expression of the algal cell-host relationship, such as the preservation of structures against the host's enzymatic systems.

In all these cases, the need for model experiments on algal cultures in interacting systems is urgent, to clarify the different situations.

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SPECIALIA

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Spiranation of phenolic diazoketones: an intermediate towards acorone synthesis

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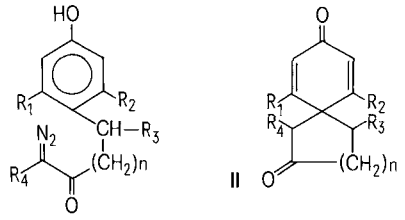
Summary. Syntheses of 4-methylspiro[4.5]deca-6,9-diene-2,8-dione (**IIb**) and 1,4-dimethylspiro[4.5]deca-6,9-diene-2,8-dione (**IIc**) by spiranation of phenolic diazoketones (**Ib**) and (**Ic**) respectively are reported. Formation of (**IIc**) illustrates the first aryl participation of phenolic diazoketone prepared from higher homologue of diazomethane.

Aryl participation of simple phenolic diazoketones toward the formation of spirodienones has been developed very recently[2]. We studied this spiroannulation reaction using phenolic diazoketones having steric interference at the site of cycloalkylation centre[3]. Boron trifluoride etherate treatment of this type of diazoketones (**Ia**), where methyl groups are present in the 2 ortho positions with respect to the cyclising moiety, yielded the spiroannulated products (**IIa**) and no rearranged products (dienone-phenol type) were isolated.

In this communication we wish to report the results of cycloalkylation, under different experimental conditions, of the diazoketones, 1-diazo-4-(4-hydroxyphenyl)-2-pentanone (**Ib**) and 2-diazo-5-(4-hydroxyphenyl)-3-hexanone (**Ic**) where methyl group/groups are linked to the cyclising moiety only. 2 spirodienones, 4-methylspiro[4.5]deca-6,9-

diene-2,8-dione (**IIb**) and 1,4-dimethylspiro[4.5]deca-6,9-diene-2,8-dione (**IIc**) were synthetised from **Ib** and **Ic** respectively and purified through column chromatography. Here, the spirodienone (**IIb**) may be considered as a suitable intermediate for total synthesis of the spiro sesquiterpenoid, acorone (**III**)[4]. To our knowledge the synthesis of the spirodienone (**IIc**) illustrates the first demonstration of aryl participation of a phenolic diazoketone obtained from a higher homologue of diazomethane, and from this reaction we speculate a shorter route for the construction of cyclopentanone part of acorone molecule via the diazoketone (**Id**) derived from diazoisobutane.

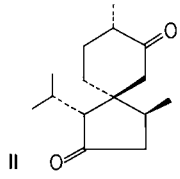
Treatment of boron trifluoride etherate on the hydroxy diazoketone (**Ib**) at room temperature (20 °C) for 15 min gave 3,4-dihydro-4-methyl-6-hydroxynaphthalen-2(1 H)-one (**IV**), m.p. 115 °C [ν_{max} 3275 (OH), 1695 cm^{-1} (C=0); δ ($CDCl_3$) 1.25 (3 H, d, CH_3), 2.44 (2 H, d, $COCH_2$), 3.20 (1 H, m, CH), 3.58 (2 H, s, $ArCH_2CO$), 5.10 (1 H, s, ArOH), 6.80-7.10 (3 H, m, ArH); MS (50 eV): m/e 176 (M^+), 134 ($M-CH_2CO$) (100%)] and 1-hydroxy-4-(4-hydroxyphenyl)-2-pentanone (**V**), m.p. 85 °C [ν_{max} 3340-3250 (OH), 1715, cm^{-1} (C=0); δ ($CDCl_3$) 4.20 (2 H, d, $COCH_2$ OH), 5.04 (1 H, t, CH_2OH)]. Here we could not isolate the aryl participation product **IIb** but its formation during the reaction may be explained by the isolation of β-tetralone derivative (**IV**) (homogeneous by TLC) which was generated by the dienone-phenol rearrangement of the initially formed spirodienone (**IIb**). We prefer to assign the structure of the rearranged product **IV** on the basis of migratory aptitude[1].



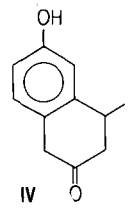
I

II

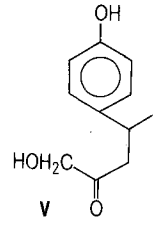
a $R_1=R_2=Me$; $R_3=R_4=H$; n=0-2.
b $R_1=R_2=R_4=H$; $R_3=Me$; n=1.
c $R_1=R_2=H$; $R_3=R_4=Me$; n=1.
d $R_1=R_2=H$; $R_3=Me$; $R_4=Pr^i$; n=1.



II



IV



V

However, aryl participation of **Ib** at low temperature (0 °C) and shorter contact time (5 min) with BF_3 catalyst afforded **IIb**, an Ar_1-5 participation product in 30% yield m.p. 112 °C [λ_{max} (MeOH) 243 nm ($\log\varepsilon$ 4.38); ν_{max} 1745 (cyclopentanone), 1662, 1622 cm^{-1} (dienone); δ ($CDCl_3$) 0.97 (3 H, d, J 7.0 Hz, CH_3), 2.14-2.82 (5 H, m, CH_2COCH_2CH), 6.42 (2 H, d, J 10 Hz 7-H, 9-H), 6.80 (2 H, d, J 10 Hz, 6-H, 10-H); MS (50 eV): m/e 176 (M^+), 106 [M-(CH_2CO, CH_3CH)] (100%) along with the rearranged product **IV** and SN_2 product **V**.

When the diazoketone (**Ib**) was refluxed for half-an-hour with water containing traces of sulphuric acid, 2 products, **IV** (undepressed mixed m.p. and identical IR-spectra) and **V** were isolated. The formation of **IV** in this reaction may be expected through the intermediacy of **IIb**.

Aryl participation of the diazoketone (**Ic**) under similar experimental conditions (BF_3-Et_2O, −10 °C, 5 min) yielded **IIc** as a semi-solid substance [ν_{max} 1730 (cyclopentanone), 1665, 1615 cm^{-1} (dienone); δ ($CDCl_3$) 1.20 (6 H, d, CH_3), 2.0-2.92 (3 H, m, $CHCH_2$), 3.30 (1 H, q, CHCO), 6.72 (2 H, d, 7-H, 9-H), 7.02 (2 H, d, 6-H, 10-H)].

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Acyclic diterpenes containing 3 enol acetate groups from the green alga *Chlorodesmis fastigiata*

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Summary. 2 new diterpenes, chlorodesmin (**4**) and dihydrochlorodesmin (**5**), each containing 3 enol acetate groups, have been isolated from Great Barrier Reef collections of the green alga *Chlorodesmis fastigiata* (Chlorophyta, Caulerpales). Didehydrotrifarin (**3**) was also characterized.

We have previously described the isolation of flexilin (**1**) and trifarin (**2**), 2 acyclic terpenes with 1,4-diacetoxybutadiene groupings from the green Caulerpalian algae *Caulerpa flexilis* and *Caulerpa trifaria* respectively[1]. Recently sesquiterpenes containing diacetoxybutadiene moieties have been isolated from *Caulerpa prolifera*[2] and *Rhipocephalus phoenix*[3], related green algae, and it was shown that rhipocephalin, the diacetoxybutadiene from *R. phoenix*, caused significant avoidance behaviour in herbivorous fishes[3]. We now report the structural elucidation of didehydrotrifarin (**3**) and 2 new diterpenes containing 3 enol acetate moieties from the green alga *Chlorodesmis fastigiata* (C. Agardh) Ducker[4].

C. fastigiata is common on the reef flats of the Great Barrier Reef, often being the only alga which occurs in quantity, and specimens show no obvious indication of being heavily grazed. Extraction of a freeze-dried collection of *C. fastigiata* from the Cairns region of the Barrier Reef with dichloromethane gave a complex extract from which didehydrotrifarin (**3**) and chlorodesmin (**4**) were isolated as oils by silica gel chromatography. A collection of *C. fastigiata* from the Capricorn-Bunker group at the southern end of the Barrier Reef gave dihydrochlorodesmin (**5**) but chlorodesmin (**4**) was absent.

The formula $C_{24}H_{36}O_4$ was established for **3** by high resolution CI mass spectrometry. No molecular ion ap-