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Note

A simple preparation of methyl 2,6-dideoxy- and methyl 3,6-dideoxy-α-D-*arabino*-hexopyranoside by photochemical deoxygenation

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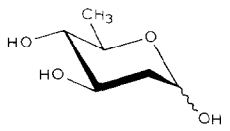
2,6-Dideoxy-D-*arabino*-hexopyranose (**1**, olivose, canarose, chromose C) is a constituent of several antibiotics (chlorotricin[1], chromomycin A_3[2], curamycin[3], olivomycin[4], venturicidin[5], flambamycin[6], the everninomycins B, C, D, and -2[7], chromocyclomycin[8], and oxamycetin[9]) and certain digitalis glycosides[10]. 3,6-Dideoxy-D-*arabino*-hexopyranose (**2**, tyvelose) has been isolated from the membranes of special types of salmonella and is responsible for the O-antigen factor 9 of the Kaufmann–White scheme[11]. For olivose (**1**) and its methyl α-D-glycoside[12–14] (**13**), as well as for tyvelose (**2**) and its methyl α-D- (**26**)[11a,15–20] and phenyl α-D-glycoside[21], laborious multistep-syntheses have been reported. The procedure now reported is a simpler approach to **13** and **26**.



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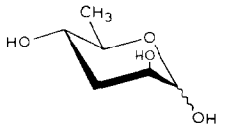

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Starting from methyl α-D-glucopyranoside (**3**) and methyl α-D-mannopyranoside (**16**), the respective 2,6- (**4**) and 3,6-diesters (**17**) are accessible by selective acylation with pivaloyl chloride at low temperature. The regioselectivity of this reaction accords with the results of other authors[22]. The 2,6-diester **4** is known[23], but the procedure given here is more suitable for large-scale preparations. The diesters **4** and **17** were further characterised as acetates (**5** and **18**) and trimethylsilyl ethers (**6** and **19**).

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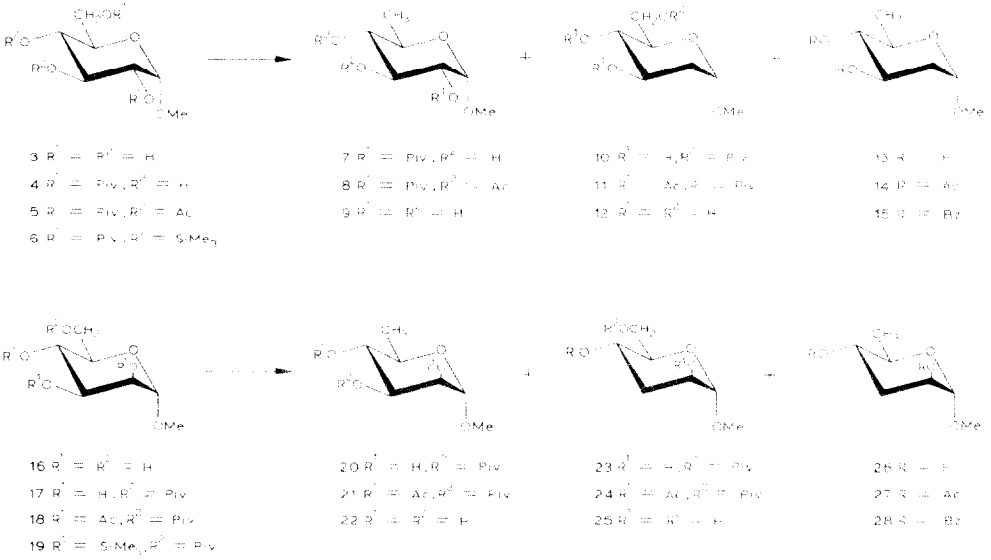
The photochemical deoxygenation of fully protected carbohydrate esters mixtures of hexamethylphosphoric triamide (HMPT) and water has been used for the preparation of deoxy sugars[24]. According to the literature[24a,25] and our own results, esters of such sterically hindered, aliphatic carboxylic acids as pivalic acid are more efficiently deoxygenated than are acetates or aromatic esters. Application of this procedure to the diesters **4** and **17** gave methyl 2,6-dideoxy-α-D-*arabino*-hexopyranoside (**13**) and methyl 3,6-dideoxy-α-D-*arabino*-hexopyranoside (**26**) in a simple manner.

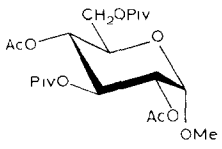


The rate of photodeoxygenation is faster at the secondary positions than at the primary positions, in agreement with earlier findings[24a]. Photolysis of **4** also pyranoside (**10**), but not methyl 6-deoxy-2-*O*-pivaloyl-α-D-glucopyranoside (**7**), whereas photolysis of **16** gave the monodeoxygenated esters methyl 6-deoxy-3-*O*- Whereas photolysis of **16** gave the monodeoxygenated esters methyl 6-deoxy-3-*O*-pivaloyl-α-D-mannopyranoside (**20**) and methyl 3-deoxy-6-*O*-pivaloyl-α-D-*arabino*-hexopyranoside (**23**) in addition to **26**. Complete conversion under the conditions used was difficult to achieve, but, because of its simplicity, the method described is superior to existing ones. For larger scale reactions, intermediate transformation of the crude deoxygenation products into the respective diacetates **8**, **11**, and **14**, and **21**, **24**, and **27**, is desirable, since these products can be purified readily without isolation.

G.l.c.–m.s. of the mixtures of diacetates obtained after incomplete reaction and comparison with authentic compounds showed that partial ester rearrangement had occurred which led to isomeric deoxygenated compounds. With **4**, <2% of the *trans*-rearranged product methyl 2,4-di-*O*-acetyl-3,6-di-*O*-pivaloyl-α-D-

glucopyranoside (**29**) was detected in addition to **5** in the acetylated, residual starting-material. *cis*-Rearrangement during the photolysis of **17** proceeded more efficiently and, in addition to the expected diacetate **18**, ~25% of methyl 3,4-di-*O*-acetyl-2,6-di-*O*-pivaloyl-α-D-mannopyranoside (**30**) was identified in the remaining non-deoxygenated material. After deacetylation of the purified diacetate mixtures, **13, 26,** and the monodeoxygenated compounds **12, 22,** and **25** were obtained pure by chromatography. Details of the mechanism of the ester rearrangement will be reported elsewhere.

Mass-spectral data for the above-mentioned compounds and for methyl 3,4-di-*O*-acetyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (**14**), methyl 2,4-di-*O*-acetyl-3,6-dideoxy-α-D-*arabino*-hexopyranoside (**27**), and the monodeoxygenated compounds **8, 11, 21,** and **24** are recorded in Table I. The mass spectra are characterised in the upper mass range by the fragments $M^+ - Me$, $- OMe$, $- AcOH$, and $- MeOH - Me$ for the pivaloyl esters, and $M^+ - H$, $- OMe$, and $- AcOH$ for the dideoxy compounds. In the lower mass range, the ions $C_4H_{13}^+$, $C_4H_{13}CO^+$, and Ac^+ were predominant.



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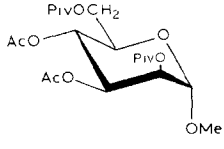

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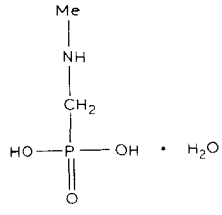

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During the irradiation procedure, a colourless, water-soluble, crystalline precipitate was formed which was identified as methylaminomethylphosphonic acid monohydrate (**31**) and is a degradation product of HMPT formed by a photochemically initiated reaction with water. The same product was obtained when the irradiation was carried out in absence of the diesters **4** or **13**. Loss of light-intensity caused by the slurry of this crystalline side-product can be avoided by continuous addition of water during the photochemical procedure.

Regioselective pivaloylation of methyl α-D-glucopyranoside and methyl α-D-mannopyranoside followed by photochemical deoxygenation constitutes a new and simple route to methyl 2,6-dideoxy-α-D-*arabino*-hexopyranoside (methyl α-D-olivoside) and methyl 3,6-dideoxy-α-D-*arabino*-hexopyranoside (methyl α-D-tyveloside).

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi Model 510 melting-point apparatus and are uncorrected. Optical rotations were measured

TABLE I

MASS-SPECTRAL DATA FOR THE DIACETATE MIXTURES OBTAINED AFTER 80% CONVERSION OF THE STARTING MATERIAL

m/z	*Relative intensity (%)*			
	5	**29**	**18**	**30**
431	0.09	0.05	0.12	0.10
415	0.53	0.47	0.90	0.46
399	0.38	0.37	0.85	0.43
386	0.07	0.10	0.11	0.05
85	57	67	80	69
57	100	100	100	100
43	36	57	53	35
	8	**11**	**21**	**24**
331		0.02		0.02
315	0.75	0.18	1.89	0.43
299	0.13	0.01	0.57	0.21
286	0.86	0.04	0.13	0.08
85	59	19	92	32
57	100	31	100	53
43	70	100	79	100
	14	**27**		
245	0.01	0.02		
215	0.08	3.30		
186	0.07	1.43		
43	100	100		

with a Perkin–Elmer Model 241 polarimeter. T.l.c. was performed on silica gel 60 (Merck) with *A*, ether; *B*, ethyl acetate; *C*, ether–methanol (3:1); and *D*, benzene–ethyl acetate (5:1); and detection with anthrone in sulfuric acid (0.2% solution). Column chromatography was carried out on Silica Woelm 32–100 (32–100 mesh), using ethyl acetate or ether. I.r. spectra were recorded with a Perkin–Elmer Model 377 spectrometer on dispersions in potassium bromide (2 mg/g). N.m.r. spectra were recorded with Varian EM 390 (^{1}H, 90 MHz) and CFT-20 (^{13}C, 20 MHz) spectrometers, for solutions (50 mg/mL) in $CDCl_3$, D_2O, or pyridine-d_5 with internal Me_4Si or sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS), as appropriate. Mass spectra (e.i.) were obtained by using a Finnegan MAT 212 spectrometer (70 eV, 0.5 mA, 200°) coupled to a Varian GC 3900 [OV 101 in a glass-capillary column (50 m × 0.3 mm i.d.); injector temperature, 240°; temperature programme, 160°→235° at 3°/min]. Irradiation was carried out in a Grantzel model 400 photoreactor[26] (200 W, 253.7 nm).

*Selective acylation of methyl α-*D*-glucopyranoside* (**3**) *and methyl α-*D*-mannopyranoside* (**16**). — To a solution of **3** or **16** (19.42 g, 0.10 mol) in dry pyridine

(300 mL) at −20° was added during 2 h, with vigorous stirring and exclusion of moisture, a solution of pivaloyl chloride (26.53 g, 0.22 mol) in dry dichloromethane (50 mL). After a further 2 h at −20°, the mixture was allowed to attain room temperature and, after 48 h, kept at 60° for 30 min. Dichloromethane and pyridine (200 mL) were distilled off under reduced pressure. Dichloromethane (500 mL) was added to the residue, and pyridine was removed by washing with aqueous 10% sulfuric acid, water, and saturated, aqueous sodium hydrogencarbonate. The organic solution was dried (Na_2SO_4) and concentrated, and the remaining syrupy residue was crystallised from hexane–benzene (7:1), to give **4** and **17**.

Methyl 2,6-di-*O*-pivaloyl-α-D-glucopyranoside (**4**; 28.81 g, 79.5%) had m.p. 90–91° (after three recrystallisations from hexane), $[\alpha]_D^{27}$ +89° (*c* 1, chloroform); lit.[23] m.p. 82–83°, $[\alpha]_D^{20}$ +57° (*c* 1, chloroform).

The 3,4-diacetate (**5**) of **4** had m.p. 105–106°, $[\alpha]_D^{26}$ +123° (*c* 1, chloroform); lit.[23] m.p. 99–101°, $[\alpha]_D^{22}$ +118° (*c* 1, chloroform).

Treatment of **4** with chlorotrimethylsilane, hexamethyldisilazane, and pyridine gave methyl 2,6-di-*O*-pivaloyl-3,4-di-*O*-trimethylsilyl-α-D-glucopyranoside (**6**, 75%), m.p. 71–72° (from hexane), $[\alpha]_D^{26}$ +120° (*c* 1.5, chloroform), R_F 0.80 (solvent *D*).

Anal. Calc. for $C_{23}H_{46}O_8Si_2$: C, 54.51; H, 9.15. Found: C, 54.55; H, 9.19.

Methyl 3,6-di-*O*-pivaloyl-α-D-mannopyranoside (**17**; 29.54 g, 81.5%) had m.p. 99–100°, $[\alpha]_D^{25}$ +52° (*c* 1, chloroform), R_F 0.27 (solvent *D*). N.m.r. data: ^1H (pyridine-d_5) δ 1.20 (s, 9 H, pivaloyl ^{t}Bu), 1.25 (s, 9 H, pivaloyl ^{t}Bu), 3.36 (s, 3 H, OMe), 4.15 (ddd, 1 H, H-5), 4.50 (m, 3 H, H-2,4,6), 4.90 (dd, 1 H, H-6′), 4.97 (d, 1 H, H-1), 5.58 (dd, 1 H, H-3), 6.58 (bs, 1 H, OH), and 6.87 (bs, 1 H, OH); $J_{1,2}$ 1.5, $J_{2,3}$ 3.3, $J_{3,4}$ 9.4, $J_{4,5}$ 9.6, $J_{5,6}$ 6.6, $J_{5,6'}$ 2.1, $J_{6,6'}$ −11.6 Hz; ^{13}C ($CDCl_3$) δ 27.16 (pivaloyl Me, $^1J_{C,H}$ 128 Hz), 27.20 (pivaloyl Me, $^1J_{C,H}$ 128 Hz), 38.91 (pivaloyl C^q), 39.07 (pivaloyl C^q), 54.84 (OMe, $^1J_{C,H}$ 143 Hz), 63.87 (C-6, $^1J_{C,H}$ 149 Hz), 66.25 (C-4, $^1J_{C,H}$ 148 Hz), 69.27 (C-2, $^1J_{C,H}$ 151 Hz), 71.00 (C-5, $^1J_{C,H}$ 148 Hz), 74.16 (C-3, $^1J_{C,H}$ 148 Hz), 100.62 (C-1, $^1J_{C,H}$ 169 Hz), 178.90 (pivaloyl COO), and 178.99 (pivaloyl COO).

Anal. Calc. for $C_{17}H_{30}O_8$: C, 56.34; H, 8.34. Found: C, 56.14; H, 8.37.

The 2,4-diacetate (**18**) of **17** had m.p. 110.5–111.5°, $[\alpha]_D^{26}$ +115° (*c* 0.8, chloroform).

Anal. Calc. for $C_{21}H_{34}O_{10}$: C, 56.49; H, 7.68. Found: C, 56.46; H, 7.76.

The 2,4-di-*O*-trimethylsilyl derivative (**19**) of **17** had m.p. 85–87° (softening at 81°) (from hexane), $[\alpha]_D^{26}$ +27° (*c* 1, chloroform), R_F 0.78 (solvent *D*).

Anal. Calc. for $C_{23}H_{46}O_8Si_2$: C, 54.51; H, 9.15. Found: C, 54.44; H, 9.07.

Photochemical deoxygenation of **4** *and* **17**. — A solution of **4** or **17** (4 g, 11.04 mmol) in HMPT–water (95:5, 200 mL) was irradiated[26] for 168 h whilst a slow stream of nitrogen was bubbled through the mixture. When the formation of the white precipitate **31** began, water was added at a rate sufficient to just dissolve the crystals; the final ratio of HMPT–water was 85:15. The reaction mixture was then worked-up as in (*a*) or (*b*).

(*a*) Water and HMPT were distilled off at 10^{-3} mmHg using a 10-cm Vigreux-column. The syrupy residue was eluted from a short column of silica gel with ether, and subsequent column chromatography (ethyl acetate) yielded **10** and **13** (from **4**), and **20, 23,** and **26** (from **17**)

Methyl 2-deoxy-6-*O*-pivaloyl-α-D-*arabino*-hexopyranoside (**10**; 0.275 g, 9.5%), syrup, $[\alpha]_D^{24}$ +70° (*c* 1.4, chloroform), R_f 0.29 (solvent *B*). N.m.r. data: ^{1}H (pyridine-d_5) δ 1.23 (s, 9 H, pivaloyl ^{t}Bu), 2.27 (ddd, 1 H, H-2*a*), 2.52 (ddd, 1 H, H-2*e*), 3.43 (s, 3 H, OMe), 4.13 (ddd, 1 H, H-5), 4.10–4.60 (m, 2 H, H-3,4), 4.58 (dd, 1 H, H-6), 4.88 (m, 1 H, H-1), 4.95 (dd, 1 H, H-6'), and 5.80 (bs, 2 H, OH); $J_{1,2a}$ 3.0, $J_{1,2e}$ 3.0, $J_{2a,2e}$ −13.0, $J_{2a,3}$ 10.2, $J_{2e,3}$ 5.4, $J_{3,4}$ 10.0, $J_{5,6}$ 7.0, $J_{5,6'}$ 2.0 Hz; ^{13}C ($CDCl_3$), δ 27.31 (pivaloyl Me, $^1J_{C,H}$ 128 Hz); 36.93 (C-2, $^1J_{C,H}$ 128 Hz); 38.92 (pivaloyl C^q); 54.36 (OMe, $^1J_{C,H}$ 142 Hz), 65.13 (C-6, $^1J_{C,H}$ 148 Hz); 62.44 ($^1J_{C,H}$ 142 Hz), 68.17 ($^1J_{C,H}$ 144 Hz), 73.24 ($^1J_{C,H}$ 148 Hz) (C-3,4,5), 101.31 (C-1, $^1J_{C,H}$ 168 Hz); and 178.26 (pivaloyl COO).

Anal. Calc. for $C_{12}H_{22}O_6$: C, 54.95; H, 8.46. Found: C, 55.17; H, 8.62.

Methyl 6-deoxy-3-*O*-pivaloyl-α-D-mannopyranoside (**20**; 0.162 g, 5.6%), syrup, $[\alpha]_D^{24}$ +52° (*c* 0.5, chloroform); R_f 0.34 (solvent *A*), 0.39 (solvent *B*). N.m.r. data ($CDCl_3$). ^{1}H, δ 1.15 (s, 9 H, pivaloyl ^{t}Bu), 1.20 (d, 3 H, Me), 2.66 (bs, 2 H, OH), 3.28 (s, 3 H, OMe), 4.54 (d, 1 H, H-1), 4.78 (m, 1 H, H-3), and 3.30–4.00 (m, 3 H, H-2,4,5); $J_{1,2}$ 2.0, $J_{3,4}$ 10.0, $J_{5,Me}$ 6.0 Hz; ^{13}C, δ 17.32 (C-6); 26.93 (pivaloyl Me); 38.88 (pivaloyl C^q); 54.70 (OMe); 68.36, 69.42, 71.24, 74.36 (C-2,3,4,5); 100.47 (C-1); and 179.06 (pivaloyl COO)

Anal. Calc. for $C_{12}H_{22}O_6$: C, 54.95, H, 8.46 Found: C, 54.65; H, 8.60.

Methyl 3-deoxy-6-*O*-pivaloyl-α-D-*arabino*-hexopyranoside (**23**; 0.295 g, 10.2%), syrup, $[\alpha]_D^{24}$ +68° (*c* 1.7, chloroform); R_f 0.16 (solvent *A*), 0.27 (solvent *B*). N.m.r. data: ^{1}H (pyridine-d_5), δ 1.22 (s, 9 H, pivaloyl ^{t}Bu), 2.10–2.70 (m, 2 H, H-3*a*,3*e*), 3.44 (s, 3 H, OMe), 4.00–5.10 (m, 6 H, H-1,2,4,5,6,6'), and 6.6 (bs, 2 H, OH); ^{13}C ($CDCl_3$), δ 27.24 (pivaloyl Me, $^1J_{C,H}$ 128 Hz); 34.75 (C-3, $^1J_{C,H}$ 130 Hz), 38.99 (pivaloyl C^q); 54.72 (OMe, $^1J_{C,H}$ 144 Hz); 62.19 ($^1J_{C,H}$ 144 Hz) 68.09 ($^1J_{C,H}$ 148 Hz), 72.05 ($^1J_{C,H}$ 148 Hz) (C-2,4,5); 64.29 (C-6, $^1J_{C,H}$ 148 Hz). 100.08 (C-1, $^1J_{C,H}$ 168 Hz); and 179.53 (pivaloyl COO)

Anal. Calc. for $C_{12}H_{22}O_6$: C, 54.95; H, 8.46 Found C, 55.12; H, 8.50.

Methyl 2,6-dideoxy-α-D-*arabino*-hexopyranoside (**13**; 0.247 g, 13.8%), $[\alpha]_D^{20}$ +84° (*c* 1.8, water); lit.[18] $[\alpha]_D$ +86.4° (water), lit.[14] +120° (water). The ^{1}H-n.m.r. spectrum was in good agreement with published data[13,14]

The 3,4-dibenzoate (**15**) of **13** had m.p. and mixture m.p. 81°, $[\alpha]_D^{25}$ 0° (*c* 1, chloroform); lit.[14] m.p. 80–83°, $[\alpha]_D$ 0° (chloroform)

Methyl 3,6-dideoxy-α-D-*arabino*-hexopyranoside (**26**; 0.278 g, 15.5%) had $[\alpha]_D^{20}$ +99° (*c* 1, water); lit.[15] $[\alpha]_D$ +102.7° (water).

The 2,4-dibenzoate (**28**) of **26** had $[\alpha]_D^{20}$ −19° (*c* 2, chloroform), lit.[18] $[\alpha]_D$ −22.9° (chloroform).

(*b*) The reaction mixture was concentrated to 150 mL, first at 8 mmHg and then at 10^{-4} mmHg. The residue was then acetylated conventionally with dry

pyridine (100 mL) and acetic anhydride (50 mL) for 24 h at room temperature. A solution of the syrupy product in ether was filtered through a short column of silica gel and concentrated, and a solution of the residue in dry methanol (50 mL) was treated with sodium methoxide (0.5 g) for 24 h at 40°. T.l.c. (solvent *B*) then indicated complete removal of the ester groups. The solution was neutralised with methanolic 1% hydrogen chloride with cooling and then concentrated, and the residue was subjected to column chromatography (elution with ether or ethyl acetate).

The elution sequence for the products of the deoxygenation of **4** was (*1*) methyl 2,6-dideoxy-α-D-*arabino*-hexopyranoside (**13**; 0.451 g, 25.2%); (*2*) methyl 2-deoxy-α-D-*arabino*-hexopyranoside (**12**; 0.384 g, 19.5%), m.p. 90–91° (from acetone–hexane), $[\alpha]_D^{20}$ +134° (*c* 1, water); lit.[27] m.p. 90–92°, $[\alpha]_D$ +135° (water).

The elution sequence for the products of the deoxygenation of **17** was (*1*) methyl 3,6-dideoxy-α-D-*arabino*-hexopyranoside (**26**; 0.475 g, 26.5%); (*2*) methyl 6-deoxy-α-D-mannopyranoside (**22**; 0.108 g, 5.5%), $[\alpha]_D^{25}$ +59° (*c* 1, water); lit.[28] $[\alpha]_D$ +64.5° (water); (*3*) methyl 3-deoxy-α-D-*arabino*-hexopyranoside (**25**; 0.299 g, 15.2%), m.p. 122–123°, $[\alpha]_D^{20}$ +126.5° (*c* 1, methanol); lit.[29] m.p. 123.5–124°, $[\alpha]_D$ +129.6° (methanol).

Methylaminomethylphosphonic acid monohydrate (**31**). — The precipitate formed after a few hours of irradiation (see above) was collected, washed with dry ether, acetonitrile, tetrachloromethane, and hexane, and dried under diminished pressure. It decomposed at 270° (sintering at 232°); ν_{max} 3400 (OH, H_2O) and 3030–2630 (NH_2^+). N.m.r. data (D_2O): ^1H, δ 3.66 (s, 3 H, Me), 4.00 (d, 2 H, CH_2, $^2J_{H,^{31}P}$ 12.6 Hz); ^{13}C, δ 43.40 (dtq, Me, $^3J_{C,^{31}P}$ 13, $^3J_{C,H}$ 4, $^1J_{C,H}$ 134 Hz), 56.25 (dt, CH_2, $^1J_{C,^{31}P}$ 138, $^1J_{C,H}$ 137 Hz).

Anal. Calc. for $C_2H_8NO_3P \cdot H_2O$: C, 16.8; H, 7.1; N, 9.8. Found: C, 17.1; H, 7.2; N, 10.3.

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