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MONOMETILOLMOCHEVINAGALLAT EFIRLARINI OLISH

ПОЛУЧЕНИЕ МОНОМЕТИЛОЛМОЧЕВИНАГАЛЛАТНЫХ ЭФИРОВ

OBTAINING MONOMETHYLOLUREAGALLATE ETHERS

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Annotatsiya

Tadqiqotlar mochevina va formaldegidning o'zaro ta'siri natijasida mono-, di- va trimetilolmochevina hosil bo'lishini o'rgandi. Ushbu tadqiqotning maqsadi gal kislotasining mono-, di- va trimetilolmochevina bilan efirlarini hosil bo'lishini o'rganishdan iborat bo'ldi.Tadqiqotda mayda organik sintez, IK, mass-spektrometriya, erish nuqtasini o'lchash, yupqa qatlam, ustunli xromatografiya usullari qo'llanildi. Efirlarning tuzilishi shuni ko'rsatdiki, eterifikatsiya reaksiyasi gallik kislotaning karboksil guruhi va metilol karbamidning gidroksil guruhi hisobiga boradi.

Аннотация

В исследованиях изучено образование моно-, ди- и триметилолмочевинов в результате взаимодействия мочевины и формальдегида. Целью данного исследования было изучение образования сложных эфиров галловой кислоты с моно-, ди- и триметилмочевиной. В исследовании использованы методы тонкого органического синтеза, ИК-, масс-спектрометрия, измерение температуры плавления, тонкослойная, колоночная хроматография. Строение сложных эфиров показало, что реакция этерификации протекает за счет карбоксильной группы галловой кислоты и гидроксильной группы метилолмочевинов.

Abstract

The studies studied the formation of mono-, di- and trimethylol ureas as a result of the interaction of urea and formaldehyde. The purpose of this study was to study the formation of esters of gallic acid with mono-, di- and trimethylurea. The study used methods of fine organic synthesis, IR, mass spectrometry, melting point measurement, thin layer, column chromatography. The structure of esters showed that the esterification reaction proceeds due to the carboxyl group of gallic acid and the hydroxyl group of methylol ureas.

Kalit so'zlar: *mochevina, formal'degid, monometilolmochevina, ammiak, gall kislotasi, gallatlar, benzoy kislotasi, polifenollar va murakkab efirlar.*

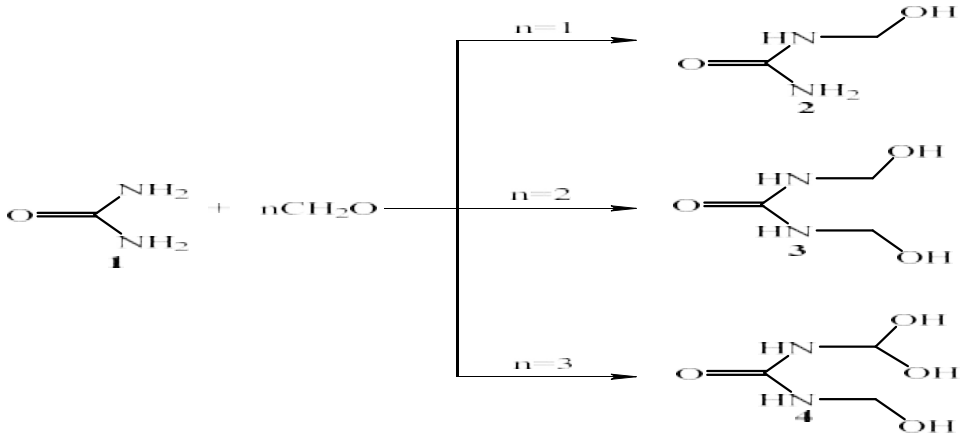
Ключевые слова: *мочевина, формальдегид, монометилмочевина, аммиак, галловая кислота, галлаты, бензойная кислота, полифенолы и сложные эфиры.*

Keys words*: urea, formaldehyde, monomethylurea, ammonia, gallic acid, gallates, benzoic acid, polyphenols and esters.*

INTRODUCTION

Methylolureas have been synthesized by different methods. Urea reacts with formaldehyde in an alkaline medium to form monomethylol urea (1) [1].

The reaction of urea with formaldehyde takes place in several stages. Their direction depends on temperature, pH value, concentration and time of reagent aggregation. At the first stage, methylol groups are formed. The presence of four reactive hydrogen atoms in urea indicates that it can combine with the same amount of formaldehyde.



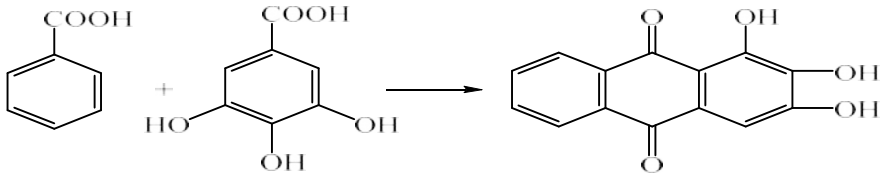
Experiments have shown that the inclusion of each methylol group reduces the reactivity of the remaining hydrogen atoms in the amino and imine groups. The equilibrium constants of the reactions for the formation of mono-, di- and trimethylolureas are 0.045, 0.274 and 1.8 at 50 ° C. The reactions for the formation of methylolurea are bimolecular, and the dissociation reaction is monomolecular. In these reactions, H_3O^+, OH^-, acids, bases and salts act as catalysts. In the reaction of urea with formaldehyde, the rate of formation of monomethylolurea increases at 35 ºC and pH 2.0-4.0 [1-3].

Gallic acid forms esters with alcohols. Esters of methyl, ethyl, propyl, and octyl alcohols with gallic acid were synthesized on a sulfuric acid catalyst.

Methyl gallate is oxidized to hexaoxidophenol. It is converted to ellagic acid by internal molecular transesterification in ammonia solution.

Ethanol is used in the fuel, polymer and cosmetic industries. It is not included in the list of approved food additives for use in the food industry in Russia and most countries of the world [4].

Since 1948, gallic acid propyl ester (1-propyl-3,4,5-trihydroxobenzoate) has been used as a food additive due to its antioxidant properties [5,6]. Gallic acid with benzoic acid forms benzoic gallate ester.



Gallic acid and its esters are used in the food industry as a food additive due to their antioxidant properties, in pharmaceuticals, medicine, in the production of paints and varnishes.

EXPERIMENTAL PART.

Synthesis of monomethylurea **(2).** 1200 g (20 mol) of urea was dissolved in 1200 ml of water. The aqueous solution was heated to 40 °C. The ammonia solution was added to 1615 ml of 34% formalin to a pH of 8-9 and the two solutions were mixed. When the mixture was kept at 10 °C for 4 h, a white precipitate formed. Then the solution was shaken and poured into a crystallizer. After 1 day, a white precipitate was isolated. M.p. = 100-101 ºC.

Synthesis of dimethylol urea (3). 60 g (1 mol) of urea was dissolved in 60 ml of water. The aqueous solution was heated to 40 °C. The ammonia solution was added to 157.5 ml of 34% formalin to pH 8.3 and the two solutions were mixed. When the mixture was kept at 10 °C for 24 h, a white precipitate formed. Then the solution was shaken and poured into a crystallizer. After 1 day, a white precipitate was isolated. M.p. = 121-122 ºC.

Synthesis of trimethylol urea (4). 60 g (1 mol) of urea was dissolved in 60 ml of water. The aqueous solution was heated to 40 °C. The ammonia solution was added to 290 ml of 34% formalin to a pH of 8.3 and the two solutions were mixed. When the mixture was kept at 10 °C for 24 h, a white precipitate formed. Then the solution was shaken and poured into a crystallizer. After 1 day, a white precipitate was isolated. M.p. = 127-128 ºC.

Synthesis of gallic acid esters. At 0 °C, 2.5 g (12 mmol) DCC (dicyclohexylabodiimide) was slowly added to a solution of 1.7 g (10 mmol) gallic acid in 100 ml of diethyl ether. To the mixture was added a solution of 50 mmol of urea in 10 ml of diethyl ether, warmed to room temperature and stirred for 24 hours. The precipitate was separated from the reaction mixture, washed 3 times with 5% $NaHCO_3$, dried over Na_2SO_4, and concentrated in vacuo. The resulting mixture was separated by column chromatography (ethanol/chloroform 4:1).

Ureidomethylgallate (5)yield 46%. M.p.=155°C. *IR spectrum.* strong 580 см$^{-1}$, middle 765 см$^{-1}$, middle 880 см$^{-1}$, strong 940 см$^{-1}$, middle 990 см$^{-1}$, strong 1035 см$^{-1}$, strong 1090 см$^{-1}$, very strong1110 см$^{-1}$, wide, strong 1130 см$^{-1}$, wide, strong1190 см$^{-1}$, strong1260 см$^{-1}$, strong см$^{-1}$, strong1570 см$^{-1}$, strong1650 см$^{-1}$, powerless, shoulder1670 см$^{-1}$, powerless3280 см$^{-1}$, powerless3355 см$^{-1}$, powerless3370 см$^{-1}$, powerless3720 см$^{-1}$, powerless3770 см$^{-1}$, powerless3830 см$^{-1}$, wide, powerless3890-3900 см$^{-1}$. *Mass spectrum:* 243,0014 m/z (100 %), 242,0016 m/z (55 %), 244,0024 m/z (23 %).

(3-(hydroxymethyl)ureido) methylgallate (6) унуми 42 %. M.p.=167°C. *IR spectrum*. strong584 см$^{-1}$, middle 697 см$^{-1}$, middle 875 см$^{-1}$, strong 935 см$^{-1}$, middle 986 см$^{-1}$, strong 1035 см$^{-1}$, strong 1090 см$^{-1}$, very strong1110 см$^{-1}$, wide, strong 1125 см$^{-1}$, wide, strong1180 см$^{-1}$, strong1235 см$^{-1}$, strong см$^{-1}$, strong1567 см$^{-1}$, strong1640 см$^{-1}$, powerless1660 см$^{-1}$, powerless3280 см$^{-1}$, powerless3270 см$^{-1}$, powerless3355 см$^{-1}$, powerless3345 см$^{-1}$, powerless3370 см$^{-1}$, powerless3755 см$^{-1}$, wide, powerless3890-3895 см$^{-1}$. *Mass spectrum*: 272,008m/z (100 %), 273,001 m/z (55 %), 274,0012 m/z (23 %).

(3,3-bis(hydroxymethyl)ureido)methylgallate **(7)** унуми 37 %. M.p.=178°C. *IR spectrum*. middle 600 см$^{-1}$, middle 740, 795 см$^{-1}$, middle 900 см$^{-1}$, strong 925 см$^{-1}$, middle 860 см$^{-1}$, very strong890 см$^{-1}$, strong 965 см$^{-1}$, very strong925, 970 см$^{-1}$, wide, strong 1110, 1230 см$^{-1}$, wide, strong1030, 1165, 1180 см$^{-1}$, strong1250, 1335 см$^{-1}$, strong 1590 см$^{-1}$, strong1690 см$^{-1}$, strong1710 см$^{-1}$, powerless3055-3135 см$^{-1}$, powerless3155-3220 см$^{-1}$, powerless3225-3275 см$^{-1}$, powerless, wide3570 см$^{-1}$, wide, powerless3570-3710 см$^{-1}$. *Mass spectrum*: 302,0014 m/z (100 %), 303,0016 m/z (55 %), 304,0024 m/z (23 %).

THE DISCUSSION OF THE RESULTS.

Based on the biological activity of urea derivatives with formaldehyde and gallic acid, it can be assumed that the products of their interaction, in particular esters, also have high biological activity. For this purpose, the reactions of gallic acid esterification with monomethyl urea, dimethyl urea, trimethyl urea were studied.

The interaction of gallic acid and methylurea is an esterification reaction and is known to take place in a mild environment. The presence of oxidants in the environment leads to the oxidation of gallic acid, and in an alkaline environment - to the polycondensation of methylurea. Therefore, a soft water extractor in a neutral solvent will be required. In view of this, in the esterification reaction, a dichloromethane solvent was used in an argon atmosphere, dicyclohexylcarbodiimide as a water absorber, and dimethylaminopyridine as a protonating agent.

When the reaction mixture was tested by TLC, it was found that the formation of products began after 30 minutes. Due to the high solubility of monomethylurea in diethyl ether in comparison with other urea derivatives and the closeness of the Rf values, a 4:1 mixture of ethanol and chloroform was used as an eluent in the separation of the reaction product from the primary monomethylurea by column chromatography. When separating the remaining esters, it was observed that a slightly easier separation occurs when using this system. It was found that as a reaction product of trimethylurea with gallic acid, two products were formed with very similar R_f values (0.34 and 0.38). The first fraction (R_f = 0.38) was formed in large quantities, and the yield of the second fraction was so low that it could not be separated in pure form. Therefore, the first fraction was used in subsequent analyzes.

The shift of the absorption line from 1760 cm^{-1} to 1565-1570 cm^{-1}, which is typical for stretching vibrations () of the carbonyl group in the carboxyl of gallic acid in the IR spectra of the obtained substances, confirm the formation of an ester. In addition, a decrease in the peak characteristic of the valency variation () of the OH group of gallic acid indicates that the hydroxyl group in the carboxyl is replaced by an alcohol residue. In the IR spectrum of 7 compounds, a

nonspecific decrease in the intensity of absorption lines 5 and 6 is observed. It can be argued that this is due to the esterification of a monosubstituted methylol group in trimethylolurea and the formation of intramolecular hydrogen bonds between di-substituted methylols in another amino group. This idea is also supported by the idea that the disubstituted methylols of the parent trimethylolurea are passive due to intramolecular hydrogen bonding.

In the mass spectra of the obtained substances, the high intensity of the peak belonging to the main molecular ion indicates the stability of the compounds.

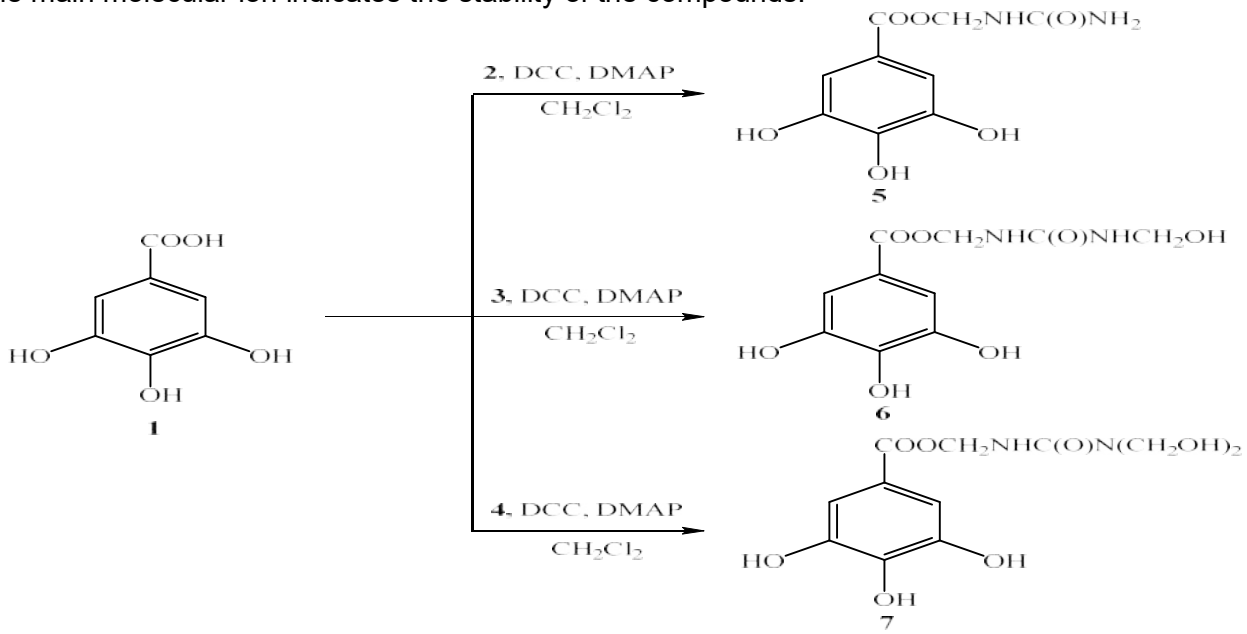


Fig.1 Scheme of ureidogallates synthesis.

CONCLUSIONS. The fact that the synthesis of derivatives of methyl urea with gallic acid occurs under mild conditions, somewhat easier, leads to their further research. In particular, the study of the biological activity of the obtained esters will serve as the center of our future research.

References.

1. Асқаров И.Р., Хожиматов М.М., Исақов Х., Қирғизов. Метилолмочевинанинг айрим ҳосилалари синтези//Илмий хабарнома. Андижон. -2014.-№4. -Б. 28-30. (Askarov IR, Khojimatov MM, Isakov H., Kirgizov. Synthesis of some derivatives of methyl urea // Scientific Bulletin. Andijan. -2014, №4, 28-30)

2. Асқаров И.Р., Исаев Ю.Т., Махсумов А.Г., Қирғизов Ш.М. Органик кимё.–Т.: Ғ. Ғулом, 2012. - 319-323б (Askarov I.R., Isaev Yu.T., Makhsumov AG, Kyrgyzov Sh.M. Organic chemistry. T.: G'. Gulom, 2012, 319-323).

3. Исақов Х., Усманов С., Горбунова В.В. ИК-спектроскопические исследования соединений тиомочевины с формальдегидом // Узбекиский химический журнал. -Тошкент.-1994. -№5. -С. 10-35. (Isaqov X., Usmanov S., Gorbunova V.V. IR-spectroscopic studies of thiourea compounds with formaldehyde // Uzbek chemical journal, Tashkent, 1994, №5, 10-35)

4. Методы получения химических реактивов и препаратов. Москва, ИРЕА, Выпуск 15, 1967, стр. 187 (Methods of obtaining chemical reagents and drugs. Moscow, IREA, No 15, 1967, 187)

5. Final Report on the Amended Safety Assessment of Propyl Gallate // International Journal of Toxicology journal. - 2007. - Vol. 26, 3. - P. 89-118. (Заключительныйотчетподополненнойоценкебезопасностипропилгаллата // Международныйжурналтоксикологии. – 2007)

6. Jerker Widengren, Andriy Chmyrov, Christian Eggeling, Per-Åke Löfdahl, and Claus A. M. Seidel. Strategies to Improve Photostabilities in Ultrasensitive Fluorescence Spectroscopy // The Journal of Physical Chemistry journal A. - 2007. - Vol. 111, 3, 429-440. (Джеркер Виденгрен, Андрей Чмыров, Кристиан Эггелинг, Пер-Оке Лёфдал и Клаус А. М. Зайдель. Стратегии улучшения фотостабильности в сверхчувствительной флуоресцентной спектроскопии // Журнал физической химии, журнал А. - 2007. - Том.)