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FREE STEROLS OF THE RED ALGA *GIGARTINA SKOTTSBERGII*

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Key Word Index—*Gigartina skottsbergii*, Gigartinales, Rhodophyceae, sterols, cholest-5-en-3β-ol

Abstract—The free sterols of the red alga *Gigartina skottsbergii* have been identified by means of GC and GC/MS analyses The mixture contained saturated and unsaturated C_{27}, C_{28} and C_{29} sterols The major component was cholest-5-en-3β-ol Cholesta-5,24-dien-3β-ol (desmosterol) was present in low proportion but no side chain hydroxylated components were detected

INTRODUCTION

The main sterols of the majority of red algae are C_{27} compounds, cholesterol being the major component of most of them, although in a few species desmosterol is present in substantial amounts and may even be the major sterol [1–3] Red algae also contain, though in minor amounts, C_{26}, C_{28} and C_{29} sterols and in some species the presence of side chain hydroxylated sterols has been reported [4–6]

We wish to report here the sterol composition of *Gigartina skottsbergii*, a red alga from the south Atlantic ocean

RESULTS AND DISCUSSION

Fresh specimens of *G skottsbergii*, collected at Puerto Madryn, Chubut, were freeze-dried and the residue was

Table 1 Free sterols of the alga *Gigartina skottsbergii*

Sterols	MS characteristic fragments	RR_t*	Composition (%)
22-*trans*-Cholesta-5,22-dien-3β-ol	384 $[M]^+$, 366, 351, 300, 273, 271, 255, 213, 111, 69, 55	0 94	0 7
Cholest-5-en-3β-ol	386 $[M]^+$, 371, 368, 301, 275, 273, 255, 231, 213, 145, 43	1 00	92 7
5α-Cholestan-3β-ol	388 $[M]^+$, 373, 370, 355, 275, 257, 233, 217, 215, 43	1 02	tr†
22-*trans*-24ξ-Methylcholesta-5,22-dien-3β-ol	398 $[M]^+$, 380, 365, 300, 271, 255, 213, 69, 55	1 04	1 1
Cholesta-5,24-dien-3β-ol	384 $[M]^+$, 369, 366, 351, 300, 299, 282, 271, 253, 231, 229, 213, 211	1 07	2 1
24ξ-Methylcholest-5-en-3β-ol	400 $[M]^+$, 385, 382, 367, 315, 289, 273, 213, 105, 43	1 10	0 8
24ξ-Methyl-5α-cholestan-3β-ol	402 $[M]^+$, 387, 384, 369, 275, 233, 217, 215, 43	1 12	tr
24-Methylcholesta-5,24(28)-dien-3β-ol	398 $[M]^+$, 383, 380, 314, 299, 281, 271, 255, 229, 213, 55	1 14	1 1
22-*trans*-24ξ-Ethylcholesta-5,22-dien-3β-ol	412 $[M]^+$, 397, 394, 379, 351, 300, 273, 271, 255, 69, 55	1 16	0 5
24ξ-Ethylcholest-5-en-3β-ol	414 $[M]^+$, 396, 381, 368, 329, 303, 255, 213, 91, 55	1 23	0 5
24ξ-Ethyl-5α-cholestan-3β-ol	416 $[M]^+$, 401, 398, 383, 275, 233, 215, 55	1 25	tr
24-Ethylcholesta-5,24(28)-dien-3β-ol	412 $[M]^+$, 397, 394, 314, 299, 281, 273, 271, 255, 229, 213, 55	1 27	0 4
24-Ethyl-5α-cholest-24(28)-en-3β-ol	414 $[M]^+$, 399, 396, 316, 301, 273, 233, 215, 55	1 28	tr

*RR_t = retention times of the free sterols relative to cholest-5-en-3β-ol
†tr = traces

extracted with methanol The residue obtained by evaporation of the solvent was partitioned between ethyl acetate and water The organic extract was dried and evaporated The residue was chromatographed on silica gel and the sterol fraction was fractionated further by HPLC Each subfraction was analysed by GC and GC/MS leading to the identification of the sterols of the mixture (see Table 1) by comparison with known standards As it has been normally found in red algae, cholesterol was by far the most abundant constituent of the mixture, which also contained C_{28} and C_{29} saturated and unsaturated components It is interesting to note that desmosterol was present, in small amount, in the free state but we were unable to detect any side chain hydroxylated sterol

EXPERIMENTAL

General HPLC was carried out on a Whatman Partisil M9 10/50 ODS-2 column using an RI detector (mobile phase MeOH) GC was on a fused silica capillary column (12 m × 0 02 mm) coated with methyl silicone fluid (Hewlett–Packard) Computerized GC/MS was on a Varian-Mat CH7-A instrument at 70 eV

Plant material Gigartina skottsbergii was collected at Puerto Madryn, Chubut, Argentina in winter at 8 m depth Voucher specimens have been deposited at the Centro Nacional Patagónico, Puerto Madryn

Extraction and analysis Fresh algae (3 4 kg) were freeze-dried and the residue (1 2 kg) was extracted with MeOH (2 × 2 l) yielding an extract which was partitioned between EtOAc and H_2O The syrup obtained by evapn of the organic solvent (4 45 g) was chromatographed twice on silica gel columns eluted with toluene and toluene–CH_2Cl_2 (1 1) to separate the free sterol fraction This fraction (99 mg) was purified by HPLC yielding four subfractions that were analysed by GC and GC/MS techniques Identification of each sterol was made by comparison with the MS data of authentic samples (see Table 1)

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ANTHRAQUINONES FROM *CASSIA SOPHERA* ROOT BARK

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Key Word Index—*Cassia sophera*, Leguminosae, 1,8-dihydroxy-3,6-dimethoxy-2-methyl-7-vinylanthraquinone, 1,3-dihydroxy-5,7,8-trimethoxy-2-methylanthraquinone

Abstract—Two new anthraquinones have been isolated from the root bark of *Cassia sophera* and characterized as 1,8-dihydroxy-3,6-dimethoxy-2-methyl-7-vinylanthraquinone and 1,3-dihydroxy-5,7,8-trimethoxy-2-methylanthraquinone

Cassia sophera (Leguminosae) is well known for its medicinal value [1], roots, flowers and heartwood have been studied chemically [2–6]

From the benzene fraction of the acetone extract of the root bark of *Cassia sophera* two new anthraquinones have now been isolated and characterized by spectral and chemical studies Both compounds (**1** and **2**) responded to characteristic colour tests for anthraquinones Their λ_{max} and IR spectra supported the above conclusion Strong peaks at 1460 cm^{-1} in the IR spectrum of **1** and at 1450 cm^{-1} in that of **2**, a signal at δ2 35 in the ^1H NMR spectrum of **1** and 2 38 in that of **2** and identification of 2-