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**ELECTROCHEMICAL METHOXYLATION OF ISOPULEGOLE (1)
AND α -PINENE (2)****

In the course of our investigation on electrochemical synthesis the electrochemical methoxylation of isopulegole (1) and α -pinene (2) was carried out. In the case of 1 product obtained was a very complex mixture with 3,4-dimethoxy-p-8(9)-menthene (3) as the major component. The methoxylation of 2 yields sobrerol dimethyl diether [6,8-dimethoxy-p-1(2)-methane] (4) as the major component. The electrochemical methoxylation of 3-carene, α -pinene or limonene gives in the described conditions a mixture of several compounds difficult to separate into individual components.

Methoxyl derivatives of acyclic and monocyclic terpene derivatives have an attractive odour impression. Examples of these derivatives are 7-methoxyelgenole (osirole), 7-methoxycitronellal and menthol methyl ether [1]. Their attractive flavour is also confirmed by our investigations on electrochemical synthesis of methoxyl derivatives of acyclic aldehydes and terpene alcohols [2].

In the present paper we aim to show some results of our investigation on the synthesis of methoxyl derivatives containing cyclic (p-methane) carbon skeleton. Taking into account these assumptions and availability of raw materials the electrochemical methoxylation of isopulegole 1 and α -pinene 2 was carried out. (Fig. 1).

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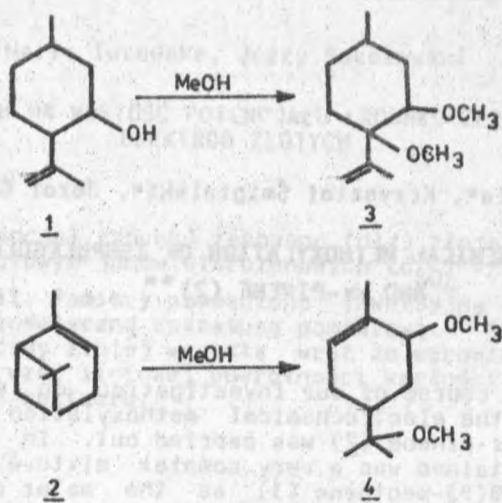


Fig. 1

Isopulegole 1 is an easily available compound as it is an intermediate in the synthesis of l-menthol from d-citronellal.

In our experiments isopulegole, chemical purity 80%, containing 20% of neo-isopulegole, was used. The process of electrochemical methoxylation was carried out in a typical three-electrode non-diaphragm cell. The reaction took place in methanol excess at a temperature close to a room temperature (28°C), the base electrolyte was sodium p-toluenesulfonate. After supplying an electric charge of 1 to 5 F/mol, the process was stopped and after distillation of unreacted methanol the product was extracted with ether and separated by gas chromatography. It was found that the reaction was complex and in each case the product obtained was a very complex mixture of many compounds. The IR spectral analysis of the reaction mixture showed that apart from ethers also other functional groups such as ketone, hydroxyl and olefine groups were present. The raw product of electrosynthesis was divided into fractions depending on boiling point. The fraction with boiling point of 80 to 110°C/1,0 mm Hg constituted 40% of the total and was the most interesting one from the perfumery's point of view. It contained about 70% of the major component. This compound was separated in a pure state by column chromatography (Kieselgel 60: petroleum ether/ether 98 : 2), and

its structure was determined by ^1H NMR and MS spectra analysis. The MS spectrum contained a distinct molecular peak at 198, while the ^1H NMR spectrum revealed the presence of two methoxyl groups at $\delta = 3.25$ and 3.15 ppm. Other characteristic signals were as follows: a triplet at $\delta = 4.42$ (1 H, $J = 6$ Hz), a multiplet at $\delta = 4.87$ (2 H) and a deformed singlet at $\delta = 1.53$ (3 H) and doublet at $\delta = 0.85$ ppm (3 H, $J = 7$ Hz).

On the basis of these data the compound structure was proposed as 3,4-dimethoxy-p-8(9)-menthene 3. This structure was also confirmed by IR 3090, 1655 ($\text{C}=\text{CH}_2$), 1125, 1100, 1060, 1020 cm^{-1} ($\text{C}-\text{O}-\text{C}$).

The other compound subjected to the electrochemical methoxylation was α -pinene 2. α -pinene is a cheap and easily available terpene hydrocarbon present in abundance, among others, in Polish turpentine. Due to the presence of a double bond and cyclobutane ring the component was expected to methoxylate and the reaction product was expected to be a compound (or a mixture of several compounds) with a preserved pinene skeleton or with an open cyclobutane ring, as it often occurs in many other transformations of α -pinene.

The process of electrochemical methoxylation was carried out in the same conditions as in the case of isopulegole. The main and almost only reaction product with 62 to 65% yield appeared to be sobrerole dimethyl ether (6,8-dimethoxy-p-1(2)-menthene) 4 whose structure was determined by ^1H NMR spectrum analysis.

^1H NMR: vinyl proton $\delta = 5.31$ ppm (1 H, br.d) two methoxyl groups $\delta = 3.24$ and 3.05 ppm (3 H each, s), proton at C-6 carbon $\delta = 3.25$ ppm/1 H, the signal overlaps with the singlet of methoxyl group 3.24 ppm/1- CH_3 group $\delta = 1.63$ ppm (3 H, br. s), gem methyl groups $\delta = 0.98$ and 0.96 ppm (6 H, two s). It is worthwhile to mention that in the ^1H NMR spectrum two additional singlets which are close to the main protons of methoxyl groups are observed ($\delta = 3.23$ and 3.03 ppm). This gives evidence that the product is a mixture of isomers with different C_6-OCH_3 group configurations. According to gas chromatography the mixture of these two compounds is in the ratio 5 : 1. It should be stressed that electrochemical methoxylation of α -pinene is a selective process resulting in a satisfactory yield of sobrerole dimethyl ether. On the other hand,

the attempts of methoxylation of the other, main component of turpentine, β -carene, in the conditions described above result in a complex reaction which yields a mixture of several compounds difficult to separate into individual components. A similar character has the electrochemical methoxylation of β -pinene and limonene.

EXPERIMENTAL

Apparatus

Typical three-electrode electrolyzer (volume 0.035 dm³) provided with a reflux condenser.

Cathodes: Platinum 0.2 x 0.2 x 0.02 dm

Anode: Platinum 0.2 x 0.2 x 0.02 dm.

The anode is placed centrally between the cathodes in a distance of 0.3 dm.

Electrolyte: Sodium *p*-toluenesulfonate (0.5 g) in methanol (0.7 mol). Current density: 5.0 A/dm².

Performance

The substrate (0.025 mol) is added to the cell and the mixture is electrolysed at 28°C until 3 F/mol has been delivered. The excess methanol is evaporated in vacuo and the product extracted with ether. The extract is washed with water, dried with sodium sulfate, and the solvent evaporated. When isopulegole 1 is used, the remaining is fractionally distilled to collect fraction boiling 80-110°C/1.0 mm Hg. The major component-3,4-dimethoxy-*p*-8(9)-menthene 3 was isolated by column chromatography and its structure determined as shown above.

In case of α -pinene 2 the remaining is fractionally distilled to give 0.016 mol of 6,8-dimethoxy-*p*-1(2)-menthene 4; b.p. 130-133°C/20 mm Hg; $n_D^{19} = 1.4658$; IR (film): 2980, 2940, 2830, 1650, 1455, 1375, 1190, 1150, 1140, 1100, 1080, 910, 800 cm⁻¹.

REFERENCES

- [1] S. A r c t a n d e r, Perfume and Flavor Chemicals, Montclair, New York 1969.
- [2] J. G ó r a, K. Ś m i g i e l s k i, J. K u l a, Zesz. Nauk. PŁ, Techn. Chem. Spoż., 39, 115 (1985).

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ELEKTROCHEMICZNE METOKSYLOWANIE IZOPULEGOLU (1)
I α -PINENU (2)

Przeprowadzono elektrochemiczne metoksylowanie izopulegolu (1) i α -pinenu (2). W przypadku 1 powstaje mieszanina składająca się z bardzo wielu związków chemicznych; głównym składnikiem jest 3,4-dimetoksy-p-8(9)-menten (3). Metoksylowanie 2 prowadzi głównie do dieteru dimetylowego sebreolu [6,8-dimetyloksy-p-1(2)-menten] (4). Elektrochemiczne metoksylowanie w podanych warunkach β -karenu, β -pinenu i limonenu prowadzi do trudnej do podzielenia mieszaniny, składającej się z kilku związków chemicznych.