Journal of Natural Products
Vol. 53, No. 5, pp. 1379-1382, Sep-Oct 1990

THREE ACETOGENINS FROM THE BROWN ALGA *CAULOCYSTIS CEPHALORNITHOS*

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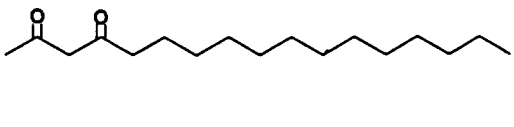
ABSTRACT.—The lipid extract of the brown alga *Caulocystis cephalornithos* was examined for secondary metabolites typical of the Cystoseiraceae. Three acetogenins were isolated and characterized by gc-ms and spectral methods.

Brown algae belonging to the family Cystoseiraceae have been extensively studied for secondary active metabolites. The Cystoseiraceae from different geographical areas, in fact, generally accumulate tetraprenyltoluquinols, and several biological activities have been reported (1–3). The majority of these compounds were found in the *Cystoseira*, the most studied and representative genus of this family, which is mainly distributed in the Mediterranean Sea (4–11). However, metabolites of this chemical type have also been isolated from other genera, such as the *Bifurcaria* occurring off the Pacific coast of the Galapagos Islands (1), the *Halidrys* from the Northern coasts of England (12), and the *Cystophora* representative of the Australian coast (13–16). Recently we obtained a sizeable amount of *Caulocystis cephalornithos* (Labill.) Areschoug (family Cystoseiraceae, order Fucales) (17,18) collected along the coast of Beacon Island, Australia, and we examined its lipid extract for secondary metabolites typical of the Cystoseiraceae. A previous phytochemical study by Australian workers on the same alga [quoted as *C. cephalornithos* (Labill.) Kuetz (family Sargassaceae, order Fucales)] (19), led to the isolation of 6-tridecyl salicylic acid, 3-tridecyl phenol, and 8-hydroxy-3-undecyl-1*H*-2-benzopyran-2-one together with two simple lipids, pentadec-1-ene and heptadec-3-en-2-one.

In the present paper, we report the identification of four additional metabolites **1**–**4**, none of which has the tetraprenyltoluquinol skeleton. All the isolated compounds have been reported as natural products from other marine or terrestrial sources. Because of the paucity of data in the literature, we describe here their spectral features.

The less polar fraction from the chromatography of the CH_2Cl_2 extract of the alga yielded an optically inactive oily compound **1**, $C_{17}H_{32}O_2$, λ max 275 nm, which showed in the ir spectrum an absorption at 1620 cm^{-1}, characteristic of a β-diketone in the enol form. This and the presence of a three-proton singlet at δ 2.10 (CH_3-CO) allowed us to establish that **1** was heptadecan-2,4-dione, a compound previously identified in the essential oil of *Ruta graveolens* (20). Heptadeca-2,4-dione in $CHCl_3$ solution is a 3:17 equilibrium mixture of the keto and enol forms, as is inferred from ^{1}H- and ^{13}C-nmr spectra. The isolation of this diketone lends support to the hypothesis that algal resorcinols and phloroglucinols are formed by condensation of a common triketocompound (13).

Compounds **2** and **3** were isolated as a mixture from the cc of the algal extract. Gas chromatography of this mixture gave two peaks, whose mass spectra indicated that they were pentadecan-2-one [**2**] and heptadecan-2-one [**3**]. Compound **2** has been previously identified as a component of cranberry oil (21),



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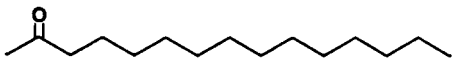

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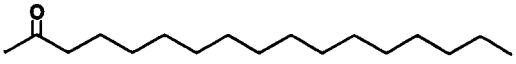

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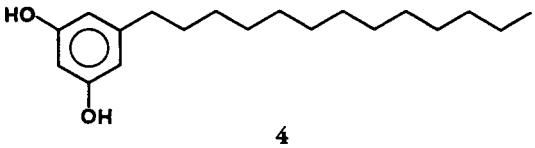

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while compound **3** has been reported previously from the essential oil of hops (22).

The more polar compound **4** was identified as 5-tridecyl resorcinol (grevillol), previously isolated from *Grevillea robusta* (23) and subsequently from *Cystophora torulosa* (13).

EXPERIMENTAL

GENERAL METHODS.—Eims were determined at 70 eV on a Kratos MS-50S instrument. Uv and ir spectra were recorded on Perkin-Elmer model 330 and model 684 spectrophotometers, respectively. Nmr spectra were measured on a Bruker AC-250 instrument, operating at 250.13 and 62.9 MHz for ^{1}H and ^{13}C, respectively; multiplicities of ^{13}C-nmr were determined by DEPT experiments; COSY and heteronuclear correlations were run using the standard Bruker microprograms. Gc-ms analysis was performed on Hewlett-Packard model 5890 instrument equipped with MSD 5971 A detector. Preparative liquid chromatography (plc) was carried out on a Jobin-Yvon LC Miniprep (LiChroprep Si 60, 25–40 μ, as the stationary phase).

PLANT MATERIAL.—*C. cephalornithos* was collected at about 3 m depth at Beacon Island, Wallaby, Australia, in September 1988. A voucher specimen was deposited at the Herbarium of the Department of Botany, Catania, Italy.

EXTRACTION AND PURIFICATION.—The air-dried and ground alga (500 g) was extracted three times with CH_2Cl_2 at room temperature with continuous stirring, and the extract was evaporated under reduced pressure. The oily residue was subjected to open cc on Si gel with a stepwise gradient of Et_2O in C_6H_{14} as the eluent. Fractions were examined by tlc and appropriately pooled. The pooled fractions were further purified by plc to give 8-hydroxy-3-undecyl-1*H*-2-benzopyran-1-one (10 mg, 0.002% dry wt), (*E*)-heptadec-3-en-2-one (210 mg, 0.04% dry wt), 3-tridecylphenol (155 mg, 0.03% dry wt), and 6-tridecyl salicylic acid (1.8 g, 0.36% dry wt), all previous reported in the lipid extract of *C. cephalornithos* (19), and the previously unreported compounds **1–4**.

HEPTADECAN-2,4-DIONE [**1**].—Compound **1** (42 mg, 0.008% dry wt): ir ν max (KBr) 3420, 1620 cm^{-1}; uv λ max (EtOH) 275 nm (ε = 12000); hreims $[M]^+$ 268.2408, calcd for $C_{17}H_{32}O_2$, 268.2402; ms *m/z* (%) 268 (2), 211 (8), 138 (4), 113 (30), 101 (22), 100 (100), 85 (74), 72 (21), 69 (11), 57 (24), 43 (76), 41 (32). ^{1}H- and ^{13}C-nmr spectra of **1** gave the following data for the keto and enolic forms of compound **1**.

Keto form.—^{1}H nmr (250 MHz, TMS, δ in $CDCl_3$) 3.57 (2H, s, H-3), 2.50 (2H, t, J = 6.5 Hz, H-5), 2.24 (3H, s, H-1), 1.59 (2H, m, H-6), 1.26 (20H, m, H-7/H-16), 0.88 (3H, t, J = 7 Hz, H-17); ^{13}C nmr (62.9 MHz, TMS, ppm in $CDCl_3$) 203.5 (s, C-2 and C-4), 57.9 (t, C-3), 43.8 (t, C-5), 31.9 (t, C-15), 31.0 (q, C-1), 29.6–29.2 (t, C-7/C-14), 23.3 (t, C-6), 22.7 (t, C-16), 14.1 (q, C-17).

Enolic form.—^{1}H nmr (250 MHz, TMS, δ in $CDCl_3$) 5.49 (1H, s, H-3), 2.26 (2H, t, J = 6.5 Hz, H-5), 2.07 (3H, s, H-1), 1.59 (2H, m, H-6), 1.26 (20H, m, H-7/H-16), 0.88 (3H, t, J = 7 Hz, H-17); ^{13}C nmr (62.9 MHz, TMS, ppm in $CDCl_3$) 194.2 (s, C-2), 191.4 (s, C-4), 99.7 (d, C-3), 38.2 (t, C-5), 31.9 (t, C-15), 29.6–29.2 (t, C-7/C-14), 25.7 (t, C-6), 25.0 (q, C-1), 22.7 (t, C-16), 14.1 (q, C-17).

PENTADECAN-2-ONE [**2**] AND HEPTADECAN-2-ONE [**3**].—These two compounds were present in the same fraction (34 mg, 0.007% dry wt) and were homogeneous by tlc. The single compounds and their ratio (9:1) were determined by gc-ms instrument equipped with a 12 m × 0.2 mm i.d. HP-1 (crosslinked dimethylsilicone gum) column. The column temperature was programmed as 100 to 250° at 10°/min; the injector temperature and the ion source temperature were 250° and 280°, respectively. The carrier gas was He.

Compound **2**.—Hreims $[M]^+$ 226.2296, calcd for $C_{15}H_{30}O$, 226.2293; ms *m/z* (%) 226 (3), 211 (2), 168 (3), 166 (2), 138 (1), 113 (2), 111 (2), 100 (2), 99 (1), 97 (3), 96 (6), 85 (11), 71 (35), 59 (51), 58 (100), 57 (12), 55 (11), 43 (66), 41 (17).

Compound **3**.—Hreims $[M]^+$ 254.2609, calcd for $C_{17}H_{34}O$, 254.2612; ms *m/z* (%) 254 (5), 239 (2), 196 (3), 194 (2), 152 (1), 138 (1), 127 (3), 113 (2), 111 (3), 100 (3), 99 (2), 97 (6), 96 (10), 85 (15), 71 (41), 59 (70), 58 (100), 57 (14), 55 (12), 43 (55), 41 (14).

5-TRIDECYL RESORCINOL [**4**].—Compound **4** (160 mg, 0.03% dry wt): ir ν max (KBr) 3320, 3250, 1600 cm^{-1}; uv λ max (EtOH) 280 nm (ε = 3150), 274 (ε = 3300), 262 (ε = 3600), 223 (ε = 8000); hreims $[M]^+$ 292.2396, calcd for $C_{19}H_{32}O_2$, 292.2402; ^{1}H nmr (250 MHz, TMS, δ in $CDCl_3$) 6.22 (2H, d, J = 2 Hz, ArH), 6.15 (1H, t, J = 2 Hz, ArH), 2.46 (2H, t, J = 6 Hz, ArCH_2-), 1.23 (22H, m, -CH_2-), 0.86 (3H, t, J = 7 Hz, C-CH_3); ^{13}C nmr (62.9 MHz, TMS, ppm in $CDCl_3$) 156.5 s (C-1 and C-3), 146.1 s (C-5), 108.0 d (C-4 and C-6), 100.1 d (C-2), 35.8 t (C-1′), 31.9 t and 31.1 t (C-2′ and C-11′), 29.7–29.3 t (C-3′–C-10′), 25.4 t (C-12′), 14.1 q (C-13′).

ACKNOWLEDGMENTS

This work was financially supported by the Ministero Pubblica Istruzione, Rome. We thank Profs. Giuseppe Giaccone and Blasco Scammacca, Department of Botany, University of Catania, for a gift of plant material collected during the "Tethys 89" expedition along the western Australian coast.

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Received 26 February 1990