SYNTHESIS OF 7- AND 9β-D-PSICOFURANOSYLGUANINE AND THEIR 1'-DEOXY DERIVATIVES*

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Reaction of halogenoses *XX—XXIII* with tris(trimethylsilyl)-N^2-acetylguanine in acetonitrile in the presence of mercuric acetate afforded the protected nucleosides *IX—XIV* and *XVII*. The ratio of the 7- to the 9-isomeric nucleoside depends on the particular halogenose. The tri-n-butyltin hydride reduction of protected nucleosides *XIII* and *XIV* gave 1'-deoxynucleosides *XV* and *XVI* in satisfactory yields. The free nucleosides *I—VIII* and *XIX* were prepared by ammonolysis of the protected nucleosides *IX—XVIII*. The CD spectra of the free nucleosides differ in their character from those of 7- and 9β-D-ribofuranosylguanine.

Psicofuranine as inhibitor of xanthosine 5'-phosphate aminase interferes with the synthesis of guanylic acid[1]. With respect to this mechanism it appeared of interest to examine the biological activity of guanine nucleosides derived from D-psicose and the activity of some related compounds. The preparation of several compounds of this type is the object of the present communication.

From psicofuranine analogues with a modified purine ring system, there have been hitherto reported only the 9β-D-psicofuranosylpurine derivatives substituted at position 6 by a hydroxy, mercapto or N-alkylamino group[2].

The most frequently used method in the synthesis of 9-glycosylguanines consists in transformation of 2-acetamido-6-chloro-9-glycosylpurines obtained in turn by glycosylation of 2-acetamido-6-chloropurine according to the mercuri process[3]. In the synthesis of guanine nucleosides, 2-fluoro-6-benzyloxypurine has been also used as the base[4]. Glycosylation of the above bases affords exclusively 9-glycosylguanines. On the other hand, glycosylation of N^2-acetylguanine according to the mercuri process[5] or the fusion procedure[6] leads to a mixture of 7- and 9-glycosylguanines. A mixture of the 7- and 9-isomers has been also obtained when the fusion method has been applied to $N^{2,3(7)}$-diacetylguanine[7] or to N^2-acylguanines[8] with acyls consisting of a greater number of carbon atoms. The silyl method has been used in the series of purine nucleosides only sporadically, *e.g.*, to prepare some 9-glycosyl derivatives of adenine[9] and 2-acetamido-6-chloropurine[10]. Reaction of tris(trimethylsilyl)guanine with tetra-O-acetyl-D-ribofuranose in the presence of an acid catalyst has furnished acetylated guanosine[11]. Reaction of tris-(trimethylsilyl)-N^2-acetylguanine with 2,5-di-O-*p*-toluyl-3-deoxy-D-ribofuranosyl bromide in ace-

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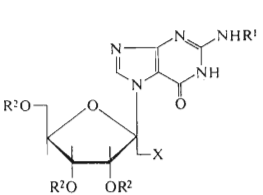
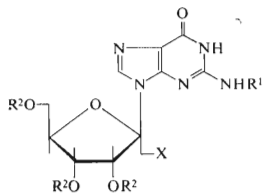
tonitrile at room temperature has afforded protected 3′-deoxyguanosine in a satisfactory yield[12]. The silyl method has also been used in the synthesis of 8-azaguanosine[13]. The unequivocal syntheses of 7- and 9-glycosylguanines starting from the corresponding glycosylimidazoles are somewhat laborious and have been previously used in the series of D-ribofuranosyl derivatives only[14,15].

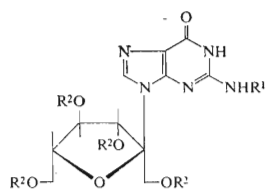
From the reported methods, the silyl procedure[12] appeared as the most suitable for the preparation of guanine ketosides. Reaction of 1,3,4,6-tetra-O-benzoyl-D-psicofuranosyl bromide (*XX*) with tris(trimethylsilyl)-N^2-acetylguanine in acetonitrile in the presence of mercuric acetate afforded a mixture of 7- and 9-(1,3,4,6-tetra-O-benzoyl-β-D-psicofuranosyl)-N^2-acetylguanine (*IX* and *X*). For the yield and ratio of isomers see Table I. In view of the similar chromatographical mobility of the two isomers, a considerable amount of silica gel was necessary for the separa-



I; $R^1 = R^2 = H$, X = OH
III; $R^1 = R^2 = H$, X = Cl
V; $R^1 = R^2 = H$, X = Br
VII; $R^1 = R^2 = X = H$
IX; R^1 = Ac, R^2 = Bz, X = BzO
XI; R^1 = Ac, R^2 = *p*-CH_3Bz, X = Cl
XIII; R^1 = Ac, R^2 = *p*-CH_3Bz, X = Br
XV; R^1 = Ac, R^2 = *p*-CH_3Bz, X = H



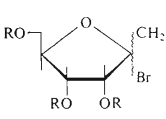
II; $R^1 = R^2 = H$, X = OH
IV; $R^1 = R^2 = H$, X = Cl
VI; $R^1 = R^2 = H$, X = Br
VIII; $R^1 = R^2 = X = H$
X; R^1 = Ac, R^2 = Bz, X = BzO
XII; R^1 = Ac, R^2 = *p*-CH_3Bz, X = Cl
XIV, R^1 = Ac, R^2 = *p*-CH_3Bz, X = Br
XVI; R^1 = Ac, R^2 = *p*-CH_3Bz, X = H



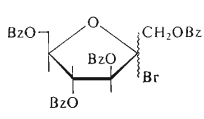
XVII; R^1 = Ac, R^2 = Bz
XVIII; $R^1 = H$, R^2 = Bz
XIX; $R^1 = R^2 = H$

tion of the mixture. The attempted separation of the free nucleosides *I* and *II* obtained by ammonolysis of the mixture of the protected nucleosides *IX* and *X*, did not meet with success. The chromatographical mobility on silica gel or cellulose was practically the same in several solvent systems. By chromatography on IRC 50 (H^+) ion exchange resin only the isomer *II* was separated while the isomer *I* underwent a hydrolytical decomposition on the column. (As shown by kinetic measurements of the acid-catalysed hydrolysis of guanine nucleosides, 7-β-D-ribofuranosylguanine is hydrolytically split much more fastly than the corresponding 9-isomer[16]). The separation on Dowex 1 (borate) ion exchange resin is only partial and is accompanied by a considerable loss of material due to hydrolysis of the nucleoside bond.

The reaction of 1-chloro-1-deoxy-3,4,6-tri-O-p-toluyl-D-psicofuranosyl bromide (*XXI*) with tris(trimethylsilyl)-N^2-acetylguanine afforded a mixture of 7- and 9-(1--chloro-1-deoxy-3,4,6-tri-O-*p*-toluyl-β-D-psicofuranosyl)-N^2-acetylguanine (*XI* and *XII*). The same procedure was used in the preparation of a mixture of 7- and 9-(1-bromo-1-deoxy-3,4,6-tri-O-*p*-toluyl-β-D-psicofuranosyl)-N^2-acetylguanine (*XIII* and *XIV*) from 1-bromo-1-deoxy-3,4,6-tri-O-*p*-toluyl-D-psicofuranosyl bromide (*XXII*). It may be seen from Table I that the ratio of the 7-isomer to the 9-isomer strongly depends on the structure of the particular halogenose. In the case of halogenoses *XXI* and *XXII*, almost equal amounts of the 7- and 9-isomers are formed while the reaction of the halogenose *XX* affords mainly the 7-isomer. With the aim to change this ratio of isomers, the reaction of the halogenose *XXII* was performed with tris--(trimethylsilyl)guanine instead of the N^2-acetyl derivative. This modification resulted in a significant increase of the content of the 7-isomer *XIII* but the overall yield was considerable lowered. To determine the ratio of the 7- to the 9-isomer in the formation of a nucleoside of the α-series, the reaction of 1,3,4,6-tetra-O-benzoyl-D-fructofuranosyl bromide (*XXIII*) with tris(trimethylsilyl)-N^2-acetylguanine was performed to afford a high yield of 9-(1,3,4,6-tetra-O-benzoyl-α-D-fructofuranosyl)-N^2-acetylguanin (*XVII*) as the single product. The reaction of the halogenose *XXIII* with tris(trimethylsilyl)guanine was also sterically uniform and afforded 9-(1,3,4,6-tetra--O-benzoyl-α-D-fructofuranosyl)guanine (*XVIII*). The limited amount of the experimental material does not allow to propose a reasonable explanation of the above observations.



XX; R = Bz, X = BzO
XXI; R = *p*-CH_3Bz, X = Cl
XXII; R = *p*-CH_3Bz, X = Br



XXIII

TABLE I

Ratio of 7- to 9-Glycosylguanines *IX—XIV*, *XVII*, and *XVIII* and Overall Yields of Glycosylations (referred to halogenoses *XX—XXIII*)

Halogenose	Method[a]	Ratio 7- to 9-isomer	Overall yield, %
XX	*A*	72/28	17·5
XXI	*A*	45/55	32·5
XXII	*A*	45/55	27·5
XXII	*B*	79/21	17·5
XXIII	*A*	0/100	88·0
XXIII	*B*	0/100	29·0

[a] Method *A*, reaction of halogenose with tris(trimethylsilyl)-N^2-acetylguanine; Method *B*, reaction of halogenose with tris(trimethylsilyl)guanine.

TABLE II

Physical and Analytical Data of Protected Nucleosides *IX—XIV*, *XVII*, and *XVIII*

Compound	$[\alpha]_D^{25}$ (*c* 0·5) (chloroform)	M.p., °C (ethanol)	Formula (m.wt.)	Calculated/Found			
				% C	% H	% N	% Hal
IX[a]	+ 41·3	sirup	$C_{41}H_{33}N_5O_{11}$ (771·75)	63·81 63·77	4·31 4·23	9·08 9·10	—
X[a]	− 42·8	sirup	$C_{41}H_{33}N_5O_{11}$ (771·75)	63·81 63·77	4·31 4·60	9·08 8·69	—
XI[b]	+159·7	185—186	$C_{37}H_{34}ClN_5O_9$ (728·2)	61·03 60·82	4·71 4·66	9·62 9·46	4·87 4·94
XII[b]	+ 27·9	144—146	$C_{37}H_{34}ClN_5O_9$ (728·2)	61·03 60·96	4·71 4·91	9·62 9·72	4·87 4·97
XIII[b]	+142·5	192—193	$C_{37}H_{34}BrN_5O_9$ (772·6)	57·52 57·66	4·44 4·54	9·06 8·96	10·34 10·40
XIV[b]	+ 25·5	158—160	$C_{37}H_{34}BrN_5O_9$ (772·6)	57·52 57·25	4·44 4·44	9·06 8·88	10·34 10·65
XVII[c]	+ 25·2	sirup	$C_{41}H_{33}N_5O_{11}$ (771·75)	63·81 63·64	4·31 4·31	9·08 8·92	—
XVIII[d]	+ 19·0[e]	252[f] (decomp.)	$C_{39}H_{31}N_5O_{10}$ (729·7)	64·20 64·02	4·28 4·26	9·60 9·50	—

Chromatographic solvent systems: [a] chloroform–acetone (10 : 3); [b] chloroform–acetone (5 : 1); [c] chloroform–methanol (97 : 3); [d] chloroform–methanol (92 : 8); [e] *c* 0·5; pyridine; [f] pyridine.

The tri-n-butyltin hydride reduction of nucleosides *XIII* and *XIV* in benzene afforded 7- and 9-(1-deoxy-3,4,6-tri-O-*p*-toluyl-β-D-psicofuranosyl)-N^2-acetylguanine (*XV* and *XVI*). Reduction of the protected nucleosides *XI* and *XII* to compounds *XV* and *XVI* proceeds under the same conditions except for a longer period of time. Such a relatively mild reduction of nucleosides *XI* and *XII* is somewhat surprising since 1-(1-chloro-1-deoxy-3,4,6-tri-O-*p*-toluyl-β-D-psicofuranosyl)uracil as well as the related thymine and N^4-acetylcytosine derivatives do not afford even traces of 1'-deoxynuclosides when heated with tri-n-butyltin hydride for 10 hours[17].

The free nucleosides *I* – *VIII* and *XIX* were prepared by ammonolysis of the corresponding protected nucleosides. Position of the glycosyl residue on the purine ring system was inferred on the basis of the similarity of UV spectra of the free nucleosides *I* – *VIII* and *XIX* with those of 7- and 9-methylguanines[18]. Configuration at the anomeric center was ascribed on the basis of Baker's rule. The CD spectra of the free nucleosides *I* – *VIII* markedly differ in their character from those of 7- and 9-β-D-ribofuranosylguanine[19–21] and cannot be therefore used for the determina-

TABLE III
Elemental Analyses of Free Nucleosides *I* – *VIII*, *XIX*

Compound	Formula (mol.wt.)	Calculated/Found			
		% C	% H	% N	% X
I	$C_{11}H_{15}N_5O_6$	42·17	4·83	22·36	—
	(313·3)	41·74	5·03	22·11	
II	$C_{11}H_{15}N_5O_6$	42·17	4·83	22·36	—
	(313·3)	42·06	5·05	22·16	
III	$C_{11}H_{14}ClN_5O_5.H_2O$	37·77	4·61	20·03	10·14
	(349·75)	37·57	4·37	19·78	9·71
IV	$C_{11}H_{14}ClN_5O_5$	39·83	4·25	21·11	10·69
	(331·7)	39·88	4·38	20·97	10·22
V	$C_{11}H_{14}BrN_5O_5.H_2O$	33·52	4·09	17·77	20·27
	(394·2)	33·81	4·14	17·53	19·88
VI	$C_{11}H_{14}BrN_5O_5$	35·12	3·75	18·62	21·24
	(376·2)	34·70	3·87	18·95	20·75
VII	$C_{11}H_{15}N_5O_5$	44·44	5·09	23·56	—
	(297·3)	43·87	5·21	23·50	
VIII	$C_{11}H_{15}N_5O_5$	44·44	5·09	23·56	—
	(297·3)	44·58	5·27	23·51	
XIX	$C_{11}H_{15}N_5O_6.H_2O$	39·88	5·17	21·14	—
	(331·3)	40·00	5·16	21·25	

tion of the configuration at the anomeric center. These differences in the character of CD spectra are probably due to different distributions of *syn* and *anti* conformers.

EXPERIMENTAL

Melting points were taken on a heated microscope stage (Kofler block). Analytical samples were dried at 25°C/0·05 Torr for 12 h. Descending paper chromatography was performed on paper Whatman No 1 in the solvent systems S_1, 1-butanol–ethanol–water (40 : 11 : 19), and S_2, 2-propanol–30% aqueous ammonia–water (7 : 1 : 2). Electrophoresis was performed on paper Whatman No 1 at 40 V/cm in buffer solutions E_1, 0·05M triethylammonium borate, and E_2, 0·05M sodium hydrogen citrate. The UV spectra were taken on an Optica Milano CF-4 apparatus. The CD spectra were measured on a Roussel-Jouan Dichrograph II Model CD-185 spectropolarimeter.

Materials

Acetonitrile was freshly distilled with calcium hydride. Tris(trimethylsilyl)-N^2-acetylguanine[12] was prepared from N^2-acetylguanine (965 mg; 5 mmol), hexamethyldisilazane (3 ml), trimethylchlorosilane (2 ml), and toluene (15 ml). This mixture was heated for 6 h, evaporated under diminished pressure, the residue dissolved in benzene (10 ml), the solution filtered, and the filtrate evaporated. The crystalline residue was used in the nucleosidation reaction. The bromide *XX* was prepared by the action of hydrogen bromide in acetic acid on methyl 1,3,4,6-tetra-O-benzoyl-D-psicofuranoside[22]. The bromides *XXI* and *XXII* were prepared similarly from the corresponding methyl 1-deoxy-1-halo-3,4,6-tri-O-*p*-toluyl-D-psicofuranosides[17]. The bromide *XXIII* was prepared by the action of hydrogen bromide on a benzene solution of 1,3,4,6-tetra-O-benzoyl-D-fructofuranose[23]. Tris(trimethylsilyl)guanine was prepared by trimethylsilylation of guanine according to the reported procedure[24].

Protected Nucleosides *IX*—*XIV*, *XVII*, and *XVIII*

A. To a solution of the freshly prepared corresponding halogenose (10 mmol) and tris(trimethylsilyl)-N^2-acetylguanine (15 mmol) in acetonitrile (20 ml) there was added with stirring mercuric acetate (2·2 g; 6·9 mmol). The mixture was stirred at 25°C for 12 h, and diluted with chloroform (150 ml). Water (0·5 ml) was then added, the mixture allowed to stand for 10 min, the precipitate filtered through Celite, and washed with three 50 ml portions of chloroform. The filtrate and washings were combined, washed with three 50 ml portions of 10% aqueous potassium iodide and two 50 ml portions of water, dried over anhydrous sodium sulfate, and evaporated under diminished pressure. The residual sirup was chromatographed on a column of silica gel (400 g; particle size, 60—120 micron) in the solvent system chloroform–acetone. The 9-isomers are eluted from the column more fastly than the 7-isomers. The chromatographically homogeneous fractions were pooled, evaporated, and the product crystallised from ethanol. For yields and ratio of the 7- and 9-isomers see Table I. Physical properties and analytical data are shown in Table II.

B. To a solution of the freshly prepared corresponding bromide (1.0 mmol) and tris(trimethylsilyl)guanine (1·5 mmol) in acetonitrile (5·0 ml) there was added with stirring mercuric acetate (0·22 g; 0·69 mmol), the mixture stirred at 25°C for 12 h, and processed similarly to method *A*. The chloroform was evaporated and the residue (a sirup in reactions of bromides *XX*—*XXII*) dissolved in a mixture of pyridine (3 ml) and acetic anhydride (1 ml). After 20 h, ethanol (2 ml) was added, the mixture kept at room temperature for 1 h, and evaporated under diminished pressure. The residue was coevaporated with toluene (to remove traces of pyridine) and chromatographed on a column of silica gel (100 g; 30—60 micron) in the solvent system chloroform–ace-

tone (see method *A*). In the reaction of the bromide *XXIII*, evaporation of the chloroform extract afforded the product *XVIII* in crystalline form (yield, 22%); work-up of mother liquors on a column of silica gel in 92 : 8 chloroform–methanol gave an additional crop of the product (overall yield, 29% of compound *XVIII*).

7-(3,4,6-Tri-O-*p*-toluyl-1-deoxy-β-D-psicofuranosyl)-N^2-acetylguanine (*XV*)

A mixture of the protected nucleoside *XIII* (1·55 g; 2 mmol), tri-n-butyltin hydride[25] (1·16 g; 4 mmol), 2,2′-azobis(isobutyronitrile) (0·05 g), and benzene (55 ml) was refluxed for 30 min and evaporated under diminished pressure. The residue was triturated with light petroleum (10 ml), the precipitate dissolved in a small volume of chloroform, reprecipitated with light petroleum, and chromatographed on a column of silica gel (100 g; particle size 30–60 micron) in the solvent system chloroform–acetone (10 : 3). Yield, 1·16 g (84%) of compound *XV* as a chromatographically homogeneous sirup; $[\alpha]_D^{25}$ +146·4° (*c* 0·46, chloroform). For $C_{37}H_{35}N_5O_9$ (693·7) calculated: 64·06% C, 5·09% H, 10·10% N; found: 63·73% C, 5·03% H, 9·89% N.

TABLE IV

Ultraviolet Spectra of Free Nucleosides *I*–*VIII* and *XIX*

Compound	λ_{max} (log ε)		
	0·1M-HCl	water	0·1M-NaOH
I	249 (3·93) 273 (3·74)	286 (3·87)	282 (3·77)
II	254 (4·09) infl. 274 (3·96)	253 (4·09)	263 (4·03)
III	248 (3·90) infl. 268 (3·72)	218 (4·26) 287 (3·89)	281 (3·63)
IV	256 (4·02) infl. 278 (3·85)	253 (4·08) infl. 273 (3·90)	262 (3·93)
V	248 (3·76) infl. 268 (3·58)	218 (4·06) 287 (3·60)	283 (3·65)
VI	257 (4·06) infl. 276 (3·91)	253 (4·50)	263 (3·99)
VII	249 (4·02) 272 (3·82)	218 (4·18) 284 (3·83)	281 (3·78)
VIII	249 (4·01) infl. 268 (3·80)	253 (4·08) infl. 273 (3·91)	262 (3·99)
XIX	253 (4·06) 277 (3·82)	253 (4·07) infl. 272 (3·90)	257–267 (3·99)

9-(1-Deoxy-3,4,6-tri-O-*p*-toluyl-β-D-psicofuranosyl)-N^2-acetylguanine (*XVI*)

The nucleoside *XIV* (1·55 g; 2 mmol) was reduced with tri-n-butyltin hydride (1·14 g; 4 mmol) in benzene (55 ml) in the presence of 2,2'-azobis(isobutyronitrile) (50 mg) analogously to the

TABLE V

CD Spectra (λ in nm) of Free Nucleosides *I*—*VIII*, *XIX*, *XXIV*, and *XXV* (water)

Compound	λ (10^{-3} . [Θ])			
I	224 (+ 2·65)	248 (−2·88)	290·5 (−1·08)	—
II	212 (−22·40)	255 (−0·24)	283·5 (−0·73)	—
III	216·5 (+ 5·45)	sh 230·5 (+1·20)	247·5 (−0·78)	288·5 (−1·98)
IV	211 (−23·40)	255·5 (−0·99)	281 (−1·54)	—
V	220 (− 3·50)	236 (+0·61)	sh 247·5 (−0·45)	284·5 (−4·85)
VI	210 (−23·80)	256 (−1·26)	279 (−1·96)	—
VII	216·5 (+19·20)	sh 231·5 (+2·40)	247·5 (−3·95)	292 (−0·90)
VIII	212 (−15·40)	sh 235 (−0·87)	279 (−1·50)	—
XIX	212·5 (+26·50)	246 (−3·70)	—	—
XXIV[a]	212·5 (−16·70)	256 (−2·85)	sh 265 (−2·50)	—
XXV[b]	215 (− 7·60)	sh 227 (−1·67)	245 (+1·70)	sh 262 (+0·30)

[a] 9β-D-Psicofuranosyladenine; [b] 9-(1-bromo-1-deoxy-β-D-psicofuranosyl)adenine[26].

TABLE VI

Paper Chromatography (R_F values) in Solvent Systems S and Electrophoresis (mobility in cm) in Buffer Solutions *E* of Free Nucleosides *I*—*VIII* and *XIX*

Compound	S_1	S_2	E_1	E_2
I	0·27	0·31	4·4	− 1·9
II	0·27	0·28	6·0	− 1·2
III	0·54	0·52	4·6	− 1·5
IV	0·52	0·50	5·4	− 0·8
V	0·52	0·54	4·4	− 1·6
VI	0·51	0·52	5·0	− 1·0
VII	0·42	0·40	2·9	− 2·3
VIII	0·42	0·38	4·6	− 1·4
XIX	0·33	0·35	0·5	− 1·7
Guanosine	0·32	0·27	5·3	− 0·7
Guanine	0·51	0·42	−2·0	−14·2

preceding paragraph. Yield, 1·25 g (90%) of compound *XVI* as a chromatographically homogeneous solid foam; $[\alpha]_D^{25} + 16{\cdot}8°$ (*c* 0·48, chloroform). For $C_{37}H_{35}N_5O_9$ (693·7) calculated :64·06% C, 5·09% H, 10·10% N; found: 63·85% C, 5·10% H, 9·92% N.

Free Nucleosides *I*—*VIII* and *XIX*

A solution of the protected nucleoside *IX*—*XVIII* (0·5 mmol) in methanol (30 ml) saturated with ammonia at 25°C was kept at room temperature for 3 days and evaporated under diminished pressure. The residue was coevaporated with methanol (10 ml) and then triturated with ether (5 ml). The solid was collected with suction and washed with two 5 ml portions of ether. The nucleosides *I*, *II*, and *XIX* were crystallised from water, the remaining ones from ethanol–water. The yields of the ammonolysis were 60—70%. The nucleosides *I*—*VIII* and *XIX* decompose above 230°C without melting. For physical properties and analytical data see Tables III—V.

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