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STEREOSELECTIVE EPOXIDATION OF DIVINYLMETHANOL: A SYNTHETIC APPROACH TO THE PENTITOLS

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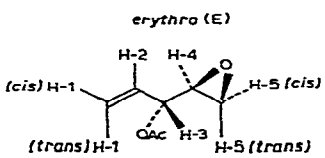
ABSTRACT

Peroxy-acid epoxidation of divinylmethanol (**9**), followed by acetylation afforded the acetylated monoepoxides **1** and **2** having the *erythro* (53%) and *threo* (47%) configurations. Peroxy-acid epoxidation of **1** and **2** yielded the acetylated diepoxides **3** (*erythro-erythro*, 36%) and **4** (*erythro-threo*, 64%) (from **1**), and **4** (*erythro-threo*, 47%) and **5** (*threo-threo*, 53%) (from **2**). Relative configurational assignments were made to **1**–**5** on the basis of (*a*) ^{1}H-n.m.r. chemical-shift and coupling-constant data, (*b*) the observation that **1** gave only **3** and **4**, and that **2** gave only **4** and **5** on epoxidation, and (*c*) the fact that **3**–**5** separately undergo epoxide-ring opening preferentially at their primary carbon atoms with acetate ion in acetic anhydride, to afford the penta-acetates of ribitol, DL-arabinitol, and xylitol, respectively, as major products. Epoxide-ring formation favours the *erythro* configuration when either peroxy acids or *tert*-butyl hydroperoxide with catalytically active Ti^{4+}, V^{5+}, or Mo^{6+} complexes are employed as epoxidation reagents. However, the diastereoselectivities characterising the epoxidations and the regioselectivities governing the epoxide-ring openings are not sufficiently high to constitute an attractive synthesis of either ribitol, DL-arabinitol, or xylitol from divinylmethanol.



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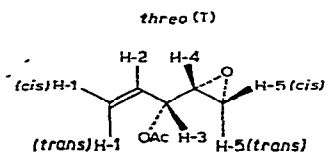

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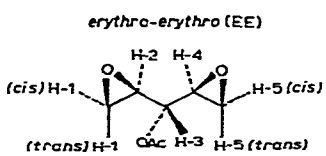

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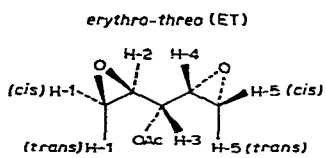

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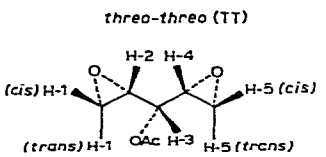

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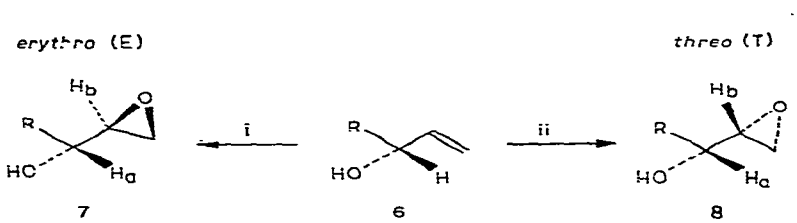
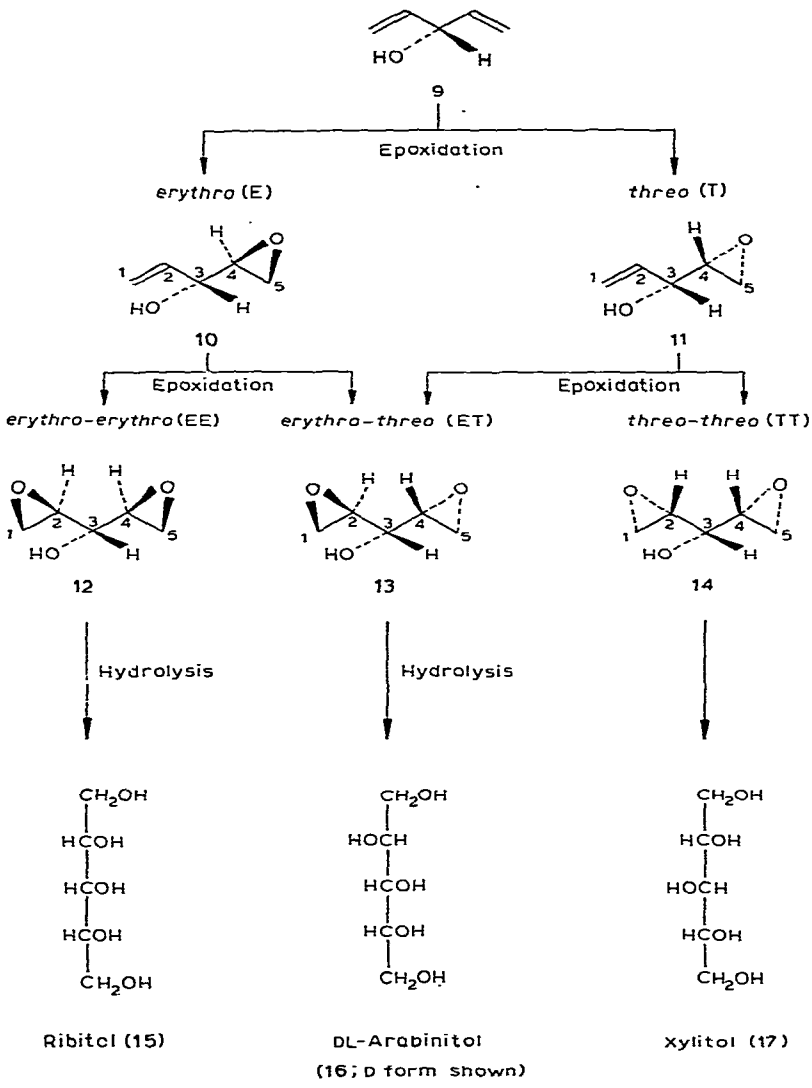


Fig. 1. The stereochemistry of epoxidation of acyclic, secondary allylic alcohols **6**. Pathway (i) is favoured by ^{t}BuOOH in the presence of catalytically active metal-complexes (*e.g.*, when R = Me, ^{t}BuOOH–VO(acac)$_2$ in CH_2Cl_2 at 0° gives[3] an *erythro/threo* ratio of 4:1, and ^{t}BuOOH–Mo(CO)$_6$ in CH_2Cl_2 at ambient temperature gives[3] a ratio of 56:44). Pathway (ii) is preferred by peroxy acids (*e.g.*, when R = Me, 3-$ClC_6H_4CO_3H$ at 0° gives[3] an *erythro/threo* ratio of 2:3).

INTRODUCTION

In recent years, the stereoselectivity of epoxidations of acyclic, secondary allylic alcohols **6** with *tert*-butyl hydroperoxide in the presence of appropriate metal catalysts[1–6] and with peroxy acids[3–10] has been investigated. In general, the *erythro/threo* ratios (**7**/**8**) observed (see Fig. 1) for the product epoxy-alcohols **7** and **8** can now be predicted on the basis of the epoxidising reagent. Thus, in the presence of catalytically active metal-complexes, *tert*-butyl hydroperoxide usually epoxidises **6** to give mainly the *erythro* isomer **7**, whereas peroxy acids preferentially yield the *threo* isomer **8**. Numerous attempts have been made[3–5,8–12] to analyse for the relative energies of the diastereoisomeric transition-states associated with these stereoselective epoxidations. However, stereoelectronic rationalisations of the small differences in energy involved (<1.5 kcal.mol^{-1}) can rarely be used to predict the outcome when a fresh problem is faced. This was the situation in considering divinylmethanol (**9**) as a possible substrate for mono- and di-epoxidation. Although the compound contains a centre of prochirality, in contrast with the one of chirality present in **6**, the faces of the C=C bonds in **9** are nonetheless diastereotopic. Thus, mono-epoxidation of **9** may lead (Scheme 1) to diastercoisomeric *erythro* (**10**) and *threo* (**11**) isomers. Further epoxidation of the vinyl groups in **10** should lead to *erythro-erythro* (**12**) and *erythro-threo* (**13**) diepoxides and, by analogy, further epoxidation of **11** must lead to the *erythro-threo* (**13**) and *threo-threo* (**14**) diepoxides. The *erythro-erythro* (**12**) and *threo-threo* (**14**) diastereoisomers are meso compounds (C_s symmetry) with centres of pseudoasymmetry at C-3 and chiral centres with opposite chiralities at C-2 and C-4. The *erythro-threo* diastereoisomer (**13**) is asymmetric and has a centre of prochirality at C-3 in addition to the two chiral centres having the *same* chiralities at C-2 and C-4. If opening of the epoxide rings in **12–14** by an appropriate oxygen nucleophile (*e.g.*, HO^- or H_2O) occurs regioselectively at the primary centres, then ribitol (**15**), DL-arabinitol (**16**), and xylitol (**17**), respectively, are the exclusive products. Thus, a selective synthesis of a particular pentitol from divinylmethanol (**9**) depends upon achieving high stereoselectivities in each epoxidation step and high regioselectivities in each epoxide-opening step.

Our investigations were concerned to devise a selective synthetic route to



Scheme 1

xylitol (**17**), which had considerable commercial importance as a sweetening agent until recently. On the basis of literature data, epoxidation by peroxy acids was expected to favour the formation of *threo* products and hence offer a stereoselective route to xylitol (**17**) from divinylmethanol (**9**). However, before our own laboratory studies began, some of the reactions based upon the chemistry outlined in Scheme 1 were reported briefly[13]. Some of the results and claims were puzzling in relation to (*a*) selectivities expected in the isomer discriminating steps, and (*b*) our investigations of 1-hydroxypenta-2,4-dienes as possible precursors to the pentitols. Since the initial

work[13] had been abstracted into the review literature[14], we decided to investigate the potential of divinylmethanol (**9**) as a starting material for a selective synthesis of pentitols.

RESULTS AND DISCUSSION

The acetylated monoepoxides **1** and **2** were prepared by treating divinylmethanol (**9**) at 60° with 1 mol.equiv. of 4-nitroperoxybenzoic acid in chloroform and then acetylating the crude, oily product. G.l.c. of the acetylated products revealed two major components (peaks 1 and 2 in Fig. 2a). The acetylated diepoxides **3**–**5** were prepared by a similar procedure, but using 2.6 mol.equiv. of 4-nitroperoxybenzoic acid with **9** and a longer reaction time. G.l.c. of the acetylated products revealed three

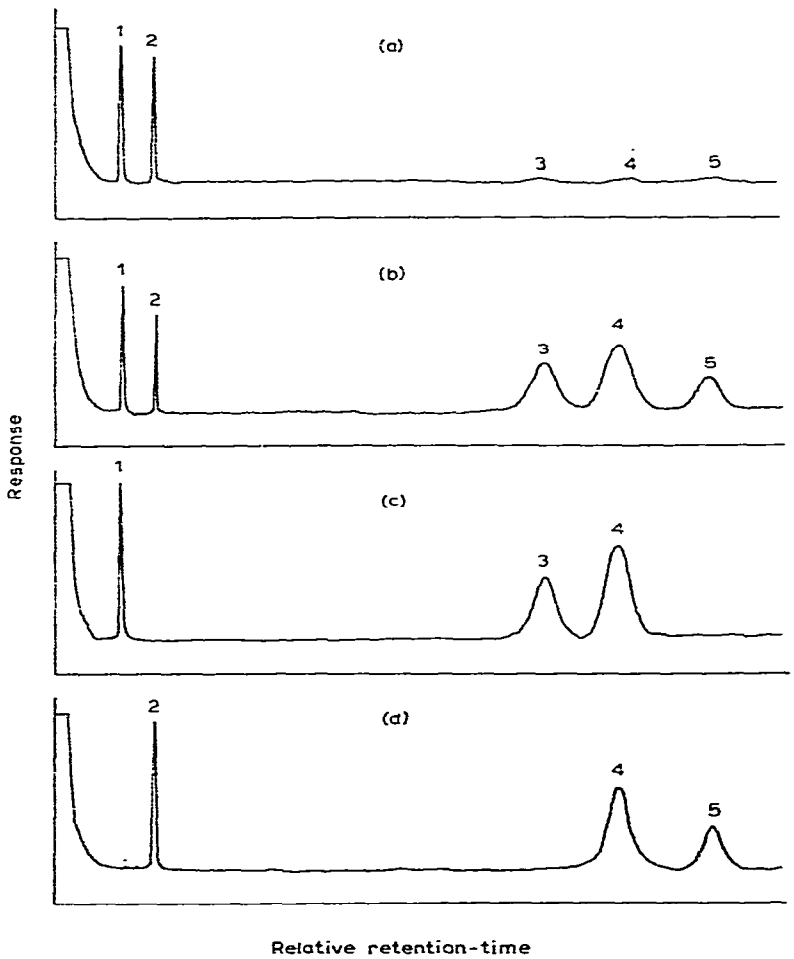


Fig. 2. G.l.c. traces of acetylated products of epoxidation with 4-nitroperoxybenzoic acid of (*a*) **9** with 1.0 mol, (*b*) **9** with 2.6 mol, (*c*) **1** with 1.7 mol, and (*d*) **2** with 1.7 mol.

additional peaks (3–5 in Fig. 2b), with retention times much longer than those for peaks 1 and 2. Although peaks 3–5 corresponded to the major products of this epoxidation, peaks 1 and 2 were also present, indicating that the formation of di-epoxides was incomplete. Pure samples of acetylated monoepoxides **1** and **2** and the acetylated diepoxides **3–5** were isolated by chromatography on silica gel, and their relative configurations were established in the first instance on the basis of high-resolution, ^{1}H-n.m.r. data.

It has been demonstrated[5] that *erythro* and *threo* epoxides of the types **7** and **8**, derived (Fig. 1) by epoxidation of secondary allylic alcohols **6**, can be characterised on the basis of certain ^{1}H-n.m.r. data: (*a*) the signal for H_a (δ 3.8 $\pm$0.1) in the *erythro* isomer **7** appears[5] consistently downfield from that of H_a (δ 3.5 $\pm$0.1) in the *threo* isomer **8**, and (*b*) the J_{H_a,H_b} value (3.25 Hz) for **7** is[5] invariably smaller than that ($\geqslant$5.0 Hz) observed for **8**. If we assume that these differences in chemical shift and coupling constant will also characterise the acetylated monoepoxides **1** and **2** (where R = CH=CH$_2$ and the hydroxyl groups are acetylated in Fig. 1), then we can assign relative configurations to the isomeric compounds giving rise to peaks 1 and 2 in Fig. 2a. The chemical shifts for the protons (including H-3) listed in Table I indicate that peaks 1 and 2 (Fig. 2a) contain the *erythro* **1** and *threo* **2** isomers, respectively. In addition to H-3 (δ 5.30) in **1** resonating at lower field than H-3 (δ 5.10) in **2**, the $J_{3,4}$ value for **1** is 4.3 Hz compared with 6.1 Hz for **2**. The isomer **1** has a shorter g.l.c. retention-time than **2**. Previously, it had been noted[5] that *erythro* isomers **7** have shorter g.l.c. retention-times than *threo* isomers **8**. The chemical shift data for the three diastereoisomeric, acetylated diepoxides which give rise to peaks 3–5 (Fig. 2b) are listed in Table I. Although, for each compound, the characteristic low-field signals at δ 4.77, 4.55, and 4.80 are associated with H-3, the relative chemical shifts do *not* permit configurational assignments to be made. Nor is a comparison of the $J_{2,3}$ and/or $J_{3,4}$ values (5.0, 5.6, and 5.0 Hz) helpful. However, the chemical shift data for the compound in peak 4 are clearly associated with the asymmetrical *erythro-threo* isomer **4**, since the signals for H-1 (*trans*), H-1 (*cis*), H-2, H-3, H-4, H-5 (*cis*), and H-5 (*trans*) are anisochronous (*seven* signals are observed for these *seven* protons). The assignment of the signals at δ 2.78, 2.83, and 3.14 (see Table I) to H-1 (*trans*), H-1 (*cis*), and H-2, respectively (*i.e.*, to the *erythro* moiety), and those at δ 2.72, 2.89, and 3.24 to H-5 (*trans*), H-5 (*cis*), and H-4, respectively (*i.e.*, to the *threo* moiety), was based upon the observation that the signal (δ 3.11) for H-4 in the *erythro* isomer **1** resonates upfield (see Table I) from that (δ 3.14) for H-4 in the *threo* isomer **2**. Thus, for the acetylated *erythro-threo* diepoxide **4**, the signal at δ 3.14 is associated with H-2 in the *erythro* moiety and the signal at δ 3.24 with H-4 in the *threo* moiety. The chemical shift assignments in Table I of signals for the protons on C-1 and C-5, made on the basis of spin–spin decoupling experiments, correlate with those observed for the stereochemically analogous protons in the acetylated *erythro* and *threo* monoepoxides **1** and **2**. The chemical shift difference between the geminal protons on C-1 (*erythro* moiety) is 0.05 p.p.m. (*cf.* 0.09 p.p.m. for **1**) and on C-5 (*threo* moiety) is 0.17 p.p.m. (*cf.*, 0.18 p.p.m. for **2**). The *erythro-erythro* (**3**) and

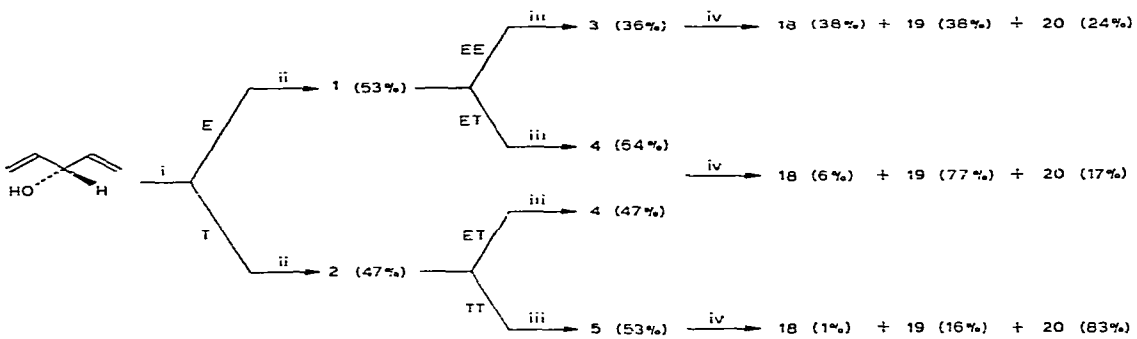
TABLE I

A COMPARISON OF PROTON CHEMICAL SHIFTS[a] FOR **1–5** AND THEIR RELATIVE CONFIGURATIONAL ASSIGNMENTS

Peak No.[b]	*Compd. No.*	*Rel. config.*[c]	*H-1 (trans)*[d]		*H-1 (cis)*[d]		*H-2*[d]		*H-3*[d]		*H-4*[d]		*H-5 (cis)*[d]		*H-5 (trans)*[d]	
			E	*T*	*E*	*T*	*E*	*T*	*E*	*T*	*E*	*T*	*E*	*T*	*E*	*T*
1	1	E	5.38[e]		5.32[e]		5.81[e]		5.30[f]		3.11[f]		2.78		2.69	
2	2	T	—	5.35[e]	—	5.29[e]	—	5.84[e]	—	5.09[g]	—	3.14[g]	—	2.85	—	2.67
3	3	EE	2.82	—	2.82	—	3.12	—	4.77	—	3.12	—	2.82	—	2.82	
4	4	ET	2.78	—	2.83	—	3.14	—	4.55[h]	4.55[h]	—	3.24	—	2.89	—	2.72
5	5	TT	—	2.72	—	2.86	—	3.20	—	4.80	—	3.20	—	2.86	—	2.72

[a]In chloroform-*d* at ambient temperature. [b]See Fig. 2. [c]E, *erythro*; T, *threo*. [d]The individual protons are identified in formulae **1–5**. [e]These chemical shifts are for the vinylic protons. [f]$J_{3,4}$ 4.3 Hz. [g]$J_{3,4}$ 6.1 Hz. [h]H-3 has the *erythro* configuration with respect to H-2 and the *threo* configuration with respect to H-4.

threo-threo (**5**) isomers contain planes of symmetry and so each should give rise to no more than four signals for H-1 (*trans*), H-1 (*cis*), H-2, H-3, H-4, H-5 (*cis*), and H-5 (*trans*): H-3 accounts for one of these signals and the three enantiotopic pairs of protons, namely, H-1 (*trans*) and H-5 (*trans*), H-1 (*cis*) and H-5 (*cis*), and H-2 and H-4, account for the other three signals. Thus, a distinction between **3** and **5** is not possible on the basis of symmetry properties. However, comparison (Table I) of the chemical shifts for H-1 (*trans*), H-1 (*cis*), H-2, H-4, H-5 (*cis*), and H-5 (*trans*) in **4** with those obtained for the constitutionally identical protons in the isomers associated with peaks 3 and 5 leads to their unambiguous assignment to the *erythro-erythro* (**3**) and *threo-threo* (**5**) isomers, respectively. The g.l.c. retention-times increase in the sequence *erythro-erythro* (**3**) to *erythro-threo* (**4**) to *threo-threo* (**5**).



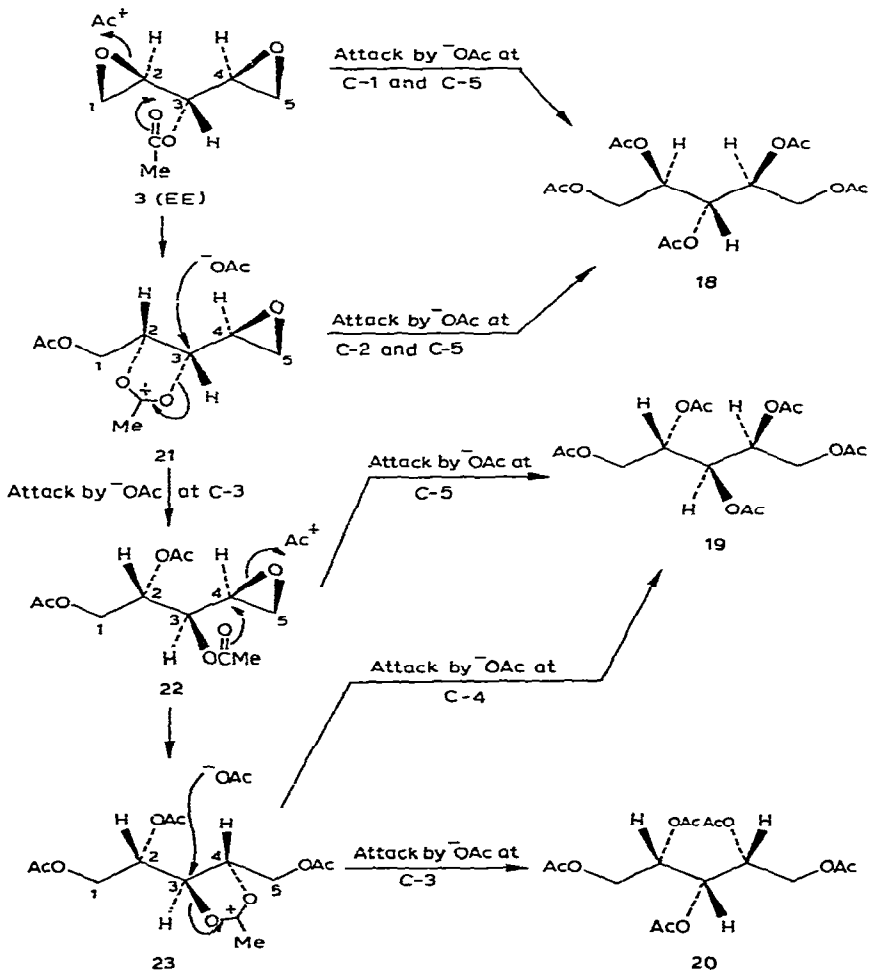
Scheme 2. Key: i, 4-$O_2NC_6H_4CO_3H$, $CHCl_3$, 60°, 6 h; ii, Ac_2O, Pyr; iii, 4-$O_2NC_6H_4CO_3H$, $CHCl_3$, 60°, 16 h; iv, Bu_4NOAc, Ac_2O, 90°, 16 h; E, *erythro*; T, *threo*.

The relative configurational assignments of **3–5** are also supported by chemical evidence. Epoxidation of the acetylated monoepoxides **1** and **2** with 1.7 mol.equiv. of 4-nitroperoxybenzoic acid gave the results summarised in Fig. 2 (c and d) and in Scheme 2. The *erythro* isomer **1** affords the acetylated *erythro-erythro* (**3**) and *erythro-threo* (**4**) diepoxides, respectively; the relative areas of peaks 3 and 4 were 36:64 and no *threo-threo* isomer **5**, corresponding to peak 5, was observed (see Fig. 2c). The *threo* isomer **2** affords the acetylated *erythro-threo* (**4**) and *threo-threo* (**5**) diepoxides, respectively; the relative areas of peaks 4 and 5 were 47:53 and *no erythro-erythro* isomer **3**, corresponding to peak 3, was observed (see Fig. 2d). These observations are consistent with the configurational assignments made above to **3–5**. In addition, the proportions of the pentitol penta-acetates **18–20** obtained on opening of the epoxide rings in **3–5** with tetrabutylammonium acetate in acetic anhydride are also in agreement with the configurational assignments. Scheme 2 summarises the quantitative results obtained during a sequence of reactions involving (*i*) epoxidation of divinylmethanol (**9**), followed by (*ii*) acetylation of the *mixture* of monoepoxides **10** and **11** to give **1** and **2**, (*iii*) further epoxidation of the *isolated* acetylated monoepoxides **1** and **2** to afford **3** and **4** and **4** and **5**, respectively, and (*iv*) epoxide-ring

openings of the *isolated* acetylated diepoxides **3–5** to give mixtures of the penta-acetates **18**, **19**, and **20** of ribitol (**15**), DL-arabinitol (**16**), and xylitol (**17**), respectively. The acetylated monoepoxides **1** and **2** were isolated by column chromatography, whereas h.p.l.c. was required in order to separate the acetylated diepoxides **3–5**. If epoxide-ring openings of **3–5** with acetate ion were regioselective at the primary carbon atoms, the sole products would be **18–20**, respectively. In fact, **4** and **5** afford **19** and **20**, respectively, as the major products of their reactions. However, **3** affords as much DL-arabinitol penta-acetate (**19**) as the expected product, ribitol penta-acetate (**18**): xylitol penta-acetate (**20**) is also a product of the epoxide-ring opening of **3** with acetate ion. Clearly, other reaction pathways are competing during the openings of the epoxide rings, particularly for those with the *erythro* configuration. Although some attack by acetate ion at the secondary carbon atoms of the epoxide rings in **3** could account for the unexpected distribution of products, it seems more likely that AcO-3 participates in the opening of the epoxide rings. There are many precedents in the literature[15] for this kind of behaviour. Scheme 3 summarises some of the possible reaction pathways, involving acetoxonium ions (*e.g.*, **21** and **23**) and acetylated epoxide (*e.g.*, **22**) intermediates, which could account for the formation of all three pentitol penta-acetates **18–20** from the acetylated diepoxide **3**. An *erythro* epoxide has the ideal stereoelectronic characteristics (antiperiplanar geometry between the attacking and leaving oxygen-functions) for acetoxy participation in the opening of the ring when the C_5 chain adopts a zigzag conformation. Also, the percentage yields (see Scheme 2) of pentitol penta-acetates **18–20** obtained from **4** and **5** support the view that participation occurs more readily for an *erythro* epoxide than for a *threo* epoxide. Other conclusions follow from the yields obtained for **1–5** recorded in Scheme 2. Somewhat unexpectedly, in view of the known[3–5,7–10] diastereoselectivities of peroxy acids to afford, usually, mainly *threo* epoxides from secondary allylic alcohols, there is a slight preference for the formation of the *erythro* epoxide **10** rather than the *threo* epoxide **11** on epoxidation of **9** with 4-nitroperoxybenzoic acid. By contrast, the epoxidation of the allylic double-bond in **1** and **2** gives mainly epoxides with *threo* stereochemistry. However, when the second epoxidation is allowed to proceed without isolation of **10** and **11**, there is a slight preference for the formation of *erythro* epoxides. Table II lists the diastereoselectivities of epoxidations of **9** with 1.0 and 2.3 mol.equiv. of various peroxy acids. The results not only reveal the relative constancy of the isomer ratios for both the mono- and di-epoxides but also demonstrate the marginal preference for the formation of *erythro* rather than *threo* epoxides. Moreover, the isomer distributions for the diepoxides **12–14**, obtained on treatment of **9** with 4-nitroperoxybenzoic acid in four different solvents, differ dramatically from those reported[13] previously using the same peroxy acid but under unspecified reaction conditions. The proportions of 5:20:75 claimed[13] for **12**:**13**:**14** and their relative configurational assignments were based upon the observation of identical ratios for xylitol (**17**):DL-arabinitol (**16**):ribitol (**15**) when the mixture of diepoxides was treated with sodium carbonate in aqueous methyl sulfoxide. However, xylitol (**17**) and ribitol (**15**) could only result from **12** and **14**, respectively, if opening of the

epoxide rings occurred exclusively at the secondary carbon atoms. When we epoxidised **9** with 4-nitroperoxybenzoic acid in dichloromethane and then hydrolysed the intermediate diepoxides with sodium carbonate in aqueous methyl sulfoxide, ratios for ribitol (**15**):DL-arabinitol (**16**):xylitol (**17**) of 10:43:47 were obtained by g.l.c. of the penta-acetates. The route does not constitute a synthesis of ribitol (**15**) as claimed[13], nor do the proportions of pentitols correspond exactly to the proportions of diepoxides from which they are derived, since g.l.c. of the intermediate diepoxides as their acetates **3**–**5** reveal ratios for **12**:**13**:**14** of 16:60:24 before their base-catalysed hydrolysis to the pentitols.

We have also examined the reaction of **9** with hexafluoroacetone–hydrogen peroxide[16] and *tert*-butylhydroperoxide in the presence of catalytically active[3–5] titanium(IV), vanadium(V), and molybdenum(VI). The results in Table III show



Scheme 3

TABLE II

THE EPOXIDATION OF DIVINYLMETHANOL (9) WITH PEROXY ACIDS

Acid	*Solvent*	*Products (%)[a] with*				
		1.0 Mol. equiv.		*2.3 Mol. equiv.*		
		10	**11**	**12**	**13**	**14**
CF_3CO_3H	CH_2Cl_2	55[b]	45[b]	23[c]	66[c]	11[c]
CH_3CO_3H	CH_2Cl_2	51[d]	49[d]	33[d]	54[d]	13[d]
$3\text{-}ClC_6H_4CO_3H$	CH_2Cl_2	56[e]	44[e]	23[e]	57[e]	20[e]
$4\text{-}NO_2C_6H_4CO_3H$	CH_2Cl_2	—	—	36[e]	55[e]	9[e]
$4\text{-}NO_2C_6H_4CO_3H$	$CHCl_3$	53[f]	47[f]	30[e]	56[e]	14[e]
$4\text{-}NO_2C_6H_4CO_3H$	CCl_4	—	—	28[e]	59[e]	13[e]
$4\text{-}NO_2C_6H_4CO_3H$	C_6H_6	—	—	25[e]	59[e]	16[e]
$4\text{-}NO_2C_6H_4CO_3H$	[g]	—	—	5[h]	20[h]	75[h]

[a]Analysed by g.l.c. of the acetates. [b]At 0° for 2.6 h. [c]At 0° for 1.3 h. [d]At 60° for 17 h. [e]At 60° for 16 h. [f]At 60° for 5 h. [g]Solvent not reported by Chautemps[13]. [h]Results reported by Chautemps[13].

TABLE III

THE EPOXIDATION OF DIVINYLMETHANOL (9) WITH HEXAFLUOROACETONE–HYDROGEN PEROXIDE AND *tert*-BUTYLHYDROPEROXIDE IN THE PRESENCE OF METAL CATALYSTS

Epoxidising agent	*Solvent*	*Products (%)[a] with*				
		1.0 Mol. equiv.		*2.3 Mol. equiv.*		
		10	**11**	**12**	**13**	**14**
$CF_3COCF_3 \cdot 1.5\ H_2O/H_2O_2$	$ClCH_2CH_2Cl$	49[b]	51[b]	—	—	—
$VO(acac)_2/{}^tBuOOH$	$ClCH_2CH_2Cl$	78[b]	22[b]	38[c]	43[c]	19[c]
$MoO_2(acac)_2/{}^tBuOOH$	$ClCH_2CH_2Cl$	84[b]	16[b]	—	—	—
$Ti(OPr^i)_4/{}^tBuOOH$	CH_2Cl_2	61[d]	39[d]	—	—	—

[a]Analysed by g.l.c. of the acetates. [b]At 60° for 16 h. [c]At 60° for 2.5 h. [d]At ambient temperature for 60 h.

that it was difficult to obtain the diepoxides **12–14** from **9** under conditions which did not lead to decomposition of the monoepoxides **10** and **11**. Formation of epoxide rings with the *erythro* configuration was favoured in all of the metal-catalysed epoxidations; 2-hydroperoxyhexafluoro-2-propanol[16] does not appear to discriminate between the two isomers in the formation of the monoepoxides.

Thus, we conclude that divinylmethanol (**9**) is not the most desirable of C_5 starting-materials from which to develop highly stereoselective syntheses of pentitols. Much better diastereoselectivities in the epoxidation steps and regioselectivities in the epoxide-ring openings would have to be achieved before **9** had the potential to challenge the constitutionally isomeric (*E*)- or (*Z*)-hydroxypenta-2,4-dienes as an attractive precursor to one or other of the pentitols[17].

EXPERIMENTAL

General. — Tetrahydrofuran was refluxed over sodium–benzophenone and then distilled under nitrogen. Pyridine (AR) was distilled from barium oxide and stored under nitrogen. Other solvents were dried using a molecular sieve (3 Å). Hydrogen peroxide (87%), used in the preparations of (*i*) solutions of peroxytrifluoroacetic acid and (*ii*) hydroperoxyfluoro-2-propanol was donated by Laporte Industries Ltd. *tert*-Butyl hydroperoxide, free from di-*tert*-butyl peroxide, was obtained from Aldrich (aqueous TBHP-70) and was dried by adding the aqueous solution to 1,2-dichloroethane[4]. The two phases were separated and the 1,2-dichloroethane–water azeotrope (b.p. 72°) was distilled until the distillate became homogeneous, leaving an anhydrous solution of *tert*-butyl hydroperoxide in 1,2-dichloroethane, the concentration of which was determined by iodometric titration. 4-Nitroperoxybenzoic acid was purified by crystallisation from chloroform, and 3-chloroperoxybenzoic acid by stirring with a phosphate buffer (pH 7.5) overnight before recrystallisation from chloroform. Peracetic acid was obtained from Phase Separation Ltd., and peroxytrifluoroacetic acid was prepared[18] from hydrogen peroxide (90%, 0.18 ml) and trifluoroacetic anhydride (1.1 ml) in dichloromethane (1 ml). 2-Hydroperoxyhexafluoro-2-propanol was prepared[16] from hexafluoroacetone sesquihydrate and 90% hydrogen peroxide. Vanadyl bis(acetylacetonate)[19] was obtained from Koch–Light. Molybdenum(VI) dioxybis(acetylacetonate)[19] and tetrabutylammonium acetate[20] were prepared according to literature procedures. The penta-acetates of ribitol, m.p. 102°, DL-arabinitol, m.p. 96°, and xylitol, m.p. 62°, were obtained conventionally. G.l.c. was carried out on a G.C.D. Pye–Unicam chromatograph equipped with a flame-ionisation detector, using a column (9 ft) of Silicone OV-17 (3%) on Chromosorb WHP and a nitrogen flow equivalent to 24 p.s.i. Column chromatography was performed[21] on silica gel 60 (40–63 μm, Merck, 9385). H.p.l.c. was carried out on a Dupont Preparative HPLC System equipped with a silica gel column. The eluate was monitored by g.l.c. High-resolution mass spectra were obtained from a Kratos MS80 instrument. ^{1}H-N.m.r. spectra (internal Me_4Si) were recorded with Bruker WH 400 (400 MHz), Perkin–Elmer R34 (220 MHz), Varian HR (220 MHz), and Jeol FX100 (100 MHz) spectrometers.

3-Hydroxypenta-1,4-diene (*Divinylmethanol*) (**9**). — Prepared[22] from methyl formate and vinylmagnesium chloride, **9** had b.p. 52.5–54°/80 mmHg; lit.[22] b.p. 56°/80 mmHg. ^{1}H-N.m.r. data ($CDCl_3$, 220 MHz): δ 5.80 [ddd, 2 H, $J_{1,2} = J_{4,5} =$ 10.5 (*cis*) and 17.0 (*trans*), $J_{2,3} = J_{3,4} = 6.0$ Hz, H-2,4], 5.22 and 5.10 [2 dd, 4 H, $J_{1,2} = J_{4,5} = 10.5$ (*cis*) and 17.0 (*trans*), $J_{1,3} = J_{3,5} = 1.0$, $J_{gem} < 0.3$ Hz, 2 H-1 and 2 H-5], 4.57 (tt, 1 H, $J_{2,3} = J_{3,4} = 6.0$, $J_{1,3} = J_{3,5} = 1.0$ Hz, H-3), and 2.53 (s, 1 H, OH).

Anal. Calc. for C_5H_8O: C, 71.4; H, 9.6. Found: C, 71.2; H, 9.8.

rel-(*3*R,*4*S)-*3-Acetoxy-4,5-epoxypent-1-ene* (**1**) *and* rel-(*3*R,*4*R)-*3-acetoxy-4,5-epoxypent-1-ene* (**2**). — To a solution of 4-nitroperoxybenzoic acid (10.9 g, 59.5 mmol) in chloroform (520 ml) was added **9** (5 g, 59.5 mmol). The mixture was kept

at 60° and the reaction was monitored by g.l.c. (80°) of acetylated samples. After 5 h, the precipitated 4-nitroperoxybenzoic acid was removed, and the filtrate was stirred overnight with anhydrous potassium carbonate, filtered, and concentrated. The resulting, pale-yellow oil (6.8 g) was treated with acetic anhydride (14 mL, 0.14 mmol) and pyridine (16 mL, 0.2 mmol) at room temperature overnight. Ether (100 mL) was added, and the solution was washed with water, dilute hydrochloric acid (10%), and saturated, aqueous sodium hydrogencarbonate, dried (Na_2SO_4), and concentrated. The resulting, pale-yellow oil (4.7 g) was purified by column chromatography [ethyl acetate–light petroleum (b.p. 40–60°), 1:9], to give a mixture of **1** and **2**. Column chromatography with tetrahydrofuran–light petroleum (b.p. 40–60°) (1:9) then gave, first, the *erythro*-monoepoxide **1** (730 mg, 5.1 mmol; 8.6%). ^{1}H-N.m.r. data ($CDCl_3$, 400 MHz): δ 5.81 [m, 1 H, $J_{1,2}$ 17.4 (*trans*) and 10.7 (*cis*), $J_{2,3}$ 6.7 Hz, H-2]. 5.38 [dt, $J_{1,2}$ 17.4 (*trans*), $J_{1,3}$ 1.2, J_{gem} 1.2 Hz, H-1 *trans* to H-2], 5.32 [dt, 1 H, $J_{1,2}$ 10.7 (*cis*), $J_{1,3}$ 1.2, J_{gem} 1.2 Hz, H-1 *cis* to H-2], 5.30 (m, 1 H, H-3), 3.11 [m, 1 H, $J_{3,4}$ 4.0, $J_{4,5}$ 4.0 (*cis*) and 2.75 Hz (*trans*), H-4], 2.78 [dd, 1 H, $J_{4,5}$ 4.0 (*cis*), J_{gem} 4.9 Hz, H-5 *cis* to H-4], 2.69 [dd, 1 H, $J_{4,5}$ 2.75 (*trans*), J_{gem} 4.9 Hz, H-5 *trans* to H-4], and 2.10 (s, 3 H, OAc). Eluted second was the *threo*-monoepoxide **2** (560 mg, 3.9 mmol; 6.6%). Mass spectrum (e.i.): *m/z* 142.0630 ($M^{+\cdot}$) (calc.: *m/z* 142.0630). ^{1}H-N.m.r. data ($CDCl_3$, 400 MHz): δ 5.84 [ddd, 1 H, $J_{1,2}$ 10.7 (*cis*) and 17.1 (*trans*), $J_{2,3}$ 6.1 Hz, H-2], 5.35 [dt, 1 H, $J_{1,2}$ 17.1 (*trans*), $J_{1,3}$ 1.2, J_{gem} 1.2 Hz, H-1 *trans* to H-2], 5.29 [dt, 1 H, $J_{1,2}$ 10.7 (*cis*), $J_{1,3}$ 1.2, J_{gem} 1.2 Hz, H-1 *cis* to H-2], 5.09 (tt, 1 H, $J_{2,3} = J_{3,4} = 6.1$, $J_{1,3}$ 1.2 Hz, H-3), 3.14 [ddd, 1 H, $J_{3,4}$ 6.1, $J_{4,5}$ 4.1 (*cis*) and 2.75 Hz (*trans*), H-4], 2.85 [dd, 1 H, $J_{4,5}$ 4.1 (*cis*), J_{gem} 4.9 Hz, H-5 *cis* to H-4], 2.67 [dd, 1 H, $J_{4,5}$ 2.75 (*trans*), J_{gem} 4.9 Hz, H-5 *trans* to H-4], and 2.12 (s, 3 H, OAc).

Anal. Calc. for $C_7H_{10}O_3$: C, 59.2; H, 7.0. Found **1**: C, 59.2; H, 7.3. **2**: C, 59.1; H, 6.9.

rel-(2R,3s,4S)-*3-Acetoxy-1,2:4,5-diepoxypentane* (**3**), rel-(2R,4R)-*3-acetoxy-1,2:4,5-diepoxypentane* (**4**), *and* rel-(2R,3r,4S)-*3-acetoxy-1,2:4,5-diepoxypentane* (**5**). — To a solution of 4-nitroperoxybenzoic acid (16.8 g, 92 mmol) in chloroform (550 mL) was added **9** (3 g, 36.0 mmol), and the mixture was maintained at 60° overnight, filtered, and stirred with a slurry of anhydrous potassium carbonate (2.5 g, 180 mmol) in acetone (25 mL) for 4 h. The mixture was filtered, treated with acetic anhydride (6.1 mL, 60 mmol) and pyridine (14.2 mL, 180 mmol) overnight, washed with water, saturated, aqueous sodium hydrogencarbonate, aqueous (10%) copper sulphate, and water, dried (Na_2SO_4), and concentrated. The resulting, deep reddish-brown oil (3.5 g) was purified by column chromatography [ethyl acetate–light petroleum (b.p. 40–60°), 1:1]. Eluted first was the *erythro-erythro*-diepoxide **3** (340 mg, 2.2 mmol; 6%). Mass spectrum (e.i.): *m/z* 158.0599 ($M^{+\cdot}$) (calc.: 158.0579). ^{1}H-N.m.r. data ($CDCl_3$, 400 MHz): δ 4.77 (t, 1 H, $J_{2,3} = J_{3,4} = 5.0$ Hz, H-3), 3.12 (m, 2 H, H-2,4), 2.82 (m, 4 H, 2 H-1 and 2 H-5), and 2.12 (s, 3 H, OAc). Eluted second was the *erythro-threo*-diepoxide **4** (176 mg, 1.1 mmol; 3%). Mass spectrum (e.i.): *m/z* 157.0470 ($M^{+\cdot}$). ^{1}H-N.m.r. data ($CDCl_3$, 400 MHz): δ 4.55 (t, 1 H, $J_{2,3}$ =

$J_{3,4}$ = 5.6 Hz, H-3), 3.24 [ddd, 1 H, $J_{4,5}$ 4.0 (*cis*) and 2.5 (*trans*), $J_{3,4}$ 5.6 Hz, H-4], 3.14 [ddd, 1 H, $J_{2,3}$ 5.6, $J_{1,2}$ 4.0 (*cis*) and 2.5 Hz (*trans*), H-2], 2.89 [dd, 1 H, $J_{4,5}$ 4.0 (*cis*), J_{gem} 5.0 Hz, H-5 *cis* to H-4], 2.83 [dd, 1 H, $J_{1,2}$ 4.0 (*cis*), J_{gem} 5.0 Hz, H-1 *cis* to H-2], 2.78 [dd, 1 H, $J_{1,2}$ 2.5 (*trans*), J_{gem} 5.0 Hz, H-1 *trans* to H-2], 2.72 [dd, 1 H, $J_{4,5}$ 2.5 (*trans*), J_{gem} 5.0 Hz, H-5 *trans* to H-4], and 2.12 (s, 3 H, OAc). The third fraction was impure and was purified by h.p.l.c. (ethyl acetate–hexane, 1:3), to give **4** and the *threo-threo*-diepoxide **5** (8.5 mg, 0.05 mmol; 0.15%). ^{1}H-N.m.r. data ($CDCl_3$, 400 MHz): δ 4.80 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 5.0 Hz, H-3), 3.20 [ddd, 2 H, $J_{1,2}$ = $J_{4,5}$ = 4.5 (*cis*) and 2.5 (*trans*), $J_{2,3}$ = $J_{3,4}$ = 5.0 Hz, H-2,4], 2.86 [dd, 2 H, $J_{1,2}$ = $J_{4,5}$ (*cis*), J_{gem} 5.0 Hz, H-1 and H-5 *cis* to H-2 and H-4, respectively], and 2.14 (s, 3 H, OAc).

Anal. Calc. for $C_7H_{10}O_4$: C, 53.2; H, 6.3. Found **3**: C, 53.0; H, 6.1. **4**: C, 52.8; H, 6.5. **5**: C, 53.1; H, 6.3.

Quantification of epoxidations. — (*a*) Divinylmethanol (**9**) was treated with 1 mol.equiv. of 4-nitroperoxybenzoic acid in chloroform at 60° for 5 h. After acetylation of the products, g.l.c. revealed the acetylated monoepoxides **1** and **2** with an *erythro*:*threo* ratio of 53:47 (see Scheme 2).

(*b*) *rel*-(3*R*,4*S*)-3-Acetoxy-4,5-epoxypent-1-ene (**1**) and *rel*-(3*R*,4*R*)-3-acetoxy-4,5-epoxypent-1-ene (**2**), when treated with 1.7 mol.equiv. of 4-nitroperoxybenzoic acid in chloroform at 60° for 16 h, underwent 80% reactions. G.l.c. of the product from **1** revealed the acetylated diepoxides **3** and **4** with an *erythro-erythro*/*erythro-threo* ratio of 36:64 (see Scheme 2). G.l.c. of the product from **2** revealed the acetylated diepoxides **4** and **5** with an *erythro-threo*/*threo-threo* ratio of 47:53 (see Scheme 2).

(*c*) The other experiments on divinylmethanol (**9**) with peroxy acids were carried out with 1 mol.equiv. of the peroxy acid to obtain monoepoxides **10** and **11**, and with 2.3 mol.equiv. of the acid to obtain the diepoxides **12**–**14** (~80% conversion). The product ratios were analysed by g.l.c., after conversion into the acetates. The other conditions employed in the individual reactions are summarised in footnotes to Table II.

(*d*) Epoxidations of divinylmethanol (**9**) with 2-hydroperoxyhexafluoro-2-propanol and with *tert*-butyl hydroperoxide in the presence of metal catalysts were carried out with 1 mol.equiv. of reagent, to obtain the monoepoxides **10** and **11**, which were converted into their acetates before g.l.c. The other conditions employed are summarised in footnotes to Table III. Apart from the one example shown in Table III, attempts to convert **9** into diepoxides **12**–**14** with 2.3 mol.equiv. of epoxidising agent were less successful.

Quantification of epoxide-ring opening in rel-(2R,3s,4S)-*3-acetoxy-1,2:4,5-diepoxypentane* (**3**), rel-(2R,4R)-*3-acetoxy-1,2:4,5-diepoxypentane* (**4**), *and* rel-(2R,3r,4S)-*3-acetoxy-1,2:4,5-diepoxypentane* (**5**). — The acetylated diepoxides **3**–**5** were treated severally with an excess of tetrabutylammonium acetate in acetic anhydride for 16 h at 90°. The reaction mixtures were then analysed directly by g.l.c., which revealed the ratios of penta-acetates recorded in Scheme 2.

Preparation of ribitol (**15**), DL-*arabinitol* (**16**), *and xylitol* (**17**) *from divinyl-*

methanol (**9**). — To a solution of 4-nitroperoxybenzoic acid (240 mg, 1.3 mmol) in dichloromethane (14 ml) was added **9** (42 mg, 0.05 mmol), and the mixture was maintained overnight at 90°. The solution was filtered, and concentrated *in vacuo* at 60°, and the residual oil was acetylated and analysed by g.l.c. Ratios for ribitol (**15**)/DL-arabinitol (**16**)/xylitol (**17**) of 10:43:47 were obtained.

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