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The adduct of the Diels-Alder levoglucosenone and isoprenein approaches to iridoids

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Abstract

One of the most widely used ways of obtaining complex natural compounds is the use of optically active, but simpler, and therefore accessible compounds in chemical syntheses. Such a chiral source is levoglucosenone, which has a unique structure, high reactivity and, at the same time, sufficient stability; he found application in the synthesis of a number of natural compounds and continues to be studied in this regard. Due to the ability of levoglucosenone to interact with 1,3-dienes by the Diels-Alder reaction under stereocontrol conditions, dinitrocompounds by the Michael reaction open the possibility for obtaining chiral derivatives that are promising for use in the synthesis of a wide class of natural compounds, including terpenoids. In continuation of the work in the direction of iridoids, we developed a new approach based on the adduct of Diels-Alder of levoglucosenone and isoprene-4-methyl-10,12-dioxatricyclo [7.2.1.02,7] dodec-4-en-8-one (**1**). Thus, taking the fact that when the Diels-Alder adduct of levoglucosenone and isoprene **1** is boiled in benzene in the presence of *p*-TsOH, isomerization of the double bond occurs, we studied the possibilities of synthesizing iridoid using the isomerized adduct 4-methyl-10,12-dioxatricyclo [7.2.1.02,7] dodec-3-en-8-one (**2**).

Ozonolitic cleavage of the double bond and subsequent treatment of Me_2S ozonides in adduct **2** led to unstable aldehyde ketone **3** – (1*S*,2*S*,3*R*,5*R*)-4-oxo-3-(3-oxobutyl)-6,8-dioxabicyclo[3.2.1]octan-2-carb-aldehyde. Oxidation of the obtained dicarbonyl compound of $KMnO_4$ proceeded with significant a resin is formed, while Jones oxidation smoothly led to acid. The attempt of chromatographic isolation of the acid was unsuccessful. Therefore, the unissolved acid was esterified with diazomethane, the resulting ester **4** – (1*S*, 2*S*,3*R*,5*R*)-methyl-4-oxo-3-(3-oxobutyl)-6,8-dioxabicyclo[3.2.1]octan-2-carboxylate was identified.

Intramolecular aldol condensation in diketone **4** was carried out in benzene in the presence of a catalytic amount of DBU (1,8-diazobicyclo [5.4.0]-undec-7-ene). The structure of the compound – methyl(1R,9S)-2-hydroxy-4-oxo-11,12-dioxatricyclo [7.2.1.02.7] dodecane-8-carboxylate (**5**) was proved on the basis of ^{1}H and ^{13}C NMR spectra. The fungicidal activity of the obtained target compound. Thus, compound **5** in a concentration of 0.5% in DMSO (dimethylsulfoxide) had a pronounced fungistatic effect on the development of *Rhizoctoniasolani*, retarding the growth of mycelium and the formation of chlamydospores.

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