*Carbohydrate Research*, 238 (1993) 313–316
Elsevier Science Publishers B.V., Amsterdam



# Note

## Crystal and molecular structure of deca-*O*-acetyl-L-*galacto*-L-*gulo*-decitol

Peter Köll [a], Jürgen Kopf [b], Martina Morf [b], Bärbel Zimmer [b] and John S. Brimacombe [c]

[a] *Department of Chemistry, The University, Carl-von-Ossietzky-Str. 9-11, D-W 2900 Oldenburg (Germany)*
[b] *Institute of Inorganic and Applied Chemistry, The University, Martin-Luther-King-Platz 6, D-W 2000 Hamburg 13 (Germany)*
[c] *Department of Chemistry, The University of Dundee, Dundee DD1 4HN (United Kingdom)*

(Received January 23rd, 1992; accepted June 2nd, 1992)

Decitols occur as 64 enantiomeric pairs and 8 *meso* forms, so that 72 diastereomers have to be considered in defining the basic conformational features of these compounds. Racemates usually behave differently in the crystalline state, so that at least 120 crystal structures have to be taken into account. Until now, only one of these structures was known[1]. The same considerations apply to simple derivatives of decitols, such as the deca-acetates. As a first example, the solid-state structure of the title compound **1**[2], which is less correctly named "D-*gluco*-D-*galacto*"-decitol deca-acetate, was determined by X-ray crystallography.

The relevant crystallographic data for **1** are given in Table I. The structure was solved by direct methods in the usual way with the help of the programs SHELXS90[3] and SHELX76[4].

All heavy atoms were refined. Hydrogens were introduced at calculated positions. The final fractional co-ordinates of C and O atoms in **1**, together with equivalent thermal parameters, are listed in Table II*. A perspective view (SCHAKAL88[5] plot) of **1** is presented in Fig. 1, together with the numbering scheme.

*Correspondence to:* Professor Dr. P. Köll, Department of Chemistry, The University, Carl-von Ossietzky-Str. 9-11, D-W 2900 Oldenburg, Germany; or to: Privatdozent Dr. J. Kopf, Institute of Inorganic and Applied Chemistry, The University, Martin-Luther-King-Platz 6, D-W 2000 Hamburg 13, Germany; or to Professor J.S. Brimacombe, Department of Chemistry, The University of Dundee, Dundee DD1 4HN, United Kingdom.

* Lists of observed and calculated structure amplitudes, anisotropic thermal parameters, fractional co-ordinates of hydrogen atoms with isotropic thermal parameters, tables of bond distances and angles, and further information (24 pages) have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/511/*Carbohydr. Res.*, 238 (1993) 313–316.

TABLE I

Crystallographic data for **1** [a]

| | | | | |
|---|---|---|---|---|
| Formula | | $C_{30}H_{42}O_{20}$ | Density (calcd) ($g \times cm^{-3}$) | 1.316 |
| Mol wt | | 722.65 | $\lambda$(Cu $K_\alpha$) (pm) | 154.051 |
| Mp (°C) | | 144 | $\mu$ ($cm^{-1}$) | 9.2 |
| Crystal size (mm) | | $0.5 \times 0.4 \times 0.1$ | $2\theta$ range (degrees) | 4.5–130 |
| Space group | | $P2_12_12_1$ | Reflections measured | 3437 |
| Cell parameters | | | Symmetry independent reflections | 3061 |
| (pm, degrees) | *a* | 1021.4(1) | Observed reflections with $F_o > 3\sigma(F_o)$ | 2411 |
| | *b* | 1578.1(1) | Number of refined parameters | 451 |
| | *c* | 2262.2(1) | Final residual factors | |
| Volume ($pm^3$) | | $3646.4(5) \times 10^6$ | *R* | 0.055 |
| *Z* | | 4 | $R_w$ | 0.052 |
| *F* (000) | | 1528 | Diffractometer | Enraf–Nonius CAD 4 |

[a] Standard deviations in parentheses.

1,2,3,4,5,6,7,8,9,10-Deca-*O*-acetyl-L-*galacto*-L-*gulo*-decitol[2] (**1**) has a bent (sickle) conformation with each of the chain segments C-1 to C-5 and C-5 to C-10 in a planar (zigzag) arrangement. Bending occurs by rotation around the C-4–C-5 bond, thereby avoiding a parallel 1,3-interaction between O-3 and O-5, but at the expense of introducing an O//O interaction between O-5 and O-7. The distance between these atoms is 277.4 pm. An alternative rotation around the C-3–C-4 bond would have resulted in a sickle conformation completely free from O//O

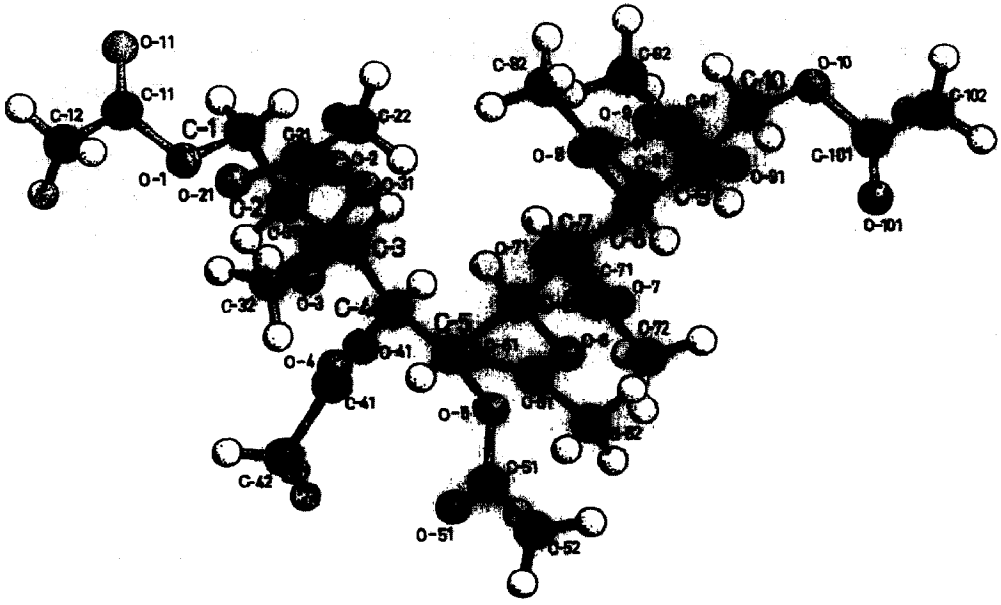


Fig. 1. SCHAKAL88[5] plot of a molecule of deca-*O*-acetyl-L-*galacto*-L-*gulo*-decitol (**1**) showing atom numbering.

TABLE II

Fractional positional parameters ($\times 10^4$)[a] and temperature factors $U_{eq}$($\times 10^3$)[b] of carbon and oxygen atoms in **1**

| Atoms | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| O-1 | −1140(5) | −2230(3) | −798(2) | 61(2) |
| O-2 | 841(4) | −2671(3) | −2090(2) | 43(2) |
| O-3 | −2300(4) | −1667(3) | −1896(2) | 36(2) |
| O-4 | −510(4) | −779(3) | −2580(2) | 41(2) |
| O-5 | −1513(5) | −1073(3) | −3679(2) | 41(2) |
| O-6 | −3804(4) | −2092(3) | −3749(2) | 36(1) |
| O-7 | −1338(5) | −2650(3) | −4214(2) | 40(2) |
| O-8 | −3081(4) | −4146(3) | −3298(2) | 40(2) |
| O-9 | −705(5) | −4573(3) | −3910(2) | 41(2) |
| O-10 | −1955(6) | −5691(3) | −4765(2) | 60(2) |
| O-11 | −357(7) | −3045(5) | −82(3) | 95(3) |
| O-21 | 2452(6) | −2007(5) | −1613(3) | 89(3) |
| O-31 | −3491(5) | −2867(3) | −1856(2) | 61(2) |
| O-41 | 1517(7) | −962(4) | −2928(4) | 105(3) |
| O-51 | −2955(8) | −11(4) | −3592(3) | 104(3) |
| O-61 | −4956(5) | −1735(3) | −2941(2) | 59(2) |
| O-71 | 669(5) | −2694(3) | −3806(2) | 61(2) |
| O-81 | −5182(6) | −4160(5) | −3565(3) | 102(3) |
| O-91 | 431(6) | −4413(4) | −4750(2) | 74(2) |
| O-101 | −2953(7) | −4908(5) | −5455(3) | 92(3) |
| C-1 | −373(8) | −2723(5) | −1208(3) | 53(3) |
| C-2 | −109(6) | −2189(4) | −1758(3) | 38(2) |
| C-3 | −1269(6) | −2110(4) | −2192(3) | 34(2) |
| C-4 | −911(6) | −1627(4) | −2749(3) | 32(2) |
| C-5 | −2063(7) | −1494(4) | −3163(3) | 34(2) |
| C-6 | −2730(6) | −2316(4) | −3363(3) | 34(2) |
| C-7 | −1908(6) | −2983(4) | −3676(3) | 30(2) |
| C-8 | −2679(7) | −3764(4) | −3848(3) | 36(2) |
| C-9 | −1903(7) | −4392(4) | −4217(3) | 42(2) |
| C-10 | −2641(8) | −5214(4) | −4323(3) | 54(3) |
| C-11 | −1028(8) | −2470(6) | −224(3) | 61(3) |
| C-12 | −1878(11) | −1938(8) | 159(4) | 108(5) |
| C-21 | 2110(8) | −2512(5) | −1972(3) | 57(3) |
| C-22 | 2988(9) | −3065(6) | −2343(4) | 81(4) |
| C-31 | −3366(7) | −2131(5) | −1737(3) | 43(3) |
| C-32 | −4345(8) | −1598(6) | −1409(3) | 63(3) |
| C-41 | 679(8) | −519(5) | −2758(3) | 51(3) |
| C-42 | 781(9) | 431(5) | −2681(4) | 71(3) |
| C-51 | −2064(10) | −333(5) | −3844(4) | 63(3) |
| C-52 | −1399(11) | −13(6) | −4388(5) | 97(4) |
| C-61 | −4899(7) | −1816(4) | −3473(3) | 45(3) |
| C-62 | −5985(9) | −1626(7) | −3895(4) | 84(4) |
| C-71 | −34(8) | −2509(5) | −4211(3) | 47(3) |
| C-72 | 416(10) | −2126(6) | −4793(4) | 80(4) |
| C-81 | −4355(9) | −4318(5) | −3213(3) | 54(3) |
| C-82 | −4578(9) | −4720(5) | −2628(4) | 67(3) |
| C-91 | 422(8) | −4574(5) | −4237(4) | 57(3) |
| C-92 | 1559(8) | −4783(6) | −3853(4) | 79(4) |
| C-101 | −2188(10) | −5431(6) | −5325(4) | 70(4) |
| C-102 | −1289(13) | −5916(7) | −5746(5) | 110(5) |

[a] Standard deviations in parentheses. [b] $U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij}\mathbf{a}_i^*\mathbf{a}_j^*\mathbf{a}_i\mathbf{a}_j$.

interactions. Until recently, the avoidance of such interactions (the so-called Hassel–Ottar effect) was regarded as the dominant factor determining alditol conformations[6]. This no longer appears to be universally true. Of the many alditol structures that have now been shown to tolerate such interactions, D-*galacto*-L-*galacto*-decitol[1] is perhaps the most impressive. That acetylated alditols in particular show a high tolerance of O//O interactions is evident in the crystal structures of the pentitol penta-acetates[7,8], the hexitol hexa-acetates[7,9,10], and heptitol hepta-acetates investigated so far[11]. Therefore, the overall conformation observed for **1** (Fig. 1) is unexpected but not without precedent. This is also true of the 1,3-parallel orientation between O-1 and O-3 (distance apart, 289.3 pm), which could have been avoided by rotation around the C-1–C-2 bond. A similar situation is encountered in the crystal structures of xylitol penta-acetate[7] and D-glucitol hexa-acetate[7,9], although the orientation of the 1-acetoxy group of **1** is unusual insofar that it is antiperiplanar (*trans*) to O-2. Neighbouring substituents at the termini of most alditol acetates[7–11] are located in *gauche* positions, as is the case with those located at the C-10 terminus of **1**. The reasons for such behaviour have been discussed[10].

ACKNOWLEDGMENTS

The Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie are thanked for financial support (to P.K. and J.K.).

REFERENCES

1 P. Köll, J. Kopf, M. Morf, B. Zimmer, and J.S. Brimacombe, *Carbohydr. Res.*, 237 (1992) 289–293.
2 J.S. Brimacombe, R. Hanna, and A.K.M.S. Kabir, *J. Chem. Soc., Perkin Trans. 1*, (1987) 2421–2426.
3 G.M. Sheldrick, *Acta Crystallogr., Sect. A*, 46 (1990) 467–473.
4 G.M. Sheldrick, SHELX76, Programs for Crystal Structure Determination, Cambridge, 1976.
5 E. Keller, *Chem. Unserer Zeit*, 14 (1980) 56–60.
6 G.A. Jeffrey, *Acta Crystallogr., Sect. B*, 46 (1990) 89–103.
7 Y.J. Park, M.H. Park, and J.M. Shin, *Daehan Hwahak Hwoejee*, 34 (1990) 517–526; *Chem. Abstr.*, 114 (1991) 82345a.
8 J. Kopf, M. Morf, B. Zimmer, and P. Köll, *Carbohydr. Res.*, 233 (1992) 35–43.
9 J. Kopf, C. Topf, M. Morf, B. Zimmer, and P. Köll, *Acta Crystallogr., Sect. C*, 47 (1991) 2425–2428.
10 J. Kopf, M. Morf, B. Zimmer, M. Bischoff, and P. Köll, *Carbohydr. Res.*, 229 (1992) 17–32.
11 P. Köll, M. Bischoff, M. Morf, B. Zimmer, and J. Kopf, *Carbohydr. Res.*, submitted.