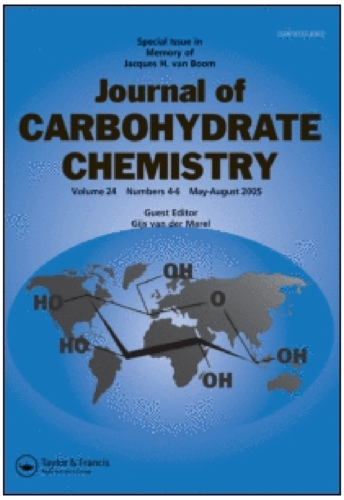

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

# Improved Yields in the Synthesis of Alkyl Glycosides

Donald E. Koeltzow[a][b]
[a] A. E. Staley Mfg. Company, Decatur, Illinois [b] Depatement of Chemistry, Luther College, Decorah, Lowa

**To cite this Article** Koeltzow, Donald E.(1985) 'Improved Yields in the Synthesis of Alkyl Glycosides', Journal of Carbohydrate Chemistry, 4: 1, 125 — 128

**To link to this Article: DOI:** 10.1080/07328308508062954

**URL:** http://dx.doi.org/10.1080/07328308508062954

J. CARBOHYDRATE CHEMISTRY, 4(1), 125-128 (1985)

Communication

# IMPROVED YIELDS IN THE SYNTHESIS OF ALKYL GLYCOSIDES

Donald E. Koeltzow[1]

A. E. Staley Mfg. Company
Decatur, Illinois 62525

Received May 8, 1984 - Final Form January 9, 1985

Recent syntheses of alkyl glycosides have involved a modification of the Koenigs-Knorr reaction in which a sugar peracetate is first brominated and finally reacted with the desired alcohol in the presence of silver ion as a catalyst. In 1980 Rosevear et al.[2] reported a simplified synthesis of alkyl glycosides in which the acetobromosugar was not isolated, but was reacted with the alcohol and the deacetylated final product was purified using column chromatography on Dowex 1. While yields obtained for alkyl glucosides by this procedure were as high as 60%, those for alkyl maltosides were only 25%. More recently Landauer et al.[3] have reported yields of 55 to 68% in the preparation of alkyl maltosides. However, their procedure involves the isolation and purification of the acetobromosugar intermediate and reported yields are calculated on the basis of this intermediate.

0732-8303/85/0401-0125$3.50/0

In the present work, reaction conditions used by Rosevear et al.[2] were examined in an attempt to maximize the yields of the higher molecular weight alkyl glycosides without isolating the acetobromosugar intermediates. Maltose octaacetate or maltotriose undecaacetate (20.0 g) were used as starting materials, with alcohol:sugar peracetate mole ratios ranging from 1:1 to 20:1. The resulting alkyl glycosides were purified on columns of Dowex 1 ($OH^-$ form) and freeze dried. Yields calculated on sugar peracetate are shown in Table 1.

The dodecyl maltosides and maltotriosides, as examples, show a direct relationship between yield and the alcohol:sugar peracetate mole ratio. For these compounds, a plateau was reached at a ratio of approximately 10:1. Spot checks of the synthesis using other alcohols support these results.

The effects of different levels of silver carbonate and iodine catalysts were also determined using a dodecanol:maltose octaacetate mole ratio of 10:1. A yield increase smaller than two percent was observed when the molar concentrations of silver carbonate and iodine were increased up to ten fold. Catalyst concentrations lower than those used by Rosevear et al.[2] were not examined.

Purity and identity of the products were established by TLC, HPLC, GC (following acid hydrolysis), and proton NMR. In the TLC work, samples were analyzed on Silica Gel G (Fisher Scientific Company, Pittsburg, PA) using alkyl maltoside and alkyl maltotrioside standards purchased from Calbiochem-Behring Corp., La Jolla,

Table 1

Percent Yields of Isolated Alkyl Maltosides and Maltotriosides

| Compound | Mole Ratio, Alcohol:Sugar Peracetate | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1:1 | 1.4:1 | 2:1 | 5:1 | 7:1 | 10:1 | 20:1 |
| n-Butyl β-D-maltotrioside | 37.2 | --- | --- | --- | --- | 44.0 | --- |
| n-Decyl β-D-maltoside | 16.5 | --- | --- | --- | --- | 51.4 | --- |
| n-Dodecyl β-D-maltoside | 11.5 | 15.8 | 32.3 | --- | 40.2 | 58.5 | 65.5 |
| n-Dodecyl β-D-maltotrioside | 10.8 | 16.5 | 34.9 | --- | 38.1 | 60.1 | 64.8 |
| n-Tridecyl β-D-maltoside | --- | --- | 35.7 | --- | --- | 41.8 | 57.3 |
| n-Tridecyl β-D-maltotrioside | --- | --- | 30.9 | --- | --- | --- | 58.3 |
| n-Pentadecyl β-D-maltotrioside | --- | --- | --- | 25.9 | --- | --- | 60.8 |
| n-Octadecyl β-D-maltoside | --- | --- | 37.6 | --- | --- | --- | 59.3 |
| n-Octadecyl β-D-maltotrioside | --- | --- | 35.0 | --- | --- | --- | 58.4 |

CA. Ethyl acetate:methanol (3:2) was used as a solvent. Plates were sprayed with aqueous 2 N $H_2SO_4$ and heated to detect the compounds. In HPLC analysis, samples were examined using a reverse phase (LC-8) column. Results here showed all compounds to be over 98% pure. For GC analysis, the alkyl glycosides were first hydrolyzed in 1 M HCl at 110 °C for 6 hours. Free alcohol levels were then measured following neutralization.

Proton NMR (200 MHz) spectra were obtained on compounds dissolved in $d_6$-DMSO in the presence of trifluroacetic acid. A Varian XL-200 NMR spectrometer was used with tetramethylsilane as an internal standard. All C-1 protons in the sugar portion of the synthesized alkyl glycosides appeared as doublets. In both the maltosides and the maltotriosides, the C-1 proton on the first sugar residue (containing the alkyl group) appeared at 4.15 ppm ($J \approx 7.7$ Hz). This agrees with the values 4.26 ppm ($J=7.6$ Hz) reported for n-dodecyl β-D-maltopyranoside.[4] The C-1 proton of the second sugar residue (the non-reducing end of the maltosides) was located at 5.05 ppm, with J values ranging from 3.42 to 4.28 Hz, depending on the compound. These numbers compare favorably with the 5.15 ppm shift ($J=3.5$ Hz) reported for this proton in n-dodecyl β-D-maltopyranoside.[4] The C-1 proton of the third sugar residue in the maltotriosides was found at 5.04 ppm ($J=4.0$ Hz).

## REFERENCES AND FOOTNOTES

1. Current address: Depatement of Chemistry, Luther College, Decorah, Iowa 52101.
2. P. Rosevear, T. VanAken, J. Baxter, and S. Ferguson-Miller, Biochemistry, 19, 4108 (1980).
3. P. Landauer, K. P. Ruess, and M. Lieflaender, Biochem. Biophys. Res. Commun., 106, 848 (1982).
4. W. J. de Grip and P. H. M. Bovee-Geurts, Chemistry and Physics of Lipids, 23, 321 (1979).