

Glycosylation of eleutheside core of the 2-*O*-acetyl-3,4-*O*-isopropylidene-*D*-arabinopyranose

© Alexey A. Pershin,⁺ Bulat T. Sharipov, and Farid A. Valeev*

Ufa Institute of Chemistry of the Russian Academy of Sciences. Oktyabrya Pr., 71. Ufa, 450054.

Fax: +7 (3472) 35-60-66. E-mail: sinvmet@anrb.ru

*Supervising author; ⁺Corresponding author

Key words: eleutherobin, eleuthesides, *D*-arabinose, glycosylation.

Abstract

A four-step synthesis of 2-trichloroacetimidate of 2-*O*-acetyl-3,4-*O*-isopropylidene-*D*-arabinopyranose by steps of regiospecific protection *D*-arabinopyranose as an acetonide, acetylation of free hydroxyl groups, selective hydrolysis of acetal center and processing trichloroacetonitrile. The possibility of using of trichloroacetimidate was studied in glycosylation eleutheside core catalyzed by TBSOTf. We obtained eleutherobin analogue with 14-methylcyclohex-12-ene A ring and glycosylated 3,4-isopropylidene-arabinopyranose by orthoether linker.

References

- [1] T. Lindel, P. R. Jensen, W. Fenical, B.H. Long, A.M. Casazza, J. Carboni, C.R. Fairchild. Eleutherobin, a New Cytotoxin that Mimics Paclitaxel (Taxol) by Stabilizing Microtubules. *J. Am. Chem. Soc.* **1997**. Vol.119. P.8744-8745.
- [2] B.H. Long, J.M. Carboni, A.J. Wasserman, L.A. Cornell, A.M. Casazza, P.R. Jensen, T. Lindel, W. Fenical, C.R. Fairchild. Eleutherobin, a Novel Cytotoxic Agent That Induces Tubulin Polymerization, is Similar to Paclitaxel (Taxol). *Cancer Res.* **1998**. Vol.58. P.1111-1115.
- [3] T. Lindel, P.R. Jensen, W. Fenical, B.H. Long, A.M. Casazza, J. Carboni, C.R. Fairchild. Eleutherobin, a New Cytotoxin that Mimics Paclitaxel (Taxol) by Stabilizing Microtubules *J. Am. Chem. Soc.* **1997**. Vol.119. P.8744 -8745.
- [4] T. Lindel. From d-Arabinose to the Marine Natural Product Eleutherobin. *Angew. Chem. Int. Ed.* **1998**. Vol.37. P.774-776.
- [5] M. Kiso, A. Hasegawa. Acetonation of some pentoses with 2,2-dimethoxypropane-N,N,-dimethylformamide *p*-toluenesulfonic acid. *Carbohydrate Research.* **1976**. Vol.52. P.95-101.
- [6] Y-J. Jian, Y. Wu. The enantioselective total synthesis of nemotin. *Org. Biomol. Chem.* **2010**. Vol.8. P.811-821.
- [7] J. Gelas, D. Horton. Acetonation of *D*-ribose and *D*-arabinose with alkyl isopropenyl ethers. *Carbohydrate Research.* **1975**. Vol.45. P.181-195.
- [8] Krasnoslobodtseva O.Yu., Sharipov B.T., Salikhov Sh.M., Safarov M.G., Spirikhin L.V., Valeev F.A. Adducts of levoglucosenone with 1,3-dienes. Cleavage of the 1,6-Anhydro Bridge. *Butlerov Communications.* **2006**. Vol.8. No.1. P.27-32. ROI: jbc-02/06-8-1-27
- [9] C. Ionescu, V. Barragan-Montero, J-L. Montero. Synthesis of a mannosyl-derived glycolipid. *Revista de Chimie (Bucharest).* **2012**. Vol.63. No.4. P.412-415.
- [10] M. Numata, M. Sugimoto, K. Koike, T. Ogawa. Total synthesis of sialosylcerebroside, GM₄. *Carbohydr. Res.* **1987**. Vol.163. P.209-225.
- [11] A.A. Pershin, B.T. Sharipov, Sh.M. Salikhov, F.A. Valeev. Eleuthesides and their analogs: X. formation of eleutheside core with methylcyclohex-12-ene A ring *Russ. J. Org. Chem.* **2015**. Vol.51. P.1536-1544. (russian)
- [12] B. Wegmann, R.R. Schmidt. The Application of the Trichloroacetimidate Method to the Synthesis of α -*D*-Gluco- and α -*D*-Galactopyranosides. *J. Carbohydr. Chem.* **1987**. Vol.6. No.3. P.357-375.
- [13] H.I. Duynstee, M.C. Koning, H. Ovaa, G.A. Marel, and J.H. Boom. Synthesis of Verbascoside: A Dihydroxyphenylethyl Glycoside with Diverse Bioactivity. *Eur. J. Org. Chem.* **1999**. Vol.10. P.2623-2632.
- [14] Kochetkov N.K., Bochkov A.F., Dmitriev B.A., Usov A.I., Chizhov O.S., Shibaev V.N. *Khimia uglevodov. Moscow: Nauka.* **1967**. 89p. (russian)