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The Synthesis of 3-Phenyl-4-(β- and -α-D-ribofuranosyl)pyrazole and the Configuration of C-Ribosylethynyl Derivatives[1]

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3-Phenyl-4-(β- and -α-D-ribofuranosyl)pyrazoles (**1a**) and (**2a**) have been synthesized from 2,3,5-tri-O-benzoyl-D-ribofuranosyl bromide (**3**) by the substitution of **3** with bis-phenylethynyl)mercury (**4a**) into 1-phenyl-2-(2,3,5-tri-O-benzoyl-β- and -α-D-ribofuranosyl)ethynes (**5a**) and (**6a**) and subsequent addition reaction with diazomethane. Ethynylation of **3** with **4a** have furnished a mixture of **5a** and **6a**, however, with phenylethynylcopper (**4b**) the ketal (**7a**) was formed together with **5a**. The configuration of the anomeric carbon of the major product (**5a**) was proved by its permanganate oxidation into the known tri-O-benzoylallonic acid (**5d**).

The nuclear magnetic resonance spectra of the 2,3-O-isopropylidene ribofuranosyl derivatives (**9a—d**) and (**10a—d**) have shown that the coupling constant of the proton at the anomeric carbon is approximately 4 Hz in the 1-α-substituted anomer, and, on the other hand, almost negligible in the 1-β-substituted anomer. Both acetylenic compounds (**5a**) and (**6a**) were converted into ribosyl pyrazole (**5f**) and (**6c**) by 1,3-dipolar addition reaction with diazomethane, which were finally debenzoylated with ammonia into the triols (**1a**) and (**2a**), respectively.

Keywords——ethynylation; 1-phenyl-2-(2,3,5-tri-O-benzoyl-β- and -α-D-ribofuranosyl)ethyne; 3-phenyl-4-(β- and -α-D-ribofuranosyl)pyrazole; configuration and coupling constant at anomeric carbon; NMR spectra

Recent publications on the structures and carcinogenic[3] and anti-viral activity[4] of C-nucleosides including formycin A, formycin B,[5] and pyrazomycin[4,6] have stimulated us to synthesize naturally-occurring compounds as well as analogous derivatives of C-nucleosides.[7] As a part of our research on the synthesis of pyrazole derivatives, we have been examining general procedures to combine pyrazole-nuclei with furanose to obtain physiologically active materials. In this article is described the synthesis of 3-phenyl-4-(β- and -α-D-

1) A part of this work has previously been communicated: *a*) K. Arakawa, T. Miyasaka, and N. Hamamichi, *Chemistry Letters*, **1974**, 1305; *b*) *Idem*, *ibid.*, **1976**, 1119; *c*) *Idem*, *Nucleic Acids Res.* Special Publication No. 2, **1976**, sl; This work was presented in part on the IVth Symposium on the Chemistry of Nucleic Acids, Kyoto, Japan, November, 26—27, 1976.

2) Location: *1-5-8 Hatanodai, Shinagawa-ku, Tokyo, 142, Japan.*

3) *a*) M. Ishizuka, T. Sawa, S. Hori, H. Takayama, T. Takeuchi, and H. Umezawa, *J. Antibiot.* (Tokyo), **21**, 5 (1968); *b*) M.J. Sweeney, F.A. Davis, G.E. Gutowski, R.L. Hamill, D.H. Hoffman, and G.A. Poore, *Cancer Res.*, **33**, 2619 (1971).

4) K. Gerzon, D.C. Delong, and J.C. Kline, *Pure Appl. Chem.*, **28**, 489 (1971).

5) *a*) G. Koyama, K. Maeda, and H. Umezawa, *Tetrahedron Lett.*, **1966**, 597; *b*) S. Aizawa, T. Hidaka, N. Otake, K. Isono, N. Igarashi, and S. Suzuki, *Agric. Biol. Chem.* (Tokyo), **29**, 375 (1965); *c*) E.M. Acton, K.J. Ryan, D.W. Henry, and L. Goodman, *Chem. Commun.* **1971**, 986.

6) *a*) J. Farkaš, Z. Flegelova, and F. Šorm, *Tetrahedron Lett.*, **1972**, 2279; *b*) S.D. Bernardo and M. Weigele, *J. Org. Chem.*, **41**, 287 (1976).

7) *a*) T.C. Jain, I.D. Jenkins, A.F. Russell, J.P.H. Verheyden, and J.G. Moffatt, *J. Org. Chem.*, **39**, 30 (1974); *b*) H.P. Albrecht, D.B. Repke, and J.G. Moffatt, *ibid.*, **39**, 2176 (1974); *c*) E.M. Acton, A.N. Fujiwara, L. Goodman, and D.W. Henry, *Carbohydr. Res.*, **33**, 135 (1974); *d*) J. Zemlicka, *J. Am. Chem. Soc.*, **97**, 5896 (1975); *e*) G. Just, and M. Ramjeesngh, *Tetrahedron Lett.*, **1975**, 985; *f*) D.B. Repke, H.P. Alrecht, and J.G. Moffatt, *J. Org. Chem.*, **40**, 2481 (1975); *g*) C.M. Gupta, G.H. Jones, and J.G. Moffatt, *ibid.*, **41**, 3000 (1976); *h*) F.G. De Las Heras, C.K. Chu, S.Y-K. Tam, R.S. Klein, K.A. Watanabe, and J.J. Fox, *J. Heterocycl. Chem.*, **13**, 175 (1976); *i*) S.Y-K. Tam, J-S. Hwang, F.G. De Las Haras, R.S. Klein, and J.J. Fox, *J. Heterocycl. Chem.*, **13**, 1305 (1976).

ribofuranosyl)pyrazoles (**1a**) and (**2a**) from 2,3,5-tri-O-benzoyl-D-ribofuranosyl bromide (**3**) by the substitution of **3** with bis(phenylethynyl)mercury (**4a**) into 1-phenyl-2-(2,3,5-tri-O-benzoyl-β- and -α-D-ribofuranosyl)ethynes (**5a**) and (**6a**), and subsequent reaction with diazomethane.

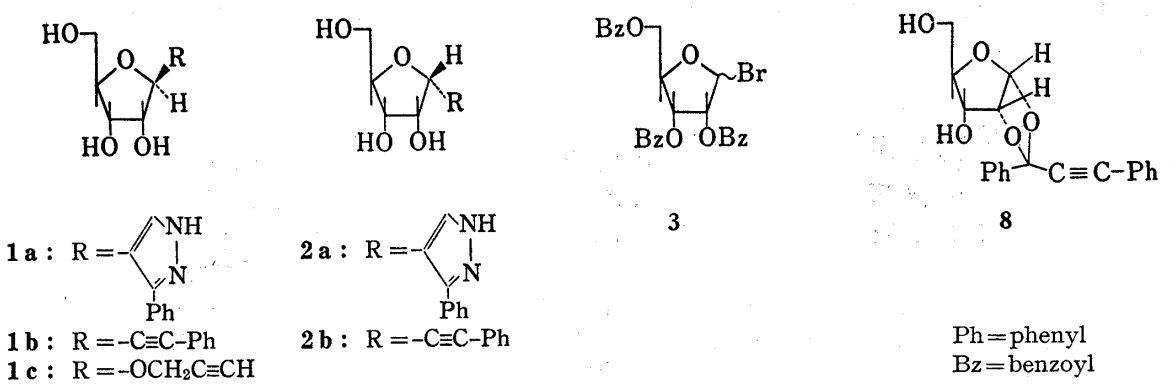


Chart 1

I. Reaction of 2,3,5-Tri-O-benzoyl-D-ribofuranosyl Bromide (3) with Heavy Metal Acetylides (4a—f)

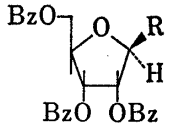
1-Ethynylribofuranosyl derivatives[7g,h,8] have been considered as important key intermediates for synthetic rout to C-nucleosides. We have intended to form C-glycoside linkage by displacement reaction of the ribosyl bromide (**3**) with various heavy metal acetylides (**4a—f**).

The reaction of the bromide (**3**) with bis(phenylethynyl) mercury (**4a**) in dry nitromethane or in dry benzene for 5 days at 35° gave, after evaporation of the solvent, light brown syrup, which revealed to be a mixture of three components by thin-layer chromatography (TLC). Column chromatography on silica gel afforded amorphous solid of 1-phenyl-2-(2,3,5-tri-O-benzoyl-D-ribofuranosyl)ethyne (**5a**) and crystalline isomer **6a**, mp 89—91°, in 36 and 17% yield, respectively. The infrared (IR) spectra of these compounds showed an absorption at 2210 cm^{-1} (–C≡C–). The nuclear magnetic resonance (NMR) spectra showed the anomeric proton signals at δ 5.19 and 5.76, respectively. Debenzoylation of **5a** and **6a** with methanolic ammonia gave the corresponding triols (**1b**) and (**2b**), the molecular formula of which were shown $C_{13}H_{14}O_4$ by elemental analysis. The mass (MS) spectra of these triols exhibited a typical fragmentation peak at *m/e* 131, which was common in the fragmentation of C-nucleosides (B+30).[9] These data strongly supported the formation of carbon-carbon linkage at 1-position of ribofuranose by this procedure. It is interesting that the products of the both β-anomer (**1b**) and α-anomer (**2b**) were obtained through heavy metal process.[10]

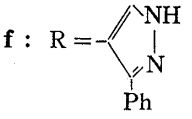
On reaction with phenylethynylcopper (**4b**) at room temperature for 5 days the bromide (**3**) gave, after separation by preparative TLC, colorless crystals (**7a**), mp 106—109°, and **5a**, in 32 and 10% yields, respectively. The NMR spectrum of **7a** showed a signal at δ 6.23 (1H, d, J=4.0 Hz, C_1H). The NMR spectra of 1,2-O-acetal derivatives of ribose reported by Hanessian[11] and Moffatt[7b] showed the signal of C_1H at δ 6.21—6.30. Debenzoylation of **7a** with methanolic ammonia gave diol (**8**), mp 143—145°, $C_{20}H_{18}O_5$, the IR spectrum of which showed

8) *a*) J.G. Buchanan, A.R. Edgar, and M.J. Power., *J. Chem. Soc.*, Perkin 1, **1974**, 1943; *b*) J.G. Buchanan, A.R. Edgar, M.J. Power, and G.C. Williams., *J. Chem. Soc., Chem. Commun.*, **1975**, 501; *c*) J.G. Buchanan, A.D. Dunn, and A.R. Edgar, *J. Chem. Soc*, Perkin 1, **1975**, 1191.
9) L.B. Townsend and R.K. Robins, *J. Heterocycl. Chem.*, **66**, 459 (1969).
10) *a*) G.T. Rogers and T.L.V. Ulbricht, *Tetrahedron Lett.*, **1968**, 1025; *b*) M. Bobek and J. Farkaš, *Collect. Czech. Chem. Commun.*, **34**, 247 (1969); *c*) R.S. Klein, M.P. Kotick, K.A. Watanabe, and J.J. Fox, *J. Org. Chem.*, **36**, 4113 (1971).
11) S. Hanessian and A.G. Peret, *Can. J. Chem.*, **52**, 1280 (1974).

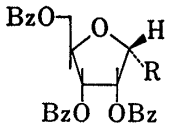
an ethynyl group band at 2210 cm^{-1}, and no carbonyl band at around 1700 cm^{-1}. The IR and NMR spectra as well as the analysis data of the debenzoylated product and **8** supported that the ethynylated product **7a** was phenylethynylated 1,2-O-benzylidene derivatives. The anomeric configuration of **5a** is tentatively supposed as β-configuration from the viewpoint of heavey metal process[10] because minor product **5a** was obtained from **3** by the reaction, but **6a** was not obtained from it.



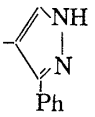
5a: R = -C≡C-Ph
5b: R = $-OCH_2C{\equiv}CH$
5c: R = $-OC_{26}H_{21}O_7$
5d: R = -COOH
5e: R = $-COOCH_3$



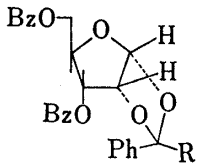
5f: R =



6a: R = -C≡C-Ph
6b: R = -COOH



6c: R =



7a: R = -C≡C-Ph
7b: R = $-OCH_2C{\equiv}CH$

Ph = phenyl
Bz = benzoyl

Chart 2

TABLE I. Reaction Products of Ribosyl Bromide (3) with **4a—f**

Reagent	Reaction products		
$Hg(C{\equiv}C\text{-}Ph)_2$ (**4a**)	**5a**	**6a**	—
$CuC{\equiv}C\text{-}Ph$ (**4b**)	**5a**	—	**7a**
$Cd(C{\equiv}C\text{-}Ph)_2$ (**4c**)	—	—	**7a**
$Hg(C{\equiv}C\text{-}CH_2OH)_2$ (**4d**)	**5b**	—	—
$CuC{\equiv}C\text{-}CH_2OH$ (**4e**)	**5b**	—	**7b**
$Hg(C{\equiv}C\text{-}COPh)_2$ (**4f**)	**5c**	—	**7b**

On reaction with bis(phenylethynyl)cadmium (**4c**) at room temperature in benzene for 20 hr the bromide (**3**) furnished the ketal **7a** as a sole product in 70% yield, which was completely identical with the reaction product **7a** obtained from the reaction of **3** with **4b**.

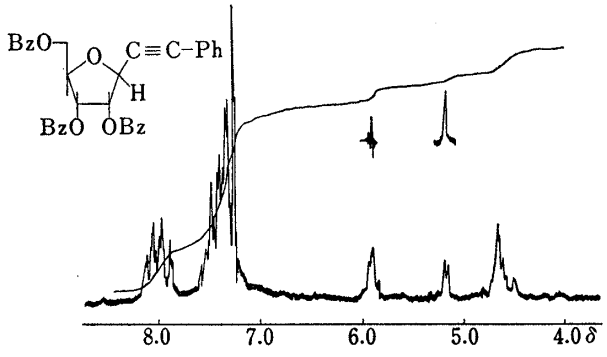


Fig. 1. NMR Spectrum (in $CDCl_3$) of **5a**

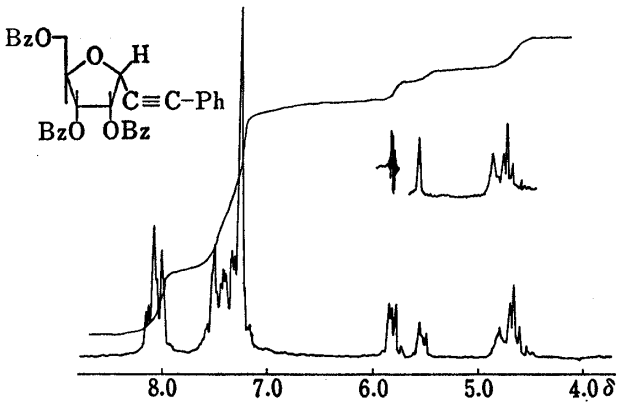


Fig. 2. NMR Spectrum (in $CDCl_3$) of **6a**

On reaction with bis(3-hydroxy-1-propynyl)-mercury (**4d**) in absolute nitromethane at 37° for 7 days the bromide (**3**) gave **5b** after separation by silica gel column chromatography. The IR spectrum of **5b** showed a band at 2210 cm^{-1} (–C≡C–). The NMR spectrum showed signals at δ 2.43 (1H, t, C≡CH), and δ 5.51 (1H, s, C_1H).[12] These data suggested that the structure of **5b** was propargyl 2,3,5-tri-O-benzoyl-β-D-ribofuranoside. Debenzoylation of **5b** with methanolic ammonia furnished propargyl ribofuranoside (**1c**) as O-glycoside.

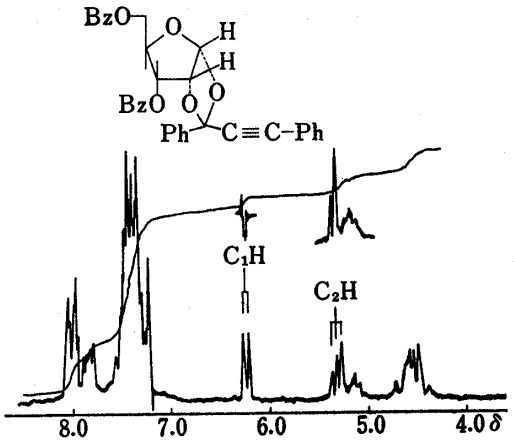


Fig. 3. NMR Spectrum (in $CDCl_3$) of **7a**

On treatment with (3-hydroxy-1-propynyl)-copper (**4e**) in benzene at room temperature for 2 days the bromide (**3**) gave, after separation by preparative TLC, the O-glycoside **5b** [21%] and small amount of **7b**. The structure of orthoester (**7b**) was confirmed by the coupling constant and chemical shift of anomeric proton in the NMR spectrum. Any crystalline product could not be isolated from the reaction mixture of **3** with bis(3-benzyloxy-1-propynyl)mercury (**4g**) in nitromethane at 40° for 5 days except small amount of resinous brown solid.

On reaction of **3** with bis(benzoylethynyl)mercury (**4f**) in benzene at 40° for 10 days any substituted product was not isolated except the dimeric β-D-ribofuranosyl β-D-ribofuranoside hexabenzoate, the structure of which was determined by direct comparison with the authentic sample prepared according to the Rosenberg's procedure.[13]

II. Chemical Proof of the Configuration at the Anomeric Carbon of 1-Phenylethynyl Ribofuranosyl Derivatives (5a) and (6a)

The configuration at the anomeric carbon of **5a** and **6a** was determined as follows: Oxidation of 1-phenyl-2-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)ethyne (**5a**), the major product of ethynylation, with potassium permanganate in acetic acid at 40° afforded, after separation by preparative TLC, carboxylic acid **5d**. For characterization of carboxylic acid group, **5d** was converted into the corresponding methyl ester (**5e**) with diazomethane in ether. The NMR spectrum exhibited a methyl signal at δ 3.79. The acid (**5d**) and the ester (**5e**) were completely identical with the authentic specimens of allonic acid and its ester prepared from the known 2,3,5-tri-O-benzoyl-β-D-ribofuranosyl cyanide,[10b,14] which had chemically been proved to be β-configurated in relationship with the natural oxoformycin.[15] Oxidation of 1-phenyl-2-(2,3,5-tri-O-benzoyl-α-D-ribofuranosyl)ethyne (**6a**), the minor product of the displacement reaction, gave, however, a different acid (**6b**) [solid], which was considered to be α-configurated at the C_1-anomeric carbon.

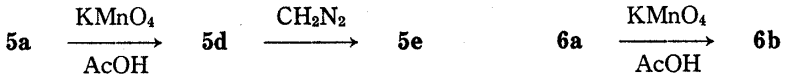


Chart 3

12) J.D. Stevens and H.G. Flether, JR, *J. Org. Chem.*, **33**, 1799 (1969).
13) E. Rosenberg and S. Zamenhof, *J. Biol. Chem.*, **237**, 1040 (1962).
14) *a*) J.A. Montgomery and K. Hewson, *J. Heterocycl. Chem.*, **7**, 443 (1970); *b*) H.S. El Khadem and T.D. Audichya, *J. Med. Chem.*, **18**, 438 (1975).
15) M. Bobek, J. Farkaš, and F. Šorm, *Tetrahedron Lett.*, **1970**, 4611.

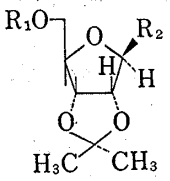
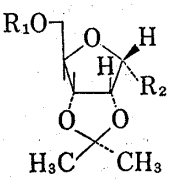
III. Comparison of the NMR Spectra of β- and -α C-Ribosyl Ethynyl Derivatives (9a—d) and (10a—d)

A considerable number of ethynylribofuranosyl derivatives[8] have been reported as intermediates for the synthesis of C-nucleosides, however, the configuration at the anomeric proton of those compounds has tentatively been discussed without chemical proof of the configuration.

We first examined the coupling constants at the C_1-proton in the NMR spectra of **5a** and **6a**, the configuration of which had been unambiguously determined by chemical method. As coupling constant must be applied with caution to configurational assignments in C-nucleoside derivatives due to uncertainties of the preferred conformation of such cyclic systems in solution, we applied Goodman's method[16] to the phenylethynylated products to stabilize the conformation of the ribofuranose ring and thereby facilitate the configurational assignments based on coupling constant ($J_{1',2'}$) of the both anomers. Also, it has recently been shown by Imbach and others[17] that the assignment of anomeric configuration by means of the difference in the chemical shifts of the two methyl groups ($\Delta\delta$) of the 2,3-O-isopropylidene derivatives of N-nucleosides was $\Delta\delta<0.10$ for the α-configuration and $\Delta\delta>0.18$ for the β-configuration.

On treatment with acetone in the presence of *p*-toluenesulfonic acid triols (**1b**) and (**2b**) gave 2′,3′-acetonides (**9a**) and (**10a**), respectively. These were converted into the monoacetates (**9b**) and (**10b**) and to the monobenzoates (**9c**) and (**10c**), which were hydrogenated into the C_1-phenethyl derivatives (**9d**) and (**10d**), respectively. The Table II summarizes the NMR data of the β- and -α-anomeric 2′,3′-O-isopropylidene derivatives. The C_1-proton signal of

Table II. NMR Spectral Data of 2,3-O-Isopropylidene Derivatives (**9a—d**) and (**10a—d**)

Compounds	No.	R_1	R_2	C_1H (δ)	$J_{1,2}$(Hz)	>C(Me)$_2$(δ)	>C(Me)$_2$($\Delta\delta$)
	**9a**	H	-C≡C-Ph	4.80—4.99	—	1.32, 1.50	0.18
	9b	Ac	-C≡C-Ph	4.87	0	1.35, 1.53	0.18
	9c	Bz	-C≡C-Ph	4.77	0	1.37, 1.55	0.18
	9d	Bz	$-CH_2CH_2Ph$	3.97	—	1.33, 1.52	0.19
	**10a**	H	-C≡C-Ph	5.01	4.1	1.33, 1.55	0.22
	10b	Ac	-C≡C-Ph	5.07	4.1	1.34, 1.55	0.21
	10c	Bz	-C≡C-Ph	4.81	4.4	1.39, 1.62	0.23
	10d	Bz	$-CH_2CH_2Ph$	3.87	3.6	1.33, 1.50	0.17

Ph=$-C_6H_5$, Ac=CH_3CO-, Bz=C_6H_5CO-

α-substituted ethynyl derivatives (**10a—c**) split into a doublet ($J_{1',2'}$=*ca.* 4 Hz) by the vicinal proton at C_2-position and the coupling constants ($J_{1',2'}$) of β-substituted ethynyl derivatives (**9a—c**) were negligible. On the other hand, the differences in the chemical shifts of the two methyl group of the β-substituted 2′,3′-O-isopropylidene derivatives are *ca.* 0.18. On the contrary, those of α-substituted compounds are *ca.* 0.21—0.23. The differences were considered too small to be useful to identify the both anomers on the contrary to the case of N-nucleosides.[17] The discrepancy between the values in C-nucleosides and the ethynyl-

16) *a*) K.J. Pyan, H. Arzoumanian, E.M. Acton, and L. Goodman, *J. Am. Chem. Soc.*, **86**, 2503 (1964); *b*) H. Maehr, T.H. Williams, M. Leach, and A. Stempel, *Helv. Chim. Acta*, **57**, 212 (1974).

17) *a*) J.-L. Imbach, J.-L. Barascut, B.L. Kam, B. Bayner, C. Tamby, and C. Tapiero, *J. Heterocycl. Chem.*, **10**, 1069 (1973); *b*) J.-L. Imbach, J.-L. Barascut, B.L. Kam, and C. Tapiero, *Tetrahedron Lett.*, **1974**, 129.

ated compounds seems to be likely the results of the reverse anisotropic effect of the pi-systems of heteroaromatic group and those of the acetylenic linkage.

IV. The 1,3-Dipolar Addition of Diazomethane on 1-Phenylethynyl Ribofuranose (5a) and (6a)

As preliminary experiment of 1,3-dipolar addition reaction, we described that addition reaction of N-phenylmaleimide with various diazomethane derivatives reacted smoothly to give pyrazole derivatives.[18] Hereupon, examination of 1,3-dipolar cycloaddition of diazoalkane on 1-phenylethynyl ribofuranose (**5a**) and (**6a**) were carried out to give pyrazole derivatives.

The reaction of the respective **5a** and **6a** with excess of diazomethane in ether at room temperature for 10 days,[19] after separation of silica gel column chromatography, gave addition products 4-(2,3,5-tri-O-benzoyl-β- and -α-D-ribofuranosyl)-3-phenylpyrazole (**5f**) and (**6c**), the IR spectra of which showed an absorption band at 3430 cm^{-1} due to >NH group. Ethyl diazoacetate did not react with the ethynyl ribofuranose (**5a**) and (**6a**) by heating in toluene at 100° for 5 hr. Debenzoylation of **5f** and **6c** with methanolic ammonia afforded the desired ribosylpyrazoles **1a** and **2a** in good yield. The MS spectra of these compounds indicated the characteristic fragmentation of C-nucleoside at *m/e* 173 (B+30).

Preliminary studies on physiological activity of these compounds revealed that **1a** and **2a** were not considerably effective in terms of growth inhibition against L 5178 Y and that anti-viral activities against Herpes Simplex virus (HSV/1) and against Influenza virus (type B) were not significantly large.

Experimental

All melting points were measured in capillary tubes and were uncorrected. Thin-layer chromatography was carried out on plates coated with silica gel (Merck GF_{254}). Preparative TLC was carried out on thick-layer plates (2 mm) of silica gel (Merck GF_{254}) and the detection was made by irradiation with an ultraviolet lamp (254 nm). Column chromatography was carried out through silica gel (Merck 70—230 mesh). NMR spectra were measured by a Hitachi R-22 90 MHz spectrometer using tetramethylsilane as an internal reference. Abbreviations are used; s=singlet, d=doublet, t=triplet, sex=sextet, m=multiplet, IR and UV spectra were measured on a JASCO IRA-1 spectrophotometer and on a Hitachi EPS-3T spectrophotometer, respectively. MS spectra were measured on a Hitachi RMU-7L or on a JEOL JMS-01SG High-resolution spectrometer with a direct inlet system.

Preparation of Bis(phenylethynyl) mercury (4a), Bis(3-hydroxy-1-propynyl)mercury (4d), Bis(benzoylethynyl)-mercury (4f), and Bis(3-benzyloxy-1-propynyl)mercury (4g)——A solution of K_2HgI_4 (26 ml)prepared by the method of J.R. Johonson *et al.*,[20] was added dropwise to a solution of ethynyl derivatives in aqueous 95% EtOH (60 ml) solution under icecooled conditions with stirring. After 10 min, the precipitated crystals were collected by filtration, washed with H_2O, dried over P_2O_5, and the corresponding mercury compounds were used in the next reactions.

2,3,5-Tri-O-benzoyl-D-ribofuranosyl Bromide[10b,11] (3)——Anhydrous hydrogen bromide was bubbled through a solution of 1-O-acetyl-2,3,5-tri-O-benzoyl-β-D-ribofuranose (ABR) in benzene at 0° for 30 min. After the flask of the reaction mixture was sealed and allowed to stand at room temperature for 30 min, the solution was evaporated under diminished pressure to give a syrup. Dry benzene (5 ml) was added to the syrup, and hydrogen bromide was removed from the mixture azeotropically by repeating this procedure three times. The residue may then be used immediately for the following reactions.

1-Phenyl-2-(2,3,5-tri-O-benzoyl-β- and -α-D-ribofuranosylethyne (5a) and (6a)——To a solution of the bromide (3, prepared from 1.0 g of ABR) in absolute benzene (4 ml) or in absolute nitromethane (4 ml) was added 1.0 g of **4a**, and the mixture was then filtered and the filtrate was washed with 20% aqueous KI (3×10 ml), and next with H_2O, and dried over Na_2SO_4. The solvent was evaporated under diminished pressure to give a syrup, which was separated by column chromatography through silica gel (3×20 cm) using benzene as the solvent.

The earlier fractions (No. 7—10, one fraction=16 ml) were identical with **4a** by TLC.

The fractions (No. 20—30) gave 0.39 g (36%) of 1-phenyl-2-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-ethyne (**5a**) as an amorphous solid. $[\alpha]_D^{20}$ −60.5° (c=0.61, chloroform). UV λ_{max}^{EtOH} nm (log ε): 231 (4.67),

18) K. Arakawa, T. Miyasaka, and N. Hamamichi, *Yakugaku Zasshi*, **97**, 410 (1977).
19) *a*) W. Kirmse and L. Horner, *Ann. Chem.*, **614**, 1 (1959); *b*) M.T. Garcia-López, G. Garcia-Muñoz, and R. Madroñero, *J. Heterocycl. Chem.*, **8**, 525 (1971).
20) J.R. Johonson and W.L. McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926).

251 (4.27), 272 (3.60), 282 (3.46). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2210 (C≡C), 1721 (C=O). NMR ($CDCl_3$) δ: 4.52—4.80 (3H, m, $C_{4'}H$ and $C_{5'}H_2$), 5.19 (1H, d, $J_{1',2'}$=2.2 Hz, $C_{1'}H$), 5.94 (2H, m, $C_{2'}H$ and $C_{3'}H$), 7.20—8.20 (20H, m, aromatic). *Anal.* Calcd. for $C_{34}H_{26}O_7$: C, 74.73; H, 4.76. Found: C, 74.55; H, 4.80.

The slowly eluting fractions (No. 40—50) gave 0.17 g (16.6%) of solid, and it was recrystallized from EtOH to give 1-phenyl-2-(2,3,5-tri-O-benzoyl-α-D-ribofuranosyl)ethyne (**6a**) as a colorless needles, mp 89—91°. $[\alpha]_D^{22}$ +87.92° (c=0.67, chloroform). UV λ_{max}^{EtOH} nm (log ε): 230 (4.94), 252 (4.54), 272 (3.87), 282.5 (3.79). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2210 (C≡C), 1720 (C=O). NMR ($CDCl_3$) δ: 4.63 (2H, m, $C_{5'}H_2$), 4.75 (1H, m, $C_{4'}H$), 5.48 (1H, m, $C_{2'}H$), 5.76 (2H, m, $C_{1'}H$ and $C_{3'}H$), 7.60—8.12 (20H, m, aromatic). *Anal.* Calcd. for $C_{34}H_{26}O_7$: C, 74.73; H, 4.76. Found: C, 74.72; H, 4.61.

1-Phenyl-2-β- and -α-D-ribofuranosyl Ethyne (1b) and (2b)——Through a solution of **5a** (0.41 g) in a mixture of anhydrous MeOH (10 ml) and benzene (5 ml) was bubbled dry gaseous ammonia for 1 hr at −20°. The reaction vessel was sealed, and the solution was allowed to stand at room temperature for 5 days. After evaporation of the solvent under reduced pressure, the residue was purified by chromatography on a column of silica gel using 2% MeOH–benzene to give 142 mg (83%) as a solid. Recrystallization from AcOEt–benzene afforded 1-phenyl-2-β-D-ribofuranosyl ethyne (**1b**) mp 66—67°. $[\alpha]_D^{19}$ −51.5° (c=0.64, methanol). UV λ_{max}^{EtOH} nm (log ε): 241.5 (4.34), 251.5 (4.25). MS *m/e*: 234 (M^+), 131 (C≡C–Ph+30). NMR (DMSO-d_6–D_2O) δ: 3.53 (2H, m, C_5H_2), 3.70—4.10 (m, C_2H, C_3H and C_4H overlapping with D_2O), 4.50 (1H, d, $J_{1,2}$=5.0 Hz, C_1H), 7.42 (5H, s, phenyl). *Anal.* Calcd. for $C_{13}H_{14}O_4$: mol wt. 234.0891. Found: mol wt. 234.0894.

In the same manner into a solution of **6a** (0.38 g) in a mixture of anhydrous MeOH (8 ml) and benzene (3 ml) was bubbled dry gaseous ammonia for 1 hr at −20°, and the reaction mixture was treated as described above. The reaction product 0.15 g (90.3%) of **2b** was recrystallized from AcOEt–hexane to give colorless needles with mp 92—93°. $[\alpha]_D^{19}$ +42.3° (c=0.52, methanol). UV λ_{max}^{EtOH} nm (log ε): 241.5 (4.27), 251.5 (4.17). MS *m/e*: 234 (M^+), 131 (C≡C–Ph+30). NMR (DMSO-d_6–D_2O) δ: 3.40—4.20 (m), 4.91 (1H, m) 7.30—7.60 (5H, m, phenyl). *Anal.* Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.13; H, 5.79.

Reaction of 3 with Phenylethynylcopper[21] (4b)——To a solution of the bromide (**3**, prepared from 1.0 g of ABR) in absolute benzene (6 ml) was added 0.79 g of **4b**, and the mixture was stirred at room temperature for 5 days. The solution was then filtered through a sintered-glass funnel, and the filtrate was washed with H_2O, dried (Na_2SO_4). After evaporation of the solvent *in vacuo*, the residual oil was purified by preparative TLC using benzene–CH_2Cl_2 (5: 1) as the developing solvent. Elution of the firstly eluting band with CH_2Cl_2 afforded 143 mg (32%) of 3,5-di-O-benzoyl-1,2-O-(1-phenylethynylbenzylidene)-α-D-ribofuranose (**7a**) as a solid. Recrystallization from EtOH–H_2O afforded colorless needles, mp 105—106°. $[\alpha]_D^{21}$ +34.2° (c=0.38, chloroform). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3030, 2210 (C≡C), 1721 (C=O). NMR ($CDCl_3$) δ: 4.40—4.80 (3H, m, C_3H and C_5H_2), 5.15 (1H, m, C_4H), 5.32 (1H, t, $J_{2,3}$=4.0 Hz, C_2H), 6.23 (1H, d, $J_{1,2}$=4.0 Hz, C_1H), 7.20—8.12 (20H, m, aromatic). *Anal.* Calcd. for $C_{34}H_{26}O_7$: C, 74.71; H, 4.80. Found: C, 74.69; H, 4.91.

Elution of the secondly eluting band with CH_2Cl_2 afforded 44 mg (10 mg) of **5a** as an amorphous solid, which was completely identical with **5a** in every respect of the TLC, UV, IR, and NMR spectra.

1,2-O-Phenylethynylbenzylidene-α-D-ribofuranose (8)——A solution of 3,5-di-O-benzoyl-1,2-O-(1-phenylethynylbenzylidene)-α-D-ribofuranose (**7a**, 78 mg) in absolute EtOH (5 ml) was previously saturated with dry NH_3 at −10°, and the reaction mixture was sealed and allowed to stand at room temperature for 5 days. After the solution was evaporated *in vacuo*, the residue was extracted with ether (4×10 ml), washed with H_2O, dried over Na_2SO_4, and evaporated *in vacuo*. The residual syrup was purified by preparative TLC using 1% MeOH–CH_2Cl_2 as the developing solvent. Elution of the major band with AcOEt gave 48.3 mg (76%) of **8**. Recrystallization from EtOH–H_2O afforded colorless needles, mp 143—145°. UV λ_{max}^{EtOH} nm (log ε): 241.5 (4.34), 250 (4.25). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2210 (C≡C), 1460, 1440. MS *m/e*: 338 (M^+), 307, 261. *Anal.* Calcd. for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found: C, 70.97; H, 5.22.

Reaction of 3 with Bis(phenylethynyl)cadmium (4c)——Into a solution of bis(phenylethynyl)cadmium[22] (**4c**) prepared from 1.0 g of phenylacetylene was added *in situ* a solution of the bromide (**3**, prepared from 0.4 g of ABR) in benzene (4 ml), and the mixture was stirred at room temperature for 20 hr. After the reaction mixture was filtered and the filtrate was washed with H_2O, dried over Na_2SO_4, and the solvent evaporated *in vacuo*. The residue was passed through a column of silica gel using benzene as the solvent to obtain the main fraction as a solid, which was recrystallized from EtOH–H_2O, giving colorless crystals (0.31 g, 71%). This material showed mp 105—106°, undepressed on admixture with **7a** obtained by the reaction of the bromide **3** with **4b**.

Reaction of 3 with Bis(3-hydroxy-1-propynyl)mercury (4d)——To a solution of the bromide (**3**, prepared from 0.4 g of ABR) in absolute nitromethane (4 ml) was added 0.48 g of **4d**, and the mixture was stirred at 37° for 7 days. The reaction mixture was then filtered and the filtrate was washed with 20% aqueous KI (3×10 ml) and H_2O, dried (Na_2SO_4). The solvent was removed *in vacuo* into syrup, which was chromatographed through a column of silica gel using benzene as the solvent. The main fractions were collected, and the solvent was evaporated *in vacuo*. Recrystallization of the residue from EtOH–H_2O afforded 0.5 g

21) R.E. Atkinson, R.F. Curtis, and J.A. Taylor, *J. Chem. Soc.* (*C*), **1967**, 578.
22) D. Nightingale and F. Wadswarth, *J. Am. Chem. Soc.*, **67**, 417 (1945).

(51%) of **5b** with mp 63—65°. $[\alpha]_D^{19}$ +43.9° (c=0.41, chloroform). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3280, 2120 (C≡C), 1725 (C=O). NMR ($CDCl_3$) δ: 2.43 (1H, t, J=2.2 Hz, C≡CH), 4.30 (2H, d, J=2.2 Hz, OCH_2–), 4.47—4.90 (3H, m, C_4H and C_5H_2), 5.51 (1H, s, C_1H), 5.77 (1H, d, J=5.0 Hz, C_2H), 5.95 (1H, t, J=5.8 Hz, C_3H), 7.22—8.23 (15H, m, aromatic). *Anal.* Calcd. for $C_{29}H_{24}O_8$: C, 69.59; H, 4.83. Found: C, 69.37; H, 5.11.

Propargyl β-D-Ribofuranoside (Ic)——A solution of **5b** (70 mg) in benzene (3 ml) was added into methanol (5 ml) saturated with dry NH_3, and the reaction mixture was kept at room temperature for 5 days. The solvent was then evaporated *in vacuo*, and the residue was purified by preparative TLC using 2% MeOH–CH_2Cl_2 as the developing solvent. Elution of the major band gave 24 mg (91%) of solid, and crystallized from AcOEt–hexane to give **1c** as colorless needles, mp 102—103°. IR ν_{max}^{KBr} cm^{-1}: 3360 (OH), 2120 (C≡C). *Anal.* Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 51.09; H, 6.42.

Reaction of 3 with (3-Hydroxy-1-propynyl)copper[21] (4e)——To a solution of the bromide (3, prepared from 0.3 g of ABR) in absolute benzene (5 ml) was added 0.2 g of **4e**, and the mixture was stirred at room temperature for 2 days. The resulting solution was filtered and the filtrate was washed with H_2O, dried (Na_2SO_4) and evaporated to give a solid, which was purified by preparative TLC using CH_2Cl_2 as the developing solvent. Elution of the major band with CH_2Cl_2 gave 64 mg (21%) of solid, which was recrystallized from EtOH–H_2O to give propargyl 2,3,5-tri-O-benzoyl-β-D-ribofuranoside (**5b**) as colorless needles, mp 63—65°. This compound was identical with **5b** obtained from the reaction of 3 and **4d** by comparring the NMR and the IR spectra.

Elution of the minor band with CH_2Cl_2 gave 15 mg (5%) of 3,5-di-O-benzoyl-1,2-O-(1-propargyloxybenzylidene)-α-D-ribose (**7b**) as an amorphous solid. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300, 2120 (C≡C), 1725 (C=O). NMR ($CDCl_3$) δ: 2.33 (1H, t, J=2.2 Hz, C≡CH), 4.05 (2H, t, J=2.2 Hz, –OCH_2–), 4.10—4.77 (3H, m, C_4H and C_5H_2), 5.05 (1H, d.d, J=9.4 Hz, J=5.4 Hz, C_3H), 5.31 (1H, d.d, J=5.4 Hz, J=4.5 Hz, C_2H), 6.23 (1H, d, J=4.0 Hz, C_1H), 7.22—8.18 (15H, m, aromatic). This compound was not further investigated because of the small amount.

Reaction of 3 with Bis(benzoylethynyl)mercury (4f)——To a solution of the bromide (3, prepared from 0.3 g of ABR) in absolute benzene (4 ml) was added 0.5 g of **4f**, and the mixture was stirred at 40° for 10 days. The solvent was filtered and the filtrate was washed with 20% aqueous KI (3×10 ml) and H_2O, dried (Na_2SO_4), and evaporated to give syrup, which was separated on chromatography (3×15 cm) of silica gel with CH_2Cl_2 as the solvent. The main fraction was evaporated under reduced pressure, and the residue was recrystallized from EtOH–AcOEt to give 0.13 g (44%) of β-D-ribofuranosyl β-D-ribofuranoside hexabenzoate (**5c**) as a colorless powder, mp 139—142° (lit.[13] 144—145°). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 (C=O), NMR ($CDCl_3$) δ: 4.88—4.50 (3H, m, C_4H and C_5H_2), 5.68 (1H, d, J=5.2 Hz, C_2H), 5.72 (1H, s, C_1H), 5.88 (1H, t, J=5.2 Hz, C_3H), 7.15—8.20 (15H, m, aromatic). *Anal.* Calcd. for $C_{52}H_{42}O_{15}$: C, 68.87; H, 4.67. Found: C, 68.80; H, 4.84. The mixed melting point of this compound with the specimens prepared according to E. Rosenberg's procedure did not show any depression.

Oxidation of 1-Phenyl-2-(2,3,5-tri-O-benzoyl-β- and -α-D-ribofuranosyl)ethyne (5a) and (6a) with $KMnO_4$——Into a solution of **5a** (0.15 g) in a mixture of AcOH (3 ml) and acetone (2 ml) was cautiously added a suspension of $KMnO_4$ (0.12 g) in AcOH (4 ml) and H_2O (2 ml). After the mixture was heated in an oil bath at 35° for 2 hr. The reaction mixture was cooled and the excess of $KMnO_4$ was decomposed by addition of MeOH. The solvent was evaporated under reduced pressure. The residue was washed with 30 ml of AcOEt and was filtered to remove the precipitated MnO_2. The filtrate was washed with 5% $NaHCO_3$ (5 ml×3), and with H_2O, dried (Na_2SO_4). After removal of the solvent under diminished pressure, the residue was separated by preparative TLC using benzene–AcOEt (85:15) as the developing solvent. Elution of the major band with AcOEt gave 35 mg (27.5%) of 3,4,6-tri-O-benzoyl-2,5-anhydro-D-allonic acid (**5d**) as an amorphous solid. Precipitation from MeOH–H_2O afforded solid (lit.[10b] solid form). $[\alpha]_D^{22}$ +39.7° (c=0.68, chloroform). UV λ_{max}^{EtOH} nm (log ε): 230 (4.36), 275 (3.37). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3240, 1721 (C=O), 1603, 1454, 1270, 1120, 1105, 1094. *Anal.* Calcd. for $C_{27}H_{22}O_9 \cdot 1/3H_2O$: C, 65.32; H, 4.59. Found: C, 65.18; H, 4.77. This compound was identical with the specimens prepared according to Bobek's procedure. The alkali solution was neutralized by the addition of AcOH and then extracted with AcOEt. The organic layer was washed well with H_2O, dried (Na_2SO_4) and evaporated to dryness *in vacuo*. The resulting residue was separated by preparative TLC using benzene–AcOEt (85:15) as the developing solvent.

Elution of the firstly eluting band with AcOEt gave 15 mg (44%) of benzoic acid, which was identical with the authentic sample.

Elution of the secondly eluting band with AcOEt afforded syrup (10 mg). This material also was identical with an authentic sample of **5d**.

In the same manner, into a solution of **6a** (0.5 g) in a mixture of AcOH (9 ml) and acetone (3 ml) was cautiously added a suspension of $KMnO_4$ (0.22 g) in AcOH (9 ml) and H_2O (6 ml). After the mixture was treated in the same manner as described above, precipitation from MeOH–H_2O afforded 134 mg (32%) of **6b** as a solid. $[\alpha]_D^{19}$ −494° (c=1.86, chloroform). UV λ_{max}^{EtOH} nm (log ε): 231 (4.69), 275 (3.69). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300, 1721 (C=O), 1454, 1270, 1110, 1095.

This compound was not identical with 3,4,6-tri-O-benzoyl-2,5-anhydro-D-allonic acid (**5d**).

Methyl 2,5-Anhydro-3,4,6-tri-O-benzoyl-D-allonate (5e)——Compound **5d** (50 mg) was added into a solution of excess amount of diazomethane in ether. The mixture was allowed to stand at room temperature

overnight. After evaporation of the solvent under reduced pressure, the residue was purified by chromatography on a column of silica gel using CH_2Cl_2 as the solvent. Precipitation from MeOH–H_2O afforded 40.5 mg (79.6%) of **5e** as a solid. $[\alpha]_D^{19}$ +18.12° (c=1.63, chloroform). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2920, 1721 (C=O), 1267, 1120, 1105, 1095. NMR ($CDCl_3$) δ: 3.78 (3H, s, $COOCH_3$), 4.73 (3H, m, C_5H and C_6H_2), 4.84 (1H, d, $J_{2,3}$=4.0 Hz, C_2H), 5.79 (1H, m, C_4H), 5.98 (1H, d.d, $J_{3,4}$=5.2 Hz, $J_{2,3}$=4.0 Hz, C_3H), 7.22—8.24 (15H, m, aromatic). *Anal.* Calcd. for $C_{28}H_{24}O_9$: C, 66.67; H, 4.76. Found: C, 67.24; H, 4.79.

Methyl ester (**5e**) was identical with the specimen prepared from authentic allonic acid (**5d**) by methylation with diazomethane.

1-Phenyl-2-(2,3-O-isopropylidene-β- and -α-D-ribofuranosyl)ethyne (9a) and (10a)——Compound **1b** (0.22 g) and anhydrous *p*-toluenesulfonic acid (21 mg) was dissolved in dry acetone (17 ml), and the solution was stirred at room temperature for 3 hr. The mixture was then neutralized by the addition of an excess of silver oxide, and filtered. The filtrate was evaporated under reduced pressure to dryness, and the residue was recrystallized from EtOH–H_2O to give 0.22 g (85.6%) of **9a** as colorless needles, mp 67—69°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (OH), 2230 (C≡C), 1374, 1383 (*gem* methyl). MS *m/e*: 274 (M^+), 259 (M^+-15). NMR ($CDCl_3$) δ: 1.32 and 1.50 (6H, 2s, 2×CH_3), 2.0 (1H, broad, OH), 3.81 (2H, d, $J_{4',5'}$=5.0 Hz, $C_5'H_2$), 4.25 (1H, sex, $J_{4',5'}$=5.0 Hz, $J_{3',4'}$=2.0 Hz, $C_4'H$), 4.80—4.99 (3H, m, $C_1'H$, $C_2'H$ and $C_3'H$), 7.22—7.55 (5H, m, phenyl). *Anal.* Calcd. for $C_{16}H_{18}O_4$: mol wt. 274.1204. Found: mol wt. 274.1211.

In the same manner compound **2b** (0.18 g) and anhydrous *p*-toluensulfonic acid (13 mg) was dissolved in dry acetone (10 ml), and the solution was treated as described above. The reaction product 0.16 g (92%) was recrystallized from EtOH–H_2O to give colorless needles **10a**. mp 104—106°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (OH), 2220 (C≡C), 1374, 1383 (*gem* methyl). MS *m/e*: 274 (M^+), 259 (M^+-15). NMR ($CDCl_3$) δ: 1.33 and 1.55 (6H, 2s, 2×CH_3), 2.0 (1H, broad, OH), 3.71 (2H, m, $C_5'H_2$), 4.26 (1H, sex, $J_{4',5'}$=4.0 Hz, $J_{3',4'}$=0.5 Hz, $C_4'H$), 4.75—4.87 (2H, m, $C_2'H$ and $C_3'H$), 5.01 (1H, d, $J_{1',2'}$=4.1 Hz, $C_1'H$), 7.25—7.60 (5H, m, phenyl). *Anal.* Calcd. for $C_{16}H_{18}O_4$: mol wt. 274.1204. Found: mol wt. 274.1197.

1-Phenyl-2-(5-O-acetyl-2,3-O-isopropylidene-β- and -α-D-ribofuranosyl)ethyne (9b) and (10b)——Compound **9a** (16 mg) was dissolved in a solution of anhydrous pyridine (0.2 ml) and acetic anhydride (0.2 ml) and the solution was heated on an oil bath for 2 hr at 45°. After cooling, the mixture was poured with stirring into ice-water (10 ml) and allowed to stand for about 5 hr at 0° until all the acetic anhydride was decomposed. The precipitated syrup was removed, washed successively with water, and then dissolved in AcOEt (5 ml). The solution was dried over Na_2SO_4, concentrated *in vacuo* to give 15 mg (81%) of **9b** as an amorphous solid. UV λ_{max}^{EtOH} nm (log ε): 240 (3.95), 251 (3.62). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2940, 2210 (C≡C), 1750 (C=O), 1373, 1383 (*gem* methyl). MS *m/e*: 316 (M^+), 301 (M^+-15). NMR ($CDCl_3$) δ: 1.35 and 1.53 (6H, 2s, 2×CH_3), 2.07 (3H, s, $COCH_3$), 4.32 (3H, s, $C_4'H$ and $C_5'H_2$), 4.77 (1H, broad s, $C_1'H$), 4.93 (2H, m, $C_2'H$ and $C_3'H$), 7.23—7.50 (5H, m, phenyl). *Anal.* Calcd. for $C_{18}H_{20}O_5$: mol wt. 316.1309. Found: mol wt. 316.1351.

In the same manner compound **10a** (20 mg) was dissolved in a solution of anhydrous pyridine (1 ml) and acetic anhydride (3 ml), and the solution was treated as described above. Amorphous solid 22.7 mg (88%) of **10b** was obtained. UV λ_{max}^{EtOH} nm (log ε): 241 (4.23), 251 (4.11). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2960, 2210 (C≡C), 1750 (C=O), 1373, 1383 (*gem* methyl). MS *m/e*: 316 (M^+), 301 (M^+-15). NMR ($CDCl_3$) δ: 1.34 and 1.55 (6H, 2s, 2×CH_3), 2.03 (3H, s, $COCH_3$), 4.13 (2H, m, $C_5'H_2$), 4.35 (1H, sex, $J_{4',5'}$=4.6 Hz, $J_{3',4'}$=1.8, $C_4'H$), 4.65 (1H, d.d, $J_{2',3'}$=5.4 Hz, $J_{3',4'}$=1.8 Hz, $C_3'H$), 4.81 (1H, d, $J_{1',2'}$=4.4 Hz, $C_1'H$), 4.95 (1H, t, $J_{2',3'}$=4.4 Hz, $C_2'H$), 7.17—7.55 (5H, m, aromatic). *Anal.* Calcd. for $C_{18}H_{20}O_5$: mol wt. 316.1309. Found: mol wt. 316.1297.

1-Phenyl-2-(5-O-benzoyl-2,3-O-isopropylidene-β- and -α-D-ribofuranosyl)ethyne (9c) and (10c)——Compound **9a** (0.18 g) and benzoic anhydride (0.4 g) was dissolved in anhydrous pyridine (5 ml), and the mixture was heated for 3 hr at 40°. After cooling, the solution was added into water (10 ml), and the aqueous phase was extracted with benzene (20 ml×3). The combined organic layers were washed with 3 N H_2SO_4 (20 ml×3), with saturated $NaHCO_3$ and with water, dried (Na_2SO_4), and evaporated *in vacuo* to give amorphous solid. This material was purified by chromatography on a column of silica gel with benzene to give 180 mg (75%) of **9c** as a solid. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2950, 2210 (C≡C), 1725 (C=O), 1373, 1383 (*gem* methyl). NMR ($CDCl_3$) δ: 1.37 and 1.55 (6H, 2s, 2×CH_3), 4.53 (3H, broad s, $C_4'H$ and $C_5'H_2$), 4.87 (1H, broad s, $C_1'H$), 4.97 (2H, m, $C_2'H$ and $C_3'H$), 7.10—8.13 (10H, m, phenyl). *Anal.* Calcd. for $C_{23}H_{22}O_5$: C, 73.00; H, 5.86. Found: C, 73.54; H, 5.51.

In the same manner compound **10a** (0.13 g) and benzoic anhydride (0.4 g) was dissolved in anhydrous pyridine (5 ml), and the mixture was treated as described above. The reaction product 0.15 g (85%) of **10c** was obtained. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2950, 2210 (C≡C), 1725 (C=O), 1373, 1383 (*gem* methyl). NMR ($CDCl_3$) δ: 1.39 and 1.62 (6H, 2s, 2×CH_3), 4.40—4.63 (3H, m, $C_4'H$ and $C_5'H_2$), 4.76—5.0 (2H, m, $C_2'H$ and $C_3'H$), 5.07 (1H, d, $J_{1',2'}$=4.0 Hz, $C_1'H$), 7.16—8.10 (10H, m, phenyl). *Anal.* Calcd. for $C_{23}H_{22}O_5$: C, 73.00; H, 5.86. Found: C, 73.54; H, 5.51.

1-Phenyl-2-(5-O-benzoyl-2,3-O-isopropylidene-β- and -α-D-ribofuranosyl)ethane (9d) and (10d)——Catalytic hydrogenation of **9c** (0.1 g) was carried out with Lindlar's catalyst (0.2 g) at atmospheric pressure until hydrogen uptake ceased. The catalyst was removed by filtration, and the filtrate was evaporated under diminished pressure to give 0.8 g (80%) of **9d** as a syrup. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 (C=O), 1374, 1384 (*gem* methyl). NMR ($CDCl_3$) δ: 1.33 and 1.52 (6H, 2s, 2×CH_3), 1.91 (2H, m, $\underline{CH_2}$–CH_2–Ph), 2.75 (2H, m, CH_2–$\underline{CH_2}$–Ph), 3.94 (1H, m, C_1H), 4.15—4.53 (4H, m), 4.64 (1H, d.d, J=6.6 Hz, J=4.0 Hz), 7.15 (5H, s,

phenyl), 7.30—8.15 (5H, m, benzoyl). *Anal.* Calcd. for $C_{23}H_{26}O_5$: mol wt. 382.1773. Found: mol wt. 382.1778.

On the other hand compound **10c** (0.1 g) was treated in the same manner as described above. Reaction product furnished 80 mg (80%) of **10d** as a syrup. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 (C=O), 1374, 1384 (*gem* methyl). NMR ($CDCl_3$) δ: 1.33 and 1.50 (6H, 2s, $2\times CH_3$), 1.86—2.25 (2H, m, $\underline{CH_2}$–CH_2–Ph), 2.75 (2H, t, $J=7.8$ Hz, CH_2–$\underline{CH_2}$–Ph), 3.87 (1H, sex, $J=7.8$ Hz, $J_{1,2}=3.6$ Hz, C_1H), 4.15—4.77 (5H, m), 7.15 (5H, s, phenyl), 7.35—8.02 (5H, m, benzoyl). *Anal.* Calcd. for $C_{23}H_{26}O_5$: mol wt. 382.1773. Found: mol wt. 382.1771.

4-(2,3,5-Tri-O-benzoyl-β- and -α-D-ribofuranosyl)-3-phenylpyrazole (5f) and (6c)——Into a solution of **5a** there was added an excess amount of diazomethane in ether, and the mixture was stored at room temperature for 10 days. Evaporation of the solvent gave solid, which was purified by preparative TLC using 1% MeOH–CH_2Cl_2 as the developing solvent. Elution of the major band gave 0.29 g (70%) of solid. Recrystallization from EtOH–H_2O gave 4-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-3-phenylpyrazole (**5f**) as pale yellow powder, mp 70—72°. UV λ_{max}^{EtOH} nm (log ε): 231 (4.68), 275 (3.77), 282 (3.69). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (NH), 3220, 1720 (C=O). NMR ($CDCl_3$) δ: 4.66 (2H, m, $C_5'H_2$), 4.73 (1H, m, $C_4'H$), 5.40 (1H, d, $J=6.8$ Hz, $C_1'H$), 5.77 (1H, t, $J=5.8$ Hz, $C_3'H$), 5.89 (1H, m, $C_2'H$), 7.23—8.22 (21H, m, aromatic). *Anal.* Calcd. for $C_{35}H_{28}N_2O_7$: C, 71.55; H, 4.59; N, 4.77. Found: C, 71.12; H, 4.78; N, 4.89.

4-(2,3,5-Tri-O-benzoyl-α-D-ribofuranosyl)-3-phenylpyrazole (**6c**) was synthesized from **6a** (0.17 g) in the same manner as described for the preparation of **5f**. The product was recrystallized from EtOH–H_2O to give colorless powder, mp 68—70°. UV λ_{max}^{EtOH} nm (log ε): 231 (4.54), 275 (3.75), 283 (3.69). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (NH), 3220, 1720 (C=O). NMR ($CDCl_3$) δ: 4.70 (2H, m,$C_5'H_2$), 4.80 (1H, m, $C_4'H$), 5.58 (1H, d, $J=3.2$ Hz, $C_1'H$), 5.92 (1H, t, $J=4.4$ Hz, $C_3'H$), 6.05 (1H, d.d, $J=4.4$ Hz, $J=3.2$ Hz, $C_2'H$), 7.20—8.04 (21H, m, aromatic). *Anal.* Calcd. for $C_{35}H_{28}N_2O_7$: C, 71.55; H, 4.78; N, 4.77. Found: C, 71.25; H, 5.00; N, 4.48.

4-β- and -α-D-Ribofuranosyl-3-phenylpyrazole (1a) and (2a)——Through a solution of **5f** (0.41 g) in a mixture of MeOH (5 ml) and absolute benzene (2 ml) was bubbled dry NH_3 at $-10°$ until saturation. The reaction vessel was sealed and allowed to stand at room temperature for 7 days. The mixture was evaporated to a syrup, which was purified by preparative TLC using 10% MeOH–CH_2Cl_2 as the developing solvent. Elution of the major band with AcOEt gave 0.14 (83%) of solid. Two recrystallizations from AcOEt–hexane afforded 4-β-D-ribofuranosyl-3-phenylpyrazole (**1a**) as crystals, mp 92—93°. UV λ_{max}^{EtOH} nm (log ε): 242.5 (3.77). MS *m/e*: 276 (M^+), 173 (B+30). *Anal.* Calcd. for $C_{14}H_{16}N_2O_4$: mol wt. 276.1109. Found: mol wt. 276.1092.

4-α-D-Ribofuranosyl-3-phenylpyrazole (**2a**) was synthesized from **6c** (0.19 g) in the same manner as described above for the preparation of **1a**. The product was recrystallized twice from EtOH–hexane to give **2a**, colorless powder (0.1 g, 70%), mp 103—105°. UV λ_{max}^{EtOH} nm (log ε): 242.5 (3.92). MS *m/e*: 276 (M^+), 173 (B+30). *Anal.* Calcd. for $C_{14}H_{16}N_2O_4$: mol wt. 276.1109. Found: 276.1102.

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