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SOMALENONE, A C_{26} STEROL FROM THE MARINE RED ALGA *MELANOTHAMNUS SOMALENSIS*

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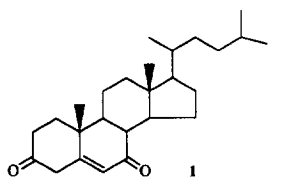
Key Word Index—Marine alga; Rhodomelaceae; *Melanothamnus somalensis*; somalenone; 24-norcholest-5-en-3,7-dione.

Abstract—A new C_{26} sterol named as somalenone has been isolated from the marine red alga *Melanothamnus somalensis* and characterized as 24-norcholest-5-en-3,7-dione. Cholesterol, 7-oxo-cholesterol and 24-methyl-enecholesterol were also isolated from the alga.

INTRODUCTION

In the course of our studies on the constituents of marine algae [1–3] and especially on red algae [4–6], we have already reported many secondary metabolites and we have now examined the marine red alga *Melanothamnus somalensis* collected from the Karachi coast of the Arabian Sea. About 10 years ago this alga was initially identified as *Odonthalia washingtoniensis*. Later, it was investigated in detail and revealed to be *Melanothamnus somalensis* [7]. We now describe the isolation and characterization of a new C_{26} sterol named as somalenone (**1**) and three known sterols from *M. somalensis*. The known sterols have not been isolated previously from the same source.



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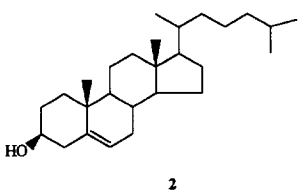

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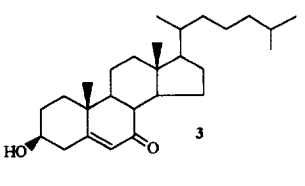

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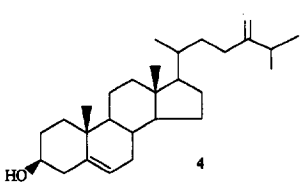

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RESULTS AND DISCUSSION

Silica gel column chromatography of the ethanolic extract of *Melanothamnus somalensis* yielded a number of fractions. The fraction eluted with hexane–diethyl ether (17:3) furnished compound **1** as an amorphous solid. The HR-mass spectrum of **1** exhibited the molecular ion peak at *m/z* 384.6069, corresponding to the molecular formula $C_{26}H_{40}O_2$. The electron impact mass spectrum also showed the molecular ion peak at *m/z* 384 and the other intense peaks appeared at *m/z* 369 $[M-CH_3]^+$, 327 $[M-C_4H_9]^+$, 234 $[C_{17}H_{30}]^+$, 204 $[C_{13}H_{16}O_2]^+$, 180 $[C_{13}H_{24}]^+$ and 118 $[C_9H_{10}]^+$, which showed the presence of a steroidal skeleton. The UV spectrum showed absorption at 240 nm due to the presence of a conjugated ketone moiety in the molecule.

The ^{13}C NMR spectrum indicated the presence of 26 carbon signals. The DEPT spectrum exhibited five methyls, nine methylenes and seven methine resonances. the remaining five signals in the broad band spectrum were due to the quaternary carbon atoms. The five methyl signals appeared at δ 12.24, 17.33, 18.86, 22.55 and 22.80. The signal due to the olefinic methine appeared at δ 122.71 and the quaternary carbon associated with this exhibited its signal at δ 162.41 in the carbon spectrum. The two ketonic carbons appeared at δ 200.34 and 206.21, corresponding to C-3 and C-7, respectively.

The ^1H NMR spectrum of **1** displayed five methyl

signals. Two signals appeared as singlets at δ 0.70 and 1.25, corresponding to Me-18 and Me-19, respectively. The other three doublets at δ 0.85, 0.86 and 0.93 were due to Me-25, Me-26 and Me-21, respectively. The olefinic proton appeared at δ 6.28 as a singlet in the spectrum.

On the basis of the above spectroscopic data the structure of **1** has been assigned as 24-norcholest-5-en-3,7-dione. Apart from the new sterol (**1**), three more sterols have been isolated and characterized as cholesterol (**2**) [8, 9], 7-oxo-cholesterol (**3**) [10] and 24-methylenecholesterol (**4**) [11].

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 and 100 MHz, respectively.

Extraction and isolation. Melanothamnus somalensis (2 kg dry wt), herbarium no. KUH-SW 4268, was extracted in a Soxhlet with $CHCl_3$ (8 hr). The solvent was then evapd under red. pres. The residue thus obtained (12.15 g) was subjected to CC with elution by hexane, hexane–Et_2O, $CHCl_3$, $CHCl_3$–MeOH and MeOH.

The fr. eluted with hexane–Et_2O (17:3) was further purified by CC to give **1** (15 mg) as an amorphous powder. UV λ_{max}^{MeOH} nm: 240 nm. HR-MS *m/z*: 384.6069 (calc. for $C_{26}H_{40}O_2$, 384.6075); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1695 (conjugated ketone), 1660 (C=C); EI-MS *m/z*: 384 $[M]^+$, 369 $[M - CH_3]^+$, 327 $[M - C_4H_9]^+$, 234 $[C_{17}H_{30}]^+$, 204 $[C_{13}H_{16}O_2]^+$, 180 $[C_{13}H_{24}]^+$, 118 $[C_9H_{10}]^+$. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.70 (3H, *s*, H-18), 0.85 (3H, *d*, J = 6.6 Hz, H-25), 0.86 (3H, *d*, J = 6.6 Hz, H-26), 0.93 (3H, *d*, J = 6.5 Hz, H-21), 1.25 (3H, *s*, H-19), 6.28 (1H, *s*, H-6); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.24 (C-1), 34.15 (C-2), 200.34 (C-3), 39.47 (C-4), 162.41 (C-5), 122.71 (C-6), 206.21 (C-7), 50.42 (C-8), 51.27 (C-9), 40.02 (C-10), 21.01 (C-11), 39.00 (C-12), 44.69 (C-13), 54.97 (C-14), 23.90 (C-15), 28.70 (C-16), 53.19 (C-17), 12.24 (C-18), 17.33 (C-19), 35.70 (C-20), 18.86 (C-21), 36.13 (C-22), 23.68 (C-23), 28.01 (C-24), 22.55 (C-25), 22.80 (C-26).

The fr. eluted with hexane–Et_2O (9:1) afforded **2** (20 mg); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1660 (C=C); EI-MS *m/z*: 386 $[M]^+$, 371 $[M - CH_3]^+$, 368 $[M - H_2O]^+$, 353 $[M - H_2O - Me]^+$, 325 $[M - H_2O -$ isopropyl$]^+$, 311 $[M - H_2O - C_4H_9]^+$, 301 $[M - C_6H_{13}]^+$, 273 [M − side chain $(C_8H_{17})]^+$, 255 [M − side chain $- H_2O]^+$; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.67 (3H, *s*, H-18), 0.85 (3H, *d*, J = 6.6 Hz, H-26), 0.86 (3H, *d*, J = 6.6 Hz, H-27), 0.91 (3H, *d*, J = 6.4 Hz, H-21), 1.00 (3H, *s*, H-19), 3.54 (1H, *m*, H-3), 5.34 (1H, distorted H-5); ^{13}C NMR ($CDCl_3$; 100 MHz): δ 37.36 (C-1), 31.98 (C-2), 71.85 (C-3), 42.43 (C-4), 140.88 (C-5), 121.70 (C-6), 31.79 (C-7), 32.03 (C-8), 50.30 (C-9), 36.59 (C-10), 21.17 (C-11), 39.59 (C-12), 42.43 (C-13), 56.39 (C-14), 24.34 (C-15), 28.24 (C-16), 56.33 (C-17), 11.90 (C-18), 19.40 (C-19), 35.81 (C-20), 18.77 (C-21), 28.24 (C-22), 36.28 (C-23), 39.91 (C-24), 28.03 (C-25), 22.55 (C-26), 22.77 (C-27).

The frs eluted with hexane–Et_2O (1:1) were mixed on the basis of the TLC profile and purified by prep. TLC developed in hexane–Et_2O (3:2) to yield 11.8 mg **3** in gummy form. UV λ_{max}^{MeOH} nm: 240 nm; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3410 (OH), 1690 (conjugated ketone); EI-MS *m/z*: 400 $[M]^+$, 385 $[M - Me]^+$, 382 $[M - H_2O]^+$, 367 $[M - H_2O - Me]^+$, 343 $[M - C_4H_9]^+$, 287 [M − side chain $(C_8H_{17})]^+$, 269 [M − side chain $- H_2O]^+$; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.67 (3H, *s*, H-18), 0.85 (3H, *d*, J = 6.6 Hz, H-26), 0.86 (3H, *d*, J = 6.6 Hz, H-27), 0.91 (3H, *d*, J = 6.5 Hz, H-21), 1.19 (3H, *s*, H-19), 3.68 (1H, *m*, H-3), 5.67 (1H, *d*, J = 1.76 Hz, H-5); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.38 (C-1), 31.94 (C-2), 70.55 (C-3), 42.27 (C-4), 165.40 (C-5), 126.13 (C-6), 202.57 (C-7), 45.44 (C-8), 49.99 (C-9), 38.32 (C-10), 21.24 (C-11), 41.80 (C-12), 43.12 (C-13), 56.21 (C-14), 23.85 (C-15), 28.55 (C-16), 54.86 (C-17), 11.98 (C-18), 17.32 (C-19), 35.79 (C-20), 18.88 (C-21), 26.33 (C-22), 36.12 (C-23), 39.51 (C-24), 28.01 (C-25), 22.56 (C-26), 22.81 (C-27).

The fraction eluted with hexane–Et_2O (3:2) yielded **4** (12.0 mg) as a gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH), 1655 (C=C); EI-MS *m/z*: 398 $[M]^+$, 314 $(M - C_6H_{12}]^+$, 271 $[M - C_9H_{17} - 2H]^+$; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.65 (3H, *s*, H-18), 0.87 (3H, *s*, H-19), 1.24 (3H, *d*, J = 7.0 Hz, H-21), 1.57 (6H, *m*, H-26, H-27), 3.52 (3β-H), 5.32 (1H, *m*, H-5), 5.34 (2H, *s*, H-28); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 34.29 (C-1), 29.76 (C-2), 73.36 (C-3), 38.59 (C-4), 146.96 (C-5), 126.42 (C-6), 32.17 (C-7), 35.74 (C-8), 53.69 (C-9), 35.77 (C-10), 20.99 (C-11), 28.59 (C-12), 41.98 (C-13), 55.92 (C-14), 24.17 (C-15), 40.11 (C-16), 50.03 (C-17), 12.03 (C-18), 12.21 (C-19), 34.29 (C-20), 19.53 (C-21), 37.15 (C-22), 22.33 (C-23), 144.64 (C-24), 29.76 (C-25), 20.99 (C-26), 22.27 (C-27), 123.45 (C-28).

The spectroscopic data for compounds **2–4** were exactly matched with the reported data for cholesterol (**2**) [8, 9], 7-oxo-cholesterol (**3**) [10] and 24-methylenecholesterol (**4**) [11], respectively.

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