Carbohydrate Research, 123 (1983) 201–207
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS OF 1,2,4-TRI-*O*-ACETYL-6-DEOXY-6-*C*-(ISOPROPYLPHOSPHINYL)-3,5-DI-*O*-METHYL-D-GLUCOSEPTANOSE AND 1,2,4-TRI-*O*-ACETYL-3-*O*-BENZYL-6-*C*-(BUTYLPHOSPHINYL)-6-DEOXY-5-*O*-METHYL-D-GLUCOSEPTANOSE

KUNIAKI SEO
Department of Industrial Chemistry, Numazu College of Technology, Numazu-shi 410 (Japan)
(Received May 23rd, 1983; accepted for publication, June 16th, 1983)

ABSTRACT

The Michaelis–Arbuzov reaction of 6-deoxy-6-iodo-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose with diethyl isopropylphosphonite afforded 6-deoxy-6-*C*-(ethoxyisopropylphosphinyl)-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (**3**). Similarly, using 3-*O*-benzyl-6-deoxy-6-iodo-1,2-*O*-isopropylidene-α-D-glucofuranose and diethyl butylphosphonite, 3-*O*-benzyl-6-deoxy-6-*C*-(ethoxybutylphosphinyl)-1,2-*O*-isopropylidene-α-D-glucofuranose (**4**) was obtained. Treatment of **3** and **4** with methyl iodide–silver oxide afforded the corresponding 5-*O*-methyl compounds, **5** and **6**, respectively. Treatment of **5** with sodium dihydrobis(2-methoxyethoxy)aluminate, followed by mineral acid, and then acetic anhydride in pyridine, gave the two isomers of 1,2,4-tri-*O*-acetyl-6-deoxy-6-*C*-(isopropylphosphinyl)-3,5-di-*O*-methyl-D-glucoseptanose and a mixture of 1,2-di-*O*-acetyl-6-deoxy-6-*C*-(isopropylphosphinyl)-3,5-di-*O*-methyl-α- and -β-D-glucofuranose, which were separated by column chromatography on silica gel. Similarly, from **6**, the two isomers of 1,2,4-tri-*O*-acetyl-3-*O*-benzyl-6-*C*-(butylphosphinyl)-6-deoxy-5-*O*-methyl-D-glucoseptanose and a mixture of 1,2-di-*O*-acetyl-3-*O*-benzyl-6-*C*-(butylphosphinyl)-6-deoxy-5-*O*-methyl-α- and -β-D-glucofuranose were obtained.

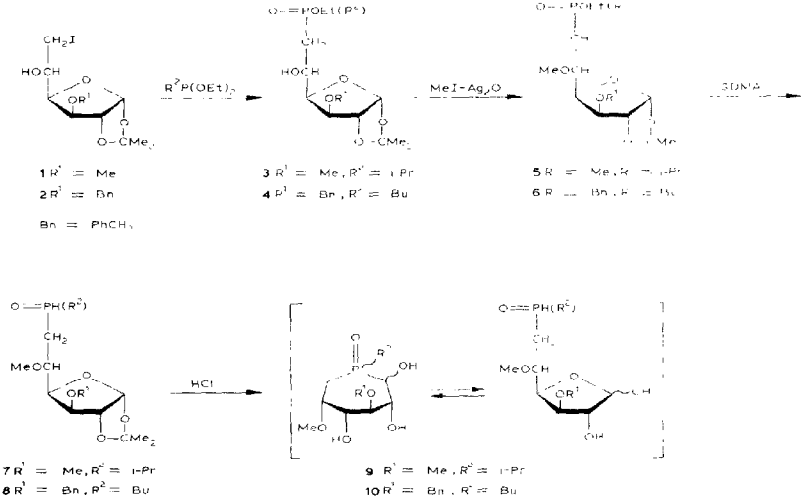
INTRODUCTION

In the chemical modification of sugar derivatives, there have been synthesized many sugar analogs having sulfur[1–3] and nitrogen[1,2,4] in the hemiacetal ring. Also, those of pentofuranoses[5,6], pentopyranoses[7–12], and hexopyranoses[13–17] having phosphorus in the ring have already been reported. However, such a hexoseptanose had not yet been prepared, and herein is reported the synthesis of the title compounds, having phosphorus in the septanoid ring.

0008-6215/83/$ 03.00

RESULTS AND DISCUSSION

6-Deoxy-6-iodo-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (**1**) and 3-*O*-benzyl-6-deoxy-6-iodo-1,2-*O*-isopropylidene-α-D-glucofuranose (**2**), respectively obtained by treating the 3-methyl (from 3-*O*-methyl-D-glucose[18]) or 3-benzyl ether of 1,2-*O*-isopropylidene-6-*O*-*p*-tolylsulfonyl-α-D-glucofuranose[19] with sodium iodide in acetone, were used as the starting materials for this synthesis.

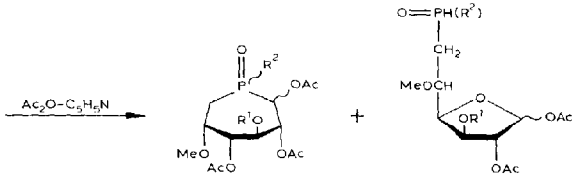


The Michaelis–Arbuzov reaction of **1** with diethyl isopropylphosphonite gave 6-deoxy-6-*C*-(ethoxyisopropylphosphinyl)-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (**3**) in 91% yield [*m/z* 352 (M^+)], which was purified by column chromatography on silica gel. Similarly, on treating **2** with diethyl butylphosphonite, 3-*O*-benzyl-6-deoxy-6-*C*-(ethoxybutylphosphinyl)-1,2-*O*-isopropylidene-α-D-glucofuranose (**4**) was obtained in 58% yield [*m/z* 442 (M^+)].

In order to avoid pyranoid-ring formation during the procedure following hydrolysis, methylation of **3** with methyl iodide and silver oxide was performed, to give 6-deoxy-6-*C*-(ethoxyisopropylphosphinyl)-1,2-*O*-isopropylidene-3,5-di-*O*-methyl-α-D-glucofuranose (**5**) in 87% yield; *m/z* 366 (M^+); similarly, **4** gave 3-*O*-benzyl-6-deoxy-6-*C*-(ethoxybutylphosphinyl)-1,2-*O*-isopropylidene-5-*O*-methyl-α-D-glucofuranose (**6**) in 72% yield; *m/z* 456 (M^+). Reduction of **5** with sodium dihydrobis(2-methoxyethoxy)aluminate (SDMA) in oxolane (tetrahydrofuran;

THF) in the usual way[7–10] afforded 6-deoxy-1,2-*O*-isopropylidene-6-*C*-(isopropylphosphinyl)-3,5-di-*O*-methyl-α-D-glucofuranose (**7**) in 82% yield; *m/z* 322 (M^+); similarly, **6** gave 3-*O*-benzyl-6-*C*-(butylphosphinyl)-6-deoxy-1,2-*O*-isopropylidene-5-*O*-methyl-α-D-glucofuranose (**8**) in 98% yield; *m/z* 412 (M^+). These compounds (**7** and **8**) respectively showed an i.r. absorption band at 2330 (2340) cm^{-1} (P–H), and, in the ^{1}H-n.m.r. spectrum, a characteristic J_{P-H} value of 456 Hz at δ 6.75 (462 Hz at δ 6.95), disappearing on deuteration.

Hydrolysis of **7** with 0.1M hydrochloric acid under argon for 3 h at 110° (bath), and acetylation of the product (**9**) with acetic anhydride–pyridine in the usual way[7–9], afforded a crude syrup (**11**). This was separated by column chromatography on silica gel, using ethyl acetate–methanol as the eluant, into three major fractions, which will be referred as A, B, and C (according to their decreasing R_F values).



11 R^1 = Me, R^2 = i-Pr
12 R^1 = Bn, R^2 = Bu

Fractions A and B were colorless syrups; each exhibited signals for three acetoxyl groups at δ 2.0–2.2 in the ^{1}H-n.m.r. spectrum, and the molecular-ion peak was at *m/z* 408, corresponding to $C_{17}H_{29}O_9P$, in the high-resolution, mass spectrum of each. Fraction C was a colorless syrup that exhibited signals for two acetoxyl groups, at δ 2.07, and 2.10, H-1 signals at δ 5.98 (β) and 6.28 (α, $J_{1,2}$ 4.2 Hz), and a P–H signal at δ 6.80 (J_{P-H} 463 Hz) in the ^{1}H-n.m.r. spectrum; it also showed an absorption band for a P–H group at 2320 cm^{-1} in its i.r. spectrum, and the molecular-ion peak at *m/z* 366, corresponding to $C_{15}H_{27}O_8P$, in the high-resolution, mass spectrum.

The ^{1}H-n.m.r. spectra of A and B showed relatively low values of δ for the H-4 signal (compared with that of fraction C), whereas the H-3 and H-5 signals were essentially similar for the three fractions, and the H-1 and H-4 signals of fraction A showed a downfield shift (compared with that of fraction B). Therefore, fractions A and B were considered to be 1,2,4-tri-*O*-acetyl-6-deoxy-6-*C*-(isopropylphosphinyl)-3,5-di-*O*-methyl-D-glucoseptanose (**11a** and **11b**; isomers) and fraction C was identified as a mixture of 1,2-di-*O*-acetyl-6-deoxy-6-*C*-(isopropylphosphinyl)-3,5-di-*O*-methyl-α- and -β-D-glucofuranose (**11c**).

Similarly, fractions D, E, and F were obtained by hydrolysis of **8**, acetylation of the resulting product (**10**), and separation of the acetates.

Fractions D and E were colorless syrups; each exhibited signals for three acetoxyl groups in the ^{1}H-n.m.r. spectrum, and a molecular-ion peak at *m/z* 498, corresponding to $C_{24}H_{35}O_9P$, in the high-resolution, mass spectrum of each. Fraction F was a colorless syrup that exhibited signals for two acetoxyl groups, at δ 2.06 and 2.08, H-1 signals at δ 6.05 (β) and 6.32 (α, $J_{1,2}$ 4.5 Hz), and half a P–H signal at δ 10.9 in the ^{1}H-n.m.r. spectrum, an absorption band for a P–H group at 2340 cm^{-1} in the i.r. spectrum, and the molecular-ion peak at *m/z* 456, corresponding to $C_{22}H_{33}O_8P$, in the high-resolution, mass spectrum. The shift patterns in the ^{1}H-n.m.r. spectra of fractions D and E, and those of fractions A and B, resembled each other. Therefore, fractions D and E were considered to be 1,2,4-tri-*O*-acetyl-3-*O*-benzyl-6-*C*-(butylphosphinyl)-6-deoxy-5-*O*-methyl-D-glucoseptanose (**12a** and **12b**), and fraction F was identified as a mixture of 1,2-di-*O*-acetyl-3-*O*-benzyl-6-*C*-(butylphosphinyl)-6-deoxy-5-*O*-methyl-α- and -β-D-glucofuranose (**12c**).

EXPERIMENTAL

The general experimental methods have been reported[11].

6-Deoxy-6-C-(ethoxyisopropylphosphinyl)-1,2-O-isopropylidene-3-O-methyl-α-D-glucofuranose (**3**). — A solution of **1** (1.75 g) in diethyl isopropylphosphonite (10 mL) was heated at 110° (bath) while more of the phosphonite (2 mL) was added in several portions. The excess of phosphonite was then evaporated off *in vacuo*, and a solution of the residue in $CHCl_3$ was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by chromatography on silica gel, using 20:1 EtOAc–methanol as the eluant, to give **3** as a colorless syrup (1.63 g, 91%); $[\alpha]_D^{24}$ −20.8° (*c* 1.00, $CHCl_3$); ^{1}H-n.m.r. data: δ 0.9–1.45 (m, 15 H, CMe_2, P-CMe_2, P-OMe), 1.16–2.50 (m, 3 H, H-6,6′, P-CH-), 3.43 (s, 3 H, OMe-3), 3.75–4.35 (m, 6 H; 1 H disappeared on deuteration, H-3,4,5, P-OCH_2-, OH), 4.50 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-2), and 5.77 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1); *m/z* 352 (M^+).

3-O-Benzyl-6-deoxy-6-C-(ethoxybutylphosphinyl)-1,2-O-isopropylidene-α-D-glucofuranose (**4**). — Compound **2** (8.0 g) was treated with diethyl butylphosphonite as just described, to give **4** as a colorless syrup (3.0 g, 57%); $[\alpha]_D^{25}$ −13.3° (*c* 3.58, $CHCl_3$); ^{1}H-n.m.r. data: δ 0.6–2.3 (m, 20 H, H-6,6′, CMe_2, P-C_4H_9, P-OCMe), 3.7–4.3 (m, 6 H; 1 H disappeared on deuteration, H-3,4,5, P-OCH_2-, OH), 4.55 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.64 (s, 2 H, OCH_2-3), 5.79 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), and 7.05–7.35 (m, 5 H, -C_6H_5); *m/z* 442 (M^+).

6-Deoxy-6-C-(ethoxyisopropylphosphinyl)-1,2-O-isopropylidene-3,5-di-O-methyl-α-D-glucofuranose (**5**). — A solution of **3** (1.5 g) in methyl iodide (5 mL) was heated under argon at 50° (bath) while silver oxide (1 g) was added in several portions. After 10 h, the mixture was filtered, and the filtrate evaporated *in vacuo*. A solution of the residue in chloroform was washed with water, dried (Na_2SO_4),

and evaporated *in vacuo*. The residue was purified by chromatography on a column of silica gel, with 50:1 EtOAc–methanol as the eluant, to give a syrup (1.40 g, 87%); $[\alpha]_D^{20}$ −26.0° (*c* 5.00, $CHCl_3$); ^{1}H-n.m.r. data: δ 0.85–1.55 (m, 15 H, CMe_2, P-CMe_2, P-OCMe), 1.8–2.45 (m, 3 H, H-6,6′, P-CH-), 3.35, 3.41 (2 s, 6 H, OMe-3,5), 3.55–4.35 (m, 5 H, H-3,4,5, P-OCH_2-), 4.58 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-2), and 5.83 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1); *m/z* 366 (M^+).

3-O-Benzyl-6-C-(ethoxybutylphosphinyl)-3-O-methyl-1,2-O-isopropylidene-α-D-glucofuranose (**6**). — Compound **4** (10 g) was treated with methyl iodide–silver oxide as already described, to give **6** as a syrup (7.4 g, 73%); $[\alpha]_D^{22}$ −9.3° (*c* 3.78, $CHCl_3$); ^{1}H-n.m.r. data: δ 0.7–2.40 (m, 20 H, H-6,6′, CMe_2, P-C_4H_9, P-OCMe), 3.36 (s, 3 H, OMe-5), 3.65–4.35 (m, 5 H, H-3,4,5, P-OCH_2-), 4.52 (s, 2 H, -OCH_2-5), 4.58 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-2), 5.80 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), and 7.1–7.4 (m, 5 H, -C_6H_5); *m/z* 456 (M^+).

6-Deoxy-1,2-O-isopropylidene-6-C-(isopropylphosphinyl)-3,5-di-O-methyl-α-D-glucofuranose (**7**). — To a solution of **5** (1.37 g) in THF (50 mL) was added a 70% solution of SDMA (2.2 g) in benzene plus THF (20 mL) at 0° under argon. After 30 min, a small amount of water containing conc. HCl (0.2 mL) was added at 0° (to decompose the excess of SDMA), the mixture filtered, and the filtrate evaporated *in vacuo*. A solution of the residue in chloroform was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*, to give **7** (0.99 g, 82%) as a syrup; $[\alpha]_D^{15}$ −24.1° (*c* 2.90, $CHCl_3$); ν_{max}^{KBr} 2330 cm^{-1} (P-H); ^{1}H-n.m.r. data: δ 0.9–1.5 (m, 12 H, CMe_2, P-CMe_2), 1.6–2.35 (m, 3 H, H-6,6′, P-CH-), 3.35, 3.42 (2 s, 6 H, OMe-3,5), 3.4–4.25 (m, 3 H, H-3,4,5), 4.51 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-2), 5.75 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), and 6.75 (d m, 1 H, disappeared on deuteration, J_{P-H} 456 Hz, P–H); *m/z* 322 (M^+).

3-O-Benzyl-6-C-(butylphosphinyl)-6-deoxy-1,2-O-isopropylidene-5-O-methyl-α-D-glucofuranose (**8**). — Compound **6** (4.3 g) was treated with SDMA (6.0 g), as already described, to give **8** (3.8 g, 98%) as a syrup; $[\alpha]_D^{23}$ −19.5° (*c* 2.57, $CHCl_3$); ν_{max}^{KBr} 2340 cm^{-1} (P–H); ^{1}H-n.m.r. data: δ 0.65–2.4 (m, 17 H, H-6,6′, CMe_2, P-C_4H_9), 3.28, 3.34 (2 s, 3 H, OMe-5), 3.65–4.35 (m, 3 H, H-3,4,5), 4.53 (s, 2 H, overlapping with H-2, OCH_2-3), 5.80 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 6.95 (d m, 1 H, J_{P-H} 462 Hz, P–H), and 7.0–7.4 (m, 5 H, -C_6H_5); *m/z* 412 (M^+).

Hydrolysis of **7**; *1,2,4-tri-O-acetyl-6-deoxy-6-C-(isopropylphosphinyl)-3,5-di-O-methyl-D-glucoseptanose* (**11a,b**) *and 1,2-di-O-acetyl-6-deoxy-6-C-(isopropylphosphinyl)-3,5-di-O-methyl-D-glucofuranose* (**11c**). — To a solution of **7** (734 mg) in methanol (10 mL) was added 0.1M HCl (30 mL). The mixture was heated under argon for 3 h at 110° (bath), the methanol being allowed to evaporate gradually, cooled, diluted with water, and the acid neutralized with Amberlite IR-45 ion-exchange resin; this was then washed with water (3 × 20 mL) and ethanol (3 × 20 mL), and filtered; the filtrate and washings were combined, and evaporated *in vacuo*, to give syrupy **9** (474 mg). This was treated with acetic anhydride (9 mL) in dry pyridine (30 mL), in the usual way[7–9], to give a crude syrup **11** (518 mg). This

syrup was separated by chromatography on a column of silica gel by elution with 50:1 EtOAc–methanol, which was gradually changed to 10:1 EtOAc–methanol, to give **11a**, **11b**, and **11c**.

Compound **11a**, R_F 0.43 (EtOAc); colorless syrup (135 mg, 20% from **9**); $[\alpha]_D^{18}$ +20.8° (*c* 1.20, $CHCl_3$); ^{1}H-n.m.r. data: δ 0.95–1.45 (m, 6 H, P-CMe_2), 1.55–2.6 (m, 3 H, H-6,6′, P-CH-), 2.01, 2.04, 2.12 (3 s, 9 H, 3 OAc), 3.31, 3.39, 3.41 (3 s, 6 H, OMe-3,5), 3.7–4.45 (m, 2 H, H-3,5), 5.05–5.3 (m, 1 H, probably H-2), and 5.65–6.4 (m, 2 H, probably H-1,4); *m/z* 408 (M^+).

Calc. for $C_{17}H_{30}O_9P$: (M + H), 409.1624. Found: 409.1609.

Compound **11b**, R_F 0.40 (EtOAc); colorless syrup (89 mg, 13% from **9**); $[\alpha]_D^{18}$ +25.9° (*c* 1.93, $CHCl_3$); ^{1}H-n.m.r. data: δ 1.05–1.5 (m, 6 H, P-CMe_2), 1.65–2.65 (m, 3 H, H-6,6′, P-CH-), 2.05, 2.10, 2.14 (3 s, 9 H, 3 OAc), 3.35–4.45 (m, 6 H, OMe-3,5), and 5.05–5.95 (m, 3 H, H-1,2,3); *m/z* 408 (M^+).

Calc. for $C_{17}H_{30}O_9P$: (M + H), 409.1624. Found: 409.1601.

Compound **11c**, R_F 0.24 (EtOAc); colorless syrup (91 mg, 11% from **9**); $[\alpha]_D^{18}$ +22.5° (*c* 2.22, $CHCl_3$); ν_{max}^{KBr} 2340 cm^{-1} (P–H); ^{1}H-n.m.r. data: δ 0.95–1.45 (m, 6 H, P-CMe_2), 1.55–2.7 (m, 9 H, H-6,6′, P-CH-, 2 OAc), 3.39, 3.46 (2 s, 6 H, OMe-3,5), 3.7–4.6 (m, 3 H, H-3,4,5), 4.11 [s and d, overlapped, $J_{1,2}$ 4.2 Hz, H-2 (β, α)], 5.89 [2, ~1/3 H, H-1 (β)], 6.28 [d, ~2/3 H, $J_{1,P}$ 4.2 Hz, H-1 (α)], and 6.75 (d m, 1 H, J_{P-H} 462 Hz, P–H); *m/z* 366 (M^+).

Hydrolysis of **8**; *1,2,4-tri-*O*-acetyl-3-*O*-benzyl-6-*C*-(butylphosphinyl)-5-*O*-methyl-*D*-glucoseptanose* (**12a,b**) *and 1,2-*O*-acetyl-3-*O*-benzyl-6-*C*-(butylphosphinyl)-5-*O*-methyl-*D*-glucofuranose* (**12c**). — Compound **8** (651 mg) was treated with 0.1M HCl (25 mL) for 12 h at 110° (bath) as already described, to give syrupy **10** (467 mg). This was treated with acetic anhydride (9 mL) in dry pyridine (30 mL) in the usual way[7, 9], to give crude, syrupy **12** (485 mg). The syrup was separated, as already described, to give **12a**, **12b**, and **12c**.

Compound **12a**, R_F 0.78 (EtOAc); colorless syrup (167 mg, 21% from **10**); $[\alpha]_D^{20}$ +25.3° (*c* 2.17, $CHCl_3$); ^{1}H-n.m.r. data: δ 0.65–2.5 (m, 11 H, H-6,6′, P-C_4H_9), 2.00, 2.09 (2 s, 9 H, 3 OAc), 3.28, 3.37 (2 s, 3 H, OMe-5), 3.8–4.45 (m, 2 H, H-3,5), 4.95 (s, 2 H, OCH_2-3), 5.1–5.3 (m, 1 H, probably H-2), 5.5–6.4 (m, 2 H, probably H-1,4), and 7.0–7.3 (m, 5 H, -C_6H_5); *m/z* 498 (M^+).

Calc. for $C_{24}H_{34}O_9P$: (M − H); 497.1939. Found: 497.1944.

Compound **12b**, R_F 0.49 (EtOAc); colorless syrup (120 mg, 15% from **10**); $[\alpha]_D^{20}$ +20.7° (*c* 1.33, $CHCl_3$); ^{1}H-n.m.r. data: δ 0.7–2.66 (m, 11 H, H-6,6′, P-C_4H_9), 2.03, 2.06, 2.13 (3 s, 9 H, 3 OAc), 3.31 (s, 3 H, OMe-5), 3.7–4.4 (m, 2 H, H-3,5), 4.68 (s, 2 H, OCH_2-3), 5.0–6.1 (m, 3 H, H-1,2,4), and 7.1–7.5 (m, 5 H, -C_6H_5); *m/z* 498 (M^+).

Calc. for $C_{24}H_{36}O_9P$: (M + H), 499.2094. Found: 499.2065.

Compound **12c**, R_F 0.44 (EtOAc); colorless syrup (69 mg, 10% from **10**); $[\alpha]_D^{20}$ +17.0° (*c* 0.88, $CHCl_3$); ν_{max}^{KBr} 2340 cm^{-1} (P–H); ^{1}H-n.m.r. data: δ 0.7–2.2 (m, 11 H, H-6,6′, P-C_4H_9), 2.06, 2.08 (2 s, 6 H, 2 OAc), 3.31, 3.37 (2 s, 3 H, OMe-5),

3.7–4.5 (m, 3 H, H-3,4,5), 4.57, 4.62 (2 s, 2 H, OCH_2-3), 5.1–5.35 (s and d overlapped, 1 H, H-2), 6.05 [s, ~1/3 H, H-1 (β)], 6.32 [d, ~2/3 H, $J_{1,2}$ 4.5 Hz, H-1 (α)], 7.1–7.4 (m, 5 H, -C_6H_5), and 10.9 (m, 1/2 H, P–H); *m/z* 456 (M^+).

ACKOWLEDGMENTS

The author thanks Prof. Dr. S. Inokawa (Okayama University, Japan) for helpful discussions, and Drs. M. Yamashita and K. Takabe (Shizuoka University, Japan) for recording the high-resolution, mass spectra.

REFERENCES

1 H. PAULSEN, *Angew. Chem.*, 78 (1966) 501–516.
2 H. PAULSEN AND K. TODT, *Adv. Carbohydr. Chem.*, 23 (1968) 115–232.
3 U. G. NAYAK AND R. L. WHISTLER, *J. Org. Chem.*, 34 (1969) 97–100.
4 S. INOUYE, T. TSURUOKA, T. ITO, AND T. NIIDA, *Tetrahedron*, 24 (1968) 2125–2144.
5 M. YAMASHITA, M. YOSHIKANE, T. OGATA, AND S. INOKAWA, *Tetrahedron*, 35 (1979) 741–743.
6 H. YAMAMOTO, Y. NAKAMURA, H. KAWAMOTO, S. INOKAWA, M. YAMASHITA, M.-A. ARMOUR, AND T. T. NAKASHIMA, *Carbohydr. Res.*, 102 (1982) 185–196.
7 K. SEO AND S. INOKAWA, *Bull. Chem. Soc. Jpn.*, 46 (1973) 3301–3302.
8 K. SEO AND S. INOKAWA, *Bull. Chem. Soc. Jpn.*, 48 (1975) 1237–1239.
9 S. INOKAWA, H. KITAGAWA, K. SEO, H. YOSHIDA, AND T. OGATA, *Carbohydr. Res.*, 30 (1973) 127–132.
10 H. YAMAMOTO, T. HANAYA, S. INOKAWA, K. SEO, M.-A. ARMOUR, AND T. T. NAKASHIMA, *Carbohydr. Res.*, 114 (1983) 83–93.
11 K. SEO, *Carbohydr. Res.*, 119 (1983) 101–107.
12 K. SEO, *Carbohydr. Res.*, 122 (1983) 81–85.
13 H. TAKAYANAGI, K. SEO, M. YAMASHITA, H. YOSHIDA, T. OGATA, AND S. INOKAWA, *Carbohydr. Res.*, 63 (1978) 105–113; P. LUGER, M. YAMASHITA, AND S. INOKAWA, *ibid.*, 84 (1980) 25–33.
14 M. YAMASHITA, Y. NAKATSUKASA, H. YOSHIDA, T. OGATA, S. INOKAWA, K. HIROTSU, AND J. CLARDY, *Carbohydr. Res.*, 70 (1979) 247–261.
15 H. YAMAMOTO, K. YAMAMOTO, H. KAWAMOTO, S. INOKAWA, M.-A. ARMOUR, AND T. T. NAKASHIMA, *J. Org. Chem.*, 47 (1982) 191–193; S. INOKAWA, K. YAMAMOTO, H. KAWAMOTO, H. YAMAMOTO, M. YAMASHITA, AND P. LUGER, *Carbohydr. Res.*, 106 (1982) 31–42.
16 H. YAMAMOTO, C. HOSOYAMADA, H. KAWAMOTO, S. INOKAWA, M. YAMASHITA, M.-A. ARMOUR, AND T. T. NAKASHIMA, *Carbohydr. Res.*, 102 (1982) 159–167.
17 H. YAMAMOTO, K. YAMAMOTO, S. INOKAWA, M. YAMASHITA, M.-A. ARMOUR, AND T. T. NAKASHIMA, *Carbohydr. Res.*, 102 (1982) C1–C3.
18 E. L. HIRST AND E. PERCIVAL, *Methods Carbohydr. Chem.*, 2 (1963) 145–150.
19 R. L. WHISTLER AND W. C. LAKE, *Methods Carbohydr. Chem.*, 6 (1972) 286–291.