rangement of (hydroxymethyl)indene **36**.

Preparation and Irradiation of 1-(1,2,3-Triphenylcyclopropen-1-yl)ethanol (39). To a solution containing 140 mg of 1,2,3-triphenyl-3-acetylcyclopropene (**28**) in 4 mL of methanol was added 125 mg of sodium borohydride. The solution was stirred at room temperature for 15 min, and then the solvent was removed under reduced pressure. The residue was taken up in ether, and the ethereal solution was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left an oil which was subjected to preparative thick-layer chromatography with a 5% acetone–hexane mixture as the eluent. The major fraction contained 132 mg of a colorless oil whose structure was assigned as 1-(1,2,3-triphenylcyclopropen-1-yl)-ethanol (**39**) on the basis of its spectral properties: IR (neat) 2.87, 5.48, 6.25, 6.69, 6.93, 9.36, 13.44, 14.70 μm; UV (95% ethanol) 228 nm (ε 5900), 316 (5400), 332 1300); NMR ($CDCl_3$, 90 MHz) δ 1.32 (d, 3 H, J = 7.0 Hz), 1.76 (s, 1 H), 5.15 (q, 1 H, J = 7.0 Hz), 7.09–7.96 (m, 15 H); mass spectrum, m/e 312 (M^+), 267 (base).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.39; H, 6.41.

A solution containing 180 mg of **39** in 150 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 1 h. Removal of the solvent under reduced pressure left a yellow oil which was shown by NMR spectroscopy to consist of a 3:2 mixture of *trans*- and *cis*-1-methyl-2,3,4-triphenyl-1,4-dihydrofuran (**40**): NMR ($CDCl_3$, 90 MHz) major isomer δ 1.51 (d, 3 H, J = 7.5 Hz), 4.76 (s, 1 H), 5.09 (q, 1 H, J = 7.5 Hz); minor isomer δ 1.73 (d, 3 H, J = 7.5 Hz), 4.90 (s, 1 H), 5.17 (q, 1 H, J = 7.5 Hz). The isomeric mixture of cis and trans isomers was oxidized to 2-methyl-3,4,5-triphenylfuran (**17**) by heating a mixture containing the isomeric dihydrofurans with 5% palladium on carbon in refluxing xylene for 24 h. Removal of the solvent followed by column chromatography afforded 2-methyl-3,4,5-triphenylfuran (**17**) as the exclusive product.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, an the National Science Foundation for financial support.

Registry No. **7**, 79918-99-3; **9**, 79919-00-9; **10**, 79919-01-0; **11**, 79919-02-1; **12**, 7404-46-8; **16**, 79919-03-2; **17**, 69490-59-1; **18**, 79919-04-3; (E)-**19**, 79919-05-4; **20**, 79919-06-5; **21**, 79919-07-6; **22**, 79919-08-7; **26**, 79919-09-8; **27**, 79919-10-1; **28**, 79919-11-2; **29**, 4970-80-3; **30**, 64749-01-5; **35**, 79919-12-3; **36**, 79919-13-4; **37**, 79919-14-5; **38**, 1801-42-9; **39**, 79919-15-6; *cis*-**40**, 79919-16-7; *trans*-**40**, 79919-17-8; 1,3-dithiane, 505-23-7; 1,2,3-triphenylcyclopropenyl perchlorate, 51778-20-2; 4-hydroxy-4-methyl-1,2,3-triphenylpenten-1-one, 79919-18-9; diphenylmethylcyclopropenyl perchlorate, 72612-89-6; 4-hydroxy-4-phenyl-(*E*)-1,2,3-triphenylpenten-1-one, 79919-19-0.

Structural Analysis of 5,6-Dideoxy-5-*C*-[(*R* and *S*)-phenylphosphinyl]-L-*ido*-hexopyranoses by 400-MHz Proton Nuclear Magnetic Resonance

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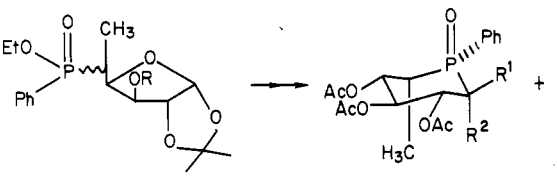
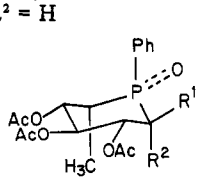
The 400-MHz ^1H NMR spectral analysis was performed on the five title compounds prepared from (5*RS*)-5,6-dideoxy-5-*C*-[(*RS*)-ethoxyphenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses upon reduction with sodium dihydrobis(2-methoxyethoxy)aluminate, followed by the action of mineral acid and acetic anhydride. The results showed that the five products all had L-ido configuration with the pyranoid ring in the $^4C_1$(L) conformation; four of them were diastereomeric isomers at C-1 and the ring phosphorus atom, and the fifth was a further reduced 1-deoxy compound.

We reported in a previous paper[2] the preparation of five kinds of 5,6-dideoxy-5-*C*-(phenylphosphinyl)hexopyranoses from (5*RS*)-5,6-dideoxy-5-*C*-[(*RS*)-ethoxyphenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses (**1** and **2**) in three steps. Of these, the two readily crystallized compounds with melting points of 199 and 215 °C were found by X-ray crystallographic analysis to possess the structures of 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-L-*ido*-hexopyranoses **3** and **4**, respectively. However the structures of the other three products could not be established because their ^1H NMR spectra were not sufficiently resolved at 100 MHz. Thus we have taken the NMR spectra of all these products at 400 MHz, and we now describe the rest of the structures together with some interesting features of the first, detailed spectral data of these sugars having phosphorus in the hemiacetal ring.



1, R = H
2, R = THP

3, R^1 = H; R^2 = OAc
4, R^1 = OAc; R^2 = H
5, R^1 = R^2 = H



6, R^1 = H; R^2 = OAc
7, R^1 = OAc; R^2 = H

Results and Discussion

The proton absorptions of the structurally established products **3** and **4** were clearly separated from each other

(1) (a) Okayama University. (b) The University of Alberta.
(2) Inokawa, S.; Yamamoto, K.; Kawamoto, H.; Yamamoto, H.; Lugar, P. *Carbohydr. Res.*, manuscript submitted for publication.

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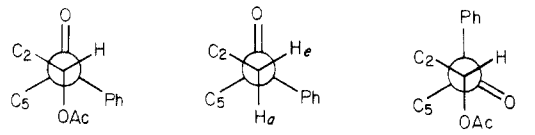
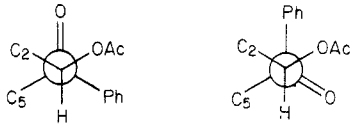
Table I. ^{1}H NMR (400 MHz) Parameters for 5-Deoxy-5-*C*-(phenylphosphinyl)-L-*ido*-pyranoses in $CDCl_3$[a]

compd	AcO-1*, H-1	AcO-2*, H-2	AcO-3*, H-3	AcO-4*, H-4	H-5	H_3-6	P-C_6H_5 (ortho, para, meta)
3	2.145* s	2.085* s	2.08* s	1.98* s			
	6.09 ddd	5.76 ddd	5.68 dd	5.78 ddd	3.05 dqdd	1.36 dd	7.78 m
	$J_{1,P}$ 11.5	$J_{2,3}$ 9.7	$J_{3,4}$ 9.9	$J_{4,5}$ 4.7	$J_{5,P}$ 21.6	$J_{6,P}$ 16.2	7.62 m
	$J_{1,2}$ 3.1	$J_{2,P}$ 0.9		$J_{4,P}$ 3.1	$J_{5,6}$ 7.6		7.54 m
	$J_{1,5}$ 2.1						
4	2.06* s	2.01* s	2.056* s	1.95* s			
	6.11 dd	5.80 ddd	5.55 dd	5.76 ddd	2.79 dqd	1.10 dd	7.80 m
	$J_{1,2}$ 10.75	$J_{2,3}$ 9.5	$J_{3,4}$ 10.1	$J_{4,5}$ 4.6	$J_{5,P}$ 21.7	$J_{6,P}$ 16.8	7.60 m
	$J_{1,P}$ 2.75	$J_{2,P}$ 2.4		$J_{4,P}$ 3.4	$J_{5,6}$ 7.6		7.54 m
5	2.50 ddd (H_a)	2.05* s	2.07* s	2.046* s			
	$J_{1,1}$ 14.0	5.60 ddd	5.44 dd	5.72 ddd	2.77 dqdd	1.04 dd	7.72 m
	$J_{1,2}$ 11.7	$J_{2,3}$ 9.5	$J_{3,4}$ 9.7	$J_{4,5}$ 4.5	$J_{5,P}$ 20.0	$J_{6,P}$ 16.9	7.60 m
	$J_{1,P}$ 5.3	$J_{2,P}$ 2.5		$J_{4,P}$ 3.7	$J_{5,6}$ 7.5		7.54 m
	2.66 dddd (H_e)						
	$J_{1,P}$ 17.5						
	$J_{1,2}$ 4.5						
	$J_{1,5}$ 2.2						
6	2.23* s	2.02* s	2.13* s	2.01* s			
	6.15 ddd	4.91 ddd	5.65 dd	5.04 ddd	3.20 dqdd	1.56 dd	7.94 m
	$J_{1,P}$ 8.6	$J_{2,3}$ 9.4	$J_{3,4}$ 9.1	$J_{4,P}$ 6.1	$J_{5,P}$ 15.5	$J_{6,P}$ 13.7	7.65 m
	$J_{1,2}$ 3.0	$J_{2,P}$ 3.4		$J_{4,5}$ 4.6	$J_{5,6}$ 7.5		7.65 m
	$J_{1,5}$ 1.7						
7	2.12* s	2.03* s	2.07* s	2.02* s			
	5.95 dd	5.24 ddd	5.49 dd	5.10 ddd	3.11 dqd	1.50 dd	8.00 m
	$J_{1,2}$ 10.6	$J_{2,3}$ 8.6	$J_{3,4}$ 9.1	$J_{4,P}$ 7.6	$J_{5,P}$ 15.6	$J_{6,P}$ 14.3	7.65 m
	$J_{1,P}$ 10.4	$J_{2,P}$ 4.5		$J_{4,5}$ 4.3	$J_{5,6}$ 7.6		7.62 m

[a] Abbreviations: s, singlet; d, doublet; q, quartet; *J*, coupling constants (hertz) confirmed by double resonance. Chemical shifts (δ values) are in parts per million from Me_4Si. An asterisk indicates the assignments of acetoxy groups are interconvertible.



3, $J_{1,P}$ = 11.5 Hz 5, $J_{1e,P}$ = 17.5 Hz, $J_{1a,P}$ = 5.3 Hz 6, $J_{1,P}$ = 8.6 Hz

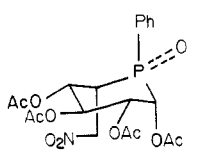


4, $J_{1,P}$ = 2.75 Hz 7, $J_{1,P}$ = 10.4 Hz

Figure 1. Newman projection along the C-1—P-5 bond and the J_{P-C-H} values.

in the 400-MHz NMR spectra. The assignments of all signals were thus readily made by employing a first-order analysis with the aid of a decoupling technique, and the results are summarized in Table I. The H-1 signal of the β-acetoxy derivative **3** consisted of a triple doublet at δ 6.09 with small $J_{1,2}$ (3.1 Hz) and large $J_{1,P}$ (11.5 Hz) values and also an additional $J_{1,5}$ (2.1 Hz) value due to the 1,5 W coupling, whereas that of the α isomer **4** showed a double doublet at δ 6.11 with large $J_{1,2}$ (10.75 Hz) and small $J_{1,P}$ (2.75 Hz) values. The remaining absorption in the spectra of **3** and **4** closely resembled each other except for the additional splitting of the H-5 signal of **3** due to the 1,5 W coupling. These values of the coupling constants are completely in conformity with the established $^4C_1$(L) conformation of the rigid pyranoid ring of compounds **3** and **4** from the viewpoint of the vicinal dihedral angles of the protons on the ring. The particularly large magnitude of $J_{5,P}$ value (21.7 Hz) of **3** and **4** appears to be a characteristic coupling of O=P—C—H in a gauche conformation (see below).

The two other diastereomers of **3** and **4**, which were produced simultaneously during the preparation, were also subjected to the 400-MHz ^{1}H NMR study. These two products showed strikingly similar absorptions except for the splitting patterns of their H-1 signals; one isomer (mp 168 °C) exhibited a large $J_{1,P}$ (8.6 Hz) and a small $J_{1,2}$ (3.0 Hz) value together with the 1,5 W coupling ($J_{1,5}$ = 1.7 Hz), whereas the other (mp 138 °C) showed large $J_{1,2}$ (10.6 Hz) and $J_{1,P}$ (10.4 Hz) values. An appreciable upfield shift (0.6–0.8 ppm) was observed for the H-2 and H-4 signals of these two products compared with those of **3** and **4**, while the remaining absorptions were essentially similar for the four products. Combination of these spectral data led to the structures **6** and **7** with *R* configuration of the ring phosphorus atom for the two additional products; the assignments of the NMR signals are also listed in Table I. The upfield shifts of the H-2 and 4 signals can be explained in terms of the shielding effect of the phenyl group linked axially to the ring P atom. The splitting patterns of the NMR spectrum (60 MHz) of compound **6** resembled that of the 6-*C*-nitro derivative **8**, which had been obtained by a different route[3] and structurally established by x-ray crystallography,[4] thus supporting the *R* configuration of the ring phosphorus atom.



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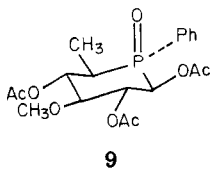

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The ^{1}H NMR spectrum of the fifth product (mp 158 °C) markedly differed from those of **3** and **4** in the following respects: (1) the presence of three AMX type proton

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signals at δ 2.5–2.8, and (2) the absence of an AcO-1 and a H-1 signal at δ 2 and 6, respectively. The remaining absorptions closely resembled those of **3**. A careful analysis of the 400-MHz spectrum with the aid of decoupling experiments therefore established the structure **5** for this product. The elementary analysis and mass spectrum supported the structure. The mechanism for the formation of such a further reduced P sugar is, however, currently under investigation.

The values of the geminal P—C—H coupling constants ($J_{1,P}$) of the presently described phosphinyl coompounds apparently depend upon the magnitude of their approximate O=P—C—H dihedral angles illustrated in the Newman projections (Figure 1). Thus the anti conformation of the O=P—C—H group exhibited a lower magnitude of coupling than the gauche conformation, providing a quick method for assignment of configuration of the P sugars. A similar dependance of the geminal P—C—H coupling constant of the O=P—C—H dihedral angle has been reported for a linear and cyclic phosphonyl compound.[5] The large values of the H—C-5—P geminal coupling constants ($J_{5,P}$ = 20-21.7 Hz for **3–5** and 15.7 Hz for **6, 7**) appear to be compatible with gauche coupling, although the exact $J_{5,P}$ value of anti coupling has not been obtained for a D-gluco-type P sugar[6] (**9**) because of the poor resolution of its ^{1}H NMR spectrum at 60 MHz. There have been reported some examples of more reliable angular dependance of P—C—C—H vicinal coupling constants upon the dihedral angles in the case of phosphonate compounds.[7] However, because of the small differences in the magnitude of the vicinal coupling ($J_{2,P}$ and $J_{4,P}$) of the present (*S*)-phosphinyl-*ido*-hexopyranose (**3, 4**) and its *R* isomer (**6, 7**), these values do not seem to have been utilized as a decisive method for assignment of the *R,S* configuration to the ring P atom.

It is not certain at present whether the predominant formation of L-ido-type P sugars from the D-*xylo*-hexofuranoses (**1, 2**) is due to a steric requirement of an intermediate. The above mechanistic study is being continued and an effective preparative method for gluco-type P sugars is currently in progress. Nevertheless, this initial work clearly demonstrates the utility of 400-MHz ^{1}H NMR studies for the effective determination of configuration and conformation of sugars containing phosphorus in the ring.

Experimental Section

^{1}H NMR spectra were obtained with a Bruker WH-400 cryospectrometer at 27 °C. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (δ 0.0) as an internal standard. Spin decoupling was performed for each proton signal to confirm the coupling constants. The NMR spectra of all compounds were completely interpretable in a first-order analysis at 400 MHz. The materials used for the measurements were prepared as described in ref 2.

Registry No. **1**, 79917-67-2; **2**, 79917-68-3; **3**, 79917-69-4; **4**, 79917-70-7; **5**, 79917-71-8; **6**, 79917-72-9; **7**, 79917-73-0.

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Stereospecific Synthesis of Muscarines and Allomuscarines in D and L Series

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D(−)-(1*R*,3*S*,4*R*)-Muscarine iodide (**4**) and L(+)-(1*S*,3*S*,4*R*)-allomuscarine iodide (**2**) were synthesized from 2-deoxy-D-ribose (**5**). Treatment of the β cyanide **6a** with a methanolic hydrogen chloride solution gave a mixture of methyl esters **7a** and **8a**. These esters reacted with dimethylamine at 90 °C to yield the corresponding deprotected dimethyl amide **10a**. Selective tosylation in dry pyridine of **10a** and reduction of the tosylamide **11a** with lithium aluminum hydride in refluxing tetrahydrofuran, followed by quaternization of the crude amine with methyl iodide, gave D(−)-muscarine iodide (**4**). The same procedure with the α cyanide **6b** gave L(+)-allomuscarine iodide (**2**). L(+)-(1*S*,3*R*,4*S*)-Muscarine iodide (**1**) and D(−)-(1*R*,3*R*,4*S*)-allomuscarine iodide (**3**) were analogously prepared from 2-deoxy-L-ribose (**13**). The anomeric purity of these compounds was established by spectroscopic data.

The interesting physiological activity of L(+)-muscarine (**1**), isolated from *Amanita muscaria*, has generated much interest over the years. Its structure elucidation[1] showed the presence of three asymetric centers (Scheme I), which implied the existence of four pairs of enantiomers in both the D and L series. All stereoisomers have been synthesized.[2]

The majority of the published syntheses afford a racemic or an isomeric mixture of natural muscarine with different stereoisomers. A few elegant stereospecific syntheses have been reported: starting from an α-amino acid as the chiral precursor, L(+)-muscarine (**1**) and L(+)-allomuscarine (**2**) were obtained after an enzymatic resolution.[3] D(−)-allomuscarine (**3**) was synthesized from an optically active diol.[4]

Among the easily accessible chiral products used as starting materials for the synthesis of muscarines, carbohydrates are the most obvious: L(+)-muscarine (**1**) has been obtained from L-arabinose, via L-chitaric acid,[5] and also from D-mannitol;[6] D(−)-muscarine (**4**) has been prepared from D-glucosamine[7] and from 2-deoxy-D-ribose.[8]

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