the inhibiting action of the cembranoids investigated on tumor cells was not specific since in approximately the same doses they caused the hemolysis of erythrocytes and inhibited the vital activity of mouse lymphocytes and macrophages.

These results permitted an explanation of the role of the individual functional groups of the compounds under investigation in the manifestation of biological activity by them. The presence of a hydroxy group, as in compound (IV), is one of the factors responsible for the efficacy of the action of these substances. The replacement of the 11,12-double bond by an epoxy ring lowers cytostatic activity, while compound (III) in which the hydroxy group has been replaced by a keto group, showed no appreciable activity in the concentrations investigated.

## LITERATURE CITED


1. L. V. Makukho and O. P. Volkolupova, Antibiotiki, No. 3, 130 (1981).
2. G. N. Likhatskaya, L. I. Strigina, A. M. Popov, N. G. Prokof'eva, M. I. Kiseleva, and M. M. Anisimov, Biol. Membr., 4, No. 3, 290 (1987).


# STEROID GLYCOSIDES OF GARDEN ONION SEEDS. STRUCTURE OF CEPOSIDE D


P. K. Kintya and L. P. Degtyareva



UDC 547.918+547.917


In the present communication we give information on the isolation of ceposide D (I) and proof of its structure. As the result of the repeated chromatography of a methanolic extract of the seeds of the garden onion Allium cepa L. (variety Dnestrovskii growing in Moldavia) on a column of silica gel, we obtained an individual fraction (I). The yields of glycoside (I) was 0.1% on the weight of the air-dry raw material. Ceposide D gave a positive reaction with the Sannié reagent [1] and a negative reaction with the Ehrlich reagent [2] which showed its spirostanol nature. The IR spectrum of (I) contained the 900-920 $cm^{-1}$ absorption bands that are characteristic for a spiroketal chain of the (25R)-series. After acid hydrolysis, diosgenin was identified as the aglycon by its physicochemical constants [3].

In a hydrolysate, D-glucose, D-galactose, L-rhamnose, and L-arabinose were identified by GLC in the form of their aldononitrile acetate derivatives [4] in a ratio of 2:1:1:1. The sequence of bonds and the sizes of the oxide rings were determined by the Hakomori methylation of (I) [5] followed by methanolysis of the permethylate obtained. The following were identified by GLC: Me 2,3,4,6-tetra-O-Me-D-$Glc_p$, Me 4,6-di-O-Me-D-$Gal_p$, Me 2,3-di-O-Me-L-$Rha_p$, and Me 3,4-di-O-Me-L-$Ara_p$. Periodate oxidation confirmed the results of methylation: only galactose was detected by paper chromatography in the hydrolysate.

The sequence of attachment of the monosaccharides was established after an investigation of the progenins obtained from the partial hydrolysis of (I). In the monoside (II) arabinose was identified, in the bioside (III) L-arabinose and L-rhamnose in a ratio of 1:1, in the trioside (IV) L-arabinose, L-rhamnose, and D-galactose (1:1:1), and in the tetraoside (V) L-arabinose, L-rhamnose, D-glucose, and D-galactose (1:1:1:1). After the methylation and methanolysis of (III) Me 2,3,4-tri-O-Me-L-$Rha_p$ and Me 3,4-di-O-Me-L-$Ara_p$ were identified; for (IV), Me 2,3,4,6-tetra-O-Me-D-$Gal_p$, Me 2,3-di-O-Me-L-$Rha_p$, and Me 3,4-di-O-Me-L-$Ara_p$; and for (V), Me 2,3,4,6-tetra-O-Me-D-$Glc_p$, Me 2,3-di-O-Me-L-$Rha_p$, Me 3,4-di-O-Me-L-$Ara_p$, and Me 2,4,6-tri-O-Me-D-$Gal_p$. The configurations of the glycosidic centers were determined according to Klyne's rule [6].

On the basis of the results presented, the following structure is proposed for ceposide D and its progenins:

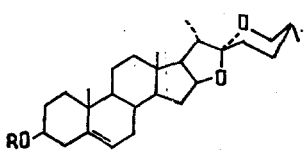
---


Institute of Ecological Genetics, Moldavian Academy of Sciences, Kishinev.


Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 139-140, January-February, 1988. Original article submitted January 21, 1988; revision submitted August 23, 1988.




0009-3130/89/2501-0124 $12.50



where R is for I: $Glc^1 \searrow^3 / Glc^1 \nearrow_2 Gal^1 \rightarrow {}^4Rha^1 \rightarrow {}^2Ara^1 \rightarrow$

II: $Ara^1 \rightarrow$

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

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

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

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. Krokhmalyuk, 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: $\lambda_{max}^{C_2H_5OH}$ 250 and 283 nm; on acidification to pH 1.0: 252 and 290 nm; on alkalinization to pH 14: 273 and 303 nm. Mass spectrum, m/z (%): 139 ($M^+$, 46), 122 ($M^+ - NH_3$, 10), 111 (26), 95 ($M^+ - CO_2$, 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: $\lambda_{max}^{C_2H_5OH}$ 250 and 283 nm; after alkalinization of the UV spectrum did not change. Mass spectrum, m/z (%): 167 ($M^+$, 5), 136 ($M^+ - OCH_3$, 11), 125 (50), 124 ($M^+ - 43$, 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 $\lambda_{max}^{C_2H_5OH}$ 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 Prirodnykh Soedinenii, No. 1, pp. 140-141, January-February, 1989. Original article submitted April 5, 1988; revision submitted July 25, 1988.