MICROBIOLOGICAL TRANSFORMATION PRODUCTS OF 1,6-DIMETHYLNAPHTHALENE

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As a continuation of our research [1-7] on the microbiological transformation of the dimethylnaphthalenes (DMN) we report the data on the identification of the transformation products of 1,6-DMN in the present communication.

EXPERIMENTAL

The transformation of 1,6-DMN was accomplished using the rinsed cells of Pseudomonas putida 71 N under the conditions described in [3]. The transformation products were isolated by TLC on Silufol UV-254 silica gel in the system: benzene–methanol–glacial CH_3COOH (45 : 4 : 2). The UV spectra were obtained on a Specord UV-VIS spectrophotometer in 96% ethanol. The IR spectra were taken as KBr pellets that contained 1 mg of the substance, and also in solution, on a UR-20 spectrophotometer. The NMR spectra were recorded on a Varian HA-100D spectrometer in d_6-acetone relative to TMS. The mass spectra were recorded on an MS-1302 mass spectrometer, with direct insertion of the sample into the ion source at an ionizing voltage of 30 eV and a vaporizer temperature of 20-100°C.

DISCUSSION OF RESULTS

Three compounds with R_f 0.47 (I), 0.39 (II), and 0.27 (III) were isolated as the transformation products of 1,6-DMN. The NMR spectra of these compounds contain a group of lines in the 7.3-9.1 ppm region, which are also present in the starting 1,6-DMN, with a total integral intensity that corresponds to six protons. This indicates that the naphthalene nucleus is retained in all of the analyzed products.

Compound (I). Ultraviolet spectrum (λ_{max}, nm): 227, 278 (272 sh, 287 sh). Infrared spectrum (ν, cm^{-1}): 415, 497, 542, 630, 706, 745, 782, 806, 828, 882, 912, 970, 1000, 1013, 1070: 1082, 1170, 1248, 1270, 1332, 1356, 1388, 1425, 1487, 1512, 1600, 1630, and a broad band in the 2800-3500 region with maxima at 2860, 2920, 3030, 3080, 3240, 3320. Mass spectrum (m/e, %): 172 (100, M^+), 157 (18), 143 (76), 141 (40), 129 (46), 128 (80), 115 (72). NMR spectrum (δ, ppm): 2.48 s (3H), 5.06 s (2H).

The presence of absorption bands at 1070, 1082, and 3320 cm^{-1} in the IR spectrum, caused by the stretching vibrations of C–OH, and also the appearance of the band of a free OH group at 3620 cm^{-1} in CCl_4 solution, indicates the presence of alcohol hydroxyl. The presence of a line with δ 5.07 (2H) in the NMR spectrum can serve as confirmation of this, and also the presence in the mass spectrum of peaks with m/e 155 (M^+-OH), 143 (M^+-HCO), and 141 (M^+-CH_2OH). Consequently, one of the substituents in product (I) is the CH_2OH group. The singlet line at 2.48 ppm (3H), observed in the NMR spectrum, belongs to the CH_3 group, the second substituent in the naphthalene nucleus of compound (I).

The fact that an intense peak of the molecular ion (M^+) with m/e 172 is observed, and all of the presented data, make it possible to identify compound (I) as being hydroxymethylmethylnaphthalene.

To determine the position of the CH_3 substituent in the naphthalene nucleus we measured the Overhauser effect (OE) for the H^5 protons when the lines at 5.07 ppm (CH_2) and 2.48 ppm ($-CH_3$) are saturated. The single singlet ($J_{5,7} < 0.8$ Hz) in the 7.3-9.1 ppm region, with δ 7.65 ppm, was assigned to the H^5 protons in the NMR spec-

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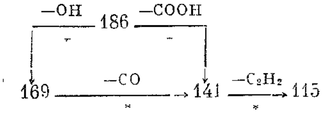
trum. The OE values were 18 and <3% when the lines of the CH_3 and CH_2OH groups were respectively saturated. This corresponds to location of the CH_3 group in the 6 position [8]. As a result, the analyzed product should be assigned the structure of 6-methyl-1-hydroxymethylnaphthalene, mp 79-80° (from EtOH). Found: C 83.70; H 6.98%. $C_{12}H_{12}O$. Calculated: C 83.66; H 6.97%.

Compound (II). Ultraviolet spectrum (λ_{max}, nm): 228, 285 (294 sh). Infrared spectrum (ν, cm^{-1}): 405, 420, 495, 515, 540, 580, 620, 657, 750, 757, 777, 787, 820, 840, 855, 883, 925, 970, 1005, 1060, 1085, 1120, 1152, 1170, 1205, 1257, 1292, 1410, 1432, 1470, 1510, 1592, 1680, and a broad band in the 2400-3200 region with maxima at 2530, 2630, 2860, 2930, 3050. Mass spectrum (m/e, %): 186 (100, M^+), 169 (25), 141 (75), 115 (95). NMR spectrum (δ, ppm): 2.50 s (3H). The IR spectrum of this product contains all of the principal absorption bands of the COOH group (925, 1257, 1292, 1410, 1680 cm^{-1}), including the characteristic absorption of the dimerized carboxyl group in the 2500-3200 cm^{-1} region.

A singlet at 2.50 ppm (3H) is present in the NMR spectrum, which testifies to the presence of a CH_3 group in compound (II). The mass spectrum of the analyzed product has the peak of M^+ with m/e 186, the character of whose decomposition can be depicted by the following scheme.



Based on the presented data, compound (II) was identified as being 6-methyl-1-naphthoic acid, mp 175-176° (from EtOH, cf. [9, 10]). Found: C 77.40; H 5.40%. $C_{12}H_{10}O_2$. Calculated: C 77.41; H 5.37%.

Compound (III). Ultraviolet spectrum (λ_{max}, nm): 246 (272 sh), 282 (292 sh), 316, 352. Infrared spectrum (ν, cm^{-1}): 410, 450, 480, 535, 557, 590, 720, 760, 778, 840, 905, 930, 1000, 1050 (sh), 1070, 1120, 1170, 1205, 1230, 1262, 1300, 1330, 1378, 1390, 1420, 1470, 1515, 1580, 1600, 1623, 1690, and a broad band in the 2400-3600 region with maxima at 2500, 2630, 2860, 2930, 3060, 3400. Mass spectrum (m/e, %): 202 (60, M^+), 185 (14), 157 (35), 129 (100), 115 (29). NMR spectrum (δ): 5.08 s (2H). The IR spectrum of compound (III) has the characteristic absorption bands of a dimerized carboxyl group (930, 1300, 1420, 1690, 2500-3200 cm^{-1}). The value of the chemical shift of the singlet line with δ 5.08 corresponds to the $ArCH_2O$ grouping.

The mass spectrum of this product has the intense peak of M^+ with m/e 202, the fragmentation of which indicates the presence of a carboxyl group. The appearance of the fragment ions with m/e 185 ($M^+ - OH$), 157 ($M^+ - COOH$), and 129 ($M^+ - COOH - CO$), is observed as the result of the decomposition of M^+.

The presented data made it possible to identify compound (III) as being 6-hydroxymethyl-1-naphthoic acid, mp 167-168° (from EtOH). Found: C 71.26; H 4.90%. $C_{12}H_{10}O_3$. Calculated: C 71.28; H 4.95%.

CONCLUSIONS

6-Methyl-1-hydroxymethylnaphthalene, 6-methyl-1-naphthoic acid, and 6-hydroxymethyl-1-naphthoic acid were isolated and identified as being the microbiological transformation products of 1,6-dimethyl-naphthalene.

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