UDC 612.398.145

102. Takeo Naito and Tomoyoshi Kawakami: Studies on Nucleosides and Nucleotides. VI.*1 Syntheses of D-Ribosylthymines and D-Xylosylthymines.

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Syntheses of glycosylthymines and glycosylthiothymines through new routes from glycosylureas and glycosylthioureas, respectively, were described in the previous papers[1~3] of this series.

In the present series of work, the same procedure was applied to 1-D-ribosyl- and 1-D-xylosylurea as a method of syntheses of their thymines. Information gathered by examination of the structures of 1-D-ribosyl- and 1-D-xylosylthymines was also reported here.

Condensation of D-ribose with urea was carried out by the same procedure as reported in Part I,[1] and an anomeric pair of 1-D-ribosylurea, (I) and (II), was obtained through purification by Celite-column chromatography. By a similar procedure two anomers of D-xylosylurea, (III) and (IV), were separated.

These ureides, (I), (II), (III), and (IV), as indicated in Table I, showed differences in physical properties, presumably due to the differences of configuration in the lactol ring and the glycosidic center.

Recently, Benn and Jones[4] synthesized two kinds of 1-D-ribosylurea, (D) and (E),*3 in a similar way, and from the results of periodate oxidation they assumed the former to be 1-D-ribopyranosylurea and the latter 1-D-ribofuranosylurea. These substances, (D) and (E), were amorphous and showed no definite melting points, but their Rf values and optical rotations were essentially identical with those of (II) and (I), respectively.

In periodate oxidation, on the contrary to the observations of Benn and Jones, these ureides, (I), (II), (III), and (IV), all consumed two moles of periodate per mole with liberation of one mole of formic acid in accord with the pyranose structure.

These experimental facts, suggested that (I) and (II), and (III) and (IV) presumably represent two pairs of α- and β-anomer, but it seemed attractive to synthesize glycosyl-

Table I. Properties of Pentopyranosylureas

	Sugar moiety	m.p.	$[\alpha]_D$	Rf	Metaperiodate oxidation (moles IO_4 consumed/mole)			
					17 hr.	25 hr.	44 hr.	HCO_2H (liberated)
(I)	1-α-D-ribopyranosyl-	184°	+22·16°	0.05		1.84	2.20	1.04
(II)	1-β-D-ribopyranosyl-	184°	−32.07°	0.03		1.87	2.22	0.90
(III)	1-α-D-xylopyranosyl-	180°	+83.47°	0.07	1.90		2.23	1.00
(IV)	1-β-D-xylopyranosyl-	201°	−17.15°	0.03	1.87		2.20	0.95

Solvent system of paper partition chromatography: iso-BuOH saturated with H_2O

*1 Part V: This Bulletin, **10**, 320 (1962).

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*3 These authors reported the separation of two 1-D-ribosylureas, (D), $[\alpha]_D$ −27°, R_G 0.91 and (E), $[\alpha]_D$ +24°, R_G 1.26. However, in the present experiments, (II), $[\alpha]_D$ −32.07°, R_G 0.96 and (I), $[\alpha]_D$ +22.16°, R_G 1.27 were obtained. Solvent system for determination of R_G: BuOH-AcOH-H_2O (4:1:5).

1) Part I: This Bulletin, **9**, 703 (1961).
2) Part II: *Ibid.*, **9**, 709 (1961).
3) Part III: *Ibid.*, **10**, 308 (1962).
4) M.H. Benn, A.S. Jones: J. Chem. Soc., **1960**, 3837.

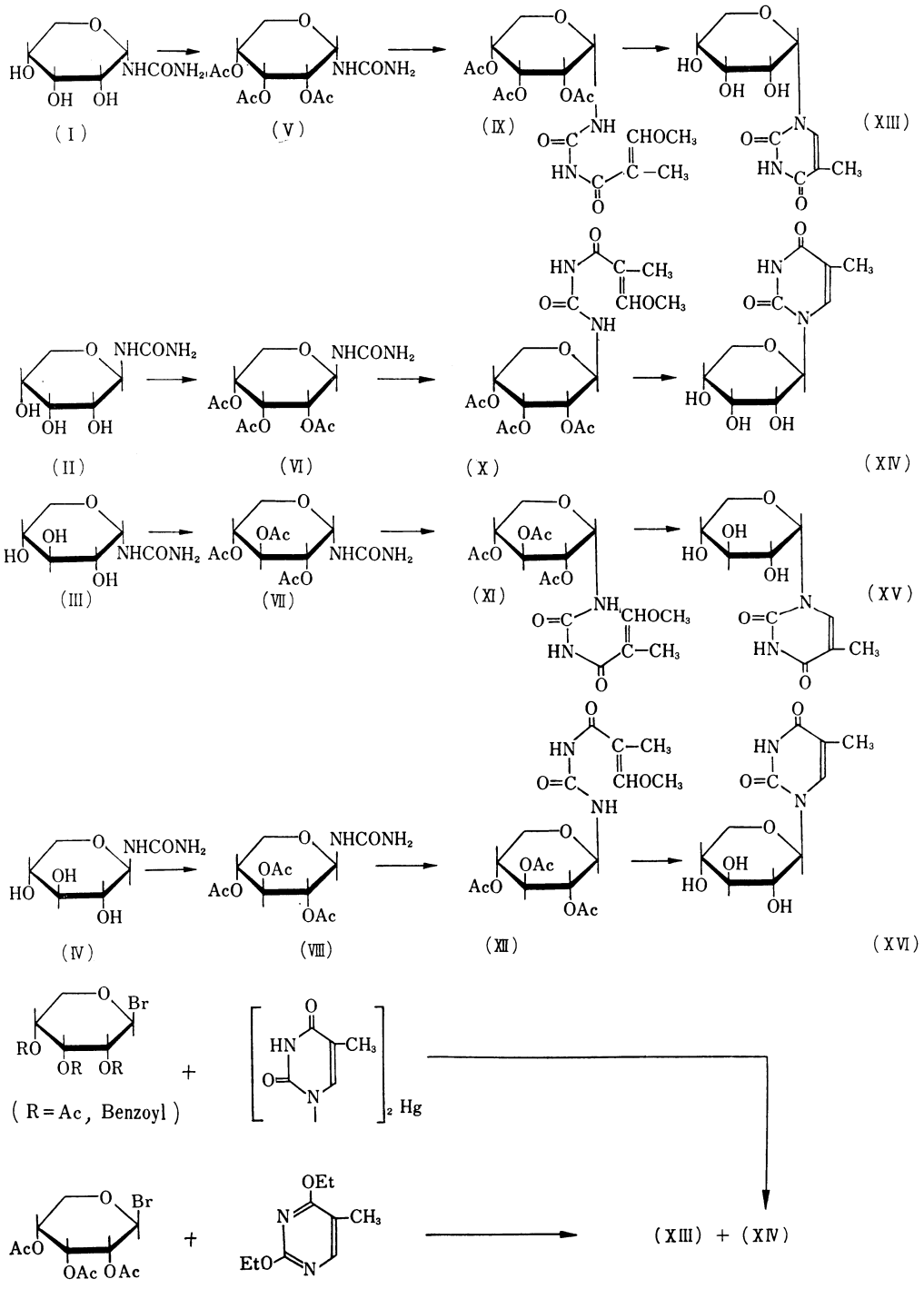
(I)
(V)
(IX)
(XIII)
(II)
(VI)
(X)
(XIV)
(III)
(VII)
(XI)
(XV)
(IV)
(VIII)
(XII)
(XVI)
(R=Ac, Benzoyl)
(XIII) + (XIV)

Chart 1.

thymines from these ureides in order to determine their lactol ring size and glycosidic configuration by comparison with the specimen of glycosylthymine synthesized in the usual way.

Following the procedure reported in Part I,[1] these ureides, (I), (II), (III), and (IV), were converted into their glycosylthymines, (XIII), (XIV), (XV) and (XVI), respectively, in the reaction sequences shown in Chart I.

The four glycosylthymines, (XIII), (XIV), (XV), and (XVI), consumed two moles of periodate per mole with liberation of one mole of formic acid; accordingly, these glycosylthymines were proved to retain their pyranose rings throughout this synthesis.

Distinct differences in physical property between (XIII) and (XIV), as well as (XV) and (XVI), could be interpreted by assuming that these four substances represent two pairs of anomeric D-ribopyranosylthymines and D-xylopyranosylthymines respectively.

The preparation of 1-D-ribopyranosyl- and 1-β-D-xylopyranosylthymines had been reported by Visser[5] and Fox,[6] respectively. The former compound obtained by Hilbert-Johnson procedure as m.p. 252°, $[\alpha]_D$ −110°, seemed to be identical with (XIII), and the latter obtained by mercury procedure as m.p. 286°, $[\alpha]_D$ +3°, corresponded to (XVI).

When the procedure reported by Visser was re-examined two components were separated with a Celite column in almost equal quantities. One m.p. 252° (Visser's compound) was confirmed to be identical with (XIII) in comparison of their melting points and infrared spectra. The other, m.p. 234°, was proved to be identical with (XIV) which was verified to be 1-β-D-ribopyranosylthymine in the following manner.

In consideration of the reaction mechanism, the formation of 1-β-D-ribopyranosylthymine was anticipated from condensation of poly-O-acylribopyranosyl halide with the mercury salt of thymine. Indeed, the reaction of dithyminylmercury with 2,3,4-tri-O-acylribopyranosyl bromide (acyl=Acetyl or Benzoyl) gave only 1-β-D-ribopyranosylthymine, m.p. 234°, which was then proved to be identical with (XIV) and also with the compound separated now by the Hilbert-Johnson procedure.

With respect to two isomers of D-xylopyranosylthymine, (XV) and (XVI), the latter was proved to be identical with the authentic specimen*4 in comparison of their melting points and infrared spectra, and the former (XV) can be regarded as the anomer of (XVI), since the xylopyranose moiety on the thymine ring was demonstrated to locate at position 1 on the basis of ultraviolet spectroscopy, as shown inTable II. Thus, it may be concluded that the syntheses of 1-D-xylosylthymines from their ureides proceed in the same pathway as 1-D-ribopyranosylthymines.

Table II. Ultraviolet Absorption of Thymine and Uracil Derivatives at Different pH

		(XIII)	(XIV)	1-Methyluracil	3-Methyluracil
$\lambda_{max}^{H_2O}$ mμ (log ε)	pH 7	268 (3.98)	268 (3.99)	267.5 (3.99)	258.5 (3.86)
	pH 12	267 (3.96)	267 (3.93)	265.0 (3.85)	282.5 (4.03)

From the foregoing results, it is clear that (XIV) and (XVI) are 1-β-D-ribopyranosyl- and 1-β-D-xylopyranosylthymine, respectively. Therefore, it follows that (II) and (IV) are 1-β-D-ribopyranosyl and 1-β-D-xylopyranosylurea, respectively, and (XIII), (XV), (I), and (III) represent the corresponding α-anomers.

With regard to the phenomenon that the specific rotations of (XIII) and (XV) were far more negative than those of their anomers, (XIV) and (XVI), in marked contrast to the typical case of their corresponding ureides, it is to be noted that this "anomaly" was also

*4 Grateful acknowledgment is expressed to Dr. J. J. Fox for his kind donation of the sample of 1-β-D-xylopyranosylthymine.

5) D. W. Visser: J. Am. Chem. Soc., **70**, 1926 (1948).
6) J. J. Fox: *Ibid.*, **78**, 2117 (1956).

observed in the two anomers of thymidine[7] and deoxycytidine[8], in which optical rotations of α-forms were negative than those of β-forms.

Experimental

1-α-D-Ribopyranosylurea (I) and 1-β-D-Ribopyranosylurea (II)——A solution of D-ribose (20 g., 0.13 mole) and urea (16 g., 0.26 mole) in 0.7% HCl (20 cc.) was kept at 50° for 10 days. The yellowish solution thus obtained was mixed with 20 g. of Celite 535. This mixture was chromatographed through a Celite column (500 g. of Celite 535 wetted with 500 cc. of H_2O). The column was eluted with H_2O-saturated *iso*-BuOH and 250 cc. fractions were collcted. Each fraction was examined by paper chromatography (solvent: H_2O-saturated *iso*-BuOH. coloring agent: Ehrlich's reagent). Fraction Nos. 42~57 showing a spot at Rf 0.05, were concentrated *in vacuo* (bath temp. 50°) to yield an opaque solution. This solution, when allowed to stand for several days, deposited 4.18 g. (16.3%) of (I), colorless plates, m.p. 184°, $[\alpha]_D^{22.5}$ +22.16°(c=2.22, H_2O). *Anal.* Calcd. for $C_6H_{12}O_5N_2$: C, 37.50; H, 6.29; N, 14.58. Found: C, 37.90; H, 6.38; N, 14.69.

From fraction Nos. 59~80, showing a spot at Rf 0.03, 3.15 g. (12.3%) of (II), colorless needles, m.p. 184°, $[\alpha]_D^{24.5}$ −32.07°(c=2.22, H_2O) was obtained. *Anal.* Calcd. for $C_6H_{12}O_5N_2$: C, 37.50; H, 6.29; N, 14.58. Found: C, 37.39; H, 6.48; N, 14.48.

1-α-D-Xylopyranosylurea (III) and 1-β-D-Xylopyranosylurea (IV)——A solution of D-xylose (20 g., 0.13 mole) and urea (16 g., 0.26 mole) in 0.7% HCl (20 cc.) was kept at 50° for 10 days. The two anomeric 1-D-xylopyranosylureas were separated by a Celite column (Celite 535, 480 g.: H_2O, 480 cc.) as described above. 250 cc. fractions were collected. Fraction Nos. 33~38 showing a spot at Rf 0.07 (solvent: described above), afforded the α-anomer (III) (1.13 g., 4.4%), colorless plates, m.p. 183°, $[\alpha]_D^{21}$ +83.47°(c=2.23, H_2O). *Anal.* Calcd. for $C_6H_{12}O_5N_2$: C, 37.50; H, 6.29; N, 14.58. Found: C, 37.66; H, 6.46; N, 14.66.

From fraction Nos. 41~81 showing a spot at Rf 0.03, the β-anomer (IV) (9.69 g., 37.8%), colorless prisms, m.p. 201°, $[\alpha]_D^{21}$ −17.15°(c=2.25, H_2O), was obtained. *Anal.* Calcd. for $C_6H_{12}O_5N_2$: C, 37.50; H, 6.29; N, 14.58. C, 37.69; H, 6.11; N, 14.13.

2,3,4-Tri-O-acetyl-α-D-ribopyrabnosylurea (V)——A mixture of (I) (3 g.), Ac_2O (15 cc.) and pyridine (30 cc.) was stirred at room temperature for 72 hr., and warmed to 60° for 1 hr. To this solution, MeOH (20 cc.) was added with stirring and ice-cooling, and the solution was concentrated *in vacuo*. A part of the resulting syrup was repeatedly triturated with petro. benzine, and the upper layer was decanted. The seeds thus obtained allowed the main batch to crystallize. Recrystallization from EtOH gave colorless prisms, m.p. 194°, $[\alpha]_D^{20}$ −8.12°(c=2.3, H_2O). Yield 3.87 g. (77.8%). *Anal.* Calcd. for $C_{12}H_{18}O_8N_2$: C, 45.28; H, 5.70; N, 8.80. Found: C, 45.69; H, 5.76; N, 8.63.

2,3,4-Tri-O-acetyl-β-D-ribopyranosylurea (VI)——A mixture of (II) (0.67 g.), Ac_2O and pyridine was stirred at 50° for 12 hr. The resulting solution was treated in the same manner as described above. Recrystallized from AcOEt-petr. benzine, (VI) was obtained as colorless needles, m.p. 194°, $[\alpha]_D^{20}$ −2.01°(c=1.62, H_2O). Yield 0.84 g. (75.6%). *Anal.* Calcd. for $C_{12}H_{18}O_8N_2$: C, 45.28; H, 5.70; N, 8.80. Found: C, 45.23; H, 5.90; N, 8.56.

2,3,4-Tri-O-acetyl-α-D-xylopyranosylurea (VII)——A mixture of (III) (0.62 g.), Ac_2O (6 cc.) and pyridine (12 cc.) was stirred at room temperature for 47 hr. After evaporation of the solvent the remaining syrup was treated as described earlier. Repeatedly recrystallized from Me_2CO and petr. benzine, (VII) formed colorless pillars, m.p. 190°, $[\alpha]_D^{23}$ −7.9°(c=1.83, H_2O). Yield, 0.65 g. (63.3%). *Anal.* Calcd. for $C_{12}H_{18}O_8N_2$: C, 45.28; H, 5.70; N, 8.80. Found: C, 45.42; H, 5.86; N, 8.63.

2,3,4-Tri-O-acetyl-β-D-xylopyranosylurea (VIII)——A mixture of (IV) (0.2 g.), Ac_2O (2 cc.) and pyridine (4 cc.) was stirred at room temperature for 44 hr. The resulting solution, after treating with MeOH, was concentrated with xylol *in vacuo* to a syrup, which was extracted with cold petr. ether. The petr. ether solution was diluted with the same solvent and upon scratching, furnished seed crystals. (VIII) was obtained as colorless leaflets, m.p. 174°, from AcOEt and petr. benzine, $[\alpha]_D^{23}$ −8.7°(c=1.75, H_2O). Yield 0.22 g. (66.5%). *Anal.* Calcd. for $C_{12}H_{18}O_8N_2$: C, 45.28; H, 5.70; N, 8.80. Found: C, 44.86; H, 5.74; N, 8.47.

1-(2,3,4-Tri-O-acetyl-α-D-ribopyranosyl)-3-(2-methyl-3-methoxyacryloyl)urea (IX)——To a solution of (V) (1.8 g.) in $CHCl_3$ (4 cc.), 2-methyl-3-methoxyacryloyl chloride (0.75 g.) was added, followed by pyridine (0.46 cc.). The reaction mixture was kept at room temperature for 4 days, warmed to 50° for 16 hr. and concentrated *in vacuo* to a light brown syrup which was mixed with 3 g. of silica gel. This mixture was chromatographed through a silica gel column (50 g., 100~200 mesh), and the column was developed with AcOEt. The fractions containing (IX) (examined by ultraviolet rays at

7) Max Hoffer: Ber., **93**, 2777 (1960).
8) J. J. Fox: J. Am. Chem. Soc., **83**, 4066 (1961).

2536 Å) were evaporated *in vacuo* to yield 1.37 g, (58.2%) of a yellowish amorphous material. UV: $\lambda_{max}^{H_2O}$ 265 mμ; $\lambda_{min}^{H_2O}$ 231 mμ.

1-(2,3,4-Tri-O-acetyl-β-D-ribopyranosyl)-3-(2-methyl-3-methoxyacryloyl)urea (X)——To a solution of (VI) (0.93 g.) in $CHCl_3$ (3 cc.), 2-methyl-3-methoxy acryloyl chloride (0.5 g.) was added, followed by pyridine (0.4 cc.). The reaction mixture was kept at room temperature for 28 hr. To this solution petr. ether was added several times and the upper layer was decanted off. The oily residue was mixed with 4 g. of silica gel. This mixture was chromatographed through an alumina column (Al_2O_3 20 g.), and the column was developed with AcOEt. The fractions of AcOEt showing the ultraviolet absorption (2536 Å) were evaporated *in vacuo* to a syrup which was crystallized from AcOEt and petro. ether to 0.34 g. (28%) of (X), colorless prisms, m.p. 82°. UV: $\lambda_{max}^{H_2O}$ 261.5 mμ; $\lambda_{min}^{H_2O}$ 227.5 mμ.

1-(2,3,4-Tri-O-acetyl-α-D-xylopyranosyl)-3-(2-methyl-3-methoxyacryloyl)urea (XI)——To a solution of (VII) (0.18 g.) in $CHCl_3$ (2 cc.), 2-methyl-3-methoxyacryloyl chloride (0.1 g.) was added, followed by pyridine (0.06 g.). The reaction mixture was refluxed for 4 hr. under anhydrous conditions and purifie through an alumina column as described above (Al_2O_3, 3 g.). The fraction of AcOEt was evaporated *in vacuo* to furnish 0.2 g. of (XI) as an amorphous colorless powder, m.p. 50°.

1-(2,3,4-Tri-O-acetyl-β-D-xylopyranosyl)-3-(2-methyl-3-methoxyacryloyl)urea (XII)——To a solution of (VIII) (0.5 g.) in $CHCl_3$ (2 cc.), 2-methyl-3-methoxyacryloyl chloride (0.2 g.) was added, followed by pyridine (0.12 cc.). The reaction mixture was kept at room temperature for 2 days and purified through an alumina column as described earlier (Al_2O_3 10 g., developing solvent: AcOEt). The fraction showing the ultraviolet absorption was evaporated *in vacuo*, and the residue was crystallized from MeOH to 0.24 g. (36.7%) of (XII), colorless plates, m.p. 160°. UV: $\lambda_{max}^{H_2O}$ 261 mμ; $\lambda_{min}^{H_2O}$ 228 mμ.

1-α-D-Ribopyranosylthymine (XIII) (A) (Cyclisation procedure)——To 3.3% NH_4OH (18 cc.), (IX) (0.64 g.) was added, and the solution was concentrated to syrup after heating at 80° for 1.5 hr. This syrup was chromatographed through an activated charcoal column (6 g. of activated charcoal, 6 g. cellulose powder) as described in Part II.[2] The column (A) was washed with distilled H_2O (400 cc.) and then elution was carried out as follows.

300 cc. of distilled H_2O was added to the mixing bottle (B), and the volume and concentration of the solvent added to the upper bottle (C) were as follows.

first: H_2O-EtOH-conc. NH_4OH (205:16:79)
second: H_2O-EtOH-conc. NH_4OH (170:65:65)
third: H_2O-iso-PrOH-conc. NH_4OH (147:62:91)

25 cc. of fractions were collected. Each fraction was examined by paper chromatography (solvent: H_2O-saturated iso-BuOH; spots were detected under ultraviolet light). Fraction Nos. 21~31 showing a single spot at Rf 0.19, were, after addition of EtOH, evaporated repeatedly *in vacuo*.

The syrup thus obtained was dissolved in AcOEt and petr. ether was added. Crystallisation occured while scratching. Recrystallized from EtOH, (XIII) was obtained as colorless prisms, m.p. 251°, $[\alpha]_D^{27}$ −108° (c=0.67, H_2O). UV: $\lambda_{max}^{H_2O}$ 268 mμ (log ε 3.98); $\lambda_{min}^{H_2O}$ 235 mμ. *Anal.* Calcd. for $C_{10}H_{14}O_6N_2$: C, 46.51; H, 5.47; N, 10.85. Found: C, 46.92; H, 5.49; N, 11.00.

(B) (Hilbert-Johnson procedure)——Tetra-O-acetyl-D-ribose[9] (6.8 g.) was added to a solution of HBr (14 g.) in AcOH (75 g.). After 3 hr. the solvents were distilled off *in vacuo*. Dry benzene was added and the mixture was evaporated *in vacuo*. This manipulation was repeated three times. A solution of 2,4-diethoxy-5-methylpyrimidine (7.1 g.) in benzene was then added and the mixture was evaporated to remove the benzene. The residue was heated at 50° in a reduced pressure (5 mm. Hg) for 140 hr.

MeOH (200 cc.) and 30% HCl in MeOH (100 cc.) were then added and, after standing at room temperature for 3 days, the solution was evaporated *in vacuo*, neutralized and filtered. The filtrate was mixed with Celite (5 g.) and this mixture was chromatographed through a Celite column (100 g. of Celite 535; 100 cc. of H_2O). The column was eluted with H_2O-saturated iso-BuOH and 25 cc. fractions were collected. Fraction Nos. 18~24 were concentrated *in vacuo* to a syrupy residue. This was dissolved in MeOH, and after addition of AcOEt; the MeOH was removed *in vacuo*. Petr. ether was added and the filtered solution was evaporated *in vacuo* to a syrup which was crystallized from iso-PrOH and petr. ether to 0.21 g. of (XIII), colorless prisms, m.p. 252°. This compound corresponding to the substance synthesized by Visser,[5] showed no depression on admixture with the specimen obtained by the procedure (A).

From fraction Nos. 27~37, 0.15 g. of (XIV) were obtained as a colorless crystalline powder, m.p. 234°. Admixture with the specimen synthesized either by mercury procedure or by cyclisation procedure gave no depression.

1-β-D-Ribopyranosylthymine (XIV). (A) (Cyclisation procedure)——To 3.3% NH_4OH (15 cc.), (X) (0.48 g.) was added, and the mixture was heated at 80° for 2 hr. Purification through an activated charcoal column as described in the case of (XIII) afforded a syrup which contained (XIV) but did not

9) P. A. Levene: J. Biol. Chem. **92**, 109 (1931); H. Zinner: Ber, **83**, 153 (1950).

crystallize. This syrup was chromatographed through a Celite column (16 g. of Celite 535, 16 cc. of H_2O). The column was eluted with H_2O-saturated iso-BuOH and 10 cc. fractions were collected. Fraction Nos. 9~27, showing a strong ultraviolet-absorbing spot at Rf 0.21 (H_2O-saturated iso BuOH), were concentrated *in vacuo* to a syrup which was crystallized from AcOEt to (XIV), colorless prisms, m.p. 234°, $[\alpha]_D^{27}$ −8.1°(c=1.1, H_2O). UV : $\lambda_{max}^{H_2O}$ 264 mμ(log ε 3.98); $\lambda_{min}^{H_2O}$ 233 mμ. *Anal.* Calcd. for $C_{10}H_{14}O_6N_2$: C, 46.51; H, 5.47; N, 10.85. Found : C, 46.91; H, 5.30; N, 11.09.

(B) **mercuri procedure**——(1) (From tri-O-benzoyl-ribopyranosyl bromide (XVII)) : (XVII) (3.7 g.) was added to a stirred suspension of dithyminylmercury (1.6 g.) in dehyd. xylene (80 cc.). After 1.5 hr. stirring under reflux, the reaction mixture was treated as described in Part I[1] and afforded 4.1 g. of a syrup. This syrup (1.8 g.) was dissolved in MeOH (50 cc.), and after addition of 1*N* MeONa in MeOH (2 cc.), the solution was refluxed for 1.5 hr. The mixture was neutralized with CO_2, evaporated *in vacuo*, and the residue chromatographed through an active charcoal column as described earlier. The syrup containing (XIV) was again purified by a Celite column (16 g. of Celite 535, 16 cc. of H_2O) as described in (A). Fraction Nos. 7~20 (each 10 cc.), showing a single spot at Rf 0.21 (H_2O-saturated iso-BuOH), were evaporated *in vacuo* to a syrup, which crystallized from MeOH and AcOEt to 0.1 g. of (XIV), colorless prisms, m.p. 234°. Admixture with the specimen synthesized by (A) gave no depression.

(2) (From tri-O-acetyl-ribopyranosyl bromide via 2,3,4-tri-O-acetyl-β-D-ribopyranosylthymine) : Tri-O-acetylribopyranosyl bromide (prepared from 6.36 g. of tetra-O-acetyl-D-ribopyranose) was added to a stirred suspension of dithyminylmercury (4.5 g.) in hot dehyd. xylene (140 cc.) and the mixture was refluxed for 1.5 hr. After treated as described earlier, crude 2,3,4-tri-O-acetyl-β-D-ribopyranosylthymine (XVIII) was absorbed on 2 g. of silica gel. This mixture was chromatographed through an alumina column (Al_2O_3 40 g.). The column was eluted with AcOEt, then with Me_2CO, and the fractions showing a strong ultraviolet absorbing spot were evaporated *in vacuo* to a syrup which was crystallized from MeOH to 0.7 g. of (XVIII), colorless prisms, m.p. 166°, $[\alpha]_D^{23}$ +17.68°(c=3.4 H_2O). UV : $\lambda_{max}^{H_2O}$ 262 mμ(log ε 3.99). *Anal.* Calcd. for $C_{16}H_{20}O_9N_2$: C, 50.00; H, 5.25; N, 7.29. Found : C, 49.98; H, 5.42; N, 6.95.

To 3.3% NH_4OH (6 cc.), (XVIII) (0.2 g.) was added and the mixture heated for 25 min. EtOH was added, and the solution was evaporated *in vacuo* to remove H_2O. Recrystallized from MeOH and AcOEt, 0.06 g. (45%) of (XIV) was obtained as a crystalline powder, m.p. 234°. Admixture with the specimen synthesized either by (A) or by (B) (1) gave no depression.

1-α-D-Xylopyranosylthymine (XV)——To 3.3% NH_4OH (3 cc.), (XI) (0.19 g.) was added and the mixture was heated at 80° for 3 hr. The solution was concentrated *in vacuo* to a syrup. This syrup was crystallized from hydr. EtOH to colorless prisms, m,p. 295°, $[\alpha]_D^{26}$ −124.9°(c=0.3, H_2O). Yield 0.01 g. UV : $\lambda_{max}^{H_2O}$ 268 mμ(log ε 3.99); $\lambda_{min}^{H_2O}$ 236 mμ. *Anal.* Calcd. for $C_{10}H_{14}O_6N_2$: N, 10.85. Found: N, 10.81.

1-β-D-Xylopyranosylthymine (XVI)——This substance was synthesized from (XII) (0.2 g.) as in the case of (XV). Recrystallization from MeOH and AcOEt yielded colorless prisms, m.p. 285°, $[\alpha]_D^{24.5}$ +2.54°(c=1.2, H_2O). Yield 0.05 g. UV : $\lambda_{max}^{H_2O}$ 264 mμ(log ε 4.01); $\lambda_{min}^{H_2O}$ 234 mμ. *Anal.* Calcd. for $C_{10}H_{14}O_6N_2$: C, 46.51; H, 5.47; N, 10.85. Found : C, 46.74; H, 5.45; N, 10.92.

2,3,4-Tri-O-benzoyl-β-ribopyranosyl bromide (XVII)——This substance was synthesized following the procedure described by Jeanloz[10] and Ness[11]; m.p. 149~150°(from petr. ether).

Metaperiodate Oxidation Studies——Concentrations of ureides ranging from 0.01 to 0.03 m*M*/cc. were treated with excess metaperiodate at 0° in the darkness and aliquots titrated iodometrically (0.01*N* I_2). The acidity of the reaction solution was determined by the usual method (0.01*N* NaOH: bromcresolpurple as an indicator). Oxidation of nucleosides with metaperiodate was carried out in a similar manner at room temperature.

The authors express their gratitude to Dr. Junzo Shinoda, President, Dr. Masao Shimizu, Director of the Research Laboratory, of this company, for their kind encouragement in the present work. The authors are also indebted to Messers. B. Kurihara and K. Abe for elemental analyses.

Summary

From the reaction mixtures of D-ribose or D-xylose and urea, two anomeric pairs of D-ribopyranosyl- and D-xylopyranosylureas were separated by a Celite column. These ureides, after acetylation followed by condensation with 2-methyl-3-methoxyacryloyl chloride, afforded the intermediates, the cyclisation of which produced two anomeric pairs of D-ribopyranosyl- and D-xylopyranosylthymines.

(Received March 12, 1962)

10) R. Jeanoloz : J. Am. Chem. Soc., **70**, 4053 (1948).
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