hydrolysis suggested that they are mono- or diglycosides (table).

Results and discussion. In earlier studies[8] a flavonoid (7-O-glycosyl-C-glycosylapigenin) was isolated from the leaves of *Bryonia dioica.* The presence of flavonoids in the other 4 plants examined in this work is reported for the first time. The major flavonoid (table) present in pollens of these 5 species is kaempferol 3-O-rutinoside; the minor flavonoids are unidentified flavonol 3-O-glycosides. Kaempferol 3-O-rutinoside is absent in all stigmas but that of *Ecballium elaterium;* the other flavonoids present in stigmas are rutin, kaempferol 3-O-glycosides, quercetin 3-O-glycosides and unidentified flavonol 3-O-glycosides. Hence all flavonoids present in pollens and stigmas of these plants are flavonol 3-O-glycosides. The flavonoid patterns of pollens of 4 species *(Lagenaria vulgaris, Cucumis citrullus, Sechium edule* and *Bryonia dioica)* are completely different from those of the corresponding stigmas and, moreover, some differences have been found between the flavonoids of pollen and stigma of *Ecballium elaterium.*

The above results show that the differences between the flavonoid patterns of pollens and corresponding stigmas are not restricted to species belonging to the genus *Cucurbita*[2,4]. Thus flavonoids of pollens and stigmas may be connected with sex expression in plants belonging to the family Cucurbitaceae. However, since only a small number (9) of species of this family (which contains about 850 species) have been examined, the above suggestion must be confirmed by further studies.

1 Acknowledgment. The author thanks Mr A. D'Urso (Botanic Institute, University of Catania) for help in acquiring the plant material.
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Sterols of Mediterranean Chlorophyceae[1]

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Summary. The distribution of sterols in 8 Mediterranean green algae has been investigated. C_{29} sterols are the major group in the species examined. 28-Isofucosterol seems to be typical for Ulotrichales, and the rare clerosterol for the genus Codium.

Recently sterols of marine algae have been widely investigated[2,3]. Chlorophyta have been much less extensively studied than Rhodophyta and Phaeophyta, but those species that have been examined show more diversity in their sterol contents. Thus the sterols of marine green algae appear to have value for the systematist as a guide for taxonomy and phylogeny.

In 1976 the most significant works in the field were reviewed by Goad, who also discussed the chemotaxonomic and phylogenetic considerations here briefly summarized[2]. Among the 6 species of Ulotrichales examined, 4 are consistent in containing 28-isofucosterol (**6**) as the main component. The occurrence of this sterol in many vascular plants seems to confirm the possible ancestral role of this order in the evolution of higher plants. The only significant feature revealed by the examination of the sterol fraction of 2 species belonging to the Cladophorales is a high content of cholesterol (**1**), and this suggested that the alkylation reaction of the side chain of the sterols in these 2 species is relatively inefficient. Finally, the 2 Siphonales examined showed a very contrasting sterol composition: in *Halimeda incrassata* clionasterol (**8**) predominates while in *Codium fragile* the major sterol is the unusual clerosterol (**7**) accompanied by minor amounts of codisterol (**5**), its C_{28} analogue.

As a part of a chemical survey on Mediterranean chlorophyta, we examined 8 green seaweeds as reported in the table, and their sterol composition is described in the present paper.

Material and methods. Algae listed in the table were collected from the littoral zone of the east coast of Sicily from Aci Castello to Capo Passero. Each alga (usually 500 g fresh weight) was freeze-dried and extracted with $CHCl_3$ (3×600 ml) at room temperature. Combined extracts were saponified and the non-saponifiable matter was chromatographed on a silica gel column (eluent: C_6H_6-ET_2O, 8:2). The crude sterol fraction, after acetylation with Ac_2O-pyridine 1:1, was further purified by a SiO_2 column using as eluent 40–70° light petroleum-C_6H_6 7:3 and analyzed by GLC-MS (AEI MS 30 instrument connected with a Pye Unicam instrument model 104 gas chromatograph; 1.5 m × 5 mm glass column packed with 2.5% SE 30; N_2 flow 30 ml/min).

When a particular fraction was shown to contain a steryl acetate in a considerable amount, the compound was isolated by PLC on $SiO_2/AgNO_3$ (40–70° light petroleum-C_6H_6 7:3 as eluent) and its identification confirmed by comparison of physical data ($[\alpha]_D$, m.p., IR and PMR) with those of an authentic sample.

Quantitation was performed by GLC of steryl acetates (cholestane as internal standard) using integrated areas of peaks.

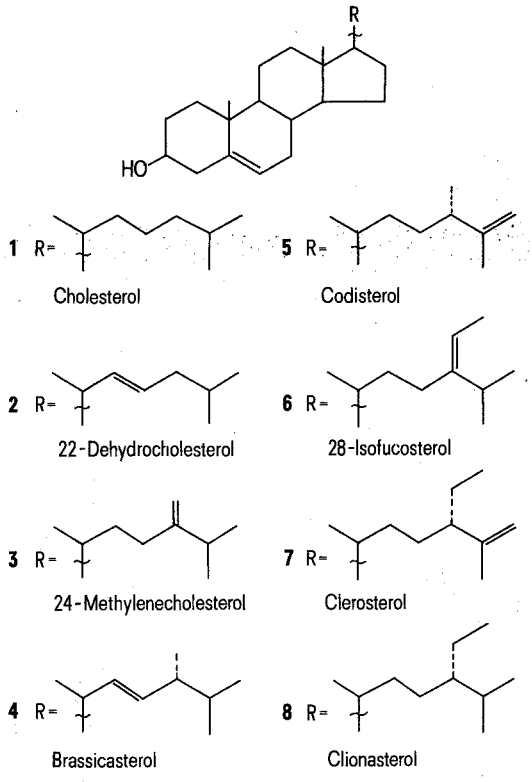
The configuration at C-24 of the steryl acetates identified only by GLC-MS was only tentatively assigned as *S,* in view the preponderance of the 24*S*-alkylsterols in the green algae[4].

Results and discussion. Our results, listed in the table, confirmed that 28-isofucosterol is representative of the

The distribution of sterols in some Mediterranean Chlorophyceae

Order	Species	Sterol (mg/kg dry alga)*							
		1	2	3	4	5	6	7	8
Ulotrichales	*Ulva rigida*	22	t	t	t	–	81	–	–
	Enteromorpha intestinalis	t	–	t	–	–	140	–	–
Cladophorales	*Cladophora echinus*	124	t	55	–	–	t	–	492
Siphonales	*Codium aderens*	–	–	–	–	t	–	629	–
	Codium bursa	t	–	–	–	–	–	250	–
	Codium tomentosum	–	–	–	–	–	122	429	–
	Halimedia tuna	92	31	72	15	–	–	–	509
Siphonocladales	*Valonia utricularis*	23	t	6	t	–	–	–	103

*Indicates not detectable, t indicates trace amounts.



seaweeds belonging to the order Ulotrichales. On the other hand the analysis of the only species of Cladophorales examined is consistent with the previous results: it contained a complex mixture of sterols with a high proportion of cholesterol. As far as the Siphonales are concerned, our analyses indicated that clerosterol is representative only of the genus *Codium*. In fact it is the dominant sterol of *C. tomentosum* and virtually the unique sterol in *C. aderens* and *C. bursa*, while it is absent in *Halimeda tuna*, where the most abundant sterol is clionasterol, the same as in the previously examined *H. incrassata*.

1 Acknowledgment. This work is a result of research sponsored by Consiglio Nazionale delle Ricerche in the frame of the Progetto finalizzato per l'Oceanografia e i Fondi Marini. Thanks are also due to Centro di Metodologie Chimico-fisiche of the University of Naples for the determination of PMR and mass spectra.

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Synthesis of 6-deoxy-6-fluoro-L-ascorbic acid[1]

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Summary. 6-Deoxy-6-fluoro-L-ascorbic acid has been synthesized in 5 steps starting from 2,3-4,6-di-O-isopropylidene-2-keto-L-gulonic acid.

Fluoro derivatives of physiologically active compounds, such as nucleosides[2], amino acids[3], carbohydrates[4], corticosteroids[5] and vitamins have attracted considerable attention in medicinal and also in preparative organic chemistry[6].

As part of a synthetic programme on vitamin C derivatives we have synthesized 6-deoxy-6-fluoro-L-ascorbic acid, i.e. the primary hydroxyl group is substituted by fluorine.

The starting material of our synthesis was the well-known intermediary product of the Reichstein-synthesis[7] for L-ascorbic acid: the 2,3-4,6-di-O-isopropylidene-L-gulosonic acid (**I**). It was converted to its methyl ester **II** using methyl iodide in the presence of potassium carbonate in dimethylformamide solution. The selective cleavage of the 4,6-O-isopropylidene protecting group was carried out in water in the presence of cuprous acetate as catalyst[8].

Methyl 2,3-O-isopropylidene-α-L-gulosonate (**III**) was then converted into its 6-toluenesulfonate ester **IV** (m.p. 127–128 °C), which with KF in dry dimethylformamide at 150 °C gave the methyl 6-deoxy-6-fluoro-2,3-O-isopropylidene-L-gulosonate (**V**) (m.p. 98–100 °C).

The last step of the synthesis was the cleavage of the protecting group and the isomerization to 6-deoxy-6-fluo-