Thin layer chromatography (TLC) was carried out on glass plates (4.5×6.0 cm) with a fixed layer of silica gel L (Chemapol, Czech Republic).

The sponges were collected by the Sigsby trawl from a depth of 400 m in the Tasman Sea during the trip No. 7 of the Research Ship "Akademik Oparin" in September, 1988. The taxonomic determination of the sponge was carried out by V. M. Koltun (Zoological Institute, RAS, St. Petersburg).

Isolation of geranylfarnesylacetone (1). The lyophilically dried sponge was thoroughly extracted by hexane and then chloroform. The combined extracts were evaporated to dryness, and the residue (3 g) was chromatographed on a column with silica gel in a petroleum ether—chloroform system. The eluates containing, according to the TLC data, compounds less polar than cholesterol were combined and concentrated *in vacuo*. The residue was chromatographed by HPLC in a petroleum ether—ethyl acetate (5 : 1) system to obtain compound **1** (3 mg) as an optically inactive yellowish oil (yield 0.0074%), R_f 0.79 (in a hexane—ethyl acetate (3 : 1) system; R_f of cholesterol = 0.33), $C_{28}H_{46}O$. MS, *m/z* (I_{rel} (%)): 398 [M^+] (24); 383 (2); 355 (4); 340 (7); 329 (19); 316 (4); 272 (24); 261 (24); 204 (30); 191 (28); 136 (52); 135 (90); 81 (100); 69 (95); 57 (15); 43 (30). The ^{1}H NMR spectral data are presented in Table 1.

Reduction of geranylfarnesylacetone (1). Compound **1** (1.9 mg) was reduced by sodium borohydride in methanol at room temperature for 10 min. After a standard treatment, compound **2** (1.9 mg, 100%) was obtained as a yellowish oil, R_f 0.50 (in a hexane—ethyl acetate (3 : 1) system; R_f of cholesterol = 0.33), $C_{28}H_{48}O$. MS, *m/z* (I_{rel} (%)): 400 [M^+] (3.4); 382 (0.8); 332 (12); 317 (2); 289 (3); 279 (15); 269 (10); 264 (10); 263 (10); 204 (31); 191 (20); 163 (20); 161 (23); 137 (100); 136 (93); 135 (68); 81 (100); 69 (95); 68 (100); 43 (95). The ^{1}H NMR spectral data are presented in Table 1.

Acetylation of alcohol (2). Compound **2** (1.6 mg) was acetylated in a acetic anhydride—pyridine (1 : 1) mixture (1 mL) at room temperature for 16 h. The compound was obtained in a 100% yield (1.8 mg) as a yellow oil. ^{1}H NMR ($CDCl_3$), δ: 2.03 (s, 3 H, CH_3CO—), and other spectral data are presented in Table 1.

References

1. T. N. Makarieva, V. A. Stonik, A. S. Dmitrenok, V. B. Krasokhin, V. I. Svetashev, and M. V. Vysotskii, *Steroids*, 1995, **60**, 316.
2. T. N. Makarieva, V. A. Stonik, L. P. Ponomarenko, and A. I. Kalinovsky, *J. Chem. Res. (S)*, 1996, No. 10, 468.
3. T. N. Makarieva, V. A. Stonik, I. I. Kapustina, V. M. Boguslavsky, A. S. Dmitrenok, V. I. Kalinin, L. M. Cordeiro, and C. Djerassi, *Steroids*, 1993, **58**, 508.
4. V. A. Stonik, T. N. Makarieva, and A. S. Dmitrenok, *J. Nat. Prod.*, 1992, **55**, 1256.
5. R. Kazlauskas, P. T. Murphy, and R. J. Wells, *Experientia*, 1978, **34**, 156.
6. J. P. Ferozou, J. Borreuer-Bonnefant, and J. J. Meusy, *Experientia*, 1977, **33**, 290.

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Preconcentration of poorly volatile impurities in thin-layer chromatography by thermodesorption of a volatile matrix

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A method for preconcentration of poorly volatile impurities by continuous thermodesorption of the major component on a TLC plate is proposed. The method provides multiple (200—500) concentration of the organic impurities present in the initial solution. A simple device for such concentration is suggested.

Key words: preconcentration, poorly volatile impurities, aqueous solutions, thin-layer chromatography, thermodesorption.

Preconcentration is a way of increasing the accuracy of an analytical determination.[1] Development of facile methods and schemes for sample enrichment is of considerable interest from the practical viewpoint.[2—4]

The so-called method of continuous evaporation for thin-layer chromatography (TLC) has been reported; according to this method, some limited evaporation of the mobile phase during separation in the working area

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of a plate narrows down the zones of the separated substances.[5—7]

In this paper, we describe a facile method for the preconcentration and preliminary isolation of impurities that are readily eluted under TLC conditions as linear zones. A volatile matrix (the major component) of the specimen being analyzed is used as the mobile phase, and the process of its evaporation is induced in a definite narrow zone on the TLC plate.

Experimental

A TLC plate coated with an adsorption layer based on silica gel was placed in a relatively low (10—20 mm) cell, which was covered with a lid containing a slot for the plate (see Ref. 8). The greater part of the plate remained outside the development chamber (the cell). An aqueous solution containing the impurities to be analyzed (in a concentration of 200 μg L^{-1}) was placed in the cell in such a way that the plate was immersed in the solution by several millimeters. Solutions of water-soluble dyes, naphthol red, 80 μg L^{-1}, methyl red, 50 μg L^{-1}, and brilliant cresyl blue, 70 μg L^{-1}, were used as model solutions. The scheme of the experiment is shown in Fig. 1.

Upon immersion of the plate, its surface was rapidly wetted by the aqueous solution being analyzed up to a length of 5—6 mm, and then it fell into an area that was blown with a stream of hot air coming from a heated blower resembling that of a household fan. In this area, the major component of the matrix (*i.e.*, water) efficiently evaporated, while the nonvolatile components being analyzed (dyes) accumulated on the plate as a relatively narrow linear band (0.5—3.0 mm, depending on the retention parameter R_f).

The degree of preconcentration was determined as a ratio of the amount of the dye mixture in the preconcentrated zone to their known content in the initial solution taking into account the consumed amount of this solution:[1] $K = Q/q$, where q and Q are the amounts of dyes on the plate before and after preconcentration, respectively. The amount of the dyes was found as the product of the dye concentration in the initial solution by the solution volume needed to wet the lower section of the plate. The time of preconcentration (20—30 min) was sufficient for a clear colored zone to appear.

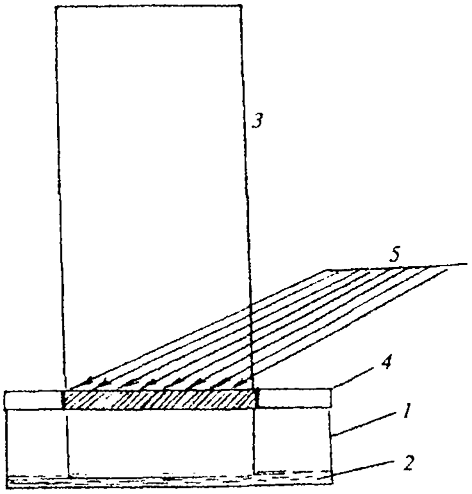

Fig. 1. Scheme of the preconcentration of impurities from a volatile matrix: *1*, cell; *2*, analyzed solution; *3*, TLC plate; *4*, the lid with a slot for a TLC plate; *5*, direction of the hot air stream.

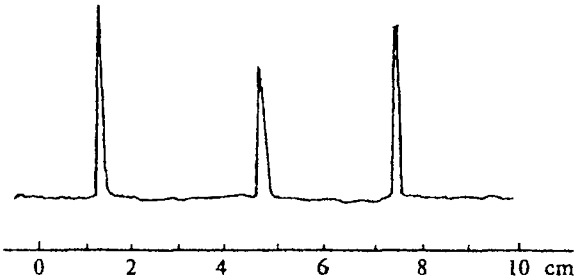

Fig. 2. Chromatogram of an aqueous solution of the dyes (*1*, brilliant cresyl blue, 70 μg L^{-1}; *2*, methyl red, 50 μg L^{-1}; *3*, naphthol red, 80 μg L^{-1}) after preconcentration by water thermodesorption on a plate and separation in a saturated chamber (elution time 30 min, propan-2-ol as the eluent).

After preconcentration, the linear zone containing the dye mixture was separated by standard TLC techniques.

All the experiments were carried out using Silufol TLC plates (Kavalier, Czech Republic; propan-2-ol was used as the eluent, elution time was 30 min). The chromatograms were scanned using a Shimadzu CS-920 high-speed densitometer (Japan) at a wavelength of 530 nm.

Results and Discussion

Figure 2 shows the chromatogram of a mixture of the dyes after its preconcentration and elution in propan-2-ol. The initial preconcentrated zone was a 2.6 mm wide rectangular band.

It can be seen from Fig. 2 that, according to densitometry, the quantitative composition of the concentrate corresponds to the initial composition to within the accuracy of determination.

The simple preconcentration procedure proposed here takes 20—30 min and makes it possible to attain a preconcentration ratio of 200—500 times and a degree of extraction of 92—97%.

References

1. N. M. Kuz'min and Yu. A. Zolotov, *Kontsentrirovanie sledov elementov* [*Preconcentration of Traces of Elements*], Nauka, Moscow, 1988, 289 pp. (in Russian).
2. Yu. A. Zolotov, *Analiticheskaya khimiya: problemy i dostizheniya* [*Analytical Chemistry: Problems and Achievements*], Nauka, Moscow, 1992, 285 pp. (in Russian).
3. K. Beyermann, *Organic Trace Analysis*, Ellis Horwood Limited Publishers, 1984.
4. *Kontsentrirovanie sledov organicheskikh soedinenii* [*Preconcentration of Traces of Organic Compounds*], Ed. N. M. Kuz'min, Nauka, Moscow, 1990, 268 pp. (in Russian).

5. K. I. Sakodynskii, V. V. Brazhnikov, S. A. Volkov, V. Yu. Zel'venskii, E. S. Gankina, and V. D. Shatts, *Analiticheskaya khromatografiya* [*Analytical Chromatography*], Khimiya, Moscow, 1993, 453 pp. (in Russian).
6. U. G. Kirchner, *Thin-Layer Chromatography*, J. Wiley, New York, 1978.
7. M. Sarsunova, V. Schwarz, and C. Michalec, *Chromatografia na tenkych vrstvach vo farmacii a v klinickey biochemii*, Bratislava, Osveta, 1977.
8. E. V. Truter, *J. Chromatogr.*, 1964, **14**, 57.

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The synthesis of menthone by ozonization of menthol

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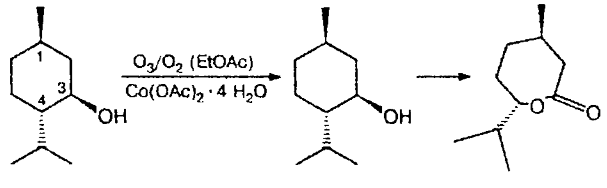
A selective method of oxidation of menthol to menthone by $Co(OAc)_2$-catalyzed ozonization in ethyl acetate or Freon-113 was developed.

Key words: menthol, oxidation, ozonization, catalyst, menthone, 3,7-dimethyl-6-octanolide.

In the synthesis of a series of optically active insect pheromones, oxidative decomposition of natural L-(−)-menthol has been carried out through the corresponding ketone obtained by oxidation of menthol with pyridinium chlorochromate.[1] At the same time, it is known that cyclic ketones can be obtained by aerobic oxidation of the corresponding cyclic alcohols, catalyzed by ruthenium and cobalt salts in the presence of acetaldehyde.[2] It is also known that the ozonolysis of arylsubstituted alicyclic compounds [3] or sulfides [4] in esters as solvents occurs selectively to yield expected stereoisomers of cycloaliphatic acids or, respectively, sulfoxides, while the ozonolysis of low-reactivity (with respect to electrophilic reagents) perfluoroolefins was successful in Freon-113 as a solvent.[5]

We found that the ozonization of racemic menthol (**1**) in EtOAc (5 mol-equiv. of O_3, ~25 °C) in the presence of a catalytic amount of $Co(OAc)_2 \cdot 4H_2O$ yields menthone (**2**) as a sole reaction product (according to GLC data). If the ozone—oxygen mixture is dosed so that a sevenfold molar excess of ozone is attained, not only is compound **2** formed, but also 3,7-dimethyl-6-octanolide (**3**) (*ca.* 10%) is detected in the reaction mixture. The identity of **3** to an authentic sample was determined by GLC.[6] When L-(−)-menthol **1a** was used instead of racemate **1**, (−)-(1*R*,4*S*)-menthone (**2a**) was obtained, which attests that the configuration at the C(1) and C(4) atoms is completely retained upon ozonization.

The ozonization of **1** in a solution of Freon-113 was carried out at a lower temperature because of high volatility of the Freon. When a fivefold excess of O_3 was passed through the reaction mixture at −30 to −40 °C, the conversion of alcohol **1** into ketone **2** reached 95%. The conversion of products **1** and **2** under the action of oxygen alone (without ozone) under the same conditions did not exceed 55%.



1, **1a** (1*R*,3*R*,4*S*) **2**, **2a** (1*R*,4*S*) **3**

Experimental

IR spectra were recorded on a Specord 75-IR spectrometer (thin film). The GLC analysis was performed on a Khrom-5 instrument with SE-30 silicon liquid (5%) as the stationary phase on Chromaton N-AW-DMCS (0.16—0.2 mm) at 50—250 °C (programmed temperature increase, 8 deg min^{-1}).

The ozonolysis of racemic menthol (1) or L-(−)-menthol (1a) in ethyl acetate. *A.* An ozone—oxygen mixture was passed at a rate of 10 L h^{-1} through a solution of **1** or **1a** (0.25 g, 1.6 mmol) and $Co(OAc)_2 \cdot 4\ H_2O$ (0.005 g) in 10 mL of EtOAc at 20 °C for 1 h (the ozonizer capacity was 8 mmol of

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