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STARFISH SAPONINS, XXXI.[1] NOVEL POLYHYDROXYSTEROIDS AND STEROIDAL GLYCOSIDES FROM THE STARFISH *SPHAERODISCUS PLACENTA*

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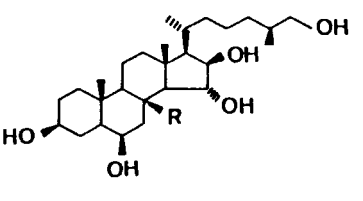
ABSTRACT.—Three novel steroidal glycosides [**6**, **7**, **10**] together with three novel polyhydroxysteroids [**2**, **3**, and **4**] have been isolated from the Mediterranean starfish *Sphaerodiscus placenta*. These compounds co-occur with three known glycosides and one known polyhydroxysteroid. The structures of the new metabolites were determined from spectral data and simple chemical transformations.

The red-yellow starfish, *Sphaerodiscus placenta* Muller-Troshel, was collected in the Gulf of Policastro near Palinuro. Extraction and fractionation of the aqueous extracts followed the steps described previously (1). In this paper we propose structures for new metabolites, the polyhydroxysteroids **2**, **3**, and **4**, and the glycosides 22-dehydrohalityloside E [**6**], 22-dehydrohalityloside D [**7**], and placentoside A [**10**]. The extracts also contained glycoside constituents, halitylosides A [**9**], B [**8**], and E [**5**], recently reported from the starfish *Halityle regularis* (2), and one polyhydroxysteroid constituent, previously isolated from the starfish *Hacelia attenuata* (3).

POLYHYDROXYSTEROIDS.—The two major components are the 24-methylenesteroids **3** and **4**, accompanied by minor amounts of their C_{27} analogs, **1** and **2**.

In the eims of **3** ($[\alpha]_D = +28.1°$) the highest peak (*m/z* 449) corresponded to loss of a methyl from the molecular formula $C_{28}H_{48}O_5$, which was determined by ^{13}C-nmr and DEPT measurements. The comparison of the ^1H- and ^{13}C-nmr spectra (Experimental Table 1) of **3** with those of the known **1** (3) immediately suggested that **3** is related to **1** by introduction of an exomethylene at C-24.

The ^1H-nmr spectrum included two 1H olefinic signals at δ 4.78 (broad s) and 4.85 (broad s), and the signals for 25-H, 26-H_2, and 27-H_3 shifted downfield to δ 2.33 (m), 3.60 (dd, J=12, 5 Hz), 3.55 (dd, J=12, 6.5 Hz), and 1.10 (d, J=7 Hz), respectively.



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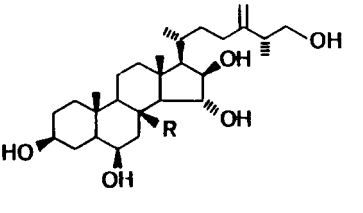
2 R=OH



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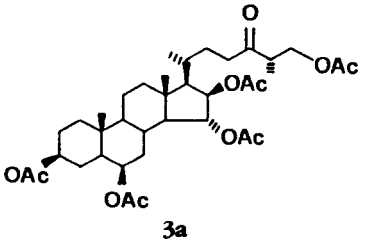
4 R=OH



3a

[1]For Part XXX, see Riccio *et al.* (9).

Irradiation of the multiplet at δ 2.33 (25-H) caused collapse of the doublet at δ 1.10 (27-H_3) to a singlet, simplified the hydroxymethylene signals into two doublets (J=12 Hz), and also sharpened the exomethylene broad singlets at δ 4.78 and 4.85 ppm.

The ^{13}C-nmr signals (Table 1) for the side chain carbons were assigned based on the data that have been published for cycloeucalenol (30-nor-24-methylenecycloartenol) (4) and the expected effects upon introduction of an hydroxyl group at C-26. The common 20*R* configuration proposed for **3** is based on the chemical shift of the C-21 methyl protons (5). The 25*R* configuration is based on the cd data of the derived 24-keto-pentaacetate **3a**. The positive Cotton effect of the cd curve of **3a** ($\Delta\epsilon_{280}$=+0.077) suggested *S* configuration at C-25 (6,7) and, accordingly, *R* configuration for the natural **3** (Note: The specification of the configuration changes on going from **3a** to **3** according to Chan, Ingold, and Prelog). We note that the 25*S* configuration was assigned to the non-alkylated, at C-24, 26-hydroxysteroids isolated from the starfish *Protoreaster nodosus* (8), *Luidia maculata*,[2] and *Coscinasterias tenuispina* (9). The same 25*S* configuration has been also established for the new steroid **2** (see below).

TABLE 1. ^{13}C-nmr Data for the Steroiol Carbons of Compounds **3**, **4**, **10** (in ppm)

Carbon Atom	Compounds			Carbon Atom	Compounds		
	3	**4**	**10**		**3**	**4**	**10**
1	39.9	41.4	39.7	15	85.1	81.0	71.1
2	32.3	31.7	26.2	16	83.1	83.1	43.4
3	72.5	72.5	73.7	17	59.9	60.6	57.8
4	36.4	36.4	69.1	18	15.1	16.8	16.6
5	[a]	[a]	57.4	19	16.2	15.8	16.9
6	72.6	74.2	64.8	20	30.9	30.6	40.8
7	40.8	45.5	[a]	21	18.6	18.4	21.2
8	31.3	76.9	77.4	22	35.9	35.6	137.1
9	55.9	57.3	58.5	23	32.9	32.9	134.5
10	36.7	36.7	38.2	24	154.0	154.0	34.5
11	21.9	19.7	19.2	25	43.6	43.5	38.2
12	42.0	43.3	43.3	26	67.6	67.6	68.8
13	44.8	45.4	44.4	27	17.2	17.2	
14	61.4	64.0	63.0	28	109.2	109.2	

[a]Signals under solvent signals: (ca. 50 ppm).

Compound **4** ([α]D=+11.7°) is related to **3** by introduction of an extra hydroxyl group at C-8, which is a common feature among polyhydroxysteroids from starfish. In the eims the highest peak was seen at *m/z* 465 (M^+-Me). In the ^{1}H-nmr spectrum the signals for the C-18 and C-19 angular methyl protons and the hydroxymethine proton at C-15) were seen shifted downfield by 0.19 ppm to δ 1.15, 0.12 ppm to δ 1.20, and by 0.37 ppm to δ 4.17, respectively. The ^{1}H-nmr spectrum of **4** also contained two doublets of doublets at δ 1.62 (J=15 and 2.5 Hz) and 2.46 (J=15 and 2.5 Hz) coupled to each other by 15 Hz and coupled by 2.5 Hz with the 6 α-proton which were assigned to H_2-7. The lack of additional coupling to the protons with δ 1.62 and 2.46 (C-7) confirmed an adjacent quaternary center (C-8).

The most significant features of the ^{13}C-nmr spectrum (Table 1) of **4**, which suggested the location of the *tert*-hydroxyl group at C-8 (76.9 ppm, -C-), were the upfield shifts (γ-effect) exhibited by C-11 (2.2 ppm) and C-15 (4.1 ppm) and the downfield shifts (β-effect) experienced by C-7 (4.7 ppm), C-9 (1.4 ppm), and C-14 (3.6

[2]Unpublished results.

ppm) relative to those in **3**. The same 25*R* configuration as in **3** is proposed for **4** because the shifts of the side chain carbons are identical in both spectra. Compound **4** has been found as the aglycone of a xyloside isolated from the starfish *Poraster superbus* (10).

The structure of 5α-cholestane-3β,6β,8,15α,16β,26-hexol for compound **2**, which was isolated in trace amounts, was derived from ^{1}H-nmr spectroscopy, eims (Experimental), and comparison with **1** and **4**.

Compound **2** is isomeric with the more common (25*S*)-5α-cholestane-3β,6α,8,15α,16β,26-hexol, first isolated from *Protoreaster nodosus* (11). The 25*S* configuration has been determined by preparing the (+)-methoxytrifluoromethylphenylacetate (MTPA ester) of **2**. The ^{1}H nmr showed a signal at δ 4.16 (2H, d, 6 Hz) for 26-H_2, thus suggesting the configuration to be 25*S* like other 26-hydroxysteroids from starfish (8). In the ^{1}H-nmr spectrum of the (+)-MTPA ester of (25*R*)-26-hydroxysteroids (*e.g.*, pavonins) signals for 26-H_2 were found at δ 4.24 (dd, 11, 6 Hz) and 4.08 (dd, 11, 7 Hz) (12).

TABLE 2. Assignments of ^{13}C-nmr (CD_3OD) Signals for 2-*O*-methyl-β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl Moiety of Compound **10** (in ppm)

	C-1	C-2	C-3	C-4	C-5	OCH_3
Xylose	103.6	81.4	76.9	71.1	66.4	=
2-*O*-Me-xylose . .	104.4	84.8	77.8	71.4	66.5	60.8

STEROIDAL GLYCOSIDES.—The known compounds, halitylosides A [**9**], B [**8**], and E [**5**] were identified by comparison (^{1}H nmr, fabms, tlc, and hplc) with authentic samples isolated from the starfish *Halityle regularis* (2).

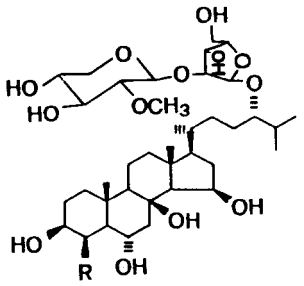
The 22-dehydrohalityloside E [**6**] and 22-dehydrohalityloside D [**7**] were identified by fabms (positive ion mode), which gave molecular ion peaks [*m/z* 743 $(M+H)^+$, **6**; *m/z* 759 $(M+H)^+$, **7**] two mass units shifted relative to their saturated analogs, ^{1}H-nmr and double resonance measurements which enabled one to determine the sequence from C-20 to C-27 [20-H: 2.21 (m), 21-H_3: 1.05 (d, J=6.3 Hz), 22-H: 5.46 (dd, J=15 and 7.5), 23-H: 5.35 (dd, J=15 and 7.5 Hz), 24-H: 3.70 (t, J=7.5 Hz), 25-H: 1.77 (m), 26-H_3 and 27-H_3: 0.90 (d, J=6.5 Hz)-0.96 (d, J=6.5 Hz)] and hydrogenation (Pd/C) to halitylosides E [**5**] (2) and D (2), respectively.

An examination of the spectral data of placentoside, $C_{38}H_{64}O_{12}$ (from fabms and ^{13}C nmr), indicated that it contains the same disaccharide moiety, i.e., 2-*O*-methyl-β-xylopyranosyl (1→2)-β-xylopyranosyl, as in halitylosides A [**9**] and B [**8**] (2). We also suppose D configuration of the sugar units as in **8** and **9**. Furthermore, ^{1}H- and ^{13}C-nmr spectra (Table 1) indicated that the aglycone of placentoside [**10**] shares the same steroidal 3β, 4β, 6α, 8, 15β-pentahydroxy-tetracyclic nucleus as in halityloside D (2).

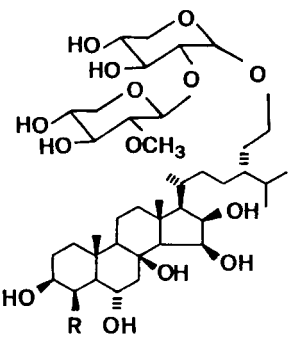
The part structure -$\overset{20}{C}H(CH_3)$-CH=CH-$\overset{24}{C}H$-$\overset{28}{C}H_3$)-$\overset{25}{C}H_2$-CH_2-O was derived by 500 MHz ^{1}H-nmr sequential decoupling [20-H: 2.20 (m), 21-H_3: 1.03 (d, J=6.5 Hz), 22-H: 5.30 (dd, J=15 and 7.6 Hz), 23-H: 5.17 (dd, J=15 and 7.5 Hz), 24-H: 2.35 (m), 28-H_3: 0.99 (d, J=6.5 Hz), 25-H_2: 1.45 (m) and 1.64 (m), 26-H_2: 3.96 (m) and 3.58 (m)]. ^{13}C nmr (Table 1) confirmed the side chain structure, already found in a sulfated glycoside, coscinasteroside D [(22*E*)-27-nor-24-methyl-26-*O*-(4-*O*-sulfoxy-β-glucopyranosyl)-5α-cholest-22-en-3β,6α,8,15β,16β,26-hexol], isolated from the starfish *Coscinasterias tenuispina* (9), and also established the location of the disaccharide moiety at C-26.

EXPERIMENTAL

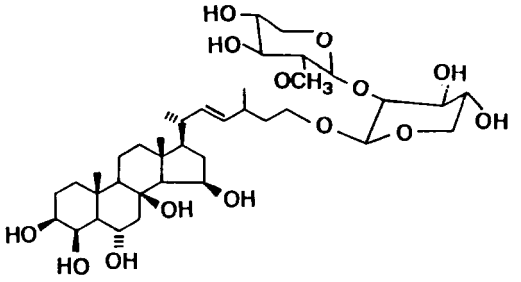
INSTRUMENTAL.—^{1}H- and ^{13}C-nmr spectra were recorded on a Bruker WM-250 instrument. The



5 R=H
6 R=H, Δ^{22E}
7 R=OH, Δ^{22E}



8 R=H
9 R=OH



10

DEPT experiments were performed using polarization transfer pulses of 90° and 135°; in the former case, only CH groups were obtained, while in the latter case positive signals for CH and CH_3 and negative ones for the CH_2 groups were obtained. Polarization transfer delays were adjusted to an average CH coupling of 135 Hz. Fab mass spectra were obtained on an AEI MS 902 mass spectrometer, equipped with a Kratos fab source. Samples were dissolved in a glycerol matrix and placed on a copper probe tip prior to bombardment with Ar atoms of 2-6 kV energy. Droplet counter-current chromatography (dccc) was carried out on a DCC-A apparatus manufactured by Tokyo Rikakikai Co., equipped with 250 tubes. Hplc separation was made on a μ-bondapack C_{18} column (7.8 mm×30 cm) using a differential refractometer detector, model 401, a U6K injector, and a solvent delivery system, M 6000A, all from Waters Associates. Rotations were taken on a Perkin-Elmer Mod. 141 Polarimeter.

EXTRACTION AND ISOLATION.—The fresh animals (3.3 kg), collected in the Gulf of Policastro and a reference specimen deposited at the Dipartimento di Chimica delle Sostanze Naturali, Università Napoli, were chopped and soaked in H_2O (4 liters) for 3 h. The aqueous extracts were passed through a column of Amberlite XAD-2 (1 kg) which was washed with H_2O (1 liter) and then with MeOH. The H_2O washings were then extracted with *n*-BuOH to give 2.1 g of glassy material in the *n*-BuOH phase, whereas the MeOH eluates were taken to dryness to give 4.4 g of glassy material. Each fraction was then chromatographed on a column of Sephadex LH-60 (4×60 cm) using MeOH-H_2O (2:1) as eluent. The fractions [10-ml fractions were collected and checked by tlc on SiO_2 with *n*-BuOH-HOAc-H_2O (60:15:25)] 90-150 contained mixed polyhydroxysteroids, glycosides, and other polar compounds (0.9 g from the *n*-BuOH extracts and 1.60 g from the MeOH eluates), which were submitted in three batches of ca. 0.89 g each to dccc, $CHCl_3$-MeOH-H_2O (7:13:8) in the ascending mode at a flow of 15 ml h^{-1}; 3.5-ml fractions were collected to give the following fractions (the first batch is described):

Fraction No.	Amount (mg)	Compounds
80-100	31	**10+8+9**
101-110	19	**8+9**
111-150	40	**2**
151-176	27	**1**, **4**
177-225	42	**3**, **4**, **7**
226-271	23	**3**, **5**, **6**

Each of the above fractions were then submitted to hplc on a C_{18} μ-bondapack column (30 cm×7.8 mm i.d.) with MeOH-H_2O (7:3) (flow rate 5 ml/min^{-1}) to give single compounds: 5 α-*Cholestane-3β,6β,15α,16β,26-pentol* [**1**], 1.6 mg, retention time (rt) in hplc 18 min, spectral data in Minale *et al.* (3). (25*S*)-5α-*Cholestane-3β,6β,8,15α,16β,26-hexol* [**2**], 2.7 mg, rt 13.5 min; eims *m/z* 450 (80% M-H_2O), 432 (100), 414 (90), 396 (40); ^{1}H nmr δ 0.94 and 0.96 (each 3H d, 6.5, 6.5, H_3-21, 27), 1.15 (3H, s, H_3-18), 1.20 (3H, s, H_3-19), 2.46 (1H, dd, 15, 2.5, H-7), 3.43 (1H, m, H-3α), 3.49 (1H, dd, 12, 7.5, H-26; the signal for the remaining H-26 hidden by the solvent), 3.89 (1H, broad s, H-6α), 4.02 (1H, dd, 7.5, 2.5, H-16α), 4.17 (1H, dd, 11.2, 7.5, H-15β). Compound **2** (1 mg) was treated with freshly distilled (+)-methoxytrifluoromethylphenylacetate (MPTA) chloride (3 liters) in 0.1 ml dry pyridine at room temperature for 3 h. After solvent removal, the product was eluted through a Pasteur pipet filled with a slurry of Si gel in $CHCl_3$ to give (+)-MPTA triester; ^{1}H nmr, δ 4.16 (2H, d, 6 Hz, H_2-26). (25R)-*24-Methyl*-5α-cholest-24(28)-*en*-3β,6β,15α,16β,*26-pentol* [**3**], 14.5 mg, rt 14 min; [α]D+28.1° (*c*=1, MeOH); eims *m/z* 449 (44%, M^+-CH_3), 446 (30, M^+-H_2O), 431 (100), 413 (90), 395 (100); ^{1}H nmr δ 0.96 (3H, s, H_3-18), 1.02 (3H, d, 7, H_3-21), 1.08 (3H, s, H_3-19), 1.10 (3H, d, 7, H_3-27), 2.33 (1H, m, H-25), 3.60 (3H, m, H-3α and H_2-26), 3.79 (1H, broad s, H-6α), 4.02 (1H, dd, 7.5, 2.5, H-16α), 4.78 and 4.85 (each 1 H broad s, H_2-28); ^{13}C nmr in Table 1. (25R)-*24-Methyl*-5α-*cholest-24(28)-en*-3β,6β,*8,15α,16β,26-hexol* [**4**], 25.7 mg, rt 14.5 min; [α]D+11.7° (*c*=0.5, MeOH); eims *m/z* 465 (12%, M^+-CH_3), 447 (30), 429 (50), 411 (100); ^{1}H nmr δ 0.99 (3H, d, 7, H_3-21), 1.09 (3H, d, 7, H_3-27), 1.15 (3H, s, H_3-18), 1.20 (3H, s, H_3-19), 2.33 (1H, m, H-25), 2.46 (1H, dd, 15, 2.5, H-7), 3.62 (3H, m, H-3α and H_2-26), 3.89 (1H broad s, H-6α), 4.02 (1H, dd, 7.5, 2.5, H-16α), 4.17 (1H, dd, 11.2, 2.5, H-15β), 4.78 and 4.85 (each 1H broad s, H_2-28). *Halityloside E* [**5**], 6.4 mg, rt 20 min [α]D−19°; spectral data in Iorizzi *et al.* (2). *22-Dehydrohalityloside E* [**6**], 0.9 mg, rt 23 min; fabms (+ve ion) *m/z* 765 $(M+Na)^+$, 743 $(M+H)^+$; ^{1}H nmr δ (aglycone) 0.90 and 0.96 (each 3H, d, 6.5, 6.5, H_3-26,27), 1.02 (3H, s, H_3-19), 1.05 (3H, d, 6.3, H_3-21), 1.32 (3H, s, H_3-18), 2.40 (2H, one dd, 15, 2.5, overlapped with a m, H-7, H-16), 3.55 (1H, m, H-3α), 3.74 (1H, td, 10.5, 5, H-6β), 4.45 (1H, m, H-15α), 5.35 (1H, dd, 15, 7.5 H-23), 5.46 (1H, dd, 15, 7.5, H-22); δ (sugar) 2.90 (1H, dd, 9, 7.5, H-2″), 3.14 (1H, t, 10.6, H-5″a), 3.20 (1H, m, H-4″), 3.42 (1H, t, 9.0, H-3″), 3.50 (3H, s, OCH_3), 3.60 (s, OCH_3), 3.65 (1H, dd, 12.5, 5, H-5′), 3.79 (1H, dd, 12.5, 3, H-5′), 3.98 (1H, m, H-4′), 4.02 (2H, one dd, 10.6, 4.0, overlapped with a m, H-5″e, H-3′), 4.08 (1H, d, 4.0, H-2′), 4.46 (1H, d, 7.5, H-1″), 5.11 (1H, broad s, H-1′). *22-Dehydrohalityloside D* [**7**], 1.5 mg, rt 16.5 min; fabms (+ve ion) *m/z* 781 $(M+Na)^+$, 759 $(M+H)^+$; ^{1}H nmr δ (aglycone) 0.93 and 0.94 (each 3H, d, 6.5, 6.5, H_3-26,27), 1.05 (3H, d, 6.3, H_3-21), 1.19 (3H, s, H_3-19), 1.30 (3H, s, H_3-18), 2.40 (2H one dd, 15, 2.5, overlapped with a m, H-7, H-16), 3.65 (1H, m, H-3α), 4.29 (1H, broad s, H-4α), 4.46 (1H, m, H-15α), 5.35 (dd, 15, 7.5, H-23), 5.46 (1H, dd, 15, 7.5, H-22); δ (sugar) identical with those of **6**. *Halityloside B* [**8**], 3.9 mg, rt 23 min, [α]D−5.0° (*c*=0.3, MeOH); spectral data in Iorizzi *et al.* (2). *Halityloside A* [**9**], 6.9 mg, rt 20 min; [α]D−3° (*c*=0.3, MeOH); spectral data in Iorizzi *et al.* (2). *Placentoside* [**10**], 3.8 mg, rt 9.5 min; fabms (−ve ion) *m/z* 743 (M−H); 597 (M-2-OMe-xyl), 465 (M-2-OMe-xyl-xyl); ^{1}H nmr δ (aglycone) 0.99 (3H, d, 6.5, H_3-28), 1.03 (3H, d, 6.5, H_3-21), 1.19 (3H, s, H_3-19), 1.31 (3H, s, H_3-18), 1.45 and 1.64 (detected by decoupling, m, H_2-25), 2.20 (1H, m, H-20), 2.28 (1H, m, H-16), 2.35 (1H, m, H-24), 2.47 (1H, dd, 12, 4, H-7β), 3.28 (1H, m, H-26), 3.87 (1H, m, H-26), 4.19 (1H, td, 10.5, 4, H-6β), 4.29 (1H, broad s, H-4α), 4.43 (1H, m, H-15α), 5.17 (1H, dd, 15, 7.6, H-23), 5.30 (1H, dd, 15, 7.5, H-22); δ (sugar) 2.95 (1H, dd, 9, 7, H-2), 3.20 (1H, dd, 12, 9.5, H-5a), 3.38 (1H, t, 9, H-3), 3.65 (3H, s, OCH_3), 3.87 (2H, two overlapped dd, 2H-5e), 4.35 (1H, d, 7.5, H-1), 4.74 (1H, d, 7.1, H-1), the remaining sugar protons gave complex overlapping signals in the region δ 3.4-3.6; ^{13}C nmr in Table 1.

CONVERSION OF **3** TO THE KETONE **3a**.—A mixture of **3** (9 mg) and excess of Ac_2O in 0.3 ml of pyridine was kept at room temperature overnight. After removal of the excess reagents in vacuo, the residue was purified by Si gel chromatography (a Pasteur pipet filled with a slurry of Si gel) with $CHCl_3$ to give the *pentaacetate*, eims *m/z* 614 (22%, M^+-CH_3CO_2H), 494 (100%, M^+-$3CH_3CO_2H$); ^{1}H nmr ($CDCl_3$) δ 0.97 (3H, d, 7, H_3-21), 0.98 (3H, s, H_3-18), 1.01 (3H, s, H_3-19), 1.04 (3H, d, 7, H_3-27), 2.02 and 2.05 (15H, s, CH_3CO), 2.40 (1H, m, H-25), 3.88 (1H, dd, 10, 7.5, H-26), 4.08 (1H, dd, 10, 7.5, H-26), 4.70 (1H, m, H-3α), 4.75 (2H, s, H_2-28), 4.98 (2H, m, H-15β, H-6α), 5.28 (1H, dd, 7.5, 2.5, H-16α). A mixture of the above pentacetate (10 mg) and OsO_4 (3.8 mg in dry pyridine 0.5 ml) was stirred at room temperature for 3 h. An aqueous solution of $NaHSO_3$ was then added, and the mixture, after 1 h stirring, was extracted with CH_2Cl_2.

Evaporation of the solvent gave a residue, which without further purification was dissolved in MeOH (1 ml). To the solution an excess of lead tetraacetate was added, and the mixture was stirred for 1 h at room temperature. Evaporation of the solvent gave a residue, which was purified by Si gel chromatography ($CHCl_3$ as solvent) to give 4.5 mg of *3β,6β,15α,16β,26-penta(acetyloxy)*-5α-*cholestan-24-one*, eims *m/z* 616 (13%, M^+-CH_3CO_2H), 514 (9), 496 (43), 473 (24), 454 (15), 436 (35), 394 (15), 376 (32), 353 (100); ^{1}H nmr ($CDCl_3$) δ 0.93 (3H, d, 6.5, H_3-21), 0.98 (3H, s, H_3-18), 1.01 (3H, s, H_3-19), 1.10 (3H,

d, 6.5, H_3-27), 2.02 and 2.10 (15H, s, CH_3CO), 2.43 (2H, m, H_2-23), 2.86 (1H, m, H-25), 4.09 (1H, dd, 11, 5, H-26), 4.20 (1H, dd, 11, 5, H-26), 4.70 (1H, m, H-3α), 4.98 (2H, m, H-15β, H-6α), 5.25 (1H, dd, 7.5, 2.5, H-16α); ir ν max ($CHCl_3$), 1710 cm^{-1}; cd (MeOH) $\Delta\epsilon_{280} = +0.077$.

HYDROGENATION OF **6** AND **7**.—Hydrogenation was carried out at room temperature and atmospheric pressure in MeOH with 10% Pd/C for 10 h. Usual work up afforded the saturated analogs which were identified by direct comparison with the authentic samples of halitylosides E [**5**] and D, respectively, isolated from *Halityle regularis* (2).

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