856. *Aspects of Stereochemistry. Part XVI.*[1] *Intramolecular Hydrogen Bonding in Ethyl* 2,3-*Dideoxy*-α-D-erythro- *and* -threo-*hexopyranosides and Related Compounds.*

By A. B. Foster, R. Harrison, J. Lehmann, and J. M. Webber.

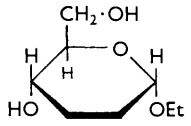
The conversion of ethyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside into the *threo*-isomer and into ethyl 2,3,6-trideoxy-α-D-*threo*-hexopyranoside is described, in which benzoate exchanges are the key steps. Deductions about the conformations of these glycosides in dilute solution in carbon tetrachloride are made from the patterns of intramolecular hydrogen bonding and in aqueous solution from optical rotations.

Continuing an investigation of the patterns of intramolecular hydrogen bonding in hydroxylated derivatives of tetrahydropyran,[2,3] we now report work on ethyl 2,3-dideoxy-α-D-*erythro*- and -*threo*-hexopyranoside and related compounds.

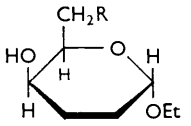
Ethyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside (I), first described by Bergmann,[4] was obtained after hydrogenation and saponification of ethyl 4,6-di-*O*-acetyl-2,3-didehydro-2,3-dideoxy-α-D-*erythro*-hexopyranoside. An additional, more direct proof of the D-*glycero*-configuration at position 4 of the latter compound was provided by ozonolysis: simultaneous reduction of the ozonide and saponification of the acetyl groups with sodium borohydride, followed by acidic hydrolysis gave erythritol, which was characterised as the di-*O*-benzylidene derivative.[5]

[1] Part XV, Buck, Foster, Lehmann, Perry, and Webber, *J.*, 1963, 4171.
[2] Brimacombe, Foster, Stacey, and Whiffen, *Tetrahedron*, 1958, **4**, 351.
[3] Barker, Brimacombe, Foster, Whiffen, and Zweifel, *Tetrahedron*, 1959, **7**, 10.
[4] Bergmann, *Annalen*, 1925, **443**, 223.
[5] Foster, Haines, and Lehmann, *J.*, 1961, 5011.

With sodium benzoate in boiling dimethylformamide, ethyl 2,3-dideoxy-4,6-di-*O*-methanesulphonyl-α-D-*erythro*-hexopyranoside gave ethyl 4,6-di-*O*-benzoyl-2,3-dideoxy-α-D-*threo*-hexopyranoside and thence ethyl 2,3-dideoxy-α-D-*threo*-hexopyranoside (II) by saponification. The diol (II) was characterised further as the di-*p*-phenylazobenzoate, as also was the *erythro*-diol (I). One methanesulphonate group was displaced from ethyl 2,3-dideoxy-4,6-di-*O*-methanesulphonyl-α-D-*erythro*-hexopyranoside on treatment with sodium iodide in acetone at 115°. By analogy with other iodine exchanges,[6] displacement

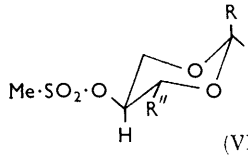


(I)



(II: R = OH)

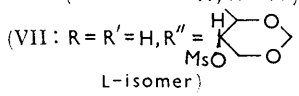
(III: R = H)



(IV: R = R′ = R″ = H)

(V: R′ = R″ = H, R = Ph)

(VI: R = R″ = H, R′ = Ph)



(VIII: R = H, R′ = Ph, R″ = Me)

of the primary methanesulphonate group would be expected, and this course of reaction was confirmed by the solution spectra considered later. Reduction of ethyl 2,3,6-trideoxy-6-iodo-4-*O*-methanesulphonyl-α-D-*erythro*-hexopyranoside with hydrogen in the presence of Raney nickel and diethylamine gave ethyl 2,3,6-trideoxy-4-*O*-methanesulphonyl-α-D-*erythro*-hexopyranoside which was converted into the corresponding *threo*-4-benzoate by sodium benzoate in dimethylformamide. Saponification then gave ethyl 2,3,6-trideoxy-α-D-*threo*-hexopyranoside (III). Attempts to obtain the *erythro*-isomer of the alcohol (III) by saponification of ethyl 2,3,6-trideoxy-4-*O*-methanesulphonyl-α-D-*erythro*-hexopyranoside with aqueous-methanolic sodium hydroxide were unsuccessful; a complex mixture of products was obtained.

The conversion of the methane sulphonates of ethyl 2,3-dideoxy- and 2,3,6-trideoxy-α-D-*erythro*-hexopyranoside into *threo*-derivatives by treatment with sodium benzoate in boiling dimethylformamide illustrates further the scope of the reagent [7] and permits additional analysis of the steric requirements. Isolated carbohydrate acyclic primary and secondary sulphonates are readily displaced,[8a] to give benzoates with inversion of configuration in the latter compounds, but reaction does not invariably occur with sulphonate groups attached to 6-membered ring systems. A sulphonate group attached to a ring-carbon atom flanked by methylene groups as, for example, in 5-methanesulphonyloxy-1,3-dioxan (IV) is readily displaced. The presence of a ring substituent remote from the sulphonate group as, for example, in *cis*- (V) and *trans*-5-methanesulphonyloxy-2-phenyl-1,3-dioxan (VI), does not inhibit displacement.[8b] Relevant to these findings is the observation [9] that cholestan-3α- and -3β-yl methanesulphonate are converted by sodium thiobenzoate in dimethylformamide into the 3β- and 3α-thiobenzoates. The effect of a substituent vicinal and *trans* to a sulphonyloxy-group in a 6-membered ring apparently depends on its bulk. Thus, a methoxy-group does not inhibit exchange since *trans*-2-methoxycyclohexyl methanesulphonate is converted into *cis*-2-methoxycyclohexyl benzoate.[10] On the other hand, 2,5-di-*O*-methanesulphonyl-1,3:4,6-di-*O*-methylene-D-mannitol (VII) does not undergo benzoate exchange; each methanesulphonate group in this compound has a bulky residue in a *trans*-vicinal position.

[6] See Tipson, *Adv. Carbohydrate Chem.*, 1953, **8**, 231.
[7] Reist, Spencer, and Baker, *J. Org. Chem.*, 1959, **24**, 1618.
[8] (*a*) Bukhari, Foster, Lehmann, and Webber, *J.*, 1963, 2287; Bukhari, Foster, Lehmann, Webber, and Westwood, *J.*, 1963, 2291; but cf. Bukhari, Foster, Lehmann, Randall, and Webber, *J.*, 1963, 4167; (*b*) Baggett, Bukhari, Foster, Lehmann, and Webber, *J.*, 1963, 4157.
[9] Foster, Lehmann, and Webber, unpublished results.
[10] Buck, Foster, Labib, and Webber, unpublshed results.

The failure of 1,3-*O*-benzylidene-4-deoxy-2-*O*-methanesulphonyl-L-erythritol (VIII) to undergo benzoate exchange appears not to be due solely to the methyl group *trans*-vicinal to the methanesulphonate residue since a similar structural feature occurs in ethyl 2,3,6-trideoxy-4-*O*-methanesulphonyl-α-D-*erythro*-hexopyranoside which does react. The balance of steric effects in these compounds must reside in the third substituent in the 1,3-dioxan and tetrahydropyran rings which, in the former case (VIII), must prevent the 1,3-dioxan ring from assuming a conformation suitable for nucleophilic displacement of the methanesulphonate group.

The infrared spectral data in Table 1 were obtained on *ca.* 0·005M-solutions of the alcohols in carbon tetrachloride. Under these conditions intermolecular hydrogen

TABLE 1.

Infrared spectral data on ethyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside and related compounds (*ca.* 0·005M-solutions in CCl_4).

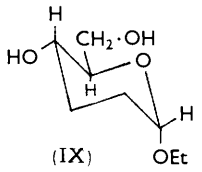
	$\nu_{max.}$ (cm.$^{-1}$) (ε)		
Alcohol	Free OH	Bonded OH	
Et 2,3-dideoxy-α-D-*erythro*-hexopyranoside	3630(62)	3607(70)	3548(28)
Et 2,3-dideoxy-α-D-*threo*-hexopyranoside	3630(27)	3596(59)	3527(56)
Et 2,3,6-trideoxy-α-D-*threo*-hexopyranoside	3630(18)	3595(38)	
2-Methoxyethanol [13]	3641(16)	3610(55)	
3-Methoxypropanol [13]	3641(34)		3554(44)
1,4-Dimethoxybutan-2-ol [13]		3598(45)	3538(28)
Tetrahydropyran-2-ylmethanol [3]		3597(55)	

bonding is negligible, absorptions in the hydroxyl stretching region may be associated with free and intramolecularly bonded hydroxyl groups,[11] and an approximate indication of their proportions is given by the relative extinction coefficients.[12] Further, providing that there is no unusual steric effect,[13] the size of the ring formed by an intramolecular hydrogen bond is indicated [13] by the magnitude of Δν, where Δν is the arithmetical difference between the absorption frequencies for free and bonded hydroxyl groups and is *ca.* 30 for a 5-membered ring (cf. 2-methoxyethanol) and *ca.* 80 for a 6-membered ring (cf. 3-methoxypropanol). By these criteria the spectra in Table 1 may be interpreted.

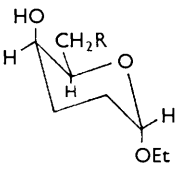
Ethyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside (I) showed strong absorption for free hydroxyl at 3630 cm.$^{-1}$ (ε 62). The strong absorption at 3607 cm.$^{-1}$ (ε 70, Δν 23, 5-membered ring) may be assigned to a hydrogen bond between the primary hydroxyl group and the ring oxygen atom (O_r) in a conformation near to that of the chair form (IX). An alternative possibility which involves the secondary hydroxyl group bonded to O_r can be largely ruled out since it would require a conformation with the dihedral angle OH–O_r *ca.* 60° and this would make the dihedral angle OH–CH_2·OH *ca.* 180° so that bonding between the two hydroxyl groups (6-membered ring) could not occur. The medium absorption at 3548 cm.$^{-1}$ (ε 28, Δν 82, 6-membered ring) must be associated with a hydrogen bond between the primary and the secondary hydroxyl group, with the primary group probably functioning as the proton donor because of its greater acidity (cf. the results of Cole and Jefferies [12]). The absorptions for bonded hydroxyl groups in ethyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside (I) are similar to those in 1,4-dimethoxybutan-2-ol (see Table 1) which suggests that the dihedral angle HO–CH_2·OH in the former compound is near the minimum value of *ca.* 60°; this arrangement occurs in the chair conformation (IX) with equatorial HO and CH_2·OH groups. The non-bonded interactions associated with the axial OEt group could cause deformation of the chair form (IX) to an extent which cannot be assessed at present but which need not change the dihedral angle

[11] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492; 1954, **76**, 4323.
[12] Cole and Jefferies, *J.*, 1956, 4391.
[13] Foster, Haines, and Stacey, *Tetrahedron*, 1961, **16**, 177.

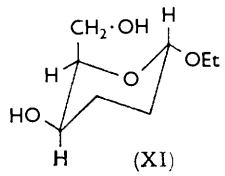
OH–CH_2·OH. Molecular models indicate that a cumulated hydrogen bond sec-OH–prim-OH–O_r could not occur in conformation (IX). Thus, the spectrum for the *erythro*-diol (I) involves absorptions for free secondary hydroxyl groups and for the primary hydroxyl group hydrogen-bonded principally to the ring-oxygen atom and, to a smaller extent, to the oxygen atom of the secondary hydroxyl group. For comparison it may be noted that in tetrahydropyran-2-ylmethanol the hydroxyl group is completely bonded to the ring-oxygen atom.[3]



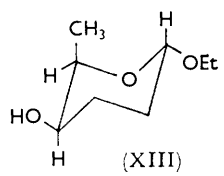
(IX)



(X: R = OH)
(XII: R = H)



(XI)



(XIII)

Ethyl 2,3-dideoxy-α-D-*threo*-hexopyranoside (II) showed weak absorption for free hydroxyl groups (3630 cm.$^{-1}$, ε 27) and strong absorptions of comparable intensity for hydroxyl groups bonded in 5- (3596 cm.$^{-1}$, ε 59, Δν 34) and 6-membered rings (3527 cm.$^{-1}$, ε 56, Δν 103). The chair conformation (X) where the dihedral angle OH–O_r is *ca.* 60° is particularly favourable for intramolecular hydrogen bonding since both primary and secondary hydroxyl groups can form bonds to the ring-oxygen atom or to each other. Because of intramolecular hydrogen bonding to the ring-oxygen atom, the axial hydroxyl group is a stabilising factor in conformation (X), *i.e.*, exerts an effect opposite to that normally associated with axial groups in 6-membered rings. The influence of this effect is also seen in tetrahydropyran-3-ol which, in dilute solution in carbon tetrachloride, exists to the extent of at least 50% in the chair conformation with the hydroxyl group axial.[3] Models suggest that a hydrogen-bond cumulation OH–CH_2·OH–O_r cannot occur in conformation (X). In the alternative chair conformation (XI) of the *threo*-diol (II) the dihedral angles OH–CH_2·OH and OH–O_r are *ca.* 60° and *ca.* 180°, respectively, an arrangement of hydroxyl groups not so favourable for hydrogen bonding as that in conformation (X). The weak absorption for free hydroxyl groups in the spectrum of the *threo*-diol (II) indicates almost complete intramolecular hydrogen bonding. As in the *erythro*-diol (I) the axial OEt group may cause deformation of the chair form in conformation (X), but the extent is not known at present; such deformation could occur without altering the dihedral angle OH–O_r.

The spectrum for ethyl 2,3,6-trideoxy-α-D-*threo*-hexopyranoside (III) showed weak absorption for free hydroxyl groups (3630 cm.$^{-1}$, ε 18) and strong absorption for bonded hydroxyl groups at 3595 cm.$^{-1}$ (ε 38, Δν 35). Intramolecular hydrogen bonding can occur in this compound only between the hydroxyl group and the ring-oxygen atom in conformations where the dihedral angle OH–O_r is *ca.* 60°. Complete existence in such a conformation is unlikely since it has been adduced [14] from other evidence that intramolecular hydrogen bonding will be complete when the dihedral angle is near to 60°. The chair conformation (XII) would be ideally suited for intramolecular hydrogen bonding, but it contains a destabilising element in the axial OEt group. It is possible that the absorption for free hydroxyl groups in the spectrum of compound (III) is a measure of the destabilisation of conformation (XII). The spectrum for ethyl 2,3,6-trideoxy-α-D-*threo*-hexopyranoside is consistent with the assigned structure, and the course of the iodine exchange noted above is thereby confirmed.

Using Whiffen's method [15] for calculating the $[M]_D$ values of pyranosides in aqueous

[14] Barker, Foster, Haines, Lehmann, Webber, and Zweifel, *J.*, 1963, 4161.
[15] Whiffen, *Chem. and Ind.*, 1956, 964.

solution, has given the results collected in Table 2; replacement of a methyl group at the glycosidic centre by an ethyl group does not significantly change the $[M]_D$ value,[16] so that no allowance was necessary for this structural change. The $[M]_D$ value of +286° for ethyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside (I) is much nearer to that (+277°) calculated

TABLE 2.

Optical rotations for ethyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside and related compounds in water.

	Calc.[15] $[M]_D$ (parameters)		Obs.
Et hexopyranoside	Conformation C1	Conformation 1C	$[M]_D$
2,3-Dideoxy-α-D-*erythro*-	+277° ($H + J + 130$)	+58° ($K - I + 130$)	+286°
2,3-Dideoxy-α-D-*threo*-	+252° ($I + J - H + 130$)	+135° ($H + K + 130$)	+184°
2,3,6-Trideoxy-α-D-*threo*-	+222° ($I + J - H + 100$)	+105° ($H + K + 100$)	+128°

Parameters taken as follows: H +34°, I +43°, J +113°, K −29°; +30° allowed for contribution of $CH_2 \cdot OH$ in D-series and +100° allowed for contribution of the glycosidic group in the α-form.

for the C1 conformation (IX) than that (+58°) for the 1C conformation, which suggests that, in aqueous solution, the glycoside exists predominantly in a shape near to that of the C1 conformation. A similar conclusion was reached above for the *erythro*-diol in dilute solution in carbon tetrachloride. On the other hand, the $[M]_D$ value for ethyl 2,3-dideoxy-α-D-*threo*-hexopyranoside is nearly midway between those calculated for the C1 and 1C conformations, which suggests that neither chair form is preferred in aqueous solution, and the $[M]_D$ value (+128°) for ethyl 2,3,6-trideoxy-α-D-*threo*-hexopyranoside is much nearer that (+105°) calculated for the 1C conformation than that (+222°) for the C1 conformation. In contrast, and as deduced from the patterns of intramolecular hydrogen bonding, the *threo*-compounds appear to exist in dilute solution in carbon tetrachloride in shapes which are near to those of the C1 conformations (X) and (XII). A possible explanation of the different conformations adopted by the *threo*-compounds in carbon tetrachloride and water is that, in the former solvent at the relevant dilution, more extensive intramolecular hydrogen bonding can occur in shapes which approach those of the C1 conformations (X) and (XII) and are therefore stabilised, whereas in the latter solvent this effect would be reduced because of intermolecular hydrogen bonding between the alcoholic hydroxyl groups and the solvent molecules. Thus, in an aqueous solution of ethyl 2,3,6-trideoxy-α-D-*threo*-hexopyranoside, if intramolecular hydrogen bonding is not significant, then the preferred shape should be near that of the 1C conformation (XIII) which has equatorial OH and OEt groups and an axial Me group (cf. the results of Cole and Jefferies [12]).

EXPERIMENTAL

Degradation of Ethyl 4,6-*Di*-O-*acetyl*-2,3-*didehydro*-2,3-*dideoxy*-α-D-erythro-*hexopyranoside*.—Ozonised oxygen (4%) was bubbled through a solution of this compound [17] (0·5 g.) in chloroform (50 ml.) in a closed-circuit apparatus; [18] uptake of ozone was complete in 30 min. A solution of sodium borohydride (0·5 g.) in ethanol (35 ml.) and water (5 ml.) was then added [19] dropwise to the chloroform solution at 25°. The mixture was boiled under reflux for 3 hr., then stored overnight at room temperature. After addition of glacial acetic acid (1 ml.) and evaporation of the solution, an aqueous solution of the residue was deionised with Amberlite resins IR-120 (H^+ form) and IRA-400 (HO^- form), then concentrated, and the residue (60 mg.) was treated with benzaldehyde (5 ml.) saturated with hydrogen chloride, at room temperature for 1·5 hr. Light petroleum (5 ml.; b. p. 60—80°) was added to the mixture and the precipitate was collected, washed with the same solvent, and recrystallised from chloroform–ethanol, to

[16] Pigman and Goepp, " Chemistry of the Carbohydrates," Academic Press, New York, 1948, p. 80.
[17] Laland, Overend, and Stacey, *J.*, 1950, 738.
[18] Dobinson, Lawson, and Ward, *Fuel*, 1956, **35**, 398.
[19] Sousa and Bluhm, *J. Org. Chem.*, 1960, **25**, 108.

yield 1,3:2,4-di-*O*-benzylidene-erythritol (0·1 g.), m. p. 196—197° alone or in admixture with authentic material.[5]

Ethyl 2,3-*Dideoxy*-α-D-threo-*hexopyranoside*.—A solution of ethyl 2,3-dideoxy-4,6-di-*O*-methanesulphonyl-α-D-*erythro*-hexopyranoside [17] (3·4 g.; m. p. 68—69°, $[\alpha]_D$ +113° in $CHCl_3$) in dimethylformamide (100 ml.) was boiled under reflux in the presence of sodium benzoate (8 g.) for 6 hr. The cooled mixture was diluted with water (100 ml.) and extracted with chloroform (2 × 100 ml.). The combined extracts were washed with aqueous sodium hydrogen carbonate, then with water, dried ($MgSO_4$), and concentrated. Distillation of the residue gave *ethyl* 4,6-*di*-O-*benzoyl*-2,3-*dideoxy*-α-D-threo-*hexopyranoside* (2·2 g., 56%), b. p. 210—240° (bath)/0·1 mm., $[\alpha]_D$ +17° (*c* 0·8 in $CHCl_3$) (Found: C, 68·5; H, 6·6. $C_{22}H_{24}O_6$ requires C, 68·8; H, 6·25%).

A solution of the redistilled, foregoing benzoate (0·5 g.) in a 13% solution of sodium hydroxide in aqueous methanol (20 ml.; 3 : 2) was boiled under reflux for 4 hr. The solution was diluted with water (25 ml.) and extracted continuously with ether for 18 hr. The dried ($MgSO_4$) ethereal solution was concentrated and the residue distilled at 100—110° (bath)/0·2 mm., to yield a product which solidified. Recrystallisation from acetone–light petroleum (b. p. 60—80°) gave *ethyl* 2,3-*dideoxy*-α-D-threo-*hexopyranoside* (0·12 g.), m. p. 56—57°, $[\alpha]_D$ +129° (*c* 0·6 in $CHCl_3$) (Found: C, 54·2; H, 8·8. $C_8H_{16}O_4$ requires C, 54·55; H, 9·1%). The *di*-O-p-*phenylazobenzoate*, prepared by the usual method,[20] had m. p. 136—137° (from ethanol–chloroform) (Found: C, 68·5; H, 5·65; N, 9·5. $C_{34}H_{32}N_4O_6$ requires C, 68·9; H, 5·4; N, 9·5%).

Ethyl 2,3,6-*Trideoxy*-α-D-threo-*hexopyranoside*.—A solution of ethyl 2,3-dideoxy-4,6-di-*O*-methanesulphonyl-α-D-*erythro*-hexopyranoside [17] (2·4 g.) and sodium iodide (1·29 g.) in acetone (30 ml.) was kept at 115° for 3 hr. The solution was filtered from sodium methanesulphonate, then concentrated, and a solution of the residue in chloroform was washed with aqueous sodium thiosulphate, dried, and concentrated. The residue was dissolved in methanol (200 ml.) containing diethylamine (1·5 ml.) and shaken with Raney nickel [21] (*ca.* 50 g.) at a slight overpressure of hydrogen. Uptake of hydrogen (1·36 l.) ceased after 3 hr. The solution was filtered and concentrated, and the residue distilled, to yield *ethyl* 2,3,6-*trideoxy*-4-O-*methanesulphonyl*-α-D-erythro-*hexopyranoside* (1·44 g., 83%), b. p. 120° (bath)/0·5 mm., $[\alpha]_D$ + 100° (*c* 1·0 in $CHCl_3$) (Found: C, 45·2; H, 7·5. $C_9H_{18}O_5S$ requires C, 45·4; H, 7·6%).

A solution of the foregoing methanesulphonate (6 g.) in dimethylformamide (200 ml.) was boiled under reflux in the presence of sodium benzoate (28 g.) for 6 hr. and then worked up as described above, to give *ethyl* 4-O-*benzoyl*-2,3,6-*trideoxy*-α-D-threo-*hexopyranoside* (3·5 g., 53%), b. p. 150° (bath)/0·07 mm., $[\alpha]_D$ +54° (*c* 1·4 in $CHCl_3$) (Found: C, 68·45; H, 7·8. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%).

Saponification of the benzoate (7 g.) essentially as described above gave *ethyl* 2,3,6-*trideoxy*-α-D-threo-*hexopyranoside* (3 g., 70%), b. p. 65°/1·8 mm., $[\alpha]_D$ +98° (*c* 0·8 in H_2O) (Found: C, 60·3; H, 10·0. $C_8H_{16}O_3$ requires C, 60·0; H, 10·0%). The *p*-phenylazobenzoate failed to crystallise. Examination of the alcohol by vapour-phase chromatography, with a Pye argon instrument including ionisation detection and a column *ca.* 120 × 0·4 cm., packed with 10% of silicone oil on 100—120 mesh Celite at 125°/40 ml. per min., revealed the presence of one major component together with traces of unidentified components.

Ethyl 2,3-*Dideoxy*-4,6-*di*-O-*phenylazobenzoyl*-α-D-erythro-*hexopyranoside*.—Under the usual conditions [20] ethyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside [17] (0·11 g.; m. p. 69—70°, $[\alpha]_D$ +133° in $CHCl_3$) gave the *di*-O-p-*phenylazobenzoate* (0·31 g., 84%), m. p. 151—152° (from ethanol–chloroform) (Found: C, 68·8; H, 5·3; N, 9·4. $C_{34}H_{32}N_4O_6$ requires C, 68·9; H, 5·4; N, 9·3%).

Saponification of Ethyl 2,3,6-*Trideoxy*-4-O-*methanesulphonyl*-α-D-erythro-*hexopyranoside*.—A solution of this compound (2·4 g.) in methanol (30 ml.) and water (50 ml.) containing potassium hydroxide (10 g.) was boiled under reflux for 20 hr. The cooled solution was then extracted continuously overnight with chloroform. Concentration of the dried ($MgSO_4$) extract and distillation of the residue gave a product (1·3 g.), b. p. 130—145°/12 mm., $[\alpha]_D$ +52° (*c* 2·0 in $CHCl_3$) (Found: C, 60·4; H, 10·2. $C_8H_{16}O_3$ requires C, 60·0; H, 10·0%). A *ca.* 0·005M-solution of the product in CCl_4 had $\nu_{max.}$ at 3630, 3619, and 3601 $cm.^{-1}$ for free and bonded hydroxyl groups; the absorptions were of similar intensity. Examination of the

[20] Baggett, Foster, Haines, and Stacey, *J.*, 1960, 3528.
[21] Adkins and Pavlic, *J. Amer. Chem. Soc.*, 1947, **69**, 3039.

product by vapour-phase chromatography under the above conditions revealed two major and five minor components.

Infrared Spectra.—The results in Table 1 were obtained by using a Unicam S.P. 100 spectrometer equipped with a grating (3000 lines per in.); the frequencies are accurate to ± 2 cm.$^{-1}$. The extinction coefficients, ε, are maximum values and are equal to $(1/cl) \log_{10} (I_0/I)$ with l in cm. and c in moles per l.

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