LITERATURE CITED

1. L. Sh. Tushishvili, S. V. Durmishidze, F. A. Medvedev, K. V. Sulaberidze, and A. V. Krokhin, Khim. Prir. Soedin., 868 (1979).
2. J. Folch, M. Lees, and G. H. S. Stanley, J. Biol. Chem., 226, 497 (1957).
3. C. Grunwald, Plant Physiol., 45, 663 (1970).
4. H. E. Nordby and S. Nagy, Phytochemistry, 13, 443 (1974).
5. H. E. Nordby and S. Nagy, Phytochemistry, 8, 2027 (1969).
6. S. Nagy and H. E. Nordby, Lipids, 6, 826 (1971).
7. B. A. Knights and A. M. M. Berrie, Phytochemistry, 10, 131 (1971).

8,13-EPOXYLABD-14-EN-19-OIC ACID — A COMPONENT OF THE NEEDLES OF *Pinus sylvestris*

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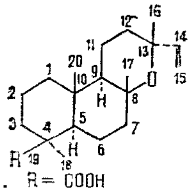
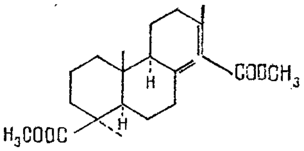
8,13-Epoxylabd-14-en-19-oic [(mannoyl oxide)-19-oic] acid, mp 64-66°C, $[\alpha]_D$ −39.2° (c 1.0; ethanol) has been isolated from the needles of *Pinus sylvestris*. The following derivatives have been obtained: methyl 8,13-epoxylabd-14-en-19-oate, with mp 83-85°C, $[\alpha]_D$ −43.2° (c 1.2; ethanol); 8,13-epoxylabd-14-en-19-ol, an oil, $[\alpha]_D$ −10.9° (c 1.0; ethanol), n_D^{25} 1.5025, cyclohexylammonium salt with mp 113-115°C, $[\alpha]_D$ −29.3° (c 1.0; ethanol); and 8,13-epoxydihydrolabd-14-en-19-oic acid with mp 61-63°C, $[\alpha]_D$ −23.1° (c 1.0; ethanol). The structures of the compounds were established by IR, mass, PMR, and ^{13}C NMR spectroscopy.

In a previous paper [1] devoted to a study of quantitative composition of the mixture of diterpene acids present in the needles of *Pinus sylvestris* L., we showed that in addition to known diterpene acids this mixture contained an acid of undetermined structure.

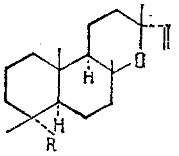
In the present investigation it has been shown that this acid is 8,13-epoxylabd-14-en-19-oic [(mannoyloxide)-19-oic] acid (I).



I. R = COOH
Ia. R = $COOCH_3$
Ib. R = CH_2OH
Ic. R = $COO^-\overset{+}{N}H_3C_6H_{11}$
Id. R = COOH; C_2H_5 at C_{13}



III



II. R = CH_3
IV. R = CH_2OAc

Table 1 gives the chemical shifts of the ^{13}C nuclei of methyl 8,13-epoxylabd-14-en-19-oate (Ia) and of related compounds: 8,13-epoxylabd-14-ene (mannoyl oxide) (II), dimethyl labda-8(17),13-diene-15,19-dioate (dimethyl agathate) (III), and 8,13-epoxylabd-14-en-18-ol acetate (yanol acetate) (IV).

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TABLE 1. Chemical Shifts of the ^{13}C Nuclei of (Ia) and Compounds Related to It, δ, TMS, ppm

Carbon atom	Compound				Carbon atom	Compound			
	Ia	II [2]	III [2]	IV [3]		Ia	II [2]	III [2]	IV [3]
C_1	39.4	38.9	39,0	38.6	C_{11}	15,5	15,2	21.5	15,4
C_2	19,2	18.4	19.8	17,2	C_{12}	35,7	35,5	39.6	35,9
C_3	38,2	41.9	38,0	35.9	C_{13}	73,3	73,0	160,5	73,3
C_4	43.9	32,5	44 2	36,6	C_{14}	148,1	147,8	114,7	148,0
C_5	57,0	55.5	56,1	50,6	C_{15}	110,0	110,0	166.9	110,2
C_6	21 6	19.8	26.1	20,0	C_{16}	28.6	28,4	19,0	28.5
C_7	43,3	42,6	38.5	43,0	C_{17}	25,1	25,4	106,2	25.4
C_8	74,8	74,9	147,4	74,9	C_{18}	28,8	32,5	28.6	73,0
C_9	55.1	55,2	55,2	56.1	C_{19}	177,8	21,3	177,3	17.8
C_{10}	37.5	36.7	40,1	37,0	C_{20}	13,1	16.6	12,4	15,8

A comparison of the chemical shifts of the carbon atoms of these compounds showed that the methyl groups at C_{13}, C_8, and C_{10} of compound (Ia) are present in the axial β position and that at C_4 in the equatorial α position while the methoxycarbonyl group occupies the axial β position.

EXPERIMENTAL

The mixture of diterpene acids isolated from the needles was separated as described elsewhere [1]. The results of the analysis of the compounds corresponded to the calculated figures. The fraction of monobasic diterpene acids was neutralized with cyclohexylamine. The salts were washed with diethyl ether and the mother solution after the separation of the salts was combined with the ether with which the precipitate had been washed and was decomposed with a 5% solution of CH_3COOH. The resulting mixture of acids was methylated with diazomethane. The methyl esters were chromatographed on a column filled with silica gel L 40/100 μm impregnated with $AgNO_3$ in a ratio of 3:1. The first fraction, eluted by pentane, contained mainly higher fatty acids; the second, eluted by pentane with 2% of diethyl ether added to it, contained a mixture of methyl esters of acids of abietane and pimarane series; and the third, eluted by pentane with the addition of 3% of diethyl ether to it contained a mixture of dimethyl pinofolate and (Ia) in a ratio of 1:1.

This mixture was subjected to rechromatography. The first fraction, eluted by pentane with the addition of 2% of diethyl ether, contained (Ia), with the composition $C_{21}H_{34}O_3$. mp 83-85°C, $[\alpha]_D$ −43.2° (c 1.2, ethanol). λ_{max}^{KBr}, cm^{-1}: 1467, 1720 (C=O), 915, 1642, 3097 (C=C), 1232 (C–O). Mass spectrum, m/z (%): M^+ 334 (1), 320 (40), 319 ($M^+ - CH_3$, 100), 302 (10), 301 ($M^+ - CH_3 - H_2O$, 35), 288 (10), 259 (26), 241 (40), 237 (44), 190 (11), 177 (29), 161 (14), 121 (23). PMR spectrum (in CCl_4, ppm): 0.54 (3 H, s), 1.10 (3 H, s), 1.14 (3 H, s), 1.20 (3 H, s), 3.56 (OCH_3, s), 4.84 (1 H, dd, J = 2 and 11 Hz), 5.0 (1 H, dd, J = 2 and 17 Hz), 5.75 (1 H, dd, J = 11 and 17 Hz).

Compound (Ia) (0.2 g) was saponified with 25 ml of 0.5 N KOH in ethylene glycol at 185°C for 2 h. After the usual working up and crystallization from pentane, the acid (I) with the composition $C_{20}H_{32}O_3$ (0.16 g) was obtained. mp 64-66°C, $[\alpha]_D$ −39.2° (c 1.0; ethanol). ORD for (I) in ethanol — smooth curve: $[\alpha]_{589}$ −39.2°, $[\alpha]_{578}$ −40.4°, $[\alpha]_{546}$ −45.2°, $[\alpha]_{436}$ −72.3°, λ_{max}^{KBr}, cm^{-1}: 1465, 1696 (C=O), 943, 1235 (OH), 1275 (C–O). Mass spectrum, m/z (%): M^+ 320 (15), 319 (57), 305 ($M^+ - CH_3$, 100), 287 ($M^+ - CH_3 - H_2O$, 54), 275 (M^+ − COOH, 11), 259 (33), 241 (44), 222 (62), 177 (49), 161 (18), 121 (49). When (Ia) (0.06 g) in ethereal solution was reduced with $LiAlH_4$ (0.2 g) in absolute ether (50 ml) for 4 h, 8,13-epoxylabd-14-en-19-ol [19-hydroxy(mannoyl oxide)] (Ib) was obtained. Oil, n_D^{25} 1.5025, $[\alpha]_D$ −10.9° (c 1.0; ethanol). λ_{max}^{KBr}, cm^{-1}: 1645, 3085 (C=C), 3360 (OH). Mass spectrum, m/z(%): M^+ 306 (1), 291 ($M^+ - CH_3$, 100), 273 ($M^+ - CH_3 - H_2O$, 38), 257 ($M^+ - H_2O - CH_2OH$, 0), 243 (8), 208 (35), 205 (28), 177 (61), 135 (34), 121 (34), 109 (49).

The mass spectra of (Ib) and of 19-hydroxy(epimannoyl oxide) [4] were identical. The cyclohexylammonium salt of the acid (I) (Ic) had mp 113-115°C, $[\alpha]_D$ −29.3° (c 1.0; ethanol). ν_{max}^{KBr}, cm^{-1}: 1645, 3045 (C=C), 1327, 1540 (COO^-).

The hydrogenation of (I) in the presence of platinum black in ethanol solution gave 8,13-epoxylabdan-19-oic acid (Id). mp 61-63°C, $[\alpha]_D$ −23.1° (c 1.0; ethanol). M^+ 322. λ_{max}^{KBr}, cm^{-1}: 1465, 1696 (C=O), 943, 1235 (OH), 1275 (C=O).

LITERATURE CITED

1. I. I. Bardyshev, A. S. Degtyarenko, A. L. Pertsovskii, and S. I. Kryuk, Khim. Drev., No. 3, 102 (1981).
2. B. L. Buckwalter, Y. R. Burfitt, A. A. Nagel, and E. Wenkert, Helv. Chim. Acta 58, 1567 (1975).
3. M. Sholichin, K. Yamasaki, R. Miyama, S. Yahara, and O. Tanaka, Phytochemistry, 19, 326 (1980).
4. A. S. Martin, Y. Rovirosa, R. Becker, and M. Castillo, Phytochemistry, 19, 1985 (1980).

GLYCOSIDES OF MARINE INVERTEBRATES.
XIV. STRUCTURE OF HOLOTHURIN B_1 FROM THE HOLOTHURIAN *Holothuria floridana*

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The complete structure of a triterpene oligoside — olothurin B_1 — from the holothurian *H. floridana* of the sublittoral of the island of Cuba has been established.

We have previously established the structure of the native aglycone of holothurin B_1 as (I) [1, 2]. The results of acid hydrolysis showed that holothurin B_1 is a sulfated bioside containing D-xylose and D-quinovose as monosaccharide residues. The structure of the carbohydrate chain of the glycoside was not established.

In the present paper we give the complete structure of holothurin B_1. Below are presented the characteristics of the ^{13}C NMR spectra of the carbohydrate chain of holothurin B_1 and its desulfated derivative (2 and 3, respectively):

Atom	*2*	*3*	**Atom**	*2*	*3*
C_1^1	105.6	105.79	C_1^2	105.1	105.4
C_2^1	83.05	83.5	C_2^2	76.48	76.8
C_3^1	76.48	77.78	C_3^2	77.52	77.78

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