GENTISIC ACID AS A MICROBIOLOGICAL OXIDATION PRODUCT OF NAPHTHALENE

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UDC 547.972.12:542.943:547.652.1

In studying the microbiological oxidation of naphthalene* by Pseudomonas fluorescens we isolated the previously unidentified [2, 3] compound (I) as the catabolism product of this hydrocarbon.

Ultraviolet spectrum in 96% C_2H_5OH (λ_{max}, nm): 212, sh 233, 328. Infrared spectrum in KBr (ν, cm^{-1}): 475, 560, 683, sh 675, 765, 785, 796, 856, 885:895, 948, 1090, 1140, 1222, 1248, 1300, 1385, 1445, 1487, 1583, 1618, 1665, and a broad band in the 2500-3500 cm^{-1} region, with maxima at 2600, 2720, 2870, 3020, 3075, and 3280. NMR spectrum (δ, ppm): 7.38 s, 7.06 q (AB), 6.82 q (J_{AB} = 8 Hz). Mass spectrum (m/e, %): 154 (43), 136 (100), 108 (42), 80 (41), 52 (40).

An analysis of the UV spectrum reveals that (I) contains a benzene ring that is conjugated with other chromophores. The IR spectrum of (I) has absorption bands that are characteristic for the dimers of carboxylic acids (1248, 1300, 1665 cm^{-1}, and a broad band in the 2500-3300 cm^{-1} region), and also bands that are responsible for the absorption of phenolic hydroxyl (1222 and 3280 cm^{-1}). The presence in the NMR spectrum of a singlet with δ 7.38 and an AB quartet testifies to the presence of three substituents in the aromatic ring of the analyzed product.

According to the mass spectrum, the molecular weight of (I) is 154 m/e. The formation of the fragment ion with m/e 136 (M^+-18) can be interpreted as being the result of the interaction of consecutively arranged COOH and OH groups in the benzene ring (ortho effect) [14]. Taking into account the molecular weight of product (I) and the nature of its two functional groups, it may be assumed that the third substituent in the aromatic ring is the OH group. This is confirmed by the character of the decomposition of the molecular ion under electron impact, caused by the successive elimination of a water molecule and three CO molecules (m/e): 136 (M^+-H_2O), 108 (M^+-H_2O-CO), 80 ($M^+-H_2O-CO-CO$), 52 ($M^+-H_2O-CO-CO-CO$).

A shift of the carbonyl absorption in the IR spectrum toward lower frequencies (ν 1665 cm^{-1}), and also the presence of the ortho effect in the mass spectrum, both indicate that the COOH and OH groups are found in the o position. A comparison of the chemical shifts of the unsubstituted protons reveals that the protons, represented by a singlet (δ 7.38), are found ortho to the COOH group. At the same time, the presence of an AB quartet testifies that the other two unsubstituted protons are arranged in a row.

Consequently, the analyzed compound must be assigned the structure of 2,5-dihydroxybenzoic (gentisic) acid (mp 199-200° (from EtOH), cf. [5]). Found: C 54.50; H 3.98%. $C_7H_6O_4$. Calculated: C 54.55; H 3.92%. In turn, the formation of gentisic acid in the microbiological oxidation of naphthalene testifies that in the given case the path for the catabolism of this hydrocarbon differs from the generally accepted scheme [2].

CONCLUSIONS

Gentisic acid was isolated and identified by physicochemical methods as being the microbiological oxidation product of naphthalene.

*The microbiological oxidation of naphthalene and identification of the oxidized product were carried out as described in [1].

Institute of the Biochemistry and Physiology of Microorganisms, Academy of Sciences of the USSR, Pushchino-on-Oka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2091-2092, September, 1975. Original article submitted December 18, 1974.

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