PREPARATION OF 3-DEOXY-3-FLUORO-D-MANNOSE AND CORRESPONDING HEXITOL*

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Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

Reaction of 1,6 : 3,4-dianhydro-β-D-altropyranose (*I*) with potassium hydrogen fluoride in hot ethylene glycol gave 1,6-anhydro-3-deoxy-3-fluoro-β-D-mannopyranose (*II*). On acid catalysed hydrolysis or acetolysis of compound *II* 3-deoxy-3-fluoro-D-mannose (*VIII*) or its tetra-O-acetyl derivative *VII*, respectively, were obtained. Reduction of compound *VIII* with sodium borohydride gave 3-deoxy-3-fluoro-D-mannitol (*IX*). The structures of the mentioned compounds were proved by ^{1}H NMR spectroscopy.

Among 3-deoxy-3-fluoro derivatives of aldohexoses only 3-deoxy-3-fluoro-D-glucose[1-3] and corresponding compounds of D-*galacto*[4,5] and L-*ido*[6,7] configuration have been described. Biochemical studies were carried out predominantly with the first of the mentioned compounds[8-12]. In view of the frequent occurrence of D-mannose in a number of glycoproteins, where they constitute the main building unit of oligosaccharide chains, and also in natural mannans, we decided to carry out – on the basis of earlier results[13] – the preparation of 3-deoxy-3-fluoro-D-mannose and some of its derivatives and so make them available for biochemical studies.

The starting compound for our synthesis, 1,6 : 3,4-dianhydro-β-D-altropyranose (*I*) was prepared by four step synthesis from 1,6-anhydro-β-D-glucopyranose, according to ref.[14]. The oxirane ring of this dianhydro derivative can be opened with various nucleophilic reagents; for the introduction of fluorine into the molecule potassium hydrogen fluoride in ethylene glycol was used, which had proved valuable earlier[15]. The reaction was carried out by heating the reaction components at 200°C under nitrogen for several hours. According to our expectation[16] the opening of the oxirane ring took place with high regioselectivity at $C_{(3)}$, and 1,6-anhydro-3-deoxy-3-fluoro-β-mannopyranose (*II*) was formed as practically the sole fluorine containing product.

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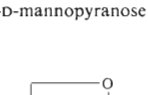
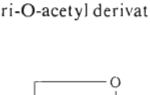
The proposed structure for compound *II* is supported by the fact that even after five days it was not oxidized with sodium periodate under the conditions when the model oxidation of 1,6-anhydro-4-deoxy-β-D-*arabino*-hexopyranose[17] did take place, and further the fact that the value of $[\alpha]_D$ −118° (water) of compound *II* is very close to the value $[\alpha]_D$ −127° found for 1,6-anhydro-β-D-mannopyranose[18] (replacement of the hydroxyl group by fluorine changes the optical rotation value only a little[16]). It was shown by means of the ^{1}H NMR spectra that compound *II* assumes the same conformation $^1C_4$(D) in water as well as in chloroform. The interaction constants $J_{2,F}$ = 26·4 or 27·4 Hz indicate an antiperiplanar arrangement of F-3 and H-2, and the values $J_{4,F}$ = 12·5 or 10·5 Hz a synclinal (gauche) arrangement of F-3 and H-4. Further parameters of compound *II* and of its di-O-acetyl derivative *III* (Table I) also confirm[19,20] their configuration and conformation $^1C_4$(D), and they are correlative[19] with the parameters of the ^{1}H NMR spectrum of 1,6-anhydro-β-D-mannopyranose (*V*) and its tri-O-acetyl derivative *VI*.

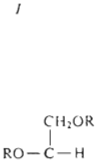


I

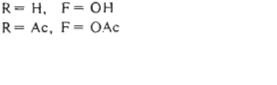


II, R = H
III, R = Ac
IV, R = Bz
V, R = H, F = OH
VI, R = Ac, F = OAc

VII, R = Ac
VIII, R = H



IX, R = H
X, R = Ac



Xa

Benzoylation of compound *II* in pyridine gave its di-O-benzoyl derivative *IV*, which is, in contrast to di-O-acetyl derivative *III*, crystalline and suitable for identification.

TABLE I

^{1}H NMR Parameters of 3-fluoro derivatives *II*, *III*, *VII*, *III*, and *X*

Proton	*II* (^2H_2O)	*II* (C^2HCl_3)	*III* (C^2HCl_3)	*VII* (C^2HCl_3)	*VIII* (^2H_2O)[a]		*X* (C^2HCl_3)	*X* ($C_6{}^2H_6$)
				Chemical shifts				
H-1	5·43	5·40	5·49	6·14	5·23	(4·91)	4·55	4·63
H-1′	—	—	—	—	—		4·13	3·97
H-2	3·83	3·72	[b]	5·36	4·19	(4·19)	5·11	5·32
H-3	4·74	4·74	[b]	4·91	4·75	(4·59)	4·85	4·87
H-4	4·12	4·01	5·04	5·46	[c]	[c]	[d]	5·66
H-5	4·63	4·53	4·65	3·97	[c]	(3·39)	5·31	5·50
H-6	4·09[e]	4·08[e]	4·20[e]	4·28[e]	[c]	[c]	4·38	4·48
H-6′	3·81[f]	3·83[f]	3·88[f]	4·13[f]	[c]	[c]	4·16	4·17
OAc	—	—	2·17	2·10	—	—	2·04	1·63
			2·19	2·13			2·06	1·66
				2·15			2·09	1·70
				2·19			2·10	1·71
							2·12	1·75
				Coupling constants				
$J_{1,1'}$	—	—	—	—	—	—	12·5	12·4
$J_{1,2}$	1·9	1·9	1·6	2·0	1·9	(1·1)	2·5	2·6
$J_{1',2}$	—	—	—	—	—	—	4·3	4·8
$J_{2,3}$	4·5	4·6	[d]	3·8	3·5	(3·5)	9·3	9·3
$J_{3,4}$	2·0	2·1	[d]	9·6	9·4	(9·4)	1·6	1·7
$J_{4,5}$	2·0	2·1	1·8	10·1	[d]	(10·0)	7·1	7·2
$J_{5,6}$	1·2	1·2	1·2	5·0	[d]	(5·9)	2·6	2·7
$J_{5,6'}$	6·0	5·9	5·9	2·5	[d]	(2·4)	5·7	5·4
$J_{6,6'}$	7·9	7·8	7·9	12·5	[d]	[c]	12·5	12·6
$J_{1,F}$	0	0	0	4·7	5·1	(2·1)	2·6	2·6
$J_{1',F}$	—	—	—	—	—	—	2·2	2·1
$J_{2,F}$	26·4	27·4	[d]	5·8	7·1	(7·4)	6·8	6·8
$J_{3,F}$	47·7	48·0	[d]	48·0	48·6	(48·0)	45·6	46·0
$J_{4,F}$	12·5	10·5	12·6	11·4	[d]	[d]	[c]	30·1
$J_{5,F}$	0·8	0·7	0	1·0	[d]	(1·2)	0	1·0
$J_{6,F}$	1·4	1·5	1·3	0	[d]	[d]	0	0
$J_{6',F}$	3·8	3·8	3·5	1·5	[d]	[d]	0	0

[a] Values for the α-anomer (in brackets for the β-anomer). [b] Complex multiplet of H-2 and H-3 at δ 4·75—5·01. [c] Strongly coupled broad multiplet of seven protons between δ 3·62 and 4·03. [d] A correct parameter value could not be determined. [e] H-6_{endo}. [f] H-6_{exo}.

Acetolysis of 1,6-anhydride bond in compound *II* with acetic anhydride, under catalysis with perchloric acid, afforded 1,2,4,6-tetra-O-acetyl-3-deoxy-3-fluoro-α-D--mannopyranose (*VII*) in 75% yield. Its structure was confirmed by ^{1}H NMR spectra. In chloroform solution it occurs in $^4C_1$(D) conformation in α-anomeric form, as evidenced by the low value of $J_{1,2} = 2{\cdot}0$ Hz (it excludes the axial orientation of H-1), the high values of the constants $J_{3,4} = 9{\cdot}6$ and $J_{4,5} = 10{\cdot}1$ Hz (hydrogens H-3, H-4 and H-5 are axial), the relatively high long-range coupling $^4J_{1,F} = 4{\cdot}7$ Hz (F-3 and H-1 in diequatorial arrangement) and also the positive optical rotation value $[\alpha]_D$ +22° (in chloroform).

After deacetylation of the tetraacetate *VII* with sodium methoxide in methanol, crystalline 3-deoxy-3-fluoro-D-mannose (*VIII*) was obtained. It was also obtained by direct hydrolysis of anhydro derivative *II* with 5% trifluoroacetic acid at 130°C in a sealed tube. Compound *VIII* reduced the Fehling's reagent rapidly under warming, in contrast to 2-deoxy-2-fluoro-D-mannose[20], which reduced it much more slowly[21].

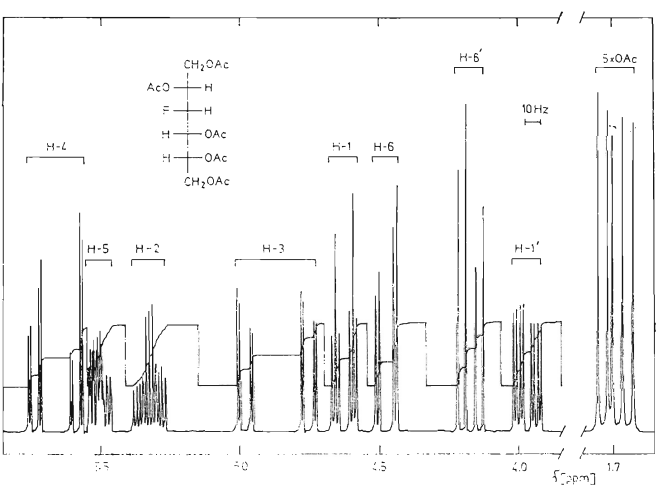


FIG. 1

^{1}H NMR Spectrum of 1,2,4,5,6-penta-O-acetyl-3-deoxy-3-fluoro-D-mannitol in hexadeuteriobenzene

The ^{1}H NMR spectrum (^2H_2O) showed that compound *VIII* after mutarotation consists of a mixture of α- and β-anomer in a 68 : 32 ratio. Both anomers exist in $^4C_1$(D) conformation (high values of $J_{3,4}$ = 9·4 and $J_{4,5}$ = 10·0 Hz), and their assignment was done on the basis of different long-range couplings $^4H_{1,F}$ (5·1 Hz in α-anomer, in contrast to 2·1 Hz in β-anomer).

Reduction of compound *VIII* with sodium borohydride gave 3-deoxy-3-fluoro--D-mannitol (*IX*), and its acetylation with acetic anhydride in pyridine afforded the corresponding 1,2,4,5,6-penta-O-acetyl derivative *X*. From the ^{1}H NMR spectrum it follows that acetate assumes in the polar solvents conformation *P* (formula *Xa*) with a planar zig-zag arrangement of the carbon chain. The spectrum in deuteriobenzene (Fig. 1) permits the extraction of all NMR parameters. Making use of the large geminal coupling constant $^2J_{3,F}$ the hydrogen H-3 could be identified. The observed long-range couplings with the fluorine atom permitted the identification of the signals of hydrogens H-1 and H-1' ($^4J_{1,F}$ = 2·2 and $^4J_{1',F}$ = 2·6 Hz). The high value of $^3J_{4,F}$ = 30·1 Hz shows an antiperiplanar arrangement of H-4 and F-3, while the value $^3J_{2,F}$ = 6·6 Hz corresponds to a synclinal arrangement. The conformations around the $C_{(1)}$—$C_{(2)}$ and $C_{(5)}$—$C_{(6)}$ bonds follow from the constants $J_{1,2}$ and $J_{1',2}$ or $J_{5,6}$ and $J_{5,6'}$ respectively. Their low values (2·6, 4·8 and 2·7, 5·4 Hz, respectively) indicate a distinct preference of the "g" rotamers in which H-2 (or H-5) is in the gauche position with respect to both neighbouring hydrogens H_1, $H_{1'}$ (or H-6, H-6'). The existence of compound *X* in conformation *Xa* is in agreement with the fact, that – for example – diethyl dithioacetal of 2,3,4,5-tetra-O-acetyl--L-rhamnose (with L-*manno* configuration at carbons $C_{(2)}$, $C_{(3)}$, $C_{(4)}$ and $C_{(5)}$) has the same conformation[22]. In both mentioned compounds the unfavourable 1,3-*syn*--interactions do not occur in the planar conformation *P*, which would destabilize it and lead to the so-called sickle conformation[23–27].

EXPERIMENTAL

The melting points were determined on micromelting point apparatus (Boëtius) and are not corrected. The optical rotation values were measured on an automatic Bendix Ericsson ETL 143A polarimeter at 23—25°C. ^{1}H NMR spectra were measured on a FT NMR spectrometer Varian XL-200 (200 MHz) in deuteriochloroform, deuteriobenzene or ^2H_2O, using tetramethylsilane (in the case of water sodium 2,2-dimethyl-2-silapentane-5-sulphonate) as internal reference. For the assignment of the signals the homonuclear decoupling of the hydrogens, the observed multiplicities of the signals and the chemical shifts were made use of. The chemical shifts and the coupling constants were obtained by first order analysis from the expanded spectra (2 Hz/cm), at a digital resolution of 0·2 Hz and using Gauss's apodization function for an increase in resolution.

The reaction course was monitored by thin-layer chromatography on silica gel according to Stahl, 0·2—0·3 mm layer thickness, using detection by spraying the plates with 50% sulfuric acid and carbonization. The solutions were concentrated on a vacuum rotatory evaporator at 40—70°C. Samples for analysis were dried over phosphorus pentoxide at 20—40°C and 20 Pa pressure.

1,6-Anhydro-3-deoxy-3-fluoro-β-D-mannopyranose (*II*)

A mixture of epoxide *I* (8·2 g) and potassium hydrogen fluoride (30 g) in ethylene glycol (200 ml) was heated under reflux (air condenser) at 200°C under stirring with nitrogen stream. According to thin-layer chromatography in benzene–dioxane–ethanol–ammonia (50 : 40 : 8 : 5) the reaction was terminated after 4 h when the mixture contained compound *II* with R_F 0·6 (relatively to the starting compound *I*) as the main product. The mixture was then diluted with 150 ml of ethanol and allowed to stand in a refrigerator overnight. The separated salts were filtered off and the solution was concentrated in a vacuum rotatory evaporator at 110°C. Acetone (100 ml) and 0·25 ml of conc. sulfuric acid were added to the residue and the mixture was shaken for 3 h at room temperature. After neutralization with a calculated amount of sodium hydroxide (0·460 g) the solution was evaporated on a water bath under reduced pressure. The residue was boiled with ethanol, filtered with charcoal and the filtrate evaporated. The residue was crystallized from methanol. Yield, 5·5 g (59%) of fluoro derivative *II*, sintering and sublimating at 110—134°C, m.p. 158—160°C, $[\alpha]_D$ −118° (*c* 0·69, water). For $C_6H_9FO_4$ (164·1) calculated: 43·90% C, 5·53% H, 11·58% F; found: 43·97% C, 5·60% H, 11·73% F.

2,4-Di-O-acetyl-1,6-anhydro-3-deoxy-3-fluoro-β-D-mannopyranose (*III*)

Anhydride *II* (200 mg) was acetylated with acetic anhydride (1 ml) in pyridine (2 ml) at room temperature for 2 h. The mixture was poured into icy water (10 ml), extracted with chloroform and the combined chloroform extracts were washed with 5% hydrochloric acid, water and dried over anhydrous calcium chloride. The chloroform solution after evaporation gave 290 mg (96%) of acetyl derivative *III*, which was distilled at 185°C bath temperature (20 Pa), $[\alpha]_D$ −106° (*c* 0·66, chloroform). For $C_{10}H_{13}FO_6$ (248·2) calculated: 48·39% C, 5·28% H; found: 48·41% C, 5·36% H.

1,6-Anhydro-2,4-di-O-benzoyl-3-deoxy-3-fluoro-β-D-mannopyranose (*IV*)

Benzoyl chloride (0·8 ml) was added to a solution of anhydride *II* (110 mg) in pyridine (1·5 ml), cooled with water. After standing overnight the mixture was diluted with a saturated sodium hydrogen carbonate solution (5 ml) and allowed to stand in a refrigerator. The separated crystals were washed with water and recrystallized from an ethanol–water mixture. Yield, 160 mg (64%) of dibenzoyl derivative *IV*, m.p. 141—142°C, $[\alpha]_D$ −186° (*c* 0·5; chloroform). For $C_{20}H_{17}FO_6$ (372·3) calculated: 64·51% C, 4·60% H, 5·10% F; found: 64·52% C, 4·48% H, 5·04% F.

1,2,4,6-Tetra-O-acetyl-3-deoxy-3-fluoro-α-D-mannopyranose (*VII*)

Perchloric acid (0·65 ml of a 70% acid) was added to a mixture of anhydride *II* (6 g) in acetic anhydride (65 ml) and the reaction course of acetolysis was followed by thin-layer chromatography in benzene–acetone (10 : 1). At room temperature the reaction was over after about 16 h. The mixture was poured into 200 ml of icy water and put into a refrigerator for crystallization. The crystals were filtered off, the filtrate extracted with chloroform. The extract was washed with sodium hydrogen carbonate, dried and evaporated to afford another part of crystals. After recrystallization of both parts of crystals from ether–light petroleum 9·5 g (74%) of acetyl derivative *VII* were obtained, m.p. 116—117°C, $[\alpha]_D$ +22° (*c* 1·4, chloroform). For $C_{14}H_{19}FO_9$ (350·3) calculated: 48·00% C, 5·47% H, 5·42% F; found: 48·28% C, 5·35% H, 5·40% F.

3-Deoxy-3-fluoro-D-mannose (*VIII*)

A) Tetraacetate *VII* (4·2 g) was deacetylated with sodium methoxide in methanol (according

to Zemplén) and the reaction course was monitored by thin-layer chromatography in benzene–acetone (10 : 1). During the reaction the formation of partially deacetylated products was observed. After complete deacetylation, which took about 24 h, the sodium ions were eliminated by means of Dowex 50 (in H^+ form) and the solution was decolorized with charcoal. The filtrate was evaporated to a syrup which was allowed to crystallize in an evacuated desiccator, over phosphorus pentoxide. After two recrystallizations from a mixture of ethanol and ether, 1·5 g (69%) of the reducing sugar *VIII* were obtained, m.p. 157–158°C, $[\alpha]_D$ + 32° → + 23° (*c* 1·4; water). Repeated crystallization from ethanol gave *VIII* of m.p. 173–175°C. For $C_6H_{11}FO_5$ (182·2) calculated: 39·56% C, 6·09% H, 10·43% F; found: 39·61% C, 6·15% H, 10·17% F.

B) Fluoromannosan *II* (6·1 g) was heated with 120 ml of 5% trifluoroacetic acid at 130 to 140°C in a sealed tube for 6 h. Chromatography on a thin layer in benzene–dioxane–ethanol–ammonia (30 : 20 : 3 : 2·5) showed that the starting compound had reacted completely. The mixture containing a small amount of carbonized substances was diluted with water, decolorized by heating with charcoal, filtered and evaporated. Yield, 6·2 g (91·7%) of syrupy fluoromannose *VIII* which can be used for the preparation of fluoromannitol *IX*.

3-Deoxy-3-fluoro-D-mannitol (*IX*)

A solution of sodium borohydride (0·4 g in 10 ml of water) was added to a stirred solution of fluoromannose *VIII* (1·5 g) in 16 ml of water over 10 minutes and the mixture was stirred for further 15 min at room temperature. Sodium ions were then eliminated from the solution by gradual addition of Amberlite IR 120 (H^+ form) ion exchanger and the solution was concentrated. The residual syrup was dissolved in 100 ml of methanol, containing a few drops of methanolic hydrogen chloride, and the solution was evaporated. This procedure was repeated until boric acid was eliminated in the form of methyl ester. The syrup was then again dissolved in water, the solution was filtered with charcoal and evaporated. The residue was allowed to stand in an evacuated desiccator over phosphorus pentoxide. Crystallization from ethanol gave 1·1 g (72%) of fluoromannitol *IX*, which was recrystallized once more for analysis. M.p. 111–113°C, $[\alpha]_D$ −4° (*c* 1·1, water). Chromatography of the concentrated mother liquors on a 30-fold amount of silica gel in chloroform–ethanol 5 : 1 gave another 0·21 g (14%) of product IX. For $C_6H_{13}FO_5$ (184·2) calculated: 39·13% C, 7·12% H, 10·32% F; found: 39·27% C, 7·12% H, 10·08% F.

1,2,4,5,6-Penta-O-acetyl-3-deoxy-3-fluoro-D-mannitol (*X*)

Fluoromannitol *IX* (100 mg) was dissolved in 2 ml of pyridine and 1 ml of acetic anhydride was added. The mixture was allowed to stand at room temperature for 18 h (thin-layer chromatography in benzene–acetone 10 : 1), then poured onto crushed ice and after 2 h the separated oil was extracted with 3 ten ml portions of chloroform. The chloroform extracts were washed with 5% hydrochloric acid, and water, dried over anhydrous calcium chloride and evaporated Yield 200 mg (93%) of a syrup. For analytical purposes the sample was purified by distillation at 160°C bath temperature and 18 kPa; $[\alpha]_D$ +10° (*c* 2; chloroform). For $C_{16}H_{23}FO_{10}$ (394·3) calculated: 48·73% C, 5·88% H, 4·82% F; found: 48·71% C, 5·85% H, 4·80% F. Gas chromatography was carried out on a Chrom 3 chromatograph (Laboratory apparatus), column length 193 cm, diameter 3 mm, packing 10% of the OV 275 phase on Chromosorb W-AW, 203°C, 60 ml N_2/min flow rate, T 203°C (T_i 230°C); retention time of fluoro derivative X 6·2 min., of 1,2,3,4,5,6-hexa-O-acetyl-D-mannitol 8·4 min.

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Note added in proof: Recently, an alternative synthesis of 3-deoxy-3-fluoro-D-mannose has been published by J. R. Rasmussen, S. R. Tafuri, and S. T. Smale in Carbohyd. Res. *116*, 21 (1983).

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