In addition, the petrol extract afforded stigmasterol and taraxasteryl and lupeyl acetates The physical constants and spectroscopic data of these compounds were consistent with those reported in the literature [6–8]

EXPERIMENTAL

Mps was measured with a Buchi apparatus and are uncorr The IR spectrum was recorded in KBr

Extraction and isolation Spilanthes ocymifolia was collected in 1979 in El Salvador Leaves (3 3 kg) were extracted with EtOH The material obtained after removal of the EtOH was diluted with H_2O, and extracted $\times 3$ with petrol and then $\times 3$ with toluene, for 30 hr The petrol extract (10 g) was chromatographed on a column of silica gel eluted with increasing proportions of toluene followed by EtOAc, yielding the following compounds in order of elution taraxasteryl acetate, lupeyl acetate, stigmasterol and *N*-2-phenylethylcinnamamide (**1**)

The toluene extract (7 5 g) was chromatographed on a silica gel column with $CHCl_3$–Me_2CO mixtures as eluents, yielding stigmasterol and *N*-2-phenylethylcinnamamide (**1**) in order of elution

The previously known products were identified by their mp and spectroscopic (IR, ^{1}H NMR, ^{13}C NMR and MS) data

N-2-*phenylethylcinnamamide* White needles, mp 125–126° (cyclohexane) IR ν_{max}^{KBr} cm^{-1} 3300, 3100, 3060, 2960, 2960, 1670, 1620, 1570, 1460, 1350, 1230, 1000, 870, 770, 750, 730, 700, etc ^{1}H NMR see Results and Discussion ^{13}C NMR see Results and Discussion MS (direct inlet) *m/z* (rel int) 252 $[M+1]^+$ (18 8), 251 $[M]^+$ (42 1), 160 $[M-C_7H_7]^+$ (21 1), 146 $[M-C_7H_7-CH_2]^+$ (12 0), 131 $[M-C_8H_{10}N]^+$ (100), 103 $[M-C_9H_{10}NO]^+$ (23 3)

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LAUREQUINONE, A CYCLOLAURANE SESQUITERPENE FROM THE RED ALGA *LAURENCIA NIDIFICA*

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Key Word Index—*Laurencia nidifica*, Rhodomelaceae, red alga, cyclolaurane-type sesquiterpene, laurequinone

Abstract—From the red alga *Laurencia nidifica* a new sesquiterpene of cyclolaurane-type was isolated, and the structure elucidated by spectral analyses and chemical means

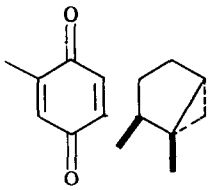
INTRODUCTION

Previous investigations of the red alga *Laurencia nidifica* (Rhodomelaceae, Rhodophyta) have revealed that this alga is a rich source of halogenated and nonhalogenated sesquiterpenes, and halogenated C_{15} nonterpenoid compounds [1–3] The present paper describes the isolation of a new cyclolaurane sesquiterpene, laurequinone (**1**) together with aplysin [4–6], debromoaplysin [4–6], laurinterol [7–10] and debromolaurinterol [7, 8]

RESULTS AND DISCUSSION

The fresh alga was extracted with acetone and the resulting extract was further extracted with ethyl acetate The oily extract was separated by column chromatography, TLC and HPLC to afford a new compound, laurequinone (**1**)

Laurequinone (**1**), $C_{15}H_{18}O_2$, pale yellow oil, $[\alpha]_D^{23}$ −53 5° (*c* 0 91, $CHCl_3$) The presence of either a 2-methyl-5-alkyl-1,4-benzoquinone group or a 2-methyl-6-alkyl-



1

1,4-benzoquinone moiety in **1** was deduced from the UV spectrum (λ_{max} at 254 and 299 nm), the ^{13}C NMR spectrum (δ23 1 *q*, 132 0 *d*, 135 2 *d*, 144 4 *s*, 154 6 *s*, 188 5 *s* and 188 9 *s*), and the ^1H NMR spectral data a vinyl methyl signal (δ2 02, *d*, J = 1 5 Hz, 3H) and two vinyl proton signals (δ6 87, *s*, 1H and 6 52, *q*, J = 1 5 Hz, 1H) The remaining part of **1** corresponded to the formula C_8H_{13}, which must be bicyclic, because no signals for the sp^2 and/or *sp* carbons were observed in the ^{13}C NMR spectrum except for those of the 1,4-benzoquinone grouping described above The ^1H NMR and ^{13}C NMR spectra indicated the presence of two methyl groups (δ1 32, *s*, 3H and 1 19, *s*, 3H, 14 7 *q* and 17 9 *q*) and a 1,1,2-trisubstituted cyclopropane (δ0 4–0 5, *m*, 2H, 16 1 *t*, 24 2 *d* and 29 1 *s*) in the C_8H_{13} moiety of **1** Thus the C_8H_{13} part of **1** was deduced to have a bicyclo[3 1 0]hexane skeleton substituted with two methyl groups

Based on the structural analyses described above together with biogenetic considerations that this alga contained debromolaurinterol [7, 8], the structure of laurequinone was deduced to be **1** This inference was unambiguously confirmed by conversion of debromolaurinterol [7, 8] into laurequinone with potassium nitrosodisulphonate (Fremy's salt) The structure and absolute stereochemistry of laurequinone was thus established to be **1** by this transformation

EXPERIMENTAL

^1H NMR (90 MHz) and ^{13}C NMR (22 5 MHz) $CDCl_3$, TMS as internal standard MS (70 eV) heated inlet system CC silica gel BW-80 (Fuji-Davison), preparative TLC silica gel 60 PF_{254} (Merck) HPLC a Jasco Tri Rotar-II liquid chromatograph with refractive index and UV detectors The isolated yield is based on fresh weight of the alga

Extraction and isolation The alga (*L. nidifica*) was collected in July off the coast of Goza, Mie Prefecture, Japan The fresh alga (8 8 kg) was extracted with Me_2CO (2 × 12 l) at room temp and the extract evaporated *in vacuo* to give an aqueous phase, which was extracted with EtOAc (12 l) Evaporation of the EtOAc extract afforded 44 5 g of an oily residue, a part of which (14 0 g) was chromatographed on silica gel (750 g) with hexane (12 l) and C_6H_6 (10 l) successively Early fractions of the C_6H_6 eluate gave a 3 1 mixture (3 05 g) of aplysin and debromoaplysin, and the middle fractions yielded a *ca* 2 1 mixture (570 mg) of laurinterol and debromolaurinterol, and the later fractions afforded crude laurequinone (**1**, 117 mg) The previously known compounds (aplysin, debromoaplysin, laurinterol and debromolaurinterol) were identified by their spectral (UV, IR, ^1H NMR and MS) data with authentic samples, respectively, after separation of each mixture by preparative TLC with hexane–Et_2O (2 1) Crude laurequinone (**1**, 117 mg) was further separated by preparative TLC with hexane–Et_2O (4 1) and HPLC [250 × 4 6 mm Cosmosil 5 C_{18}, MeOH–H_2O (4 1), flow rate 1 ml/min] to give **1** (8 5 mg, 0 00031 %) Pure **1** was obtained b GC separation (1 5 m × 5 0 mm packed with 5 % SE 30 on Chromosorb W, isothermal 150°, injector temp 190°, detector temp 200°, TC as detector, He at 44 ml/min, R_t 17 3 min)

Compound **1** Pale yellow oil, $[\alpha]_D^{23}$ −53 5° (*c* 0 91, $CHCl_3$), UV λ_{max}^{MeOH} nm (ε) 254 (13 300), 299 (850), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1640, 1595, 1160, 1110, 1000, 910, ^1H NMR δ6 87 (1H, *s*), 6 52 (1H, *q*, J = 1 5 Hz), 2 02 (3H, *d*, J = 1 5 Hz), 1 32 (3H, *s*), 1 19 (3H, *s*), 0 4–0 5 (2H, *m*), 1 0–2 2 (5H, *m*), ^{13}C NMR δ188 9 *s*, 188 5 *s*, 154 6 *s*, 144 4 *s*, 135 2 *d*, 132 0 *d*, 48 7 *s*, 35 8 *t*, 29 1 *s*, 25 4 *t*, 24 2 *d*, 23 1 *q*, 17 9 *q*, 16 1 *t*, 14 7 *q*, MS *m/z* (rel int) 230 $[M]^+$ (88), 215 (51), 202 (43), 189 (100), 188 (46), 175 (69), 174 (44), 161 (42), HRMS *m/z* 230 1290 $[M]^+$ calc for $C_{15}H_{18}O_2$, 230 1305

Transformation of debromolaurinterol into **1** To a stirred soln of debromolaurinterol (18 8 mg) in Me_2CO (5 1 ml) was added a KH_2PO_4 buffer soln (0 055 M, 5 1 ml) of Fremy's salt [$ON(SO_3K)_2$, 238 mg] After the mixture was stirred for 30 min at 40°, an additional amount (238 mg) of $ON(SO_3K)_2$ in KH_2PO_4 buffer (0 055 M, 2 0 ml) was added The mixture was stirred at 40° for a further 3 hr and extracted with CH_2Cl_2 (2 × 6 ml) Evaporation of the CH_2Cl_2 extracts *in vacuo* gave an oily residue, which was separated by preparative TLC (× 2) with hexane–Et_2O (2 1) to afford **1** (11 9 mg, 59 %) and unreacted debromolaurinterol (2 0 mg, 11 %) The synthetic **1** was proved to be identical with natural **1** by comparison of the spectral (UV, IR, ^1H NMR, ^{13}C NMR and MS) data, the optical rotation and chromatographic behaviour

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