tion has been noted in biological systems and has been reported to occur frequently in microbial transformations of several natural aromatic compounds[7]. Moreover, the main metabolic reaction of *Cuninghamella echinulata*, in the presence of laudanosine, has been reported to be O-demethylation in the benzylic portion of the molecule[8]. The nature of the 2 oxygenation steps and the sequence of these 3 transformation steps are at present under investigation.

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Petiodial, a new monocyclic diterpenoid from the Mediterranean green alga *Udotea petiolata*[1]

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Summary. The structure of a new monocyclic diterpenoid, petiodial (**4**), present in the green seaweed *U. petiolata*, has been determined on the basis of physico-chemical data. This alga also produces udoteal (**3**), a feeding deterrent metabolite previously isolated from the taxonomically related species *U. flabellum*.

In 1981 Nakatsu et al.[2] reported the presence in the Caribbean green alga *Udotea flabellum* of 2 monocyclic aldehydic diterpenes, udoteafuran (**1**) and udoteatrial (**2**); the latter, which seems to be responsible for the antimicrobial activity of the crude extract, was isolated as a cyclic diacetate after treatment with Ac_2O. More recently udoteal (**3**), a 1,4-diacetoxybutadiene-containing diterpene, biogenetically related to **1** and **2**, was found in the same material by Paul et al.[3]. Sesqui- and di-terpenes with this unusual functionality have been isolated from some other algae belonging to the families Caulerpaceae and Codiaceae (Siphonales)[4–7], and apparently function as chemical defence agents, since many of them have been proved to induce pronounced feeding avoidance in herbivorous fishes.

On pursuing our chemotaxonomically oriented studies on marine green algae[8,9], we have been investigating *Udotea petiolata*, a seaweed very common in the Mediterranean, and belonging to the same genus of *U. flabellum*. We wish to report here that this alga also produces udoteal (**3**), as well as a new related metabolite (**4**), that we named petiodial.

Material and methods. Samples of *U. petiolata* were collected in the bay of Naples, Italy, during the spring 1982. The dried powdered whole plants (29 g, after extraction) were extracted 3 times with $CHCl_3$ and the solvent was evaporated to afford a residue (2.4 g) which was partitioned by a Si gel column using as eluant increasing amounts of Et_2O in n-hexane. Fractions eluted with n-hexane-Et_2O (8:2) afforded mg 128 of udoteal. Fractions eluted with n-hexane-Et_2O (75:25) were rechromatographed on PLC using C_6H_6-AcOEt (7:3) as eluant. The band Rf 0.75 (UV-light), scraped and eluted with Et_2O, gave mg 39 of pure petiodial as a colorless oil.

Results and discussion. Udoteal was identified by comparison of its spectral (PMR, CMR, UV, IR and MS) data with those reported by Paul et al.[3].

Petiodial, $[\alpha]_D = -25.7$ (c = 0.5, in $CHCl_3$) has molecular formula $C_{22}H_{32}O_4$ (from HRMS on the parent ion).

The part structure C_9-C_{18} in **4** could be deduced by comparison of its PMR- and CMR-spectra, performed in $CDCl_3$ using a Bruker WH 270 spectrometer, with those of nerolidol[10] and udoteal [PMR: δ 5.10 (1H, bt, J = 7Hz, 10-H), 5.05 (1H, bt, J = 7Hz, 14-H), 1.67 (3H, bs, 16-H_3), 1.60 (3H, bs, 17-H_3) and 1.58 (3H, bs, 18-H_3). CMR: δ 134.8 (s, C_{11}), 131.3 (s, C_{15}), 124.0 (d, C_{14}), 123.2 (d, C_{10}), 39.5 (t, C_{12}), 29.4 (t, C_9), 27.0 (t, C_{13}), 25.8 (q, C_{16}), 17.5 (q, C_{17}) and 15.9 (q, C_{18})].

The IR-spectrum of **4** indicated the presence of 2 aldehydic groups, one of which is α,β-unsaturated ($\nu_{max}^{CCl_4}$ 2740, 1720 and 1670 cm^{-1}). These assignments were confirmed by the expected PMR bands at δ 10.11 (1H, s, 1-H) and 9.64 (1H, d, J = 2Hz, 19-H) and by off resonance CMR signals at δ 204.3 (d, C_{19}), 187.6 (d, C_1), 158.4 (s, C_3) and 140.6 (s, C_2).

The presence of the CH_3COOCH_2-group linked to a fully substituted olefinic carbon was deduced from IR ($\nu_{max}^{CCl_4}$ 1740, 1235 cm^{-1}) and PMR [δ 5.06 (2H, s, 20-H_2) and 2.10 (3H, s, Me-CO-)] spectra.

Consideration of the molecular formula and overall unsaturations delineated from the CMR-spectrum which presents, in addition to the above mentioned bands and those of the acetoxyl group, only sp^3 carbon signals [δ 59.5 (t), 52.6 (d), 45.2 (d), 34.9 (t), 28.9 (t) and 26.4 (t)] showed petiodial to be a monocyclic diterpenoid.

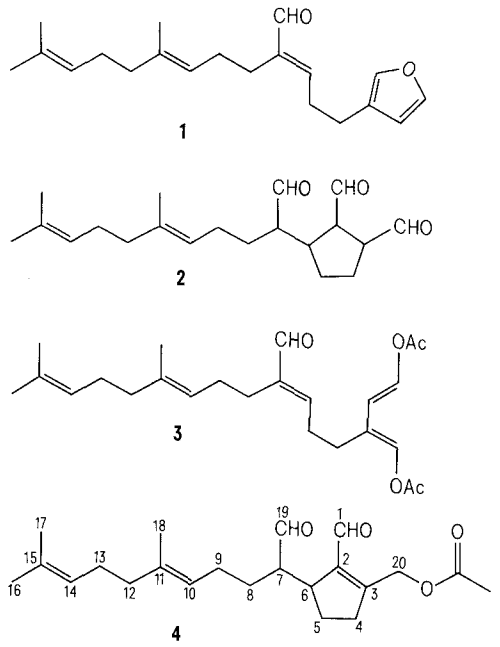
We were able to determine the complete structure of petiodial from a detailed analysis of PMR-spectrum which contains further signals at δ 3.41 (1H, m, 6-H), 2.90 (1H, m, 7-H), 2.60 (2H, t, J = 4Hz, 4-H_2) and 1.82 (2H, m, 8-H_2). By irradiation at δ 2.90, the aldehydic signal at δ 9.64 collapsed into a singlet and the multiplets at δ 3.41 and 1.82 were simplified. On the other hand, the latter multiplet is also simplified by irradiation at δ 2.00 (9-H_2 frequency). Finally irradiation at δ 1.95 (tentatively the frequency of 5-H_2) caused the triplet at δ 2.60 to collapse into a singlet and simplified the multiplet at 3.41.

What remained for the final assignment of petiodial was the location of the aldehydic and CH_3COOCH_2-groups which could be linked to C_2 and C_3 respectively or vice

versa. The second possibility was excluded on the basis of additional ^{1}H NMR-data. NOE effect was registered for the 20-H_2 signal while no detectable effect was observed for the 1-H resonance when the 4-H_2 (2.60 ppm) signal was saturated in a difference NOE experiment. Confirming evidence was obtained by mass spectrum which exhibits an intense peak at m/z 342 (10% of the base peak) deriving from the loss of a molecule of water from the 2 aldehydic groups to give a pyrane ring. The mass spectrum shows other significative peaks at m/z 300 (16%, M^+-AcOH), 282 (14%, $300-H_2O$), 231 (8%, $300-C_5H_9$), 107 (91%, $300-C_{13}H_{21}O$) and 69 (base peak, C_5H_9).

UV-spectrum ($\lambda_{max}^{n\text{-hexane}}$ 247 nm, ε 7450) is also consistent with the proposed structure, being indicative of a strained trisubstituted α,β-unsaturated aldehyde.

The carbon skeleton of petiodial has previously been found only in udoteatrial (**2**) and this could have a chemotaxonomic significance.



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Gossypol. Synthesis and in vitro spermicidal activity of isomeric hemigossypol derivatives[1]

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Summary. Three isomeric hemigossypol derivatives (**3**, **4**, **5**) have been synthesized. Two of these derivatives (**3**, **4**) and one synthetic intermediate (**7**) have been shown to have activity comparable to gossypol (**1**) in a sperm motility assay.

Gossypol (**1**), a cotton seed pigment, has been reported[4] to be an effective, reversible orally administered male contraceptive. This antifertility activity has stimulated wide interest in the development of a profile of structure-activity relationships for gossypol (**1**) and its sesquiterpene precursor, hemigossypol (**2**). Although the precise mechanism of action is not clear, it is known that gossypol damages stage 18 and 19 spermatids in the testis[5]. Additionally gossypol has been demonstrated to be an effective spermicidal agent[6]. Because of the instability of hemigossypol and some of its derivatives towards dimerization and the long term nature of in vivo feeding experiments, a rapid, reliable in vitro assay is desirable as an initial screen. For this purpose a sperm motility assay has been developed to measure the in vitro spermicidal activity of the gossypol derivatives with the hope of establishing a correlation between this activity and in vivo antifertility activity similar to that which exists for gossypol itself. We wish to report in this preliminary communication the synthesis of 3 isomeric hemigossypol derivatives (**3**, **4** and **5**) and their effect on sperm motilities.

Chemistry. All 3 of the isomeric naphthaldehydes are the result of regioselective formylations of 1,6,7-trimethoxy-3-methyl-5-(1-methylethyl)naphthalene (**6**). This key inter-

Inhibition of hamster sperm by gossypol derivatives

Compound (50 μM)	% Inhibition (5 min)
1	100
3	84
4	96
5	3
6	4
7	100
9	20