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ACETOXONIUM IONS FROM ACETOXYOXIRANES AND ORTHOESTERS: THEIR CONVERSION INTO ETHYLIDENE ACETALS, REARRANGEMENT, AND SOLVOLYSIS*†

J. GRANT BUCHANAN AND ALAN R. EDGAR

Department of Organic Chemistry, The University, Newcastle upon Tyne NE1 7RU, and Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS (Great Britain)

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ABSTRACT

The acid-catalysed ethylidenation of some methyl pentopyranosides has been studied and the configuration at the acetal carbon atom assigned by p.m.r. spectroscopy. There is a strong preference for the isomer in which the methyl group has the *endo* configuration. Several cyclic alkyl orthoacetates derived from methyl pentopyranosides have been prepared by orthoester exchange and the *endo* *C*-methyl isomer shown to preponderate. Treatment of vicinal acetoxyoxiranes and orthoacetates with boron trifluoride followed by lithium borohydride, or with diborane, yields ethylidene acetals in which the *C*-methyl group is *endo*. Rearrangements of the hexachloroantimonate salts of acetoxonium ions derived from methyl lyxo- and arabino-pyranosides, possessing *trans*-vicinal acetoxyl groups, have been studied. The ions having the *arabino* configuration are preferred in both the α and β series. The reaction of cyclic orthoacetates of methyl β-L-arabinopyranoside and some derivatives with dry acetic acid proceeds *via* an acyclic acetoxonium ion to yield only products having the L-*arabino* configuration.

INTRODUCTION

The acid-catalysed ring-opening of oxiranes bearing a neighbouring *trans*-acetoxyl group is believed[2] to involve acetoxonium ions as intermediates. We wished to extend our studies in two ways. Firstly, to obtain further evidence for the presence of these ions by converting their salts into ethylidene acetals, a process for which there is a precedent in the steroid field[3]. Secondly, to prepare some related carbohydrate orthoesters and to study their behaviour under similar reaction conditions. From our previous experience[2,4], methyl pentopyranosides appeared to be the best substrates for this work.

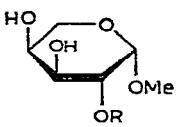
*Dedicated to the memory of Professor Edward J. Bourne.

†For a preliminary report of part of this work, see Ref. 1. Presented in part at a meeting of the Chemical Society Carbohydrate Discussion Group held in Bedford College, University of London, September 15th, 1970.

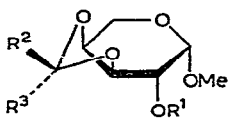
As a first step, it was necessary to prepare, as reference compounds, *O*-ethylidene derivatives of known stereochemistry at the acetal carbon atom. The chemistry of cyclic acetals was a lifelong interest of Professor Bourne, and he was coauthor of a pioneering review of the subject[5].

RESULTS AND DISCUSSION

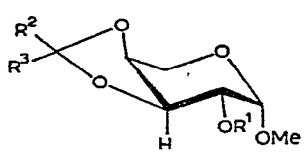
Oldham and Honeyman[6] showed that treatment of methyl β-L-arabinopyranoside (**1**) with paraldehyde and sulphuric acid yielded two isomeric 3,4-*O*-ethylidene compounds. We have re-examined this reaction using toluene-*p*-sulphonic acid as catalyst and have separated the isomeric acetals by chromatography on alumina. The major component, shown by p.m.r. spectroscopy to constitute 80–90% of the mixture, was isolated as a crystalline solid, m.p. 73–75°, in 55% yield; it was clearly the isomer of m.p. 76° previously isolated[6]. Its p.m.r. spectrum contained a doublet centred at δ 1.45 due to the ethylidene methyl group, and a corresponding methine signal as a quartet centred at δ 5.10. The minor component was isolated as a syrup whose p.m.r. spectrum contained signals due to the ethylidene group at δ 1.35 (CH_3) and 5.40 (CH). These data indicate[7–12] that the crystalline isomer has the *endo*-methyl structure **3** and that the syrupy isomer has structure **4**. The reliability of the p.m.r. method has been reaffirmed recently[12] by determination of the structure of one of the isomers of methyl 3,4-*O*-ethylidene-β-D-galactopyranoside by X-ray crystallography.



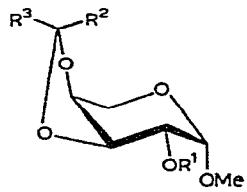
1 R = H
2 R = Me



3 $R^1 = R^3 = H, R^2 = Me$
4 $R^1 = R^2 = H, R^3 = Me$
5 $R^1 = H, R^2 = Me, R^3 = OMe$
6 $R^1 = H, R^2 = OMe, R^3 = Me$
7 $R^1 = H, R^2 = Me, R^3 = OEt$
8 $R^1 = H, R^2 = OEt, R^3 = Me$
9 $R^1 = R^2 = Me, R^3 = OMe$
10 $R^1 = R^3 = Me, R^2 = OMe$
11 $R^1 = R^2 = Me, R^3 = H$
12 $R^1 = Ac, R^2 = Me, R^3 = OMe$
13 $R^1 = Ac, R^2 = OMe, R^3 = Me$



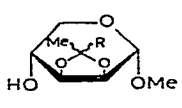
3a
4a
5a
6a



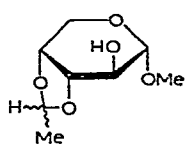
4b
6b

In order to confirm that the acetal mixture had equilibrated under the reaction conditions, we treated each isomer separately with toluene-*p*-sulphonic acid in chloroform. Examination of the resulting mixtures by p.m.r. spectroscopy revealed that the *endo*-methyl compound **3** was the major product in both cases, and **3** was isolated in 70% yield after acid treatment of **4**. The strong preference for the *endo*-methyl isomer is in keeping with work on other 1,3-dioxolane systems[10,12–15]. Kankaanperä[14,15] and Eliel and his coworkers[10] have made an extensive study of 2,4-dialkyl-1,3-dioxolanes and 2,4,*cis*-5-trialkyl-1,3-dioxolanes. With the exception of two cases involving *tert*-butyl substituents[10], the isomer having the *endo*-2-alkyl substituent preponderated. Kankaanperä has suggested that this can be rationalised by assuming that the 1,3-dioxolane ring adopts a half-chair (or twist) conformation, a conclusion also reached by other workers[10]. Thus, a probable conformation[16] of the acetal **3** is **3a**, in which the pyranoside ring is in the form of a flattened-chair intermediate between $^4C_1$ and $^OH_5$ (*cf.* Ref. 17) and the dioxolane ring is in the $^4T_{O-4}$ conformation. The minor isomer may exist as **4a**, in which there is a destabilising a,a′ interaction between the acetal methyl group and H-4, or as **4b** whose pyranose ring is $^4C_1$ and whose dioxolane ring is $^{O-3}T_3$. In **4b**, there is a destabilising interaction between the acetal hydrogen and the C-2–C-3 bond of the pyranose ring. The general preference for the methyl group in a 2-methyl-1,3-dioxolane to have the *endo* configuration was illustrated further by acid-catalysed ethylidenation of the methyl ether (**2**) of **1**, methyl α-D-lyxopyranoside, methyl α-D-arabinopyranoside, and cyclohexane-*cis*-1,2-diol, to give **11**, **14**, **16**, and **17**, respectively, each of which is preponderantly the *endo*-methyl isomer, as shown by p.m.r. spectroscopy (Table I). It has recently been shown[12] that methyl 2,6-di-*O*-benzyl-β-D-galactopyranoside gives mainly the *endo*-methyl ethylidene acetal under conditions of acidic catalysis.

We have previously postulated[2,4] that acetolysis of the anhydrolyxoside **20** proceeds *via* the acetoxonium-ion intermediate **21**. We anticipated that if such an ion could be prepared under anhydrous conditions[3], its reduction by a hydride



14 R = H
15 R = OMe



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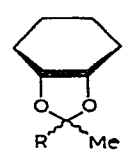
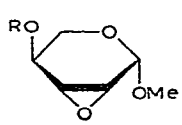
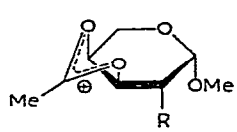


17 R = H
18 R = OMe



19 R = H
20 R = Ac



21 R = OH
22 R = $OBF_3^{\ominus}$

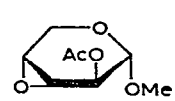


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TABLE I

P.M.R. SPECTRA[a] OF ETHYLIDENE ACETALS AND ORTHOACETATES

Compound	endo-*Me*	exo-*Me*	endo-*H*	exo-*H*	endo-*OMe*	exo-*OMe*	*Glycosidic OMe*	*Other signals*	*Ratio* exo-*Me*/endo-*Me* *at equilibrium*
3	1.45(d)			5.10(q)			3.45(s)	4.64 (d, 1 H, H-1)	~1:8
4		1.35(s)	5.40(q)				3.45(s)	4.64 (d, 1 H, H-1)	
11	1.39(d)			5.03(q)			3.40(s)	3.30 (s, 3 H, OMe) 4.58 (d, 1 H, H-1)	Only one isomer observed
14	Not resolved		5.10(q)	4.95(q)			3.42(s)	4.60 (d, 1 H, H-1)	~1:2.5
16	Not resolved		5.26(q)	4.92(q)			3.40(s)	Not resolved	~1:2
17	1.30(d)	1.20(d)	5.24(q)	4.92(q)					~1:2
5,6	1.54(s)	1.44(s)			3.33(s)	3.22(s)	3.45(s)	4.60 (s, 1 H, H-1)	~1:5
7,8	1.57(s)	1.47(s)					3.45(s)	1.15 (t, 3 H, OCH_2*Me*) 4.65 (d, 1 H, H-1)	~1:5
12,13	1.54(s)	1.44(s)			3.33(s)	3.22(s)	3.30(s)	1.04 (s, 3 H, COMe)	~1:7
18	1.45(s)	1.36(s)			3.23(s)	3.13(s)			~1:7

[a] CCl_4, 60 MHz, δ scale.

reagent should yield the acetal **3**, since approach of the reagent should be from the less-hindered *exo* side. We therefore treated the oxirane **20** in benzene with boron trifluoride etherate. A gummy precipitate, presumably **22**, formed immediately and was treated with lithium borohydride in ether to give the acetal **3** in 37% yield. None of the isomer **4** could be detected by t.l.c., indicating that the hydride had attacked exclusively from the *exo* side[18–20].

It is known that oxiranes undergo ring-opening when treated with diborane[21,22]. We therefore treated the anhydrolyxoside **20** with a solution of diborane in ether and isolated the acetal **3** in 45% yield. The oxirane **19** was also isolated (26%), arising by reductive cleavage of the ester grouping[21]. Once again, none of the *exo*-methyl isomer **4** could be detected. Reductive cleavage of the acetal ring[23] was not a major reaction under our conditions.

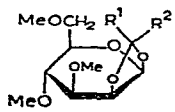
Cyclic orthoesters are an alternative source of cyclic acetoxonium ions[9,24–27]. Many examples of alkoxy alkylidene derivatives of carbohydrates are known, but in most cases the 1,3-dioxolane ring involves the anomeric centre[9,11,18–20,28–30]. The first examples to be characterised in which C-1 was not part of the dioxolane ring were ribonucleoside derivatives[31–34]; an orthoester was used as an intermediate in the monoacylation of a hexopyranoside[35]. Contemporary with this work, Paulsen[36] described a 4,6-*O*-ethoxyethylidene derivative of D-idose.

We have prepared a series of cyclic orthoesters of the methyl pentopyranosides from the glycoside and trimethyl orthoacetate by the technique of acid-catalysed orthoester exchange[34,37]. Examination of the products by p.m.r. spectroscopy revealed that a diastereoisomeric mixture was obtained in each case and, by using the arguments of Perlin[19] and of Lemieux and Morgan[20], it was shown that the isomer in which the alkoxy group had the *exo* configuration was always preponderant (Table I). Since orthoesters are extremely acid-labile, the method of preparation ensures that the systems have attained equilibrium. The preparation of 1,2-orthoesters from *O*-acetylglycosyl halides normally leads to the preferential formation of the *exo*-alkoxy isomer as a result of nucleophilic attack on the acetoxonium-ion intermediate[18–20] from the less-hindered *exo* side. Under non-acidic conditions, subsequent isomerisation cannot occur. It is apparent that the isomer having an *exo*-alkoxy group is preferred under conditions of both kinetic and thermodynamic control. The thermodynamic preference for the *exo*-alkoxy isomer is in agreement with the behaviour of *O*-ethylidene acetals, and the conformational arguments are similar[10,14,15]. It is known that a methoxyl group has a lower conformational free-energy difference than an alkyl group[38]. Thus, the L-*arabino* orthoesters **5** and **6** may exist in the conformations **5a** and **6a** or **6b**. In **6a**, there is a destabilising a,a′ interaction between the orthoester methyl group and H-4, while in **6b** there is a similar interaction between the orthoester methoxyl group and the C-2–C-3 bond. The orthoester **5**, in conformation **5a**, should therefore be preferred thermodynamically.

We have used orthoester formation as a further test for acetoxonium-ion formation in an acid-catalysed reaction of an acetoxyoxirane. When methyl 2-*O*-acetyl-3,4-anhydro-α-D-arabinopyranoside (**23**) was treated with antimony penta-

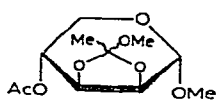
chloride, and the resulting solid was treated with sodium methoxide in methanol, the α-D-*lyxo* orthoester **15** was produced in 80% yield; its n.m.r. spectrum was almost indistinguishable from that of the same orthoester prepared from methyl α-D-lyxopyranoside by orthoester exchange. The ratio of diastereoisomers, determined from the OCH_3 signals in the p.m.r. spectrum, was 4.5:1 in favour of the *exo*-methoxy compound (4:1 for the preparation using orthoester exchange). Here again, the *endo*-methyl compound is favoured under conditions both of kinetic and thermodynamic control.

We then studied the reactions of the orthoesters with boron trifluoride etherate[27]. Since the orthoesters could not be separated from each other by chromatography, it was necessary to use diastereoisomeric mixtures. Treatment of the *arabino* orthoesters **7** and **8** in benzene with boron trifluoride etherate yielded a gummy salt, presumably **22** or the fluoroborate salt of **21**, which was reduced with excess of lithium borohydride in ether to give the acetal **3** in 44% yield. P.m.r. spectroscopy of the crude product indicated that **3** and **4** had been formed in a ratio of ~9:1. Under similar conditions, the orthoesters **9** and **10** afforded the acetal **11** in 49% yield without a detectable amount of the *exo*-methyl isomer. Bhattacharjee and Gorin[9] have shown that only the acetal **26**, having the *endo*-methyl group, is produced by treatment of the orthoesters **24** and **25** with aluminium chloride–lithium aluminium hydride. The direct conversion of the orthoesters **7** and **8** into the acetal **3**, in 66% yield, was accomplished by treatment with diborane in ether; a trace (2%) of the isomeric acetal **4** was isolated.



24 R^1 = Me, R^2 = OMe
25 R^1 = OMe, R^2 = Me
26 R^1 = Me, R^2 = H

Acetoxonium-ion migrations have been observed in systems where a cyclic acetoxonium-ion has a neighbouring *trans*-acetoxyl group[39,40]. When the *lyxo* derivative **27** in dichloromethane was treated with antimony pentachloride[27], a pale yellow solid formed immediately. The p.m.r. spectrum of a solution of this solid in acetonitrile showed signals due to acetoxonium methyl groups at δ 2.45 and 2.64 and to acetyl methyl groups at δ 2.38 and 2.58, indicating that the salt was probably a mixture of **28** and **29** in the ratio ~1:2. The mixture of salts was treated with aqueous potassium acetate; isolation of the products, followed by deacetylation, gave crystalline methyl α-D-arabinopyranoside in 32% yield. The mother liquors contained equal amounts of methyl α-D-arabinopyranoside and methyl α-D-lyxopyranoside. No xylopyranosides were detected, showing the absence of ions such as **31** in the equilibrium. A similar result was obtained on treatment of the arabinoside **30** with antimony pentachloride. In this case, the total yields of crystalline material were higher (58% of arabinoside and 11% of lyxoside), probably because the reaction was carried out using carbon tetrachloride in which the salts are less soluble.



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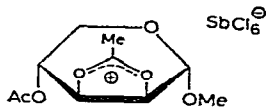

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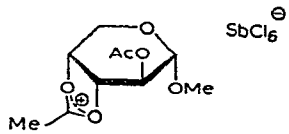

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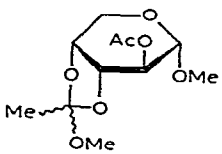

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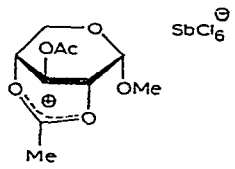

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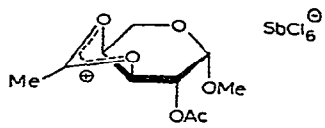

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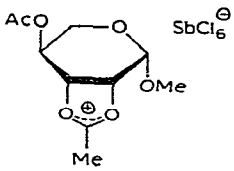

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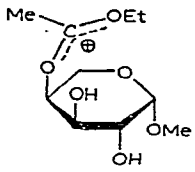

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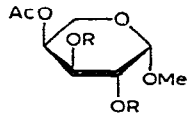


35 R = H
36 R = Ts

The corresponding rearrangement (32⇌33) in the β-L-series was also examined. Treatment of the arabinosides **12** and **13** under the same conditions gave crystalline methyl β-L-arabinopyranoside (**1**) in 66% yield, presumably *via* the salt **32**, while paper chromatography of the mother liquors showed the presence of **1** and of methyl β-L-lyxopyranoside in the ratio ~2:1; again, no xylopyranosides were detected. In both α and β series, there is a strong preference for an ion of *arabino* configuration, a result also found by Paulsen[41] and by Pedersen[42] for similar compounds.

Previously[2], we described the acetolysis, under anhydrous conditions, of a number of acetoxyoxiranes. A feature of these reactions was that there were three products from each substrate, corresponding to the three possible modes of ring-opening of the derived acetoxonium ion. For example, when the anhydrolyxoside **20** was heated with a mixture of acetic acid and acetic anhydride and the product deacetylated, the major glycoside was the arabinoside **1** together with methyl β-L-lyxopyranoside and methyl α-D-xylopyranoside in progressively smaller amounts. The formation of each of these products from the acetoxonium ion **21** can be rationalised.

The L-*arabino* orthoesters **5** and **6** were treated with boron trifluoride, and the resulting salt (**22** or the fluoroborate of **21**) was heated with dry acetic acid containing potassium acetate for 6 h. The major products were diacetates which yielded the same three glycosides on deacetylation. Again, the arabinoside **1** was the major

product, together with lyxoside and xyloside in approximately equal amounts. The minor difference in the isomer ratio compared with the earlier acetolysis is probably due to a variation in the relative amount of anionic species in the two reactions[2].

Since the orthoesters yielded acetoxonium ions on treatment with boron trifluoride or antimony pentachloride, we expected that cyclic ions would also be produced on treatment with anhydrous acetic acid[24–26]. However, when the arabinosides **7** and **8** were heated with anhydrous acetic acid at 100°, only derivatives of methyl β-L-arabinopyranoside (**1**), present as two monoacetates and a diacetate (t.l.c.), were formed. No products derived from ring-opening, with inversion, of the acetoxonium ion **21** could be detected. This strongly suggested that a cyclic acetoxonium ion was not formed as an intermediate in this reaction, but since the arabinosides **7** and **8** are alcohols, water could be produced in their acylation by acetic acid[2], leading to *cis*-opening of a cyclic acetoxonium ion[24–26]. We therefore repeated the reaction using the orthoesters **9** and **10** and also **12** and **13**, each of which lacks a free hydroxyl group. In both cases, only derivatives of methyl β-L-arabinoside were obtained. The result with **12** and **13** is particularly interesting because we have shown that the ion **32** is at least partly converted into the corresponding L-*lyxo* ion **33**. It appears, therefore, that protonation of the orthoesters that we have studied leads to the formation of an acyclic acetoxonium ion, *e.g.*, **34**, in contrast to the behaviour of the cyclohexane system[24–26] and that of our orthoesters with Lewis acids. Further work is necessary to establish the precise mechanism of the acetolysis (see Refs. 43–45 for some current views of carbohydrate orthoester hydrolysis).

King and Allbutt[46] have observed that hydrolysis of acetoxonium ions leads to preferential formation of an axial ester and have cited several carbohydrate examples. They have commented that this effect may also be observed in acid-catalysed hydrolysis of orthoesters, regardless of whether a cyclic or acyclic acetoxonium ion is involved. Treatment of the orthoesters **7** and **8** with 5% sulphuric acid gave two monoacetates. The axial monoacetate **35** was isolated as the bis(toluene-*p*-sulphonate)[4] **36** in 62% yield.

EXPERIMENTAL

General. — Infrared spectra were measured for potassium bromide discs. P.m.r. spectra were recorded with a Perkin–Elmer R10 spectrometer operating at 60 MHz, with tetramethylsilane as internal standard. T.l.c. was performed on plates of Kieselgel G (Merck), carbohydrates being detected with anisaldehyde–sulphuric acid spray[47]. Epoxides were detected with sodium iodide–Methyl Red spray[48]. Adsorption chromatography was carried out on silica gel (Hopkin and Williams) or aluminium oxide (Martindale Samoore). Paper chromatography was performed on Whatman No. 1 paper with water-saturated butanone; glycosides were detected with the periodate–Schiff spray[49]. Removal of solvents was performed under reduced pressure.

Comparison with authentic samples was performed by mixture m.p., t.l.c., and i.r. and p.m.r. spectroscopy.

Methyl 3,4-O-ethylidene-β-L-arabinopyranosides (**3** *and* **4**). — The glycoside **1** (2.2 g) was stirred overnight with paraldehyde (20 ml) containing toluene-*p*-sulphonic acid (150 mg) and Drierite (2 g). The solution was neutralised with solid sodium carbonate and filtered, and the product was isolated using chloroform. The acetal **3** (1.4 g, 55%), m.p. 73–75°, crystallised from light petroleum; lit.[6] m.p. 76°. For p.m.r. data, see Table I.

The mother liquors were chromatographed on alumina (15 g). Benzene–ether (9:1) eluted first 1,2:5,6 di-*O*-ethylidene-β-L-arabinopyranose (50 mg), followed by the acetal **4** (260 mg, 10%), $[\alpha]_D$ +182° (*c* 0.48, chloroform). For p.m.r. data, see Table I. Further elution yielded a mixture of **3** and **4** (150 mg).

Equilibration of acetals **3** *and* **4**. — (*a*) The acetal **3** (20 mg) was dissolved in dry chloroform (1 ml) containing toluene-*p*-sulphonic acid (20 mg). After 18 h, t.l.c. (ethyl acetate) revealed that **3** and **4** were present in the ratio ~8:1.

The reaction was repeated in an n.m.r. tube using **3** (50 mg) in *p*-dioxane (0.5 ml) containing toluene-*p*-sulphonic acid (20 mg). After 1 day at room temperature, the ratio of **3**:**4** was ~8:1 as shown by the intensity of the signals at δ 1.45 and 1.35.

(*b*) The acetal **4** (100 mg) was dissolved in dry chloroform (1 ml) containing toluene-*p*-sulphonic acid (25 mg). After 1 h, the solution was neutralised with solid sodium carbonate. Isolation yielded the acetal **3** (70 mg, 70%), m.p. 73°, mixture m.p. 72–73°.

Methyl 3,4-O-ethylidene-2-O-methyl-β-L-arabinopyranoside (**11**). — (*a*) The acetal **3** (1.5 g) in methyl iodide (25 ml) containing silver oxide (1 g) was heated under reflux for 6 h. Isolation using chloroform, with crystallisation and recrystallisation of the product from light petroleum, yielded **11** (1.21 g, 75%), m.p. 47°, $[\alpha]_D$ +210° (*c* 0.69, chloroform). For p.m.r. data, see Table I.

Anal. Calc. for $C_9H_{16}O_5$: C, 52.95; H, 7.8. Found: C, 53.35; H, 7.9%.

(*b*) The glycoside $\mathbf{2}^{50}$ (100 mg) was stirred overnight with paraldehyde (5 ml), toluene-*p*-sulphonic acid (25 mg), and anhydrous copper sulphate (100 mg). The solution was neutralised (Na_2CO_3) and the product isolated using chloroform. Crystallisation and recrystallisation from light petroleum yielded **11** (92 mg, 80%), m.p. 47°, $[\alpha]_D$ +212° (*c* 0.9, chloroform). None of the isomeric acetal could be detected by t.l.c. or n.m.r.

Ethylidenation of methyl α-D-lyxopyranoside and methyl α-D-arabinopyranoside. — The glycosides were ethylidenated by treatment overnight with paraldehyde containing toluene-*p*-sulphonic acid and Drierite as described for the ethylidenation of **1**. Isolation using chloroform gave syrups in yields of 91% and 74%, respectively. T.l.c. (ethyl acetate) of each crude product revealed the presence of two isomeric acetals, the major component having the lower R_F value. The p.m.r. spectra of the crude products are described in Table I.

2-Methyl-cis-4,5-tetramethylene-1,3-dioxolane[26,51] (**17**). — Cyclohexane-*cis*-

1,2-diol (100 mg) was stirred overnight with paraldehyde (200 mg) in benzene (1 ml) containing toluene-*p*-sulphonic acid (100 mg) and Drierite (200 mg). Isolation using chloroform yielded **17** as a syrup (115 mg, 94%) which could not be resolved on t.l.c. The p.m.r. spectrum of the crude product is described in Table I.

Treatment of epoxide **20** *with boron trifluoride etherate followed by lithium borohydride.* — The acetoxyepoxide[4] **20** (290 mg) in dry benzene (5 ml) was treated with boron trifluoride etherate (0.6 ml). The gummy precipitate, which formed immediately, was washed by decantation with benzene (10 ml), and lithium borohydride (100 mg) in dry ether (20 ml) was added. After 18 h, water (10 ml) was added and the product isolated with chloroform to yield a syrup (120 mg). T.l.c. (ethyl acetate) revealed the presence of the acetal **3** and the absence of the acetal **4**. The syrup was chromatographed on alumina (5 g). Benzene-ether (3:1) eluted the acetal **3** (107 mg, 37%), m.p. 70–73°, mixture m.p. 71–72°.

Reaction of acetoxyepoxide **20** *with diborane.* — A solution of the epoxide **20** (400 mg) in ether (200 ml) saturated with diborane was kept overnight, water (20 ml) was then added, and the ether layer was separated after the evolution of gases had ceased. The water layer was extracted with chloroform (2 × 50 ml), and the combined ether and chloroform extracts were evaporated to a syrup (305 mg). T.l.c. (ethyl acetate) revealed the presence of **3** and **19**, and the mixture was chromatographed on alumina (20 g). Ether–methanol (19:1) eluted the acetal **3** (180 mg, 45%), m.p. 70–72° (from light petroleum). Ether–methanol (9:1) then eluted the epoxide **19**[4] (80 mg, 26%), m.p. 66–68°, mixture m.p. 65–67°.

Preparations of orthoesters. — (*a*) *Methyl 3,4-O-methoxyethylidene-β-*L*-arabinopyranoside* (**5** *and* **6**). A mixture of glycoside **1** (250 mg), dry benzene (2 ml), toluene-*p*-sulphonic acid (50 mg), and trimethyl orthoacetate (350 mg) was stirred overnight at room temperature. The acid was neutralised (solid Na_2CO_3) and the product isolated using chloroform. The resulting chromatographically homogeneous syrup (310 mg, 92%) was distilled at 100°/10^{-3} mmHg to give a mixture of **5** and **6**, $[\alpha]_D$ +106° (*c* 1.23, chloroform). The p.m.r. data are shown in Table I; sublimation did not change the p.m.r. spectrum.

Anal. Calc. for $C_9H_{16}O_6$: C, 49.1; H, 7.3. Found: C, 48.7; H, 7.45.

(*b*) *Methyl 3,4-O-ethoxyethylidene-β-*L*-arabinopyranoside* (**7** *and* **8**). A mixture of glycoside **1** (500 mg), dry benzene (5 ml), triethyl orthoacetate (750 mg), and toluene-*p*-sulphonic acid (50 mg) was stirred overnight at room temperature. Isolation of the product as in (*a*) gave a syrup (850 mg) which was chromatographed on alumina (15 g) with benzene–ether (1:1) to give the orthoesters **7** and **8** as a syrup. After distillation *in vacuo* (120°/10^{-2} mm), the product (490 mg, 68%) had $[\alpha]_D$ +100.3° (*c* 2.86, pyridine). The p.m.r. data are shown in Table I; chromatography and distillation did not significantly alter the p.m.r. spectra.

Anal. Calc. for $C_{10}H_{18}O_6$: C, 51.3; H, 7.7. Found: C, 51.2; H, 7.7.

*Methyl 2-O-methyl-3,4-O-methoxyethylidene-β-*L*-arabinopyranoside* (**9** *and* **10**). The ether **2**[50] (0.5 g) was stirred for 3 h with trimethyl orthoacetate (0.5 ml) containing toluene-*p*-sulphonic acid. Isolation as described in (*a*) yielded a syrup, which

was distilled *in vacuo* (120°/10^{-3} mmHg) to give **9** and **10** (0.51 g, 77%), $[\alpha]_D$ +101.0° (*c* 1.32, chloroform). For p.m.r. data, see Table I; distillation did not alter the p.m.r. spectrum.

Anal. Calc. for $C_{10}H_{18}O_6$: C, 51.3; H, 7.7. Found: C, 50.9; H, 7.7.

(*d*) *Methyl 2-O-acetyl-3,4-O-methoxyethylidene-β-L-arabinopyranoside* (**12** *and* **13**). Methyl 2-*O*-acetyl-β-L-arabinopyranoside[4] (500 mg) was stirred with trimethyl orthoacetate (0.5 ml) in benzene (5 ml) containing toluene-*p*-sulphonic acid (100 mg) for 4 h. Isolation as described in (*a*) yielded a syrupy product, which was distilled *in vacuo* to give the orthoesters **12** and **13** as a syrup (580 mg, 91%), $[\alpha]_D$ +80.3° (*c* 0.69, chloroform). For p.m.r. data, see Table I; distillation did not change the p.m.r. spectrum.

Anal. Calc. for $C_{11}H_{18}O_7$: C, 50.4; H, 6.9. Found: C, 50.3; H, 6.9.

(*e*) *Methyl 4-O-acetyl-2,3-O-methoxyethylidene-α-D-lyxopyranoside* (**27**). Methyl 4-*O*-acetyl-α-D-lyxopyranoside[5,2] (45 mg) was stirred for 24 h with benzene (1 ml) containing trimethyl orthoacetate (50 mg) and toluene-*p*-sulphonic acid (5 mg). Isolation as described in (*a*) yielded the syrupy orthoesters which were distilled *in vacuo* (120°/10^{-2} mmHg) to yield **27** (48 mg, 84%), $[\alpha]_D$ +18.3° (*c* 2.84, chloroform).

Anal. Calc. for $C_{11}H_{18}O_7$: C, 50.4; H, 6.9. Found: C, 50.1; H, 7.0.

(*f*) *Methyl 2-O-acetyl-3,4-O-methoxyethylidene-α-D-arabinopyranoside* (**30**). The crude ethylidene derivative of methyl α-D-arabinopyranoside (100 mg) previously described was treated overnight with acetic anhydride (1 ml) in dry pyridine (5 ml). Isolation using chloroform yielded a crude product (100 mg), which was heated at 100° for 30 min with 80% acetic acid (5 ml). Evaporation then yielded a syrup which crystallised spontaneously. Recrystallisation from ethyl acetate yielded methyl 2-*O*-acetyl-α-D-arabinopyranoside (72 mg, 68%), m.p. 89–91°, $[\alpha]_D$ −12.0° (*c* 2.0, chloroform).

Anal. Calc. for $C_8H_{14}O_6$: C, 46.6; H, 6.8. Found: C, 47.0; H, 6.6.

Methyl 2-*O*-acetyl-α-D-arabinopyranoside (50 mg) in dry benzene (3 ml) was stirred overnight with trimethyl orthoacetate (50 mg) and toluene-*p*-sulphonic acid (10 mg). Isolation as described in (*a*) yielded a syrup which was distilled (120°/10^{-2} mmHg) to give **30** (53 mg, 83%), $[\alpha]_D$ −10.1° (*c* 2.0, chloroform).

Anal. Calc. for $C_{11}H_{18}O_7$: C, 50.4; H, 6.9. Found: C, 50.3; H, 7.0.

(*g*) *Methyl 2,3-O-methoxyethylidene-α-D-lyxopyranoside* (**15**). (*i*) Methyl α-D-lyxopyranoside (175 mg) was stirred with trimethyl orthoacetate (0.2 ml) in benzene (1 ml) containing toluene-*p*-sulphonic acid (20 mg) for 4 h. After neutralisation (solid Na_2CO_3), the product was isolated using chloroform to give the orthoester **15** as a syrup (242 mg, 103%) which was purified by distillation (100°/10^{-3} mmHg); $[\alpha]_D$ +29.0° (*c* 1.51, chloroform). The p.m.r. spectrum (CCl_4) indicated that the ratio of *exo*-OCH_3:*endo*-OCH_3 was ~4:1.

Anal. Calc. for $C_9H_{16}O_6$: C, 49.1; H, 7.3. Found: C, 49.1; H, 7.4.

(*ii*) The anhydroarabinoside[4] **23** (200 mg) in carbon tetrachloride–dichloromethane (5:1, 25 ml) was treated with antimony pentachloride (0.2 ml) in dichloro-

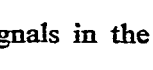
methane (5 ml). A gummy precipitate formed within a few seconds and was allowed to settle. The precipitate was washed by decantation with carbon tetrachloride and finally dissolved in methanolic sodium methoxide (25 ml, from 0.5 g of Na). The solution was evaporated, water added, and the product isolated using chloroform. The syrupy product (190 mg, 81%) had a p.m.r. spectrum (CCl_4) very similar to that of the product in (*i*) and showed a ratio of *exo*-OCH_3:*endo*-OCH_3 of ~4.5:1. After further purification (prep. t.l.c.; alumina, ether), it had $[\alpha]_D$ +30.2° (chloroform) and an *exo*-OCH_3:*endo*-OCH_3 ratio of 5:1.

Reaction of orthoesters **7** *and* **8** *with boron trifluoride etherate followed by lithium borohydride.* — A mixture of the orthoesters **7** and **8** (0.5 g) in dry benzene (10 ml) was treated with boron trifluoride etherate (0.5 ml). A gummy precipitate formed immediately, and was washed by decantation with benzene (10 ml). Lithium borohydride (200 mg) in dry ether (50 ml) was then added and the mixture left overnight at room temperature. Water (10 ml) was added, and the ether layer separated. Isolation yielded a syrup (280 mg) which crystallised from light petroleum, yielding the acetal **3** (180 mg, 44%), m.p. 70–73°, P.m.r. spectroscopy of the mother liquors in CCl_4 revealed the presence of the acetal **4** and indicated that the ratio of **3**:**4** in the crude product was ~9:1.

Reaction of orthoesters **9** *and* **10** *with boron trifluoride etherate and lithium borohydride.* — A mixture of **9** and **10** (100 mg) in dry benzene (10 ml) was treated with boron trifluoride etherate (0.2 ml). The gummy salt, which precipitated immediately, was washed by decantation and then treated overnight with a solution of lithium borohydride (100 mg) in dry ether (20 ml). Isolation as described above yielded a syrup (60 mg), which was chromatographed on alumina (2 g). Benzene–ether (9:1) eluted the acetal **11**; crystallised from light petroleum, **11** (42 mg, 48%) had m.p. 45–46°, mixture m.p. 44–46°. P.m.r. spectroscopy of the mother liquors in CCl_4 did not reveal any of the *exo*-Me isomer.

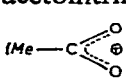
Reaction of a mixture of orthoesters **7** *and* **8** *with diborane.* — A mixture of **7** and **8** (0.5 g) was dissolved in dry ether (30 ml) which had been saturated with diborane. After 6 h, water (10 ml) was added and the product isolated from the ether layer as a syrup (400 mg) which partially crystallised. The crude product was chromatographed on alumina (15 g). Benzene–ether (7:3) eluted the acetal **4** (10 mg, 2%), identified by t.l.c., and benzene–ether (1:1) eluted the acetal **3** (270 mg, 66%), m.p. 74–75°, mixture m.p. 71–73°.

Acetoxonium-ion migrations. — (*a*) **28** *and* **29**. (*i*) The orthoester mixture **27** (0.9g) in dry dichloromethane (10 ml) was treated with antimony pentachloride (0.8 ml) in dichloromethane (5 ml). The pale-yellow precipitate which formed immediately was washed by decantation with dichloromethane (3 × 20 ml). The p.m.r. spectrum in dry acetonitrile included signals at δ 2.38 (*Me*CO), 2.45 (Me—C(=O)—O⊕), 2.58 (*Me*CO), and 2.64 (Me—C(=O)—O⊕); the signals at δ 2.38 and 2.45 and those at δ 2.58 and 2.64 were

in the ratio ~1:2. There were no signals in the region δ 1.5  or 3.5 (OMe). Evaporation of the acetonitrile *in vacuo* yielded a solid (1 g) which was treated with water (20 ml) containing potassium acetate. After 3 h, the solution was extracted with chloroform (3 × 100 ml). Evaporation of the chloroform extracts yielded a syrup (450 mg) which contained (t.l.c., ethyl acetate) two diacetates, the diacetate of lower R_F value constituting 80–90% of the mixture. A portion of the syrup (300 mg) was deacetylated with sodium methoxide in methanol; after deionisation [Dowex 50 (NH_4^+) resin], evaporation yielded methyl α-D-arabinopyranoside (120 mg, 32%), m.p. 130–131° (from ethyl acetate–methanol). Paper chromatography of the mother liquors showed the presence of approximately equal quantities of methyl α-D-arabinopyranoside and -lyxopyranoside.

(*ii*) The orthoester mixture **30** (160 mg) in dry carbon tetrachloride (5 ml) was treated with antimony pentachloride (0.1 ml) in carbon tetrachloride (2 ml). The precipitate, which formed immediately, was washed by decantation with carbon tetrachloride (2 × 20 ml), and then treated with a solution of potassium acetate (1 g) in water (10 ml) overnight. Isolation using chloroform yielded a syrup (135 mg), which contained (t.l.c., ethyl acetate) two diacetates, the diacetate of lower R_F value constituting ~90% of the mixture. The mixture was deacetylated with sodium methoxide in methanol, deionised [Dowex 50 (NH_4^+) resin], and evaporated to a syrup (91 mg) which yielded crystalline methyl α-D-arabinopyranoside (58 mg, 58%), m.p. 130° (from ethyl acetate–methanol), mixture m.p. 131–132°. The mother liquors were evaporated to a syrup (20 mg), which was resolved by preparative t.l.c. in ethyl acetate–methanol (95:5), yielding methyl α-D-lyxopyranoside (11 mg, 11%), m.p. 102–103°, mixture m.p. 103–104°.

(*b*) **32** *and* **33**. A mixture of orthoesters **12** and **13** (1 g) in dry carbon tetrachloride (20 ml) was treated with antimony pentachloride (2 g) in carbon tetrachloride (10 ml). The pale-yellow precipitate was washed by decantation with dry carbon tetrachloride (2 × 25 ml), yielding the salts **32** and **33** (2.05 g, 95%). The salts (2.0 g) were treated with potassium acetate (5 g) in water (25 ml). After 3 h, the products were isolated using chloroform (3 × 50 ml), yielding a syrup (730 mg) that contained (t.l.c., ethyl acetate) two diacetates, the major component having the lower R_F value. The product was deacetylated with sodium methoxide in methanol, and the deionised [Dowex 50 (NH_4^+) resin] solution was evaporated to yield a syrup (500 mg) that crystallised from methanol, yielding the arabinoside **1** (402 mg, 66% overall), m.p. 167–169°. Paper chromatography of the mother liquors revealed **1** and methyl β-L-lyxopyranoside in the ratio 2:1.

Reaction of the acetoxonium salt **21** *tetrafluoroborate with potassium acetate in dry acetic acid.* — A mixture of the orthoesters **5** and **6** (1 g) in dry benzene (20 ml) was treated with boron trifluoride etherate (1.5 ml). The gummy precipitate, which formed immediately, was washed by decantation with ether, and then dissolved in dry acetonitrile (10 ml). The p.m.r. spectrum of this solution showed a singlet at δ 2.4  . A portion (5 ml) of this solution was evaporated *in vacuo* and the residue

was dissolved in dry acetic acid (10 ml) containing anhydrous potassium acetate (1 g). The solution was heated under reflux for 6 h. T.l.c. (ethyl acetate) then revealed that the product was largely diacetate with a small proportion of monoacetate. The solution was evaporated *in vacuo*, water (40 ml) added, and the solution extracted with ethyl acetate (3 × 50 ml). Evaporation of the extracts yielded a syrup which was deacetylated with sodium methoxide in methanol, and the solution was deionised [Dowex 50 (NH_4^+) resin] and evaporated. Paper chromatography revealed methyl β-L-arabinopyranoside (**1**) as the major product, together with methyl β-L-lyxopyranoside and α-D-xylopyranoside in approximately equal amounts.

Reaction of orthoesters **7** *and* **8** *with dry acetic acid.* — A mixture of (**7**) and (**8**) (20 mg) in dry acetic acid (2 ml) was heated at 100° for 6 h. T.l.c. (ethyl acetate) then revealed the absence of (**7**) and (**8**), and the presence of two monoacetates and a diacetate. The solution was evaporated *in vacuo*, yielding a syrup, which was deacetylated by treatment with sodium methoxide in methanol. The solution was deionised [Dowex 50 (NH_4^+) resin], and evaporated to yield a syrup, which was examined by paper chromatography. Only the arabinoside **1** could be detected; no lyxopyranosides or xylopyranosides were present. The syrup crystallised on standing, yielding the arabinoside **1** (9 mg, 64%), m.p. 170°, which was identical with an authentic sample.

Reaction of orthoesters **9** *and* **10** *with dry acetic acid–acetic anhydride.* — A mixture of the orthoesters **9** and **10** (100 mg) was dissolved in dry acetic acid–acetic anhydride (1:1, 0.5 ml) in an n.m.r. tube. After 30 min at 20°, there was a slight decrease in the intensity of the signals at δ 1.45 (*endo*-Me) and 3.1 (*exo*-OMe). After 24 h at 20° followed by 30 min at 60°, the signals at δ 1.45 and 3.1 had almost disappeared and there was a strong signal at δ 3.56 (MeCOO*Me*). Evaporation of the solution yielded a syrupy diacetate, which was catalytically deacetylated with sodium methoxide in methanol to yield the ether **2**. Crystallisation of **2** from ether gave the hydrate[50] (45 mg, 54%), m.p. 45°, mixture m.p. 44–46°. Examination of the mother liquors by t.l.c. revealed only the ether **2**.

Reaction of orthoesters **12** *and* **13** *with acetic acid–acetic anhydride.* — A mixture of (**12**) and (**13**) (200 mg) in acetic acid–acetic anhydride (1:2) (2 ml) was heated at 110° for 6 h. T.l.c. indicated that the product was a single triacetate. Water (5 ml) was added and the solution evaporated *in vacuo* to a syrup (250 mg), which was deacetylated with sodium methoxide in methanol. Deionisation [Dowex 50 (NH_4^+) resin], followed by evaporation of the solution, yielded a crystalline solid (115 mg). Recrystallisation from methanol yielded the arabinoside **1** (90 mg, 72%), m.p. 169°, mixture m.p. 169–170°. Paper chromatography of the mother liquors revealed only **1**; xylopyranoside and lyxopyranoside were absent.

Aqueous, acidic hydrolysis of orthoesters **7** *and* **8**. — A mixture of **7** and **8** (100 mg) was treated with 5% aqueous sulphuric acid (5 ml) for 30 min at room temperature. The solution was neutralised ($BaCO_3$), filtered, and evaporated to yield a syrup (95 mg). T.l.c. (ethyl acetate) indicated the presence of two monoacetates, that of lower R_F value constituting ~80% of the mixture. The syrup was treated with toluene-*p*-sulphonyl chloride (3 mol. equiv.) in pyridine (5 ml) at room temperature

for 2 days. Isolation using chloroform yielded the disulphonate[4] **36** (120 mg, 62%), m.p. 162°, which was identical with an authentic sample.

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