DISTRIBUTION OF 2-AMINOIMIDAZOLE AND N-METHYLTAURINE IN MARINE SPONGES

N. K. Utkina and S. A. Fedoreev

UDC 539.4+547.78+547.466

In the process of searching for physiologically active compounds of sponges, we have investigated ethanolic extracts of several marine sponges belonging to the families Halichondriidae and Haliclonidae from the collections of the twelfth tropical voyage of the scientific-research vessel "Professor Bogorov" (1981-1982). From an extract of the marine sponge *Halichondria* sp. 1 by column chromatography on Polikhrom-1 in water and subsequently separating the aqueous fraction on silica gel in the $CHCl_3$—MeOH—H_2O (75:25:2) system we isolated two compounds — 2-aminoimidazole hydrochloride (I), and the β-amino sulfonic acid N-methyltaurine (II).

The constants of substance (I) with mp 150-152°C (1-butanol—xylene) and of its monoacetate with mp 270-275°C (decomp.) [λ_{max}^{MeOH}:245 nm (log ε 3.97); PMR (CD_3OD, δ, ppm): 6.8 (s, 2H;, 2.2 (s, 3H); m/z (%) 125 (M^+, 70), 83 (M — CH_2=C=O, 100), 56 (M — CH_2=C=O — HCN, 100), 43 (100)] corresponded to literature figures [1, 2].

Substance (II) [mp 251-253°C (H_2O — MeOH); PMR (D_2O, δ, ppm) 2.91 (s, 3H), 3.41 (t, J = 6.4 Hz, 2H), 3.58 (t, J = 6.4 Hz, 2H); monoacetate (II), mp 154-156°C (MeOH); m/z (%) 181 (M^+, 50), 139 (M — CH_2=C=O, 60), 138 (M — CH_2=C=O — H, 40), 101 (100), 100 (80), 86 (100), 73 (100), 64 (50), 57 (100), 43 (100)] corresponded to N-methyltaurine [3].

Extracts of other samples were separated by TLC on silica gel in the n-BuOH—HOAc—H_2O (12:3:5) system. The zones containing substances (I) and (II) (staining with the Pauly reagent and with a 1% solution of ninhydrin in acetone) were eluted with ethanol and the products, after drying, were weighed and acetylated by the usual method. The presence in the mass spectra of the acetates of peaks with m/z 125 and 181 and their intensities served as a confirmation of the nature and purity of the compounds (I) and (II), respectively, that had been isolated.

2-Aminoimidazole had previously been detected in the sponge *Reniera cratera* [1]. N-Methyltaurine is widely distributed in marine algae [4], but among invertebrate animals it has previously been found only in the marine sponge *Calix nereis* [3]. The results of the screening performed have shown that these compounds are encountered fairly frequently in sponges of the families Halichondriidae and Haliclonidae.

The distribution of 2-aminoimidazole and N-methyltaurine in sponges* was as follows (+ means that they were not determined quantitatively):

Species	Collection site	Compound (amount on the dry weight of the sponge, %) *	
		I	II
Halichondriidae			
Halichondria sp. 1	Madagascar	0.3	0.1
Halichondria sp. 2		+	+
Halichondria sp. 3	Vietnamese littoral	0.01	0.2
Halichondriidae gen. sp.	Socotra	0.1	0.2
Trachyopsis halichondrioides	Madagascar	+	+
Haliclonidae			
Haliclona sp.	"	+	0.1
Callyspongia subarmigera	"	—	+

---

*The sponges were determined by V. V. Sholov.

Pacific Ocean Institute of Biorganic Chemistry of the Far Eastern Scientific Center of the Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 124-125, January-February, 1984. Original article submitted July 14, 1983.

LITERATURE CITED

1. G. Cimino, S. De Stefano, and L. Minale, Comp. Biochem., Physiol., 47 B, 895 (1974).
2. R. Fargner and F. Pyman, J. Chem. Soc., 115, 217 (1919).
3. D. Ackermann and P. List, Naturwissenschaften, 46, 354 (1959).
4. G. Impellizzeri, S. Mangiafico, G. Oriente, M. Piattelli, and S. Sciuto, Phytochemistry, 14, 1549 (1975).

ISOCUPRESSIC ACID AND NEW ESTERS OF IT FROM THE NEEDLES OF *Pinus sibirica*

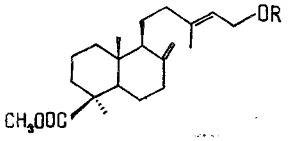
V. A. Raldugin and V. A. Pentegova

UDC 547.595.9

In view of the potential significance of diterpene acids from needles in the chemosystematics of coniferous plants [1], we have investigated the "polar" resin acids [2] of the needles of *Pinus sibirica* R. Mayr. (Siberian stone pine).

It has been shown previously [3] that the ordinary resin acids of these needles are represented by lambertianic acid and tricyclic acids of the abietane and isopimarane series.

The acid fraction of an ethereal extract of the air-dry needles collected in March, 1983, was methylated with diazomethane and chromatographed on silica gel as described previously [2]. In this way, three compounds were obtained, with yields of 4, 1, and 0.2% on the initial acid fraction. The main compound was identified from its PMR spectrum and its constants as methyl cupressate (I), which has been found previously in the oleoresin of the Siberian stone pine [4]. The other two proved to be new substances, not previously described, and their structures have been established as the dimethyl ester of 15-O-succinylisocupressic acid (II) and methyl 15-O-methylisocupressate (III).



I. R = H
II. R = CH_3
III. R = $COCH_2CH_2COOCH_3$

In the PMR spectrum (here and below, 60 MHz, CCl_4, HMDS, δ scale) of substance (II), which was obtained in the form of an oil with n_D^{27} 1.5000, $[\alpha]_D^{27}$ +34.8° (c 8.93; chloroform), the characteristic singlet [2] of the four protons of the methylene groups of a succinyl residue was observed at 2.47 ppm, the singlets of two methoxycarbonyl groups at 3.53 and 3.59 ppm, and a doublet (J = 7 Hz, 2H) of the protons of the C_{15}-methylene group at 4.53 ppm. In addition, there were signals at (ppm) 0.43, 1.10, and 1.63 (3H each, singlets, Me_{10}, Me_4, and Me_{13}, respectively), 4.47 and 4.80 (1H each, narrow multiplets, $>C=CH_2$), and 5.25 ppm (1H, triplet, J = 7 Hz, H_{14}). When the ester (II) was reduced with lithium tetrahydroaluminate in diethyl ether, the known [4] agathadiol with mp 108-109°C was obtained.

The ester (III) (yield 0.2%) was obtained in the form of an oil with n_D^{20} 1.5070, $[\alpha]_D^{20}$ +38° (c 1.45; chloroform). PMR spectrum (ppm): 5.23 (1H, triplet, J = 7 Hz), 3.80 (2H, doublet, J = 7 Hz) and 3.16 (3H, singlet) — the protons of a $>C=CH-CH_2-OCH_3$ grouping, 4.81 and 4.48 (1H each, narrow multiplets, $>C=CH_2$), 3.53 (3H, singlet, $COOCH_3$), 1.58, 1.10, and 0.43 (3H each, singlets, Me_{13}, Me_4, and Me_{10}, respectively). The structure of this ester was shown by its formation in the methylation of methyl isocupressate (I) with methyl iodide in tetrahydrofuran in the presence of sodium hydroxide.

15-O-Succinylisocupressic acid is present in the needles in the form of a free diacid, and not the monomethyl ether since, like agathic acid [2], it is selectively extracted by an aqueous solution of sodium bicarbonate from ethereal solutions both of the acid fraction and of the whole extract of the needles. 15-O-Methylisocupressic acid is not the product of

---

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 125-126, January-February, 1984. Original article submitted September 26, 1983.