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SYNTHESIS OF 3-*O*-SUBSTITUTED D-MANNOSES

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ABSTRACT

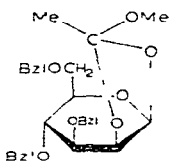
1,2,4,6-Tetra-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranose (**7**) was obtained in good yield from 3,4,6-tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose (**1**) by acetolysis. Hydrogenolysis of **7** afforded 1,2,4,6-tetra-*O*-acetyl-α-D-mannopyranose which is a versatile intermediate for the preparation of other 3-*O*-substituted D-mannoses, such as 3-*O*-methyl-D-mannose and 3-*O*-α-D-mannopyranosyl-D-mannose. 3,4-Di-*O*-methyl-D-mannose was readily prepared from 1,2,6-tri-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranose, which was also obtained from **1** by controlled acetolysis.

INTRODUCTION

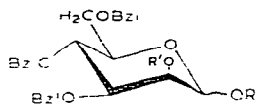
D-Mannose is commonly found in glycoproteins, glycolipids, and many polysaccharides. The methyl ethers of D-mannose are important reference samples in structural elucidation in the polysaccharide field[1]. Mono-, di-, and tri-methyl ethers of D-mannose have been synthesized by partial methylation[2] of methyl α-D-mannopyranoside which produced a mixture of methyl ethers that was fractionated by extraction with chloroform, followed by chromatography on hydrocellulose. 3-*O*-Methyl-D-mannose[3] and 3,4,di-*O*-methyl-D-mannose[4] have been synthesized[5] from methyl 4,6-*O*-ethylidene-α-D-mannopyranoside and 1,6-anhydro-β-D-mannopyranose, respectively, by selective esterification of their equatorial hydroxyl groups. The synthesis[5] of 3-*O*-methyl-D-mannose was quite laborious. It involved the selective blocking of the 3-OH of methyl 4,6-*O*-ethylidene-α-D-mannopyranoside with a nitrate function. This was followed by *p*-toluenesulfonylation, reductive denitration, methylation, treatment with sodium amalgam, and acid hydrolysis. 3-*O*-(α-D-Mannopyranosyl)-D-mannose has been obtained by acid hydrolysis of D-mannane phosphate[6] and acid-catalyzed reversion of D-mannose[7]. In this paper, we report a convenient synthesis of **5** and **7** which can be used to prepare 3,4-di-O-methyl-D-mannose and 3-*O*-substituted-D-mannoses, respectively.

RESULTS AND DISCUSSION

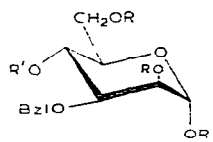
Acid hydrolysis of 3,4,6-tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose[8] (**1**) with aqueous acetic acid, followed by acetylation gave 1,2-di-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-mannose (**3**) which was further transformed into the 2-*O*-acetyl derivative **4**. Acetolysis[9] of the orthoester **1** with 2% sulfuric acid at 0–5° for 2 h gave crystalline 1,2,6-tri-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranose (**5**) in good yield. This is not surprising in view of the lability of benzyl ethers[10] toward acetolyzing reagents. It is noteworthy that acetolysis of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose with 0.22% sulfuric acid for 3 min gave 1,6-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-D-glucopyranose[11], whereas 2% sulfuric acid for 18 h gave α-D-glucopyranose pentaacetate[12]. The n.m.r. spectrum of **5** shows three acetoxy



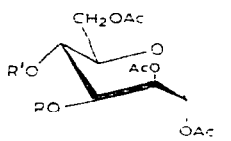
1



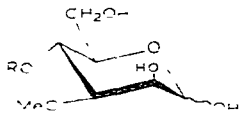
2 R = R′ = H
3 R = R′ = Ac
4 R = H, R′ = Ac



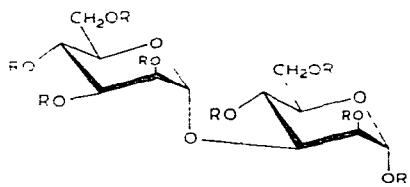
5 R = Ac, R′ = Bzl
6 R = H, R′ = Bzl
7 R = R′ = Ac
8 R = R′ = H



9 R = R′ = H
10 R = R′ = Me
11 R = H, R′ = Ac
12 R = Me, R′ = Ac



13 R = Me
14 R = H



15 R = Ac
16 R = H

signals corresponding to nine protons. In addition to the aromatic signals, only H-1 (τ 3.90) and H-2 (τ 4.63) absorb in the lowerfield region. The α-D configuration is indicated by the chemical shift[13] of H-1. This was confirmed by the sequence of *O*-deacetylation and *O*-acetylation of **5** to give a mixture of α and β anomers. The chemical shift of H-1 for the β anomer is at τ 4.27.

When the acetolysis of **1** was continued for 16 h at ambient temperature it gave 1,2,4,6-tetra-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranose (**7**) as a major product. The signal for H-3 appeared at τ 6.16 as a quartet, whereas that for H-4 appeared at τ 4.83 as a triplet. This assignment was confirmed by spin decoupling[14]. Thus, the

ease of cleavage of the benzyl ethers by acetolysis appears to be in the order of 6-OBzl > 4-OBzl > 3-OBzl.

The 3-*O*-benzyl ether **7** is a precursor of 1,2,4,6-tetra-*O*-acetyl-α-D-mannopyranose (**11**), which is a versatile intermediate for the preparation of 3-*O*-glycosyl-D-mannoses or other 3-*O*-substituted derivatives. Thus, treatment of **11** with diazomethane in the presence of a catalytic amount of boron trifluoride etherate[15] gave the 3-*O*-methyl derivative **12** in nearly quantitative yield. Saponification (Zemplén) of **12** afforded 3-*O*-methyl-D-mannose[3] (**14**) which had previously been obtained in a laborious way[5]. Condensation of **11** with 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide in acetonitrile in the presence of mercury salts[16] gave, upon deblocking, 3-*O*-α-D-mannopyranosyl-D-mannose (**16**) which had been obtained by acid-catalyzed reversion of D-mannose[7]. 1,2,4,6-Tetra-*O*-acetyl-β-D-glucopyranose[17] has also been used as an intermediate for the preparation of 3-*O*-glycosyl-D-glucoses.

Hydrogenolysis of 1,2,6-tri-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranose (**5**) gave the diol **9** which was converted into 3,4-di-*O*-methyl-D-mannose[4,5] (**13**) in good yield.

EXPERIMENTAL

General methods. — Melting points were taken in a Thomas–Hoover Unimelt apparatus, and are uncorrected. Optical rotations were measured with a Zeiss polarimeter. Thin-layer chromatography (t.l.c.) was performed on Silica gel G (Analtech) plates, and the spots were detected by a ceric sulfate (1%)–sulfuric acid (10%) spray. Column chromatography was conducted on Silica gel 60 (70–230 mesh ASTM). N.m.r. spectra were recorded for solutions in chloroform-*d* (unless stated otherwise) at 60 or 100 MHz, with tetramethylsilane as the internal standard. Conventional processing consisted in drying organic solutions with anhydrous sodium sulfate, filtration, and evaporation of the filtrate under diminished pressure.

3,4,6-Tri-O-benzyl-1,2-O-(1-methoxyethylidene)-β-D-mannopyranose (**1**). — 3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose, m.p. 98–101°, $[\alpha]_D^{27}$ −17.2±0.3° (*c* 1.53, chloroform) (*Anal.* Calc. for $C_{15}H_{22}O_{10}$: C, 49.72; H, 6.12. Found: C, 49.70; H, 6.14), {lit.[18] m.p. 111–113°, $[\alpha]_D$ −23.5° (chloroform)} was prepared by the method of Mazurek and Perlin[18]. The orthoester triacetate (80 g) was *O*-deacetylated with methanolic ammonia to give a homogeneous syrup (53 g) upon evaporation. The material (53 g) in dry *N*,*N*-dimethylformamide (400 ml) containing sodium hydride (30 g) was benzylated with benzyl bromide (96 ml) with stirring for 24 h at room temperature. Excess sodium hydride was eliminated by addition of methanol, and the mixture was partitioned between chloroform and water. The organic layer was washed with water five times, dried, and concentrated to a crystalline mass. Recrystallization from ethyl ether–petroleum ether afforded **1** (70 g), m.p. 77–79°, $[\alpha]_D^{27}$ +35.6±0.3° (*c* 1.75, chloroform); lit.[8] m.p. 76–78°, $[\alpha]_D^{23.5}$ +12.1° (*c* 1.65, chloroform); lit.[19] m.p. 75–77°, $[\alpha]_D$ +29° (chloroform). The OMe-*exo*-diastereoisomer was formed as a major product (88%); n.m.r. (chloroform-*d*): τ 4.70 (d, $J_{1,2}$ 3.0 Hz, H-1), 6.75 (s,

OMe), 8.28 (s, 88% OMe-*exo*-diastereoisomer, CMe), 8.52 (s, 12% OMe-*endo*-diastereoisomer, CMe).

Anal. Calc. for $C_{30}H_{34}O_7$: C, 71.13; H, 6.77. Found: C, 71.36; H, 6.80.

1,2-Di-O-acetyl-3,4,6-tri-O-benzyl-D-mannose (**3**). — A solution of **1** (12 g) in glacial acetic acid (140 ml) and water (90 ml) was heated on a steam bath for 4 h, and then concentrated to dryness. The syrup was dissolved in dichloromethane and washed with aqueous sodium hydrogencarbonate and water. The dried solution was evaporated *in vacuo* to a syrup which was acetylated with acetic anhydride–pyridine. The reaction mixture was processed in the normal manner to yield **3** (12 g, 95%) as a mixture of α- and β-anomers in the ratio of 7:3, $[\alpha]_D^{27}$ +29.9±0.7° (*c* 1.50, chloroform); n.m.r. (chloroform-*d*): τ 2.74 and 2.83 (15 aromatic), 3.90 (d, $J_{1,2}$ 2.0 Hz, H-1α), 4.29 (d, $J_{1,2}$ 1.5 Hz, H-1β), 4.43 (q,H-2β), 4.65 (t, H-2α), and 7.85, 7.90, and 8.0 (2 OAc).

Anal. Calc. for $C_{31}H_{34}O_8$: C, 69.65; H, 6.41. Found: C, 69.43; H, 6.45.

A portion of **3** was *O*-deacetylated with a catalytic amount of sodium methoxide in methanol to give crystalline 3,4,6-tri-*O*-benzyl-D-mannose (**2**), m.p. 96–98° (from ethyl ether–petroleum ether), $[\alpha]_D^{27}$ +25.9±0.3° (c 1.55, chloroform); lit.[8] m.p. 98–99°, $[\alpha]_D^{24}$ +22.7° (*c* 1.92, chloroform).

Anal. Calc. for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 72.26; H, 6.90.

1,2,6-Tri-O-acetyl-3,4-di-O-benzyl-α-D-mannopyranose (**5**). — Conc. sulfuric acid (1.2 ml) was added dropwise with stirring to an ice-cold solution of **1** (5.0 g) in 1:1 (v/v) acetic acid–acetic anhydride (60 ml). The stirring was continued for 2 h at 0–5°. Aq. sodium acetate and ice were added to the reaction mixture, and the products were extracted with chloroform. The organic layer was washed with aq. sodium hydrogencarbonate and water, dried, and concentrated to a syrup (5.4 g) which contained, as shown by t.l.c. (1:9, v/v, ethyl acetate–chloroform), **5** (R_F 0.44, a major product) and minor amounts of 1,2,4,6-tetra-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranose (**7**) (R_F 0.31), the unreacted **1**, and some slower-moving components. Benzyl acetate was also present in the crude syrup (5.4 g) as indicated by n.m.r. (chloroform-*d*): τ 2.70 (aromatic protons), 4.90 (s, OCH_2), and 7.92 (s, Ac). Crystallization of the crude syrup from ethyl ether–petroleum ether gave **5**, m.p. 80–81.5°, $[\alpha]_D^{27}$ +32.5±0.6° (*c* 1.63, chloroform); n.m.r. (chloroform-*d*): τ 2.63 (10 aromatic protons), 3.90 (d, $J_{1,2}$ 2.0 Hz, H-1), 4.63 (q, $J_{2,3}$ 2.5 Hz, H-2), and 7.83, 7.91, and 7.94 (3 OAc). Additional amount of **5** (total yield 3.4 g, 71%) was obtained by column chromatography on Silica gel with 1:19 (v/v) ethyl acetate–chloroform as eluent.

Anal. Calc. for $C_{26}H_{30}O_9$: C, 64.18; H, 6.22. Found: C, 63.96; H, 6.27.

1,2,4,6-Tetra-O-acetyl-3-O-benzyl-α-D-mannopyranose (**7**). — Conc. sulfuric acid (3 ml) was added dropwise with stirring to an ice-cold solution of **1** (15 g) in 1:1 (v/v) acetic acid–acetic anhydride (150 ml). The stirring was continued for 2 h at 0–5°. T.l.c. indicated the formation of **5** as a major product. The reaction mixture was stirred for 16 h at room temperature and processed in the usual manner to give a crude syrup. This was chromatographed on a column of Silica gel with chloroform followed by 1:9 (v/v) ethyl acetate–chloroform as eluents. Fractions containing **7**

were pooled and concentrated to a syrup which was rechromatographed on Silica gel with the same eluents. The major product was identified by n.m.r. as **7** (7.99 g, 59%), $[\alpha]_D^{27}$ +0.28±0.6° (*c* 1.79, chloroform); n.m.r. (chloroform-*d*): τ 2.77 (5 aromatic), 3.95 (d, $J_{1,2}$ 2.0 Hz,H-1), 4.67 (q, $J_{2,3}$ 3.5 Hz, H-2), 4.83 (t, $J_{3,4}$ $J_{4,5}$ 9.0 Hz, H-4), 6.16 (q, H-3), 6.09 (m, H-5): 5.87 (q, $J_{5,6}$ 5.5 Hz, $J_{6,6'}$ 12.0 Hz, H-6), 5.96 (q, $J_{5,6'}$ 2.8 Hz, H-6'), and 7.87, 7.91, 7.94, and 7.99 (4 OAc).

Anal. Calc. for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.19; H, 6.04.

The slow-moving component was isolated as a crystalline material and shown by m.p., R_F and n.m.r. to be α-D-mannose pentaacetate (0.83 g, 7%).

2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranose (**4**). — A solution of **3** (1.0 g) in anhydrous ether (25 ml) was saturated with hydrogen chloride and kept overnight at room temperature. The solution was concentrated *in vacuo* and partitioned between dichloromethane and cold water. The organic layer was washed with cold water a few times, dried, and evaporated to give 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl chloride (821 mg, 86%); n.m.r. (chloroform-*d*): τ 2.80 and 2.85 (15 aromatic), 4.0 (d, $J_{1,2}$ 2.0 Hz, H-1), 4.58 (t, $J_{2,3}$ 2.0 Hz, H-2), and 7.96 (OAc). Treatment with aq. acetone in the presence of silver carbonate afforded **4**, $[\alpha]_D^{27}$ +10.2±0.8° (*c* 1.32, chloroform).

Anal. Cal. for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55. Found: C, 70.76; H, 6.70.

1,2,4,6-Tetra-O-acetyl-α-D-mannopyranose (**11**). — A solution of **7** (3.0 g) in ethyl acetate (30 ml) containing 5% palladium-on-charcoal (1.0 g) was hydrogenated for 3 h. The catalyst was filtered off and washed with ethyl acetate. The combined filtrates were concentrated *in vacuo* to give **11** (2.11 g, 87 %), $[\alpha]_D^{27}$ +19.5±0.7° (*c* 1.51, chloroform); n.m.r. (chloroform-*d*): τ 3.95 (d, $J_{1,2}$ 2.0 Hz, H-1), 6.87 (d, OH), and 7.83, 7.87, 7.92, and 7.95 (4 OAc).

Anal. Calc. for $C_{14}H_{20}O_{10}$: C, 48.28; H, 6.79. Found: C, 48.37; H, 6.62.

3-O-α-D-Mannopyranosyl-D-mannose (**16**). — A solution of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (590 mg) in dry dichloromethane (2 ml) was added to a solution of **11** (500 mg) in dry acetonitrile (4 ml) containing mercuric cyanide (172 mg) and mercuric bromide (248 mg). The reaction mixture was stirred for 1 h at room temperature and concentrated to dryness. The residue was extracted with dichloromethane, and the combined extracts were filtered and washed successively with M potassium bromide and water. The dried solution was evaporated *in vacuo* to a syrup (1.03 g) which was chromatographed on a column of Silica gel with 1:3 (v/v) ethyl acetate–chloroform as eluent. 1,2,4,6-Tetra-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-mannopyranose (**15**) was isolated as a foam (490 mg, 50%), $[\alpha]_D^{27}$ +35.9±0.7° (*c* 1.52, chloroform); n.m.r. (chloroform-*d*): τ 3.95 (d, $J_{1,2}$ 2.0 Hz, H-1), 5.0 (s, H-1') and 7.78, 7.87, 7.93, 7.95, and 8.02 (8 OAc).

Anal. Calc. for $C_{28}H_{38}O_{19}$: C, 49.56; H, 5.64. Found: C, 49.08; H, 5.75.

A solution of **15** (372 mg) in dry methanol (10 ml) was *O*-deacetylated with sodium methoxide (15 mg). The solution was de-ionized with an acid resin, filtered, and concentrated to give a syrup (282 mg). The material was purified by chromatography on a Silica gel column (6:4:1, v/v, chloroform–methanol–water) to give **16**

(155 mg, 83%), $[\alpha]_D^{27}$ +40° (*c* 1.55, methanol); R_F 0.2; lit.[6,7] $[\alpha]_D$ +50° (*c* 2.86, methanol).

3-O-Methyl-D-mannose (**14**). — Boron trifluoride etherate (0.02 ml) was added to a solution of **11** (0.5 g) in dichloromethane (5 ml) at 0°. An excess of diazomethane in dichloromethane was added to the stirred mixture. The reaction appeared to be complete in 10 min (t.l.c., 1:1, v/v, ethyl acetate–chloroform). After 1 h, the white solid (polymethylene) was removed by filtration, and the filtrate was washed succesively with aq. sodium hydrogencarbonate and water. The dried solution was concentrated to give 1,2,4,6-tetra-*O*-acetyl-3-*O*-methyl-α-D-mannopyranose (**12**) (0.52 g, quantitative yield), $[\alpha]_D^{27}$ +25.9±0.6° (*c* 1.66, chloroform); n.m.r. (chloroform-*d*): τ 3.98 (d, $J_{1,2}$ 2.0 Hz, H-1), 4.73 (q, $J_{2,3}$ 3.0 Hz, H-2), 5.0 (t, $J_{4,3} = J_{4,5}$ 9.0 Hz, H-4), 6.39 (q, H-3), 6.67 (OMe), 7.87, 7.93, and 7.96 (4 OAc).

Anal. Calc. for $C_{15}H_{22}O_{10}$: C, 49.72; H, 6.12. Found: C, 49.62; H, 6.03.

Compound **12** (100 mg) was saponified with sodium methoxide in methanol to give **14** (40 mg), $[\alpha]_D^{27}$ +8.5±1.1° (*c* 0.95, methanol); R_F (10:3, v/v, chloroform–methanol) 0.27; lit.[3] $[\alpha]_D$ +15° (*c* 1.2, 50% ethanol); lit.[5] $[\alpha]_D^{25}$ +2.7° (*c* 2.50, water).

3-O-Benzyl-D-mannose (**8**). — Compound **7** (300 mg) was *O*-deacetylated with sodium methoxide in methanol to give **8** (165 mg). The purified material had R_F (10:3, v/v, chloroform–methanol) 0.4; $[\alpha]_D^{27}$ +2.8±1.0° (*c* 1.03, methanol).

Anal. Calc. for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.67; H, 6.76.

1,2,6,-Tri-O-acetyl-D-mannopyranose (**9**). — A solution of **5** (as a mixture of α- and β-anomers, 414 mg) in ethyl acetate (10 ml) containg 10% palladium-on-charcoal (200 mg) was hydrogenated for 3 h. The mixture was filtered and the filtrate concentrated *in vacuo* to give **9** (16.5% of β anomer) (216 mg, 91%), $[\alpha]_D^{27}$ +4.8±1.0° (*c* 0.92, chloroform); n.m.r. (chloroform-*d*): τ 4.0 (d, $J_{1,2}$ 2.0 Hz, H-1α), 4.25 (H-1β, 16.5%), 4.65 (H-2β), 4.92 (q, $J_{2,3}$ 3.0 Hz, H-2α), 7.87, and 7.90 (3 OAc).

Anal. Calc. for $C_{12}H_{18}O_9$: C, 47.06; H, 5.92. Found: C, 47.12; H, 6.07.

3,4-Di-O-methyl-D-mannose (**13**). — Boron trifluoride etherate (2–3 drops) was added to a solution of **9** (a mixture of α- and β-anomers, 200 mg) in dichloromethane (5 ml) at 0°. An excess of diazomethane in dichloromethane was added to the reaction mixture with stirring. After 4 h, more dichloromethane was added and the filtered solution was washed successively with aq. sodium hydrogencarbonate and water. The dried solution was concentrated to a syrup (201 mg, 91%); n.m.r. (chloroform-*d*): τ 3.95 (d, $J_{1,2}$ 2.0 Hz, H-1α), 4.17 (d, $J_{1,2}$ 1.0 Hz, H-1β), 4.48 (H-2β), 4.73 (q, $J_{2,3}$ 3.0 Hz, H-2α), 6.43 and 6.54 (α-OMe), 6.49 and 6.59 (β-OMe), 7.82, 7.85, and 7.89 (α-OAc). The α-anomer **10** was isolated by column chromatography (1:3, v/v, ethyl acetate–chloroform), $[\alpha]_D^{27}$ +48.3±0.7° (*c* 1.39, chloroform).

Anal. Calc. for $C_{14}H_{22}O_9$: C, 50.30; H, 6.63. Found: C, 49.92; H, 6.72.

Compound **10** was saponified with sodium methoxide in methanol to give 3,4-di-*O*-methyl-D-mannose, m.p. 94–97° (ethyl acetate), $[\alpha]_D^{27}$ +20.5° (*c* 0.633, methanol); R_F (10:3, v/v, chloroform-methanol, 0.5); m.s.: *m/e* 191 ($M^+ - 17$), 173 ($M^+ - 17 - H_2O$), 159 ($M^+ - 17 - MeOH$).

3,4-Di-O-benzyl-D-mannose (**6**). — Compound **4** (330 mg) was *O*-deacetylated

in the usual manner to give **5**, Crystallization from ethyl acetate afforded pure material (190 mg), m.p. 129–130°, $[\alpha]_D^{27}$ $+0.3\pm0.6°$ (*c* 1.54, methanol).

Anal. Calc. for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71. Found: C, 66.90, H. 6.82.

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