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SYNTHESIS OF TWO ENANTIOMERIC TETRASUBSTITUTED CYCLOHEXANONES FROM 6-DEOXYHEX-5-ENOPYRANOSIDE DERIVATIVES

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ABSTRACT

The conversion of various 6-deoxyhex-5-enopyranoside derivatives in the presence of a catalytic amount of mercury(II) sulfate into chiral cyclohexanones has been studied. Under the experimental conditions used, the stereochemistry at position 5 of the tetrasubstituted cyclohexanones appears to depend on the conformation of the starting carbohydrate derivatives which was indicated by the ^{13}C-n.m.r. data. Reaction of methyl 4-*O*-benzoyl-2,3-di-*O*-methyl-β-L-*arabino*- and -α-D-*arabino*-hex-5-enopyranoside furnished the enantiomeric 2-benzoyloxy-5-hydroxy-3,4-dimethoxycyclohexanones **19** and **21**, respectively.

INTRODUCTION

In 1979, Ferrier reported a reaction for converting a 6-deoxyhex-5-enopyranoside **1** into a chiral cyclohexanone derivative **3** in high yield[1]. The value of this reaction in the aminoglycoside antibiotic field was immediately recognised[2–6] since it provided a route for the modification of the cyclitol unit of these compounds. The scope of the Ferrier reaction has not been thoroughly explored and it has been used in only a few synthetic schemes[2–6].

In studies of the synthesis of anthracycline antibiotics modified in the carbohydrate moiety, we were interested in the preparation of a carbocyclic analogue of daunosamine and have investigated the conversion of various 6-deoxyhex-5-enopyranosides into cyclohexanone derivatives.

RESULTS AND DISCUSSION

Under the experimental conditions used by Ferrier, although methyl 3,4-di-*O*-benzoyl-6-deoxy-2-*O*-tosyl-α-D-*xylo*-hex-5-enopyranoside (**1**) afforded the cyclohexanone **3** in a yield close to that reported, methyl 2,4-di-*O*-benzoyl-6-deoxy-3-*O*-tosyl-α-D-*xylo*-hex-5-enopyranoside (**2**) did not give the expected 2L-2,4,5/3-2,4-dibenzoyloxy-5-hydroxy-3-toluene-*p*-sulphonyloxycyclohexanone (**4**), and only 27% of the elimination product 4L-4,5/0-2,4-dibenzoyloxy-5-hydroxycyclohex-2-enone (**5**) could be isolated. However, when the Ferrier reaction was carried out in

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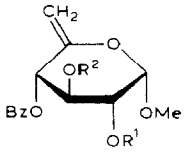
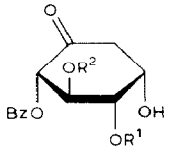
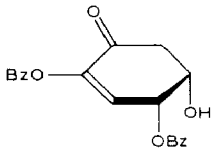
the presence of only catalytic amounts of mercury(II) sulfate[7] instead of 1.1 equiv. of mercury(II) chloride as originally advocated, **2** gave 72% of **4**. Therefore, in all subsequent Ferrier reactions, catalytic amounts of mercury(II) sulfate were used.



1 R^1 = Ts, R^2 = Bz
2 R^1 = Bz, R^2 = Ts



3 R^1 = Ts, R^2 = Bz
4 R^1 = Bz, R^2 = Ts



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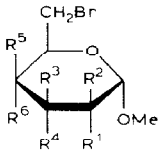
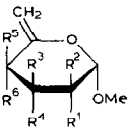


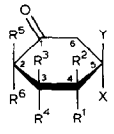
6 R^2 = R^4 = R^6 = H, R^1 = R^3 = R^5 = OBz
7 R^2 = R^4 = R^6 = H, R^1 = R^3 = OMe, R^5 = OBz
8 R^1 = R^4 = R^5 = H, R^2 = R^3 = R^6 = OBz
9 R^1 = R^3 = R^5 = H, R^2 = R^4 = OAc, R^6 = OBz
10 R^1 = R^3 = R^5 = H, R^2 = R^4 = OMe, R^6 = OBz
11 R^2 = R^3 = R^5 = H, R^1 = R^4 = R^6 = OBz

From another investigation, methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-hexopyranosides in the *galacto, manno,* and *allo* series, methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-galactopyranoside, methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-altropyranoside, and methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-altropyranoside[8] were available, and each was converted[9], using *N*-bromosuccinimide–carbon tetrachloride, into the corresponding 6-bromo-6-deoxy derivatives (**6**–**11**). Reaction with silver fluoride in dry pyridine[10] then yielded the respective 6-deoxyhex-5-enopyranosides **12**–**17**. Storage of solutions of **12** (*galacto*), **13** (*galacto*), **14** (*manno*), and **16** (*altro*) in 1,4-dioxane containing a catalytic amount of mercury(II) sulfate at 60–80° gave **18**–**21**, respectively, in excellent yields. However, under similar conditions, **17** (*allo*) afforded 80% of the cyclohexanone derivative **22**. Surprisingly, the configuration at position 5 of **21** and **22** was the opposite of that of the cyclohexanones **18**–**20**. Evidence for the configuration at position 5 of the cyclitol derivatives was obtained from 200- or 250-MHz ^{1}H-n.m.r. studies; large $J_{5,6a}$ values were observed for **21** and **22**.

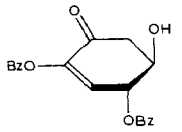
The cyclohexanone derivatives **19** and **21** are enantiomers, as indicated by identical ^{1}H-n.m.r. spectra and $[\alpha]_{546}^{20}$ values of +7.0° and −6.8° (*c* 0.7,



12 $R^2 = R^4 = R^6 = H, R^1 = R^3 = R^5 = OBz$
13 $R^2 = R^4 = R^6 = H, R^1 = R^3 = OMe, R^5 = OBz$
14 $R^1 = R^4 = R^5 = H, R^2 = R^3 = R^6 = OBz$
15 $R^1 = R^3 = R^5 = H, R^2 = R^4 = OAc, R = OBz$
16 $R^1 = R^3 = R^5 = H, R^2 = R^4 = OMe, R^6 = OBz$
17 $R^2 = R^3 = R^5 = H, R^1 = R^4 = R^6 = OBz$



18 $R^2 = R^4 = R^6 = Y = H, R^1 = R^3 = R^5 = OBz, X = OH$
19 $R^2 = R^4 = R^6 = Y = H, R^1 = R^3 = OMe, R^5 = OBz, X = OH$
20 $R^1 = R^4 = R^5 = Y = H, R^2 = R^3 = R^6 = OBz, X = OH$
21 $R^1 = R^3 = R^5 = X = H, R^2 = R^4 = OMe, R^6 = OBz, Y = OH$



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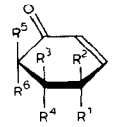

23 $R^2 = R^4 = R^6 = H, R^1 = R^3 = OMe, R^5 = OBz$
24 $R^1 = R^3 = R^5 = H, R^2 = R^4 = OMe, R^6 = OBz$

chloroform). If the 6-deoxyhex-5-enopyranosides **13** and **16** were left for 24 h in the reaction medium in the presence of mercury(II) sulfate, the only compounds subsequently isolated were the enantiomeric cyclohexanones **23** and **24**, respectively. This finding led to the conclusion that the stereochemistry at position 5 of the cyclohexanone derivatives, which was not obviously related to the anomeric configuration of the 6-deoxyhex-5-enopyranosides, might be related to their conformation and this was studied by ^1H- and by ^{13}C-n.m.r. spectroscopy. Compounds **1** (*gluco*), **12** (*galacto*), and **14** (*manno*) had large $J_{2,3}$, $J_{2,3}$, and $J_{3,4}$ values indicative of the $^4C_1$ conformation. Compound **15** (*altro*) also had a large $J_{2,3}$ value and an intermediate value (5.5 Hz) for $J_{1,2}$ reflecting a $^1C_4$ conformation. The ^1H-n.m.r. spectrum of **17** did not afford any proof for either conformation because of the all-*cis* substitution pattern. Therefore, the ^{13}C-n.m.r. spectra of the above compounds were recorded with both the broad-band and the gated decoupling techniques (see Table I). Although, the signals for C-2, C-3, and C-4 could not be differentiated without the application of two-dimensional ^{13}C–^1H shift-correlated experiments[11], the data in Table I furnished evidence for the conformation of the unsaturated carbohydrates. In **1**, **12**, and **14** where MeO-1 is axial, both MeO-1 and C-1 are shielded relative to the corresponding signals in **15** where MeO-1 is equatorial. Furthermore, C-6 is deshielded in **12** and **15**, in which the substituent at C-4 is axial. The anomalous chemical-shift data of **17** (*allo*) is not surprising since, whatever its conformation, the steric strain resulting from a 1,3-diaxial interaction made comparison of its spectra with those of the other unsaturated carbohydrates meaningless. However, the gated decoupling experiments furnished unambiguous information on the conformation of all compounds in Table I. In agreement with previous literature data, if the anomeric carbon atom carries an axial substituent,

TABLE I

^{13}C-N.M.R. DATA ($CDCl_3$, INTERNAL Me_4Si) FOR THE 6-DEOXYHEX-5-ENOPYRANOSIDES

Atom	α-D-xylo (**1**)	β-L-arabino (**12**)	α-D-lyxo (**14**)	α-D-arabino (**15**)	α-D-ribo (**17**)
C-1	98.6	98.8	99.7	102.4	99.4
C-2	76.4	67.7[a]	70.5[a]	69.6[a]	68.8[a]
C-3	69.9[a]	68.9[a]	69.7[a]	69.4[a]	68.2[a]
C-4	69.4[a]	70.7[a]	68.1[a]	68.3[a]	67.6[a]
C-5	149.4	149.7	151.4	150.4	149.5
C-6	98.4	104.3	97.5	101.4	99.4
OMe	56.0	55.7	55.8	56.6	56.6
$J_{C\text{-}1,H\text{-}1}$	176.0	175.1	174.6	168.0	170.2

[a]Assignments may be interchanged

the $^1J_{C,H}$ value at C-1 is significantly higher than in compounds having equatorial anomeric substituents[11]. The $^1C_4$ conformation of **15** and **17** is reflected by the $^1J_{C,H}$ values.

Thus, the stereochemistry at position 5 of the cyclohexanone derivatives described above appears to depend on the conformation of the 6-deoxyhex-5-enopyranoside precursors. Thus, **15–17** (*altro* and *allo* series), which have the $^1C_4$ conformation, afford cyclohexanones with HO-5 directed upward, whereas, in the products derived from the 6-deoxyhex-5-enopyranosides, which adopt a $^4C_1$ conformation, HO-5 is directed downward.

EXPERIMENTAL

General. — Melting points were determined with a Büchi apparatus and are uncorrected. Optical rotations (1-dm tube) were measured with a Perkin–Elmer Model 141 MC polarimeter. ^{1}H-N.m.r. spectra (internal Me_4Si) at 80, 200, and 400 MHz were recorded with Bruker WM-80, WM-200, and WM-400 spectrometers, and at 250 MHz with a Cameca spectrometer. ^{13}C-N.m.r. spectra at 50.31 and 100.62 MHz were recorded with Bruker WM-200 and WM-400 spectrometers. Microanalysis were performed by the Service Central de Microanalyse du C.N.R.S. Kieselgel Pf_{254} (Type 60, Merck) activated at 120° was used for t.l.c.

Methyl 6-bromo-6-deoxy-α-D-hexopyranosides. — A suspension of methyl 4,6-*O*-benzylidene-α-D-hexopyranoside (1 mmol), *N*-bromosuccinimide (1.23 mmol), and barium carbonate (1.5 mmol) in dry carbon tetrachloride (8 mL) was boiled under reflux for 2 h, filtered, washed with aqueous 10% sodium hydrogensulfite (3 × 2 mL) and water (3 × 3 mL), dried, and concentrated. The residue was purified by column chromatography, t.l.c., or crystallisation, to afford the 6-bromo-6-deoxy compounds.

Methyl 6-deoxyhex-5-enopyranosides. — To a solution of methyl 6-bromo-6-deoxy-α-D-hexopyranoside (1 mmol) in dry pyridine (7 mL) was added silver

fluoride (1.5 mmol). The mixture was stirred in the dark for 24–48 h at room temperature, diluted with ether (40 mL), filtered through a column of silica gel, and concentrated to give the unsaturated compound.

*Tetrasubstituted cyclohexanones**. — (*a*) A solution of 6-deoxyhex-5-enopyranoside (1 mmol) and mercury(II) chloride (1 mmol) in aqueous acetone (2:3, 7 mL) was boiled under reflux for 2–4 h. The reaction was monitored by t.l.c. On cooling of the solutions, the cyclohexanone derivatives crystallised.

(*b*) A solution of 6-deoxyhex-5-enopyranoside (1 mmol) in 1,4-dioxane (6 mL) containing an aqueous solution (3 mL) of sulfuric acid (5mM) and mercury(II) sulfate (0.02 mmol) was stirred under nitrogen at 60–80° for 15–60 min. The reaction was monitored by t.l.c. After the addition of water (9 mL) and cooling, some of the cyclohexanone derivatives crystallised. Otherwise, ether extraction was applied.

*Methyl 2,4-di-*O*-benzoyl-6-deoxy-3-*O*-tosyl-α-*D*-xylo-hex-5-enopyranoside* (**2**). — Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-tosyl-α-D-glucopyranoside[8] was converted into methyl 2,4-di-*O*-benzoyl-6-bromo-6-deoxy-3-*O*-tosyl-α-D-glucopyranoside (1.075 g, 75%), and thence into **2** (0.77 g, 82%), m.p. 80–82° (from methanol), $[\alpha]_D^{20}$ +59° (*c* 0.34, chloroform). Mass spectrum: *m/z* 538 (M^+). ^{1}H-N.m.r. data (C_6D_6, 200 MHz): δ 8.27–6.37 (m, 14 H, aromatic protons), 6.02 (m, 1 H, H-4), 5.85 (t, 1 H, $J_{2,3} = J_{3,4} = 10$ Hz, H-3), 5.35 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 10 Hz, H-2), 5.10 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.70 (bs, 1 H, H-6a), 4.58 (bs, 1 H, H-6b), 3.10 (s, 3 H, OMe), and 1.63 (s, 3 H, PhMe).

Anal. Calc. for $C_{28}H_{26}O_9S$: C, 62.45; H, 4.83; S, 5.95. Found: C, 62.16; H, 4.92; S, 5.92.

*2L-2,4,5/3-2,4-Dibenzoyloxy-5-hydroxy-3-toluene-*p*-sulphonyloxycyclohexanone* (**4**). — Prepared from **2** (0.10 g, 0.19 mmol) by method (*b*), **4** (0.07 g, 72%) had m.p. 112–114° (from carbon tetrachloride), $[\alpha]_D^{20}$ −22° (*c* 0.35, chloroform). Mass spectrum: *m/z* 524 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 250 MHz): δ 8.16–6.77 (m, 14 H, aromatic protons), 5.75–5.65 (m, 3 H, H-2,3,4), 4.59 (bs, 1 H, H-5), 2.87 (bs, 2 H, H-6*a*,6*e*), and 2.06 (s, 3 H, PhMe).

Anal. Calc. for $C_{27}H_{24}O_9S$: C, 61.83; H, 4.58; S, 6.10. Found: C, 61.62; H, 4.60; S, 6.01.

4L-4,5/0-2,4-Dibenzoyloxy-5-hydroxycyclohex-2-enone (**5**). — Prepared from **2** (0.25 g, 0.47 mmol) by method (*a*), **5** (44 mg, 27%) was a syrup, $[\alpha]_D^{20}$ −112° (*c* 0.11, chloroform). Mass spectrum: *m/z* 352 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 250 MHz): δ 8.08–7.44 (m, 10 H, 2 Ph), 6.67 (dd, 1 H, $J_{3,4}$ 4, $J_{3,5}$ 1.5 Hz, H-3), 6.08 (t, 1 H, $J_{3,4} = J_{4,5} = 4$ Hz, H-4), 4.67 (m, 1 H, H-5), 3.07 (dd, 1 H, $J_{5,6a}$ 7, J_{gem} 17 Hz, H-6*a*), and 2.91 (dd, 1 H, $J_{5,6e}$ 4, J_{gem} 17 Hz, H-6*e*).

Anal. Calc. for $C_{20}H_{16}O_6$: C, 68.18; H, 4.55. Found: C, 67.83; H, 4.78.

*Methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-α-*D*-lyxo-hex-5-enopyranoside* (**14**). —

*For nomenclature, see *Biochem. J.*, 153 (1976) 23–31.

Prepared from **8**[9] (2.3 g, 4.1 mmol), **14** (1.54 g, 78%) had m.p. 53–54° (from methanol), $[\alpha]_D^{20}$ −150° (*c* 0.85, chloroform). Mass spectrum: *m/z* 488 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 80 MHz): δ 8.09–7.10 (m, 15 H, 3 Ph), 6.34 (dt, 1 H, $J_{4,6a}$ = $J_{4,6b}$ = 2, $J_{3,4}$ 9 Hz, H-4), 5.88 (dd, 1 H, $J_{2,3}$ 3, $J_{3,4}$ 9 Hz, H-3), 5.75 (dd, 1 H, $J_{1,2}$ 2, $J_{2,3}$ 3 Hz, H-2), 5.01 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 4.86 (t, 1 H, $J_{4,6a}$ = J_{gem} = 2 Hz, H-6a), 4.73 (t, 1 H, $J_{4,6b}$ = J_{gem} = 2 Hz, H-6b), and 3.50 (s, 3 H, OMe).

Anal. Calc. for $C_{28}H_{24}O_8$: C, 68.85; H, 4.92 . Found: C, 68.46; H, 4.96.

2L-2,5/3,4-2,3,4-Tribenzoyloxy-5-hydroxycyclohexanone (**20**). — Prepared from **14** (0.3 g, 0.62 mmol) by method (*a*) or (*b*), **20** (0.25 g, 83%) had m.p. 138–140° (from methanol), $[\alpha]_D^{20}$ −169° (*c* 0.8, chloroform). Mass spectrum: *m/z* 474 (M^+). ^{1}H-N.m.r. data (C_5D_5N, 400 MHz): δ 8.35–7.15 (m, 15 H, 3 Ph), 6.90 (dd, 1 H, $J_{2,3}$ 11, $J_{3,4}$ 3.5 Hz, H-3), 6.78 (d, 1 H, $J_{2,3}$ 11 Hz, H-2), 6.62 (t, $J_{3,4}$ = $J_{4,5}$ = 3.5 Hz, H-4), 4.92 (m, 1 H, H-5), 3.56 (dd, 1 H, $J_{5,6e}$ 3, J_{gem} 15 Hz, H-6*e*), 3.53 (dd, 1 H, $J_{5,6a}$ 1.5, J_{gem} 15 Hz, H-6*a*), and 3.13 (d, 1 H, $J_{5,OH}$ 18 Hz, OH).

Anal. Calc. for $C_{27}H_{22}O_8$: C, 68.35; H, 4.64. Found: C, 68.00; H, 4.68.

*Methyl 2,3,4-tri-O-benzoyl-6-deoxy-β-*L-arabino-*hex-5-enopyranoside* (**12**). — Prepared from **6**[9] (0.22 g, 0.39 mmol), **12** (0.13 g, 68%) was a syrup, $[\alpha]_D^{20}$ −101° (*c* 0.18, chloroform). Mass spectrum: *m/z* 488 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 80 MHz): δ 8.00–7.24 (m, 15 H, 3 Ph), 6.10 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 5.83 (m, 2 H, H-2,3), 5.25 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.91 (bs, 1 H, H-6a), 4.88 (bs, 1 H, H-6b), and 3.45 (s, 3 H, OMe).

Anal. Calc. for $C_{28}H_{24}O_8$: C, 68.85; H, 4.95 . Found: C, 68.70; H, 4.82.

2D-2,3/4,5-2,3,4-Tribenzoyloxy-5-hydroxycyclohexanone (**18**). — Prepared from **12** (0.05 g, 0.1 mmol), **18** (0.05 g, 99%) had m.p. 51–53°, $[\alpha]_D^{20}$ −41° (*c* 0.02, chloroform). Mass spectrum: *m/z* 474 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 250 MHz): δ 8.12–7.31 (m, 15 H, 3 Ph), 6.10 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 4 Hz, H-3), 6.01 (d, 1 H, $J_{2,3}$ 4 Hz, H-2), 5.93 (m, 1 H, H-4), 4.66 (m, 1 H, H-5), 3.12 (dd, 1 H, $J_{5,6}$ 11, J_{gem} 14 Hz, H-6*a*), and 3.04 (dd, 1 H, $J_{5,6e}$ 5.5, J_{gem} 14 Hz, H-6*e*).

Anal. Calc. for $C_{27}H_{22}O_8$: C, 68.35; H, 4.64. Found: C, 68.07; H, 4.63.

*Methyl 2,3,4-tri-O-benzoyl-6-bromo-6-deoxy-α-*D-*allopyranoside* (**11**). — Prepared from methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-allopyranoside[13] (0.57 g, 1.14 mmol), **11** (0.31 g, 48%) was a syrup, $[\alpha]_D^{20}$ +60° (*c* 0.1, chloroform). Mass spectrum: *m/z* 569 (M^+). ^{1}H-N.m.r. data (C_6D_6, 200 MHz): δ 8.16–7.33 (m, 15 H, 3 Ph), 6.18 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 3 Hz, H-3), 5.37 (dd, 1 H, $J_{1,2}$ 4, $J_{2,3}$ 3 Hz, H-2), 5.35 (dd, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 9.5 Hz, H-4), 5.30 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.67 (m, 1 H, H-5), 3.65–3.53 (m, 2 H, H-6,6′), and 3.63 (s, 3 H, OMe).

Anal. Calc. for $C_{28}H_{25}BrO_8$: C, 59.05; H, 4.39; Br, 14.06. Found: C, 59.11; H, 4.50; Br, 14.05.

*Methyl 2,3,4-tri-O-benzoyl-6-deoxy-α-*D-ribo-*hex-5-enopyranoside* (**17**). — Prepared from **11** (0.31 g, 0.54 mmol), **17** (0.23 g, 85%) was a syrup, $[\alpha]_D^{20}$ +127° (*c* 0.17, chloroform). Mass spectrum: *m/z* 488 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 200 MHz): δ 8.15–7.31 (m, 15 H, 3 Ph), 6.05 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 3.5 Hz, H-3), 5.93

(m, 1 H, H-4), 5.58 (t, 1 H, $J_{1,2} = J_{2,3}$ 3.5 Hz, H-2), 5.27 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.02 (s, 1 H, H-6a), 4.88 (s, 1 H, H-6b), and 3.62 (s, 3 H, OMe).

Anal. Calc. for $C_{28}H_{24}O_8$: C, 68.85; H, 4.92 . Found: C, 68.62; H, 4.87.

4L-4/5-2,4-Dibenzoyloxy-5-hydroxycyclohex-2-enone (**22**). — Prepared from **17** (0.6 g, 0.12 mmol) by method (*b*), **22** (0.036 g, 80%) was a syrup, $[\alpha]_D^{20}$ +88° (*c* 0.19, chloroform). Mass spectrum: *m/z* 366 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 200 MHz): δ 8.12–7.43 (m, 10 H, 2 Ph), 6.83 (d, 1 H, $J_{3,4}$ 3 Hz, H-3), 5.98 (dd, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 7 Hz, H-4), 4.53 (m, 1 H, H-5), 3.12 (dd, 1 H, $J_{5,6e}$ 5, J_{gem} 17 Hz, H-6*e*), and 2.82 (dd, 1 H, $J_{5,6a}$ 10.5, J_{gem} 17 Hz, H-6*a*).

Anal. Calc. for $C_{20}H_{16}O_6$: C, 68.18; H, 4.55 . Found: C, 68.01; H, 4.51.

*Methyl 2,3-di-O-acetyl-4-O-benzoyl-6-deoxy-α-*D-arabino-*hex-5-enopyranoside* (**15**). — Prepared from methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-altropyranside (274 mg, 0.75 mmol), **9** (233 mg, 70%) was converted (200 mg, 0.45 mmol) without purification into **15** (145 mg, 89%), which was a syrup, $[\alpha]_D^{20}$ −5° (*c* 0.1, chloroform). Mass spectrum: *m/z* 364 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 200 MHz): δ 8.17–7.48 (m, 5 H, Ph), 6.00 (d, 1 H, $J_{3,4}$ 4.5 Hz, H-4), 5.43 (dd, 1 H, $J_{1,2}$ 5.5, $J_{2,3}$ 9.5 Hz, H-2), 5.23 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 4.5 Hz, H-3), 4.97 (d, 1 H, J_{gem} 1.5 Hz, H-6a), 4.87 (d, 1 H, J_{gem} 1.5 Hz, H-6b), 4.68 (d, 1 H, $J_{1,2}$ 5.5 Hz, H-1), 3.60 (s, 3 H, OMe), 2.17 (s, 3 H, OAc), and 2.03 (s, 3 H, OAc).

Anal. Calc. for $C_{18}H_{20}O_8$: C, 59.34; H, 5.49. Found: C, 59.56; H, 5.38.

*Methyl 4-O-benzoyl-6-bromo-6-deoxy-2,3-di-O-methyl-α-*D-*altropyranoside* (**10**). — Prepared from methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-altropyranoside[8] (1.42 g, 4.58 mmol), **10** (1.02 g, 57%) was a syrup, $[\alpha]_D^{20}$ +75° (*c* 1.6, chloroform). Mass spectrum: *m/z* 389 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 250 MHz): δ 8.05–7.41 (m, 5 H, Ph), 5.28 (dd, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ 9 Hz, H-4), 4.76 (s, 1 H, H-1), 4.43 (m, 1 H, H-5), 3.88 (m, 2 H, H-2,3), and 3.64–3.45 (m, 11 H, H-6,6′ and 3 OMe).

Anal. Calc. for $C_{16}H_{21}BrO_6$: C, 49.36; H, 5.40; Br, 20.57. Found: C, 49.11; H, 5.38; Br, 20.73.

*Methyl 4-O-benzoyl-6-deoxy-2,3-di-O-methyl-α-*D-arabino-*hex-5-enopyranoside* (**16**). — Prepared from **10** (0.89 g, 2.29 mmol), **16** (0.62 g, 87%) was a syrup, $[\alpha]_D^{20}$ +61° (*c* 0.3, chloroform). Mass spectrum: *m/z* 308 (M^+). ^{1}H-N.m.r. data ($CDCl_3$, 250 MHz): δ 8.08–7.40 (m, 5 H, Ph), 5.96 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 4.81 (s, 1 H, H-6a), 4.74 (s, 1 H, H-6b), 4.54 (d, 1 H, $J_{1,2}$ 5.5 Hz, H-1), and 3.60–3.41 (m, 11 H, H-2,3 and 3 OMe).

Anal. Calc. for $C_{16}H_{20}O_6$: C, 62.33; H, 6.49 . Found: C, 62.30; H, 6.44.

2L-2,3/4,5-2-Benzoyloxy-5-hydroxy-3,4-dimethoxycyclohexanone (**21**). — Prepared from **16** (93 mg, 0.3 mmol) by method (*b*), **21** (45 mg, 50%) had m.p. 99–101° (from hexane–ether, 8:2), $[\alpha]_D^{20}$ ~0° (*c* 0.1, chloroform), $[\alpha]_{546}^{20}$ −7° (*c* 0.7, chloroform). Mass spectrum: *m/z* 294 (M^+). ^{1}H-N.m.r. data [$(CD_3)_2CO$, 250 MHz]: δ 8.07–7.42 (m, 5 H, Ar), 5.74 (d, 1 H, $J_{2,3}$ 3 Hz, H-2), 4.29 (t, 1 H, $J_{2,3} = J_{3,4} = 3.5$ Hz, H-3), 4.22 (m, 1 H, H-5), 3.92 (bs, 1 H, H-4), 2.86 (t, 1 H, $J_{5,6a} = J_{gem} = 12.5$ Hz, H-6*a*), and 2.58 (dd, 1 H, $J_{5,6e}$ 4.5, J_{gem} 12.5 Hz, H-6*e*).

Anal. Calc. for $C_{15}H_{18}O_6$: C, 61.22; H, 6.12 . Found: C, 60.84; H, 5.98.

2L-2,3/4-2-Benzoyloxy-3,4-dimethoxycyclohex-5-enone (**24**). — Application of method (*b*) for 24 h at 80° to **16** (0.295 g, 0.96 mmol) gave **21** (15 mg, 5%), and **24** (16 mg, 6%) as a syrup, $[\alpha]_D^{20}$ −12° (*c* 1.1, chloroform). Mass spectrum: *m/z* 276 (M^+). ^{1}H-N.m.r. data [$(CD_3)_2CO$, 250 MHz]: δ 8.06–7.48 (m, 5 H, Ph), 7.02 (dq, 1 H, $J_{5,6}$ 10, $J_{4,5}$ 5, $J_{3,5}$ 2 Hz, H-5), 6.07 (d, 1 H, $J_{5,6}$ 10 Hz, H-6), 5.93 (d, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 4.26–4.18 (m, 2 H, H-3,4), and 3.56 (s, 6 H, 2 OMe).

*Methyl 4-O-benzoyl-6-deoxy-2,3-di-O-methyl-β-*L*-arabino-hex-5-enopyranoside* (**13**). — Prepared from **7**[14] (1.01 g, 2.6 mmol), **13** (0.7 g, 88%) was a syrup, $[\alpha]_D^{20}$ +29° (*c* 0.25, chloroform). Mas spectrum: *m/z* 292 (M^+). ^{1}H-N.m.r. data (C_6D_6, 200 MHz): δ 8.25–6.68 (m, 5 H, Ph), 6.22 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 4.90 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1), 4.78 (s, 1 H, H-6a), 4.75 (s, 1 H, H-6b), 3.91 (m, 2 H, H-2,3), 3.33, 3.25, and 3.23 (3 s, 9 H, 3 OMe).

Anal. Calc. for $C_{16}H_{20}O_6$: C, 62.33; H, 6.49 . Found: C, 62.30; H, 6.44.

2D-2,3/4,5-2-Benzoyloxy-5-hydroxy-3,4-dimethoxycyclohexanone (**19**). — Prepared from **13** (0.18 g, 0.59 mmol) by method (*b*) but for 4 h at 60°, **19** (0.126 g, 73%) had m.p. 99–101°, $[\alpha]_D^{20}$ ~0° (*c* 0.3, chloroform), $[\alpha]_{546}^{20}$ +7° (*c* 0.7, chloroform). Mass spectrum: *m/z* 294 (M^+). ^{1}H-N.m.r. data [$(CD_3)_2CO$, 250 MHz]: δ 8.07–7.42 (m, 5 H, Ph), 5.74 (d, 1 H, $J_{2,3}$ 3 Hz, H-2), 4.23 (m, 2 H, H-3,5), 3.92 (t, 1 H, $J_{3,4} = J_{4,5}$ = 4.5 Hz, H-4), 2.85 (t, 1 H, $J_{5,6a} = J_{gem}$ = 12.5 Hz, H-6*a*), and 2.58 (dd, 1 H, $J_{5,6e}$ 4.5, J_{gem} 12.5 Hz, H-6*e*).

Anal. Calc. for $C_{15}H_{18}O_6$: C, 61.22; H, 6.12 . Found: C, 61.29; H, 6.05.

2D-2,3/4-2-Benzoyloxy-3,4-dimethoxycyclohex-5-enone (**23**). — Application of method (*b*) for 24 h at 80° to **13** (0.29 g, 0.94 mmol) gave **19** (17 mg, 6%), and **23** (43 mg, 17%) as a syrup, $[\alpha]_D^{20}$ +14° (*c* 1.3, chloroform). Mass spectrum: *m/z* 276 (M^+). ^{1}H-N.m.r. data [$(CD_3)_2CO$, 250 MHz]: δ 8.06–7.48 (m, 5 H, Ph), 7.02 (dq, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 5, $J_{3,5}$ 2 Hz, H-3), 6.07 (d, 1 H, $J_{2,3}$ 10 Hz, H-2), 5.93 (d, 1 H, $J_{5,6}$ 2.5 Hz, H-6), 4.26–4.18 (m, 2 H, H-4,5), and 3.56 (2 s, 6 H, 2 OMe).

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