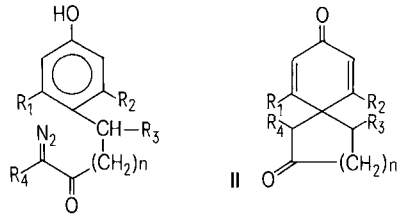
diene-2,8-dione (**IIb**) and 1,4-dimethylspiro[4.5]deca-6,9-diene-2,8-dione (**IIc**) were synthetised from **Ib** and **Ic** respectively and purified through column chromatography. Here, the spirodienone (**IIb**) may be considered as a suitable intermediate for total synthesis of the spiro sesquiterpenoid, 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.

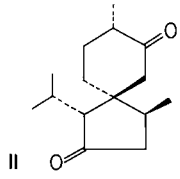
Treatment of boron trifluoride etherate on the hydroxy diazoketone (**Ib**) at room temperature (20 °C) for 15 min gave 3,4-dihydro-4-methyl-6-hydroxynaphthalen-2(1 H)-one (**IV**), m.p. 115 °C [ν_{max} 3275 (OH), 1695 cm^{-1} (C=0); δ ($CDCl_3$) 1.25 (3 H, d, CH_3), 2.44 (2 H, d, $COCH_2$), 3.20 (1 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].



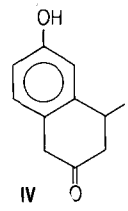
I

II

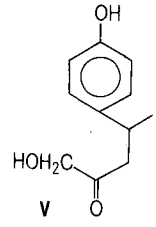
a $R_1=R_2=Me$; $R_3=R_4=H$; n=0-2.
b $R_1=R_2=R_4=H$; $R_3=Me$; n=1.
c $R_1=R_2=H$; $R_3=R_4=Me$; n=1.
d $R_1=R_2=H$; $R_3=Me$; $R_4=Pr^i$; n=1.



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)].

1 Author for reprint request.
2 L.N. Mander and D.J. Beams, Aust. J. Chem. *27*, 1257 (1974).
3 K.K. Bhattacharya and P.K. Sen, Synth. Comm., in press; Bull. chem. Soc. Japan, in press.
4 D.A. McCrae and L. Dolby, J. org. Chem. *42*, 1607 (1977).

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

R.J. Wells and K.D. Barrow

Roche Research Institute of Marine Pharmacology, P.O. Box 255, Dee Why (N.S.W. 2099, Australia) and Department of Biochemistry, University of New South Wales, Kensington (N.S.W. 2033, Australia), 17 April 1979

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.

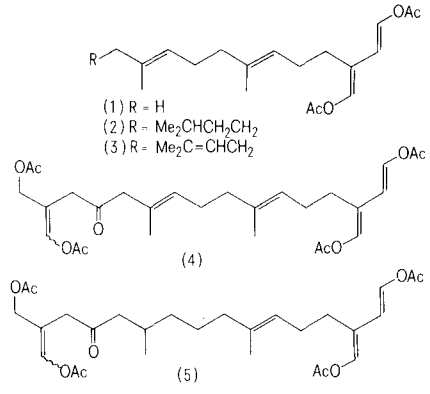
We have previously described the isolation of flexilin (**1**) and trifarin (**2**), 2 acyclic terpenes with 1,4-diacetoxybutadiene groupings from the green Caulerpalian algae *Caulerpa flexilis* and *Caulerpa trifaria* respectively[1]. Recently sesquiterpenes containing diacetoxybutadiene moieties have 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-

peared in the 70 e.v. EI-MS of **3** which showed the 1st observable ion at m/e 328 ($M^+ - 60$) with other prominent ions at m/e 286, 191, 149, 109, 69, 43. Comparison of the ^1H and ^{13}C-NMR data of **3** with that of **1** and **2** established the structure of **3**. The ^1H-NMR-spectrum of **3** in CCl_4 showed resonances at δ 7.32 (1H, d, J = 12 Hz). 7.08 (1H, bs), 5.82 (1H, d, J = 12 Hz), 5.05 (3H, m), 2.08 (3H, s), 2.06 (3H, s), 1.84 (3H, bs) and 1.59 (9H, bs) and the ^{13}C-NMR-spectrum in $CDCl_3$ gave resonances at δ 167.5 (s), 167.1 (s), 135.9 (s), 135.4 (s), 134.2 (d), 131.0 (s), 124.3 (d), 124.1 (d), 123.2 (d), 121.1 (d), 113.2 (d), 39.6 (t), 26.7 (t), 26.6 (2C, t), 25.6 (q), 25.3 (t), 20.5 (2C, q), 17.6 (q), 16.0 (2C, q). UV- and IR-spectra of **3** (ν_{max} 1760 cm^{-1}; λ_{max} 252 nm (log ε 4.49) were almost identical to those of **1** and **2**.

Chlorodesmin (**4**) gave a very weak molecular ion in the CI-MS and the molecular formula was extrapolated as $C_{28}H_{38}O_9$ from high resolution data on the 1st major fragment ion at m/e 458 ($M^+ - 60$). The ^1H-NMR-spectrum demonstrated the presence of a diacetoxybutadiene moiety with signals at δ (CCl_4) 7.34 (1H, d, J = 12 Hz), 7.09 (1H, bs) and 5.85 (1H, d, J = 12 Hz) and the appearance of dominant ions at m/e 191 ($C_{12}H_{15}O_2$) and 149 ($C_{10}H_{13}O$) parallelled the MS behaviour of **1**–**3**. The remainder of the ^1H-NMR-spectrum of **4** consisted of resonances at δ 7.01 (1H, bs), 5.16 (2H, m), 4.64 (2H, s), 3.09 (2H, s), 3.00 (2H, s), 2.13 (3H, s), 2.10 (3H, s), 2.08 (3H, s), 1.95 (3H, s) and 1.60 (6H, bs). The ^{13}C-NMR-spectrum of **4** [δ ($CDCl_3$) 205.5 (s), 169.8 (s), 167.1 (s), 166.7 (2C, s), 135.5 (d), 135.2 (s), 135.2 (d), 133.8 (d), 129.2 (d), 128.2 (s), 123.1 (d), 120.5 (s), 113.5 (s), 112.6 (d), 59.2 (t), 52.7 (t), 41.4 (t), 38.6 (t), 26.0 (t), 26.0 (t), 24.7 (t), 20.0 (4C, each q), 15.7 (q) and 15.3 (q)] demanded the presence of 1 ketonic carbonyl, 4 ester carbonyls, 4 trisubstituted and 1 disubstituted double bonds, and a $-CH_2-O$ grouping. Thus **4** must be acyclic. Fully coupled ^{13}C-NMR-spectra showed that the coupling constants of the doublets at δ 135.2, 135.0 and 133.8 were between 189 and 193 Hz attributable to the presence of 3 enol acetate groups in **4** and the absence of a methyl signal at about δ 25 showed the absence of a Z terminal methyl. The majority of the spectrum was very similar to that of (**3**) suggesting that the 3rd enol acetate, the $-CH_2OAc$ group and the nonconjugated ketone were grouped at the opposite end of the diterpene chain to that of the diacetoxydiene moiety.



2 proton singlets at δ 4.64, 3.09 and 3.00 in the ^1H-NMR-spectrum of (**4**) indicated the presence of 1 allylic acetoxymethyl group and 2 doubly allylic methylenes in the molecule and only structure **4** satisfies all spectral data.

Dihydrochlorodesmin (**5**) had mass spectral and NMR features very similar to those of (**4**). Thus dominant mass spectral ions appeared at m/e 191, 149 and 91 as in (**4**) and the ^1H-NMR-spectrum [δ ($CDCl_3$) 7.37 (1H, d, J = 12 Hz), 7.10 (1H, bs), 7.06 (1H, bs), 5.88 (1H, d, J = 12 Hz) 5.14 (1H, bt, J = 7 Hz), 4.72 (2H, s), 3.08 (2H, s), 2.12 (6H, s), 2.10 (3H, s), 1.99 (3H, s), 1.53 (3H, bs), 0.88 (3H, d, J = 7 Hz)] was similar to that of (**4**) with the exception that 1 doubly allylic methylene group was missing and a $-C(Me)=CH-$ grouping now appeared as a $-CH(Me)-CH_2-$group. The ^{13}C-NMR-spectrum [δ ($CDCl_3$) 207.0 (s), 170.4 (s), 167.6 (s), 167.2 (s), 167.0 (s), 135.5 (2C, each d), 134.2 (d), 123.4 (d), 121.0 (s), 114.0 (s), 113.2 (s), 113.2 (d), 59.7 (t), 49.5 (t), 43.7 (t), 39.5 (t), 36.4 (t), 29.0, 26.5, 25.2, 20.5 (4C, q), 19.7 (q), 15.7 (q)] also was fully in accord with structure (**5**) for dihydrochlorodesmin.

Attempted hydride reduction, hydrogenation or gentle acid and base hydrolysis of both **4** and **5** resulted in complex product mixtures and paucity of material precluded further chemical work.

1 A.J. Blackman and R.J. Wells, Tetrahedron Lett. *1978*, 3063.
2 V. Amico, G. Oriente, M. Piatelli, C. Tringali, E. Fattorusso, S. Magno and L. Mayol, Tetrahedron Lett. *1978*, 3593.
3 H.H. Sun and W. Fenical, Tetrahedron Lett. *1979*, 689.
4 RRIMP Museum Specimen FN 1912/000.

Concerning the anchoring of acetylcholinesterase in biomembranes

H. Grossmann, K.-P. Ruess and M. Liefländer

Chemisches Institut der Universität Regensburg, Universitätsstrasse 31, D-8400 Regensburg (Federal Republic of Germany)
22 March 1979

Summary. Highly purified acetylcholinesterases from various sources do not contain hydroxyproline and hydroxylysine, indicating the absence of a collagenlike 'tail'. The enzymes examined are therefore bound to the membrane in a different way compared with acetylcholinesterase isolated from electric organ.

At the present time a great deal of interest is focussed on the possibility that highly purified acetylcholinesterase may contain hydroxyproline and hydroxylysine. A percentage of 0.3–0.8% of these amino acids is considered to show that the acetylcholinesterase in question contains a collagen-like 'tail'. Highly purified 18S- and 14S-molecular forms of acetylcholinesterase from electric organ tissue do contain such significant amounts of hydroxyproline and hydroxylysine, although a more detailed description of the collagen-like 'tail' cannot yet be given. The putative role of the 'tail' in anchoring acetylcholinesterase to the fibrillar matrix of the basement membrane (even in the case of mammalian muscle endplate) and in self-association of the various molecular forms at low ionic strength is open to speculation and is under investigation[1].

The electric organ is a highly specialized tissue, which evolved from muscle tissue with its known collagen content. We were interested in analyzing our several highly