Original article

DEVELOPMENT OF A MODIFIER FOR GIVING MATERIALS FROM EFFICIENTLY PROCESSED WOOD BIOMASS SPECIAL PROPERTIES


**Background.** Wood is a unique material in its structure. However, materials made from wood raw materials have such negative properties as insufficient bio- and fire-resistance. In turn, when organizing and improving the efficiency of logging activity, large amounts of practically unused cutting residues is produced. Their modification for the purposes of the forest industry is an effective tool for creating many valuable and demanded products. In particular, arilazo-β-dicarbonyl compounds are widely used as syntons for the production of heterocyclic compounds. Among heterocycles, a large number of compounds have found application in the form of biologically active substances that have been successfully and for a long time used as pesticides for the wood processing industry.

**Purpose.** Synthesis of p-nitrophenyl hydrobutanons, cyclocondensation to form pyrazoles and study of their chemical properties of the substances first obtained. Proof of structure by modern spectral analysis methods.

**Materials and Methods.** Research methods include: organic synthesis; UV spectrometry, $^1$H NMR, $^{13}$H NMR.

**Results.** Four new compounds were synthesized: 4-methoxy-1-(p-chloro(bromo)phenyl)-2-(p-nitrophenylhydrazo)-1,2,3-butantrions and 3(5)-methoxy-5(3)-(p-chloro(bromo)phenyl)-4-(p-nitrophenylhydrazo)-1H-pyrazoles. Amines were prepared by the reduction of the related nitrosopyrazoles. The acylation reaction was demonstrated for the obtained amine. The structures of all synthesized compounds were proved by modern methods of analysis.

**Conclusion.** Thus, we synthesized p-nitrophenylhydrazobutanetriones with a chloro(bromo)phenyl substituent, their cyclization products with hydrazine, and N-(5-(4-chloro(bromo)phenyl)-3-(methoxymethyl)-1H-pyrazole-4-yl)acetamides based on them. The structure of the obtained substances was determined by spectral methods of analysis.
Keywords: p-nitrophenylhydrazobutantrione; reduction; cyclocondensation; hydrazine hydrate; acylation; UV spectroscopy

Результаты. Синтезировано 4 новых соединения: 4-метокси-1-(p-хлор(-бром)фенил)-2-(p-нитрофенилгидразо)-1,2,3-бутантрионы и 3(5)-метокси-5(3)-(p-хлор(бром)фенил)-4-(p-нитрофенил-гидразо)-1H-пиразолы. Восстановлением соответствующих нитрозопиразолов получены амины. Для полученного амина показана реакция ацилирования. Доказано строение всех синтезированных веществ современными методами анализа.

Заключение. Таким образом, нами были синтезированы п-нитрофенилгидразобутантрионы с наличием хлор(бром)фенильного заместителя, продукты их циклизации с гидразином, а также N-(5-(4-хлор(бром)фенил)-3-(метоксиметил)-1H-пиразол-4-ил)ацетамиды на их основе. Структура полученных веществ определена спектральными методами анализа.

Ключевые слова: п-нитрофенилгидразобутантрион; восстановление; циклоконденсация; гидразингидрат; ацилирование; УФ-спектроскопия


Introduction

Modern timber industry is characterized by many problems and difficulties. Some of them find a proper scientific solution and justification, others do not. In particular, solutions in the field of organization of industrial production activities, processing of raw materials and materials at large industrial sites, economic, environmental and other issues are described in some detail in the scientific literature. On the other hand, there are quite a few theoretical and applied works on the processing of wood biomass remaining from logging industries. At the same time, the problem of involving these resources in production is extremely relevant. During the research of the team of authors, work was carried out to modify the efficiently processed biomass of the tree. The main task is to give new, relevant properties.

On the basis of b-dicarbonyl compounds, various nitrogen-containing heterocyclic systems are obtained, for example, five-membered furans, pyrroles, thiophenes, as well as six-membered quinolines and pyridazines [1-3, 15-17].

Among the nitrogen-containing heterocycles, pyrazole derivatives attract the most attention because they are used as medicinal preparations [4]. It is also known that their amino derivatives have a strong bactericidal and fungicidal effect [10, 12, 14, 17]. Such properties make it possible to use heterocyclic compounds as pesticides for diseases in forest nurseries [8].
In addition, the introduction of halogen into an organic compound significantly expands the range of its application. It is known that aromatic halogeno-proiz-water have insecticidal activity, which is very important for their use in the field of timber processing [8, 11]. Such properties prompted us to introduce chlorine (bromine)a substituent in the molecule of b-dicarbonyl synthon.

During cyclocondensation of b-dicarbonyl compounds with hydrazine, all substituents in the initial aliphatic compounds are stored in the pyrazole nucleus. Thus, the introduction of a halogen-containing fragment into the reaction causes its presence in the resulting pyrazole.

In addition, the introduction of a nitrogen-containing fragment allows you to switch to different classes of organic compounds. Diazonium salts are the key to the synthesis of (p-nitrophosphylhydrazo)-butantriones by the azo combination reaction. Further reduction to the arylazo group makes it possible to obtain amines. Acylation of the final nitrogen-containing group is carried out to study the properties of new compounds. Modern spectral methods of analysis were used to prove the structure of the obtained substances.

**Materials and Methods**

UV spectrometry using high performance liquid chromatography (HPLC/MS) was used to identify and qualitatively determine the obtained compounds [19].

UV spectra were recorded on a Shimadzu LC/MS-2020 instrument with a RAPTOR ARC-18 100 column (diameter 2.1 mm, grain size 0.1 mm, length 100 mm). A sample was prepared with a concentration of 0.01 mg/ml, eluent was acetonitrile-water (9:1), recording was carried out in isocratic mode, at t=35°C in a thermostated column.

$^1$H NMR spectra were recorded in DMSO-d$_6$ with TMS as internal standard.

$^{13}$C NMR spectra were recorded in CDCl$_3$ with TMS as internal standard.

**Results of the research and Discussion**

As a result of the ester condensation of Kleisen carried out in the presence of sodium alcoholate in absolute diethyl ether between the methyl ether of methoxyacetic acid and p-haloacetophenones, sodium (Z)-4-(4-chloro(bromine) phenyl)-1-methoxy-4-oxobut-2-en-2-olates were obtained [23].

For the introduction of a nitrogen-containing group into the molecule of the b-dicarbonyl compound, the reaction of the nitrogen combination of sodium salt with p-nitrobenzene diazonium chloride was carried out (Fig. 1) according to a well-known technique [5].
Fig. 1. Scheme for the preparation of (p-nitrophenylhydrazo)-butanetriones

Thus, for the first time, we obtained β-dicarbonyl synthons based on the p-nitrophenylhydrazo group with the presence of chlorine(bromine)phenyl substitution. UV spectrometry using high-performance liquid chromatography (HPLC/MS) was used to identify and qualitatively determine the compounds obtained [13].

First obtained (p-nitrophenylhydrazo)-butanetrones were introduced into the cyclocondensation reaction [18]. To do this, the corresponding butanetione was dissolved in ethyl alcohol and an equimolar amount of 95% hydrazine hydrate solution was added drop by drop at room temperature (Fig. 2).

The disappearance of the starting substance was controlled by TLC. Then the reaction mass was diluted with water, precipitated in the form of large flakes, which were removed by filtration. An additional amount of the target product was obtained by extraction with diethyl ether. UV spectra were recorded to identify and determine the formed azo compounds [13].

Fig. 2. Synthesis of azopyrazoles

For unambiguous proof of the structure of new compounds, we reduced aryldiazopyrazoles to already known amines [6]. The reduction was carried out with hydrazine hydrate in the presence of palladium on coal in ethanol (Fig. 3) [9].
It should be noted that the total yield of amino compounds obtained by reducing the arylase derivative exceeds the total yield of amino compounds through the nitrosation reaction of substituted β-diketones followed by cycloaromatization to nitrosopyrazole and its reduction. Thus, the total yield of products in the case of reduction of arylazopyrazoles was 31.2%, while through nitrosation of β-diketone and cyclocondensation with reduction was about 17.5%. As a result of comparing the two methods, it was proved that the preparation of 5-(4-chloro(bromine)phenyl)-3-(methoxymethyl)-1H-pyrazole-4-amine through the arylase group is more effective.

It is known that many amines are labile and can be easily oxidized in air, therefore, an unambiguous proof of the structure is the production of an N-acyl derivative. To carry out acylation, aminopyrazole was suspended in an absolute diethyl ether medium, an acetylyating agent was added. The solution was stirred at a t = 0–5 °C for 30 minutes. The thickened mixture was recrystallized from ethanol, white crystals were formed (Fig. 4).

For the purposes of optimize the reaction conditions of N-acylation [22], the influence of solvents, time and amount of aceto-acetic anhydride on the reaction was studied (Table 1).
Table 1.

<table>
<thead>
<tr>
<th>№</th>
<th>Solvent</th>
<th>Time, h</th>
<th>Temperature, °C</th>
<th>Yield, %</th>
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</thead>
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<tr>
<td>1</td>
<td>Ethanol</td>
<td>8</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol</td>
<td>6</td>
<td>100</td>
<td>74</td>
</tr>
<tr>
<td>3</td>
<td>Ethanol + two-fold excess of anhydride</td>
<td>4</td>
<td>25</td>
<td>80</td>
</tr>
<tr>
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<td>Two-fold excess of anhydride</td>
<td>1</td>
<td>25</td>
<td>89</td>
</tr>
</tbody>
</table>

Experimental data show that this reaction has the greatest efficiency with a two-fold excess of anhydride without the addition of a solvent.

**Experimental part**

*Synthesis of 4-methoxy-1-(p-chloro(bromo)phenyl)-2-(p-nitrophenylhydrazo)-1,2,3-butanetrione (Fig. 1).* p-Nitroaniline (0.004 mol) was dissolved in 4.5 ml of water, a threefold excess of 6N was added of hydrochloric acid. The resulting solution was cooled to -5 to -10°C and an equimolar amount of sodium nitrite was sprinkled in small portions, maintaining the temperature regime. The solution was stirred for an hour. The buffer solution was prepared separately.

Mixed 0.04 mol of the sodium salt of the diketone, 5-10 ml of ethanol and 0.04 mol of sodium acetate. The solution was chilled for 30 minutes, filtered. The mother liquor was introduced into the machine with a buffer solution. The color of the solution changed to bright yellow. Thermostated at a temperature not exceeding 5 °C for 30 minutes. Filtered out. Recrystallized from ethanol [20].

4-methoxy-1-(p-chlorophenyl)-2-(p-nitrophenylhydrazo)-1,2,3-butanetrione. Yield 74%, mp 148-150 °C. UV spectrum: 369 nm (N=N).

4-methoxy-1-(p-bromophenyl)-2-(p-nitrophenylhydrazo)-1,2,3-butanetrione. Yield 80%, mp 178-180 °C. UV spectrum: 387 nm (N=N).

*Synthesis of 3(5)-methoxy-5(3)-(p-chloro(bromo)phenyl)-4-(p-nitrophenylhydrazo)-1H-pyrazole (Fig. 2).* 4-Methoxy-1-(p-chloro(bromo)phenyl)-2-(p-nitrophenylhydrazo)-1,2,3-butanetione (0.1 mol) was dissolved in a minimum amount of ethyl alcohol. Avoiding heating, the calculated amount of hydrazine hydrate (0.1 mol) was added. The solution was stirred for 6 hours at a temperature of 20°C. The yellow-orange precipitate was filtered off, recrystallized from ethanol. An additional amount of the target product was obtained by extraction with diethyl ether [20].

3(5)-methoxy-5(3)-(p-chlorophenyl)-4-(p-nitrophenylhydrazo)-1H-pyrazole. Yield 85%, mp 205-207 °C. UV spectrum: 360 nm (N=N), 201, 234 nm (pyrazole cycle).
3(5)-methoxy-5(3)-(p-bromophenyl)-4-(p-nitrophenyl-hydrazo)-1H-pyrazole. Yield 75%, mp 219-222 °C. UV spectrum: 364 nm (N=N), 205, 250 nm (pyrazole cycle).

Reduction of 3(5)-methoxy-5(3)-(p-chloro(bromo)phenyl)-4-(p-nitrophenyl-hydrazo)-1H-pyrazole (Fig. 3). To 4-azopyrazole (0.1 mol) was added a twofold excess of hydrazine hydrate on a palladium-on-charcoal catalyst in a minimum amount of ethanol. The mixture was stirred for 2 hours, then filtered off the coal. The mother liquor was evaporated. The resulting light brown crystals were recrystallized from ethanol [20].

Acylation of substituted 4-aminopyrazoles (Fig. 4). Aminopyrazole (0.13 mol) was suspended in absolute diethyl ether (2 ml), acetic anhydride was added in a two-fold molar excess [21]. The solution was stirred at a t = 0–5 °C for 30 minutes. The thickened mixture was filtered off, the resulting precipitate was recrystallized from ethanol.

N-(5-(4-chlorophenyl)-3-(methoxymethyl)-1H-pyrazol-4-yl)acetamide. Yield 64%. White crystals, mp 165-166 °C. ¹H NMR (DMSO-d₆), δ, ppm: 13.19 s (1H, NH), 9.64s (1H, NH), 7.61-7.66 m (4H bromophenyl rings), 2.05s (3H, CH₃ of acyl subst.), 3.34 and 4.36 s (5H, CH₂ and CH₃ groups of the methoxymethyl subst.) ¹³C NMR spectrum, δ, ppm: 23.23, 58.26, 63.38, 122.08, 128.68, 129.39, 130.82, 132.24, 139.23, 148.62, 169.85.

N-(5-(4-bromophenyl)-3-(methoxymethyl)-1H-pyrazol-4-yl)acetamide. Yield 63%. White crystals, mp 185-186 °C. ¹H NMR (DMSO-d₆), δ, ppm: 13.1 s (1H, NH), 9.3 s (1H, NH), 7.70-7.50 m (4H bromophenyl rings), 2.02 s (3H, CH₃ of acyl subst.), 3.25 and 4.29 s (5H, CH₂ and CH₃ groups of the methoxymethyl subst.) ¹³C NMR spectrum, δ, ppm: 23.21, 58.00, 63.11, 128.37, 129.10, 129.33, 134.27, 139.13, 148.67, 169.91.

Conclusion
Thus, for the first time we obtained b-dicarbonyl compounds based on a p-phenylhydrazogroup with a chlorine(bromine)phenyl substituent, which we then introduced into the cyclization reaction to form a pyrazole cycle. The structure of the newly synthesized compounds was confirmed by spectral analysis methods (¹H NMR, ¹³C NMR, UV spectroscopy). It is shown that when azopyrazoles are reduced, 4-amino derivatives are formed with higher yields than when identical compounds are obtained from b-dicarboxyl compounds by nitrosation followed by cyclo-condensation. The effect of solvents, time and amount of acetoacetic acid anhydride on the course of the N-acylation reaction was studied in order to optimize this process.
Conflict of interest information. The authors declare that there is no conflict of interest.

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