follow (compound, per cent in original mixture, per cent unreacted hydrocarbon in final hydrocarbon mixture): **2**, 35, 0; **3**, 38, 5; **4**, 1, 80; **5**, 13, 0; **6**, 3, 15; **7**, 3, 0.

Registry No.—*meso*-**1**, 32388-93-5; *dl*-**1**, 32388-94-6; **2**, 18265-39-9; **3**, 2417-88-1; **4**, 21293-01-6; **5**, 32388-98-0; **6**, 32388-99-1; **7**, 16356-05-1.

Reaction of Ethynyl Compounds with Lactones

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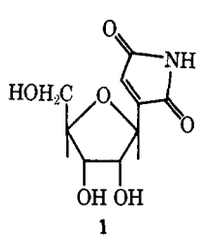
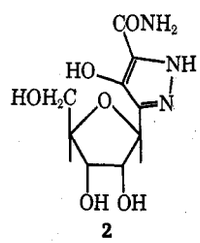
Acetylenic lactols, 3-butyl-3,3′-dihydroxy-1,5-diphenylpenta-1,4-diyne, 6-hydroxy-1-phenylheptan-3-one, 1-(2-substituted ethynyl)-β-L-gulofuranose, and 1-(2-substituted ethynyl)-α-D-ribofuranose, were synthesized *via* the lithium derivative of ethynyl compounds. The reaction mechanism involving the lactone carbonyl is similar to the reaction of aldehyde or ketone with the ethynyllithium compound.

The nucleoside antibiotics, showdomycin[1] (**1**), pyrazomycin[2] (**2**), and formycin[3,4] (**3**), are carbon-linked nucleosides. The carbon-linked nucleosides are interesting compounds with potent biological activity, and the synthetic studies on these compounds have been reported by Šorm, *et al.*,[5] and by Goodman, *et al.*[6]



1



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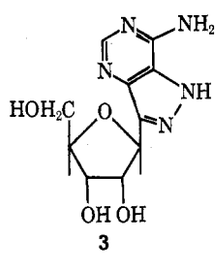
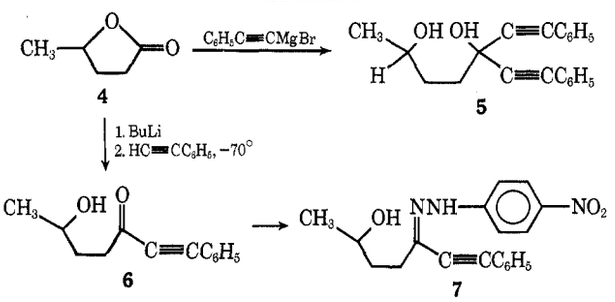


3

Tronchet and Perret[7] reported the synthesis of an analog of pyrazomycin (**2**), 3-β-D-erythrofuranosyl-1-*p*-nitrophenylpyrazole. On the other hand, Asbun and Binkley[8] synthesized 5-substituted pyrimidine nucleosides from the reaction of diisopropylidene aldehydopentose with 2,4-dibenzyloxy-5-lithiopyrimidine.

The present paper concerns attempted reaction of ethynyl compounds with lactones and sugar lactones, which was expected as a model experiment for the preparation of the carbon-linked nucleoside.[9] γ-Valerolactone (**4**) (Scheme I) was treated with the

SCHEME I



Grignard compound of phenylacetylene to obtain 3-butyl-3,3′-dihydroxy-1,5-diphenylpenta-1,4-diyne (**5**). This is similar to the reaction of γ-butyrolactone and phenylmagnesium bromide.[10] Butyllithium was used in place of the Grignard compound of γ-butyrolactone (**4**) to form 6-hydroxy-1-phenylhepta-1-yn-3-one (**6**), which was confirmed as its *p*-nitrophenylhydrazone (**7**) through examination of ir, nmr, and mass spectra.

By application of this method to sugar lactones, it has been possible to obtain acetylenic lactols. Treatment of 5-*O*-(tetrahydropyran-2-yl)-2,3-*O*-isopropylidene-D-ribonolactone (**9**) with butyllithium and phenylacetylene in ether failed to afford phenylacetylenic lactol. On the other hand, reaction of 2,3-*O*-isopropylidene-D-ribonolactone (**8**) or 2,3-*O*-isopropylidene-5-*O*-acetyl-D-ribonolactone (**10**) with lithium acetylenic compounds gave 1-(2-substituted ethynyl)-2,3-*O*-isopropylidene-D-ribofuranose (**11a,b**) in 30% yield (Scheme II). The ir spectra of these compounds (**11a,b**) show hydroxyl bands at 3380 and 3280 cm^{-1} and acetylenic band at 2180–2190 cm^{-1}, and no lactonic band at around 1780 cm^{-1}.

In case of L-gulonolactone, 2,3:5,6-di-*O*-isopropylidene derivative (**12**) was treated with various lithium acetylenic compounds to obtain 1-substituted 2,3:5,6-di-*O*-isopropylidene-L-gulofuranose (**13a–g**) in a reasonable yield (40–50%) (Scheme III). The ir spectra of these compounds (**13a–g**) showed a hydroxyl band at around 3300–3400 cm^{-1} and an acetylenic band at 2160–2180 cm^{-1}, and the mass spectra of these compounds showed molecular ion (M^+) peaks.

The nmr spectra of these compounds (**13a–g**) showed a broad singlet due to C_1-hydroxyl group at around δ

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(9) H. Ogura and H. Takahashi, unpublished work.

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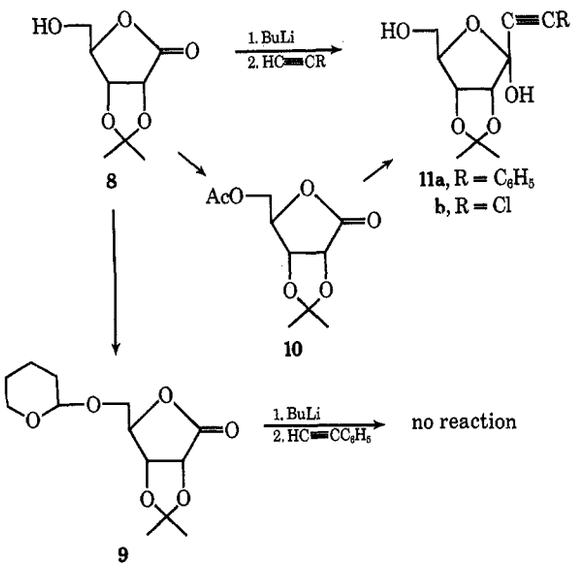
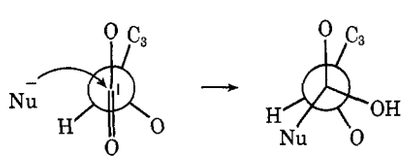
SCHEME II



3.20–3.50 ppm, and four singlets at around δ 1.20–1.55 ppm due to the isopropylidene group. Therefore, the structure of these compounds (**13a–g**) was firmly established.

Hydrolysis of both 1-(3-phenylethynyl)-2,3:5,6-di-*O*-isopropylidene-L-gulofuranose (**13a**) and 1-(3-tetrahydropyranyloxypropynyl)-2,3:5,6-di-*O*-isopropylidene-L-gulofuranose (**13e**) by treatment with 70% acetic acid[11] yielded 1-(3-phenylethynyl)-L-gulofuranose (**14a**) and 1-(3-hydroxypropynyl)-L-gulofuranose (**14b**), respectively. Further acetylation of these compounds in acetic anhydride in the presence of pyridine afforded 1,2,3,5,6-penta-*O*-acetyl derivatives (**15a,b**). This result was confirmed by ir spectra, by the absence of a hydroxyl band at around 3000–3500 cm^{-1} and the presence of a molecular peak in the mass spectra. Easy acetylation of the anomer hydroxyl group may be explained by small steric hindrance. This was confirmed by the acetylation of **13a** under the same condition to yield 1-acetoxy-1-phenylethynyl-2,3:5,6-di-*O*-isopropylidene-L-gulofuranose (**16**). For a similar reason, acetylation of a tertiary hydroxyl group occurred in steroid[12] and in pikromycin (amaromycin), a macrolide antibiotic, under the same conditions.[13]

The ethynyl group in these acetylenic lactols is assumed to have the configuration depicted in the structural formulae because the nucleophilic addition reaction would probably take place from the least hindered side of the molecule, namely opposite to the 2,3-*O*-isopropylidene ring. The reaction proceeds stereospecifically and the isomeric lactols were not detected by tlc or gas chromatography.



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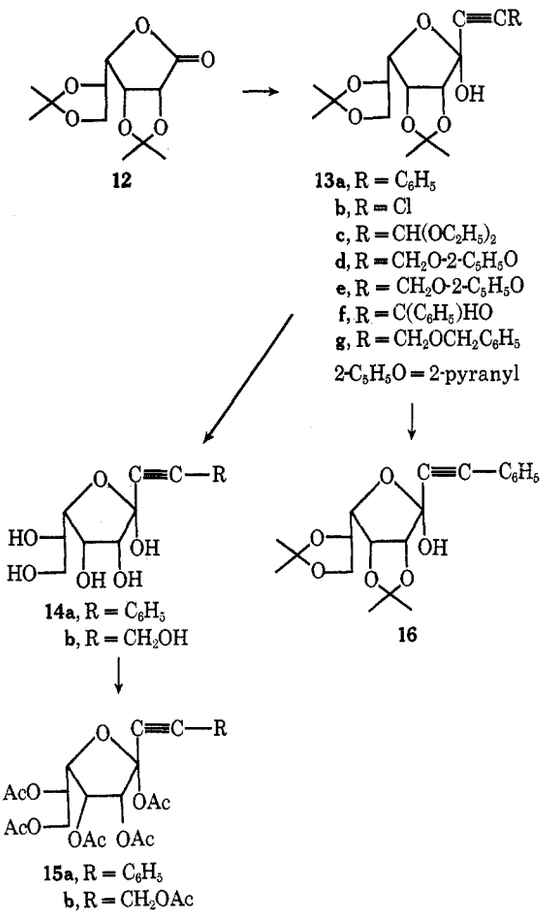
SCHEME III



Experimental Section

All melting points were obtained on a Mettler FP-1 melting point apparatus and are corrected. Gas chromatography was performed with a JGC-810 gas chromatograph and a OV-1 column was used at 180°. Optical rotations were measured in chloroform solution, in a 0.1-dm tube with a JASCO automatic polarimeter DIP-SL, unless otherwise noted. Nmr spectra were recorded in deuteriochloroform at 60 MHz with a Varian Associates C-60 spectrometer and tetramethylsilane was used as an internal reference. Mass spectra were taken with a Japan Electron Optics JMS-01S high-resolution spectrometer with a direct inlet system.

3-Butyl-3,3′-dihydroxy-1,5-diphenylpenta-1,4-diyne (5).—To a solution of isopropylmagnesium bromide prepared from magnesium (1.4 g, 0.06 mol) and isopropyl bromide (6.5 g, 0.05 mol) in ether (50 ml), 5.1 g (0.05 mol) of phenylacetylene was added dropwise, with stirring under introduction of dry nitrogen. After stirring for 0.5 hr, the solution was refluxed for 1.5 hr and γ-valerolactone (5.7 g, 0.06 mol) was added to the hot solution, which was stirred for 2 hr and allowed to stand overnight at room temperature. The reaction solution was treated with saturated NH_4Cl solution and extracted with ether. The ether solution was washed with $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed under reduced pressure to give **5** (3.0 g, 20%) as colorless prisms: mp 102.2° [recrystallized from ether–petroleum ether (bp 30–60°)]; ir λ_{max}^{KBr} 3360 (OH), 2180 (C≡C), 1600 and 1570 cm^{-1} (phenyl); nmr δ 7.24–7.64 (10 H, m, aromatic proton), 3.82–5.90 (1 H, m), and 1.26 (3 H, d, CH_3); mass spectrum *m/e* 304 (M^+).

6-Hydroxy-1-phenylhepta-1-yn-3-one (6).—To a solution of lithium (0.39 g, 0.06 mol) in anhydrous ether (50 ml), butyl bromide was added dropwise under introduction of dry nitrogen at room temperature. When the solution became turbid, the solution was cooled to −10° and the remaining butyl bromide (total amount, 3.4 g, 0.03 mol) was added during 30 min. After stirring for 1.5 hr at 0–2°, phenylacetylene (2.5 g, 0.03 mol) in ether (5 ml) was added dropwise at −70°. To the reaction solution γ-valerolactone (2.5 g, 0.03 mol) was added dropwise at −60 to −70° during 30 min. After stirring for 3 hr, the reaction

mixture was worked up as described for the preparation of **5** to give an orange oil: ir λ_{max}^{film} 3380 (OH) and 1665 cm^{-1} (unsaturated ketone). *Anal.* Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.25; H, 7.03.

p-Nitrophenylhydrazone (7) was prepared from **6** (0.5 g, 0.02 mol) and *p*-nitrophenylhydrazine (0.37 g, 0.02 mol) in glacial acetic acid (3 ml). The reaction mixture was poured into water (200 ml) and extracted with ether. The ether solution was washed with $NaHCO_3$ solution and water, dried, and ether was evaporated to leave yellow crystals. This was recrystallized from ethanol to **7** as yellow needles: mp 108.3°; ir λ_{max}^{KBr} 3290 (NH), 3380 and 1115 (OH), and 1600 cm^{-1} (phenyl); nmr δ 1.30 (3 H, d, CH_3), 1.60 (1 H, s, OH), 3.95 (1 H, m, CH), and 7.50 (5 H, m, phenyl), 7.10 and 8.15 (2 H, d, proton of hydrazine); mass pectrum *m/e* 337 (M^+). *Anal.* Calcd for $C_{19}H_{19}O_3N_3$: mol wt 337.143. Found: mol wt 337.144.

3-(2-Tetrahydropyranyloxy)-1-propyne.—This compound was prepared by the procedure of Crombie,[14] in 80% yield: bp 45–50° (3–4 mm) (reported[15] bp 63–65° (9 mm); ir λ_{max}^{film} 2100 cm^{-1} (C≡C); tlc R_f 0.78 (benzene–acetone, 4:1).

3-Phenyl-3-(2-tetrahydropyranyloxy)-1-propyne.—To a stirred solution of α-phenylpropargyl alcohol (25.4 g, 0.5 mol) in ether (20 ml), 2,3-dihydropyran (16.8 g, 0.2 mol) and a catalytic amount of *p*-toluenesulfonic acid were added under ice cooling.[16] After stirring for 2 hr at room temperature, the reaction mixture was treated by the general method as described above in the preparation of **5** to give a colorless liquid: bp 100–103° (1 mm); ir λ_{max}^{film} 2100 (C≡C) and 1600 cm^{-1} (phenyl); tlc R_f 0.68 (benzene–acetone, 4:1).

2,3-*O*-Isopropylidene-D-ribonolactone (8).[17]—To a solution of D-ribonolactone[18] (25 g, 0.13 mol) in acetone (500 ml), concentrated H_2SO_4 (10 ml) was added dropwise under ice cooling, and then the whole was stirred continuously for 5 hr at room temperature. After the reaction, ammonia gas was passed through into the reaction solution under ice cooling. The filtrate was evaporated under reduced pressure and the resulted crystalline residue was recrystallized from benzene to 26.6 g (80%) of **8** as colorless needles: mp 138.0–139.0°; $[\alpha]^{26}D$ −84.17° (*c* 0.9); ir λ_{max}^{KBr} 3420, 1080 (OH), 1780 (lactone), 1390, and 1380 cm^{-1} (*gem*-CH_3); nmr δ 1.49 and 1.42 (6, H, s, isopropylidene), 3.28 (1 H, s, OH), 3.90 (2 H, d, C_5H_2), and 4.64 (1 H, t, C_4H); mass spectrum *m/e* 188 (M^+). *Anal.* Calcd for $C_8H_{12}O_6$: C, 51.06; H, 6.43. Found: C, 50.88; H, 6.52.

5-*O*-(Tetrahydropyran-2-yl)-2,3-*O*-isopropylidene-D-ribonolactone (9).—A solution of 2,3-*O*-isopropylidene-D-ribonolactone (**8**, 3.76 g, 0.02 mol) in dimethylformamide (30 ml) was treated with 2,3-dihydropyrane (1.68 g, 0.02 mol) in the presence of *p*-toluenesulfonic acid at room temperature. After standing at room temperature for 2 days, ether was added and the reaction mixture was worked up to give **9** as colorless needles (from water) (4.0 g, 74%): mp 105–107°; $[\alpha]^{26}D$ −69.78° (*c* 0.9); mass spectrum *m/e* 272 (M^+). *Anal.* Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.28; H, 7.45.

5-*O*-Acetyl-2,3-*O*-isopropylidene-D-ribonolactone (10).—A solution of 2,3-*O*-isopropylidene-D-ribonolactone (**8**, 11.7 g, 0.06 mol) in acetic anhydride (15 ml) and pyridine (15 ml) was stirred for 30 hr at room temperature. The slightly brownish solution was concentrated, poured into ice–water (500 ml), and extracted with $CHCl_3$ (300 ml). The organic layer was washed with $NaHCO_3$ solution (100 ml) and dried over $MgSO_4$, and the solvent removed to give 13 g (90%) of **10** as colorless needles: mp 47.5°; ir λ_{max}^{KBr} 1790 (lactone), 1760 (acetate), 1390 and 1380 cm^{-1} (*gem*-CH_3); nmr δ 1.36, 1.48 (6 H, s, isopropylidene) and 2.12 (3 H, s, $OCOCH_3$); mass spectrum *m/e* 230 (M^+). *Anal.* Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.28; H, 6.18.

1-Phenylethynyl-2,3-*O*-isopropylidene-α-D-ribofuranose (11a). A.—A solution of 2,3-*O*-isopropylidene-D-ribonolactone (**8**, 1.0 g, 0.005 mol) was treated with phenylacetylene (1.02 g, 0.01 mol) in the same manner as described for **6**, and **11a** was obtained (0.5 g, 30%) as colorless needles: mp 152.3°; ir λ_{max}^{KBr} 3380 (OH), 2180 (C≡C), 1600 and 700 cm^{-1} (phenyl); nmr δ 1.45, 1.64 (6 H, s, isopropylidene), 3.75, 3.95 (2 H, dd, C_5H_2), and 7.40 (5 H, m,

TABLE I
1-(2-SUBSTITUTED ETHYNYL)-2,3:5,6-DI-*O*-ISOPROPYLIDENE-β-L-GULOFURANOSE (13)

Compd	R	Yield, %	Mp, °C	Ir, λ_{max}^{KBr}, cm^{-1}	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H	$[\alpha]D$ (temp, °C)	*m/e* Calcd	*m/e* Found	Nmr (CDCl$_3$), δ
13a	C_6H_5	50	145.0–147.0[a]	3320, 2180 1600, 695	$C_{20}H_{24}O_6$	66.65	6.75	66.62	6.72	+13.31° (21) (*c* 1.0)	360.157	360.162	1.35, 1.42, 1.50, 1.58 (12 H, s, isopropylidene), 3.20 (1 H, s, OH), 7.40 (5 H, m, phenyl)
13b	Cl	45	172.6[b]	3380, 2180 1385, 1375	$C_{14}H_{19}O_6Cl$	52.75	6.01	52.56	6.11	+39.25° (21) (*c* 1.0)	318	318	1.35, 1.40, 1.48, 1.54 (12 H, s, isopropylidene), 3.50 (1 H, s, OH)
13c	$CH(OC_2H_5)_2$	45	87.3[a]	3380, 1385 1375	$C_{19}H_{30}O_8$	59.05	7.83	58.88	7.93	−35.82° (26) (*c* 1.2)	386.194	386.188	1.34, 1.38, 1.48, 1.53 (12 H, s, isopropylidene), 3.65 (4 H, q, OCH_2CH_3), 5.32 (1 H, s, $CH(OC_2H_5)_2$)
13d	CHOO C_6H_5	40	85.0–86.0[a]	3360, 1385 1375	$C_{26}H_{34}O_8$	65.81	7.22	65.72	7.20	−10.56° (25) (*c* 1.0)	474	474	1.20, 1.32, 1.40, 1.45 (12 H, s, isopropylidene), 1.68 (6 H, m, tetrahydropyran), 7.40 (1 H, s, phenyl)
13e	CH_2OO	40	124.9[b]	3260, 1380 1365 (KBr)	$C_{20}H_{30}O_8$	60.29	7.59	60.04	7.68	+25.87° (24) (*c* 0.9)	398.194	398.194	1.35, 1.38, 1.44, 1.45 (12 H, s, isopropylidene), 1.68 (6 H, m, tetrahydropyran), 3.40 (1 H, s, OH)
13f	CHOH C_6H_5	5	87.6[a]	3400, 2180 1385, 1375 700	$C_{21}H_{26}O_7$						390.168	390.167	
13g	$CH_2OCH_2C_6H_5$	17	88.3[a]	3300, 1600 700 (KBr) 2180 ($CHCl_3$)	$C_{22}H_{28}O_7$	65.33	6.98	65.18	7.05	+18.67° (20) (*c* 1.0)	404.184	404.180	1.25, 1.27, 1.40, 1.48 (12 H, s, isopropylidene), 3.20 (1 H, s, OH), 7.35 (5 H, m, phenyl)

[a] Colorless needles. [b] Colorless fine needles.

(14) L. Crombie and A. G. Jocklin, *Chem. Ind. (London)*, 1197 (1954); L. Crombie, *J. Chem. Soc.*, 1007 (1955).
(15) R. G. Jones and M. J. Mann, *J. Amer. Chem. Soc.*, **75**, 4048 (1953).
(16) D. N. Robertson, *J. Org. Chem.*, **25**, 931 (1960).
(17) L. Hough, J. K. N. Jones, and D. L. Mitchell, *Can. J. Chem.*, **36**, 1720 (1958).
(18) Available from SIGMA Chemical Co., St. Louis, Mo.

phenyl). *Anal.* Calcd for $C_{16}H_{18}O_5$: C, 66.20; H, 6.25. Found: C, 66.36; H, 6.25.

B.—A solution of 5-*O*-acetyl derivative (**10**, 2.3 g, 0.01 mol) was treated with phenylacetylene (1.0 g, 0.01 mol) in the same manner as described for A; **11a** (0.5 g, 20%), mp 153.0°, was obtained. This was identical in all respects with a sample prepared by A.

1-(2-Chloroethynyl)-2,3-*O*-isopropylidene-α-D-ribofuranose (11b).—This compound was prepared by the procedure similar to that described for the preparation of **13b**. **11b** was obtained (0.7 g, 30%) as colorless needles: mp 130.5°; $[\alpha]^{27}D$ −71.45° (*c* 0.9); ir λ_{max}^{KBr} 3380 (OH), 2190 (C≡C), 1390 and 1380 cm^{-1} (gem-CH_3); nmr δ 1.38, 1.60 (6 H, s, isopropylidene), and 3.67, 3.84 (2 H, dd, C_5H_2); mass spectrum *m/e* 248 (M^+). *Anal.* Calcd for $C_{10}H_{13}O_5Cl$: C, 48.30; H, 5.27. Found: C, 48.24; H, 5.31.

2,3:5,6-Di-*O*-isopropylidene-L-gulonolactone (12).—To a suspension of L-gulonolactone[19] (20 g, 0.11 mol) in acetone (400 ml), concentrated H_2SO_4 (8 ml) was added slowly and the mixture was stirred at room temperature for 7 hr. After reaction, ammonia gas was passed through the reaction solution under ice cooling and the reaction mixture was treated by the similar method as described for the preparation of **6**. **12** (12 g, 55%) was obtained as colorless needles: mp 153–154°; $[\alpha]^{24}D$ +91.48° (*c* 1.0); nmr δ 1.40, 1.49 (12 H, s, isopropylidene); mass spectrum *m/e* 258 (M^+). *Anal.* Calcd for $C_{12}H_{18}O_6$: C, 55.81; H, 7.03. Found: C, 55.66; H, 7.05.

1-Phenylethynyl-2,3:5,6-di-*O*-isopropylidene-β-L-gulofuranose (13a). General Procedure for 13c–g (Table I).—By a similar procedure to that described for the preparation of **6**, a solution of phenylethynyllithium (prepared from 1.2 g, 0.01 mol of phenylacetylene) was obtained. To this reaction solution 2,3:5,6-di-*O*-isopropylidene-L-gulonolactone (2.58 g, 0.01 mol) in tetrahydrofuran (10 ml) was added dropwise at −70° during 30 min, stirring was continued for 3 hr at the same temperature, and the mixture was left overnight at room temperature. The brownish solution was treated as mentioned above for the preparation of **5** to give 1.8 g (50%) of **13a** as colorless needles, mp 145–147°. Recrystallization from ether–petroleum ether gave a product of mp 151.1°: uv λ_{max}^{EtOH} 240.0 nm (log ε 4.2), 251.0 (3.5), and 282.5 (3.3).

1-Chloroethynyl-2,3:5,6-di-*O*-isopropylidene-β-L-gulofuranose (13b).—To a mixture of lithium (1.3 g, 0.02 mol) in anhydrous ether (50 ml), butyl bromide (3 g, 0.02 mol) in ether (5 ml) was added under a current of dry nitrogen and under stirring at −10 to 0° during 30 min and the reaction mixture was stirred for 1.5 hr at −5 to 0°. To this reaction solution, *cis*-1,2-dichloroethylene (1 g, 0.01 mol) in ether was added dropwise at −2 to 0° during 20 min. After stirring for 1.5 hr at 5–15°, the solution wash chilled to −60°, 2,3:5,6-di-*O*-isopropylidene-L-gulonolactone (2.58 g, 0.01 mol) in tetrahydrofuran (10 ml) was added to the cooled reaction at −60° during 30 min, and stirring was continued for 3 hr. This reaction solution was treated as above in the preparation of **6** and gave 1.4 g (45%) of **13b**.

1,2,3,5,6-Penta-*O*-acetyl-1-phenylethynyl-β-L-gulofuranose (15a).—A solution of **13a** (1 g, 0.003 mol) in 70% acetic acid (10 ml) was warmed at 50° for 2.5 hr. The solvent was completely removed by distillation under a reduced pressure. Remaining liquid was dissolved in ether which was washed with a minimum amount of $NaHCO_3$ solution, and then dried and evaporated. There was obtained 1-phenylethynyl-L-gulofuranose (**14a**) as a white powder: $[\alpha]^{22}D$ +19.53° (*c* 1.1, MeOH); ir λ_{max}^{film} 3360 (OH), 2180 (C≡C), 1600 and 695 cm^{-1} (phenyl).

This compound (**14a**), without further purification, was acetylated with acetic anhydride (5 ml) in the presence of pyridine (5 ml). After the reaction solution was stirred for 24 hr at room temperature, this was worked up to obtain **15a** as a brownish liquid. Thin layer chromatography showed a spot at R_f 0.58 in benzene–acetone (3:2): $[\alpha]^{26}D$ +5.45° (*c* 1.0); ir λ_{max}^{film} 2220 (C≡C), 1750 (acetyl), and 762 cm^{-1} (phenyl); mass spectrum *m/e* 490 (M^+). *Anal.* Calcd for $C_{24}H_{26}O_{11}$: mol wt, 490.148. Found: mol wt, 490.147.

1,2,3,5,6-Penta-*O*-acetyl-1-(3-acetyloxypropyn-1-yl)-β-L-gulofuranose (15b).—1-(3-Tetrahydropyranyloxypropynyl)-2,3:5,6-di-*O*-isopropylidene-L-gulofuranose (**13e**, 1 g, 3 mmol) was hydrolyzed by the same procedure as that of **15a** to obtain 1-(3-hydroxypropyn-1-yl)-L-gulofuranose (**14b**) as a brownish liquid: $[\alpha]^{22}D$ +47.11° (*c* 0.8, MeOH); ir λ_{max}^{film} 3280 (OH) and 2160 cm^{-1} (C≡C).

This compound (**14b**) was acetylated in the same way as described for the preparation of **15a** to yield **15b** as a pale brown liquid (0.6 g, 39%): $[\alpha]^{25}D$ +13.87° (*c* 1.0, MeOH); ir λ_{max}^{film} 2250 (C≡C) and 1750 cm^{-1} (acetyl); mass spectrum *m/e* 486 (M^+).

1-*O*-Acetyl-1-(2-phenylethynyl)-2,3:5,6-di-*O*-isopropylidene-β-L-gulofuranose (16).—1-(2-Phenylethynyl)-2,3:5,6-di-*O*-isopropylidene-β-L-gulofuranose (**13a**, 0.13 g, 0.3 mmol) was acetylated in the same way as described for the preparation of **15a** to yield **16** as colorless needles (0.08 g, 54%): mp 112.5°; $[\alpha]^{22}D$ +32.83° (*c* 0.5); ir λ_{max}^{KBr} 2190 (C≡C), 1745 (acetyl), 1385 and 1375 (gem-CH_3), 760 and 693 cm^{-1} (phenyl); uv λ_{max}^{EtOH} 240.2 nm (log ε 4.32) and 250.8 (4.25); mass spectrum *m/e* 402 (M^+). *Anal.* Calcd for $C_{22}H_{26}O_7$: C, 65.66; H, 6.51; mol wt, 402.168. Found: C, 65.59; H, 6.55; mol wt, 402.168.

Registry No.—**5**, 32257-12-8; **6**, 32257-13-9; **7**, 32257-14-0; **8**, 30725-00-9; **9**, 31858-77-2; **10**, 32257-17-3; **11a**, 32257-18-4; **11b**, 32257-19-5; **12**, 7306-64-1; **13a**, 32257-21-9; **13b**, 32257-22-0; **13c**, 32257-23-1; **13d**, 32257-24-2; **13e**, 32257-25-3; **13f**, 32257-26-4; **13g**, 32257-27-5; **14a**, 32257-28-6; **14b**, 32257-29-7; **15a**, 32304-30-6; **15b**, 32304-31-7; **16**, 32257-30-0; 3-phenyl-3-(2-tetrahydropyranyloxy)-1-propyne, 32257-31-1.

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