Reference Object Identifier – ROI: jbc-02/15-42-4-41 The article is published on materials of the report on "International Scientific Forum Butlerov Heritage - 2015". http://foundation.butlerov.com/bh-2015/ Submitted on March 20, 2015.

Some transformation of adducts of levoglucosenone and 1,3-diens in approaches to iridoides

© Ilgiz M. Biktagirov,² Lilia Kh. Faizullina,¹⁺ Shamil M. Salihov,¹ and Farid A. Valeev^{1*} ¹Ufa Institute of Chemistry of the Russian Academy of Sciences. Okttober Ave., 71. Ufa, 450054. Russia. Fax: +7 (3472) 35-60-66. E-mail: sinvmet@anrb.ru ² Bashkir State University.

*Supervising author; ⁺Corresponding author

Keywords: levoglucosenone, 1,6-anhydro sugar, iridoides, the Diels-Alder adducts, cyclopentanoides.

Abstract

Worldwide iridoids, contained in medicinal plants have a broad spectrum of biological activity. They possess antiinflammatory, antifungal, algal, anti-tumor, anti-oxidant, antibiotic, neuroprotective, immunosuppressive and many other types of activity. Despite on the apparent availability, content of iridoid glycosides in plants is usually around 1%, which limits not only the possibility of their practical use, but also to find of effective modifikats. Therefore, research in the field of synthesis of iridoids and their analogs are promising, both in the development of the methodology of organic synthesis, and search of new biologically active compounds We studied some the possibility of using levoglucosenone as chiral source in synthesis iridoids and their analogs in

this work. Attractive in terms of the starting compounds are Diels-Alder adducts levoglucosenone and 1,3-diene. The synthesis of iridoids from these adducts is possible in resolve of the two main problems – modification of the cyclohexane in cyclopentane part and transformation of carbohydrate part in the lactone fragment of iridoids.

The problem of reducing the cyclohexane ring cyclopentane adduct levoglucosenone and butadiene it has been studied previously by ozonolysis cleavage of double-bond, oxidation in the dicarboxylic acid and its Dieckmann condensation her diester. In continuation of these studies, possibility of modification of cyclohexane ring to cyclopentane by ozonolysis cleavage and intermolecular aldol cyclization was studied on the base of the Diels-Alder adduct of levoglucosenone and piperylene – 6-methyl-10,12-dioxatricyclo[7.2.1.02,7]dodec-4-ene-8one. On the basis of the adduct levoglucosenone and piperylene obtained functionalized cyclopentane, annelated with the carbohydrate moiety to be used in the synthesis of iridoids and cyclopentanoids.

At the same time studied way of conversion of the cyclohexane ring in cyclopentane studied by us using the Wagner-Meerwein rearrangement on the dioxolane derived of Diels-Alder adduct of levoglucosenone pipervlene -6-methyl-8,8-ethylenedioxy-10,12-dioxatricyclo-[7.2.1.02,7]dodec-4-ene was action by BF₃·Et₂O.

It was carried out reaction of allyl oxidation of the Diels-Alder adducts of levoglucosenone and 1,3-dienes by action CrO₃·2Py in CH₂Cl₂. It was found that this transformation occurs upon prolonged storage on atmospheric oxygen and to light.