Treatment of IXb with *o*-Phenylenediamine——A solution of IXb (100 mg.) and *o*-phenylenediamine (100 mg.) in EtOH (20 ml.) was refluxed for 2 hr. and then concentrated until crystals started separating. After cooling, the crystals (99 mg.), m.p. 237～239°, were collected and recrystallized from $CHCl_3$–EtOH yielding pale yellow needles of the quinoxaline derivative (84 mg.), m.p. 238～239°, $[\alpha]_D$ +230° (c=1.00). UV λ_{max} mμ (ε): 217 (27,700), 223 (26,400), 259 (22,800), 342 (11,500), 358 (10,000). IR ν_{max}^{Nujol} cm^{-1}: 3230, 1737, 1635, 1610 (w), 1556, 1186, 763. *Anal.* Calcd. for $C_{28}H_{34}O_3N_2$: C, 75.30; H, 7.67; N, 6.27. Found: C, 75.24; H, 7.78; N, 6.56.

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Summary

Oxidation of 2,17β-dihydroxyandrosta-1,4-dien-3-one (IIa) with manganese dioxide in acetone resulted in the ring contraction giving 17β-hydroxy-A-norandrost-3(5)-ene-1,2-dione (IIIa) whereas the reaction, in the presence of acid, afforded 1ξ,17β-dihydroxy-2-oxaandrost-4-en-3-one (IV). Oxidation of 4,17β-dihydroxyandrosta-1,4-dien-3-one (V), even in the absence of acid, resulted in the ring cleavage yielding 5ξ,17β-dihydroxy-4-oxaandrost-1-en-3-one (VI). Possible mechanisms for their reactions were discussed.

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186. Kin-ichi Imai, Akira Nohara, and Mikio Honjo: Synthesis of Purine Nucleosides Using Iodine as Catalyst.

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The so-called fusion method for the synthesis of purine nucleosides which has been developed by Sato, *et al.*[1] involves heating of 1,2,3,5-tetra-O-acyl-D-ribofuranose with various purines in the presence of Lewis acids as catalysts. The method is simple and superior to the conventional method which utilizes heavy metal salts of the bases and halogenosugars to accomplish nucleosides formation.

We have paid our attention to iodine for its catalytic activity in Koenigs-Knorr's reaction[2] and the condensation[3] of propylene glycol with glucose, and tried this catalyst for the synthesis of nucleosides by the fusion method. This paper deals with a nucleoside synthesis using iodine as a catalyst and detailed studies of the reaction products.

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1) *a*) T. Sato, T. Simadate, Y. Ishido: Nippon Kagaku Zasshi, **81**, 1440, 1442 (1960). *b*) T. Simadate, Y. Ishido, T. Sato: *Ibid.*, **82**, 938 (1961). *c*) T. Simadate: *Ibid.*, **82**, 1268, 1270 (1961). *d*) Y. Ishido, T. Sato: Bull. Chem. Soc. Japan, **34**, 1347 (1961). *e*) T. Simadate: Nippon Kagaku Zasshi, **83**, 212, 214 (1962). *f*) Y. Ishido, A. Hosono, S. Isome, A. Maruyama, T. Sato: Bull. Chem. Soc. Japan, **37**, 1389 (1964). *g*) Y. Ishido, Y. Kikuchi, T. Sato: Nippon Kagaku Zasshi, **86**, 240 (1965). *h*) Y. Ishido, T. Matsuba, A. Hosono, K. Fujii, H. Tanaka, K. Iwabuchi, S. Isome, A. Maruyama, Y. Kikuchi, T. Sato: Bull. Chem. Soc. Japan, **38**, 2019 (1965). *i*) Y. Ishido, A. Hosono, Y. Nagasawa, K. Iwabuchi, S. Isome, A. Maruyama, T. Sato: Abstracts of Papers, the 18th Annual Meeting of the Chemical Society of Japan (April 1965, Osaka), p. 224.

2) B. Helferich, E. Bohn, S. Winkler: Ber., **63**, 989 (1930).

3) U. S. Pat. 2,407,001; 2,407,002; 2,407,003 (Sept. 1946).

Fusion of theophylline (I) and 1-O-acetyl-2,3,5-tri-O-benzoyl-β-D-ribofuranose[4] (II) in the presence of iodine, followed by debenzoylation with sodium methoxide gave colorless needles. This substance had the melting point, analytical values, ultraviolet absorption spectrum and specific rotation identical with those[1a,5] of 7-β-D-ribofuranosyltheophylline (III). The nuclear magnetic resonance (NMR) spectrum, however, showed that the product was very likely a mixture of isomers. The yield*2 of the reaction product reached 81% in our method, while it was only 65% when *p*-toluenesulfonic acid*3 was used as a catalyst.

Since the reactivity of amino- or hydroxypurines is poor in the fusion method, attempts[1f,6] have been made to use their acyl derivatives to improve yields of the products. Fusion of 2,6-diacetamido-9 (or 7)-acetylpurine[7] (IV) and II in the presence of iodine, followed by de-blocking and purification by Dowex-1 (chloride), afforded 2,6-diamino-9-β-D-ribofuranosylpurine[8,9] (IV) in yields of 45~50%; while when *p*-toluenesulfonic acid was used as a catalyst, the yield was 31%. The product de-blocked was confirmed to be practically pure β-anomer on the basis of the NMR spectrum. Furthermore we have synthesized III and V using bromine or iodine trichloride as a catalyst.

Halogenopurines have been known to be more readily fusible than amino- or hydroxypurines and hence may come into reaction with sugar components to some extent in the absence of catalyst.[1h] Thus, when 2,6-dichloropurine (VI) and II were heated in the presence of iodine and the product was purified by the silica gel column chromatography, 2,6-dichloro-9-(2′,3′,5′-tri-O-benzoyl-β-D-ribofuranosyl)purine (VII) was obtained in a yield of 90%. The fusion of VI and 1,2,3,5-tetra-O-acetyl-β-D-ribofuranose has already been reported[1f,1g,10] to give the 9-β-ribonucleoside derivative. In our case, the NMR spectrum of VII indicated that the reaction product was homogeneous. Furthermore, the β-configuration of the compound was established from the following reactions: treatment of VII with methanolic ammonia gave 2-chloroadenosine[1g,10,11] (VIII). While alkaline hydrolysis of VII afforded 2-chloroinosine (IX), which was catalytically reduced to give inosine (X).

The conventional method involving mercury salts of the bases and 2,3,5-tri-O-acyl-D-ribofuranosyl halides has an advantage because of the predominant formation of naturally occurring 9-β-ribonucleoside derivatives. The fusion method, however, gives an anomeric mixture[6,12] depending upon the nature of the bases employed. Thus, from the reaction of N^6,$N^{9(or7)}$-diacetyladenine[13,14] (XI) with II in the presence of iodine, after deacylation and purification by the ion-exchange chromatography with Dowex-1 (chloride), was obtained adenine riboside (the yield, 8%). The ultraviolet absorption spectrum of this substance was superimposable with that of adenosine. However, the NMR spectrum clearly indicated that this was an anomeric mixture of the nucleosides; the one being 9-β-D-ribofuranosyladenine (XII) and the other the

*2 Calculated from optical density in terms of III.
*3 Whereby we also found that isomers were given.

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12) L. Pichat, P. Dufay, Y. Lamorre: Compt. Rend., **259**, 245 (1964).
13) L. Birkofer: Ber., **76**, 769 (1943).
14) A. H. Schein: J. Med. Pharm. Chem., **5**, 302 (1962).

α-anomer[15~17] (XIII), for the NMR signal of $H_{1'}$ of the latter compound (δ 6.25) appeared in a lower field than that of adenosine (δ 5.85). The ratio of β-anomer (XII) to α-anomer (XIII) was estimated as 2:1. Although XI was less reactive, the use of N^6-benzoyladenine (XIV) gave an improved yield (53~55%)[19] of a mixture of XII and XIII. XII was isolated by simple recrystallization of the mixture from water.

Fusion of acetylhypoxanthine[16] (XV), II and iodine gave, after purification by the silica gel chromatography and de-blocking, hypoxanthine riboside (yield, 12%). This was chromatographed with Dowex-50 (hydrogen) to fractionate into two parts. Fraction 1 was proved to contain 9-β-D-ribofuranosylhypoxanthine (XVI) from the paper electrophoretic and chromatographic behavior, ultraviolet absorption and NMR spectra. Similary, fraction 2 was presumed to contain α-anomer (XVII) from the ultraviolet absorption spectrum and paper chromatographic behavior.

A mixture of acyl derivatives of guanine ribosides was obtained in 51% yield by the fusion of N^2,$N^{9(or7)}$-diacetylguanine[16] (XVIII) with II in a manner similar to that described with XV. After fractionation by the silica gel chromatography three glassy substances were separated. Each substance was deacylated and confirmed to be 7-β- (XIX), 7-α- (XX) and an anomeric mixture of 9-D-ribofuranosylguanines (XXI and XXII), on the basis of the paper chromatographic behavior, the ultraviolet absorption and NMR spectra. Of a pair of the anomeric 7-D-ribonucleosides, the one showing the NMR signal of $H_{1'}$ in a higher field was assigned the β-configuration.[15] This demonstrated that the β-nucleoside was more dextrorotatory than the α-anomer. This discrepancy from Hudson's rules of isorotations might be due to the effect of the 6-carbonyl group of guanine N^7-nucleosides which is located at a close position to the ribose moiety.*4

Experimental

All melting points were uncorrected. Paper chromatography (PC) was carried out on Whatman filter paper No. 1 using as developing solvent, (A) H_2O, (B) *n*-BuOH-AcOH-H_2O (2:1:1), (C) *n*-BuOH-AcOH-H_2O (5:2:3) or (D) isobutyric acid-0.5*N* NH_4OH (10:6), by the ascending method unless otherwise mentioned. Paper electrophoresis (PE) was done on Whatman filter paper No. 1 at 22 v/cm., for 30~60 min. using 0.05*M* borate buffer (pH 9.2). The spots were detected visually under UV lamp. NMR spectra were measured with Varian A 60 NMR spectrometer (60 Mc.) at 40°. Chemical shifts in p.p.m. were recorded relative to tetramethylsilane as a standard.

D-Ribofuranosyltheophylline——a) A mixture consisting 1-O-acetyl-O-2,3,5-tri-O-benzoyl-β-D-ribofuranose (II) (1.512 g., 3 mmoles), theophylline (I) (540 mg., 3 mmoles) and I_2 (30 mg.) was heated at 160~170° for 5 min. and additional 10 min. *in vacuo* (20 mmHg). After cooling, the melt was extracted with $CHCl_3$ (15 ml.), and the extract distilled to remove $CHCl_3$. To the residue was added 2.5% sodium methoxide (15 ml.) and the solution was refluxed for 30 min., neutralized with AcOH and concentrated to dryness. The residue was dissolved in H_2O and the solution was subjected to steam distillation to remove methyl benzoate. The aqueous residue was kept at 5° to give colorless crystals (617 mg., 66%), which were recrystallized from MeOH to give colorless needles, m.p. 193°. *Anal.* Calcd. for $C_{12}H_{16}O_6N_4$: C, 46.15; H, 5.16; N, 17.94. Found: C, 46.23; H, 4.99; N, 18.12. $[\alpha]_D^{22}$ +25.1° (c=1.0, H_2O). UV: $\lambda_{max}^{H_2O}$ 274.5 mμ, $\lambda_{min}^{H_2O}$ 246 mμ. NMR (NaOD): δ 8.32 (H_8), 6.05 ($H_{1'}$, J=4.0 c.p.s., doublet), 3.52, 3.35 (CH_3, 70% from integrated intensity), besides, 8.07, 8.01 (H_8), 6.30, 6.10 ($H_{1'}$), 3.20, 3.17, 2.97, 2.74 (CH_3, 30% from integrated intensity). PC (solvent A), R theophylline 1.2. PE, M theophylline 1.04.*5 b) A mixture consisting of II (504 mg., 1 mmole), I (180 mg., 1 mmole) and *p*-toluenesulfonic acid (5 mg.) or I_2 (10 mg.) was worked up as described under a). After treating the residue with 2.5% sodium methoxide, the aqueous solution was adjusted to pH 11 with *N* NH_4OH and passed through a column of Dowex-1 x-8 (chloride), 100~200 mesh (50 ml.).

*4 Such an instance is in good agreement with the optical rotations of the pyrimidine nucleosides having a carbonyl group at position 2 (T. R. Emerson, T. L. V. Ulbricht: Chem. Ind., **1964**, 2129). On the contrary to this, the pyridine nucleotides, which lack the carbonyl group at position 2 (N. O. Kaplan, M. M. Ciotti, F. E. Stolzenbach, N. R. Bachur: J. Am. Chem. Soc., **77**, 815 (1955)), obey Hudson's rules.

*5 The ratio of the migration distance of a sample to that of theophylline

15) T. Nishimura, B. Shimizu: This Bulletin, **13**, 803 (1965).
16) J. A. Montgomery, H. J. Thomas: J. Am. Chem. Soc., **87**, 5442 (1965).
17) T. Nishimura, B. Shimizu: Agr. Biol. Chem., **28**, 224 (1964).

The column was eluted with 0.01*M* NH_4Cl buffer (pH 10.5). From the optical density of the eluate, the yield was 65% in case of *p*-toluenesulfonic acid and 81% in case of I_2. c) A mixture consisting of II (1.008 g., 2 mmoles), I (360 mg., 2 mmoles) and Br_2 (2 drops) was worked up as described under b). The yield of the reaction product reached 51%. The eluate was treated with activated charcoal and concentrated *in vacuo*. The crystals obtained were recrystallized from H_2O to give colorless needles (III), m.p. 188~190°. $[\alpha]_D^{22}$ +23° (c=0.3, H_2O). UV : λ_{max}^{H2O} 273.5 mμ, λ_{min}^{H2O} 246.5 mμ. NMR (NaOD) : δ 8.30 (H_8), 6.30 ($H_{1'}$, J= 4.0 c.p.s., doublet), 3.52, 3.35 (CH_3). PC (solvent A), R theophylline 1.2.

2,6-Diamino-9-β-D-ribofuranosylpurine (V)——a) A mixture consisting of II (5 g., 10 mmoles), 2,6-diacetamido-9 (or 7)-acetylpurine (IV) (1.38 g., 5 mmoles) and I_2 (200 mg.) was worked up as described above except the temperature (170~175°). Colorless prisms, m.p. 238~240°. *Anal.* Calcd. for $C_{10}H_{14}O_4N_6$: C, 42.55; H, 5.00; N, 29.78. Found : C, 42.37; H, 5.28; N, 29.64. $[\alpha]_D^{20}$ −39.5 (c=0.65, 0.1*N* HCl). UV : $\lambda_{max}^{0.1N\ HCl}$ 292.5 mμ (ε 9.7×10^3), 253 mμ (ε 1.15×10^3), $\lambda_{min}^{0.1N\ HCl}$ 270 mμ, 232 mμ; $\lambda_{max}^{H_2O,\ 0.1N\ NaOH}$ 280.5 mμ (ε 9.7×10^3), 256.5 mμ, $\lambda_{min}^{H_2O\ 0.1N\ NaOH}$ 266 mμ, 236.5 mμ. NMR (NaOD) : δ 8.07 (H_8), 5.84 ($H_{1'}$, J=5.5 c.p.s., doublet). b) A mixture consisting of II (504 mg., 1 mmole), IV (276 mg., 1 mmole) and I_2 (5~10 mg.) was kept heating at 160~170° for 1 hr. and additional 30 min. *in vacuo*. The melt was treated as described under a) (yield, 45~50%). The eluate was concentrated *in vacuo* to give residue, in which no signal of anomer was detected by NMR spectrum. c) A mixture consisting of II (2.5 g., 5 mmoles), IV (1.38 g., 5 mmoles) and ICl_3 (20 mg.) was worked up as described under b) to obtain colorless prisms, m.p. 238°. This substance was found identical with V obtained in a) from its specific rotation, UV absorption, IR absorption and NMR spectra.

2,6-Dichloro-9-(2',3',5'-tri-O-benzoyl-β-D-ribofuranosyl)purine(VII)——A mixture consisitng of II(2.520 g., 5 mmoles), 2,6-dichloropurine (945 mg., 5 mmoles) and I_2 (25 mg.) was allowed to react at 150~154° for 15 min. *in vacuo*. After cooling, the melt was dissolved in CH_2Cl_2 (20 ml.) and applied on the top of a column of silica gel (50 g., Merck). The column was eluted with CH_2Cl_2. The eluate was concentrated to give a tan glass (2.85 g., 90%). *Anal.* Calcd. for $C_{31}H_{22}O_7N_4Cl_2$: C, 59.09; H, 3.40; N, 8.59. Found : C, 58.78; H, 3.50; N, 8.84. $[\alpha]_D^{24}$ −55.3° (c=1.0, $CHCl_3$). UV : λ_{max}^{EtOH} 275 mμ (ε 11.5×10^3), 230.5 mμ (ε 39.9×10^3), λ_{min}^{EtOH} 258 mμ. NMR (CCl_4) : δ 8.37 (H_8), 6.45 ($H_{1'}$).

2-Chloroinosine (IX)——VII (5 g., 7.9 mmoles) was dissolved in dioxane (70 ml.) and to this was added *N* NaOH (50 ml.). The mixture was heated at 60° for 2 hr., neutralized with *N* HCl and taken up to dryness *in vacuo*. The residue was dissolved in H_2O (120 ml.), acidified with *N* HCl and extracted with ether to remove benzoic acid. The aqueous layer was treated with activated charcoal (12 g.) and concentrated *in vacuo* to 150 ml. and applied on the top of a column of Dowex-1 x-8 (chloride), 100~200 mesh (15 ml.). The column was first washed with H_2O and eluted with 0.1*N* HCl. The eluate was treated with activated charcoal (7.5 g.) and concentrated *in vacuo* to give a colorless powdery substance (1.3 g., 55%). UV : $\lambda_{max}^{0.1N\ HCl}$ 253 mμ, $\lambda_{min}^{0.1N\ HCl}$ 225 mμ; $\lambda_{max}^{H_2O}$ 254 mμ, $\lambda_{min}^{H_2O}$ 227 mμ; $\lambda_{max}^{0.1N\ NaOH}$ 257 mμ, $\lambda_{min}^{0.1N\ NaOH}$ 227 mμ. NMR (NaOD) : δ 8.12 (H_8), 5.78 ($H_{1'}$, J=6.5 c.p.s., doublet). PC (solvent B), R inosine 1.3; PC (solvent D), Rf 0.65.

Inosine (X)——PdO-$BaSO_4$[18] (200 mg.) was suspended in 2% AcOH (25 ml.) and shaken in an atmosphere of H_2 and to this was added an aqueous solution (25 ml.) of IX (147 mg., 0.49 mmole). The mixture was shaken for 4.5 hr. in an atmosphere of H_2. The catalyst was filtered off and the filtrate was treated with activated charcoal (700 mg.) to obtain a powdery substance (94 mg., 72%). This was found identical with an authentic sample of inosine from its PE and PC (solvent B, Rf 0.39) behavior, UV absorption and NMR spectra.

Anomeric Mixture of 9-D-Ribofuranosyladenine (XII and XIII)——a) A mixture consisting of II (5.04 g., 10 mmoles), N^6,$N^{9(or7)}$-diacetyladenine (XI) (2.19 g., 10 mmoles) and I_2 (200 mg.) was kept heating at 170~175° for 1 hr. and additional 30 min. *in vacuo*. After cooling, the melt was extracted with $CHCl_3$ (150 ml.) and the extract was applied on the top of a column of silica gel (130 g.). The column was eluted with EtOAc and the eluate was concentrated to give a colorless syrup. The syrup was treated with 2.5% sodium methoxide (15 ml.) and applied on the top of a column (2×14 cm.) of Dowex-1 x-8 (chloride), 100~200 mesh. The column was eluted with 0.01*M* NH_4Cl buffer (pH 10.5) (yield, 8%). The eluate was treated with activated charcoal (1 g.) to obtain a powdery substance. UV absorption spectrum was superimposable with that of adenosine. NMR (NaOD) : δ 8.30 (H_8 of α-anomer, 33% from integrated intensity), 8.23 (H_8 of β-anomer, 67% from integrated intensity), 7.98 (H_2 of anomers), 6.25 ($H_{1'}$ of α-anomer), 5.83 ($H_{1'}$ of β-anomer, J=5.0 c.p.s., doublet). PE, M adenosine 1.0. b) A mixture consisting of II (2.5 g., 5 mmoles), N^6-benzoyladenine (1.2 g., 5 mmoles) and I_2 (50 mg.) was kept at 160~170° for 15 min. and additional 30 min. *in vacuo*. The melt was treated as described under a) (yield, 53%). The powdery substance was recrystallized from H_2O to give colorless needles (XII, 206 mg., 15%), m.p. 230°. *Anal.* Calcd. for $C_{10}H_{13}O_4N_5$: C, 44.94; H, 4.90; N, 26.21. Found: C, 45.15; H, 5.12; N, 26.49. $[\alpha]_D^{22}$ −60.0° (c=0.7, H_2O). This was found identical with an authentic sample of adenosine from its PE and PC (solvent C, Rf 0.64) behavior, UV absorption and NMR spectra.

Anomeric Mixture of 9-D-Ribofuranosylhypoxanthine (XVI and XVII)——A mixture consisting of II (7.55 g., 15 mmoles), acetylhypoxanthine (2.67 g., 15 mmoles) and I_2 (150 mg.) was worked up as described

18) R. Kuhn, H. J. Haas : Angew. Chem., **67**, 785 (1955).

with XI (yield, 12%). An aliquot of the solution of the de-blocked product (200, O.D. units at 250 mμ) was applied on the top of a column (0.9×6 cm.) of Dowex-50 x-8 (hydrogen), 100~200 mesh. The column was eluted with H_2O to obtain fraction 1 (65, O.D. units) and fraction 2 (66, O.D. units). Each fraction was concentrated *in vacuo* to give a colorless syrupy residue. The syrup obtained from fraction 1 was found identical with an authentic sample of inosine from its PE and PC (solvent B, descending method, Rf 0.40) behavior, UV absorption and NMR spectra. The syrup obtained from fraction 2 showed M inosine 0.94 by PE, R inosine 0.98 by PC (solvent B, descending method) and UV absorption spectrum was superimposable with those of inosine.

7- and 9-D-Ribofuranosylguanine (XIX, XX, XXI, and XXII)——A mixture consisting of II (504 mg., 1 mmole), $N^2,N^{9(or7)}$-diacetylguanine (XVIII) (193 mg., 0.83 mmole) and I_2 (20 mg.) was allowed to react as already described with XI. The extract was applied on the top of a column of silica gel (20 g.) and the column was eluted with EtOAc. The eluate was concentrated to give a colorless glass (272 mg., 51% calcd. from XVIII). This was again subjected to the silica gel chromatography using EtOAc as eluant to give fraction 1, 2 and 3. Each fraction was treated as described to obtain colorless crystals. 7-β-D-Ribofuranosylguanine (XIX): XIX was isolated from fraction 1. *Anal.* Calcd. for $C_{10}H_{13}O_5N_5 \cdot \frac{1}{2}H_2O$: C, 41.10; H, 4.83; N, 23.97. Found: C, 41.14; H, 4.92; N, 24.03. $[\alpha]_D^{25}$ −16° (c=0.63, 0.1*N* NaOH). UV: $\lambda_{max}^{0.1N\ HCl}$ 251.5 mμ (ε 8.8×10^3), 275 mμ (shoulder), $\lambda_{min}^{0.1N\ HCl}$ 231.5 mμ; $\lambda_{max}^{H_2O}$ 287 mμ (ε 7.1×10^3), $\lambda_{min}^{H_2O}$ 261 mμ; $\lambda_{max}^{0.1N\ NaOH}$ 283.5mμ (ε 6.2×10^3), $\lambda_{min}^{0.1N\ NaOH}$ 258 mμ. NMR (NaOD): δ 8.30 (H_8), 6.21 ($H_{1'}$, J=5.5 c.p.s., doublet). PC (solvent D), R guanosine 1.1. Mixture of 9-β- and 9-α-D-ribofuranosylguanine (XXI and XXII): A mixture of XXI and XXII were isolated from fraction 2. UV absorption spectrum was superimposable with that of guanosine. NMR (NaOD): δ 8.04 (H_8 of α-anomer), 7.95 (H_8 of β-anomer), 6.22 ($H_{1'}$ of α-anomer, J=4.5 c.p.s., doublet), 5.75 ($H_{1'}$ of β-anomer, J=6.5 c.p.s., doublet). PC (solvent D), R guanosine 1.0. 7-α-D-Ribofuranosylguanine (XX): XX was isolated from fraction 3. *Anal.* Calcd. for $C_{10}H_{13}O_5N_5 \cdot H_2O$: C, 39.87; H, 5.02; N, 23.25. Found: C, 40.19; H, 5.01; N, 23.40. $[\alpha]_D^{25}$ −59.2° (c=0.62, 0.1*N* NaOH). UV absorption spectrum was superimposable with that of XIX. NMR (NaOD): δ 8.20 (H_8), 6.67 ($H_{1'}$, J=4.0 c.p.s., doublet). PC (solvent D), R guanosine. 1.1.

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Summary

Iodine has been found to be an excellent catalyst for the synthesis of nucleosides, *i.e.*, the reaction of 1-O-acetyl-2,3,5-tri-O-benzoyl-β-D-ribofuranose with various purines in the presence of iodine resulted in the formation of corresponding 9-β-D-ribonucleosides, and/or their isomers in good yields.

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