°, $[\alpha]_D$ +79°. Analytical data indicated the formula $C_9H_{10}O_6$. The u.v. spectrum [$\lambda_{max.}$ 256 nm (ε 16 600)] was consistent with a furoic ester and the i.r. spectrum showed the retention of a hydroxy-ester [$\nu_{max.}$ 3 500 and 1 740 cm^{-1}] and unsaturated (aryl) ester (1 720 and 1 600 cm^{-1}) functions. The n.m.r. spectrum confirmed the furan structure, with two aryl doublets (J 4 Hz) centred at τ 2.93 and 3.58.

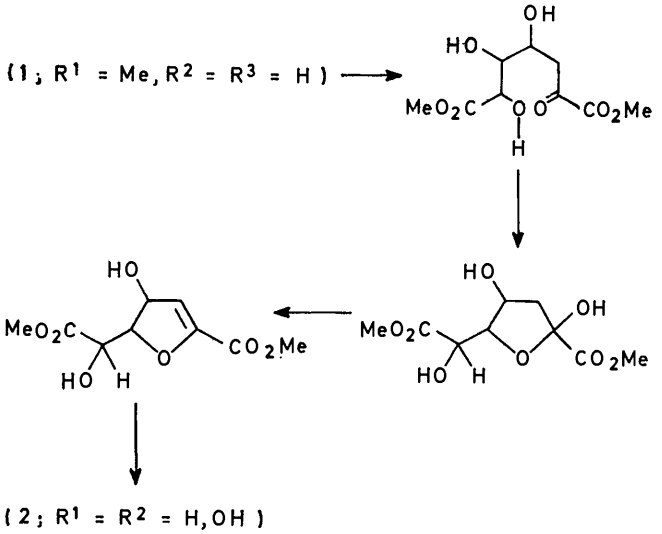
Oxidation of the furan ester (2; R^1R^2 = H,OH) with selenium dioxide gave the optically inactive furyl ketone

† Preliminary communication, ref. 4.

[1] M. R. Atkinson and A. G. Eckermann, *Austral. J. Biol. Sci.*, 1965, **18**, 437.
[2] M. J. Cornelius and A. J. Keys, unpublished results.
[3] C. J. Leaver, Ph.D. Thesis, University of London, 1966.
[4] A. J. Keys, C. L. Leaver, D. H. R. Barton, B. D. Brown, and D. A. Widdowson, *Nature*, 1971, **232**, 423.
[5] A. J. Keys, *Biochem. J.*, 1968, **103**, 1.

(2; R^1R^2 = O), with the expected spectroscopic properties. Finally, oxidation of (2; R^1R^2 = O) with alkaline hydrogen peroxide and methylation of the resultant diacid gave dimethyl furan-2,5-dicarboxylate, identical with authentic material obtained by conventional synthesis.[6]

At this stage, the evidence was consistent with either a dihydropyran or a dihydrofuran structure (3) for daucic acid. The n.m.r. evidence favoured the pyran alternative, but further chemical confirmation was sought. Oxidation of dimethyl daucate with chromium trioxide in pyridine gave dimethyl 4-oxo-4*H*-pyran-2,6-dicarboxylate (4), which finally confirmed the pyranoid alternative. The mechanisms of this oxidation deserved further investigation. The formation of the dimethyl ester (2; R^1R^2 = H,OH) from the pyran (1; R^1 = Me, R^2 = R^3 = H) is readily explained by the mechanism in Scheme 1.



SCHEME 1

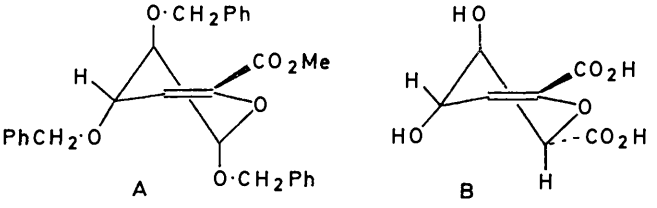
With the constitution of daucic acid established, attention was turned to the stereochemistry. The relative stereochemistry has been determined largely by ^{1}H n.m.r. spectroscopy. Assignments were made on the basis of chemical shifts and coupling constants. The lack of significant change in the coupling constants in dimethyl daucate on acetylation showed that no marked conformational change was produced and the data could be directly compared.

The ^{1}H n.m.r. coupling constants for dimethyl daucate and dimethyl daucate diacetate, determined by double resonance experiments and the INDOR technique,[7] are given in the Table, together with data for the uronate (5) (numbered as indicated for comparison). This compound has been shown to exist in the $^1H_2$ (here $^6H_5$) conformation (conformation A) with all the substituents axially oriented.[8] This conformation is dictated by the anomeric effect of the 6-benzyloxy-group. A comparison of the coupling constants of daucic acid derivatives with those of (5) show that as with (5) there are no *trans*-diaxial couplings. The values of $J_{3,4}$ and $J_{4,5}$ are comparable in both systems but $J_{5,6}$ is significantly less (2.0 and 1.8 Hz) in the daucic acid system than in the uronate (5) (5.5 Hz). These facts are consistent with H-4, -5, and -6 in (1) being equatorial, equatorial, and axial respectively (conformation B). The lower $J_{5,6}$ value would be a consequence of the larger (closer to 90°) torsion angle between axial and equatorial C–H than between the equatorial C–H bonds of (5). This structure requires that the methoxycarbonyl group at C-6 be equatorial, which is consistent with the known [9] inverse anomeric effect of this group. Conversely, for a methoxycarbonyl group at C-5 in hexopyranoses, a strong preference for equatorial orientation, irrespective of the remaining configurations, has been established.[8] By either consideration, methyl daucate would be expected to adopt a conformation with the methoxycarbonyl group equatorially oriented. It follows that the hydroxy-groups at C-4 and -5 are axial. The long-range coupling of H-3 to -5 (J 1.5 Hz) is consistent with a planar W conformation. Some chemical evidence for the *trans*-diaxial disposition of the hydroxy-groups arises from our inability to prepare a cyclic carbonate of dimethyl daucate under a variety of conditions. The compound is too unstable to acid for the alternative acetal formation.

Coupling constants (Hz)

Compound	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{3,5}$
Dimethyl daucate (1; R^1 = Me, R^2 = R^3 = H)	3	*a*	2.0	1
Dimethyl daucate diacetate (1; R^1 = Me, R^2 = R^3 = Ac)	2.6	4.4	1.8	1.5
(5)	3.5	4.5	5.5	*b*

[a] Indeterminate. [b] Not reported.



With the relative stereochemistry thus established, determination of the absolute stereochemistry of one of the asymmetric centres was necessary. Attention was thus turned to the absolute stereochemistry of the furan (2; R^1R^2 = H,OH).

The potential of this approach was readily realised. Racemic methyl 2-hydroxy-2-(5-methoxycarbonyl-2-furyl)acetate (2; R^1R^2 = H,OH) was synthesised by Friedel–Crafts alkylation of methyl 2-furoate with n-butyl glyoxylate. The resulting n-butyl ester was transesterified with methanol–toluene-*p*-sulphonic acid to give the required racemic diester (2; R^1R^2 = H,OH). This was reduced selectively with sodium borohydride in tetrahydrofuran to the racemic diol (6), which on treat

[6] P. A. Yoder and B. Tollens, *Ber.*, 1901, **34**, 3446.
[7] V. J. Kowalewski, D. G. Kowalewski, and E. C. Ferra, *J. Mol. Spectroscopy*, 1966, **20**, 203.
[8] J. Kiss and W. Arnold, *Helv. Chim. Acta*, 1975, **58**, 297.
[9] R. U. Lemieux and A. R. Morgan, *Canad. J. Chem.*, 1965, **43**, 2205.

ment with acetic anhydride in the presence of pyridine afforded the racemic diacetate (7). Ozonolysis of this diacetate in ethyl acetate at 0 °C, followed by methylation of the total acidic product with ethereal diazomethane, then gave racemic methyl 2,3-diacetoxypropionate in 55% yield.

Optically active methyl 2-hydroxy-2-(5-methoxycarbonyl-2-furyl)acetate was then required for correlation of the asymmetric centre with that of D-glyceraldehyde. It could be obtained from natural daucic acid, but since extraction was tedious and yielded only very small amounts of pure material, it appeared more readily available from synthesis. Accordingly the racemic furan (2; R^1R^2 = H,OH) was hydrolysed with an excess of potassium hydroxide in methanol and afforded the corresponding diacid, or was hydrolysed with sodium carbonate in aqueous tetrahydrofuran to the monoacid, 5-methoxycarbonyl-2-furylglycolic acid. Resolution of each of these acids was attempted with a variety of optically active bases [(−)-methylbenzylamine, brucine, quinine methohydroxide,[10] and (−)-amphetamine] under standard conditions but in all cases either amorphous solids or oils were obtained and no separation of the diastereoisomeric salts was achieved.

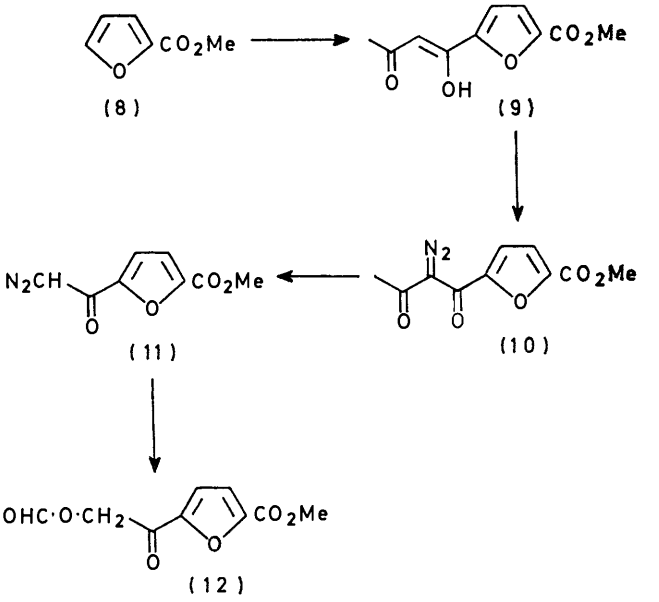
The preparation of the desired optically active diester by asymmetric reduction of a suitable ketone was then investigated. Enzymic reductions of functionalised ketones have been reported recently [11] and this method appeared attractive. Attention was thus turned to the synthesis of the precursors (2; R^1R^2 = O) and (12).

Oxidation of racemic methyl 2-hydroxy-2-(5-methoxycarbonyl-2-furyl)acetate with buffered aqueous potassium permanganate gave the oxo-ester (2; R^1R^2 = O) in 72% yield. Reduction of the oxo-ester with bakers yeast (*Saccharomyces cerevisiae*)–sucrose then afforded the furan (2; R^1 = OH, R^2 = H), $[\alpha]_D^{20}$ −66.5° (in acetone), in 55% yield. It was thus evident that this compound was enantiomeric with the compound, $[\alpha]_D^{25}$ +79% (acetone), obtained from daucic acid and that the extent of asymmetric synthesis achieved was 92%. Reduction of this furan derivative with sodium borohydride as described above then gave (−)-1-(5-methoxycarbonyl-2-furyl)-ethane-1,2-diol (6), $[\alpha]_D^{20}$ −24.2° (in $CHCl_3$).

This diol was also prepared as follows (Scheme 2). Although acetylation of methyl furoate had previously been reported, the yields of the monoacyl derivative were low and complex mixtures of products were obtained.[12] However, treatment of methyl furoate with two equiv. of acetic anhydride and of tin(IV) chloride in carbon disulphide gave the enol (9) in good yield. This product was readily converted into the diazo-diketone (10), which on treatment with sodium methoxide in methanol at 0 °C gave the diazo-ketone (11) together with dimethyl furan-2,5-dicarboxylate in 82 and 12% yield, respectively. Reaction of the diazo-ketone (11) with cold formic acid afforded the oxo-formate (12) quantitatively; the overall yield of compound (12) from the enol (9) was 78%. Finally, reduction of this oxo-formate with bakers yeast–sucrose gave the diol (6) (70%), $[\alpha]_D^{20}$ −25.2° (in $CHCl_3$).

Acetylation of the (−)-diol obtained by either route, followed by ozonolysis and then methylation of the crude acidic product, afforded methyl 2,3-diacetoxypropionate (15), $[\alpha]_D^{20}$ −5.9° (in $CHCl_3$).

For comparison purposes, methyl (+)-(*R*)-2,3-diacetoxypropionate (14), $[\alpha]_D^{20}$ +11.3° (in $CHCl_3$), was prepared from D-glyceric acid (13) by esterification with methanol–hydrogen chloride [13] and treatment of the



SCHEME 2

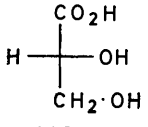
methyl ester with acetic anhydride–pyridine. It followed that the methyl (−)-2,3-diacetoxypropionate (15) had the *S*-configuration, and hence that the (−)-diol the *S*-configuration and the hydroxy-ester from reduction of the oxo-ester the *R*-configuration (2; R^1 = OH, R^2 = H). These stereochemical results from yeast reductions were not unexpected since in the reported reductions of methyl phenylglyoxylate and phenacyl alcohol, the alcohols produced had the corresponding absolute stereochemistries.[1]

Since the (−)-hydroxy-ester (2; R^1 = OH, R^2 = H) was enantiomeric with the derivative obtained from dimethyl daucate, this latter substance had the *S*-configuration (2; R^1 = H, R^2 = OH), and hence daucic acid is 2,6-anhydro-3-deoxy-D-*xylo*-hept-2-enaric acid (1; R^1 = R^2 = R^3 = H).

As the basis for a possible synthesis of daucic acid, we studied the reduction of dimethyl 4-oxo-4*H*-pyran-2,6-dicarboxylate (4). Treatment of this ester with sodium borohydride in methanol gave four isolable products (16)—(19). These could be separated by preparative

[10] R. J. Major and J. Finkelstein, *J. Amer. Chem. Soc.*, 1941, **63**, 1368.
[11] D. D. Ridley and M. S. Stralow, *J.C.S. Chem. Comm.*, 1975, 400.
[12] R. Ercoli, E. Mantica, G. Claudia, S. Chiozzotto, and E. Santambrogio, *J. Org. Chem.*, 1967, **32**, 2917.
[13] E. Baer, J. M. Grosheintz, and H. O. L. Fisher, *J. Amer. Chem. Soc.*, 1939, **61**, 2607.

layer chromatography and their characterisation followed from their spectral properties (see Experimental section), and additionally, for the dihydropyran (16), from oxidation with lead tetra-acetate to dimethyl 2,3-dihydro-4-oxopyran-2,6-dicarboxylate. In each case, the compounds were further characterised as acetates and benzoates. The products arose from a combination of conjugate addition of hydride ion and ester reduction. No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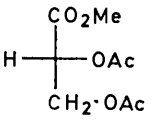
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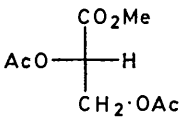
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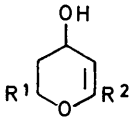
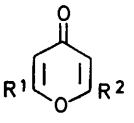
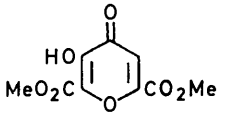


(16) $R^1 = R^2 = CO_2Me$
(17) $R^1 = CH_2 \cdot OH, R^2 = CO_2Me$




(20)

(18) $R^1 = CH_2 \cdot OH, R^2 = CO_2Me$
(19) $R^1 = R^2 = CH_2 \cdot OH$

conditions were found whereby selective conjugate addition could be achieved. The best yield of the 2,3-dihydropyran (16) was an unsatisfactory 16%. The analogous reduction of dimethyl 3-hydroxy-4-oxopyran-2,6-dicarboxylate (20) gave no isolable quantities of the corresponding daucic acid derivatives.

Although daucic acid has been detected in many plants, it became evident from the increasing u.v. absorbance during work-up that some at least of the compound was being generated during the treatment with charcoal. The possibility remains that the natural material is a hydrated form of daucic acid which undergoes elimination under the mild work-up conditions.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Optical rotations were determined for solutions in $CHCl_3$ unless otherwise stated. U.v. spectra were taken for solutions in MeOH, and n.m.r. spectra for solutions in $CDCl_3$ at 60 MHz, with tetramethylsilane as internal standard. P.l.c. refers to preparative layer chromatography on silica gel $PF_{254.366}$ (Merck). Light petroleum was the fraction, b.p. 40—60°.

Extraction of Daucic Acid (1; $R^1 = R^2 = R^3 = H$).—Mature carrots (20 kg) were washed and pulped, after removal of the tops. The pulp was added to boiling water (3 l) with vigorous stirring. The solution was left to cool (overnight) and filtered through asbestos wool. The clear filtrate was acidified to pH 1.5—2 (N-HCl). The acidified carrot juice solution was treated with activated charcoal (2 × 30 g). The charcoal was collected and washed with distilled water (1 l).

The charcoal filter cakes were suspended in dilute ammonia solution (0.02N; 600 ml) and 2N-ammonia solution was added dropwise to pH 7.5—8. After ½ h with occasional stirring, the charcoal was collected and subjected to two more extractions with dilute ammonia solution. The ammoniacal filtrate (1 800 ml) was concentrated (to 3 ml) by distillation at 30 °C under nitrogen at *ca.* 1 cmHg. The solution was introduced on to a column of Sephadex G 50 (15 g; 20 × 1.8 cm). The acids were eluted with water. Fractions (1 ml) of the effluent were collected and examined by u.v. spectroscopy. The high molecular weight fractions (1—40) showed very little 240 nm absorption. Those of low molecular weight (40—100) showed a strong 240 nm absorption.

This solution was concentrated (to 3 ml) by vacuum distillation as above and introduced on to a column of Sephadex G 10 (25 g; 20 × 1.8 cm). The acids were eluted with water, and fractions collected (1 ml) and examined by u.v. spectroscopy. The 240 nm compound appeared in fractions 20—35. Partial purification could be improved by successive reintroductions of the combined 240 nm fractions on to the column. Seven runs, however, still resulted in impure compound.

The impure combined fractions were introduced on to a Dowex 1 × 4, 200—400 mesh ion-exchange column [5] (2.8 cm diam., 15 cm long) which had been equilibrated with a solution (450 ml) containing AnalaR formic acid (90%; 63 ml l^{-1}), ammonium formate (13.5 g l^{-1}), and sodium chloride (29.5 g l^{-1}). The column was washed with distilled water until the u.v. absorption had fallen to a low level. The acidic material was eluted with a gradient of the above buffered salt solution (1 050 ml) against distilled water (6 050 ml). Fractions (25 ml) were collected at a flow rate of 5 ml min^{-1} and the column effluent was continuously monitored by u.v. spectroscopy.

The fractions containing the required compound (nos. 177—200; $E^{1\%}_{1\,cm}$ 150 for the purest fractions) were combined. Charcoal (1.5 g) was added and the solution stirred occasionally during 15 min. The charcoal was collected and washed thoroughly with distilled water (500 ml). The procedure was repeated four times, until the filtrate and washings showed no 240 nm absorption.

The combined portions of charcoal (4 × 1.5 g) were suspended in 0.02N-ammonia solution (60 ml). 2N-Ammonia was added dropwise to pH > 7.5. The solution was left with occasional stirring for 15 min.

The charcoal was collected and the extraction procedure repeated twice more. The combined charcoal extracts (180 ml) were concentrated under vacuum (to 3 ml) and introduced on to a cation-exchange resin column (H^+ form; Zeo Karb 225 or Dowex). The extracts were eluted with distilled water and the fractions (1 ml) analysed by u.v. spectroscopy until no more 240 nm acid compound was eluted. The combined 240 nm fractions were evaporated to dryness under vacuum. An oil (190—285 mg) was obtained, which could be crystallised from ethyl acetate to give impure *daucic acid* (1; $R^1 = R^2 = R^3 = H$), m.p. 85—87° (Found: C, 41.9; H, 4.5. $C_7H_8O_7$ requires C, 41.2; H, 4.0%).

Dimethyl Daucate and its Monomethyl Ethers.—The oil (1; $R^1 = R^2 = R^3 = H$) (30 mg) was dissolved in methanol (10 ml). Dry diazomethane in ether was added in excess. The solution was left at room temperature for 5 min. Evap-

oration, which removed the solvent and the excess of diazomethane, gave an oil which was purified by t.l.c. (30% acetone–petroleum, with plates developed three times; or 40% acetone–petroleum, with plates developed twice) to give *dimethyl daucate* (1; R^1 = Me, R^2 = R^3 = H) (77 mg), m.p. 130—131° (from ethyl acetate–light petroleum), $[\alpha]_D^{24.5}$ −102° (*c* 0.9 in Me_2CO), *m/e* 232 (M^+), 169, 155, 145 (100%), 139, and 127, $\lambda_{max.}$ (EtOH) 242 nm (ε 5 600), $\nu_{max.}$ (Nujol) 3 500, 1 740, 1 720, and 1 650 cm^{-1}, τ ($CDCl_3$) 3.96 (1 H, m, H-3), 5.34 (1 H, m, H-6), 5.49 (1 H, m, H-4), 5.70 (1 H, m, H-5), 6.20 (3 H, s OMe), 6.23 (3 H, s, OMe), and 6.72 (2 H, m, OH) (decoupling experiments gave $J_{3,4}$ 3, $J_{4,5}$ indeterminate, $J_{3,5}$ 1, $J_{3,6}$ 0, $J_{5,6}$ 2 Hz) (Found: C, 46.4; H, 5.0. $C_9H_{12}O_7$ requires C, 46.6; H, 5.2%); and dimethyl daucate monomethyl ether mixture [(1; R^1 = R^2 = Me, R^3 = H) and (1; R^1 = R^3 = Me, R^2 = H)] (inseparable; 28 mg), m.p. 114—115° (from methyl acetate–light petroleum), $[\alpha]_D^{23}$ −86° (*c* 0.2 in $CHCl_3$), M^+ 246, $\nu_{max.}$ (Nujol) 3 500, 1 740, 1 720, and 1 650 cm^{-1}, $\lambda_{max.}$ (EtOH) 242 nm (ε 5 490) (Found: C, 48.8; H, 5.7. Calc. for $C_{10}H_{14}O_7$: C, 48.8; H, 5.7%).

Dimethyl Daucate Diacetate (1; R^1 = Me, R^2 = R^3 = Ac).—Dimethyl daucate (19 mg) was acetylated with acetic anhydride–pyridine at room temperature. T.l.c. (40% acetone–light petroleum) gave the diacetate (29 mg) (as an oil), *m/e* 316 (M^+), 285, and 197, $\lambda_{max.}$ (EtOH) 237 nm, $\nu_{max.}$ ($CHCl_3$) 1 755, 1 745sh, and 1 665 cm^{-1}, τ (C_6D_6) 3.98 (1 H, m, H-3), 4.15 (1 H, m, H-5), 4.37 (1 H, m, H-4), 5.65 (1 H, m, H-6), 6.56 (6 H, s, OMe), and 8.21 (6 H, s, Ac), $J_{3,4}$ 2.6, $J_{4,5}$ 4.4, $J_{3,5}$, 1.5, $J_{3,6}$ 0, $J_{5,6}$ 1.8 Hz, τ ($CDCl_3$) 4.04 (1 H, m, H-3), 4.27 (1 H, m, H-5), 4.27 (1 H, m, H-4), and 5.18 (1 H, m, H-6), $J_{3,4}$ 2.3, $J_{5,6}$ 1.2, $J_{3,6}$ 0 Hz, $J_{4,5}$ not observable.

Dimethyl Daucate Dibenzoate (1; R^1 = Me, R^2 = R^3 = Bz).—Dimethyl daucate (26 mg) was benzoylated with benzoyl chloride in pyridine. T.l.c. (40% acetone–petroleum) gave the crystalline *dibenzoate* (46 mg), m.p. 112° (from methanol), $\lambda_{max.}$ (EtOH) 231 nm, $\nu_{max.}$ ($CHCl_3$) 1 763, 1 757, 1 743, 1 737, 1 723, and 1 684 cm^{-1}, *m/e* 218, 259, and 197; τ ($CDCl_3$) 2.07 (4 H, m), 2.64 (6 H, m), 3.90 (3 H, m), 4.93 (1 H, m), 6.10 (3 H, s), and 6.27 (3 H, s) (Found: C, 62.7; N, 4.7. $C_{23}H_{20}O_9$ requires C, 62.7; H, 4.6%).

Methyl 2-Hydroxy-2-(5-methoxycarbonyl-2-furyl)acetate (2; R^1R^2 = H,OH).—Dimethyl daucate (200 mg) in anhydrous methanol was treated with an excess of a saturated solution of dry hydrogen chloride in anhydrous methanol. The solution was refluxed until reaction was complete (4 h). The solvent and the excess of reagent were removed under vacuum. The oily residue was dissolved in anhydrous methanol, and dry diazomethane in ether was added. Evaporation gave a crystalline compound, which could be purified by t.l.c. (40% acetone–light petroleum) to give the *diester* (2; R^1R^2 = H, OH) (102 mg), m.p. 134—135° (from ethyl acetate–light petroleum), $[\alpha]_D^{25}$ + 79.3° (*c* 0.2 in Me_2CO), *m/e* 214 (M^+), 183, 155 (100%), and 122, $\lambda_{max.}$ (EtOH) 256 nm (ε 16 600), $\nu_{max.}$ ($CHCl_3$) 3 550, 1 740, 1 720, and 1 600 cm^{-1}, τ($CDCl_3$) 2.93 (1 H, d, *J* 4 Hz, H-3), 3.58 (1 H, d, *J* 4 Hz, H-2), 4.80 (1 H, s, α-H), 6.16 (3 H, s, OMe), 6.23 (3 H, s, OMe), and 6.74br (1 H, exchangeable with D_2O, OH) (Found: C, 50.3; H, 4.6. $C_9H_{10}O_6$ requires C, 50.5; H, 4.7%), identical except for m.p. and optical rotation with a racemic synthetic sample (see below).

Treatment of the product (10 mg) with acetic anhydride–pyridine, followed by t.l.c. (40% acetone–light petroleum) gave the *O*-acetyl derivative (2; R^1R^2 = H,OAc) (13.8 mg) as an oil, $\lambda_{max.}$ (EtOH) 253 nm (ε 15 820), M^+ 256, τ ($CDCl_3$) 2.91 (1 H, d, H-3), 3.50 (1 H, d, H-2), 3.92 (1 H, s, α-H), 6.20 (6 H, d, OMe), and 7.86 (3 H, s, COMe).

Methyl (5-Methoxycarbonyl-2-furyl)glyoxylate (2; R^1R^2 = O).—(*a*) Compound (2; R^1R^2 = H,OH) (90 mg) was dissolved in dry xylene (3 ml). Selenium dioxide was added and the mixture was refluxed until reaction was complete (1 h; t.l.c. in 40% acetone–light petroleum). The selenium and excess of selenium dioxide were filtered off and washed with small portions of hot xylene. The combined filtrate and washings were concentrated *in vacuo*, to yield a yellow crystalline solid which was purified by t.l.c. (40% acetone–light petroleum). Further purification was achieved by repeated p.l.c. as above, to give the crystalline *glyoxylate* (44 mg), m.p. 115—116° (from ethyl acetate–light petroleum or ethyl acetate), *m/e* 212 (M^+), 181, 153 (100%), and 140, $\nu_{max.}$ ($CHCl_3$) 3 050, 1 735, and 1 685 cm^{-1}, $\lambda_{max.}$ (EtOH) 293 (ε 13 000) and 257sh nm, τ ($CDCl_3$) 2.2 (1 H, d, H-3), 2.63 (1 H, d, H-4), and 6.00 (6 H, d, OMe) (Found: C, 51.1; H, 3.6. $C_9H_8O_6$ requires C, 51.0; H, 3.8%).

(*b*) Compound (2; R^1R^2 = H,OH) (12.1 mg) was dissolved in acetone (3 ml), Chromic acid (1 ml ≡ 20.16 mg [O], by standardisation) was added dropwise. Twice the theoretical amount of chromic acid solution was consumed, to obtain complete reaction. Work-up gave the glyoxylate in poor yield (1.4 mg), identical with the foregoing sample.

Dimethyl Furan-2,5-dicarboxylate.—The foregoing glyoxylate (25 mg) in methanol (2 ml) was treated with a mixture of 10% potassium hydroxide (2 ml) and methanol (2 ml) at 0—5 °C. When hydrolysis was complete (>5 min), hydrogen peroxide (30% w/v) was added in excess. The oxidative decarboxylation could be followed by the shift in the u.v. (EtOH) from $\lambda_{max.}$ 293 to 261 nm (2 h). The methanol was removed *in vacuo* and distilled water (4 ml) was added. The solution was acidified (dilute HCl), saturated with ammonium sulphate, and continuously extracted with ether (8 h). The extract was evaporated to yield an oil. This, in methanol (3 ml), was treated with dry diazomethane in ether in excess. T.l.c. (30% acetone–light petroleum) gave the furan diester (6 mg), m.p. and mixed m.p. 109—110° (from light petroleum), M^+ 184, $\lambda_{max.}$ ($CHCl_3$) 1 720 and 1 590 cm^{-1}, τ ($CDCl_3$) 2.90 (2 H, s) and 6.18 (6 H, s, OMe), identical (physical data and t.l.c. behaviour) with authentic material.[6]

Degradation to Dimethyl 4-Oxo-4H-pyran-2,6-dicarboxylate (4).—Chromium trioxide–pyridine complex (43.12 mg) was stirred in dry pyridine (3 ml) with dimethyl daucate (15.4 mg; molar ratio 1 : 2.5) at room temperature overnight. The mixture was poured into water, saturated with ammonium sulphate, and extracted continuously with ether (8 h). Removal of the solvent *in vacuo* gave an oil. T.l.c. (30% acetone–light petroleum; twice developed) of the combined product from two batches gave the pyran diester (6 mg), m.p. 115—116° (from ethyl acetate–light petroleum), M^+ 212, $\lambda_{max.}$ (EtOH) 270 (ε 10 660) and 280sh nm, $\nu_{max.}$ ($CHCl_3$) 1 750, 1 665, 1 637, and 1 605 cm^{-1}, τ ($CDCl_3$) 2.92 (2 H, s) and 6.08 (6 H, s), identical with an authentic sample.[14]

Methyl 2-Hydroxy-2-(5-methoxycarbonyl-2-furyl)acetate.—To finely crushed, anhydrous zinc chloride (45 g) were added methyl furan-2-carboxylate (12 g) and butyl glyoxylate (50 ml). The viscous suspension was stirred at 40 °C for 48 h, then diluted with ethyl acetate (500 ml) and dilute sulphuric acid (200 ml). The organic layer was washed with water, dried, and evaporated. The residue was distilled under reduced pressure. After a forerun of starting materials, *butyl 2-hydroxy-2-(5-methoxycarbonyl-2-furyl)acetate*

[14] R. Willstatter and R. Pummerer, *Ber.*, 1904, **37**, 3740.

(11.5 g, 47%) was obtained, b.p. 145—152° at 1 mmHg, $\nu_{max.}$ (film) 1 745 and 3 400 cm^{-1} (Found: C, 56.2; H, 6.2. $C_{12}H_{16}O_6$ requires C, 56.2; H, 6.3%).

The butyl ester (11.5 g) and toluene-*p*-sulphonic acid (1 g) were refluxed in methanol (200 ml) for 10 h. The solvent was evaporated off under reduced pressure and the residue was dissolved in ethyl acetate. The organic layer was washed with saturated sodium hydrogen carbonate solution, then with water, dried, and evaporated. The *methyl ester* was recrystallised from methanol to yield plates, m.p. 134—135°, $\nu_{max.}$ ($CHCl_3$) 1 750 and 3 550 cm^{-1}, τ ($CDCl_3$) 2.92 (1 H, d, *J* 3.6 Hz, H-4), 3.58 (1 H, d, *J* 3.6 Hz, H-3), 4.80 (1 H, s, α-H), 6.12 (3 H, s, OMe), and 6.60br (1 H, s, OH) (Found: C, 50.5; H, 4.3. $C_9H_{10}O_6$ requires C, 50.5; H, 4.7%).

Oxidation of Methyl 2-Hydroxy-2-(5-methoxycarbonyl-2-furyl)acetate.—To the methyl ester (2.20 g) in acetone (100 ml) were added potassium permanganate (1.6 g), potassium dihydrogen phosphate (0.34 g), and saturated aqueous magnesium sulphate (50 ml).[15] The solution was stirred at room temperature for 24 h, then further potassium permanganate (1 g) and potassium dihydrogen phosphate (0.18 g) were added and the mixture was stirred for another 24 h. The solution was decolourised with sodium disulphite solution, then evaporated under vacuum to remove most of the acetone. The residue was diluted with water and ether and the ether layer was washed with saturated sodium hydrogen carbonate solution, then with water. The dried extract was evaporated. The residue was chromatographed on silica gel to give *methyl 2-(5-methoxycarbonyl-2-furyl)glyoxylate* (1.6 g), m.p. 115—116°, $\nu_{max.}$ ($CHCl_3$) 1 700 and 1 735 cm^{-1}, τ ($CDCl_3$) 2.20 (1 H, d, *J* 3.8 Hz, H-4), 2.63 (1 H, d, *J* 3.8 Hz, H-3), 5.97 (3 H, s, OMe), and 6.02 (3 H, s, OMe) (Found: C, 51.0; H, 3.9. $C_9H_8O_6$ requires C, 51.0; H, 3.8%).

The hydrogen carbonate solution was acidified and extracted 3 times with ethyl acetate. The dried organic layer was evaporated and treated with a slight excess of ethereal diazomethane. The ethereal solution was worked up in the usual manner and afforded dimethyl furan-2,5-dicarboxylate (0.4 g), m.p. 114—115° (lit.,[6] 112°).

(−)-(R)-*Methyl 2-Hydroxy-2-(5-methoxycarbonyl-2-furyl)-acetate.*—To a stirred suspension of actively fermenting yeast (100 g) and sucrose (100 g) in water (500 ml) was added methyl 2-(5-methoxycarbonyl-2-furyl)glyoxalate (0.5 g) and the mixture was allowed to ferment at 25 °C for 2 days. The extract was diluted with ethyl acetate (500 ml) and filtered. The filtrate was separated and the aqueous layer was re-extracted with ethyl acetate (500 ml). The combined organic layers were dried and evaporated. The residue was subjected to p.l.c. and afforded the (−)-(R)-*ester* (0.28 g), m.p. 132—134°, $[\alpha]_D^{20}$ −66.5° (*c* 1 in Me_2CO), $\nu_{max.}$ and τ ($CDCl_3$) identical with those of the racemic compound (above).

Reduction of Methyl 2-Hydroxy-2-(5-methoxycarbonyl-2-furyl)acetate.—The racemic methyl ester (1.0 g) in tetrahydrofuran (50 ml) was stirred with sodium borohydride (1.0 g) at room temperature for 12 h. The solvent was evaporated off under reduced pressure and the residue was diluted with ethyl acetate and dilute sulphuric acid. The organic extract was dried and evaporated to leave an oil, $\nu_{max.}$ ($CHCl_3$) 3 500—3 200 and 1 740 cm^{-1}, τ ($CDCl_3$) 2.90 (1 H, d, *J* 3.5 Hz, H-4), 3.48 (1 H, d, *J* 3.5 Hz, H-3), 4.91 (1 H t, *J* 6 Hz, α-H), 5.30br (2 H, s, OH), 6.05 (2 H, d, *J* 6 Hz, CH_2O), and 6.18 (3 H, s, OMe). The oil was pure enough for use in the following step, but for analytical purposes a sample was further purified by p.l.c. This afforded 1-(5-*methoxycarbonyl-2-furyl)ethane-1,2-diol* (6) as an oil (Found: C, 51.3; H, 5.2. $C_8H_{10}O_5$ requires C, 51.6; H, 5.4%). Reduction of the (−)-(*R*)-methyl ester under similar conditions afforded the (−)-(*S*)-diol, $[\alpha]_D^{20}$ −24.2° (*c* 2 in $CHCl_3$), $\nu_{max.}$ and τ ($CDCl_3$) identical with those of the racemic compound (above).

1-(5-*Methoxycarbonyl-2-furyl)ethylene Diacetate* (7).—The racemic diol (0.5 g) was treated with acetic anhydride (0.5 ml) and pyridine (1 drop) at room temperature for 14 h. The excess of reagents was evaporated off at 40° at 0.2 mmHg to leave the *racemic diacetate*, an oil, $\nu_{max.}$ ($CHCl_3$) 1 755 and 1 745 cm^{-1}, τ ($CDCl_3$) 2.88 (1 H, d, *J* 3.5 Hz, H-4), 3.44 (1 H, d, *J* 3.5 Hz, H-3), 3.88 (1 H, t, *J* 6.0 Hz, α-H), 5.46 (2 H, d, *J* 6.0 Hz, CH_2O), 6.08 (3 H, s, OMe), 7.84 (3 H, s, OAc), and 7.88 (3 H, s, OAc) (Found: C, 53.2; H, 5.2. $C_{12}H_{14}O_7$ requires C, 53.3; H, 5.2%). Similar acetylation of the (−)-(*S*)-diol afforded the (−)-(*S*)-diacetate, an oil, $[\alpha]_D^{20}$ −68.1° (*c* 1.5 in $CHCl_3$), $\nu_{max.}$ and τ ($CDCl_3$) identical with those of the racemic compound (above).

4-*Hydroxy-4-(5-methoxycarbonyl-2-furyl)but-3-en-2-one* (9).—To an ice-cold solution of methyl furan-2-carboxylate (31.5 g) in acetic anhydride (51 g, 2 equiv.) was added tin(IV) chloride (130 g, 2 equiv.).[12] The mixture was stirred at room temperature for 24 h, poured into cold iced dilute sulphuric acid, and then extracted twice with ether. The combined extracts were washed three times with water, dried, and evaporated. A small amount of starting material was removed by triturating the residue with light petroleum, whereupon the residue crystallised as cubes. Recrystallisation from methanol–water afforded pale yellow cubes (38 g, 72%), m.p. 107—108°, $\nu_{max.}$ (Nujol) 1 705 cm^{-1}, τ ($CDCl_3$) −4.3br (1 H, s, OH), 2.7—2.9 (2 H, m, H-3 and -4), 3.72 (1 H, s, CH), 6.05 (3 H, s, OMe), and 7.78 (3 H, s, Ac), $\lambda_{max.}$ 276, 285, and 325 nm (log ε 4.0, 4.02, and 4.29), $\lambda_{max.}$ (MeOH–NaOH) 267 and 350 nm (log ε 4.33 and 4.33) (Found: C, 57.1; H, 4.85. $C_{10}H_{10}O_5$ requires C, 57.1; H, 4.8%).

2-*Diazo-1-(5-methoxycarbonyl-2-furyl)butane-1,3-dione* (10).—To an ice-cold, rapidly stirred solution of the enone (9) (31.5 g) in acetonitrile (400 ml) under nitrogen was added methanesulphonyl azide (18.3 g) and then triethylamine (15.2 g), dropwise.[16] The solution was stirred for 30 min after which the solvent was removed at 0 °C under reduced pressure. The residue was diluted with chloroform and the chloroform extract was washed with iced, dilute sulphuric acid, water, and brine. The dried organic layer was evaporated and gave the *diazo-diketone* (32.4 g), pale yellow cubes (from methanol), m.p. 81—82°, $\nu_{max.}$ (Nujol) 2 130 and 1 730 cm^{-1}, τ ($CDCl_3$) 2.65br (2 H, s, H-3 and -4), 6.02 (3 H, s, OMe), and 7.40 (3 H, s, Ac), $\lambda_{max.}$ 270 and 278 nm (log ε 4.2 and 4.2) (Found: C, 50.8; H, 3.4; N, 12.2 $C_{10}H_8N_2O_5$ requires C, 50.8; H, 3.4; N, 11.9%).

Methyl 5-Diazoacetylfuran-2-carboxylate (11).—To a stirred solution of sodium methoxide in anhydrous methanol [from sodium hydride as a 50% oil suspension (0.42 g) in methanol (100 ml)] at −15 °C under nitrogen was added the diazo-diketone (10) (2.06 g) in methanol (20 ml). The solution was stirred in the cold for 1 h, then rapidly poured into iced 0.5M sulphuric acid–chloroform with the minimum contact with air. The chloroform extract was dried and evaporated and the residue was chromatographed on silica gel. Elution with benzene afforded dimethyl furan-2,5-

[15] F. J. Wolf and J. Weijland, *Org. Synth.*, Coll. Vol. IV, 1963, p. 124.

[16] M. Regitz, *Angew. Chem. Internat. Edn.*, 1967, **6**, 733.

dicarboxylate (0.2 g); elution with benzene–ether (5 : 1) gave the *diazo-ketone* (11) (1.4 g), yellow plates (from methanol), m.p. 113—114°, $\nu_{max.}$ (Nujol) 2 120 and 1 740 cm^{-1}, τ ($CDCl_3$) 2.72 (2 H, m, H-3 and -4), 3.78 (1 H, s, $COCHN_2$), 6.05 (3 H, s, OMe), $\lambda_{max.}$ 274, 285, and 313 nm (log ε 4.20, 4.20, and 4.23) (Found: C, 49.5; H, 3.1; N, 14.2. $C_8H_6N_2O_4$ requires C, 49.5; H, 3.1; N, 14.4%).

Methyl 5-Formyloxyacetylfuran-2-carboxylate (12).—To ice-cold formic acid (10 ml) was added the diazo-ketone (11) (3 g). The mixture was stirred for 3 h, then poured into iced, saturated sodium hydrogen carbonate solution, and extracted twice with ether. The combined extracts were washed with water, dried, and evaporated. The *oxo-formate* (2.8 g) crystallised from methanol–ether as needles, m.p. 96—97°, $\nu_{max.}$ (Nujol) 1 720 and 1 695 cm^{-1}, τ ($CDCl_3$) 1.70 (1 H, s, CHO), 2.58—2.72 (2 H, m, H-3 and -4), 4.61 (2 H, s, CH_2), and 6.03 (3 H, s, OMe), $\lambda_{max.}$ 275 nm (log ε 4.3) (Found: C, 51.0; H, 3.7. $C_8H_8O_6$ requires C, 51.0; H, 3.8%).

Reduction of Methyl 5-Formyloxyacetylfuran-2-carboxylate (12).—To a stirred suspension of actively fermenting yeast (100 g) and sucrose (100 g) in water (500 ml) was added the oxo-formate (1 g) and the mixture was allowed to ferment at 25 °C for 2 days. The extract was diluted with ethyl acetate (500 ml) and filtered. The filtrate was separated and the aqueous layer was re-extracted with ethyl acetate (500 ml). The combined organic layers were dried and evaporated. The residue was subjected to p.l.c. and afforded (−)-(*S*)-1-(5-methoxycarbonyl-2-furyl)ethane-1,2-diol (6; antipode) (0.65 g), $[\alpha]_D^{20}$ −25.2° (*c* 1 in $CHCl_3$). Apart from the slightly higher rotation recorded here, this sample was identical with the sample described above.

Ozonolysis of 1-(5-Methoxycarbonyl-2-furyl)ethylene Diacetate (7).—Ozone was passed slowly through a solution of the racemic diacetate (1 g) in ethyl acetate (50 ml) at 0 °C for 3 h. The mixture was then flushed with nitrogen and treated with zinc dust (5 g) and acetic acid (1 ml) overnight. The mixture was filtered and the filtrate evaporated. The residue was treated with a slight excess of ethereal diazomethane at 0 °C and the mixture was worked up in the usual manner. The crude product was subjected to p.l.c. and afforded racemic methyl 2,3-diacetoxypropionate (14; racemate) (0.25 g). The spectra of this compound were identical with those obtained from authentic racemic methyl 2,3-diacetoxypropionate: $\nu_{max.}$ (film) 1 750—1 730 cm^{-1}, τ ($CDCl_3$) 4.72 (1 H, t, *J* 6 Hz, CH), 6.20 (3 H, s, OMe), 7.88 (3 H, s, OAc), and 7.94 (3 H, s, OAc).

Ozonolysis of the (−)-(*S*)-diacetate under similar conditions afforded (−)-(*S*)-methyl 2,3-diacetoxypropionate (15), $[\alpha]_D^{20}$ −5.9° (*c* 1·0 in $CHCl_3$), which similarly showed spectral properties identical with those given above.

(+)-(R)-*Methyl 2,3-Diacetoxypropionate* (14).—To (+)-(*R*)-methyl 2,3-dihydroxypropionate (13) (0.5 g),[13] prepared from (+)-(*R*)-glyceraldehyde, were added acetic anhydride (1 ml) and pyridine (1 drop) and the mixture was kept at room temperature for 10 h. The excess of reagents was evaporated off at 40° and 0.2 mmHg to leave the (+)-(R)-*triester* (0.52 g), $[\alpha]_D^{20}$ +11.3° (*c* 1 in $CHCl_3$) (Found: C, 47.0; H, 5.9. $C_8H_{12}O_6$ requires C, 47.1; H, 5.9%), $\nu_{max.}$ and τ ($CDCl_3$) identical with those obtained of the authentic, racemic compound (above).

2-(5-Carboxy-2-furyl)-2-hydroxyacetic Acid.—To a solution of methyl 2-hydroxy-2-(5-methoxycarbonyl-2-furyl)acetate (5 g) in methanol (100 ml) was added 3M-sodium hydroxide (10 ml). The mixture was kept at room temperature for 3 h, then acidified with dilute sulphuric acid and concentrated under reduced pressure to remove most of the methanol. The suspension was extracted three times with ethyl acetate and the combined organic layers were dried and evaporated. The residue was recrystallised from methanol to give cubes of the *acid*, m.p. 154—155°, $\nu_{max.}$ (Nujol) 2 550—3 400 cm^{-1}, τ [$(CD_3)_2SO$] 1.75br (3 H, s, OH), 2.72 (1 H, d, *J* 3.6 Hz, H-4), 3.35 (1 H, d, *J* 3.6 Hz, H-3), and 4.90 (1 H, s, CH) (Found: C, 44.9; H, 3.2. $C_7H_6O_6$ requires C, 45.2; H, 3.25%).

Reduction of Dimethyl 4-Oxo-4H-pyran-2,6-dicarboxylate (4) *with Sodium Borohydride–Methanol*.—The diester (179 mg) was dissolved in the minimum volume of dry methanol. Sodium borohydride (40 mg; molar ratio 1 : 1.25) was added to the stirred solution at room temperature. The reduction was followed by t.l.c. (40% acetone–light petroleum) until completion (20 min). The solvent was removed *in vacuo*. T.l.c. (30% acetone–light petroleum) gave four products. They were, in order of decreasing R_F value the 2,3-dihydropyran (16) (25 mg), the γ-pyrone (18) (38 mg), the 2,3-dihydropyran (17) (7 mg), and the γ-pyrone (19) (7 mg). A larger-scale reaction of the diester (48.3 mg) in dry methanol with sodium borohydride (64.05 mg) at room temperature gave unchanged diester (15 mg) and compounds (16) (47 mg), (18) (76 mg), (17) (15 mg), and (19) (15 mg).

Characterisation of the γ-pyrone (18). The *γ-pyrone* (18) had m.p. 138—139° (from ethyl acetate–light petroleum), M^+ 184, $\lambda_{max.}$ (EtOH) 261 nm (ε 7 570), $\nu_{max.}$ (Nujol) 3 200, 1 755, 1 740, 1 670, 1 650, 1 615, and 1 593 cm^{-1}, τ ($CDCl_3$) 3.00 (1 H, d), 3.50 (1 H, m), 5.45 (2 H, d), 6.05 (3 H, s), and 6.4 (1 H, OH), τ (C_2D_6CO) 3.58 (1 H, d), 4.00 (1 H, s), 5.93 (2 H, s), and 6.50 (3 H, s) (Found: C, 52.4; H, 4.6. $C_8H_8O_5$ requires C, 52.2; H, 4.4%). Acetylation gave the *monoacetate*, M^+ 226, τ ($CDCl_3$) 2.90 (1 H, d), 3.55 (1 H, d), 5.00 (2 H, s), 6.00 (3 H, s), and 7.80 (3 H, s). Benzoylation gave the *monobenzoate*, m.p. 121—122° (from dry methanol), M^+ 288, $\lambda_{max.}$ (EtOH) 255 (ε 21 190) and 261 nm (10 070), $\nu_{max.}$ ($CHCl_3$) 1 740, 1 670, 1 664, 1 630, and 1 605 cm^{-1}, τ ($CDCl_3$) 1.90 (2 H, m), 2.40 (3 H, m), 2.94 (1 H, d), 3.43 (1 H, d), 4.75 (2 H, s), and 6.00 (3 H, s) (Found: C, 62.4; H, 4.1. $C_{15}H_{12}O_6$ requires C, 62.5; H, 4.2%).

Characterisation of the γ-Pyrone (19).—The *γ-pyrone* (19) had m.p. 111—112° (from ethyl acetate–light petroleum), M^+ 156, $\lambda_{max.}$ (EtOH) 247 nm (ε 13 550), $\nu_{max.}$ (Nujol) 3 160—3 340, 1 665, and 1 610 cm^{-1} (Found: C, 53.6; H, 5.1. $C_7H_8O_4$ requires C, 53.8; H, 5.2%). The *dibenzoate* had m.p. 145—146° (from dry methanol), M^+ 364, $\lambda_{max.}$ (EtOH) 232 (ε 34 620) and 256sh nm; $\nu_{max.}$ ($CHCl_3$) 1 730, 1 675, 1 630, and 1 604 cm^{-1}, τ ($CDCl_3$) 2.00 (4 H, m), 2.50 (6 H, m), 3.50 (2 H, s), and 4.80 (4 H, s) (Found: C, 69.0; H, 4.6. $C_{21}H_{16}O_6$ requires C, 69.2; H, 4.4%).

Characterisation of the 2,3-dihydropyran (16). The *dihydropyran* showed M^+ 216, $\lambda_{max.}$ (EtOH) 236 nm, $\nu_{max.}$ (film) 3 440, 1 730, and 1 647 cm^{-1}, τ ($CDCl_3$) 3.80 (1 H, d), 5.10 (1 H, m), 5.65 (1 H, m), 6.15 (3 H, s), 6.23 (3 H, s), 7.80 (2 H, m), and 7.8 (1 H, OH) (Found: C, 51.1; H, 6.0. $C_9H_{12}O_6$ requires C, 50.0; H, 5.6%). The monoacetate showed M^+ 258, τ ($CDCl_3$) 3.83 (1 H, d), 4.65 (1 H, m), 5.05 (1 H, m), 6.13 3 H, s), 6.20 (3 H, s), 7.55 (2 H, m), and 7.98 (3 H, s). The *monobenzoate* had m.p. 115—116° (from dry methanol), M^+ 320, $\lambda_{max.}$ (EtOH) 234 (ε 19 410) and 240sh nm, $\nu_{max.}$ ($CHCl_3$) 1 762, 1 740, 1 723, 1 655, and 1 605 cm^{-1} (Found: C, 59.8; H, 4.8. $C_{16}H_{16}O_7$ requires C, 60.0; H, 5.0%).

Characterisation of the 2,3-dihydropyran (17). The dihydropyran showed M^+ 188. The *dibenzoate* had m.p. 120—

122° (from dry methanol), M^+ 396, $\lambda_{max.}$ (EtOH) 232 nm (ε 29 750), $\nu_{max.}$ ($CHCl_3$) 1 725, 1 655, and 1 605 cm^{-1}, τ ($CDCl_3$) 1.90 (4 H, m), 2.45 (6 H, m), 3.75 (1 H, m), 4.27 (1 H, m), 5.35 (2 H, s), 5.52 (1 H, m), 6.15 (3 H, s), and 7.80 (2 H, m) (Found: C, 66.7; H, 5.1. $C_{22}H_{20}O_7$ requires C, 66.7; H, 5.1%).

Synthesis of Dimethyl 2,3-Dihydro-4-oxopyran-2,6-dicarboxylate.—The 2,3-dihydropyran (16) (33.6 mg) was dissolved in dry chloroform. Activated manganese dioxide (270 mg; molar ratio 1 : 20) was added to the stirred solution at room temperature. The reaction was followed by t.l.c. (30% acetone–light petroleum) to completion (1 h). The manganese dioxide was filtered off and washed with chloroform. Evaporation of the combined filtrate and washings yielded a brown oil, which could be crystallised (ethyl acetate–light petroleum) to give the *γ-pyrone* (34.2 mg), m.p. 76—77°, M^+ 214, $\lambda_{max.}$ (EtOH) 276 nm (ε 10 240); $\nu_{max.}$ ($CHCl_3$) 1 749, 1 690, and 1 613 cm^{-1}, τ ($CDCl_3$) 3.70 (1 H, s), 4.83 (1 H, t), 6.10 (3 H, s), 6.19 (3 H, s), and 7.07 (2 H, d) (Found: C, 50.7; H, 4.7. $C_9H_{10}O_6$ requires C, 50.5; H, 4.7%).

Reductions of Dimethyl 3-Hydroxy-4-oxopyran-2,6-dicarboxylate (20).—The diester (20; 48 mg) was dissolved in dry methanol (2 ml). Sodium borohydride (40 mg; molar ratio 1 : 5) was added to the stirred solution at room temperature. The methanol was removed *in vacuo* and the residue acetylated. T.l.c. (40% acetone–petroleum) gave six products. These were isolated and their u.v. spectra (EtOH) checked. None agreed with that of dimethyl daucate diacetate.

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