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Synthesis and analysis of 1-octen-3-ol, the main flavour component of mushrooms

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The most abundant volatile occurring in mushrooms and responsible for the mushroom odour is 1-octen-3-ol. To meet the demand for a flavour compound yielding a mushroom odour a study was carried out on the possibility of obtaining 1-octen-3-ol synthetically. On the basis of literature data and experiments performed, the synthesis of this compound was carried out by two methods, i.e. by GRIGNARD reaction between acrolein and amyl iodide and by selective reduction of 1-octen-3-on. The purity of the 1-octen-3-ol obtained was determined by GLC chromatography and by spectroscopic methods. The compound obtained by GRIGNARD reaction had its IR, ^{13}C NMR spectra and GLC chromatogram identical with those of the standard. The yield of 1-octen-3-ol by GRIGNARD reaction was 65%, while the reduction of the ketone to the alcohol gave a yield of 90%.

Introduction

Insufficient production of mushrooms and their high price determine the importance of search for compounds of mushroom flavour, which would be applicable for the aromatization of food, i.e. concentrates, powdered soups, sauces, certain kinds of cheese etc. As it has been found, the volatile compound occurring in the greatest amount in the mushrooms is 1-octen-3-ol [1]. Even in high dilution this compound exhibits a strong mushroom flavour. Its threshold value is 0.001 ppm in water and 0.01 ppm in milk [2].

The paper presented demonstrates the possibility of obtaining this compound via chemical synthesis in the maximum pure state.

On the basis of the literature available and general methods of chemical synthesis, the following processes of obtaining 1-octen-3-ol have been considered.

1. Synthesis of 1-octen-3-ol in the GRIGNARD reaction between amylomagnesium bromide and acrolein [3].

$$C_5H_{11}MgBr + CH_2{=}CH{-}CHO \xrightarrow[-Mg(OH)Br]{H_2O} CH_2{=}CH{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}C_5H_{11}.$$

   The yield of the reaction is about 65—85%. The disadvantage is the necessity of application of great amounts of anhydrous ethyl ether as a solvent.
2. Obtaining of 1-octen-3-ol by selective reduction of the suitable ketone i.e. 1-octen-3-on, according to the following reaction:

$$C_5H_{11}-\underset{\underset{O}{\|}}{C}-CH=CH_2 \xrightarrow{H_2} C_5H_{11}-\underset{\underset{OH}{|}}{CH}-CH=CH_2$$

The ketone can be obtained by one of the following methods:

2.1. By the aldol condensation between heptanone-2 and formaldehyde.
This reaction is relatively easy to be carried out, however the formation of other by-products is unavoidable. 1-Octen-3-on is thought to be the dominating product when the proper conditions of the reaction are chosen i.e. the proper ratio of substrates, adequate time, temperature and with sufficiently selective catalytic agents used [4].

$$C_5H_{11}-\underset{\underset{O}{\|}}{C}-CH_3 + CH_2O \xrightarrow[-H_2O]{NaOH} C_5H_{11}-\underset{\underset{O}{\|}}{C}-CH=CH_2$$

2.2. By MANNICH reaction between heptanone-2, formaldehyde and dimethylamine hydrochloride.

$$C_5H_{11}-\underset{\underset{O}{\|}}{C}-CH_3 + CH_2O + (CH_3)_2NH\cdot HCl \xrightarrow[-HCl]{} C_5H_{11}-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-N\begin{matrix}CH_3\\CH_3\end{matrix}\cdot HCl$$

$$\xrightarrow[-(CH_3)_2NH]{NaHCO_3} C_5H_{11}-\underset{\underset{O}{\|}}{C}-CH=CH_2 .$$

In this reaction, besides the compound I, other byproducts are also formed, so disadvantage of this method is the difficulty in obtaining pure β-amino compound (compound I) which after deamination gives 1-octen-3-on [5].

2.3. In the reaction of acid chlorides [6]

$$C_5H_{11}-\overset{\overset{O}{\|}}{C}\begin{matrix}\diagup\\\diagdown\end{matrix}Cl + CH_2=CH_2 \xrightarrow{AlCl_3} C_5H_{11}-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-Cl \xrightarrow{140\,^\circ C}$$

$$C_5H_{11}-\underset{\underset{O}{\|}}{C}-CH=CH_2$$

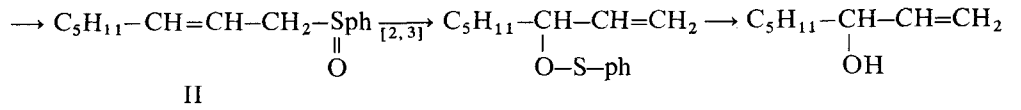
The method depends on subjecting capronyle chloride to the activity of ethylene and next, on thermal dehalogenization of the β-chloroketone formed. The yield of the whole process is about 30% and of the last stage about 85%.

3. Recently, 1-octen-3-ol has been obtained by the condensation reaction of heptanal with methylosulfinylobenzene to the proper vinyl sulfoxide (compound I), which undergoes isomerization to allyl sulfoxide (compound II) and through sigmatropic rearrangement [2.3], giving the proper allyl alcohol [7].

$$C_6H_{13}CHO + CH_3-\underset{\underset{O}{\|}}{S}-ph \xrightarrow[-H_2O]{} C_6H_{13}-CH=CH-\underset{\underset{O}{\|}}{S}-ph$$

I

$$\longrightarrow C_5H_{11}-\bar{C}H-\overset{\ominus}{\bar{C}}H-\bar{C}H-\underset{\underset{O}{\|}}{S}-ph$$



II

The method is useless however as far as eatables are concerned as sulphuric bonds are toxic and yields unpleasant odour. Also, the cost of obtaining 1-octen-3-ol according to this method is high.

Of the procedures described above the methods 1, 2.1 and 2.3 were chosen as the most promising in obtaining 1-octen-3-ol high purity, which could be applied in production of food.

Experimental

Reagents

The reagents used in the synthesis were supplied by Polish Chemical Reagents in Gliwice. Acrolein was obtained by dehydrogenation of glycerine with a mixture of potassium sulfate and potassium bisulfate [8], directly before it was used in GRIGNARD reaction.

Methods

1. *Synthesis of 1-octen-3-ol in* GRIGNARD *reaction*

300 ml of anhydrous ethyl ether, 21 g of magnesium filings for GRIGNARD synthesis and 0.5 g of iodine were placed in a three necked 1000 ml round-bottomed flask, equipped with a mechanical stirrer, a reflux condenser of high efficiency and a dropper. The condenser and the dropper were protected by pipes with anhydrous calcium chloride. The flask was slowly heated in water bath up to the boiling point of the content and then a 80 ml of freshly distilled amyl iodide was slowly added. When the reaction proceeded too violently, the flask was cooled in water with ice. After the whole amount of amyl iodide was added, the mixture was still heated for 30 min, with continuous stirring. Then, the mixture was cooled in water with ice down to 5 °C and then, 41 ml of acrolein dissolved in 150 ml of ether was added. When the higly exothermic reaction stopped, the flask was kept at room temperature for 1 h. After the reaction was completed the liquid from over the magnesium filings was transfered to 500 ml of water. The white precipitate of hydroxy magnesium iodide that formed in the water was acidified with 100 ml of 30% sulfuric acid. Next the ether layer was separated from the water layer which was then 5 times extracted with ether. The combinated ether solutions were dried with andydrous magnesium sulfate. After the ether was distilled off, the crude 1-octen-3-ol was distilled under vacuum. The product obtained was 51 g of colourless liquid with the main fraction collected at 72—75 °C and 15 mm Hg, which means the yield of the process was 67%. In order to obtain 1-octen-3-ol of higher purity, the compound was subjected to vacuum redistillation in a column filled with FENSKY rings.

2. *Synthesis of 1-octen-3-ol by aldol condensation*

In a two necked 250 ml flask equipped with a mechanical stirrer and a dropper, 61 ml of heptanone-2 was placed. Then, during strong stirring at room temperature, 20 ml of water, 40 ml of formalin (36%) and 20 ml of 10% sodium hydroxide was added to the flask. After 5 h of intensive stirring the flask was heated in water bath at 50 °C for 2 h. After 24 h the reaction mixture was neutralized with 20 ml of 10% hydrochloric acid. Then, the organic and water layers were separated and the latter was extracted two times with benzene. The combined organic solutions were dried with anhydrous magnesium sulfate concentrated in a vacuum evaporator and distilled under vaccum. The product obtained was a mixture of ketones with boiling points between 60 and 85 °C at 15 mm Hg.

Then, the ketone fraction obtained was subjected to MEERWEIN-PONNDORF-VERLEY reduction.

30 g of the fraction was placed in a 500 ml flask, equipped with VIGREUX column connected with LIEBIG condenser. Next, 300 ml of anhydrous isopropyl alcohol and 30 ml 1 M solution of aluminium isopropylate in

isopropyl alcohol, were added. The flask was heated up to the point providing a temperature between 60 to 70 °C at the top of the column. Simultaneously, the acetone which was forming in the reaction was distilled off at a rate of 5—10 drops per min. The heating was stopped when the test of the distillate with 2,4-dinitrophenylhydrazine to prove the acetone presence in the distillate gave the negative result. When the isopropyl alcohol was distilled off, 100 ml of 20% sulfuric acid were added to the remaining mixture. The upper layer was washed with water for the second time, dried with anhydrous magnesium sulfate and subjected to vacuum distillation.

The main fraction was collected at 70—80 °C and 15 mm Hg. The product obtained was 24 g of colourless liquid of mushroom flavour. The liquid mixture was redistilled in a column filled with FENSKY rings giving 13 g of 1-octen-3-ol.

Analysis

IR spectra of the compounds studied were measured within the range of 4000—5000 cm^{-1} by 75 IR Specord spectrometer. The compounds were placed in 0.24 mm thick cuvettes in chloroform.

^{13}C-NMR spectra were taken by FX 900 Jeol spectrometer by Noise Band Decoupling technique, with TMS as a standard.

Gas Chromatography analysis was performed with 2700 Varian Aerograph. The glass column was 3 m long, outer diameter 3 mm, packed with 15% Carbowax 20 M terminated with terephthalic acid on 80/100 mesh, acid washed DMCS treated chromosorb W. Nitrogen was used as a carrier gas at a flow rate of 20 ml/min. The column temperature was held isothermally at 120 °C.

Results and Discussion

Synthesis of 1-octen-3-ol by GRIGNARD *reaction*

1-octen-3-ol obtained by the reaction between amylomagnesium iodide and acrolein with the yield of 70%, was found to have IR spectrum identical with the standard, however its GLC chromatogram (Fig. 1), proved the presence of other components, so the purity of the compound was 91%. The preparation was additionally purified by vacuum redistillation using a column after which its chromatogram showed only one peak.

The purity of the compound was higher than 99%. The identification and determination of 1-octen-3-ol can be accurately performed by the ^{13}C-NMR method. In ^{13}C-NMR spectrum registered by Noise Band Decoupling (NBD) technique, each carbon atom is responsible for one signal and each has a significantly different chemical shift in respect to the standard (Fig. 2) [9].

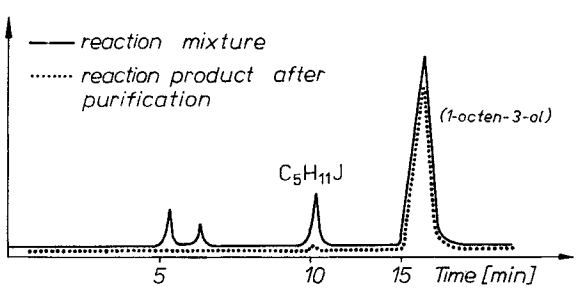


Fig. 1.
Purity of 1-octen-3-ol obtained by the GRIGNARD method

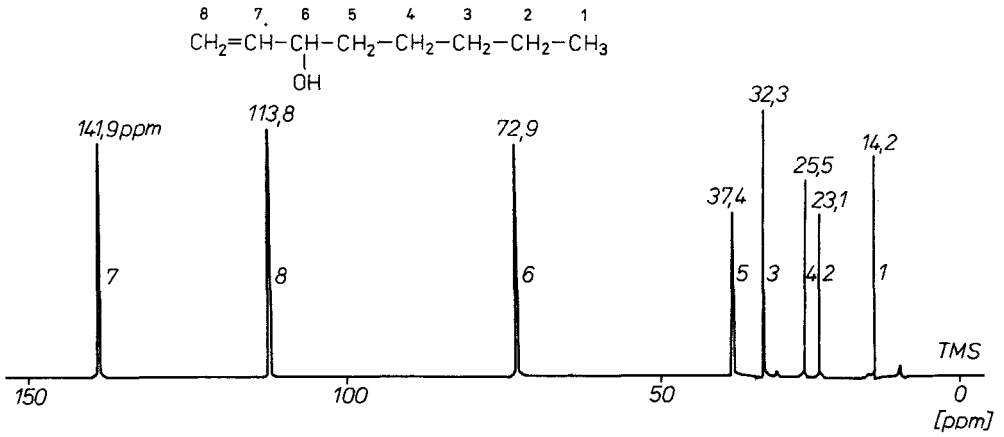


Fig. 2.
^{13}CNMR spectrum of 1-octen-3-ol obtained by the GRIGNARD method

Synthesis of 1-octen-3-ol by aldol condensation

Aldol condensation between heptanone-2 and formaldehyde catalyzed with sodium hydroxide was found to give a mixture of ketones and other by-products. In the IR spectrum of the reaction mixture, presented in Fig. 3, the band at 1660 cm^{-1} is due to a carbonyl group conjugated with the double bond, while the peak at 1620 cm^{-1} is due to the double bond. As it follows from the spectrum presented, the initial ketone is still present in a high concentration (the band C = 0 at 1710 cm^{-1}), which is also conformed by the chromatogram presented in Fig. 4. Such a great amount of the heptanone-2 which did not take part in the reaction, made the yield of the whole process considerably lower. On the other hand, the application of higher amount of formaldehyde is rather not taken into account, because of the by-products that can appear in great amounts.

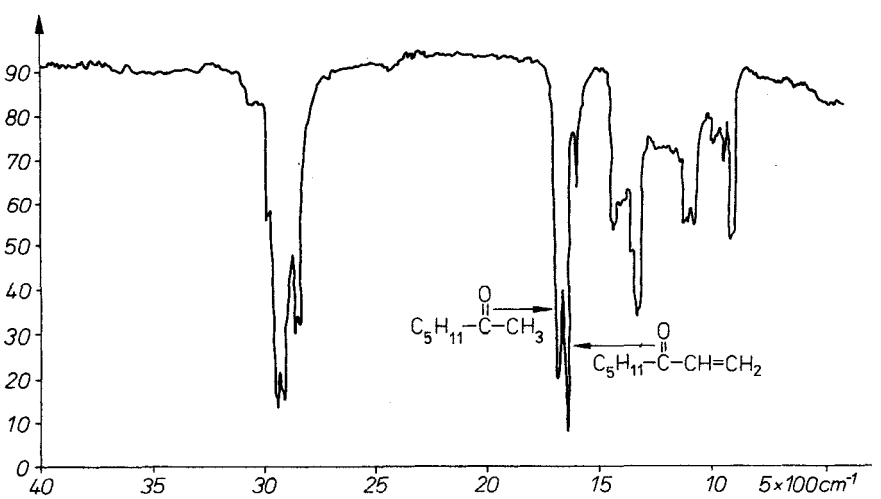


Fig. 3.
IR spectrum of reaction products obtained acc. aldol condensation method before reduction

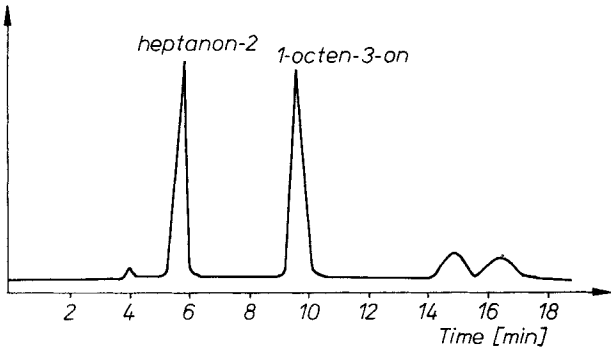


Fig. 4.
Gas chromatogram of the reaction products obtained acc. aldol condensation method before reduction

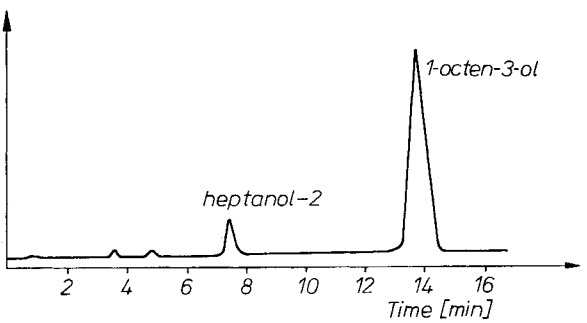


Fig. 5.
Gas chromatogram of the reaction products obtained acc. aldol condensation method after reduction and purification

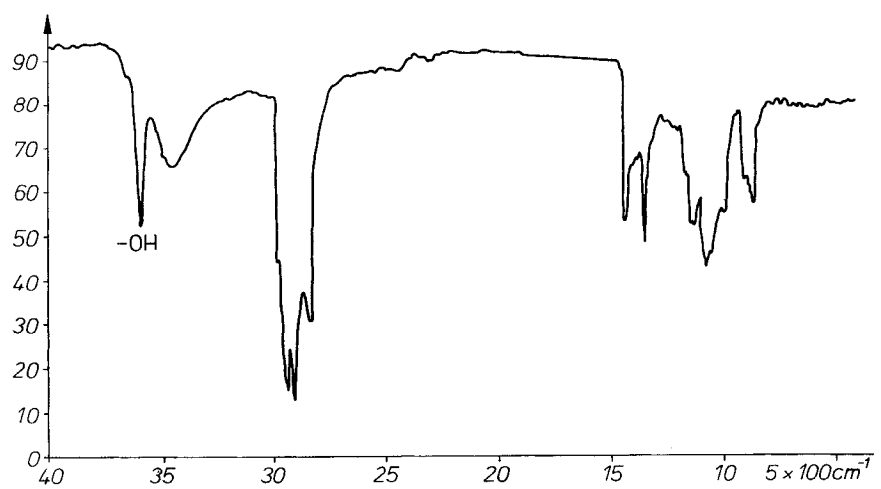


Fig. 6.
IR spectrum of reaction product obtained acc. aldol condensation method after reduction and purification

The mixture of ketones was not separated but subjected to selective reduction of carbonyl group with the double bond conserved, taking into regard the instability of 1-octen-3-on as α/β-unsaturated ketone undergoing polymerization. The mixture yielded a fruit-herbal flavour, i.e. the flavour significantly different from the mushroom odour of the mixture after the reduction. The appearance of the mushroom odour after the reduction proves, that a new compound was formed. As it can be seen from the chromatogram (Fig. 5) and IR spectrum (Fig. 6), in which carbonyl peaks disappeared and hydroxy groups vibrations appeared, a mixture of alcohols was obtained after reduction. The stable alcohols were separated by normal vacuum distillation in a column, so the 1-octen-3-ol obtained could be additionally purified. The yield of 1-octen-3-ol as calculated in respect to the initial heptanone-2 amount, was 25% and its purity was about 91%.

Finding such a low efficiency of the method described above, pure 1-octen-3-on was synthesised according to the other method described by WOODWARD [10] with using capronyl chloride and ethylene as the initial compounds. The ketone obtained by this method was subjected to reduction. The yield of 1-octen-3-on was 40% while the yield of the selective reduction of ketone to alcohol was over 90%. The resulting 1-octen-3-ol was purified according to the method described above and its purity as determined by GLC chromatography was over 97%.

Conclusions

1. GRIGNARD reaction between amyl iodide and acroleine gave a spectroscopically pure 1-octen-3-ol exhibiting a mushroom flavour with the yield of 65%.
2. To meet the requirements a large scale production is necessary. The most suitable method seems to be that of aldol condensation followed the reduction of ketone to alcohol with the double bond conserved. The condition required for this method to be profitable is the obtaining of 1-octen-3-on in excess with respect to the other products of the condensation step. Relatively pure 1-octen-3-on can be obtained in the reaction between capronyl chloride and ethylene.
3. In the aldol condensation method, the reaction mixture exhibits mushroom odour only after reduction which unequivocally means that it is 1-octen-3-ol and not 1-octen-3-on.
4. In order to determine the purity of 1-octen-3-ol, GLC chromatography and ^{13}C NMR method were found to be the most useful.

Zusammenfassung

S. WNUK, S. KINASTOWSKI und E. KAMIŃSKI: Synthese und Analyse von 1-Octen-3-ol, der Hauptaromakomponente von Pilzen

Die am häufigsten vorkommende und für das Pilzaroma verantwortliche flüchtige Verbindung ist 1-Octen-3-ol. Um den Forderungen nach Bereitstellung von Verbindungen mit einem Pilzaroma nachzukommen, wird eine Studie über die Möglichkeiten der synthetischen Herstellung von 1-Octen-3-ol angefertigt. Auf Grund von Literaturangaben und eigenen Untersuchungen wird die Synthese dieser Verbindung nach zwei Verfahren, der GRIGNARD-Reaktion zwischen Acrolein und Amyljodid sowie durch selektive Reduktion von 1-Octen-3-on ausgeführt. Die Reinheit des erhaltenen 1-Octen-3-ol wird durch Gaschromatographie und spektroskopische Methoden bestimmt. Die nach der GRIGNARD-REAKTION erhaltene Verbindung ist gemäß IR- und ^{13}C NMR-Spektren sowie GLC-Chromatogramm mit dem Standard identisch. Die Ausbeute von 1-Octen-3-ol nach der GRIGNARD-Reaktion beträgt 65% und diejenige der Ketonreduktion des Alkohols 90%.

Резюме

С. Внук, С. Кинастовски и Е. Камински: Синтез и анализ 1-октен-3-ола — основным компонентом аромата грибов

1-остен-3-ол является наиболее часто встречающимся и отвечающим за аромат грибов летучим соединением. Чтобы удовлетворить требования заготовки соединений с ароматом грибов, проводилась экстпертиза о возможностях синтетического получения 1-октен-3-ола. На основе литературных данных и собственных исследований синтез этого соединения проводился двумя способами, реакцией Гринярда между акролеином и амилйодидом и путем избирательной редукции 1-октен-3-ола. Чистота полученного 1-октен-3-ола определялась с помощью газовой хроматографии и спектроскопическими методами. Полученное при реакции Гринярда соединение согласно ИК- и ^{13}C NMR-спектрам идентично со стандартом. Выход 1-октен-3-ола после реакции Гринярда составляет 65%, а при кетоновой редукции алкоголя 90%.

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