617. *Aspects of Stereochemistry. Part XXII.*[1] *Structure, Conformation, and Absolute Configuration of Some Carbohydrate Benzylidene Acetals Containing Fused Ring Systems* [2]

By N. Baggett, K. W. Buck, A. B. Foster, and J. M. Webber

The correlation between stereochemical environment and chemical shift for the benzyl proton in benzylidene acetals established in the preceding Paper has been extended to carbohydrate benzylidene derivatives containing: (a) two *cis*-fused five-membered rings (*e.g.*, 2,3-*O*-benzylidene-1,4-anhydroerythritol); (b) *cis*-fused five- and six-membered rings (*e.g.*, methyl 3,4-*O*-benzylidene-β-L-arabinopyranoside, 1,2:3,4-di-*O*-benzylidene-D-galactopyranose, and methyl 2,3:4,6-di-*O*-benzylidene-α-D-mannopyranoside); (c) *trans*-fused six-membered rings (*e.g.*, derivatives of methyl 4,6-*O*-benzylidene-D-glucopyranoside and 1,3:2,4-di-*O*-benzylidene-erythritol); (d) *cis*-fused six-membered rings (*e.g.*, derivatives of methyl α-D-galactopyranoside and 1,3:2,4-di-*O*-benzylidene-L-threitol). Clear evidence has been obtained which indicates that members of group (d) exist in the predicted " O "-inside structures.

In the preceding Paper [1] the structures of various benzylidene derivatives of acyclic di- and poly-hydric alcohols containing isolated cyclic acetal rings were related to the chemical shifts of the benzyl proton signals in the n.m.r. spectra of these compounds. An extension to certain fused ring systems is now described.

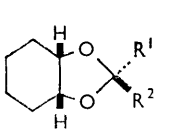
Acid-catalysed benzylidenation of cyclohexane-*cis*-1,2-diol gave a mixture of cyclic acetals (2-*endo*,*exo*-phenyl-1,3-dioxa-*cis*-bicyclo[4,3,0]nonanes) with benzyl proton signals of comparable integrated areas at τ 4·32 and 4·60 (these and subsequent τ values are for *ca.* 10% solutions in dioxan). The chemical shift of the latter signal is similar to that (4·66) for the corresponding proton in 2-phenyl-1,3-dioxolan and may be assigned to isomer (I) where the *exo*-benzyl proton is *cis*-related to the ring-junction protons. The former signal (4·32) is further to lower field than those (*ca.* 4·50) for the *trans*-4-alkyl-2-phenyl-1,3-dioxolan derivatives considered in the preceding Paper [1] and reflects the deshielding influence [1,3] of the two methylene groups attached to the ring-junction carbon atoms and *cis*-related to the *endo*-benzyl proton in structure (II).

Comparable results have been obtained with various carbohydrate derivatives containing a 2-phenyl-1,3-dioxolan ring *cis*-fused to a tetrahydropyran ring. Thus, Oldham and Honeyman [4] observed that an old sample of methyl 3,4-*O*-benzylidene-β-L-arabinopyranoside (originally prepared by the Gerhardt method [5]) on benzoylation gave mainly an acid-stable (hot 0·05N-hydrochloric acid in aqueous acetone) benzoate, *A*, m. p. 126—127°, $[\alpha]_D$ +174° (in $CHCl_3$), which was probably a pure diastereoisomer. However, a freshly prepared sample gave mainly a mixture of benzoates, *B*, m. p. 100—102°, $[\alpha]_D$ +214·9° (in $CHCl_3$), the predominant isomer being acid-labile. Fractionation of the latter product gave what was probably the second diastereoisomeric form of methyl 2-*O*-benzoyl-3,4-*O*-benzylidene-β-L-arabinopyranoside, *C*, m. p. 120—122°, but unfortunately no $[\alpha]_D$ value was given. When methyl β-L-arabinopyranoside was benzylidenated using Oldham and Honeyman's method,[4] the crude 3,4-*O*-benzylidene derivative had benzyl proton

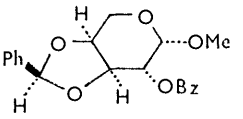
[1] Part XXI, preceding Paper.
[2] Preliminary report of some of these results, N. Baggett, K. W. Buck, A. B. Foster, M. H. Randall, and J. M. Webber, *Proc. Chem. Soc.*, 1964, 118.
[3] N. S. Bhacca and D. H. Williams, " Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, 1964, pp. 184—190.
[4] M. A. Oldham and J. Honeyman, *J.*, 1946, 986.
[5] W. Gerhardt, Ger.P. 253,083/1910; *Chem. Zentr.*, 1912, **83**, 1953.

signals at 4·30 and 4·56 with integrated areas in the ratio *ca.* 1 : 2·5. The marked predominance of one diastereoisomer suggested that the crude product was not a true equilibrium mixture since near equimolar mixtures of 4- or 4,6-di-substituted 2-phenyl-1,3-dioxolan derivatives are usually formed at equilibrium effected by vigorous acid catalysis. Support for this view is provided by the observation that, on acid-catalysed benzylidenation of cyclohexane-*cis*-1,2-diol [6,7] and methyl 2,6-di-*O*-methyl-α-D-galactopyranoside [7] under homogeneous conditions, kinetic control was operative initially and the diastereoisomer with the high-field benzyl proton signal (*exo*-benzyl proton) was formed preferentially.

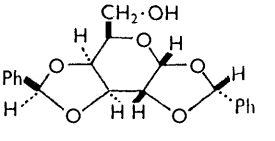
Benzoylation of the crude 3,4-*O*-benzylidene derivative gave a product with benzyl proton signals at 4·18 and 4·53 from which was separated a benzoate, *D*, m. p. 119—120°, $[\alpha]_D$ +224° (in $CHCl_3$), with a single benzyl proton signal at 4·51. The compound *D*, which is probably identical with the benzoate *C*, is a pure diastereoisomer and may be



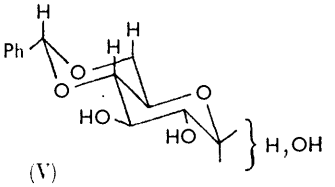
(I : R^1 = Ph, R^2 = H)
(II : R^1 = H, R^2 = Ph)



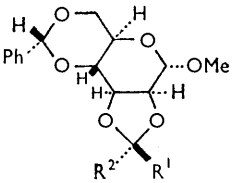
(III)



(IV)



(V)



(VI) R^1 = H, R^2 = Ph (m. p. 180—181°, $[\alpha]_D$ −1° in $CHCl_3$)
(VII) R^1 = Ph, R^2 = H (m. p. 97—99°, $[\alpha]_D$ −63° in $CHCl_3$)

assigned the structure (III) which contains an *exo*-benzyl proton. On the basis of the above $[\alpha]_D$ values for benzoates *A* and *D*, the mixture *B* contains 82% of diastereoisomer *D*.

The reaction of D-galactose with benzaldehyde has been studied by various workers [8-11] and, in the presence of zinc chloride, the main product is the 4,6-*O*-benzylidene derivative together with a small amount of 1,2:3,4-disubstituted compound. Four isomers of 1,2:3,4-di-*O*-benzylidene-α-D-galactose are theoretically possible, and there is some variation of physical constants recorded by the various groups. However, a comparison of specimens prepared by Wallenfels,[11] Zinner and Thielebeule,[8] and Foster [10] established their identity, and the last two compounds had benzyl proton signals of equal integrated area at 4·55 and 4·62 [cf. 4·60 for the cyclohexane derivative (I)], indicative of structure (IV) with an *exo*-benzyl proton in each benzylidene acetal. The crude di-*O*-benzylidene-D-galactose had benzyl proton signals at 4·02, 4·30, 4·62, and 4·68 with integrated areas in the ratio 1 : 0·5 : 3 : 3. The high-field signals (4·62 and 4·68) are associated with the isomer ultimately isolated, and its predominance in the mixture makes it likely that the same product was isolated by the various workers.[8-11] The low-field signals are probably associated with diastereoisomers containing *endo*-benzyl protons, but attempts to separate these isomers were unsuccessful.

It has been shown [12] that 4,6-*O*-benzylidene-D-glucose has a *trans*-decalin type ring

[6] N. Baggett, A. B. Foster, J. M. Webber, D. Lipkin, and B. E. Phillips, *Chem. and Ind.*, 1965, 136.
[7] N. Baggett, J. M. Duxbury, A. B. Foster, and J. M. Webber, *Carbohydrate Res.*, 1965, in the press.
[8] H. Zinner and W. Thielebeule, *Chem. Ber.*, 1960, **93**, 2791.
[9] J. Pacak and M. Cerny, *Coll. Czech. Chem. Comm.*, 1961, **26**, 2212; E. G. Gros and V. Deulefeu, *Chem. and Ind.*, 1962, 1502.
[10] A. B. Foster, Ph.D. Thesis, Birmingham, 1950.
[11] Professor K. Wallenfels, personal communication.
[12] A. B. Foster, A. H. Haines, J. Homer, J. Lehmann, and L. F. Thomas, *J.*, 1961, 5005.

system (V) with the phenyl group equatorial to the 1,3-dioxan ring so that the benzyl proton is axial and there are axial protons at positions 4 and 6. There can be little doubt that a similar stereochemical arrangement is present in methyl 4,6-*O*-benzylidene-α-D-glucopyranoside and its derivatives and in methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (see Table). The chemical shift for the benzyl protons in these compounds (4·81—4·84) is only slightly to lower field than those (4·86—5·02) for the equatorially substituted derivatives of 2-phenyl-1,3-dioxan described in the preceding Paper.[1]

Condensation of methyl α-D-mannopyranoside with benzaldehyde in the presence of zinc chloride gave a crude product mixture having benzyl proton signals at 4·15, 4·47, 4·74, 4·82, and 4·84 with integrated areas in the ratio 1 : 1 : 1 : *ca.* 2·5 : 1. Fractionation of the mixture gave methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (4·82) and the two 2,3:4,6-di-*O*-benzylidene derivatives, *E* {m. p. 180—181°; $[\alpha]_D$ −1° (in $CHCl_3$); 4·16, 4·76} and *F* {m. p. 97—99°; $[\alpha]_D$ −63° (in $CHCl_3$); 4·46, 4·84} originally described by Robertson.[13] The signals at 4·76 and 4·84 for isomers *E* and *F*, respectively, may be assigned to the 4,6-*O*-benzylidene group, and those at 4·16 and 4·46 to the 2,3-*O*-benzylidene acetal with *endo*- and *exo*-benzyl protons, respectively; *i.e.*, structures (VI) and (VII) may be allocated to compounds *E* and *F*.

1,4-Anhydroerythritol on vigorous acid-catalysed benzylidenation gave a near-equimolar mixture of 2-*exo*,*endo*-phenyl-1,3,5-trioxa-*cis*-bicyclo[3,3,0]octanes with benzyl proton signals at 4·36 and 4·67 (Δτ 0·31). The isomer with the low-field signal (4·36) was obtained crystalline (m. p. 57—58°) and, in parallel with the preceding examples, may be assigned the structure (VIII) with an *endo*-benzyl proton. When benzylidenation of 1,4-anhydroerythritol was effected under homogeneous conditions[6] using the system benzaldehyde–nitromethane–toluene-*p*-sulphonic acid at *ca.* 25°, rapid appearance of the high-field benzyl proton signal (4·96) occurred followed by much slower appearance of a signal at 4·66 (Δτ 0·30) paralleled by diminution in intensity of the first signal until equilibrium was reached. Interruption of the reaction in the early stage gave the selectively formed isomer (m. p. 73—75°, τ 4·67 in dioxan) with an *exo*-benzyl proton (IX). Other

Benzyl proton signals for certain benzylidene acetals

trans-Decalin type ring systems	
Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside	4·84
2,3-di-*O*-acetate	4·83
2,3-di-*O*-methyl ether	4·81
Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside	4·82
1,3:2,4-Di-*O*-benzylidene-erythritol	4·75
1,3:2,4-Di-*O*-benzylideneribitol	4·63, 4·73
5-*O*-acetate	4·65, 4·77
cis-Decalin type ring systems	
Methyl 4,6-*O*-benzylidene-α-D-galactopyranoside	4·81
2-deoxy	4·82
2,3-di-*O*-methyl ether	4·81
1,3:2,4-Di-*O*-benzylidene-L-threitol	4·82
1,3:2,4-Di-*O*-benzylidenexylitol	4·79, 4·85
5-*O*-acetate	4·80, 4·84
5,6-Di-*O*-benzoyl-1,3:2,4-di-*O*-benzylidene-D-glucitol	4·71, 4·86
1,3:2,4:5,6-Tri-*O*-benzylidene-D-glucitol	4·51, 4·75, 4·80

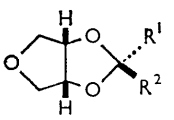
examples of homogeneous benzylidenations together with the mechanistic implications will be considered elsewhere. Assignment of absolute configuration to various 2,3-*O*-benzylidene-nucleosides, for which the acetals (VIII) and (IX) are model compounds, has already been reported.[6]

1,3:2,4-Di-*O*-benzylidene-erythritol has a *trans*-decalin type ring system with equatorial phenyl groups[14] (X), and its benzyl proton signal (4·75) was only slightly to lower field than those (4·81—4·84) for the 4,6-*O*-benzylidene-D-glucopyranose derivatives in

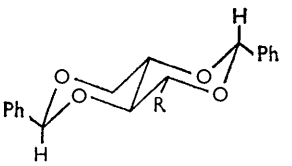
[13] G. J. Robertson, *J.*, 1934, 330.
[14] A. B. Foster, A. H. Haines, and J. Lehmann, *J.*, 1961, 5011.

the Table. 1,3:2,4-Di-*O*-benzylideneribitol [15] had benzyl proton signals at 4·63 and 4·73 (5-*O*-acetate, τ 4·65, 4·77) which are consistent with the structure (XI). The signal at 4·73 (cf. 4·75 for 1,3:2,4-di-*O*-benzylidene-erythritol) may be assigned to the benzyl proton in the 1,3-dioxan ring carrying the hydroxymethyl substituent since it is clear from the results in the preceding Paper (Table 1) that the signal for the benzyl proton in 2-phenyl-1,3-dioxan is not significantly influenced by the introduction of equatorial alkyl or oxyalkyl substituents at positions 4 and 6. On the other hand, the benzyl proton in the second 1,3-dioxan ring and the hydroxymethyl group can approach closely enough for deshielding to occur, and this accounts for the slight shift to lower field.

A more complex situation was encountered in the *cis*-fused series. Proof has been presented that the 1,3:2,4-di-*O*-methylene [16] and 1,3:2,4-di-*O*-benzylidene (XII) derivatives [14] of L-threitol have the predicted [17] " O "-inside conformations with equatorial phenyl groups in the case of the latter compound. The benzyl proton signal (4·82) for the 1,3:2,4-di-*O*-benzylidene derivative is slightly to higher field than that (4·75) for the erythritol analogue (X) and reflects the essentially similar environment of the benzyl protons, *i.e.*, axial and on the same side of the 1,3-dioxan ring as axial protons at positions 4 and 6 [see formula (XII)]. It is interesting to note that the alternative, " H "-inside structure (XV; R = H) with equatorial phenyl groups, which might be formed in the reaction of L-threitol with benzaldehyde, has each benzyl proton axial and on the same side

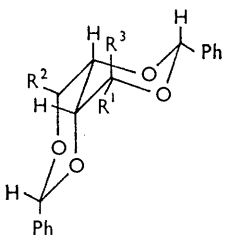


(VIII) R^1 = H, R^2 = Ph (m. p. 57—58°)
(IX) R^1 = Ph, R^2 = H (m. p. 73—75°)

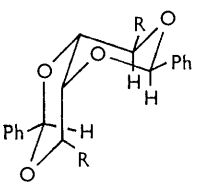


(X) R = H
(XI) R = CH_2·OH

of a 1,3-dioxan ring as an axial hydrogen atom and an axial methylene group attached to one of the ring junction carbon atoms. The effect of the latter group would be to deshield the benzyl proton and shift its signal to lower field.[1,3] The situation is comparable with that in the benzylidene acetals of DL-pentane-2,4-diol and 2-methylpentane-2,4-diol [formulæ (III) and (IV) in the preceding Paper], for which the benzyl proton signals occur at 4·58 and 4·66, respectively.



(XII) R^1 = R^2 = R^3 = H
(XIII) R^1 = CH_2·OH, R^2 = R^3 = H
(XIV) R^1 = CH_2(OBz)·CH·OBz, R^2 = R^3 = H
(XVI) R^1 = R^2 = CH_2·OBz, R^3 = H (L-form)
(XVII) R^1 = H, R^2 = R^3 = CH_2·OBz (L-form)



(XV) R = CH_2·OBz

Xylitol affords a di-*O*-benzylidene derivative of undetermined structure although some evidence [18] has been reported which indicates the presence of a free primary hydroxyl

[15] D. J. J. Potgeiter and D. L. MacDonald, *J. Org. Chem.*, 1961, **26**, 3934.
[16] R. U. Lemieux and J. Howard, *Canad. J. Chem.*, 1963, **41**, 393.
[17] J. A. Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 1.
[18] M. L. Wolfrom and E. J. Kohn, *J. Amer. Chem. Soc.*, 1942, **64**, 1739; M. L. Wolfrom, W. J. Burke, and E. A. Metcalf, *ibid.*, 1947, **69**, 87.

group. Condensation of xylitol with benzaldehyde in the presence of toluene-*p*-sulphonic acid gave a product (m. p. 167—168°) which had benzyl proton signals at 4·79 and 4·85 (the 5-*O*-acetate had signals at 4·80 and 4·84) indicative of six-membered acetals and consistent with a 1,3:2,4-distribution of the benzylidene groups and the existence of the molecule in an " O "-inside conformation with equatorial phenyl groups and an equatorial hydroxymethyl group (XIII). A similar situation exists in 5,6-di-*O*-benzoyl-1,3:2,4-di-*O*-benzylidene-D-glucitol [19] (XIV) which had benzyl proton signals at 4·86 and 4·71, but in this case one of the signals is shifted to lower field. The latter signal is tentatively assigned to the benzyl proton in the 1,3-acetal because of the closer possible approach of the benzoyl groups to this proton (with consequent greater deshielding) than to the benzyl proton in the 2,4-acetal.

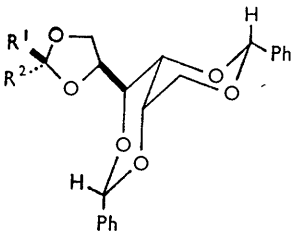
1,6-Di-*O*-benzoyl-2,4:3,5-di-*O*-benzylidene-D-glucitol [20] had benzyl proton signals at 4·71 and 4·37. The high-field signal (4·71) is indicative of a six-membered benzylidene acetal, and this requires that the second acetal ring be of similar size and confirms the structure previously assigned. The ring system is *cis*-fused, and the two structures possible involve " O "- and " H "-inside arrangements [(XVI) and (XV), respectively] of two chair forms of 1,3-dioxan rings with equatorial phenyl groups and one axial and one equatorial benzoyloxymethyl group. The close approach of the *endo*-protons (including both benzyl protons) and the *endo*-benzoyloxymethyl group in the " H "-inside structure (XV), in addition to causing adverse non-bonded interactions,[17] would also result in significant deshielding [3] of both benzyl protons, supplementing the deshielding of the type commented on above for the " H "-inside structure (XV; R = H) for 1,3:2,4-di-*O*-benzylidene-L-threitol. Only one of the benzyl proton signals (4·37) for 1,6-di-*O*-benzoyl-2,4:3,5-di-*O*-benzylidene-D-glucitol was significantly shifted to lower field. On the other hand, the signals are entirely consistent with the " O "-inside structure (XVI) since only the benzyl proton in the 1,3-dioxan ring carrying an axial benzoyloxymethyl group [R^2 in formula (XVI)] would be significantly deshielded (cf. the results in the preceding Paper for the benzylidene derivatives of DL-pentane-2,4-diol and 2-methylpentane-2,4-diol).

Benzylidenation of 1,6-di-*O*-benzoyl-D-mannitol affords a 3,4-*O*-benzylidene compound together with a 2,3:4,5-disubstituted derivative [21] of undetermined structure (combined yield of the two products was 85%). The di-*O*-benzylidene derivative showed a single benzyl proton signal (4·37), and two of the three possible structures are thereby eliminated: first, a 2,3:4,5-diacetal since this would involve diastereoisomeric 2-phenyl-1,3-dioxolan derivatives with characteristic benzyl proton signals as discussed above, and, secondly, a 2,5:3,4-diacetal since this would involve two dissimilar benzylidene acetals and, moreover, can exist in two isomeric forms which are not obviously different in thermodynamic stability as revealed by molecular models. A 2,4:3,5-distribution of the acetals would enable the molecule to adopt an " O "-inside structure with equatorial phenyl groups and axial benzoyloxymethyl groups (XVII). Each benzyl proton signal in such a structure would be significantly shifted to low field, and it is important to note the precise correspondence of the signal with that assigned to the benzyl proton in a comparable environment in 2,4:3,5-di-*O*-benzylidene-1,6-di-*O*-benzoyl-D-glucitol (XVI).

Zissis and Richtmyer [22] obtained two di-*O*-benzylidene derivatives (*A*, m. p. 159—160°, $[\alpha]_D$ −47·5° in $CHCl_3$, cf. +45·2° in $CHCl_3$ for 2,4:3,5-di-*O*-benzylidene-1,6-di-*O*-benzoyl-D-mannitol; and *B*, m. p. 131—134°, $[\alpha]_D$ +12·3° in $CHCl_3$) on benzylidenation of 1,6-dideoxy-L-mannitol. A sample of the major isomer, *A*, kindly provided by Dr. N. K. Richtmyer, was found to have a single benzyl proton signal at 4·40, and by analogy with the di-*O*-benzoate (XVII) it may be assigned a 2,4:3,5-distribution of the acetal groups and a structure (XVII; R^1 = H, R^2 = R^3 = Me) (D-form). The correspondence in optical

[19] J. K. Wolfe, R. M. Hann, and C. S. Hudson, *J. Amer. Chem. Soc.*, 1942, **64**, 1493.
[20] L. von Vargha, *Ber.*, 1935, **68**, 18, 1377.
[21] W. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Amer. Chem. Soc.*, 1943, **65**, 1419.
[22] E. Zissis and N. K. Richtmyer, *J. Amer. Chem. Soc.*, 1952, **74**, 4373.

rotations of the 1,6-dideoxy-derivative and the 1,6-di-*O*-benzoate (XVII) is noteworthy. Unfortunately, insufficient of isomer *B* was available for n.m.r. spectroscopy, but it seems likely that it is one of the two theoretically possible 2,5:3,4-di-*O*-benzylidene derivatives. Molecular models indicate such structures to be stereochemically acceptable, and it has been



(XVIII) R^1 = H, R^2 = Ph (m. p. 160—161°)
(XIX) R^1 = Ph, R^2 = H (m. p. 173—177°)

observed that reaction of 1,6-di-*O*-methyl-3,4-di-*O*-isopropylidene-D-mannitol [23] with benzylidene bromide in a t-butyl alcohol–potassium t-butoxide mixture gave the 2,5-*O*-benzylidene derivative.[24] In this case, however, the symmetry of the system is such that only one isomer can be formed.

The preceding arguments emphasise the desirability of comparing the benzyl proton signal pattern for crude and purified products in reaching a decision on the correlation of signals with particular ring sizes of benzylidene acetals and with particular diastereoisomers. This is especially true in the case of 2-phenyl-1,3-dioxolan derivatives where normally, at equilibrium, near equimolar amounts of diastereoisomers will be present and selective crystallisation is a possibility.

Although a tri-*O*-2-nitrobenzylidene derivative of galactitol has been reported,[25] apparently the corresponding benzylidene derivatives are unknown. Condensation of galactitol with benzaldehyde under forcing conditions (acid-catalysis with azeotropic removal of water) gave two tri-*O*-benzylidene derivatives,[26] *G* (m. p. 160—161°, τ 4·20, 4·41, 4·82) and *H* (m. p. 174—177°, τ 4·23, 4·63, 4·84). The benzyl proton signals for these isomers are best accounted for by postulating a 1,3:2,4:5,6-distribution of the acetals and a structure (XVIII) or (XIX) involving an " O "-inside structure with equatorial phenyl groups and C-5 axial to the 2,4-acetal ring. By analogy with the preceding results and arguments the signals at 4·82 and 4·84 for isomers *G* and *H* may then be assigned to the benzyl proton in the 1,3-acetal, and the respective low-field signals at 4·20 and 4·23 to the 2,4-acetal benzyl proton which is deshielded by the axial group at C-4. The signals at 4·41 and 4·63 may be assigned to the benzyl proton in the 5,6-benzylidene group, which is, respectively, *cis* and *trans* to C-4 in isomers *G* (XVIII) and *H* (XIX). These compounds are being further investigated.

All the above results and interpretations accord with the theoretical considerations presented by Mills.[17]

Experimental

The n.m.r. spectra were determined using a Varian A60 instrument on *ca.* 10% solutions in dioxan with tetramethylsilane (6%) and benzyl alcohol (10%) separately in chloroform as external references.

Benzylidenation of Methyl β-L-*arabinopyranoside.*—A mixture of this compound (5 g.) and benzaldehyde (25 ml.) was heated at 135° for 3·5 hr. with removal of water as described by Oldham and Honeyman.[4] Excess of benzaldehyde was then removed by distillation at diminished temperature and pressure. The residue, which had benzyl proton signals at 4·30 and 4·56 in the ratio *ca.* 1 : 2·5, was treated with benzoyl chloride (5 ml.) and pyridine (10 ml.) at room temperature overnight. The mixture was poured into ice–water and extracted with chloroform. The dried ($MgSO_4$) extract was evaporated and the residue recrystallised first

[23] L. F. Wiggins, *J.*, 1946, 384.
[24] N. Baggett, A. B. Foster, K. Palmork, and J. M. Webber, unpublished results.
[25] I. Tanasecu and I. Iliescu, *Bull. Soc. chim. France*, 1938, **5**, 1446.
[26] N. Baggett, A. B. Foster, and J. M. Webber, unpublished results.

from chloroform–light petroleum (b. p. 60—80°) and then from dioxan–light petroleum, to give *methyl* 2-O-*benzoyl*-3,4-O-*benzylidene*-β-L-*arabinopyranoside* (0·66 g.), m. p. 119—120°, $[\alpha]_D^{30}$ +224° (*c* 1·0 in $CHCl_3$) (Found: C, 67·4; H, 5·8. $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·7%).

Benzylidenation of 1,4-*Anhydroerythritol.*—(*a*) A mixture of 1,4-anhydroerythritol [27] (3·1 g.), benzaldehyde (3·6 ml.), toluene (30 ml.), and toluene-*p*-sulphonic acid (50 mg.) was boiled under reflux for 2·5 hr. using a device for the azeotropic removal of water. The cooled solution was washed with aqueous 10% potassium carbonate and water, dried ($MgSO_4$), and concentrated, to give 2-*exo*,*endo*-phenyl-1,3,5-trioxa-*cis*-bicyclo[3,3,0]octane (4·1 g., 70%), b. p. 160—165° (bath)/0·05 mm. (Found: C, 68·8; H, 6·45. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

The above product solidified on storage, and four recrystallisations from ethanol gave the 2-exo-*phenyl* isomer, m. p. 57—58° (Found: C, 68·8; H, 6·1%).

(*b*) The development of benzyl proton signals was followed for a mixture of 1,4-anhydroerythritol (1·02 g.), toluene-*p*-sulphonic acid (108 mg.), nitromethane (5 ml.), and benzaldehyde (5 ml.) at 25—30°. A single signal (τ 4·96), due to the *endo*-phenyl isomer appeared during 4 min. and the mixture was then poured into water containing an excess of sodium carbonate. The solution was extracted with ether, the extract was dried ($MgSO_4$), and the residue was distilled from sodium carbonate. The initial fraction, b. p. 88—160°(bath)/12 mm., was discarded and the second fraction (1·43 g., 78%), b. p. 160—164°(bath)/12 mm., which solidified on storage, was recrystallised from ether–light petroleum (b. p. 60—80°), to give the 2-endo-*phenyl* isomer (1·13 g.), m. p. 73—75° (Found: C, 68·8; H, 6·3%).

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[27] J. S. Brimacombe, A. B. Foster, M. Stacey, and D. H. Whiffen, *Tetrahedron*, 1958, **4**, 351.