

oils (fractional composition – 350–570 °C). A study concerning the changes in the physicochemical properties and hydrocarbon composition of vacuum gas oil during hydrotreating at the combined unit KT-1/1 was conducted. The obtained data is presented in tables 1 and 2.

The following methods were used during the work: liquid adsorption chromatography method for separating a fraction into a hydrocarbon type composition; cryoscopic method on KRION 1 to determine the molecular weight; SPECTROSCAN S X-ray fluorescence energy dispersive sulfur analyzer for determination of total sulfur content; Stabinger viscometer SVM3000 (Anton Paar) for determining the density and viscosity of petroleum products.

During hydrotreatment, vacuum gas oil is fed to the top of the reactor and gradually passes through the catalyst bed. At high temperatures and pressure

hydrogen binds sulfur on the catalyst converting it to hydrogen sulfide. It also saturates aromatic hydrocarbons with hydrogen, turning them into naphthenic ones [2].

As can be seen from the above data, the sulfur content decreases to 0.078–0.152 wt. %. The hydrocarbon composition of the vacuum gas oil changes with content of the saturated hydrocarbons increase and decrease of the content of aromatic hydrocarbons and resins.

The data obtained will then be used to develop a mathematical model of the catalytic cracking process of vacuum gas oil, which will take into account the conversion of hydrocarbons and sulfur compounds. Also this model will be applicable to optimize the technological modes of operation of the apparatus of the reactor-regenerative unit, control the catalyst, and increase the efficiency of the catalytic cracking process.

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## DEVELOPING OF ARYL GLYCOSIDES ACYLATION METHODS

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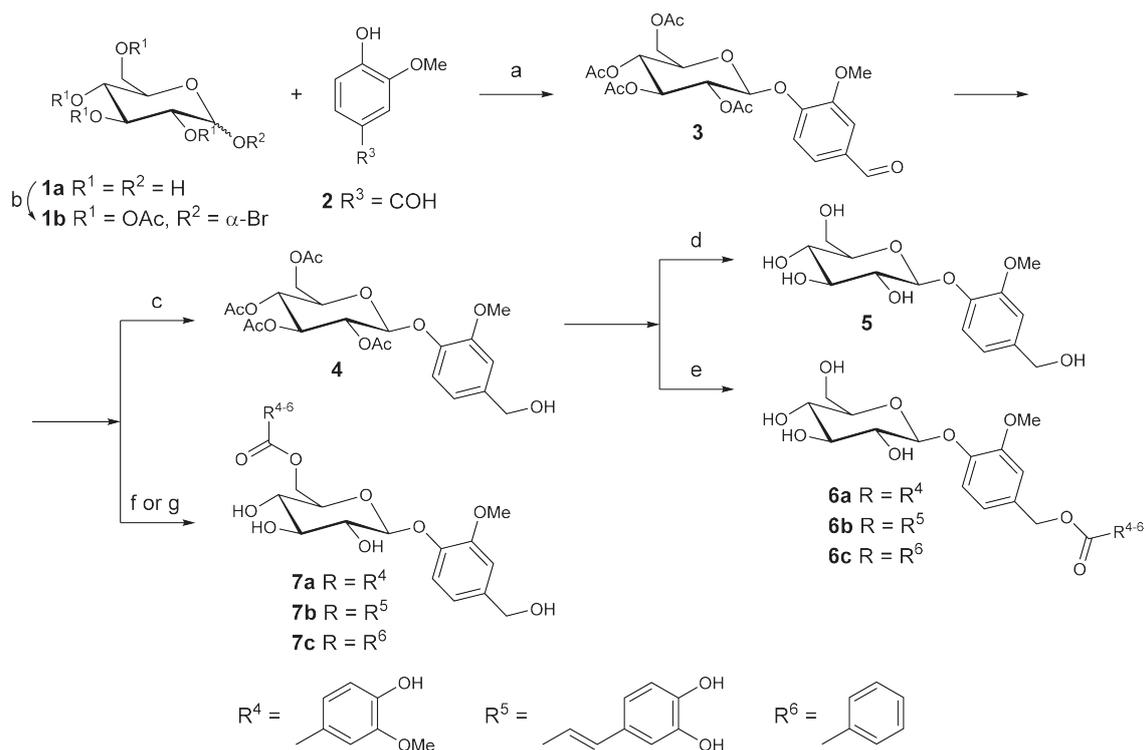
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Glycosides, a broad class of natural organic compounds, are extremely interesting objects for chemical research. They are mostly bioavailable and thus can alter this parameter for other organic compounds. Aryl glucopyranosides (and other glycosides with phenolic (aryl) residue as an aglycon) can be modified at 4 positions at least, depending on a structure of aglycon, and all these compounds might have different bioactivity also different from original glycoside [1–2].

One of such natural glycosides is vanilloloside **5** (Scheme 1) which itself shows almost no anti-cancer activity [1] whilst its 6–O ester saccharumside-B and other analogs with different acyl groups shows high antiproliferative effect on the same cancer cells [2]. There are also natural glycosides acylated at aglycon positions with prospectively high biological activity [1–3]. Besides, aryl glycosides are of low toxicity [4] and have variety of other bio-

activities: anti-inflammatory [5], antibacterial [1], etc.

As aryl glycosides are common constituents of different plants, the most common way to obtain them is extraction. However, it is not very efficient, and tends to be expensive as the extraction requires kilograms of plant parts to give milligrams of product [6]. To obtain the pure product from extract it should be separated from other substances with similar structures and properties, and very often it is not pure enough to be used in further tests. Moreover, the plant itself might be expensive or hard to get collected, or even protected from collection by law. The chemical synthesis in this case gives higher yields, is easily scaled up, and can be started with easily available reagents such as glucose **1a** and vanillin **2**, etc. The resulting products can also be used as chemotaxonomic markers in biological research [7].



Scheme 1. Total synthesis of acyl aryl glycosides:

a – KOH, acetone/H<sub>2</sub>O; b – 1. Ac<sub>2</sub>O, H<sup>+</sup>; 2. PBr<sub>3</sub>; 3. H<sub>2</sub>O; c – NaBH<sub>4</sub>, CTMAB, H<sub>2</sub>O/CHCl<sub>3</sub>; d – MeONa/MeOH; e – 1. R<sup>4-6</sup>(O)Cl, Py, DCM; or R<sup>4-6</sup>(O)OH, DCC/DMAP, DCM; 2. HCl/EtOH/CHCl<sub>3</sub> (1 : 3 : 1 vol.); or 1. CBr<sub>4</sub>, PPh<sub>3</sub>, DCM; 2. R<sup>4-6</sup>(O)OK, DMF; 3. HCl/EtOH/CHCl<sub>3</sub> (1 : 3 : 1 vol.); f – 1. MeONa/MeOH; 2. R<sup>4-6</sup>(O)Cl, Py, DCM; 3. NaBH<sub>4</sub>, MeOH; g – 1. Lipase, MeCN; 2. R<sup>4-6</sup>(O)Cl, Py, DCM; 3. NaBH<sub>4</sub>, MeOH; 4. HCl/EtOH/CHCl<sub>3</sub> (1 : 3 : 1 vol.).

Thus, our goal was to develop the efficient way of acyl aryl glycoside synthesis starting from glucose **1a** and vanillin **2**. To carry this out we considered two options of acylation: at aglycon and at carbohydrate fragment (Scheme 1).

First, we glycosylated vanillin **2** with aceto-bromoglucose **1b** (Scheme 1–b) synthesized from glucose **1a** (Scheme 1–a). The resulted product **3** was a starting point for all other synthesis. For instance, by reduction with NaBH<sub>4</sub> in the presence of CTMAB (cetyltrimethylammoniumbromide) in biphasic system we obtained glycoside **4** which

was deacetylated to give vanilloloside **5** (Scheme 1–d), and acylated in different manners with following deacetylation to give corresponding esters at aglycon **6a–c** (Scheme 1–e). The other path was to deacetylate glycoside **3** and further modify it with different chlorides with following reduction with NaBH<sub>4</sub> to obtain target compounds acylated at 6–O position of carbohydrate moiety **7a–c** (Scheme 1–f). Another way to get to the same products **7a–c** is to use fermentative catalysis to selectively deacetylate 6–OH group enabling it to further acylation with chlorides (Scheme 1–g).

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