REACTION OF NUCLEOSIDES WITH THIONYL CHLORIDE; PREPARATION OF THE DEOXY DERIVATIVES OF CYTIDINE AND ADENOSINE*

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On reaction of thionyl chloride with cytidine and adenosine in refluxing acetonitrile, the 5'-chloro-2',3'-sulphinyl derivatives *I* and *VII* are formed in a quantitative yield. On heating in dimethylformamide, compound *I* affords 5'-chloro-5'-deoxycyclocytidine (*II*) which is hydrolyzed in alkali to the arabinosyl derivative *III*; reduction of *III* with tributyltin hydride gives the 5'-deoxyarabinosyl derivative *IV*. The sulphinyl derivative *I* is hydrolyzed to 5'-chloro-5'-deoxycytidine (*V*) which is reduced to 5'-deoxycytidine (*VI*). Analogously, the sulphinyl derivative *VII* affords 5'-chloro-5'-deoxyadenosine (*VIII*) and the reduction of *VIII* gives 5'-deoxyadenosine (*IX*). Of these compounds, the 5'-chloro-5'-deoxyarabinosyl derivative as the only one shows an inhibitory effect towards the L1210 cell growth.

In the course of the study of protecting groups of polyfunctional molecules that are used in syntheses of nucleosides and nucleotides, we achieved new results even at well-known reactions, as *e.g.* at the reactions of nucleosides with acyl halides[1,2], 1,1'-carbonyldiimidazole[3,4], diphenyl carbonate[5], or thionyl chloride[6-8]. The recently described reaction of cytidine with thionyl chloride in acetonitrile at room temperature affords 2',3'-O-sulphinyl cytidine[9], in dimethylformamide cyclocytidine[10,11] while in hexamethylphosphortriamide the 5'-halogeno derivative of the nucleoside is formed[12]. Thus, thionyl chloride affords quite different reaction products under conditions which differ only in the solvent used. Besides, during the study[6-8] of the reaction of nucleosides with thionyl chloride in hexamethylphosphortriamide we found that, in contrast to the earlier observation[12,13], two epimers of the 5'-chloro-2',3'-O-sulphinyl derivative of ribonucleosides[6-8], stereoisomeric at the sulphur atom, were formed. The highly reactive sulphinyl derivatives were utilized in the conversion of ribonucleosides to the 5'-halogeno and 5'-deoxy derivatives of ribo, arabino, 2'-halogeno-2'-deoxyribo, and 2'-deoxyribonucleosides[6-8].

The aim of the present paper was to study the influence of different solvents on the formation of 5'-halogeno-2',3'-O-sulphinyl derivatives in reactions of nucleo-

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sides with thionyl chloride; in particular, the possibility of formation of the 5′-chloro-2′,3′-sulphinyl derivatives of cytidine and adenosine on reaction with thionyl chloride in acetonitrile and their ability to give epimers was studied. In the reaction of cytidine with thionyl chloride in acetonitrile, in contrast to the reaction at room temperature[9], enhancement of the reaction temperature afforded, in analogy to our earlier findings[6–8], an almost quantitative yield of a new product, the hydrochloride of 5′-chloro-2′,3′-sulphinyl derivative *I*. For the sake of comparison and confirmation of the structure, 5′-chloro-5′-deoxy-2′,3′-O-sulphinylcytidine (*I*) was alternatively prepared from 5′-chloro-5′-deoxy-cytidine[12] by reaction with thionyl chloride in acetonitrile at room temperature (in an 89% yield), analogously to the preparation of 2′,3′-O-sulphinylcytidine[9].

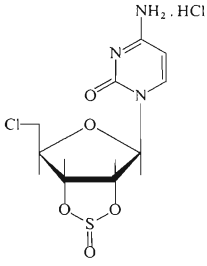
The hydrochloride of the sulphinyl derivative *I* was converted to the corresponding 5′-chloro-5′-deoxycyclocytidine hydrochloride (*II*) in 78% yield by heating in dimethylformamide. In contrast to the other pyrimidine nucleosides[6–8], it is not necessary to catalyze the conversion by the presence of imidazole. *II* can only be isolated as a salt, otherwise it is hydrolyzed to the arabinosyl derivative *III*. The opening of the anhydro ring was achieved by a strongly basic ion exchange resin in carbonate cycle; this technique is convenient because of preventing the inorganic salts to contaminate the reaction mixture. The arabinosyl derivative *III* is obtained as free nucleoside in a high yield. The following reduction of the 5′-chloro derivative *III* with tributyltin hydride[14,15] (ref.[3] and references therein) afforded 5′-deoxy-arabinosylcytosine (*IV*) in 51% yield. Instead of using alkaline methanolysis[6], the 2′,3′-sulphinyl group in the 5′-chloro derivative *I* was hydrolyzed in aqueous solution by the action of a strongly basic ion exchange resin in carbonate cycle; the 5-chloro-5′-deoxyribosyl derivative *V* was obtained in 80% yield. Subsequent reduction with tributyltin hydride in methanol afforded 5′-deoxycytidine (*VI*) in 38% yield; when carried out in dimethyl sulphoxide, the yield was 51%.

In analogy to cytidine, the reaction of thionyl chloride with adenosine in refluxing acetonitrile afforded the crystalline 5′-chloro-5′-deoxy-2′,3′-O-sulphinyladenosine (*VII*) in 93·5% yield. The hydrolysis of *VII* by a strongly basic ion exchange resin in carbonate cycle led to the 5′-chloro-5′-deoxyadenosine (*VIII*). Subsequent reduction of *VIII* with tributyltin hydride in dimethyl sulphoxide afforded 5′-deoxy-adenosine (*IX*) in crystalline form in 50% yield while the analogous reduction in tetrahydrofurane yielded[18] 82% of *IX*.

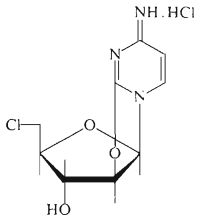
The formation of the 5′-chloro-2′,3′-O-sulphinyl derivatives *I* and *VII* in the reaction of thionyl chloride with cytidine and adenosine in acetonitrile in almost quantitative yield excludes unambiguously the original assumption of Hogenkamp[13] about the course of the formation of 5′-chloro derivatives of cytidine and adenosine. At the same time, however, a suggestion comes into consideration that in the reaction course thionyl chloride reacts with both primary and secondary hydroxyl groups of the nucleoside under formation of 2′(3′),5′-bis-O-chlorosulphinyl derivative,

whereby the 2′(3′)-chlorosulphinyl group is immediately transformed to 2′,3′-cyclic sulphite. The 5′-chlorosulphinyl group is further transformed, by way of nucleophilic substitution, to the 5′-chloro group to afford the final product, the 5′-chloro-2′,3′-O-sulphinyl derivative.

With regard to the observation that the reaction of uridine[6], 5-fluorouridine[6], and 6-azauridine[8] with thionyl chloride in hexamethylphosphortriamide gives rise to the 5′-chloro-2′,3′-O-sulphinyl derivatives in the form of a mixture of two isomeric compounds, we studied derivatives *I* and *VII* in order to decide whether they are homogeneous compounds or mixtures of two isomers. From the ^{1}H-NMR spectra of *I* and *VII* it follows that the products are isomeric mixtures indeed. We succeeded to assign spectral signals to only one isomer out of two in both cases. It appeared



I



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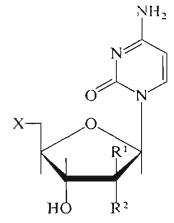
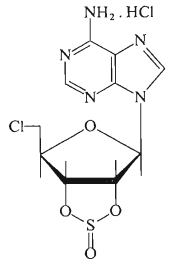
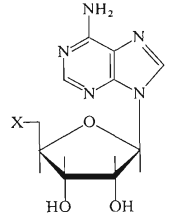


III, X = Cl, R^1 = OH, R^2 = H
IV, X = H, R^1 = OH, R^2 = H
V, X = Cl, R^1 = H, R^2 = OH
VI, X = R^1 = H, R^2 = OH



VII



VIII, X = Cl
IX, X = H

impossible to assign stereochemistry to the single isomers. However, quantum chemistry calculations[16] seem to support the assumption on the stereochemistry of isomers mentioned in the earlier paper[6] dealing with the 5'-chloro-2',3'-O-sulphinyl derivatives of uridine and 5-fluorouridine. According to that, the epimers differ in the location of oxygen of the sulphinyl group, with respect to the plane defined by the atoms $C_{2'}$—$O_{(2')}$—S—$O_{(3')}$—$C_{3'}$ (observed clockwise). Thus, in case of the epimer which was specified as (+)-isomer (arising in higher yield, the more mobile one on TLC) that oxygen is before reference plane while in the other isomer, oxygen is behind that plane.

In a study performed by Dr A. Bloch, Roswell Park Memorial Institute, the analogues *III* – *VI*, *VIII*, *IX* were tested for inhibition of L1210 cell growth and for antiviral activity. Out of the compounds prepared, the 5'-chloro-5'-deoxy-arabinosyl derivative *III* as the only one shows a remarkable biological activity ($9 \cdot 10^{-7}$M, a concentration causing 50% inhibition of L1210 cell growth), although lower than that of arabinosylcytosine ($1 \cdot 10^{-8}$M). Contrary to the arabinosylcytosine, compound *III* shows no activity against herpes simplex virus Type I and II. The results of the test for inhibition of nucleic acids synthesis done at Stanford Research Institute are subject of a separate paper[17].

EXPERIMENTAL

Melting points were taken on a heated microscope stage (Kofler block). The ultraviolet spectra were recorded on a Unicam SP 8000 apparatus. The infrared spectra were taken on a UR-20 (Carl Zeiss, Jena) apparatus. Optical rotations were measured on an automatic Perkin–Elmer 141 MC polarimeter. The ^{1}H-NMR spectra were recorded on a Varian HA-100 100 MHz instrument, using hexamethyldisiloxane as internal standard; chemical shift (δ values) are expressed in ppm and the coupling constants in Hz. Column chromatography was performed on the Pitra silica gel (particle size 30—60 μ, produced by Service Laboratories of this Institute) in the system ethyl acetate–acetone–ethanol–water (15 : 3 : 4 : 3). Solutions were taken down under diminished pressure on a rotatory evaporator at 30—40°C. Analytical samples were dried at 65 Pa.

5'-Chloro-5'-deoxy-2',3'-O-sulphinylcytidine Hydrochloride (*I*)

A) A mixture of cytidine (486 mg; 2 mmol), thionyl chloride (0·6 ml), and acetonitrile (5 ml) was refluxed for 45 min. Resulting mixture was cooled and set aside at +3°C for 2 h. Deposited *I* was filtered off and washed with acetonitrile (2 . 1 ml) and ether (3 . 3 ml). Yield, 677 mg (98%) of *I*, m.p. 148°C (decomp.), $[\alpha]_D^{25}$ —10·1° (*c* 0·50, dimethylformamide). IR spectrum (KBr): 3330, 3250, 3210, 3170, and 3117 cm^{-1} (NH), 1737 cm^{-1} (C=O), 1682 cm^{-1} (C=$\overset{+}{\text{N}}$H), 1546 cm^{-1} ($\overset{+}{\text{N}}$H), 1273 cm^{-1} (C—NH_2), 1221 cm^{-1} (S=O). ^{1}H-NMR spectrum (hexadeuteriodimethyl sulphoxide): 3·91 (m, 2 H, 2 $H_{5'}$), 4·73 (m, 1 H, $H_{4'}$, $J_{4',3'} = 4{\cdot}0$, $J_{4',5'} = J_{4',5''} = 7{\cdot}0$), 5·57 (dd, 1 H, $H_{3'}$, $J_{3',2'} = 7{\cdot}5$, $J_{3',4'} = 4{\cdot}0$), 5·90 (dd, 1 H, $H_{2'}$, $J_{2',1'} = 2{\cdot}5$, $J_{2',3'} = 7{\cdot}5$), 6·22 (d, 1 H, $H_{1'}$, $J_{1',2'} = 2{\cdot}5$), 6·27 (d, 1 H, H_5, $J_{5,6} = 7{\cdot}6$), 8·20 (d, 1 H, H_6). For $C_9H_{10}N_3O_5S.HCl$ (344·2) calculated: 31·41% C, 3·22% H, 12·21% N, 20·60% Cl, 9·32% S; found: 31·52% C, 3·16% H, 12·22% N, 20·66% Cl, 9·50% S.

B) Pulverized 5'-chloro-5'-deoxycytidine[12] (*V*; 1·11 g; 4 mmol) was added under stirring to a mixture of acetonitrile (12 ml) and thionyl chloride (0·75 ml). The whole was stirred for 3 h. Deposited *I* was filtered off, washed with ether (3 . 3 ml) and dried over potassium hydroxide *in vacuo*. Yield, 1·23 g (89%) of *I* (identical in all respects with the sample prepared according to the procedure *A*).

[2*R*-(2α,3β,3aβ,9aβ)]-2-Chloromethyl-2,3,3a,9a-tetrahydro-3-hydroxy-6-imino-6*H*-furo[2',3':4,5]oxazolo[3,2-*a*]pyrimidine Hydrochloride (*II*)

Sulphite *I* (3·44 g; 10 mmol) was heated in dimethylformamide (30 ml) at 100°C for 45 min. Dimethylformamide was removed *in vacuo* and the residue was crystallized from aqueous ethanol to give 1·52 g (54%) of *II*, m.p. 253°C (decomp.); reported[11], m.p. 263—265°C (decomp.). Mother liquors furnished additional 680 mg (24%) of the same compound, $[\alpha]_D^{25}$ —14·7° (*c* 0·49; water); reported[11], $[\alpha]_D$ —25·3° (*c* 0·5; water). IR spectrum (KBr): 3292 and 3115 cm^{-1} (NH_2), 1664 cm^{-1} (NH_2), 1568 and 1500 cm^{-1} (ring).

4-Amino-1-(5-chloro-5-deoxy-β-D-arabinofuranosyl)pyrimidin-2(1*H*)-one (*III*)

To a solution of compound *II* (280 mg; 1 mmol) in water (10 ml), Dowex 1X4 (CO_3^{2-}; 10 ml) was added and the whole was stirred for 1 h at room temperature. The resin was filtered off, washed with water (150 ml) and the combined filtrates were evaporated *in vacuo*. Crystallization of the residue from water afforded 202 mg (77%) of compound *III*, m.p. 206—208·5°C; reported[11], m.p. 202—204·5°C. Mother liquors afforded additional 17 mg (6·5%) of the same compound. $[\alpha]_D^{25}$ +150° (*c* 0·52; water); reported[11], $[\alpha]_D^{25}$ +163·8° (*c* 0·5; water). IR spectrum (KBr): 3439, 3372, 3318, sh 3288, and 3211 cm^{-1} (OH, NH), 1646 cm^{-1} (C=O).

4-Amino-1-(5-deoxy-β-D-arabinofuranosyl) pyrimidin-2-(1*H*)-one (*IV*)

A solution of the 5'-chloro derivative *III* (262 mg; 1 mmol) in dimethyl sulphoxide (5 ml) was heated up to 110°C and then 1M benzene solution of tributyltin hydride (6 . 2 ml) along with 2,2'-azobis(2-methylpropionitrile) (6 . 7 mg) were added gradually over 6 h. The mixture was cooled and ether (5 ml) and water (15 ml) were added. After extraction the aqueous layer was separated, washed with ether (2 . 5 ml), and evaporated *in vacuo*. The residue was chromatographed on a column of silica gel (150 g). The UV-absorbing fraction was evaporated and crystallized from water to afford 124 mg (51%) of *IV* (monohydrate), m.p. 172—173°C. $[\alpha]_D^{25}$ +135° (*c* 0·45; water). IR spectrum (KBr): 3439, 3345, 3233, sh 3120 cm^{-1} (OH, NH_2), 1660 and 1634 cm^{-1} (C=O, NH_2), 1607 cm^{-1} (C=N), 1281 cm^{-1} (C—NH_2). For $C_9H_{13}N_3O_4.H_2O$ (245·2) calculated: 44·08% C, 6·17% H, 17·13% N; found: 43·96% C, 6·14% H, 17·28% N.

5'-Chloro-5'-deoxycytidine (*V*)

To a solution of *I* (172 mg; 0·5 mmol) in water (4 ml), Dowex 1X4 (CO_3^{2-}; 3 ml) was added and the whole was stirred for 15 min. The resin was filtered off, washed with water (50 ml), and the combined filtrates were evaporated *in vacuo*. Crystallization of the residue from water furnished 105 mg (80%) of compound *V*, m.p. 170—177°C (decomp.); reported[12], m.p. 160—168°C (decomp.). IR spectrum of *V* is identical with that of the compound prepared according to ref.[12]. IR spectrum (KBr): 3532, 3482, 3399, 3350, sh 3259, and 3232 cm^{-1} (OH, NH_2), 1673 and 1651 cm^{-1} (C=O, NH_2), 1605 cm^{-1} (ring).

5'-Deoxycytidine (*VI*)

A) A solution of *V* (262 mg; 1 mmol) in methanol (15 ml) was heated to reflux and then 1M solution of tributyltin hydride in benzene (10 . 3 ml) along with 2,2'-azobis(2-methylpropionitrile) (10 . 10 mg) were added gradually over 4 days. The mixture was evaporated *in vacuo*, treated with ether (20 ml), and extracted with water (10 ml). The aqueous layer was washed with ether (3 . 10 ml) and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (100 g). Crystallization of the first UV-absorbing fraction from water afforded 35 mg of the starting compound *V*; crystallization of the residue of fraction 2 from water yielded *VI* in the form of monohydrate, m.p. 209—211°C (81 mg; 38%, referred to the reacted *V*), $[\alpha]_D^{25}$ +31° (*c* 0·45; water). UV spectrum (water): λ_{max} 211 and 270 nm (log ε 4·04 and 3·98), λ_{min} 249 nm (log ε 3·83). IR spectrum (KBr): 3530, sh 3448, 3425, 3327, and 3199 cm^{-1} (OH, NH), sh 1657 and 1643 cm^{-1} (C=O, NH_2), 1597 and sh 1580 cm^{-1} (ring). For $C_9H_{13}N_3O_4.H_2O$ (245·2) calculated: 44·08% C, 6·17% H, 17·13% N; found: 43·98% C, 6·05% H, 17·09% N.

B) A solution of *V* (262 mg; 1 mmol) in dimethyl sulphoxide (5 ml) was heated to 110°C and then 1M solution of tributyltin hydride in benzene (6 . 2 ml) along with 2,2'-azobis(2-methylpropionitrile) (6 . 7 mg) were added gradually over 6 h. The mixture was cooled, ether (5 ml) and water (15 ml) were added, and after extraction the aqueous layer was separated, washed with ether (2 . 5 ml), and evaporated at 250 Pa. Crystallization of the residue from water afforded 125 mg (51%) of the deoxy derivative *VI*, identical with the sample prepared according to the procedure *A*.

5'-Chloro-5'-deoxy-2',3'-O-sulphinyladenosine Hydrochloride (*VII*)

Adenosine (535 mg; 2 mmol) was added to a mixture of acetonitrile (5 ml) and thionyl chloride (0·6 ml) and the whole was refluxed for 45 min. The mixture was left to stand at +3°C for 4 h, the deposited *VII* was filtered off, and washed with acetonitrile (2 . 2 ml) and ether (3 . 4 ml). Yield, 690 mg (93·5%) of *VII*, m.p. 220°C (decomp.), $[\alpha]_D^{25}$ —17° (*c* 0·33; dimethyl sulphoxide).

IR spectrum (KBr): 3260 cm^{-1} (NH_2), 2550 cm^{-1} $(\overset{+}{N}H)$, 1711 and 1690 cm^{-1} (NH_2), 1601, 1514, and sh 1506 cm^{-1} (ring), 1214 cm^{-1} (S=O).^{1}H-NMR spectrum (hexadeuteriodimethyl sulphoxide): 3·96 (m, 2 H, 2 $H_{5'}$), 4·60 (m, 1 H, $H_{4'}$), $J_{4',3'}$ = 3·8, $J_{4',5'}$ = 6·0), 5·91 (dd, 1 H, $H_{3'}$, $J_{3',2'}$ = 6·5, $J_{3',4'}$ = 3·8), 6·32 (dd, 1 H, $H_{2'}$, $J_{2',1'}$ = 2·7, $J_{2',3'}$ = 6·5), 6·55 (d, 1 H, $H_{1'}$, $J_{1',2'}$ = 2·7), 8·64 (s, 1 H, H_2), 8·81 (s, 1 H, H_8). For $C_{10}H_{11}Cl_2N_5O_4S$ (368·2) calculated: 32·62% C, 3·01% H, 19·26% Cl, 19·02% N, 8·71% S; found: 32·58% C, 3·09% H, 19·53% Cl, 19·22% N, 8·52% S.

5'-Chloro-5'-deoxyadenosine (*VIII*)

Dowex 1X4 (CO_3^{2-}; 5 ml) was added to a solution of *VII* (184 mg; 0·5 mmol) in water (4 ml) and the mixture was stirred for 20 min at room temperature. The resin was filtered off and washed with water until the UV absorption of the filtrate disappeared (c. 200 ml). The combined filtrates were evaporated *in vacuo*. Crystallization of the residue from water afforded 121 mg (84·5%) of *VIII*, m.p. 114—115°C; reported[12], m.p. 190°C (decomp.).

The compound *VIII* crystallized with 1 1/2 molecule of water. The analytical sample was dried at 20 °C for 6 h. For $C_{10}H_{12}N_5O_3Cl$. 1 1/2 H_2O (312·7) calculated: 38·41% C, 4·83% H, 11·34% Cl, 22·40% N; found: 38·23% C, 4·76 H, 11·28% Cl, 22·19% N. The sample *VIII* when dried at 135 °C for 8 h lost its crystalline water, m.p. 193 °C (decomp.). For $C_{10}H_{12}ClN_5O_3$ (285·7) calculated: 42·04% C, 4·23% H, 12·41% Cl, 24·51% N; found: 41·67% C, 4·23% H, 12·56% Cl, 24·16% N.

5'-Deoxyadenosine (*IX*)

A solution of the chloro derivative *VIII* (286 mg; 1 mmol) in dimethyl sulphoxide (4 ml) was heated to 100°C and then 1M solution of tributyltin hydride in benzene (14 . 2 ml) along with 2,2'-azobis(2-methylpropionitrile) (14 . 7 mg) were added over 14 h. The mixture was partly evaporated *in vacuo*, diluted with water (30 ml), and washed with ether (3 . 20 ml). The aqueous solution was evaporated initially in the vaccum of water pump and then at 250 Pa. The residue was chromatographed on a silica gel column (100 g). Crystallization from water afforded 127 mg (50·5%) of *IX*, m.p. 133—134°C; $[\alpha]_D^{25}$ —44° (*c* 0·51; water). Reported[18], m.p. 130—133°C.

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