348. *A Synthesis of* 6-*Deoxy*-L-*talose*

By P. M. COLLINS and W. G. OVEREND

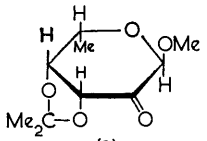
A synthesis of 6-deoxy-L-talose is reported. The mutarotation of the deoxy-sugar has been shown to be complex. The stereochemistry of the catalytic and metal hydride reductions of methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosidulose and methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose is discussed with reference to recent views concerning similar reductions of cyclic ketones.

6-DEOXY-L-TALOSE was first isolated from the cardiac glycoside sarmentoside A.[1] More recently it has been identified as a component of the glycolipids produced by *Mycobacterium avium* [2] and *Mycobacterium marianum*.[3] The " K " lipopolysaccharide antigen of *Pseudomonas pseudomallei* also contains this sugar [4] which was also isolated in crystalline form

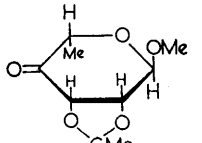
[1] J. Schmutz, *Helv. Chim. Acta*, 1948, **31**, 1719.
[2] P. Jolles, F. Bigler, T. Gendre, and E. Lederer, *Bull. Soc. Chim. Biol.*, 1961, **43**, 177.
[3] M. Chaput, G. Michel, and E. Lederer, *Experientia*, 1961, **17**, 107.
[4] A. P. MacLennan, *Biochem. J.*, 1962, **82**, 394.

from a hydrolysate of the cell walls of *Actinomyces bovis*.[5] The enantiomer was isolated from the capsular polysaccharide of a Gram-negative organism.[6]

Syntheses of 6-deoxy-L-talose have resulted from studies of the basic epimerisation of L-fuconic acid [1] and of the behaviour of 2-*O*-tosyl-L-fucose in basic solution.[7] Stemming from an investigation of the preparation and reactions of methyl hexopyranosiduloses we have developed an alternative preparation of this naturally-occurring deoxy-sugar.[8] Oxidation of methyl 3,4-*O*-isopropylidene-α-L-fucoside with chromium trioxide–pyridine complex [9] gave methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosidulose (I). This acetonated glycoside is a derivative of the novel sugar angustose (6-deoxy-L-*lyxo*-hexosulose) which occurs in angustmycin A, a nucleoside-type antibiotic.[10] Catalytic hydrogenation of the hexopyranosidulose (I) yielded a mixture of methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-hexosides which could be readily deacetonated by partial hydrolysis. From the acetylated hydrolysate a crystalline methyl 6-deoxyhexoside triacetate was isolated. The same compound could be prepared from methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside as initial material since oxidation of this glycoside gave methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (II) [11] which by sequential hydrogenation, deacetonation, and acetylation afforded the triacetate. As the triacetate was obtainable from both (I) and (II) it must have the L-*talo*-configuration and is methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-L-taloside (III; R = Ac). Zemplén deacetylation of the



(I)



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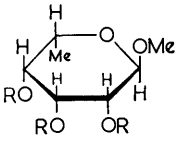


(III)

triacetate afforded crystalline methyl 6-deoxy-α-L-talopyranoside (III; R = H) from which 6-deoxy-L-talose was obtained by acid hydrolysis. The deoxy-sugar was identical with the 6-deoxy-L-talose isolated from *Actinomyces bovis* by MacLennan.[5] The crystalline synthetic 6-deoxy-L-talose probably has the α-pyranose structure since its specific rotation in pyridine, a solvent in which its mutarotation is extremely slow, is similar to that of methyl 6-deoxy-α-L-talopyranoside. In water the sugar undergoes very rapid mutarotation and this fast change and the decrease in the mutarotation coefficient calculated from the integrated first-order rate equation is indicative of complex mutarotation.[12] This is not surprising since talose is also reported to exhibit complex mutarotation.[12]

Although catalytic reduction of compounds (I) and (II) leads predominantly to products with the L-*talo*-configuration, paper chromatographic analysis indicated that small amounts of substances with respectively the L-*fuco*- and L-*rhamno*-configurations were also present. Similar results were found for the reductions of compounds (I) and (II) with lithium aluminium hydride. By visual comparison against controls of the intensity of spots on the chromatograms it appeared that at least 80% of the derivative with the L-*talo*-configuration was formed from (I) and about 90% from (II). A more accurate determination of the isomer distribution in the products from the catalytic reductions was made by gas

[5] A. P. MacLennan, *Biochim. Biophys. Acta*, 1961, **48**, 600.
[6] A. Markovitz, *J. Biol. Chem.*, 1962, **237**, 1767.
[7] J. K. N. Jones and W. H. Nicholson, *J.*, 1955, 3050.
[8] For a preliminary account see P. M. Collins and W. G. Overend, *Chem. and Ind.*, 1963, 375.
[9] See J. S. Burton, W. G. Overend, and N. R. Williams, *J.*, 1965, in the press.
[10] H. Yüntsen and H. Yonehara, *Bull. Agric. Chem. Soc. Japan*, 1957, **21**, 261; H. Yüntsen, *J. Antibiotics* (*Tokyo*), 1958, **11***A*, 79, 233; quoted by J. D. Dutcher in *Adv. Carbohydrate Chem.*, 1963, **18**, 290.
[11] B. M. Gough, Ph.D. Thesis, University of London, 1961.
[12] F. J. Bates, "Polarimetry, Saccharimetry and the Sugars," National Bureau of Standards, Washington, 1942, C440, p. 442.

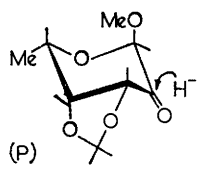
chromatography and by polarimetric analysis as described in the Experimental section. The following results were obtained:

Compound reduced		Percentage of configurational isomers in product L-*fuco*	L-*talo*	L-*rhamno*
(I)	(*a*)	11	89 (±1)	
	(*b*)	14	86	
(II)	(*a*)		92	8 (±2)
	(*b*)		98	2

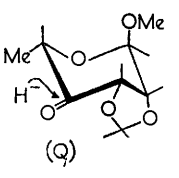
Determinations based on (*a*) optical rotation measurements, and (*b*) gas chromatographic estimation.

Both methods of estimation clearly indicate the preponderance of the isomer with the L-*talo*-configuration and to explain these results it is necessary to know the conformation of each oxo-glycoside (I) and (II). For sugars containing a pyranoid ring Reeves [13] and Kelly [14] have assigned instability ratings which enable the favoured chair conformation to be confidently predicted in many cases. For pyranosiduloses the situation is likely to be more complex for it is known [15] that for substituted cyclohexanones, the trigonal carbon atom results in internal interactions that differ from those present in substituted cyclohexanes. For the latter the preferred chair form has its bulky substituents in equatorial positions, but with either 2- or 3-substituted cyclohexanones the equatorial position for a substituent is not so energetically favoured owing to the " 2- or 3-alkyl ketone " effect.[15-17]

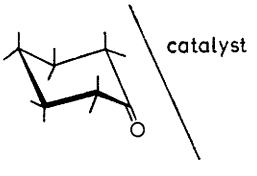
Methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosidulose (I) in the IC conformation (P) might suffer some destabilisation akin to the " 2-alkyl ketone " effect between the equatorial substituent at C-3 and the carbonyl group. In the CI conformation a similar interaction would occur between the equatorially disposed methoxyl group at C-1



(P)



(Q)



and the carbonyl group. (In this conformation there will also be a large interaction between the axial methyl group at C-5 and the axial substituent at C-3.)

Methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose in the IC conformation (Q) has equatorial substituents at C-3 and C-5 which can interact with the carbonyl group as mentioned above. However this effect for a methyl substituent is known to be insignificant.[16,17] In the alternative CI conformation there would be a large interaction between the axial methyl group at C-5 and the axial substituent at C-3 which would probably outweigh any destabilisation caused by interactions mentioned for the IC conformation. Consequently of the two possible chair conformations for compounds (I) and (II), those depicted (P and Q) are likely to be the most stable.

Catalytic hydrogenations of cyclohexanones have been explained by assuming that the catalyst is approached by the least hindered side of the ketone as shown and is there reduced by the hydrogen adsorbed on the catalyst surface. Applying these ideas to compounds (I) and (II) in conformations P and Q the products would be expected to have the L-*talo*-configuration, *i.e.*, an alcohol would be formed with the hydroxyl group axial

[13] R. E. Reeves, *J. Amer. Chem. Soc.*, 1949, **71**, 215.
[14] R. B. Kelly, *Canad. J. Chem.*, 1957, **35**, 149.
[15] E. L. Eliel, " Stereochemistry of Carbon Compounds," McGraw-Hill, New York, 1962, p. 239.
[16] B. Rickborn, *J. Amer. Chem. Soc.*, 1962, **84**, 2414.
[17] N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, 1962, **84**, 2201.

when the product is in the same conformation as the ketone. Similar results are found in steroid [18] and cyclitol [19] chemistry and with other pyranosiduloses.[20]

As the reduction of methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosidulose with lithium aluminium hydride gives predominantly a product with the L-*talo*-configuration the nucleophilic hydride-donating reagent attacks the carbonyl group from above to give an axial hydroxyl group at C-2. Similarly hydride attack on the hexopyranosid-4-ulose must have been from above in order to give mainly the L-*talo*-isomer.

These results are consistent with explanations of the stereochemistry of metal hydride reductions of alicyclic ketones that have been forwarded by Dauben, Fonken, and Noyes [21] and by Kamernitzky and Akrem.[22] Although the two views are not congruous they both attach importance to axial substituents in the β-position to the reaction centre. Thus the strong preference for the isomer found in our hydride reductions arises from hindrance to approach of the reagent from the other direction owing to the axial substituent at C-4 in (P) and at C-2 in (Q). Although these workers [21,22] did not consider the reduction of inososes or pyranosiduloses, the metal-hydride reduction products of these substances show the importance of the orientation of β-substituents to the reaction centre.[19,20]

Experimental

Whatman No. 1 paper was used for chromatography. The descending method was employed with the organic phase of either ethyl acetate–propan-1-ol–water (5 : 3 : 2) (1) or ethyl acetate–pyridine–water (2 : 1 : 2) (2) mixtures as solvent. Borate buffer [23] was used for ionophoresis. Products were located on papers by spraying with aqueous ammoniacal silver nitrate and sodium hydroxide. For thin-layer chromatography silica gel G. (supplied by Merck A.G., Darmstadt) was used as adsorbent and detection was with anisaldehyde–sulphuric acid.[24] Infrared spectra were measured in the solid phase in potassium bromide discs. Mutarotation changes were determined with a Bendix Ericsson E.T.L.-N.P.L. automatic polarimeter coupled with a Honeywell Brown recorder.

Methyl 6-*Deoxy*-3,4-O-*isopropylidene*-α-L-lyxo-*hexopyranosidulose*.—Methyl 3,4-*O*-isopropylidene-α-L-fucoside (20 g.), b. p. 84—89°/0·2 mm., $[\alpha]_D^{20}$ −165° (*c* 0·8 in H_2O), was oxidised in pyridine (1 l.) with chromic oxide (60 g.) according to the method of Burton *et al.*[9] The oily product was re-oxidised and afforded a substance (16·2 g.) which partially crystallised. The crystals (6·0 g.) were separated on a porous tile and dried over phosphoric oxide. Oxidation of the oil extracted from the tile afforded more crystalline material (2·0 g.). The solid was recrystallised from light petroleum (b. p. 60—80°) to give the *hexopyranosidulose* (7·2 g., 36%), m. p. 73—74°, $[\alpha]_D^{20}$ −111° (*c* 1·1 in $CHCl_3$), $\nu_{max.}$ 1765 cm.$^{-1}$ (C=O) (Found: C, 55·7; H, 7·7. $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·5%).

Methyl 6-*Deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosid*-4-*ulose*.—This compound was prepared from methyl 2,3-*O*-isopropylidene-α-L-rhamnoside {$[\alpha]_D^{20}$ −18·0° (*c* 1·4 in EtOH)} by the same oxidative procedure. The oily product was purified by distillation and was shown to be identical with a sample first prepared by Dr. B. M. Gough of this department [11] {$[\alpha]_D^{20}$ −107° (*c* 3·5 in EtOH), reported −103°}.

Methyl 2,3,4-*Tri*-O-*acetyl*-6-*deoxy*-α-L-*taloside*.—Methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosidulose (1·02 g.) in 95% ethyl alcohol (20 ml.) was added to Adams catalyst (0·5—1·0 g.) which had been prereduced by shaking with ethanol in an atmosphere of hydrogen. The mixture was shaken with hydrogen until the uptake ceased (10 hr.) when 1·1 equivalents of hydrogen had been consumed. The solution was filtered and evaporated to an oil (1·0 g.) (X) which had no carbonyl absorption in the infrared region of its spectrum. Analysis by thin-layer chromatography also indicated complete reduction. This product (1·0 g.) in ethanol (9 ml.) was hydrolysed at room temperature with 0·3N-hydrochloric acid (21 ml.). The liberation of acetone was followed by determination of the ultraviolet absorption of the solution at 278 mμ

[18] D. H. R. Barton, *J.*, 1953, 1027.
[19] T. Posternak, *Helv. Chim. Acta*, 1936, **19**, 1333; 1941, **24**, 1045; D. Reymond, *ibid.*, 1957, **40**, 492.
[20] O. Theander, *Acta Chem. Scand.*, 1958, **12**, 1883.
[21] W. G. Dauben, G. J. Fonken, and D. S. Noyes, *J. Amer. Chem. Soc.*, 1956, **78**, 2579.
[22] A. V. Kamernitzky and A. A. Akrem, *Tetrahedron*, 1962, **18**, 705.
[23] J. L. Frahn and J. A. Mills, *Austral. J. Chem.*, 1959, **12**, 65.
[24] E. Stahl and U. Kaltenbach, *J. Chromatog.*, 1961, **5**, 357.

and was complete in 40 min. The solution was neutralised (Ag_2CO_3), filtered through a charcoal–Celite pad, and evaporated to a colourless gum (0·79 g.), $[\alpha]_D^{20}$ −129° (*c* 0·7 in H_2O), (A) which was dried over phosphoric oxide. A small portion of the oil X (15 mg.) was further hydrolysed with 2N-hydrochloric acid (2 ml.) at 100° for 2 hr. The solution was neutralised (Ag_2CO_3) and filtered to a clear solution (B) of the free sugar.

Likewise, methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (0·33 g.) was hydrogenated, but 48 hours' treatment was necessary for complete reduction [no absorption at 1750 $cm.^{-1}$ (C=O)]. Deacetonation of the oily product (Y) with 0·3N-hydrochloric acid at room temperature as above afforded a gum (C) (0·25 g.), a portion (15 mg.) of which was further hydrolysed with 2N-hydrochloric acid at 100° for 2 hr. to afford a solution (D) of the free sugar. A chromatographic and ionophoretic examination of the products indicated that A and C consisted mainly of methyl 6-deoxy-α-L-talopyranoside, *e.g.*:

Compound	M_G	R_F Solvent 1	R_F Solvent 2
Methyl α-L-fucopyranoside	0·20	0·61	
Methyl α-L-rhamnopyranoside		0·76	0·65
Product A	0·39	0·80s, 0·61w	
Product C		0·82s	0·74s
6-Deoxy-L-talose	0·71		0·60
L-Fucose	0·85		0·43
L-Rhamnose			0·48
Product B	0·71		0·60s, 0·40w
Product D			0·60s, 0·48w

s = strong intense spot; w = weak spot.

The product C (0·24 g.) was dissolved in dry pyridine (7 ml.) and freshly distilled acetic anhydride (5·5 ml.). After 20 hr. at 30° the solution was poured on to crushed ice (17 g.), and the product was extracted with methylene dichloride. The extract was washed successively with water, sodium hydrogen carbonate (saturated), and water, and evaporated to a solid which was recrystallised from light petroleum (b. p. 40—60°). *Methyl* 2,3,4-*tri*-O-*acetyl*-6-*deoxy*-α-L-*taloside* (0·2 g., 57%) was obtained as fine needles, m. p. 91—92°, $[\alpha]_D^{20}$ −73·3° (*c* 1·2 in MeOH) (Found: C, 51·3; H, 6·7; OMe, 10·2. $C_{13}H_{20}O_8$ requires C, 51·3; H, 6·6; OMe, 10·2%).

In a similar manner product A (0·77 g.) was acetylated with acetic anhydride (16 ml.) in pyridine (20 ml.). After recrystallisation from light petroleum (b. p. 40—60°) the triacetate (0·87 g., 66%) had m. p. 91—92° (alone or when mixed with the sample prepared from product C), $[\alpha]_D^{20}$ −75·9° (*c* 3·9 in MeOH). Nucleation of the mother-liquors with methyl 2,3,4-tri-*O*-acetyl-α-L-fucoside failed to induce crystallisation.

Methyl 6-*Deoxy*-α-L-*talopyranoside*.—Deacetylation of the triacetate (0·79 g.) in methanol (50 ml.) with a small piece of clean sodium at 0° for 20 hr. gave after neutralisation (solid CO_2) an oily product which solidified. Distillation gave a colourless oil (0·33 g., 71%), b. p. 120°(bath temp.)/10^{-3} mm., which rapidly solidified, m. p. 63—65°, $[\alpha]_D^{20}$ −104° (*c* 2·1 in H_2O). The *glycoside* was non-reducing to Fehling's solution (Found: C, 46·8; H, 7·6; OMe, 17·2. $C_7H_{14}O_5$ requires C, 47·2; H, 7·9; OMe, 17·4%).

6-*Deoxy*-L-*talose*.—Methyl 6-deoxy-α-L-talopyranoside (0·7 g.) in water (20 ml.) was stirred and heated under reflux with ZeoKarb 225 (H^+ form) resin until the optical rotation of the liquid was constant (2 hr.). Filtration and evaporation of the solution yielded a gum which solidified and was recrystallised from ethanol–acetone to give the deoxy-hexose (0·4 g., 62%), m. p. 126—127°, $[\alpha]_D$ −20·5° ± 1·4° (*c* 2·28 in H_2O). Schmutz [1] gives m. p. 116—118°, $[\alpha]_D^{20}$ −20·9° ± 2° in H_2O for a synthetic sample of 6-deoxy-L-talose and for the enantiomer Markovitz [6] gives m. p. 129—131°. For a sample of the deoxy-sugar isolated from natural sources, MacLennan [5] reports m. p. 119—121°, $[\alpha]_D^{21}$ −18·9° (H_2O). Our 6-deoxy-L-talose and a sample of that isolated and kindly provided by Dr. A. P. MacLennan had infrared spectra and chromatographic and ionophoretic behaviours which were identical. There was no depression of melting point on admixture of the samples.

Alternatively the sugar could be obtained less readily and less pure from the glycoside (0·22 g.) by treatment with 2N-hydrochloric acid (15 ml.) at 60° for 24 hr. The cooled solution was neutralised (Ag_2CO_3), filtered through a charcoal–Celite pad, and evaporated to a gum. An aqueous solution of the gum (0·14 g. in 1 ml.) was applied to two sheets of Whatman No. 3

paper (46 × 57 cm.) and developed with the organic phase of ethanol–butanol–water (1 : 4 : 5). Elution of the sugar-containing band produced a gum (85 mg.) which solidified on drying *in vacuo* over phosphoric oxide. This solid had m. p. 119—121°, $[\alpha]_D^{20}$ −20·5° ± 1·4° (*c* 2·28 in H_2O).

The mutarotation of 6-deoxy-L-talose (0·0684 g.) in water (3 ml.) was measured, as soon as possible after dissolution, with an automatic polarimeter. The temperature was maintained at 24·8°. Rate coefficients were calculated from the integrated first-order rate equation.

Time (sec.) ...	110	120	130	140	150	160	170	180	190	200	220	240	260	300
10^3k (sec.$^{-1}$) ...	9·15	8·44	8·42	8·27	8·01	7·67	7·49	7·27	7·18	7·03	6·72	6·45	6·23	5·79

The coefficients decrease with increasing time. The agreement between separate determinations was better than ±1·5%. The initial specific rotation could not be obtained by extrapolation of these results. However the mutarotation of 6-deoxy-L-talose in pyridine was very slow and the sugar had $[\alpha]_D$ −108°.

Procedure for Lithium Aluminium Hydride Reductions.—The methyl *O*-isopropylidenehexopyranosidulose (I) or (II) (0·2 g.) in diethyl ether (10 ml.) was stirred under reflux for 20 hr. with the hydride (80 mg.). Excess of hydride was decomposed with water, and the reduction product was isolated by evaporation of an ether extract. The product in water was heated under reflux for 2 hr. with ZeoKarb 225 resin (H^+ form). The volume of the solution was then adjusted to give a sugar concentration of 2% and this solution was examined by paper chromatography. The intensities of spots were compared with those of standard mixtures [L-fucose and 6-deoxy-L-talose for the product from (I) and L-rhamnose and 6-deoxy-L-talose for that from (II)]. The same chromatographic procedure was used with the products from the catalytic reduction of compounds (I) and (II). On a preparative scale methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (2·2 g.) in ether (70 ml.) was added to lithium aluminium hydride (0·25 g.) in ether (150 ml.). After heating under reflux for 3 hr. water was added and the filtered solution was evaporated to a gum. This material was partially hydrolysed and acetylated in the usual manner to afford methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-L-taloside (1·8 g., 58%), m. p. 88—90°, $[\alpha]_D$ −73° (*c* 1·2 in MeOH). Methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosidulose (0·28 g.) on similar treatment yielded the same triacetate (0·18 g., 40%), m. p. 89—91°.

Isomer Distribution Determinations.—(i) The oil (X) (*ca.* 0·2 g.) from the catalytic reduction of compound (I) was treated with 0·3N-hydrochloric acid (10 ml.) for 2 hr. at 20° and then the optical rotation of the solution was measured. Optical rotations of the following in 0·3N-hydrochloric acid were also determined: methyl 3,4-*O*-isopropylidene-α-L-fucoside similarly treated with the acid, methyl α-L-fucopyranoside in acid containing acetone (1 mol.) (both solutions gave the same value for the specific rotation of the glycoside when allowance was made in the calculation for loss of the isopropylidene group by the former substance), and methyl 6-deoxy-α-L-talopyranoside. (It was shown that the presence of a 10M-excess of acetone had no effect on the rotation of this taloside.) A similar procedure was adopted with the product (Y) obtainable from the reduction of compound (II) but in this case the optical rotation of methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside after standing in 0·3N-hydrochloric acid was also measured. That hydrolysis of the glycoside linkage or anomerisation had not occurred was checked. The following results were obtained for the average of several measurements of the optical rotations of the reference compounds and for the products obtained from three independent reductions of each compound (I) and (II).

Compound after treatment with 0·3N-hydrochloric acid	$[\alpha]_D$
Methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside	−61·7° ± 0·1°
Methyl 3,4-*O*-isopropylidene-α-L-fucoside	−192·2° ± 0·2°
Methyl α-L-fucopyranoside (with added acetone)	−191·8°
Methyl 6-deoxy-α-L-talopyranoside	−102° ± 0·5°
Methyl α-L-rhamnopyranoside (with added acetone)	−61·5°
Oil X	−112·0° ± 0·3°
Oil Y	−98·9° ± 0·2°

(ii) The oils (X and Y) were analysed directly by a gas chromatographic method. The apparatus was constructed by Dr. G. B. Gill of this department and employed a 4 ft. vertical column packed with Apiezon L grease (10%) on Celite (100—120 mesh) with argon as carrier gas. The column was operated at 166° and a β-ray ionisation detector was used. Only two

peaks were produced for each oil. By comparison with retention times for authentic samples it was shown that the first peaks for oils X and Y were respectively due to methyl 3,4-*O*-isopropylidene-α-L-fucoside and methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside. In each case the second peak represented the bulk of the sample and must have been respectively the 3,4- and 2,3-*O*-isopropylidene derivative of methyl 6-deoxy-α-L-talopyranoside. The accuracy of a quantitative analysis of the chromatograms was slightly reduced owing to the fact that in each the first peak tailed into the second. Moreover standard mixtures of the two isomers produced in each reduction could not be prepared as only one isopropylidenated isomer was available in each case. However the compounds available were those shown to be present in each oil in small amount. Consequently known weights of methyl 3,4-*O*-isopropylidene-α-L-fucoside was added to oil X, and of methyl 2,3-*O*-isopropylidene-α-L-rhamnoside to oil Y, and analysis of the mixtures so produced permitted detector linearity and reproducibility to be ascertained.

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