

where R is for I: $\text{Glc}^1 \rightarrow^3 \text{Gal}^1 \rightarrow^4 \text{Rha}^1 \rightarrow^2 \text{Ara}^1 \rightarrow$

II: $\text{Ara}^1 \rightarrow$

III: $\text{Rha}^1 \rightarrow^2 \text{Ara}^1 \rightarrow$

IV: $\text{Gal}^1 \rightarrow^4 \text{Rha}^1 \rightarrow^2 \text{Ara}^1 \rightarrow$

V: $\text{Glc}^1 \rightarrow^3 \text{Gal}^1 \rightarrow^4 \text{Rha}^1 \rightarrow^2 \text{Ara}^1 \rightarrow$

The compounds isolated had the following constants: (I) mp 197-198°, $[\alpha]_D^{20}$ -68.1° (c 1.01; methanol); (II) mp 159-160°, $[\alpha]_D^{20}$ -80.3° (c 1.00; methanol); (III) mp 179-181°, $[\alpha]_D^{20}$ -52.0° (c 1.20; methanol); (IV) mp 189-190°, $[\alpha]_D^{20}$ -55.3° (c 1.00; methanol); (V) mp 193-195°, $[\alpha]_D^{20}$ -45.0° (c 1.09; methanol).

LITERATURE CITED

1. C. Sannié, S. Heitz, and H. Lapin, C. R. Acad. Sci., Paris, 233, 1670 (1951).
2. S. Hijosawa, M. Huton, T. Komori, et al., Chem. Pharm. Bull., 16, 1162 (1968).
3. L. Fieser and M. Fieser, Steroids, Rheinhold, New York (1959) [Russian translation, Mir, Moscow (1964), pp. 562, 854].
4. V. V. Krokhamlyuk, P. K. Kintya, and V. Ya. Chirva, Izv. Akad. Nauk MSSR, Ser. Biol. Khim. Nauk, No. 1, 85 (1975).
5. S. Hakomori, J. Biochem. (Tokyo), 55, 205 (1964).
6. W. Klyne, Biochem. J., 47, No. 4, xli (1950).

IDENTIFICATION OF 5-HYDROXYPICOLINIC ACID AMONG THE PRODUCTS BIOSYNTHESIZED BY *Nocardia* sp.

T. N. Makar'eva, A. I. Kalinovskii,
V. A. Stonik, and E. V. Vakhrusheva

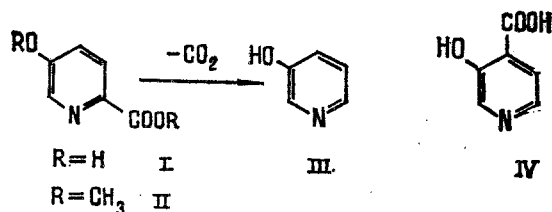
UDC 547.826/827:579.8

Microorganisms, including those living in sea water, are a rich source of various organic compounds [1, 2]. In a culture medium upon which *Nocardia* sp. isolated from residues of marine macrophytes of the Sea of Japan was growing [3], substance (I) has been detected, and it has been obtained in the form of an amorphous powder by column chromatography on Sephadex G-25 and silica gel [chloroform-ethanol-water (10:10:1)] and purified by high-performance liquid chromatography on Whatman ODS columns (with water as eluent). UV spectrum: $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 250 and 283 nm; on acidification to pH 1.0: 252 and 290 nm; on alkalization to pH 14: 273 and 303 nm. Mass spectrum, m/z (%): 139 (M^+ , 46), 122 ($\text{M}^+ - \text{NH}_3$, 10), 111 (26), 95 ($\text{M}^+ - \text{CO}_2$, 100). ^1H NMR spectrum (D_2O): 7.59 (1H, d, J = 9 Hz), 8.01 (1H, s), 8.09 (1H, d, J = 9 Hz). ^{13}C NMR (D_2O): 127.0; 129.3; 134.5; 135.5; 138.3; 169.7.

The methylation of (I) with diazomethane led to the dimethyl derivative (II). UV spectrum: $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 250 and 283 nm; after alkalization of the UV spectrum did not change. Mass spectrum, m/z (%): 167 (M^+ , 5), 136 ($\text{M}^+ - \text{OCH}_3$, 11), 125 (50), 124 ($\text{M}^+ - 43$, 100), 109 (66), 108 (20). ^1H NMR (CD_3OD): 3.69 (3H, s); 3.96 (3H, s); 7.52 (1H, dd, J = 9 and 2.5 Hz), 8.15 (1H, d, J = 9 Hz), 8.22 (1H, d, J = 2.5 Hz).

To determine the position of the hydroxy group in the pyridine ring, the Na salt of (I) was decarboxylated by heating at 300-350°C. This gave the hydroxypyridine (III). UV spectrum $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 286 nm (literature figures for 3-hydroxypyridine - 287; for

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Branch, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnikh Soedinenii, No. 1, pp. 140-141, January-February, 1989. Original article submitted April 5, 1988; revision submitted July 25, 1988.



2-hydroxypyridine - 297; and for 4-hydroxypyridine - 246 nm [4]). ^1H NMR (CDCl_3): 7.45 (1H, dd, $J = 5$ and 9 Hz), 7.56 (1H, d, $J = 9$ Hz), 8.10 (1H, d, $J = 5$ Hz), 8.6 (1H, br. s).

The position of the carboxy group was established from an analysis of the ^1H NMR spectra of compounds (I) and (II). In actual fact, the value of the meta spin-spin coupling constant of the protons of the pyridine nucleus in substance (II), which was 2.5 Hz, excluded structure (IV) for the compound isolated. In the hydroxy acid (IV) this constant has a value of 0.4 Hz [5].

From the results that we had obtained and those of a quantitative determination of Na^+ ions on a Shimadzu AA 610S atomic absorption spectrometer (found: Na 14.2%, calculated for $\text{C}_6\text{H}_4\text{NO}_3\text{Na}$: Na 14.0%) it followed that the compound isolated was the Na salt of 5-hydroxypicolinic acid (I). Substance (I) has been synthesized previously by the reduction of 4-chloro-5-hydroxypicolinic acid [6].

So far as we are aware, a hydroxypicolinic acid has not previously been described in the culture medium of a microorganism. Similar compounds such as the phytopathotoxin fusaric acid have been isolated previously from various representatives of *Fusarium* [7].

LITERATURE CITED

1. D. J. Faulkner, Nat. Prod. Rep., **1**, 551 (1984).
2. Y. Okami, Pure Appl. Chem., **54**, 1951 (1982).
3. L. M. Kondrat'eva, Ten Khak Mun, and E. V. Vakhrusheva, Mikrobiologiya, **57**, No. 1, 47 (1988).
4. M. L. Peterson, J. Org. Chem., **25**, 565 (1960).
5. W. Brugel, Nuclear Magnetic Resonance Spectra and Chemical Structure, Academic Press, New York, Vol. 1 (1967), p. 153.
6. Beilstein, **22**, 213 (1935).
7. J. B. Harborne, An Introduction to Ecological Biochemistry, Academic Press, London (1977).

AMINO ACID COMPOSITION OF *Pirus communis* AND ITS CHANGE DURING STORAGE

É. B. Farzaliev, Z. D. Gusar,
A. F. Radova, and V. N. Golubev

UDC 582.734.3:577.1.004.4

Pears are distinguished by a variety of free amino acids. Of the 20 commonest amino acids we have identified 16 in pears, seven of them being essential (Table 1).

Two varieties of pears with different times of ripening were investigated. The dynamics of the changes in the amino acids during storage were established by determining these constituents extracted from weighed specimens of average samples of the skin and flesh with 85% ethanol (allowing for the moisture content of the tissues investigated) before and after storage for 50 days. For the best extraction of the amino acids, the homogeneous mass

M. V. Lomonosov Odessa Technological Institute of the Food Industry. Translated from Khimiya Prirodnikh Soedinenii, No. 1, pp. 142-143, January-February, 1989. Original article submitted April 21, 1988; revision submitted August 3, 1988.