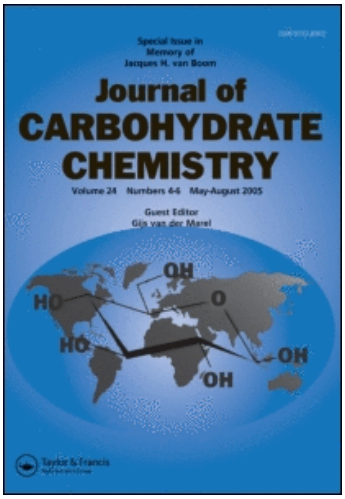

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Synthesis of Substituted 1-\C\-Phenyl-D-Tetritols and 1-*C*-(1*H*-Pyrazol-4-yl)-D-tetritols by Ring Transformation of 2-Formylglycals

Alina Montero[ab]; Manfred Michalik[c]; Holger Feist[a]; Helmut Reinke[a]; Ivo Rudloff[ad]; Klaus Peseke[a]
[a] Fachbereich Chemie, Universität Rostock, Rostock, Germany [b] Centro de Bioactivos Químicos, Universidad Central de Las Villas, Santa Clara, Cuba [c] Leibniz-Institut für Organische Katalyse, Rostock, Germany [d] Oswel Research Products Ltd., Lab 5005 — Medical and Biological Science Building, University of Southampton-Boldrewood, Southampton, UK

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Synthesis of Substituted 1-*C*\-Phenyl-D-Tetritols and 1-*C*-(1*H*-Pyrazol-4-yl)-D-tetritols by Ring Transformation of 2-Formylglycals[#,‡]

Alina Montero,[1,2] Manfred Michalik,[3] Holger Feist,[1] Helmut Reinke,[1] Ivo Rudloff,[1,4] and Klaus Peseke[1,*]

[1]Fachbereich Chemie, Universität Rostock, Rostock, Germany
[2]Centro de Bioactivos Químicos, Universidad Central de Las Villas, Santa Clara, Cuba
[3]Leibniz-Institut für Organische Katalyse, Rostock, Germany
[4]Oswel Research Products Ltd., Lab 5005 — Medical and Biological Science Building, University of Southampton-Boldrewood, Southampton, UK

CONTENTS

[#]Dedicated to Professor Dr. Dr. hc. Adolf Zschunke on the occasion of his 65th birthday.
[‡]Presented at the XXth International Carbohydrate Symposium, Hamburg, Germany, 2000.
[*]Correspondence: Klaus Peseke, Fachbereich Chemie, Universität Rostock, D-18051, Rostock, Germany; Fax: +49-381-498-6412; E-mail: klaus.peseke@chemie.uni-rostock.de.

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ABSTRACT

2-Formylglycals **1a,b** reacted with dialkyl 3-oxoglutarates in the presence of base to furnish the 5-[(1*R*,2*R*(*S*),3*R*)-1,2,4-tris(benzyloxy)-3-hydroxy-butyl]-2-hydroxy-isophthalic acid dialkyl esters **2a–d**. Treatment of **1a,b** with hydrazine derivatives afforded the substituted 1,2,4-tri-*O*-benzyl-1*C*-(1*H*-pyrazol-4-yl)-D-tetritols **5a–d**. Deprotection of **5a,b** was achieved with Pd/H_2 to yield the 1*C*-(1-methyl-1*H*-pyrazol-4-yl)-D-tetritols **6a,b**.

Key Words: Formylglycals; Acyclo–*C*–nucleosides; Pyrazoles; Isophthalic acid esters; Ring transformation; Push–pull alkenes.

INTRODUCTION

Owing to their potential biological properties, substantial efforts have been devoted to the synthesis of modified nucleosides since their discovery.[1–8] In order to obtain less toxic, less susceptible to viral resistance or more active compounds of this type new syntheses have been developed. Furthermore, the syntheses of heterocycles with a polyhydroxyalkyl chain have attracted great interest in synthetic organic chemistry.[9–11]

In earlier studies, we investigated the ring transformations of *C*-branched, unsaturated sugars with *push–pull* functionalisation to furnish a new class of modified acyclo-*C*-nucleosides.[12–15] We describe in this paper the reactions of 2-formylglycals using 1,3-*C*,*C*′- and 1,2-*N*,*N*′-dinucleophiles to obtain new acyclo-*C*-nucleoside analogues.

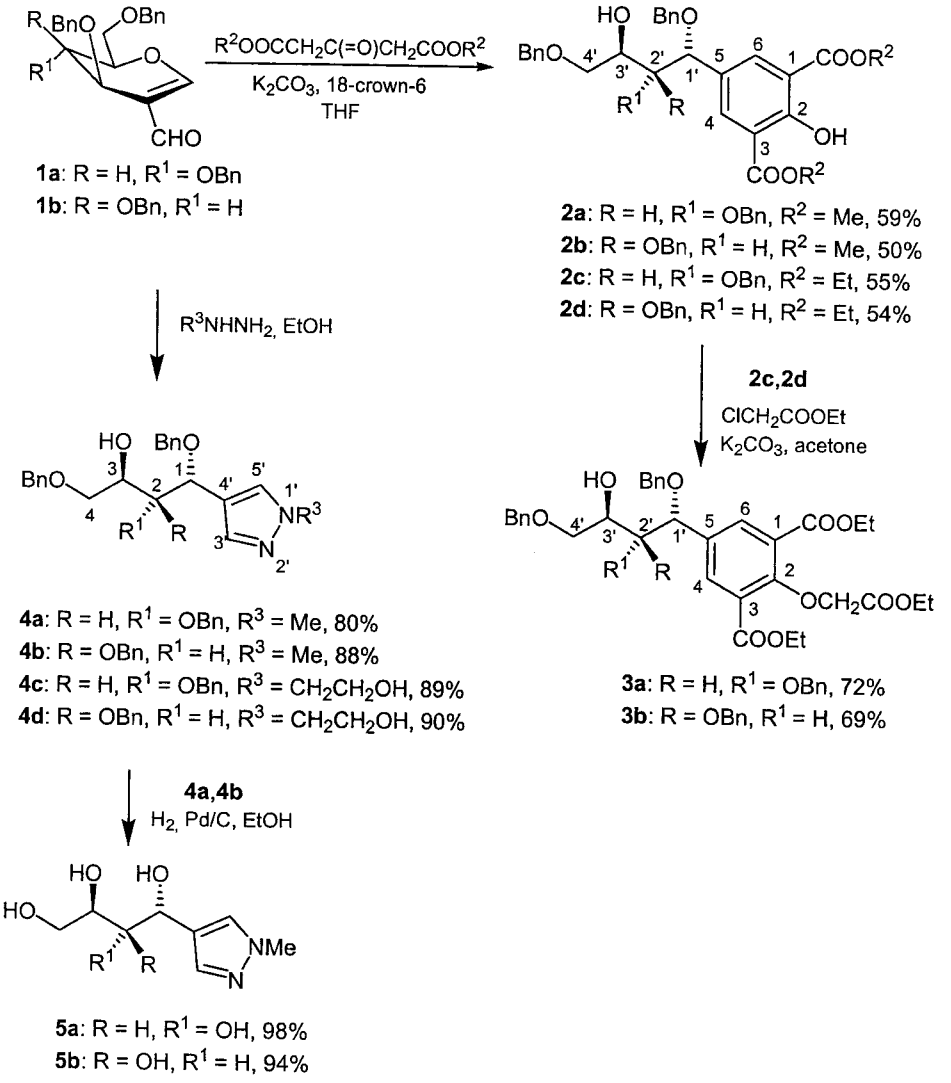
RESULTS AND DISCUSSION

Because of their *push–pull* activated carbon–carbon double bond,[16–18] 2-formylglycals **1a,b**[19] synthesised by a Vilsmeier–Haack reaction of *O*-benzyl protected glycals are a versatile class of compounds, which should allow the nucleophilic attack of dinucleophiles at C-1 under ring opening of the glycals followed by cyclisation involving the formyl group. Treatment of **1a,b** under reflux with dialkyl 3-oxoglutarates as 1,3-*C*,*C*′-dinucleophiles and potassium carbonate in presence of crown ether afforded the expected 5-[(1*R*,2*R*(*S*),3*R*)-1,2,4-tris(benzyloxy)-3-hydroxy-butyl]-2-hydroxy-isophthalic acid dialkyl esters **2a–d** in such ring transformation reactions (Sch. 1).

The NMR spectra of these compounds showed the absence of signals for the formyl group and the presence of two hydroxy and alkoxycarbonyl groups. All the other analytical data are in accordance with the proposed open-chain sugar structures as well. The NMR signals of the carbon and hydrogen atoms could unambiguously be assigned with ^{13}C, ^{1}H correlation experiments confirming the postulated structures.

Furthermore, an x-ray structure of compound **2d** could be obtained. An ORTEP drawing is shown in Fig. 1.

The crystal structure of **2d** is dominated by the formation of hydrogen bridges. The infinite chains of molecules along the *b* axis are formed by bridges between the hydroxyl group at C-3 and one of the carbonyl groups of a neighbouring molecule. The other hydroxyl group at C-4′ is involved in an intramolecular hydrogen bridge towards one of



Scheme 1.

the carbonyl groups in the same molecule. This phenomenon helps to explain the complex infrared spectra of **2d.**

In order to obtain benzofuran derivatives, we carried out the reactions of **2c**,**d** with ethyl chloroacetate in the presence of potassium carbonate in acetone. After a first step, the 5-[(1*R*,2*R*(*S*),3*R*)-1,2,4-tris(benzyloxy)-3-hydroxy-butyl]-2-ethoxycarbonylmethoxy-isophthalic acid diethyl esters **3a,b** were isolated. However, the desired heterocyclisation to yield the corresponding 5-[(1*R*,2*R*(*S*),3*R*)-1,2,4-tris(benzyloxy)-3-hydroxy-butyl]-3-hydroxy-benzo[*b*]furan-2,7-dicarboxylic acid diethyl esters could not be achieved.

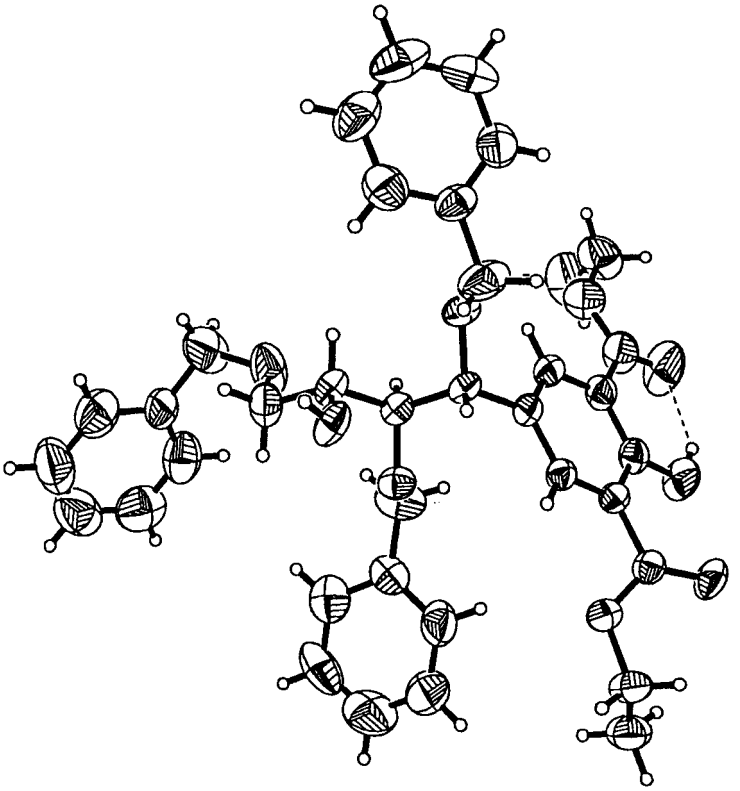


Figure 1. ORTEP drawing of **2d**.

The *push–pull* functionality of **1a**,**b** should also allow reactions with 1,2-*N*,*N*′-dinucleophiles. In analogy to similar *push–pull* compounds,[17–19] the nucleophilic attack of hydrazine derivatives at C-1 was accompanied by cyclisation involving the formyl group to furnish the corresponding pyrazole ring. In this manner, treatment of the starting materials with methylhydrazine and 2-hydrazinoethanol, respectively, under reflux afforded the substituted (1*R*)-1,2,4-tri-*O*-benzyl-1-*C*-(1*H*-pyrazol-4-yl)-D-alditols **4a–d**. The IR and the ^{13}C NMR spectra of these products showed the absence of signals for the formyl group. Furthermore, the successful ring transformation was proven by observing the typical long range coupling between the pyrazol protons H-3′ and H-5′ ($^4J \sim 0.6$ Hz for **4a**,**b** and 0.9 Hz for **4c**,**d**, respectively) in the ^1H NMR spectrum due to the W-arrangement. Furthermore, in the ^1H NMR spectra of **4c**, **d** appeared an additional signal for an OH group. ^{13}C, ^1H and ^1H, ^1H correlation spectra allowed the unambiguous assignment of all signals for the proposed structures. Thus, the distinction of H-3′ and H-5′ was possible by a correlation found for H-5′ and N–Me in the NOESY spectrum of **4b**.

Finally, we examined the deprotection of the synthesised systems for two examples. The catalytic hydrogenation[20] of compounds **4a,b** was successful and afforded the

acyclo-*C*-nucleoside analogues **5a,b** in very good yields. In the ^{1}H NMR of **5a**,**b** spectra signals for benzyl groups were absent and instead four signals for OH groups were found.

In conclusion, we described here starting from *push–pull* functionalised unsaturated sugars a simple method to prepare aryl and hetaryl *C*-substituted alditoles to be considered as new acyclo-*C*-nucleoside analogues.

EXPERIMENTAL

General Procedures

TLC was carried out on silica gel 60 GF_{254} (Merck) with detection by UV light ($\lambda = 254$ nm) and/or by charring with 5% sulfuric acid in methanol. Silica gel 60 (63–200 mesh) (Merck) was used for column chromatography. Melting points were determined by using a Boetius melting point apparatus and are corrected. Specific rotations were determined with a Polar LμP (IBZ Messtechnik). IR spectra were recorded with a Nicolet 205 FT-IR spectrometer. ^{1}H NMR (300.13 and 250.13 MHz, respectively) and ^{13}C NMR (75.5 and 62.9 MHz, respectively) spectra were recorded on Bruker instruments ARX 300 and AC 250, respectively, with $CDCl_3$ or DMSO-d_6 as solvent. The calibration of spectra was carried out on TMS (internal, ^{1}H) and solvent (^{13}C) signals (δ^1H TMS = 0; δ^{13}C $CDCl_3$ = 77.0, DMSO-d_6 = 39.7). The ^{1}H and^{13}C NMR signals were assigned by DEPT and/or two-dimensional ^{1}H, ^{13}C correlation experiments. The mass spectra were recorded on an AMD 402/3 spectrometer (AMD Intectra GmbH). Elemental analysis was performed on a Leco CHNS-932 instrument. For chromatography Merck silica gel 60 (230–400 mesh) was used.

5-[(1*R*,2*R*,3*R*)-1,2,4-Tris(benzyloxy)-3-hydroxy-butyl]-2-hydroxy-isophthalic acid dimethyl ester (2a). Potassium carbonate (60 mg), 18-crown-6 (50 mg), and dimethyl 3-oxoglutarate (0.043 mL, 0.3 mmol) were added to a solution of 2-formyl-3,4,6-tri-*O*-benzyl-D-glucal **1a** (100 mg, 0.225 mmol) in THF (5 mL). The mixture was then heated under reflux and stirred for 6 hr. After this time another amount of dimethyl 3-oxoglutarate (0.043 mL, 0.3 mmol) was added. The solution was refluxed again and stirring was continued up to the disappearance of **1a** (7 hr, TLC control). After filtration, the solvent was evaporated and the residue purified by column chromatography (toluene/EtOAc 9 : 1). Compound **2a** was isolated as a colourless syrup. Yield 80 mg (59%); $[\alpha]_D^{23}$ − 50.3 ($c = 1$, $CHCl_3$); R_f 0.24 (toluene/EtOAc 9 : 1). IR (film), (cm^{-1}): 3446 (OH); 1732, 1720, 1678 (C═O); 1613 (C═C). ^{1}H NMR (300.13 MHz, $CDCl_3$), δ 1.92 (br, 1H, OH-3′); 3.50 (dd, 1H, $^3J_{1,2} = 3.0$ Hz, $^3J_{2,3} = 7.3$ Hz, H-2′); 3.52–3.56 (m, AB part of ABX, 2H, H-4′a,b); 3.84 (s, 6H, Me); 3.94 (m, 1H, H-3′); 3.98 (d, 1H, $^2J = 11.0$ Hz, C*H*HPh); 4.17 (d, 1H, $^2J = 11.8$ Hz, C*H*HPh); 4.26 (d, 1H, $^2J = 11.0$ Hz, C*H*HPh); 4.43 (s, 2H, CH_2Ph); 4.47 (d, 1H, $^2J = 11.8$ Hz, C*H*HPh); 4.61 (d, 1H, H-1′); 6.91–6.97 (m, 2H, Ph); 7.07–7.14 (m, 3H, Ph); 7.17–7.30 (m, 10H, Ph); 7.99 (s, 2H, H-4, H-6); 11.69 (s, 1H, OH-2). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ 52.3 (Me); 70.1 (C-3′); 70.9, 71.3, 73.5, 74.6 (C-4′, CH_2Ph); 78.7 (C-1′); 82.0 (C-2′); 116.4 (C-1, C-3); 127.6, 127.8 (*p*-Ph); 128.0, 128.1, 128.3, 128.4, 128.5 (*o*-, *m*-,*p*-Ph); 129.0 (C-5); 135.6 (C-4, C-6); 137.4 (2x), 137.8 (*i*-Ph); 161.1 (C-2); 167.9 (C═O). MS (FAB positive, NBA/NaCl), m/z (%): 623 (100) $[M + Na]^+$.

Anal. calcd for $C_{35}H_{36}O_9$(600.65): C, 69.99; H, 6.04. Found: C, 69.96; H, 5.79.

5-[(1*R*,2*S*,3*R*)-1,2,4-Tris(benzyloxy)-3-hydroxy-butyl]-2-hydroxy-isophthalic acid dimethyl ester (2b). The reaction of **1b** with dimethyl 3-oxoglutarate was carried out as described above for the preparation of **2a**. Compound **2b** was isolated as a white solid after recrystallisation from *n*-heptane. Yield 68 mg (50%); mp 78–81°C; $[\alpha]_D^{23}$ −29.0 ($c = 1$, $CHCl_3$); R_f 0.24 (toluene/EtOAc 9 : 1). IR (KBr), ν (cm^{-1}): 3414 (OH); 1742, 1705, 1682 (C═O); 1610 (C═C). ^1H NMR (300.13 MHz, $CDCl_3$), δ 2.00 (br, 1H, OH-3′); 3.45 (dd, 1H, $^2J_{4a,4b} = 9.5$ Hz, $^3J_{3,4a} = 6.1$ Hz, H-4′a); 3.51 (dd, 1H, $^3J_{3,4b} = 6.1$ Hz, H-4′b); 3.54 (dd, 1H, $^3J_{1,2} = 8.1$ Hz, $^3J_{2,3} = 2.2$ Hz, H-2′); 3.86 (s, 6H, Me); 3.86 (d, 1H, $^2J = 10.8$ Hz, C*H*HPh); 4.10 (dt, 1H, H-3′); 4.16 (d, 1H, $^2J = 10.8$ Hz, C*H*HPh); 4.21 (d, 1H, $^2J = 11.6$ Hz, C*H*HPh); 4.36 (d, 1H, $^2J = 11.6$ Hz, C*H*HPh); 4.45 (d, 1H, H-1′); 4.43, 4.47 (q(AB), 2H, $^2J = 11.9$ Hz, CH_2Ph); 6.80–6.88 (m, 2H, Ph); 7.05–7.14 (m, 3H, Ph); 7.15–7.31 (m, 10H, Ph); 7.98 (s, 2H, H-4, H-6); 11.69 (s, 1H, OH-2). ^{13}C NMR (62.9 MHz, $CDCl_3$), δ 52.4 (Me); 69.4 (C-3′); 71.0 (*C*H_2Ph); 71.1 (C-4′); 73.5, 74.4 (*C*H_2Ph); 79.4 (C-1′); 81.1 (C-2′); 116.3 (C-1, C-3); 127.7–128.4 (Ph); 129.7 (C-5); 135.6 (C-4, C-6); 137.0, 137.4, 137.8 (*i*-Ph); 161.2 (C-2); 167.8 (C═O). MS (FAB positive, NBA/NaCl), m/z (%): 623 (100) $[M + Na]^+$.

Anal. calcd for $C_{35}H_{36}O_9$(600.65): C, 69.99; H, 6.04. Found: C, 70.01; H, 6.16.

5-[(1*R*,2*R*,3*R*)-1,2,4-Tris(benzyloxy)-3-hydroxy-butyl]-2-hydroxy-isophthalic acid diethyl ester (2c). Diethyl 3-oxoglutarate (0.108 mL, 0.6 mmol) and 2-formyl-3,4,6-tri-*O*-benzyl-D-glucal **1a** (100 mg, 0.225 mmol) were reacted as described for the preparation of **1a**. Compound **2c** was isolated as a colourless syrup. Yield 78 mg (55%); $[\alpha]_D^{24}$ −33.7 ($c = 1$, $CHCl_3$); R_f 0.29 (toluene/EtOAc 9 : 1). IR (film), ν (cm^{-1}): 3429 (OH); 1731, 1717, 1672 (C═O); 1612 (C═C). ^1H NMR (300.13 MHz, $CDCl_3$), δ 1.31 (t, 6H, $^3J = 7.3$ Hz, Me); 2.42 (br, 1H, OH-3′); 3.49 (dd, 1H, $^3J_{1,2} = 3.0$ Hz, $^3J_{2,3} = 7.6$ Hz, H-2′); 3.52–3.60 (m, AB part of ABX, 2H, H-4′a,b); 3.96 (d, 1H, $^2J = 11.0$ Hz, C*H*HPh); 3.97 (m, 1H, H-3); 4.18 (d, 1H, $^2J = 11.8$ Hz, C*H*HPh); 4.22 (d, 1H, $^2J =$ 11.0 Hz, C*H*HPh); 4.32 (m, 4H, CH_2); 4.44 (s, 2H, CH_2Ph); 4.48 (d, 1H, $^2J = 11.8$ Hz, C*H*HPh); 4.63 (d, 1H, H-1′); 6.90–6.96 (m, 2H, Ph); 7.06–7.13 (m, 3H, Ph); 7.14–7.31 (m, 10H, Ph); 7.98 (s, 2H, H-4, H-6); 11.76 (s, 1H, OH-2). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ 14.2 (Me); 61.5 (CH_2); 70.1 (C-3′); 70.9, 71.3, 73.5, 74.7 (C-4′, *C*H_2Ph); 78.6 (C-1′); 82.0 (C-2′); 116.7 (C-1, C-3); 127.6, 127.9 (*p*-Ph); 128.0, 128.1, 128.4, 128.4, 128.5 (*o*-, *m*-, *p*-Ph); 128.9 (C-5); 135.2 (C-4, C-6); 137.4, 137.5, 137.8 (*i*-Ph); 161.2 (C-2); 167.5 (C═O). MS (CI, *iso*-butane), m/z (%): 629 (0.5) $[M + H]^+$, 91 (100).

Anal. calcd for $C_{37}H_{40}O_9$(628.71): C, 70.68; H, 6.41. Found: C, 70.74; H, 6.32.

5-[(1*R*,2*S*,3*R*)-1,2,4-Tris(benzyloxy)-3-hydroxy-butyl]-2-hydroxy-isophthalic acid diethyl ester (2d). The reaction of **1b** with diethyl 3-oxoglutarate was carried out as described above for the preparation of **2c**. Recrystallisation from dichloromethane/*n*-heptane yielded **2d** as colourless crystals. Yield 76 mg (54%); mp 78–81°C; $[\alpha]_D^{24}$ − 23.4 ($c = 0.5$, $CHCl_3$); R_f 0.33 (toluene/EtOAc 9 : 1). IR (KBr), ν (cm^{-1}): 3429 (OH); 1732, 1708, 1665 (C═O); 1612 (C═C). ^1H NMR (250.13 MHz, $CDCl_3$), δ 1.34 (t, 6H, $^3J = 7.3$ Hz, Me); 2.53 (br, 1H, OH-3′); 3.45 (dd, 1H, $^2J_{4a,4b} = 9.5$ Hz, $^3J_{3,4a} = 6.1$ Hz, H-4′a); 3.52 (dd, 1H, $^3J_{3,4b} = 6.1$ Hz, H-4′b); 3.53 (dd, 1H, $^3J_{1,2} = 8.2$ Hz, $^3J_{2,3} = 2.1$ Hz, H-2′); 3.82 (d, 1H, $^2J = 11.0$ Hz, C*H*HPh); 4.12 (d, 1H, $^2J = 11.0$ Hz, C*H*HPh); 4.14 (br m, 1H, H-3′); 4.21 (d, 1H, $^2J = 11.5$ Hz, C*H*HPh); 4.34 (q, 4H, CH_2); 4.36 (d, 1H, $^2J = 11.5$ Hz, C*H*HPh); 4.46 (d, 1H, H-1′); 4.45, 4.48

(q(AB), 2H, $^2J = 11.8$ Hz, CH_2Ph); 6.80–6.88 (m, 2H, Ph); 7.05–7.14 (m, 3H, Ph); 7.15–7.30 (m, 10H, Ph); 7.99 (s, 2H, H-2′, H-6′); 11.82 (s, 1H, OH-4′). ^{13}C NMR (62.9 MHz, $CDCl_3$), δ 14.2 (Me); 61.6 (CH_2); 69.4 (C-3′); 71.0, 71.2, 73.5, 74.4 (C-4′, CH_2Ph); 79.4 (C-1′); 81.1 (C-2′); 116.6 (C-1, C-3); 127.7–128.5 (Ph); 129.6 (C-5); 135.3 (C-4, C-6); 137.0, 137.4, 137.9 (*i*-Ph); 161.4 (C-2); 167.4 (C═O). MS, (CI, *iso*-butane), m/z (%): 629 (0.5) $[M + H]^+$.

Anal. calcd for $C_{37}H_{40}O_9$(628.71): C, 70.68; H, 6.41. Found: C, 70.78; H, 6.66.

Compound **2d** was subjected to x-ray analysis at 293 K and wavelength 0.71073 Å. The crystal was sealed onto a glass fiber and mounted on a Bruker P4 automated four circle diffractometer. The structure was solved by direct methods (XS program for crystal structure solution, version 4.2 for MS-DOS, copyright Bruker Analytical X-ray Inst. Inc.) and refined by the full-matrix least squares method on F^2 (SHELXL-97; G.M. Sheldrick, Universität Göttingen, 1997). Non-H atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed into theoretical positions and were refined by using the riding model. **2d**, ($C_{37}H_{40}O_9$); formula weight = 628.69; crystal system: monoclinic; space group: $P2_1$; unit cell dimensions: $a = 11.781(3)$ Å, $b = 10.783(2)$ Å, $c = 13.171(2)$ Å, $\beta = 92.58(2)^\circ$; volume: 1671.5(6) Å^3; $Z = 2$; density (calculated): 1.249 Mg/m^3; absorption coefficient: 0.089 mm^{-1}; $F(0\,0\,0) = 668$; crystal size: $0.76 \times 0.63 \times 0.53$ mm^3; Θ range for data collection: 2.270 to 22.00°; index ranges: $-12 \le h \le 12$, $-11 \le k \le 11$, $-13 \le l \le 13$; reflections collected: 4560; independent reflections: 4075 [R(int) = 0.0489]; completeness to $\Theta = 22.00^\circ$: 99.8%; absorption correction: none; data/restraints/parameters: 4075/1/417; goodness-of-fit on F^2: 1.028; final R indices [$I > 2\sigma(I)$]: $R1 = 0.0504$, $wR2 = 0.1311$; R indices (all data): $R1 = 0.0565$, $wR2 = 0.1377$; absolute structure parameter: 0.1(13); largest different peak and hole: 0.187 and −0.161 e Å^{-3}.

CCDC-190061 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

5-[(1*R*,2*R*,3*R*)-1,2,4-Tris(benzyloxy)-3-ethoxycarbonylmethoxy-butyl]-2-hydroxy-isophthalic acid diethyl ester (3a). Ethyl chloroacetate (0.017 mL, 0.159 mmol) and potassium carbonate (43 mg) were added to a solution of **2c** (100 mg, 0.159 mmol) in acetone (5 mL). The mixture was then heated under reflux and stirring for 5 hr. After this time, the solution was filtered, the solvent was evaporated, and the residue purified by column chromatography (toluene/EtOAc 9 : 1). Compound **3a** was obtained as a colourless syrup.

Yield 82 mg (72%); $[\alpha]_D^{21}$ −35.5 ($c = 0.4$, $CHCl_3$); R_f 0.22 (toluene/EtOAc 5 : 1). IR (film), ν (cm^{-1}): 3514 (OH); 1763, 1731 (C═O). ^{1}H NMR (250.13 MHz, $CDCl_3$), δ 1.25 (t, 3H, $^3J = 7.1$ Hz, CH_3CH$_2$OC(═O)CH$_2$); 1.28 (t, 6H, $^3J = 7.1$ Hz, CH_3CH$_2$OC(═O)); 1.97 (br, 1H, OH-3′); 3.50 (dd, 1H, $^3J_{1,2} = 2.8$ Hz, $^3J_{2,3} = 7.6$ Hz, H-2′); 3.55 (m, 2H, H-4′a,b); 3.86 (d, 1H, $^2J = 10.7$ Hz, C*H*HPh); 3.95 (dt, 1H, $^3J_{3,4a} = {}^3J_{3,4b} = 4.0$ Hz, H-3′); 4.12 (d, 1H, $^2J = 10.7$ Hz, C*H*HPh); 4.19 (d, 1H, $^2J = 11.6$ Hz, C*H*HPh); 4.24 (q, 2H, CH$_3$CH_2OC(═O)CH$_2$); 4.28 (q, 4H, CH$_3$CH_2OC(═O)); 4.43 (s, 2H, CH_2Ph); 4.50 (d, 1H, $^2J = 11.6$ Hz, C*H*HPh); 4.70 (d, 1H, H-1′); 4.75 (s, 2H, CH$_3$CH$_2$OC(═O)CH_2); 6.86–6.96 (m, 2H, Ph); 7.06–7.34 (m, 13H, Ph); 7.94 (s, 2H, H-4, H-6). ^{13}C NMR (62.9 MHz, $CDCl_3$), δ 14.1 (*C*H$_3$CH$_2$OC(═O)); 14.2 (*C*H$_3$CH$_2$OC(═O)CH$_2$); 61.0 (CH$_3$*C*H$_2$OC(═O)CH$_2$); 61.5 (CH$_3$*C*H$_2$OC(═O)); 69.9 (C-3′);

70.8, 71.6, 73.5, 74.6 (C-4′, *C*H$_2$Ph); 72.2 (CH$_3$CH$_2$OC(=O)*C*H$_2$); 78.6 (C-1′); 81.8 (C-2′); 127.2 (C-1, C-3); 127.7–128.5 (Ph); 134.0 (C-4, C-6); 135.6 (C-5); 137.2, 137.3, 137.7 (*i*-Ph); 156.5 (C-2); 165.1 (CH$_3$CH$_2$O*C*(=O)); 168.7 (CH$_3$CH$_2$O*C*(=O)CH$_2$). MS (CI, *iso*-butane), *m*/*z* (%): 715 (3) [M + H]$^+$.

HRMS Calcd for C$_{41}$H$_{46}$O$_{11}$–OCH$_2$Ph: 669.26996, Found: 669.26870.

5-[(1*R*,2*S*,3*R*)-1,2,4-Tris(benzyloxy)-3-ethoxycarbonylmethoxy-butyl]-2-hydroxy-isophthalic acid diethyl ester (3b). The reaction of **3b** with chloroacetic acid ethylester was carried out as described above for the preparation of **3a** yielding a colourless syrup. Yield 78 mg (69%); $[\alpha]_D^{21}$ −19.7 (*c* = 1, CHCl$_3$); R_f0.25 (toluene/EtOAc 5 : 1). IR (film), ν (cm^{-1}): 3514 (OH); 1763, 1731 (C=O). ^{1}H NMR (300.13 MHz, CDCl$_3$), δ 1.25 (t, 3H, ^3J = 7.1 Hz, C*H*$_3$CH$_2$OC(=O)CH$_2$); 1.29 (t, 6H, ^3J = 7.1 Hz, C*H*$_3$CH$_2$OC(=O)); 2.22 (br, 1H, OH-3′); 3.42 (dd, 1H, $^2J_{4a,4b}$ = 9.4 Hz, $^3J_{3,4a}$ = 6.2 Hz, H-4′a); 3.50 (dd, 1H, $^3J_{3,4b}$ = 6.0 Hz, H-4′b); 3.53 (dd, 1H, $^3J_{1,2}$ = 8.3 Hz, $^3J_{2,3}$ = 2.0 Hz, H-2′); 2.74 (d, 1H, ^2J = 10.7 Hz, C*H*HPh); 4.04 (d, 1H, ^2J = 10.7 Hz, C*H*HPh); 4.10–4.22 (m, 2H, H-3′, C*H*HPh); 4.23 (q, 2H, CH$_3$C*H*$_2$OC(=O)CH$_2$); 4.29 (q, 4H, CH$_3$C*H*$_2$OC(=O)); 4.37 (d, 1H, ^2J = 11.3 Hz, C*H*HPh); 4.42, 4.47 (q, AB), 2H, ^2J = 11.9 Hz, C*H*$_2$Ph); 4.54 (d, 1H, H-1′); 4.73 (s, 2H, CH$_3$CH$_2$OC(=O)C*H*$_2$); 6.82–6.86 (m, 2H, Ph); 7.05–7.30 (m, 13H, Ph); 7.95 (s, 2H, H-4, H-6). ^{13}C NMR (75.5 MHz, CDCl$_3$), δ 14.1 (*C*H$_3$CH$_2$OC(=O)); 14.2 (*C*H$_3$CH$_2$OC(=O)CH$_2$); 61.0 (CH$_3$*C*H$_2$OC(=O)CH$_2$); 61.5 (CH$_3$*C*H$_2$OC(=O)); 69.3 (C-3′); 71.1, 71.3, 73.5, 74.4 (C-4′, *C*H$_2$Ph); 72.2 (CH$_3$CH$_2$-OC(=O)*C*H$_2$); 79.3 (C-1′); 81.1 (C-2′); 127.2 (C-1, C-3); 127.7–128.4 (Ph); 134.3 (C-4, C-6); 136.2 (C-5); 136.9, 137.3, 137.8 (*i*-Ph); 156.6 (C-2); 165.0 (CH$_3$CH$_2$O*C*(=O)); 168.7 (CH$_3$CH$_2$O*C*(=O)CH$_2$). MS, (CI, *iso*-butane), *m*/*z* (%): 715 (2) [M + H]$^+$.

HRMS calcd for C$_{41}$H$_{46}$O$_{11}$–OCH$_2$Ph: 669.26996, Found: 669.26840.

(1*R*)-1,2,4-Tri-*O*-benzyl-1-*C*-(1-methyl-1*H*-pyrazol-4-yl)-D-erythritol (4a). A solution of **1a** (100 mg, 0.225 mmol) in ethanol (5 mL) and methylhydrazine (0.024 mL, 0.45 mmol) was 10 min refluxed under stirring. After this time the solvent was evaporated and the residue purified by column chromatography (toluene/EtOAc 1 : 1). Compound **5a** was isolated as a colourless syrup.

Yield 85 mg (80%); $[\alpha]_D^{23}$ −29.9 (*c* = 0.5, CHCl$_3$); R_f 0.40 (toluene/EtOAc 1 : 1). IR (film), ν (cm^{-1}): 3423 (OH). ^{1}H NMR (300.13 MHz, CDCl$_3$), δ 2.76 (br, 1H, OH-3); 3.53–3.62 (m, AB-part of ABX, 2H, H-4a,b); 3.68 (dd, 1H, $^3J_{1,2}$ = 4.1 Hz, $^3J_{2,3}$ = 6.7 Hz, H-2); 3.87 (s, 3H, Me); 3.93 (m, 1H, H-3); 4.30 (d, 1H, ^2J = 11.9 Hz, C*H*HPh); 4.45 (d, 1H, ^2J = 11.3 Hz, C*H*HPh); 4.50 (s, 2H, C*H*$_2$Ph); 4.51 (d, 1H, ^2J = 11.3 Hz, C*H*HPh); 4.54 (d, 1H, ^2J = 11.9 Hz, C*H*HPh); 4.67 (d, 1H, H-1); 7.16–7.37 (m, 15H, Ph); 7.28 (d, 1H, H-5′); 7.47 (d, 1H, $^4J_{3',5'}$ = 0.6 Hz, H-3′). ^{13}C NMR (75.5 MHz, CDCl$_3$), δ 38.9 (Me); 70.4 (C-3); 70.7 (*C*H$_2$Ph); 71.0 (C-4); 73.4, 74.3 (*C*H$_2$Ph); 73.4 (C-1); 81.4 (C-2); 119.0 (C-4′); 127.7, 127.7, 127.8 (*p*-Ph); 127.9, 128.0, 128.1, 128.3, 128.4, 128.4 (*o*-, *m*-Ph); 129.7 (C-5′); 137.8, 138.1, 138.1 (*i*-Ph); 138.6 (C-3′). MS, (CI, *iso*-butane), *m*/*z* (%): 473 (27) [M + H]$^+$, 91 (100).

Anal. calcd for C$_{29}$H$_{32}$N$_2$O$_4$(472.58): C, 73.71; H, 6.82; N, 5.93. Found: C, 73.75; H, 6.80; N, 5.84.

1,2,4-Tri-*O*-benzyl-1*C*-(1-methyl-1*H*-pyrazol-4-yl)-D-threitol (4b). The reaction of **1b** with methylhydrazine was carried out as described above for the preparation of **5a**. Compound **5b** was obtained as a colourless syrup. Yield 94 mg (88%); $[\alpha]_D^{25}$ −51.2 (*c* = 0.45, CHCl$_3$); R_f 0.46 (toluene/EtOAc 1 : 1). IR (film), ν (cm^{-1}): 3423 (OH). ^{1}H NMR (300.13 MHz, CDCl$_3$), δ 2.32 (br, 1H, OH-3); 3.44 (d, 2H, $^3J_{3,4}$ = 5.7 Hz,

H-4a,b); 3.63 (dd, 1H, $^3J_{1,2} = 6.4$ Hz, $^3J_{2,3} = 3.2$ Hz, H-2); 3.79 (s, 3H, Me); 3.96 (dt, 1H, H-3); 4.25 (d, 1H, $^2J = 11.6$ Hz, C*H*HPh); 4.32, 3.34 (q(AB), 2H, $^2J = 8.5$ Hz, CH_2Ph); 4.41, 4.42 (q(AB), 2H, $^2J = 10.8$ Hz, CH_2Ph); 4.45 (d, 1H, $^2J = 11.6$ Hz, C*H*HPh); 4.51 (d, 1H, H-1); 7.03–7.07 (m, 2H, Ph); 7.15–7.29 (m, 13H, Ph); 7.23 (d, 1H, H-5′); 7.40 (d, 1H, $^4J_{3',5'} = 0.6$ Hz, H-3′). ^{13}C NMR (62.9 MHz, $CDCl_3$), δ 38.9 (Me); 69.7 (C-3); 70.5 (*C*H_2Ph); 71.0 (C-4), 73.4, 74.4 (*C*H_2Ph); 73.5 (C-1); 81.3 (C-2); 119.7 (C-4′); 127.6, 127.7, 128.1 (*p*-Ph); 127.8 (2x), 127.9, 128.3, 128.3 (2x) (*o*-, *m*-Ph); 129.6 (C-5′); 137.8, 137.9, 138.0 (*i*-Ph); 138.8 (C-3′). MS, (CI, *iso*-butane), m/z (%): 473 (71) $[M + H]^+$, 91 (100).

Anal. calcd for $C_{29}H_{32}N_2O_4$(472.58): C, 73.71; H, 6.82; N, 5.93. Found: C, 73.48; H, 6.89; N, 5.84.

1,2,4-Tri-*O*-benzyl-1*C*-[1-(2-hydroxy-ethyl)-1*H*-pyrazol-4-yl]-D-erythritol (4c). A solution of **1a** (100 mg, 0.225 mmol) in ethanol (5 mL) and 2-hydrazinoethanol (0.031 mL, 0.45 mmol) were reacted as described for preparation of **5a**. The resulting residue was purified by column chromatography (chloroform/methanol 9 : 1). Compound **5c** was isolated as a colourless syrup.

Yield 101 mg (89%); $[\alpha]_D^{24}$ −9.8 ($c = 1$, $CHCl_3$); R_f 0.34 (chloroform/methanol 9 : 1). IR (film), ν (cm^{-1}): 3415 (OH). ^{1}H NMR (250.13 MHz, $CDCl_3$), δ 2.78 (br, 2H, OH-3, CH_2CH_2O*H*); 3.51 (m, 2H, H-4a,b); 3.60 (dd, 1H, $^3J_{1,2} = 4.0$ Hz, $^3J_{2,3} = 7.0$ Hz, H-2); 3.82–3.91 (m, 3H, H-3, CH_2C*H*$_2$OH); 4.10–4.15 (m, 2H, CH_2CH_2OH), 4.24 (d, 1H, $^2J = 11.9$ Hz, C*H*HPh); 4.36, 4.43 (q(AB), 2H, $^2J = 11.3$ Hz, CH_2Ph); 4.42 (s, 2H, CH_2Ph); 4.49 (d, 1H, $^2J = 11.9$ Hz, C*H*HPh); 4.62 (d, 1H, H-1); 7.08–7.14 (m, 2H, Ph); 7.16–7.30 (m, 13H, Ph); 7.32 (d, 1H, H-5′); 7.44 (d, 1H, $^4J_{3',5'} = 0.9$ Hz, H-3′). ^{13}C NMR (62.9 MHz, $CDCl_3$), δ 53.7 (*C*H_2CH_2OH); 61.8 (CH_2*C*H_2OH); 70.3 (C-3); 70.8, 70.9 (C-4, *C*H_2Ph); 73.2 (C-1); 73.4, 74.2 (*C*H_2Ph); 81.1 (C-2); 118.7 (C-4′); 127.7–128.5 (Ph); 129.7 (C-5′); 137.6, 137.9, 137.9 (*i*-Ph); 139.0 (C-3′). MS, (CI, *iso*-butane), m/z (%): 503 (8) $[M + H]^+$, 91 (100).

Anal. calcd for $C_{30}H_{34}N_2O_5$(502.61): C, 71.69; H, 6.82; N, 5.57. Found: C, 71.30; H, 6.65; N, 5.40.

1,2,4-Tri-*O*-benzyl-1*C*-[1-(2-hydroxy-ethyl)-1*H*-pyrazol-4-yl]-D-threitol (4d). The reaction of **1b** with 2-hydrazinoethanol was carried out as described above for the preparation of **5c**. Compound **5d** was obtained as a colourless syrup. Yield 102 mg (90%); $[\alpha]_D^{22}$ −36.1 ($c = 1$, $CHCl_3$); R_f0.34 (chloroform/methanol 9 : 1). IR (film), ν (cm^{-1}): 3415 (OH). ^{1}H NMR (250.13 MHz, $CDCl_3$), δ 2.78 (br, 2H, OH-3, CH_2CH_2O*H*); 3.43 (dq, AB-part of ABX, 2H, $^3J_{4a,4b} = 8.6$ Hz, H-4a,b); 3.64 (dd, 1H, $^3J_{1,2} = 6.5$ Hz, $^3J_{2,3} = 3.2$ Hz, H-2); 3.83–3.92 (m, 2H, CH_2C*H*$_2$OH); 3.96 (dt, 1H, $^3J_{3,4a} = {}^3J_{3,4b} = 5.8$ Hz, H-3); 4.10–4.15 (m, 2H, CH_2CH_2OH); 4.27 (d, 1H, $^2J = 11.6$ Hz, C*H*HPh); 4.30, 4.33 (q(AB), 2H, $^2J = 11.0$ Hz, CH_2Ph); 4.40, 4.44 (q(AB), 2H, $^2J = 12.0$ Hz, CH_2Ph); 4.45 (d, 1H, $^2J = 11.6$ Hz, C*H*HPh); 4.53 (d, 1H, H-1); 7.01–7.07 (m, 2H, Ph); 7.16–7.30 (m, 13H, Ph); 7.32 (d, 1H, $^4J_{3',5'} = 0.9$ Hz, H-5′); 7.46 (d, 1H, H-3′). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ 53.8 (*C*H_2CH_2OH); 61.8 (CH_2*C*H_2OH); 69.7 (C-3); 70.6 (*C*H_2Ph); 71.1 (C-4); 73.4 (*C*H_2Ph); 73.5 (C-1); 74.4 (*C*H_2Ph); 81.3 (C-2); 119.6 (C-4′); 127.6–128.4 (Ph); 129.8 (C-5′); 137.8, 137.9, 137.9 (*i*-Ph); 139.1 (C-3′). MS, (CI, *iso*-butane), m/z (%): 503 (17) $[M + H]^+$, 91 (100).

Anal. calcd for $C_{30}H_{34}N_2O_5$(502.61): C, 71.69; H, 6.82; N, 5.57. Found: C, 71.30; H, 6.99; N, 5.58.

1*C*-(1-Methyl-1*H*-pyrazol-4-yl)-D-erythritol (5a). A suspension of **5a** (300 mg, 0.630 mmol) and palladium over active carbon (10%) in anhydrous ethanol (10 mL) was stirred under a H_2-atmosphere. After 15 hr, the mixture was filtered over diatomite and then evaporated. Recrystallisation from ethanol yielded **6a** as colourless crystals. Yield 125 mg (98%); mp 183–187°C; $[\alpha]_D^{23}$ −35.5 ($c = 0.5$, MeOH); R_f 0.26 (chloroform/methanol 2 : 1). IR (KBr), ν (cm^{-1}): 3393, 3314, 3278 (OH). ^{1}H NMR (250.13 MHz, DMSO), δ 3.25–3.50 (m, 3H, H-2, H-3, H-4a); 3.56 (dd, 1H, $^2J_{4a,4b} =$ 10.4 Hz, $J = 2.5$ Hz, H-4b); 3.76 (s, 3H, Me); 4.25–4.65 (br, 3H, 3x OH); 4.70 (br, 2H, H-1, OH); 7.30 (d, 1H, $^4J_{3',5'} = 0.9$ Hz, H-3′); 7.50 (d, 1H, H-5′). ^{13}C NMR (62.9 MHz, DMSO), δ 38.5 (Me); 63.6 (C-4); 65.1 (C-1); 71.7 (C-3); 75.0 (C-2); 124.2 (C-4′); 129.0 (C-5′); 137.4 (C-3′). MS, (CI, *iso*-butane), m/z (%): 203 (22) $[M + H]^+$, 185 (100) $[M - H_2O]^+$.

Anal. calcd for $C_8H_{14}N_2O_4$(202.21): C, 47.52; H, 6.98; N, 13.85. Found: C, 47.50; H, 7.02; N, 13.73.

1*C*-(1-Methyl-1*H*-pyrazol-4-yl)-D-threitol (5b). The deprotection of **5b** was carried out as described above for the preparation of **6a**. Recrystallisation from ethanol yielded **6b** as colourless crystals. Yield 120 mg (94%); mp 53–55°C; $[\alpha]_D^{23}$ − 4.1 ($c = 0.5$, H_2O); R_f 0.26 (chloroform/methanol 2 : 1). IR (KBr), ν (cm^{-1}): 3564, 3388, 3237 (OH). ^{1}H NMR (250.13 MHz, DMSO), δ 3.25–3.55 (m, 3H, H-2, H-4a,b); 3.72 (m, 1H, H-3); 3.77 (s, 3H, Me); 4.16 (d, 1H, $^3J = 7.6$ Hz, OH-2/4); 4.26 (d, 1H, $^3J_{3,OH\text{-}3} = 5.8$ Hz, OH-3); 4.45 (dd, 1H, $^3J_{1,2} = 7.6$ Hz, H-1); 4.45 (br, 1H, OH-2/4); 4.97 (d, 1H, $^3J_{1,OH\text{-}1} = 5.6$ Hz, OH-1); 7.29 (d, 1H, $^4J_{3',5'} = 0.9$ Hz, H-3′); 7.48 (d, 1H, H-5′). ^{13}C NMR (75.5 MHz, DMSO), δ 38.5 (Me); 63.2 (C-4); 66.1 (C-1); 70.4 (C-3); 73.7 (C-2); 124.8 (C-4′); 129.0 (C-5′); 137.6 (C-3′). MS, (CI, *iso*-butane), m/z (%): 203 (60) $[M + H]^+$, 185 (100) $[M - H_2O]^+$.

Anal. calcd for $C_8H_{14}N_2O_4$(202.21): C, 47.52; H, 6.98; N, 13.85. Found: C, 47.14; H, 6.81; N, 13.67.

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