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Note

myo-Inositol 4,6-carbonate: an easily prepared small molecule with three syn-axial hydroxyl groups☆

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Dedicated to Professor Pierre Sinaÿ on the occasion of his 62nd birthday

Abstract

myo-Inositol 4,6-carbonate, a compound having three syn-axial hydroxyl groups, was synthesized in four steps suitable for gram-scale preparation. It readily forms complexes with cations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: syn-Axial hydroxyls; Carbonylation; Complexes with cations

Compounds that have three syn-axial hydroxyl groups on a six-membered ring are of interest because they form complexes with cations [2]; they also form tridentate esters with oxyacids: borates, phosphates, and orthoacetates. However, such compounds are rare. The best-known example is *cis*-inositol; when it was first obtained [3], it was believed that it was the only known example of such a structure. However, it was soon found [4] that ouabagenin, a natural product, also had such a feature. Another natural product, muellitol, was discovered later [5]; this interesting compound has two sets of three cis-axial hydroxyl groups on one cyclohexane ring. Since then, several other compounds with three syn-axial hydroxyl groups have been synthesized. However, none of these compounds is readily available. Two syntheses of *cis*-inositol have been published [1,6], but neither is suitable for multigram preparations. This Note describes the easy synthesis of another such compound, *myo*-inositol 4,6-carbonate, from the readily available *myo*-inositol, on a multigram scale.

Our aim was achieved by bridging O-4 and O-6 of *myo*-inositol by a short bridge, thereby forcing it into a conformation that has three axial hydroxyl groups. The starting material was the readily available *myo*-inositol 1,3,5-orthoformate (**1**) [7,8] (Scheme 1), which is already in the inverted conformation. In order to prevent C-2 from reacting, it must be converted into its 2-*tert*-butyldimethylsilyl (TBDMS) ether (**2**). Surprisingly, a methylene bridge could not be placed between the two axial oxygen atoms. Reaction under alkaline conditions (Ag_2O or NaH and CH_2Br_2 or CH_2I_2; also $BrCH_2CH_2Br$), or under acidic conditions [$CH_2(OMe)_2$] failed to give any

☆ Cyclitols, Part 53. For Part 52, see Ref. [1].

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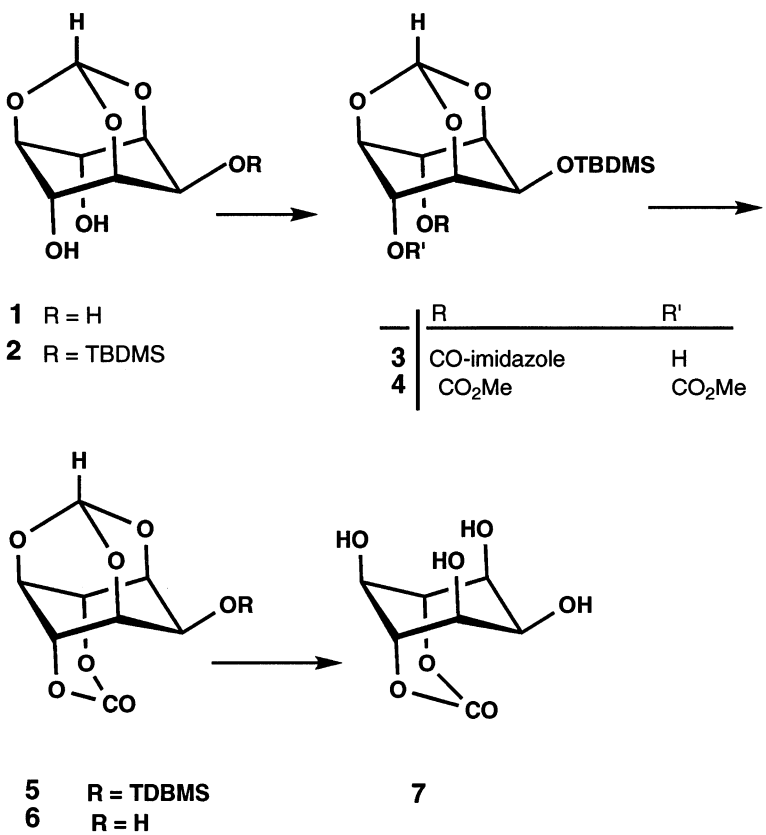
bridged product. The special conditions for alkylation of Das and Shashidhar [9], involving benzoates rather than free hydroxyl groups, were equally unsuccessful.

Success was achieved by carbonylation with 1,1-*O*-carbonyldiimidazole (CDI) [10,11]. This reagent has been applied very successfully to carbohydrates by Kutney and Radcliffe [12], but unfortunately only a preliminary communication was published that gave no experimental details. Nicolaou et al. [13] applied this reagent to the synthesis of taxol derivatives having vicinal hydroxyl groups, but working with very small quantities, they used a very large excess of solvent. Applying their conditions to **2**, the 4,6-carbonate **5** was obtained in good yield; but when attempts were made to carry out the reaction on a large scale, and consequently with a much reduced amount of solvent, the yield fell and a mixture of by-products was obtained. One of these was isolated and proved, by its NMR spectrum, to be the 4,6-di(methylcarbonyl) derivative **4**.

The first step in the carbonylation is the formation of the imidazole-*N*-carboxylic ester **3** [11], which cyclizes to the desired product **5**, but this latter reaction seems to be slower with syn-axial hydroxyl groups than with vicinal ones. The monosubstituted product **3** can also react with another molecule of CDI to give the bis(imidazole-*N*-carbonyl) derivative which, on crystallization from methanol, would have yielded the dimethyl ester **4** that we obtained. The bis(imidazole-*N*-carbonyl) derivative was not isolated in our experiments; however, such a compound has been described [12], without a detailed report of its properties.

The ring closure to **5** is a first-order reaction, whereas all other ones are of second order; hence, great dilution favours the desired reaction. This is, however, experimentally inconvenient, involving the handling of large volumes of solvents. Thus, another method was used: adding CDI in several aliquots, thereby keeping its concentration low [12]. In this way, a 74% yield was reliably obtained.

Both the TBDMS group and the orthoester were removed from **5** by hot trifluoroacetic



Scheme 1.

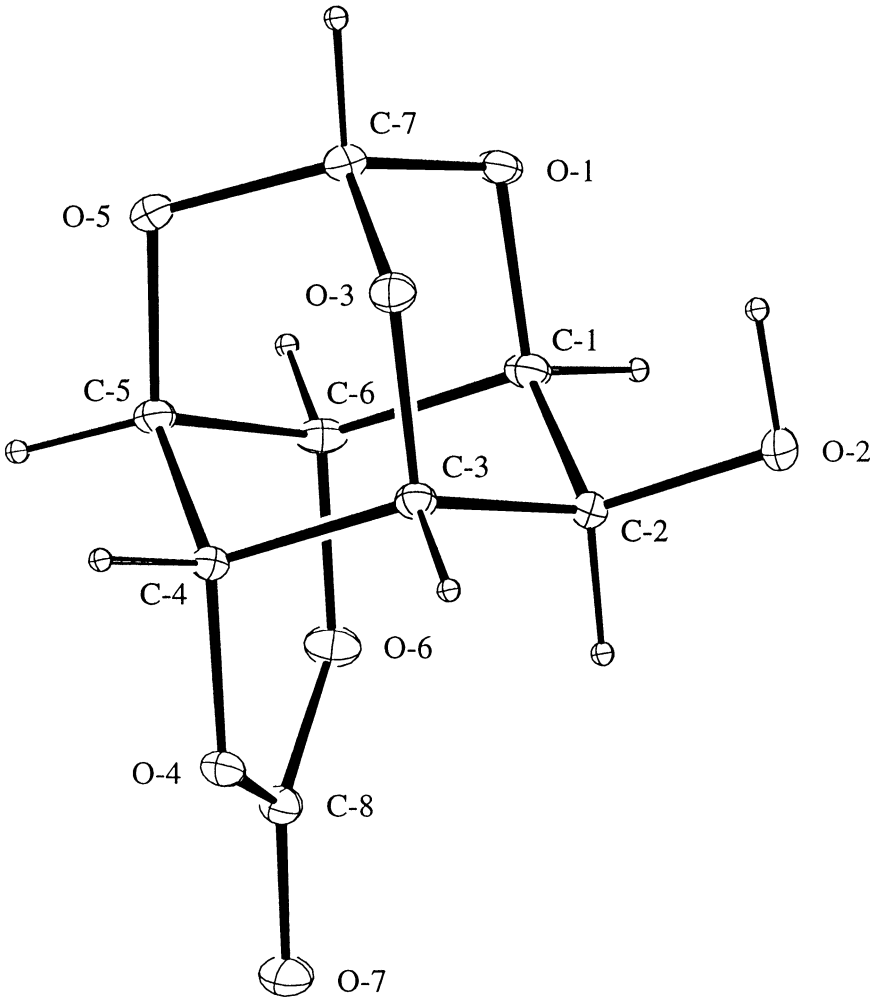


Fig. 1. X-ray structure of compound **6**.

acid, yielding *myo*-inositol 4,6-carbonate (**7**) in good yield. As shown by its NMR spectrum, this compound is in the chair form with three syn-axial hydroxyl groups. There seems to be very little of the boat or skew conformation in solution, as judged by the coupling constants. It forms complexes with cations, which are almost as strong as those formed with *cis*-inositol: by TLC on a cation-exchange plate in the calcium form, the R_f is 0.14, compared with 0.07 for the latter; on a lanthanum plate [14], the values are 0.14 and 0.08, respectively. *cis*-Inositol, of course, forms somewhat stronger complexes because it has three groups of ax, eq, ax hydroxyls in addition to the syn-axial hydroxyl groups.

Trifluoroacetic acid will remove both of the protecting groups even at room temperature. The experiment was first conducted in this way, but then a solid, which was not the desired product, separated from the solution. It turned out to be the carbonate orthoformate **6**, only the TBDMS group having been removed. This compound was found to be almost insoluble in water, as well as in all common organic solvents, and could be dissolved only in *N*,*N*-dimethylformamide and DMSO. Even in trifluoroacetic acid it had a low solubility and hence precipitated. When the reaction was conducted at higher temperature, this intermediate had increased solubility and a higher rate of reaction that prevented its precipitation.

Such a low solubility is quite unexpected for a compound with the structure of *myo*-inositol 4,6-carbonate 1,3,5-orthoformate (**6**); thus, an X-ray crystal structure determination was carried out that confirmed the structure (Fig. 1).

The crystal structure also suggests a reason for the low solubility. In the crystal, the molecules are in long zig-zag chains formed by hydrogen bonding of the (only) hydroxyl group with the O-5 of another molecule. However, the carbonyl oxygen atoms are close to three carbon-bound hydrogen atoms of other molecules: H-1 of a molecule in one chain and H-5 of another molecule and the orthoformate hydrogen atom of a third molecule in another chain, the O–H distances being 2.47, 2.53 and 2.39 Å, respectively (Fig. 2). These can be regarded as C–H···O hydrogen bonds [15]. Their lengths fall within the accepted limits for such bonds [16]. It appears then that in *myo*-inositol 2,4-carbonate 1,3,5-orthoformate the strands of molecules are held together by C–H···O bonds, resulting in a very stable crystal structure that causes the compound to have low solubility.

This compound may be a useful intermediate for the synthesis of *myo*-inositol derivatives with substituents on O-2. It can be hydrolysed to **7** under the same conditions as **5**.

1. Experimental

myo-*Inositol 1,3,5-orthoformate* (**1**) *{(1*R*, 3*S*,5*R*,7*S*,8*R*,9*R*)-2,4,10-trioxatricyclo-[3,3,1,1^{3,7}]decane-6,8,9-triol}*.—This compound was prepared essentially by the method of Ref. [8]. However, it was not easy to purify, and chromatography on a larger scale appeared undesirable. It was found to be more

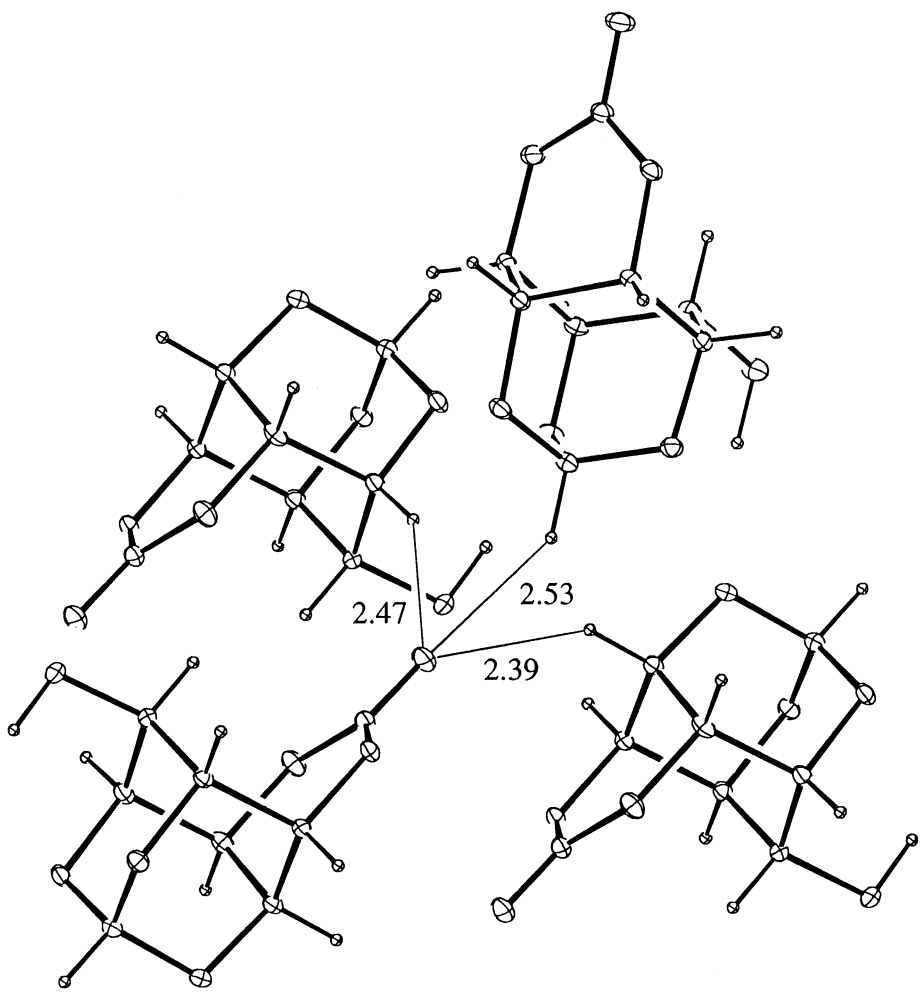


Fig. 2. The C–H···O bonds in the crystals of compound **6**.

convenient to use a modification suggested by Andersch and Schneider [17]: acetylation of the reaction mixture to give the readily crystallizing triacetate [7], followed by deacetylation.

To a stirred mixture of *myo*-inositol (30 g, 0.167 mol), dry DMF (240 mL) and triethyl orthoformate (50 mL, 0.30 mol), held at 120–130 °C, a solution of *p*-toluenesulfonic acid (7.5 g) in DMF (20 mL) was added. The inositol dissolved in 30 min (if it did not completely dissolve, the solution was decanted). After 2 h, the solvent was evaporated in vacuo. Pyridine (100 mL) and Ac_2O (100 mL) were added, all dissolving in about 2 min. Crystallization was slow, and it was assisted by the addition of seed crystals. Next day, the crystals (42 g, mp 172–174 °C, lit. 173–174 °C [7]) were filtered and dried at 100 °C. Addition of water to the mother liquor produced more substance, which, however, had to be recrystallized from MeOH to yield an additional 5 g (mp 156–162 °C).

The acetate, suspended in dry MeOH (80 mL), was heated to boiling, and NaOMe (3.0 mL, 2 M solution) was added. Solution occurred in a few minutes, and crystallization soon started (and, again, could be assisted by the addition of seed crystals). After cooling, the crystals of **1** (20 g) were separated; after evaporating the mother liquor to 25 mL, another 5.5 g was obtained. Total yield: 25.5 g (80%). For NMR spectra, see Ref. [18].

2-O-tert-*Butyldimethylsilyl*-myo-*inositol 1,3,5-orthoformate* (**2**).—A mixture of the orthoformate **1** (16 g, 0.083 mol), dry DMF (140 mL), 2,6-lutidine (23 mL), and *tert*-butyldimethylsilyl chloride (12.5 g, 0.083 mol) was left to stand for 2 days. Crystals of lutidine hydrochloride had separated. The mixture was evaporated in vacuo (bath at 80 °C) until 75 mL distilled over, and water (75 mL) was added. On cooling (and, if possible, seeding) crystals of **2** separated: 19.9 g (74%), mp 167–169 °C, lit. 179–181 °C [7]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.49 (d, 1 H, $J_{2,7}$ 1.3 Hz, H-7), 4.57 (t, 2 H, $J_{3,4} = J_{4,5}$ 4.0 Hz, H-4,6), 4.28 (q, 1 H, $J_{1,2}$ 1.9 Hz, H-2), 4.25 (sept, 1 H, $J_{1,5}$ 1.8 Hz H-5), 4.14 (dt, 2 H, H-1,3), 0.94 (s, 3 Me), 0.16 (s, 2 Me). Ref. [7] gives fewer details of the spectrum. It is of interest to note that the proton of the orthoformate (H-7) is coupled to H-2, but not to any other ring proton; this has been confirmed by decoupling. This sample was sufficiently pure for the next reaction; however, it could be purified by recrystallization from MeOH. The yield obtained was higher than in Refs. [7] and [8], and chromatographic purification was avoided. The previous authors used 1.2 equiv of TBDMS-Cl, which was reduced in this preparation to 1.0 equiv in order to minimize the formation of 2,4-di-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 1,3,5-orthoformate. This latter compound was obtained by fractional crystallization of material in the mother liquors of the above reaction; crystallized from MeOH, it had mp 77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.49 (d, 1 H, $J_{2,7}$ 1.3 Hz, H-7), 4.59 (t, 1 H, $J_{1,6} = J_{5,6}$ 4.1 Hz, $J_{4,6}$ 2.1 Hz, H-6), 4.44 (m, 1 H, H-6), 4.26 (q, 1 H, H-4), 4.26 (q, 1 H, $J_{1,2}$ 1.3 Hz, H-2), 4.15 (sextet, 2 H, $J_{1,5}$ 1.8 Hz, H-1,3), 4.04 (sextet, 1 H, H-5), 0.95 (s, 3 Me), 0.92 (s, 3 Me), 0.18 (s, Me), 0.16 (s, Me), 0.5 (s, 2 Me); ^{13}C NMR: δ 102.28 (C-7), 75.06, 74.51, 69.45, 68.76, 68.50, 60.55, 25.95 (3 Me), 25.60 (3 Me), 18.27 (quat. C), 17.62 (quat. C), −4.60 (2 Me), −5.20 (2 Me); Anal. Calcd for $C_{19}H_{38}O_6Si_2$ (418.7): C, 54.50; H, 9.15. Found: C, 54.06; H, 9.19.

2-O-tert-*Butyldimethylsilyl*-myo-*inositol 4,6-carbonate 1,3,5-orthoformate* (**5**).—To a solution of the TBDMS ether **2** (10 g, 0.030 mol) in dry THF (400 mL), heated to 65–70 °C, four aliquots of CDI (4.0 g each, a total of 2.8 equiv) were added at 90-min intervals. Heating was continued for 3 h. Next day, the mixture was again warmed to 65–70 °C, and hot water (500 mL) was added. The mixture was kept at 5 °C overnight (not any cooler because the solvent mixture sets solid at lower temperatures). Crystallization was slow, but ultimately shiny crystals (8.0 g, 74%) of **5** were obtained. For analysis the compound was crystallized from five parts of EtOAc, plus 20 parts of light petroleum. On heating, the compound's behaviour was very characteristic: it crystallized in thin flakes, which began to sublime at 150 °C; at about 170 °C they rapidly turned into thin long needles, which then melted at 195–200 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.40 (s, H-7), 5.03 (t, 2 H,

$J_{3,4}$ 4.4 Hz, H-4,6), 4.59 (t, 1 H, $J_{5,6}$ 4.4 Hz, H-5), 4.37 (dt, 2 H, $J_{1,2}$ 1.8 Hz, H-1,3), 3.98 (t, 1 H, H-2), 0.94 (s, 3 Me), 0.15 (s, 2 Me); ^{13}C NMR: 145.03 (C=O), 101.87 (C-7), 71.92 (2 C), 70.27 (2 C), 60.66, 60.00, 25.68 (3 Me), 18.21 (quat. C), −4.72 (2 Me); Anal. Calcd for $C_{14}H_{22}O_7Si$ (330.4): C, 50.89; H 6.71. Found: C, 50.7; H, 7.1.

2-O-tert-*Butyldimethylsilyl*-myo-*inositol 4,6-di(methylcarbonate) 1,3,5-orthoformate* (**4**).—Obtained from the mother liquors of the foregoing preparation by chromatography; mp 110 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.56 (d, $J_{2,7}$ 1.7 Hz, H-7), 4.74 (t, 2 H, H-4,6), 4.70 (quint, 1 H, H-5), 4.22 (d, 2 H, H-1,3), 4.14 (d, 1 H, H-2), 3.80 (s, 2-OMe), 0.94 (s, 3 Me), 0.13 (s, 2 Me); ^{13}C NMR: δ 154.28 (C=O), 102.97 (C-7), 71.68 (2 C), 70.99 (2 C), 66.00, 61.03, 55.32 (2 OMe), 25.81 (3 Me), 18.34 (quat. C), 7.05 (2 Me); Anal. Calcd for $C_{17}H_{28}O_{10}Si$ (420.5): C, 48.54; H, 6.66. Found: C, 49.2; H, 6.7.

myo-*Inositol 4,6-carbonate* (**7**).—Compound **5** (10.00 g, 0.030 mol) was dissolved in trifluoroacetic acid (80 mL) at 65–70 °C, and water (10 mL) was added with stirring. After 10 min, more water (10 mL) was added, and 45 min later the solution was evaporated in vacuo until it started to crystallize, at which point hot EtOH (60 mL) was added. After several hours in the refrigerator, 5.4 g (87%) of **7** was obtained. It could be crystallized from a small amount of 1:1 water–EtOH, but the recovery was found to be poor; mp 172 °C; ^{1}H NMR (300 Hz, D_2O): δ 4.93 (tt, 2 H, $J_{3,4}$ 3.6 Hz, 0.7 Hz long-range coupling, H-4,6), 4.61 (tt, 1 H, $J_{1,5}$ 1.8, $J_{5,6}$ 4.6 Hz and some small long-range coupling, H-5), 4.43 (tq, 2 H, some long-range coupling, H-1,3), 4.01 (t, 1 H, $J_{1,2}$ 4.3 Hz, H-2); ^{13}C NMR: 149.6 (C=O), 76.10 (C-1,3), 69.55 (C-4,6), 63.47 (C-5), 62.24 (C-2). Anal. Calcd for $C_7H_{10}O_7$ (206.2): C, 40.78; H, 4.89. Found: C, 40.80; H, 4.65. The crystals usually contained some *myo*-inositol, which could not be readily removed by recrystallization. The contaminant did not interfere with complex formation. It could, however, be removed by chromatography on a small cation-exchange resin column in the lanthanum [14], or an even smaller one in the neodymium form [19]. The compound was stable in aqueous solution at rt, but in boiling water it was shown to be gradually converted into *myo*-inositol with loss of CO_2. This process was slowed down if the pH was lowered to pH 4.0. In alkaline solution, of course, the compound decomposed rapidly.

myo-*Inositol 4,6-carbonate 1,3,5-orthoformate* (**6**).—In order to obtain a reasonable yield of product, the concentration was increased and the temperature lowered to reduce its solubility; judicious addition of seed crystals (if they were already available) was shown to increase the yield. Compound **5** (1.0 g, 3.00 mmol) was dissolved in warm trifluoroacetic acid (4.0 mL), water (1.0 mL) was added with stirring, and the mixture was cooled to rt, at which point separation of crystals soon started. After 1 h, another 1.0 mL of water was added. Filtration 4 h later yielded 0.32 g (48%) of **6** that was crystallized from Me_2SO by addition of water; mp 250 °C; ^{1}H NMR (300 MHz, Me_2SO-d_6): δ 5.80 (d, 2 H, $J_{2,OH}$ 6.2 Hz, OH), 5.67 (s, 1 H, H-7), 5.10 (t, 2 H, $J_{3,4}$ 4.7 Hz, H-4,6), 4.82 (t, 1 H, $J_{5,6}$ 4.3 Hz, H-5), 4.38 (dd, 2 H, $J_{1,2}$ 1.4 Hz, H-1,3), 3.68 (d, 1 H, some long-range coupling, H-2); ^{13}C NMR: δ 145.57 (C=O), 101.34 (C-7), 71.25 (2 C), 70.54 (2C), 59.12 (C-5), 59.00 (C-2). Anal. Calcd for $C_8H_8O_7$ (216.2): C, 44.45; H, 3.75. Found C, 44.4; H, 3.5. This compound could also be crystallized from a lot of water; its solubility was 8 g L^{-1} at 90 °C and 1.3 g L^{-1} at 0 °C.

Crystallography of **6**.—Crystal data: $C_8H_8O_7$, M_w 216.1, monoclinic, space group $C2/c$, a 9.438(2), b 10.123(1), c 16.613(4) Å, β 92.98(1)°, V 1585.1(6) Å^3, D_c 1.81 g cm^{-3}, Z 8, μCu 13.77 cm^{-1}. Crystal size 0.05 × 0.22 × 0.29 mm; $2\theta_{max}$ 140°; min and max transmission factors 0.73 and 0.93. The number of reflections was 1298 considered observed out of 1512 unique data, with R_{merge} 0.013 for 48 pairs of equivalent $hk0$ reflections. The final residuals R, R_w were 0.036, 0.065 for the observed data.

Structure determination.—Reflection data were measured with an Enraf–Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromatized copper radiation (λ 1.54184 Å). Data were corrected for ab-

Table 1
Non-hydrogen atomic parameters for compound **6** [a]

	x	y	z	$(U_{11}+U_{22}+U_{33})/3$
O-1	0.33993(12)	0.37419(13)	0.73414(7)	0.0354(3)
O-2	0.31050(16)	0.19067(16)	0.60417(8)	0.0452(8)
O-3	0.10674(12)	0.33672(12)	0.68880(7)	0.0337(3)
O-4	0.15200(13)	0.55822(11)	0.51751(7)	0.0351(4)
O-5	0.17505(14)	0.54214(12)	0.73836(7)	0.0366(4)
O-6	0.38540(14)	0.59450(14)	0.56115(8)	0.0414(4)
O-7	0.30879(17)	0.63218(14)	0.43603(8)	0.0528(4)
C-1	0.3819(2)	0.4073(2)	0.6538(1)	0.0332(4)
C-2	0.2895(2)	0.3285(2)	0.5936(1)	0.0299(4)
C-3	0.1369(2)	0.3672(2)	0.6066(1)	0.0291(4)
C-4	0.11363(17)	0.51581(17)	0.59679(9)	0.0296(4)
C-5	0.2052(2)	0.5882(2)	0.6594(1)	0.0324(4)
C-6	0.3577(2)	0.5561(2)	0.6428(1)	0.0351(4)
C-7	0.1980(2)	0.4050(2)	0.7444(1)	0.0327(4)
C-8	0.2829(2)	0.5962(2)	0.5020(1)	0.0367(4)

[a] Estimated standard deviation in parentheses.

Table 2
Hydrogen atom positional parameters for compound **6** [a]

	x	y	z
HO-2	0.28028	0.16948	0.65951
HC-1	0.48418	0.38534	0.64820
HC-2	0.31345	0.35362	0.53772
HC-3	0.07096	0.31772	0.56844
HC-4	0.01160	0.53708	0.60405
HC-5	0.18845	0.68552	0.65519
HC-6	0.42279	0.60560	0.68146
HC-7	0.17482	0.37683	0.79988

[a] Thermal parameters are equal to those of the bonded atom.

sorption using the analytical method of De Meulenaer and Tompa [20]. Reflections with $I > 3\sigma(I)$ were considered observed. The structure was determined by direct phasing and Fourier methods. Hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atoms to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full-matrix least-squares. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from

$$\sigma(I_o) = [\sigma^2(I_o) + 0.04I_o)^2]^{1/2}$$

The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from the International Tables for X-ray Crystallography [21]. Structure solution was by SIR92 [22] and refinement used RAELS [23]. ORTEP-II [24] running on a Power Macintosh was used for the structural diagrams, and a DEC Alpha-AXP workstation was used for calculations. The non-hydrogen atom parameters for **6** are shown in Table 1, and those of the hydrogen atoms in Table 2. The bond lengths and the dihedral angles are normal.

2. Supplementary material

Full crystallographic details, including structural features, have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Tel. +44 1223-336-408, fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

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