2. L. I. Gornostaeva, Author's abstract of Candidate's dissertation [in Russian], Riga (1979).
3. L. I. Gornostaeva, S. M. Repyakh, and É. D. Levin, Khim. Drevesiny, No. 4, 93 (1979).
4. N. K. Kashtanova, A. I. Lisina, A. K. Dzizenko, and V. A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 2, Series No. 1, 126 (1967).
5. V. A. Raldugin, V. L. Salenko, N. S. Gamov, T. F. Titova, V. A. Khan, and V. A. Pentegova, Khim. Prir. Soedin., 199 (1980).
6. R. M. Beri and H. W. Lemon, Can. J. Chem., 48, 67 (1970).
7. K. Yoshihara, Y. Ohta, T. Sakai, Y. Hirose, Tetrahedron Lett., 2263 (1969).

MASLINIC ACID FROM THE LEAVES OF *Eucalyptus viminalis*

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UDC 547.597

According to the literature, the leaves of the ribbon eucalyptus contain cineol, β-sitosterol, 5-hydroxy-4',7-dimethoxy-6,8-dimethylflavone, 4',5-dihydroxy-7-methoxy-6,8-dimethyl flavone [1], and quercitrin [2].

When the total acidic components of a chloroform extract of the leaves of the ribbon eucalyptus were chromatographed on silica gel 40/100 mμ, we obtained a fraction (eluent ethyl acetate—petroleum ether (15 : 85)) containing, according to GLC, a triterpene compound (R_f 0.65, Silufol, chloroform—methanol (4 : 1), visualization with a 20% ethanolic solution of tungstophosphoric acid). From a concentrated ethereal solution of this fraction previously washed with 0.5% aqueous sodium bicarbonate and with water, a precipitate deposited, and from an ethanolic solution of this, by repeated purification on a column with acidic activated carbon of type B and silica gel 40/100 mμ, we obtained a compound $C_{30}H_{48}O_4$, mp 265-268°C (from aqueous ethanol).

Its mass spectrum showed that this substance belonged to the pentacyclic triterpenes. The spectrum contained the following characteristic peaks: M^+ 472 (2.76%), m/z 248 (93.98%), 223 (25.84%), 203 (100%). The nature of the retrodiene breakdown indicates the presence of a double bond in the 12,13 position. The peak with m/z 248 is characteristic for ion **a** [3], including rings D and E of a pentacyclic triterpene and containing a carboxy group, the splitting off of which led to the ion with m/z 203. The presence in the mass spectrum of the peak of an ion with m/z 223 including rings A and B shows the position of the two hydroxy groups in rings A and B (or only in ring A) [3].

The PMR spectrum (pyridine-d_5, TMS) contained a doublet at 3.35 ppm, J = 9 Hz, and a sextet at 4.02 ppm, $J_1 = 9$ Hz, $J_2 \approx 9$ Hz, and $J_3 \approx 4$ Hz, 1 H each. These signals are due to two vicinal hemihydroxylic protons, H-3 and H-2, respectively. A multiplet at 5.44 ppm, 1 H, is due to an olefinic H-12 proton. The PMR spectrum (CD_3OD, TMS) contains in the 0.8-1.1 ppm region five singlets with an intensity ratio of 1 : 2 : 1 : 1 : 2, which shows that the substance belongs to the β-amyrin derivatives.

Thus, on the basis of its physical constants and spectral characteristics, the compound isolated can be identified as maslinic acid, or 2,3-dihydroxyolean-12-ene-28-carboxylic acid [4, 5]. This conclusion was confirmed by the production on the methylation of the substance described with diazomethane of a compound $C_{31}H_{50}O_4$, mp 227-229°C, in the mass spectrum of which the mass of ion **a** [3] had been increased by 14 mass units, while the IR spectrum proved to be identical with that of methyl maslinate [4].

LITERATURE CITED

1. J. A. Lamberton, Aust. J. Chem., 17, 692 (1964).
2. N. M. Dzhanashiya and V. I. Glyzin, Khim. Prir. Soedin., 764 (1970).
3. H. Budzikiewicz, J. M. Wilson, and C. Djerassi, J. Am. Chem. Soc., 85, 3688 (1963).

All-Union Scientific-Research Institute of Medicinal Plants, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 113-114, January-February, 1983. Original article submitted July 20, 1982.

4. L. Cagliotti, G. Cainelli, and F. Minutilli, Gazz. Chim. Ital., 91, 1387 (1961).
5. R. Caputo, L. Mangoni, P. Monaco, and P. Privitera, Phytochemistry, 13, 2825 (1974).

24,25,26,26-TETRAMETHYLCHOLEST-23-ENE-2β,3α,6α-TRIOL TRIS(SODIUM SULFATE) — A NEW POLYHYDROXYLATED STEROID FROM THE SPONGE HALICHONDRIIDAE GEN. SP.

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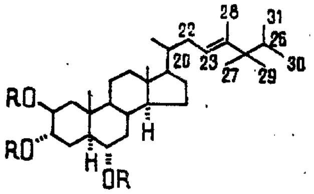
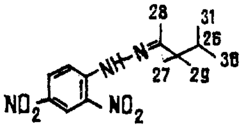
UDC 547.92

Sponges of the class Demospongiae form a rich source of steroid compounds of unique structure [1, 3]. From an aqueous ethanolic extract of the sponge *Halichondriidae* gen. sp., collected off the island of Socotra (People's Democratic Republic of Yemen) during the twelfth voyage of the Scientific-Research Vessel "Professor Bogorov," by column chromatography on Polikhrom 1 (50% ethanol) we have obtained the previously unknown 24,25,26,26-tetramethylcholest-23-ene-2β, 3α, 6α-triol tris (sodium sulfate) (Ia, $C_{31}H_{51}O_{12}S_3Na_3 \cdot 3H_2O$, mp 170-172°, $[\alpha]_D^{20}$ + 35.9° (c 0.46; pyridine). IR spectrum: λ^{KBr} 1236 cm^{-1} ($-OSO_3$). Mass spectrum (direct introduction, m/z, %): 420 ($M^+ - 3NaHSO_4$, 43); 377 ($M^+ - C_3H_7 - 3NaHSO_4$, 100).



R = SO_3Na (Ic)
R = H (Ib)
R = $COCH_3$ (Ia)



II

Acid hydrolysis (9% HCl, 90°C, 1.5 h) of (I) gave sulfuric acid and the triol (Ib), $C_{31}H_{54}O_3$, mp 223-226°, $[\alpha]_D^{20}$ + 45.6° (c 0.45; ethanol). Mass spectrum (direct introduction, m/z, %): 431 ($M^+ - C_3H_7$, 13); 413 ($M^+ - C_3H_7 - H_2O$, 73); 395 ($M^+ - C_3H_7 - 2H_2O$, 80); 377 ($M^+ - C_3H_7 - 3H_2O$, 100).

The acetylation of (Ib) with acetic anhydride in pyridine led to the triacetate (Ic), $C_{37}H_{60}O_6$, mp 140-142°, $[\alpha]_D^{20}$ + 71.2° (c 0.43; ethanol). Mass spectrum (direct introduction, m/z, %): 557 ($M^+ - C_3H_7$, 16); 497 ($M^+ - C_3H_7 - C_3H_7 - CH_3COOH$, 43); 437 ($M^+ - C_3H_7 - 2CH_3COOH$, 95); 377 ($M^+ - C_3H_7 - 3CH_3COOH$, 100).

Recently Japanese authors [3] have obtained a compound similar to (Ia), 24ξ, 25-dimethylcholestane-2β, 3α, 6α-triol tris (sodium sulfate) (halistanol sulfate), from the sponge *Halichondria* cf. *moorei* [3]. A comparison of the ^{13}C NMR spectra of (Ia-c) with the corresponding spectra of halistanol sulfate, halistanol, and halistanol acetate showed their complete coincidence for the signals of the C_1-C_{20} atoms.

The structure of the side chain of (Ia) was shown by spectral methods (Bruker WM-250) and by ozonolysis. The presence of a $CH_3-\underset{|}{C}H-CH_2-CH=C<$ fragment in the side chain followed from differential decoupling and double resonance experiments for (Ib). Thus, when the vinyl proton (5.34 ppm) was irradiated by the method of differential decoupling the signals of the protons of the neighboring methylene group (C_{22}) appeared at 2.20 and 1.85 ppm. Irradiation at 2.20 or 1.85 ppm enabled the chemical shift of the C_{20} methine proton to be determined (1.52 ppm). Under double-resonance conditions, irradiation at 1.52 ppm converted the doublet signal of the C_{21} methyl group into a singlet. The presence of a methyl group at a double bond follows from the ^1H NMR spectra of (Ia-c), in which the corresponding singlet signal (3 H) is observed in the 1.49-1.52 ppm region.

The ozonolysis of (Ic) gave 3,3,4-trimethylpentan-2-one, which was isolated in the form of the 2,4-dinitrophenylhydrazone (II), $C_{14}H_{20}N_4O_4$, mp 153-154°C. Mass spectrum (direct introduction): M^+ 308 (100). Its ^1H NMR spectrum contained the signals of C_{30} and C_{31}

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 114-115, January-February, 1983. Original article submitted November 9, 1982.

0009-3130/83/1901-0115$07.50