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TRITERPENOIDS AND STEROIDS OF SOME SPECIES OF THE ORDER ERICALES

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Plants of the order Ericales (Ericaceae) are producing agents of substances of phenolic nature and also of compounds of the isoprenoid class [1]. We have investigated 17 species of the families Ericaceae, Pyrolaceae, Monotropaceae, and Empetraceae. It was found that all the plants studied contained triterpenoids both of neutral nature and of the acid type. On GLC analysis of methylated extracts of the materials under investigation [2], two triterpene acids were detected - oleanolic and ursolic. The relative amounts of the latter $(K_{01/urs})$ expressed as the ratio of the areas of the peaks of the methyl esters of these acids were determined:

Plant	$K_{ol/urs}$
Family Ericaceae Juss.	
Andromeda polifolia L. (bog rosemary andromeda)	0.80
Arctostaphylos uva-ursi (L.) Spreng. (bearberry)	2.70
Arctous alpina (L.) Niedenzu (arctic ptarmiganberry)	0.35
Calluna vulgaris (L.) Hull. (Scotch heather)	0.22
Cassiope ericoides (Pall.) D. Don	0.54
Chamaedaphne calyculata (L.) Moench. (leatherleaf)	0.65
Oxycoccus palustris Pers. (cranberry)	0.59
Phyllodoce caerulea (L/) Bab. (blue mountain heath)	0.39
Vaccinium arctostaphylos L. (Caucasian whortleberry)	0.22
V. ovalifolium Smith (ovalleaf whortleberry)	2.65
V. uliginosum L. (bog blueberry)	0.75
V. vitis-idaea L. (cowberry)	0.50

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Family Pyrolaceae Dumort.	
Chimaphila umbellata (L.) W. Barton (common pipsissewa)	0.33
Ortilia secunda (L.) House	0.39
Pyrola minor L. (snowline pyrola)	0.20
Family Monotropaceae Nutt.	
Hypopitus monotropa Crantz.	0.63
Family Empetraceae S. F. Gray	
Empetrum subholarcticum V. Vassil.	0.93

Calluna vulgaris (I), Chamaedaphne calyculata (II), Chimaphila umbellata (III), Ortilia secunda (IV), and Hypopitus monotropa (V) were investigated with the aim of isolating triterpenoids of neutral nature. Chloroform extracts of the epigeal parts of the plants, after the separation of the triterpene acids, were chromatographed of silica gel with elution by benzene-chloroform mixtures. Uvaol was found in (I) and (II) and taraxerol in (III) and (IV), while β -sitosterol was isolated from (I), (II), and (V). The identities of the substances obtained were confirmed by IR spectra and mixed melting points.

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IDENTIFICATION OF ECDYSTEROIDS OF HEXACTINIC CORALS

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Until recently, ecdysteroids had been isolated only from insects, crustaceans, and terrestrial plants [1, 2]. In 1982, Italian workers first reported the isolation of crustecdysone from a marine animal not belong to the Arthropoda type — the hexactinic coral <u>Gerardia savaglia</u> [3].

On studying alcoholic extracts of hexactinic corals Palythoa sp. and Parazoanthus sp. gathered during the thirteenth voyage of the Scientific Research Ship Professor Bogorov on the shores of Vietnam, we isolated 20-hydroxyecdysone (I) and, for the first time from marine invertebrates, its 2- and 3-acetoxy derivatives [(II) and (III), respectively]. The extracts were chromatographed on Polikhrom ($\rm H_2O \rightarrow 50\%$ ethanol) and silica gel [CHCl3:EtOH (6:1)]. The mixture of (II) and (III) was separated by the HPLC method (Zorbax C-8; 4.6 × 250 mm; 30% EtOH in H₂O; 1 ml/min; λ 248 nm). The structure of (I) [mp 235-238°C, [α]D²⁰ +57° (c 1.0; CH₃OH)] was established by a comparison of ¹³C and ¹H NMR high-resolution spectra, and also by UV, IR and mass spectroscopy and literature information [3-9]. After acetylation, compounds (I), (II), and (III) gave one and the same derivative (IV). The positions of the acetate groups in (II) and (III) were determined from their ¹³C NMR spectra (Table 1). In solutions, compounds (II) and (III) were partially converted into one another as a result of the epimerization described previously [8, 10].

OH
$$R_1 = R_2 = R_3 = OH$$
II. $R_1 = R_2 = R_3 = OH$
III. $R_1 = OAC$; $R_2 = R_3 = OH$
III. $R_1 = R_3 = OH$; $R_2 = OAC$
IV. $R_1 = R_2 = R_3 = OAC$

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