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Fluorination of (+)-*chiro*-inositol with SF_4/HF to give 2α,3β-difluoro-7-oxabicyclo[2.2.1]heptane-5α,6α-sulfite

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Abstract

The fluorination of (+)-*chiro*-inositol with SF_4/HF under moderate conditions affords a single product studied by ^1H and ^{19}F and ^{13}C NMR spectroscopy. These have been fully assigned with the aid of other physical techniques and compared with a computer-generated model. This data indicate the product to be 2α,3β-difluoro-7-oxabicyclo[2.2.1]heptane-5α,6α-sulfite **3** which was subsequently confirmed by single-crystal X-ray analysis. A mechanism for the reaction is proposed and is compared with that proposed for the formation of the product obtained from the fluorination of *myo*-inositol.

Keywords: Inositols; Fluorination; Sulfur tetrafluoride; 2α,3β-Difluoro-7-oxabicyclo[2.2.1]heptane-5α,6α-sulfite

1. Introduction

There has been considerable interest in the chemistry and biology of inositol derivatives since the discovery that (+)-*myo*-inositol-1,4,5-triphosphate acts as a second messenger concerned with calcium mobilisation and receptor stimulation [1,2]. Interest also arises because second messengers, their receptors and enzymes involved in their metabolism, are potential targets for rational drug design. Not surprisingly attention has been given to fluorinated analogues of *myo*-inositol and many derivatives have been made [3–12]. In most cases the syntheses involved a number of steps which often involve either expensive starting materials, multi-protection and de-protection and almost always a resolution step. Of particular interest to us was the work of Kozikowski et al. [13] who have shown that fluorination of quebrachitol (2-*O*-methyl-(−)-*chiro*-inositol) with DAST led to the formation of a mixture of fluorinated methyl ethers which on demethylation afforded (−)-1-deoxy-1-fluoro-*myo*-inositol. Further, they subsequently showed [7] that (+)-pinetol ((+)-5-*O*-methyl-*chiro*-inositol) yielded a difluoro product, (+)-1,5-dideoxy-1,5-difluoro-*neo*-inositol. These results suggested to us that it might be possible to directly fluorinate inositols to their corresponding fluorinated analogues. Previously [14], we have investigated the possibility of direct fluorination of *myo*-inositol under mild conditions with SF_4/AHF as a means of preparing monofluoroinositols. We discovered a very unusual reaction in that the product was the bicyclic compound, 2β,3β-difluoro-7-oxabicyclo[2,2,1]heptane-5α,6α-sulphite **1**, which could be hydrolysed to the corresponding 5α,6α-diol **2**. In the light of the differing results found by Kozikowski et al., we repeated this experiment with *chiro*-inositol to see if the structural changes between *myo*- to *chiro*-inositol might have a significant effect on the reaction. At the time of our initial study *chiro*-inositol was not readily available since it does not itself occur naturally and is found as its methyl ethers (quebrachitol) in natural rubber and (pinetol) in certain pine woods these are also relatively difficult to obtain. Fortunately, we have subsequently been able to obtain good supplies of optically pure (+)-*chiro*-inositol from Dr. Andrew Falshaw which enabled us to complete the work we now report. *Chiro*-inositol itself is of considerable interest, it is believed to be important, probably as its phosphate, in many mammalian regulatory systems and is implicated as being involved in some way with diabetes. Thus, derivatives of it may be important biologically.

2. Results and discussion

We first attempted to fluorinate both *myo*- and *chiro*-inositols with DAST under a variety of conditions using

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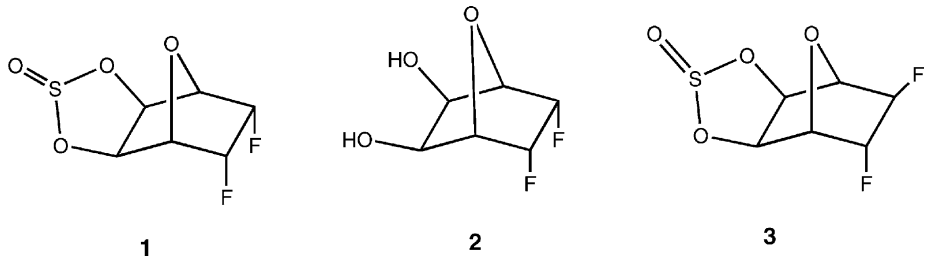


1 2 3

Fig. 1. Fluorination products from inositols and SF_4.

freshly prepared DAST of high purity both alone and in the presence of re-distilled AHF. Under all of the conditions tried we found that no reaction or significant decomposition of the starting material had occurred. This is a somewhat surprising result since we and others have shown that even mono protected inositols are readily fluorinated. We have as yet no clear explanation of this observation.

We next repeated the reaction of *myo*-inositol with SF_4 and obtained the same result as before, thus confirming the reaction parameters. Reaction of *chiro*-inositol with SF_4/AHF as described previously [13] yielded a crystalline product shown by TLC to be a single component using a number of eluants and gave a single peak on HPLC. The product was recrystallised from acetonitrile and was subjected to a complete structural analysis.

Preliminary ^1H and ^{19}F NMR studies gave spectra, which were much more complex than those found for **1**. The mass spectrum indicated a product of the same molecular mass of **1** with a similar breakdown pattern to **1**. We thus concluded that the product was of the same type as **1** and elemental analysis confirmed this view and we assigned the product as 2α,3β-difluoro-7-oxabicyclo[2.2.1]heptane-5α,6α-sulfite **3** (see Fig. 1).

3. Structural analysis

The full structure of the molecule was determined by the Chemical Technologies Department of Roche Discovery Welwyn using ^1H, ^{19}F and ^{13}C NMR spectroscopy including the use of COSY spectra to determine which atoms coupled to which and by single-crystal X-ray diffraction analysis. The full ^1H and ^{19}F NMR spectra are shown in Fig. 2 and the simulated spectrum is shown in Fig. 3. In the interests of space the expansion of the individual signals from which coupling constants were determined are not shown.

As can be seen in Figs. 2 and 3 both the proton and fluorine spectra are very complex with multiple coupling leading to some complex coupling patterns (atom numbering referred to below is that shown on the structure in Fig. 2). The COSY spectra, which are not reproduced, were less helpful than they might have been owing to overlap of signals but allowed us to confirm which protons coupled together, and also revealed that some protons were in some cases somewhat surprisingly not coupled (or had a zero coupling constant). The coupling relationships between the atoms are shown in Tables 1–5. It was easier to assign the fluorine spectrum and the analysis is as follows: the fact that there are two fluorine signals shows a lack of symmetry within the molecule and the presence of a coupling of ca. 50 Hz in each signal indicates that the fluorine is attached to a CH group. The fluorine atoms clearly must be in either the *endo* or *exo* configuration. This is confirmed by the similarity of the chemical shifts −190.9 and −206.3 with the values from 2,3-difluoro-bicyclo[2.2.1]heptane [15] of F *exo* −189.6, F *endo* −219 ppm. The signal for the *endo* fluorine atom shows a dddddd splitting pattern with the large geminal HF coupling of 50.68 Hz being a key feature and the signal for the *exo* fluorine atom shows a ddddddd splitting again with the large $^2J_{HF}$ coupling.

We next examined the ^1H spectrum the analysis of which was not trivial owing to the overlap of multiplets. However, certain couplings were crucial to the analysis which ultimately led us to the full assignment. The signals centered at

Table 1
Proton coupling patterns nuclei which couple are indicated by asterisks

Nucleus	H_1	H_2	H_3	H_4	H_5	H_6	F_7	F_8
H_1		0	*	*	*	0	*	*
H_2	0		*	*	0	*	*	*
H_3	*	*		0	0	0	*	*
H_4	*	*	0		0	*	*	0
H_5	*	0	0	0		*	*	*
H_6	0	*	0	*	*		*	*
F_7	*	*	*	*	*	*		*
F_8	*	*	*	0	*	*	*	

Table 2
Chemical shifts and multiplicities

Nucleus	H_1	H_2	H_3	H_4	H_5	H_6	F_7	F_8
$\delta(CH_3CN)$	4.85	5.1	4.9	4.74	5.12	5.26	−190.9	−206.3
Multiplicity	dddddd	ddddd	dddd	dddd	dddd	ddddd	ddddddd	dddddd

The δ values are given for the centre of muliplets.

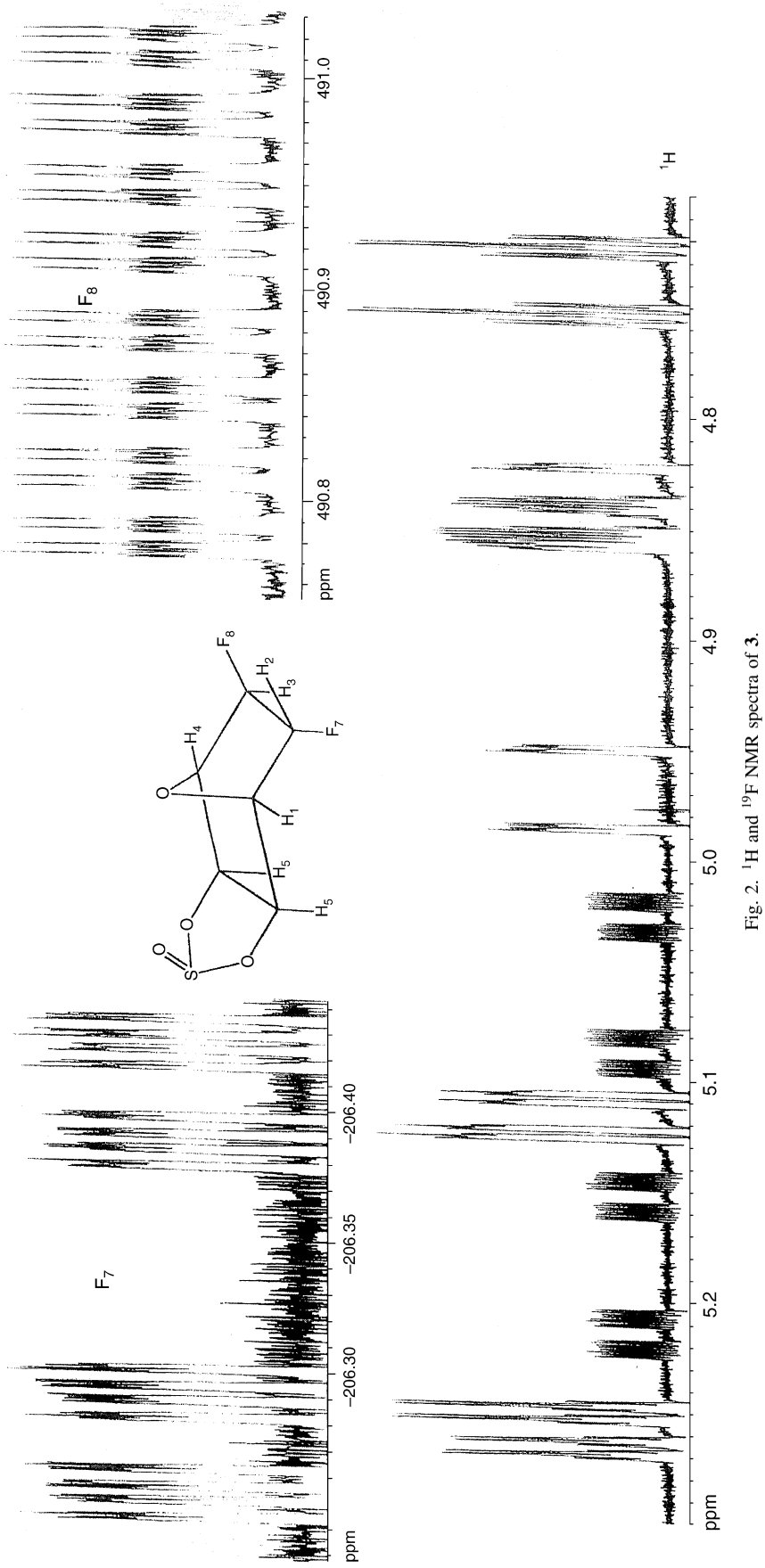


Fig. 2. ^{1}H and ^{19}F NMR spectra of **3**.

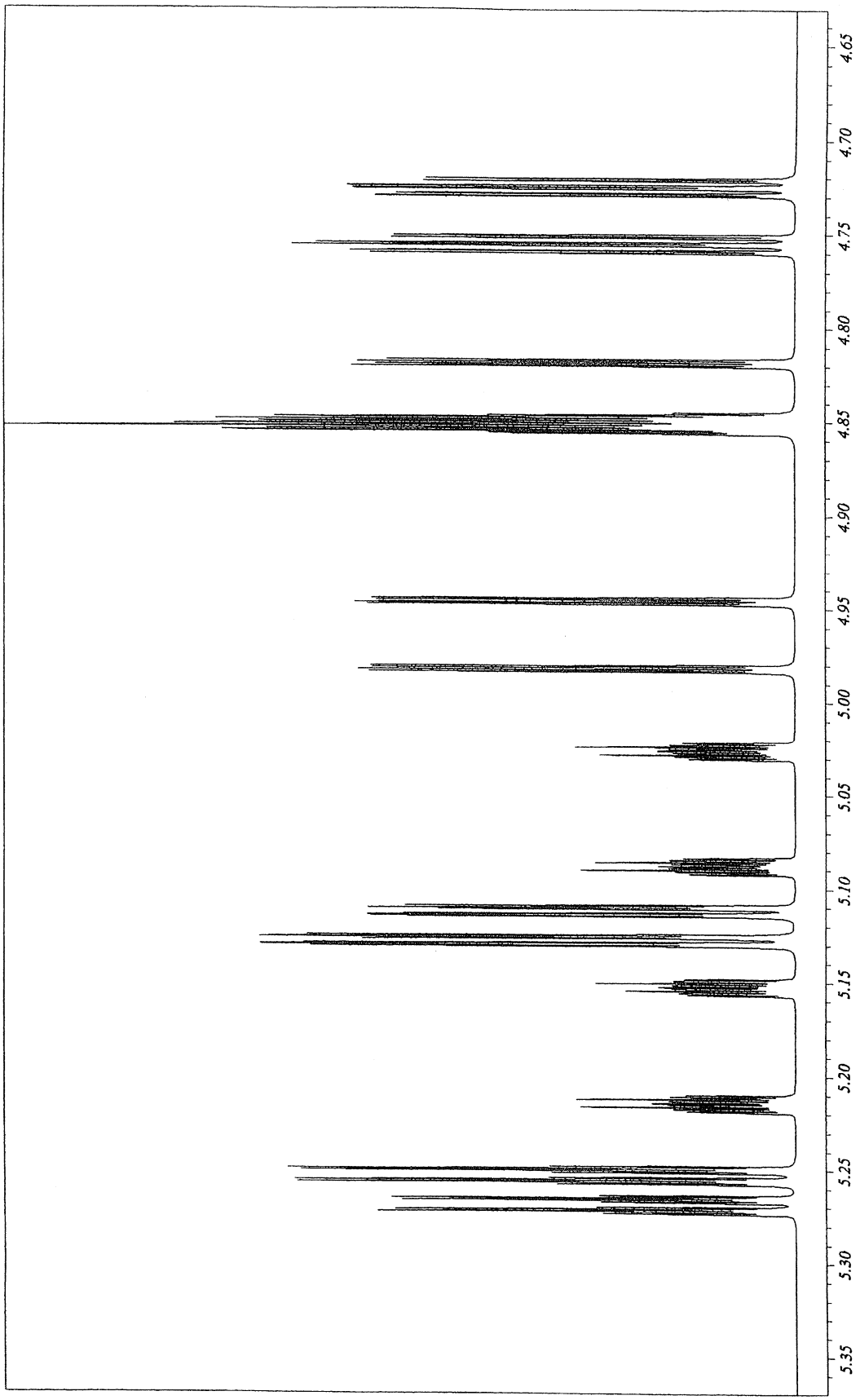


Fig. 3. Simulated ^{1}H NMR spectrum of **3**.

Table 3
Coupling constants (Hz)

Nucleus	H_1	H_2	H_3	H_4	H_5	H_6	F_7	F_8
H_1		0	0.4	1.54	0.44	0	0.64	0.52
H_2	0		0.88	1.68	0	0.37	50.68	24.72
H_3	0.4	0.88		0	0	0	14.42	50.96
H_4	1.54	1.68	0		0	0.48	12.17	0
H_5	0.44	0	0	0		6.3	1.62	0.28
H_6	0	0.37	0	0.48	6.3		0.46	2.46
F_7	0.64	50.68	14.42	12.17	1.62	0.46		4.5
F_8	0.52	24.72	50.96	0	0.28	2.46	4.5	

Table 4
^{13}C chemical shifts

Carbon	Carbon	C_2	C_3	C_4	C_5	C_6
$\delta(CH_3CN)$	78.2	93.8	93.5	84.4	85.6	85.2
Multiplicity	dd	dd	dd	dd	d	d

Table 5
CF coupling constants (Hz)

^1J	C_2F_7 188.9, C_3F_8 195.5
^2J	C_1F_7 20.1, C_2F_8 24.5, C_3F_7 29.4, C_4F_8 27.5
^3J	C_1F_8 2.7, C_2F_7 7.1, C_3F_8 11.8, C_4F_7 6.2

δ 4.90 and 5.12 clearly were due to the CHF groups (H_3 and H_2) as they both showed the large $^2J_{HF}$ couplings The H_2 was much more coupled than H_3 (ddddd versus ddd) suggesting that H_2 is in the *exo* configuration and H_3 is in the *endo* configuration. This view is further strengthened by the COSY spectrum which indicates (Table 1) that H_2 couples to H_1, H_6, H_4 and H_3 whereas H_3 couples with H_1, and H_6 and both couple to fluorine. Protons adjacent to the cyclic sulfite (H_5 and H_6) were assigned to the signals centered at δ 5.12 and 5.26 as multiplets (dddd and ddddd), respectively. The COSY spectrum suggested that H_5 was coupled to H_1, H_6 and H_6 was coupled to H_2, H_4, H_5 and both were coupled to both fluorine atoms with H_6 having the larger HF coupling constants. This is consistent with the well known through space contribution to HF coupling leading to the assignment of H_6 being nearer to the *endo* fluorine atom F_7. The common coupling constant of 6.3 Hz between the two protons further confirms their position as being adjacent to the cyclic sulfite. Finally, the bridgehead (H_4 and H_1) were assigned as giving the signals centered at δ 4.74 and 4.85. The absence of any significant coupling, as confirmed by the COSY spectrum, of these protons to the protons adjacent to the sulfite strongly suggested that the sulfite has the *exo* orientation with a proton–proton torsion angle of ca. 90°. It was then necessary to determine the stereochemical relationship between the individual bridgehead protons and the CHF groups. One of the protons had a large 12.17 Hz coupling to the fluorine atom at −190.9 indicating that these protons are vicinal and that the fluorine atom is *exo*. The second proton had a much smaller 0.64 Hz coupling suggesting the fluorine is *endo*. Thus, the signal at δ 4.74 is due to H_4 and the signal at 5.26 is due to H_1. The COSY spectrum indicated that H_4 couples to H_1, H_2 and H_6 and F_7, whilst H_1 couples to H_2, H_3, H_4 and H_5 and both fluorine atoms. These data are consistent with the assigned positions. Thus we have completely assigned the ^1H and ^{19}F spectra as being entirely consistent with the structure proposed. A compilation of the chemical shifts and multiplicities is shown in Table 2 and the coupling constants from both ^1H and ^{19}F spectra are shown in Table 3. The ^{13}C spectrum was very complex because of the overlap of signals, but it was possible to determine the chemical shifts and coupling constants for all of the carbon atoms. Although this data confirms the gross structure it is only included for information as it does not particularly aid structural assignment. The chemical shifts and coupling constants are shown in Tables 4 and 5.

The proposed structure was finally confirmed as (**3**) by means of a single-crystal X-ray diffraction analysis. The molecular structure is shown in Fig. 4 and consists of a cyclic five-membered 1,3,2-dioxathiolane-2-oxide system fused directly to the difluoro-7-oxa-bicyclo[2.2.1]heptane moiety with fluorine atoms F(1) and F(2) clearly occupying *exo* and *endo* configurations, respectively. In common with many other 1,3,2-dioxathiolane-2-oxide structures [17–22] the present structure adopts a half-chair (envelope) conformation with a dihedral angle between the planes defined by O(1), S(1), O(2) and O(1), C(1), C(2), O(2) of 8.2(1)°. The S=O group is pseudo-axial with an S(1)–O(3) bond length of 1.440(1) Å. The endocyclic S–O bond lengths [S(1)–O(1), 1.626(1), S(1)–O(2), 1.631(1) Å] can be considered as equivalent. The absence of any asymmetry in these endocyclic S–O bonds along with the slightly increased S=O bond length suggests that the pseudo-axial lone electron pairs on both of the endocyclic oxygen atoms are interacting with the S=O group on this molecule [17]. This anomeric effect has been cited as being the predominant cause of the preferred pseudo-axial orientation of the S=O bond [23].

The relatively small torsion angle around the C(1)–C(2) bond [O(1)–C(1)–C(2)–O(2), 5.1(1)°] is typical for a fused five-membered ring sulfite and may be compared to two similar fused cyclic sulfites containing a bicyclo[3.1.1]heptane ring system, *cis* and *trans*-3a,8,8-trimethyl-3a,4,5,6,7,7a-hexahydro-4,6-methano-1,3,2-dioxathiolane-2-oxide, which have O–C–C–O torsion angles of −3.4(7) and 21.1(7)°, respectively [20]. The typical value expected for a simple substituted five-membered cyclic sulfite is about 35°, however, this value can increase markedly if the cyclic sulfite ring system is stereochemically constrained, for example, in dispiro[1,3,2-dioxathiolane-4,5-bis(cyclohexane)]-2-oxide [18] and 8,8′-di(pentacyclo-(5.4, $0.0^{2.6}$, $0.0^{3.10}$, $0.0^{5.9}$) undecanyl)-spiro-4,5-(1,3,2-dioxothiolane-2-oxide) [24] both of which have O–C–C–O torsion angles of 39.4 and −43.5°, respectively.

The crystal packing is dominated primarily by van der Waals forces and although there are no formal hydrogen or secondary bonds there are two H–F contacts of F(1)–H(5A)^i

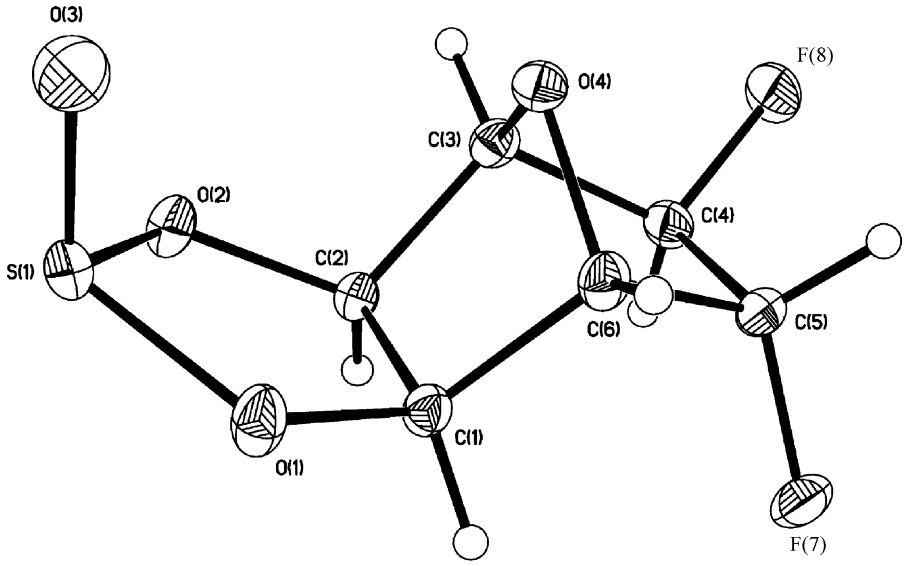


Fig. 4. Single crystal X-ray structure of 2α,3β-difluoro-7-oxabicyclo[2.2.1]heptane-5α,6α-sulphite showing atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level.

2.53(2) Å and F(1)–H(5A)^{i} 2.49(2) Å ($i = -1/2 + x$, $3/2 - y$, $-z$), these being approximately equal to the sum of the van der Waals radii of 2.50 Å as defined by Pauling [25].

In our earlier paper [14] we proposed a mechanism for the formation of the bicyclic derivative **1** from *myo*-inositol and SF_4 which involved the formation of a cyclic intermediate which fixed the conformation sufficiently to enable the subsequent processes to proceed giving the isolated product. Thus, we applied this mechanistic reasoning to the current reaction and found that it predicted a product with different stereochemistry to the observed product. We therefore had to slightly modify the suggested mechanism to obtain the required stereochemistry. The proposed mechanism is shown graphically in Scheme 1. We propose that the first step in the reaction is the formation of the cyclic intermediate A in the same way that we proposed previously [14], similar intermediates have also been proposed in the fluorination of pinetol with DAST [7] and are well documented in the fluorination of sugars with DAST [16] In this case, because of the C-2 rotational symmetry of the parent *chiro*-inositol, either pair of *cis* hydroxyl groups could equally react, but examination of models shows that these lead to the same intermediate **A**. The next step in the reaction must involve a change of conformation as shown to allow for the formation of the 1,4-epoxide bridge since clearly the hydroxyl groups must ultimately be in the *trans* arrangement to give intermediate **B**. Further, fluorination leads to intermediate **C** which can now eliminate SOF_2 and fluoride ion to form the epoxide **D**. Fluoride ion opening of the epoxide as shown results in the formation of intermediate **E** which now has the required stereochemistry at C_1 and C_4 and inverts the stereochemistry at C_1. A second conformational change and fluorination results in the formation of intermediate **F** which is now set-up correctly for the formation of the 1,4-oxygen bridge. We obviously cannot discount the possibility that the fluorination occurs before the conformation change. The formation of the oxygen bridge now fixes the conformation and subsequent fluorination with a further inversion on configuration leads after hydrolysis in the work up to the observed product.

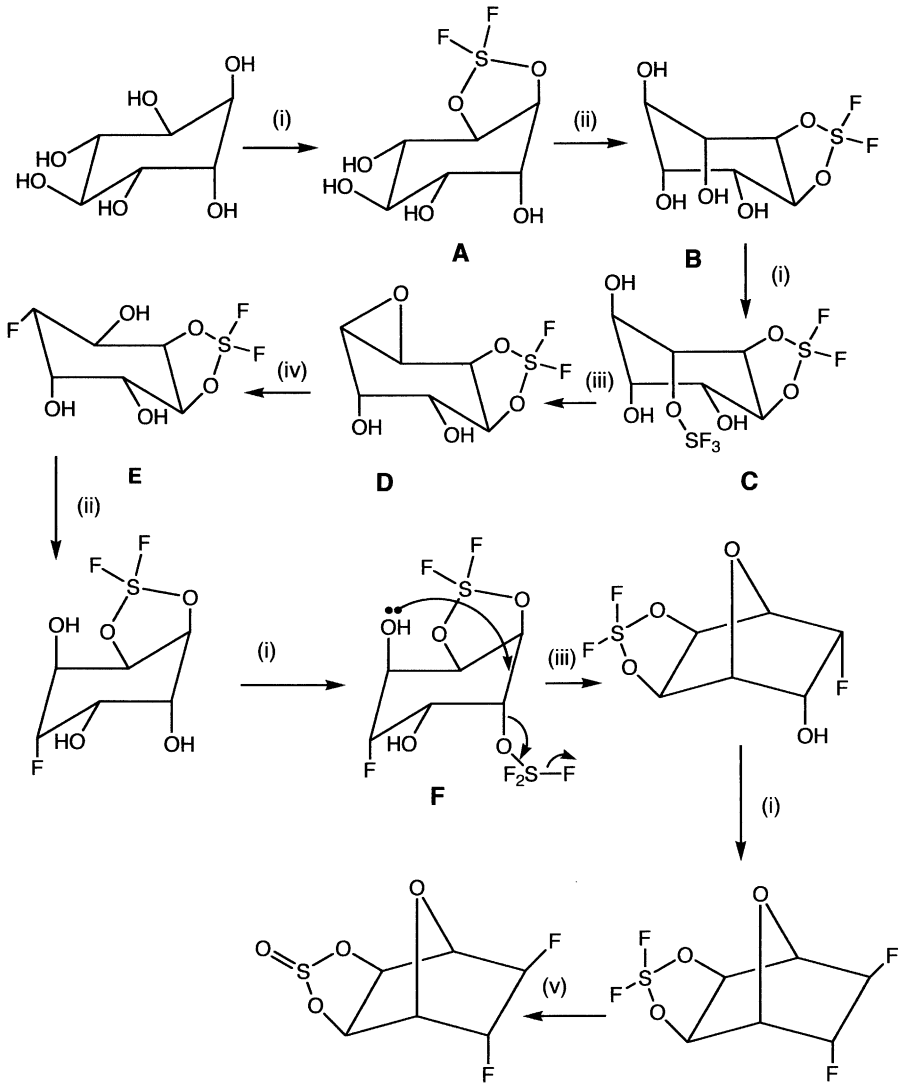
As with the product from *myo*-inositol, it is possible to remove the sulfite to obtain the diol, but we were unable to open the epoxide bridge to obtain the desired difluoro-dideoxy cyclitol. Thus we have confirmed that the reaction of cyclitols with SF_4 to form bicyclic compounds seems to be a general reaction. Whilst the failure to open the epoxide is disappointing we have clearly demonstrated the power of modern methods of structural assignment.

4. Experimental

Mass spectra were carried out using a Kratos MS 80RF instrument. ^{1}H, ^{19}F and ^{13}C NMR spectra were carried out using a Bruker DRX 400 spectrometer using TMS (^{1}H and ^{13}C) and $CFCl_3$ (F) as references.

4.1. Reaction of (+)-chiro-inositol with SF_4/AHF

Liquefied sulfur tetrafluoride (10cm^3) and anhydrous hydrogen fluoride (10 cm^3) were added to *chiro*-inositol (1.3 g) in a stainless steel Parr reaction vessel cooled to −78 °C. The bomb was sealed and the contents stirred for 12 h at 18 °C. The vessel was then re-cooled to −78 °C opened and the contents poured into a polythene beaker. The excess sulfur tetrafluoride and AHF were vented and the residue was dissolved in dichloromethane (50 cm^3), the organic phase was washed with sodium hydrogen carbonate solution, and then water (2 cm × 25 cm^2) and dried ($MgSO_4$). Evaporation of the solvent yielded a pale brown



Scheme 1. Reaction mechanism: (i) SF_4; (ii) flip; (iii) $-SOF_2-HF$; (iv) HF; (v) work up.

solid which on recrystallisation from methanol afforded 2α,3β-difluoro-7-oxabicyclo[2.2.1]heptane-5α,6α-sulfite **3** (nc) (0.6 g, 43%) mp 148–149 °C (found: C, 34.2; H, 2.9%. $C_6H_6F_2O_4S$ requires C, 34.0; H, 3.0%); *m/z* 212 $[M]^+$, 148 $[M\text{-}SO_2]^+$.

4.2. Single crystal X-ray structure

A colourless needle crystal, 0.50 mm × 0.30 mm × 0.20 mm was mounted on a Rigaku AFC7R four-circle diffractometer equipped with an Oxford Cryosystems Cryostream Cooler [27] using graphite-monochromated Mo Kα radiation.

4.2.1. Crystal data

$C_6H_6O_4F_2S_1$, $M = 212.17$, orthorhombic, space group $P2_12_12_1$ $a = 9.5368(8)$, $b = 15.6030(8)$, $c = 4.9287(8)$ Å, $U = 733.40(14)$ Å^3 (from 2θ values of 25 reflections measured at $\pm\omega$ ($35.80 \leq 2\theta \leq 39.6°$ Mo Kα, $\lambda = 0.71069$ Å)), $Z = 4$, $D_c = 1.922$ g cm^{-1}, $\mu = 0.457$ mm^{-1}, $F(0\,0\,0) = 432$, $T = 123(1)$ K.

4.2.2. Data collection and processing

A total of 1940 reflections were collected with $\omega - 2\theta$ scans, scan-width $= (1.00 + 0.35 \tan\theta)°$, to a θ_{max} of 26.98° (h − 12 to 12, k − 19 to 19, l − 6 to 6, one set of Bijvoet pairs collected). The 1607 unique reflections ($R_{int} = 0.0192$) and 1568 observed with $I < 2\sigma(I)$. Analysis of the intensities of three standard reflections recorded every 150 reflections showed an overall decrease in the intensity of 0.07% and the data were scaled accordingly. The data were corrected for Lorentz and polarisation effects. No absorption correction was applied since preliminary ψ-scans revealed no significant absorption effects [26].

4.2.3. Structure solution and refinement

The structure was solved by direct methods. Full-matrix least-squares refinement on F^2 with weighting scheme

$w^{-1} = \sigma^2(F_o^2) + (0.0550P)^2 + 0.2000P$, where $P = (F_o^2 + 2F_o^2)/3$, anisotropic displacement parameters, riding hydrogen atoms (U_{iso} free to refine), and a secondary extinction correction $x = 0.036(4)$, where $F_c^* = kF_c[1 + 0.001 \times F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$, converged with a Δ/σ_{max} of 0.000. Final $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}\} = 0.0755$ for all data, conventional $R = 0.0260$ on F values of 1607 reflections with $I > 2\sigma(I)$, $S = 1.015$ for all data and 125 parameters. Absolute structure parameter 0.06(8) [29]. Final difference map between +0.34 and −0.33 e Å^{-3}. Further details of the structural investigation including supplementary data are available on request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK quoting the depository number CSD 145411, the authors' names and the full citation of the journal [28].

References

[1] H. Streb, R.F. Irvine, M.J. Berridge, I. Schultz, Nature 306 (1983) 67.
[2] M.J. Berridge, R.F. Irvine, Nature 312 (1984) 315.
[3] J.D. Moyer, D. Reizes, N. Malinowski, J. Jiang, D.C. Baker, ACS Symp. Ser. 374 (1988) 42.
[4] C. Jiang, J.D. Moyer, D.C. Baker, J. Carbohydrate Chem. 6 (1987) 3193.
[5] S.S. Yang, T.R. Beattie, T.Y. Shen, Synth. Commun. 16 (1986) 131.
[6] G. Lowe, F. McPhee, J. Chem. Soc., Perkin Trans. 1 (1991) 1249.
[7] A.P. Kozikowski, A.H. Fauq, G. Powis, D.C. Melder, J. Am. Chem. Soc. 112 (1990) 4528.
[8] J.L. Offer, J.C. Metclafe, G.A. Smith, J. Chem. Soc., Chem. Commun. (1990) 1313.
[9] A.P. Kozikowski, A.H. Fauq, J. Am. Chem. Soc. 112 (1990) 7403.
[10] C. Jiang, D.J.A. Schedler, P.E. Morris, A.-H.A. Zayd, D.C. Baker, Carbohydrate Res. 207 (1990) 7403.
[11] S.V. Ley, M. Parra, A.J. Redgrave, F. Sternfeld, Tetrahedron 30 (1989) 5401.
[12] J.F. Marek, G.D. Prestwich, Tetrahedron Letts. 30 (1989) 5401.
[13] A.P. Kozikowski, A.H. Fauq, J.M. Rusnak, Tetrahedron Letts. 30 (1989) 3365.
[14] P.L. Coe, L.D. Proctor, J.A. Martin, W.A. Thomas, J. Fluorine Chem. 58 (1992) 87.
[15] M. Zupan, A. Gregorcic, A. Pollak, J. Org. Chem. (1977) 1562.
[16] P.J. Card, J. Carbohydrate Chem. 4 (1985) 451.
[17] G. Lowe, S.J. Salamone, R.H. Jones, J. Chem. Soc., Chem. Commun. (1984) 262.
[18] M. Mottevalli, M.B. Hursthouse, D.G. Hellier, H.G. Liddy, Acta Cryst. C46 (1990) 1912.
[19] F. Rebiere, O. Samuel, L. Ricard, H.B. Kagan, J. Org. Chem. 56 (1991) 5991.
[20] D.G. Hellier, M. Mottevalli, Acta Cryst. C51 (1995) 116.
[21] D.G. Hellier, M. Mottevalli, Acta Cryst. C51 (1995) 129.
[22] D.G. Hellier, M. Mottevalli, Acta Cryst. C52 (1996) 739.
[23] A.J. Kirby, The Anomeric Effect and Related Stereoelectronic Effects at Oxygen, Springer, Berlin, 1983, p. 31.
[24] S.G. Bott, A.P. Marchand, V.R. Gadgil, J. Chem. Cryst. 25 (1995) 215.
[25] L. Pauling, The Nature of the Chemical Bond, 3rd Edition, Cornell University Press, Ithaca, 1960.
[26] teXsan Single Crystal Structure Analysis Software, Version 1.6, Molecular Structure Corporation, Woodlands, TX 77381, USA, 1993.
[27] J. Cosier, A.M. Glazer, J. Appl. Cryst. 19 (1986) 105.
[28] G. Sheldrick, SHELXTL, Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.
[29] H.D. Flack, Acta Cryst. A38 (1983) 876.