NEW DITERPENOID OF THE XENIANE SERIES FROM THE GORGONIAN *Paragorgia arborea*

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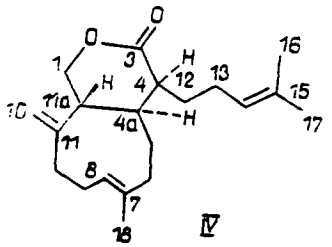
The terpenoids of marine organisms living in the seas of the USSR have not been studied completely. During an expedition to the Kurile islands (seventh voyage of the scientific-research ship "Akademik Oparin," June, 1988) we collected the gorgonian *Paragorgia arborea* in Rikorda bay at a depth of 150 m, with a Sigsbee trawl. This animal also lives in the southern hemisphere. Italian scientists have recently isolated the xeniolides (I-III) from extracts of *P. arborea* collected in the southern part of the Indian Ocean [1]. Compounds (I-III) were absent from our material, but the xeniolide (IV) was present with mp 32-34°C, $[\alpha]_{578}^{25}$ +32° (c 0.1; chloroform), M^+ 302 m/z.



IV

I. 12(13)-Dehydro-(IV)
II. 4(12) E-Dehydro-(IV)
III. 4(12) Z-Dehydro-(IV)
V. $\Delta^{12(13)}$-Isomer of (IV)

The presence in (IV) of a six-membered lactone ring followed from its spectral characteristics (Table 1; IR spectrum: 1736 cm^{-1}) and from the formation from (IV) under the action of HCl-saturated methanol of the methyl ester of the corresponding hydroxy acid, the mass spectrum of which had a peak at m/z 334 (M^+). The H-1α and H-1β signals in the PMR spectrum of (IV) appeared as characteristic doublets of doublets at 4.03 and 4.17 ppm, agreeing completely in respect to chemical shifts and SSCCs with the corresponding signals in the spectra of (I-III).

The ^{13}C NMR spectrum of (IV) was close to the spectrum of coraxeniolide A (V) from *Corallium* sp. [2]. The differences related mainly to the signals of the side-chain, which is explained by a different position of the double bond in (V) from that in (IV).

The structure of the side-chain in (IV) was confirmed by its PMR spectrum, in which all the signals of the methyl groups were observed at 1.64-1.69 ppm; consequently, CH_3-16 and CH_3-17 were located at the double bond.

TABLE 1. ^{13}C and ^1H NMR Spectra of Compound (IV) (δ, ppm; deuterochloroform)

C atom	δ	C atom	δ	H atom	δ	J, Hz
C-1	67,0	C-11	152,6	H-1α	4,03 dd	(11,4; 3,3)
C-3	175,0	C-11a	49,3	H-1β	4,17 dd	(11,4; 4,0)
C-4	44,8	C-12	26,5	H-8	5,35 m	
C-4a	46,1	C-13	29,6	H-14	5,13 m	
C-5	35,4[c]	C-14	123,7[b]	CH_3-16	1,69 br.s	
C-6	40,0	C-15	132,3[a]	CH_3-17	1,64 br.s	
C-7	135,2[a]	C-16	17,8	CH_3-18	1,67 br.s	
C-8	124,4[b]	C-17	25,6	H-19	4,9 br.s	
C-9	25,1	C-18	16,3	H-19	4,7 br.s	
C-10	35,3[c]	C-19	113,3			

Notes. a, b, c) Assignment of the signals ambiguous.

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Thus, we have isolated the previously unknown xeniolide (IV) with a 14(15)-double bond in the side chain. Cases of differences in the chemical compositions of terpenoids from gorgonians of one species but different habitats were known previously for cembranolides [3].

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CHROMATOSPECTROPHOTOMETRIC DETERMINATION OF CYTISINE IN ÉKSTRAKT TERMOPSIS ZHIDKII (LIQUID EXTRACT OF THERMOPSIS)

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The standardization of medicinal plant material and preparations from it must be carried out in relation to identical biologically active substances. In view of this, the aim of the present investigation was to develop a method for the quantitative evaluation of ékstrakt termopsis zhidkii [liquid extract of thermopsis] (1:2) with respect to cytisine.

As the standard sample we used cytisine corresponding to the demands of the State Pharmacopeia of the USSR, 10th edn. Ékstrakt termopsis zhidkii (1:2) marketed by the Geguzhes Pirmoi pharmaceutical factory was investigated.

The total *Thermopsis* alkaloids were separated by thin-layer chromatography. For this purpose, about 10 g (accurately weighed) of the liquid extract was placed in a 100-ml flask and evaporated on the water bath to a volume of 2-3 ml. After cooling, 2 ml of a solution of ammonia and 60 ml of chloroform, accurately measured, were added and the mixture was shaken on a vibration apparatus for 5-10 min. Then 5 g of anhydrous sodium sulfate was added and shaking was continued for 5 min. The chloroform extract was strained through absorbent cotton, with protection of the liquid from evaporation. Then 40-50 ml, accurately measured, of the chloroform extract was filtered into a flask through a paper filter containing 3 g of anhydrous sodium sulfate and 1.5 g of alumina [activity grade (II)] that had previously been wetted with chloroform. This was washed with chloroform (3 × 5 ml), the washings being added to the main filtrate. The chloroform was distilled off on the water bath to dryness. The dry residue in the flask was dissolved in 2 ml of 95% ethanol.

On a Silufol plate (15 × 15 cm) divided into five equal sections 0.075-ml portions of the alcoholic extract of liquid ékstrakt termopsis zhidkii were deposited on the starting line (bands 2, 3, and 4), and in the fifth position 0.075 ml (150 μg) of a 0.2% ethanolic solution of cytisine, one band being left as control. The plate with the deposited substances was placed in a previously saturated chamber containing the mixed solvent chloroform–acetone–diethylamine (5:4:1) [1]. When the solvent front had traveled 12 cm, the plate was removed from the chamber and dried, and the substances were detected in UV light (254 nm): cytisine (R_f 0.29), pachycarpine (0.48), methylcytisine (0.60), and an unidentified alkaloid (0.70).

As the comparison solution we used the eluate from the control band corresponding to the zone of the standard cytisine, which was prepared in the following way. Cytisine (0.15 g, accurately weighed) was placed in a 100-ml measuring flask and dissolved in 95% ethanol, the solution was made up to the mark with ethanol and was carefully mixed, and 5 ml of the resulting solution was placed in a 50-ml measuring flask, made up to the mark with 95% ethanol, and carefully mixed. This solution contained 0.00015 g of cytisine in 1 ml.

The sections of the sorbent with the standard and experimental samples and the control bands at the level of the zone of the standard sample of cytisine were transferred quantitatively to flasks with ground-in stoppers and were each covered with 10 ml of 95% ethanol and shaken in the vibration apparatus for 10 min, after which the extracts were filtered through folded paper filters.

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