# CHEMISTRY

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## Abstract

## Full Text

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# SYNTHESIS OF NEW C-GLYCOSIDES

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Organometallic synthesis has opened broad possibilities for obtaining substituted carbohydrates in which the first carbon atom is linked by a direct carbon —carbon bond to some aglycone (C-glycosides). By this route, starting from the corresponding Grignard reagent and acetohalogeno sugar, we have obtained a series of new C-glycosides: 1-(2′, 3′, 4′-tri-O-acetyl-*L*-rhamnopyranosyl)butane, 1-(2′, 3′, 4′, 6′-tetra-O-acetyl-*D*-mannopyranosyl)butane, *m*-(2, 3, 4, 6-tetra-O-acetyl-*D*-mannopyranosyl)toluene, *m*-(2, 3, 4, 6-tetra-O-acetyl-*D*-glucopyranosyl)toluene. Using the method of deacetylation with hydrochloric acid proposed by us earlier ($^1$), we synthesized 1-*L*-rhamnopyranosylbutane, *m*-*D*-mannopyranosyltoluene, and *m*-*D*-glucopyranosyltoluene.

A number of new C-glycosides were obtained by carrying out substitution reactions in the aglycone. Starting from the previously synthesized ($^2$) *p*-(2, 3, 4, 6-tetra-O-acetyl-*D*-glucopyranosyl)anisole, its mercurated product was obtained. By iodination of the corresponding C-glycosides obtained earlier ($^3$), 4-(2′, 3′, 4′-tri-O-acetyl-*L*-arabinopyranosyl)-2,6-diiodoanisole and 4-(2′, 3′, 4′-tri-O-acetyl-*L*-arabinopyranosyl)-2,6-diiodophenol were synthesized.

The individual character of the compounds obtained was established by means of thin-layer chromatography.

## Experimental Part

**1-(2′, 3′, 4′-tri-O-acetyl-*L*-rhamnopyranosyl)butane.** To a solution of butylmagnesium bromide, obtained from 5.82 g (0.24 mole) of magnesium and 32.88 g (0.24 mole) of *n*-butyl bromide in 100 ml of absolute ether, a solution of 7.5 g (0.024 mole) of acetochlororhamnose in 100 ml of absolute ether is added dropwise. The reaction mixture is stirred for 1 hour at room temperature and for 4 hours with heating on a water bath. After decomposition of the reaction product with water, the aqueous layer is separated and evaporated to dryness; the dry residue is acetylated by heating for 25 min with 70 ml of acetic anhydride containing 0.1–0.2 g of magnesium perchlorate ($^4$). The acetylated product is extracted with chloroform; the extracts are neutralized with a saturated sodium bicarbonate solution, washed with water, clarified with activated charcoal, and dried over calcium chloride. The chloroform is distilled off; the residue is dissolved in ether, and the ethereal solution is clarified with charcoal and dried over calcium chloride. After evaporation of the ether, 1.7 g (27% of theory) of a colorless glassy product is obtained, from which, after storage in a vacuum desiccator over phosphorus pentoxide and repeated recrystallizations, a crystalline substance with m.p. 58–59° is isolated. The product is soluble in common organic solvents. The substance is described for the first time.

Found, %: C 57.91; H 8.16
$C_{16}H_{28}O_7$. Calculated, %: C 58.10; H 7.93

The structure of the compound is described by the formula

[[structural formula]]

**1-*L*-rhamnopyranosylbutane.** A solution of 1 g of the triacetate described above in 10 ml of absolute methanol is heated with 3 drops of hydrochloric acid for 2 hours. After neutralization of the mixture, the solvent is evaporated; the residue is dissolved in ethyl acetate, the extracts are clarified with charcoal and dried over sodium sulfate. After evaporation of the solvent and storage in a vacuum desiccator over $P_2O_5$, 0.48 g (78% of theory) of a colorless glassy substance is obtained. The substance is soluble in water and methanol, insoluble in ether. Described for the first time.

Found, %: C 58.61; H 10.10
$C_{10}H_{20}O_4$. Calculated, %: C 58.79; H 9.86

**1-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-*D*-mannopyranosyl)butane.** To a solution of butylmagnesium bromide, prepared from 4.71 g (0.1 mol) of magnesium and 26.9 g (0.19 mol) of butyl bromide in 80 ml of absolute ether, a solution of 6 g (0.016 mol) of acetochloromannose is added. The work-up is carried out as indicated in the preceding synthesis. The final acetylation of the dry residue is performed with acetic anhydride in the presence of sodium acetate. From the ether extract, 4 g of a viscous substance (63% of theory) is obtained. Recrystallization from isopropyl alcohol gave 1.5 g (23.6%) of crystalline substance in the form of transparent quadrangular plates with m.p. 105–106°. The product is soluble in organic solvents. Described for the first time.

Found, %: C 55.60; H 7.25
$C_{18}H_{28}O_9$. Calculated, %: C 55.65; H 7.26

***m*-(2, 3, 4, 6-tetra-*O*-acetyl-*D*-mannopyranosyl)toluene.** To the Grignard reagent prepared from 6.1 g (0.25 mol) of magnesium and 42.75 g (0.25 mol) of *m*-bromotoluene in 100 ml of absolute ether, a solution of 8 g (0.021 mol) of acetochloromannose in 100 ml of absolute ether is added dropwise. The reaction mixture is stirred for 1 hour at room temperature and for 3 hours while heating on a water bath. After the usual work-up, the product is acetylated with acetic anhydride in the presence of sodium acetate. 6.12 g of a viscous mass is obtained, from which 2.9 g (31.4% of theory) of crystalline substance is isolated in the form of small transparent plates with m.p. 123-123.5°. Oxidation of the substance with permanganate gave isophthalic acid. Described for the first time.

Found, %: C 59.80; H 6.13
$C_{21}H_{26}O_9$. Calculated, %: C 59.70; H 6.20

The structure of the compound is represented by the formula:

[[structural formula]]

***m*-*D*-mannopyranosyltoluene.** A solution of 0.6 g of the product described in 15 ml of absolute methanol is heated for 2 hours on a water bath with 3 drops of hydrochloric acid. The acid is neutralized with sodium bicarbonate, the solvent is distilled off, and the residue is recrystallized from methanol. 0.3 g of substance with m.p. 170-172° is obtained. Oxidation of the product gives isophthalic acid. Described for the first time.

Found, %: C 61.68; H 7.20
$C_{18}H_{18}O_5$. Calculated, %: C 61.41; H 7.09

**m-(2, 3, 4, 6-tetra-O-acetyl-D-glucopyranosyl)toluene.** To a Grignard reagent prepared from 7.86 g (0.32 mole) of magnesium and 81.28 g (0.32 mole) of *m*-bromotoluene in 150 ml of absolute ether, a solution of 10 g (0.026 mole) of acetochloroglucose in 150 ml of absolute ether is added gradually. After the usual work-up the product is acetylated for 30 min with 60 ml of acetic anhydride containing 2 drops of hydrochloric acid. From the chloroform extracts, 4 g (34.8% of theory) of a crystalline substance was obtained in the form of small shiny needles, m.p. 141-142°. On oxidation of it, isophthalic acid was isolated. Described for the first time.

$C_{21}H_{26}O_9$. Found, %: C 59.57; H 6.15
Calculated, %: C 59.70; H 6.20

**m-D-glucopyranosyltoluene.** A solution of 1.7 g of the above-described product in 20 ml of absolute methanol is heated for 3 hours with five drops of hydrochloric acid. After neutralization the solvent is distilled off, and the residue is dissolved in hot ethyl acetate. The extracts are decolorized with charcoal and dried over sodium sulfate. On evaporation of the solvent, 0.9 g (88.3% of theory) of a colorless glassy product was obtained. The substance is soluble in water and methanol, and insoluble in ether. On acetylation with acetic anhydride in the presence of anhydron, the starting tetraacetate was obtained in good yield. Described for the first time.

structural formula of 4-(2′, 3′, 4′, 6′-tetra-O-acetyl-D-glucopyranosyl)-2-chloromercurianisole

Figure 1: structural formula of 4-(2′, 3′, 4′, 6′-tetra-O-acetyl-D-glucopyranosyl)-2-chloromercurianisole

chemical structure

Figure 2: chemical structure

| | | |
|---|---|---|
| $C_{13}H_{18}O_5$. | Found, %: | C 61.30; H 7.13 |
| | Calculated, %: | C 61.41; H 7.09 |

**4-(2′, 3′, 4′, 6′-tetra-O-acetyl-D-glucopyranosyl)-2-chloromercurianisole.** To a solution of 0.7 g (0.016 mole) of 4-(2′, 3′, 4′, 6′-tetra-O-acetyl-D-glucopyranosyl)anisole in 10 ml of glacial acetic acid is added a solution of 0.6 g (0.019 mole) of mercuric acetate in 10 ml of acetic acid. The mixture is heated on a water bath for 2 hours, after which it is poured into a cold saturated solution of common salt in water. The precipitate is filtered off, washed well with water, and recrystallized twice from alcohol. A product with m.p. 113-115° was obtained. Described for the first time.

| | | |
|---|---|---|
| $C_{21}H_{25}O_{10}HgCl$. | Found, %: | Hg 30.23 |
| | Calculated, %: | Hg 29.80 |

We give the structure of the compound obtained:

**4-(2′, 3′, 4′-tri-O-acetyl-L-arabinopyranosyl)-2,6-diiodoanisole.** To a solution of 0.5 g of 4-(2′, 3′, 4′-tri-O-acetyl-L-arabinopyranosyl)anisole in 5 ml of carbon tetrachloride, 1.2 g of iodine chloride in the same solvent is added. After two hours the solution is poured into water, the lower layer is separated, washed with water, with solutions of sodium bicarbonate and sodium thiosulfate, again with water, and dried over anhydrous sodium sulfate. After removal of the solvent, 0.5 g of a light-yellow syrup remains, which does not crystallize. The product is soluble in ordinary organic solvents. Described for the first time.

| | | |
|---|---|---|
| $C_{18}H_{20}O_7I_2$. | Found, %: | I 41.60 |
| | Calculated, %: | I 41.08 |

The structure of the substance is described by the formula:

4-(2′, 3′, 4′-tri-*O*-acetyl-*L*-arabopyranosyl)-2,6-diiodophenol. The substance was obtained by the method described above from 0.5 g of the corresponding phenetole derivative. It is a noncrystallizing syrup, soluble in ordinary organic solvents. Described for the first time.

$C_{19}H_{22}O_8J_2$. Found, %: J 40.52
Calculated, %: J 40.08

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## CITED LITERATURE

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*Note: Figure translations are in progress. See original paper for figures.*