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FLEXILIN AND TRIFARIN, TERPENE 1,4-DIACETOXYBUTA-1,3-DIENES FROM TWO *CAULERPA* SPECIES (CHLOROPHYTA).

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We have previously reported[1] the occurrence of the diterpene alcohol caulerpol (1) in the green alga *Caulerpa brownii*. We now describe the isolation of a new acyclic sesquiterpene (2), for which we suggest the name flexilin from *C. flexilis* and a related diterpene trifarin (3) from *C. trifaria*. Each compound contained a 1,4-diacetoxybuta-1,3-diene moiety which, to our knowledge is the first report of this functionality in a natural product.

Hexane soluble material obtained from *C. flexilis*[2a] as described previously[1] was purified by dry column and preparative thin layer chromatography on silica gel to give (2) as a colourless oil (1.3% dry algal weight) b.p. $100^{\circ}/0.1$ mm. The formula $C_{19}H_{28}O_4$ was established by elemental analysis. No molecular ion was observed in the mass spectrum but prominent peaks occurred at 260(M^+ -AcOH), 218, 191 and 149 a.m.u. The i.r. spectrum showed strong absorptions at ν_{max} 1760 and 1632 cm^{-1} and the u.v. spectrum was: λ_{max} 251 nm (log ε4.67).

The ^1H n.m.r. spectrum of (2) in CCl_4 showed signals at δ7.37(1H, d, J 12Hz), 7.13(1H,s), 5.88(1H, d, J 12Hz, coupled to 7.37, d), 5.1(2H, m), 2.14(3H, s), 2.11(3H, s), 1.67(3H, bs), 1.62 (6H, bs) together with a further eight allylic protons in the range δ2.4-1.9. The ^{13}C n.m.r. confirmed the presence of two ester carbonyls [δ167.8(s) and 167.4(s)] and eight olefinic carbons at δ136.0(s), 135.6(d), 134.3(d), 131.3(s), 124.3(d), 122.2(d), 121.2(s) and 113.4(d). The remaining nine carbon resonances occurred at δ39.7(t), 26.8(t), 26.6(t), 25.7(q), 25.5(t), 20.7 (2C)(q), 17.7(q) and 16.0(q).

I.r., u.v. and ^1H n.m.r. spectral data reported for E,E-1,4-diacetoxy-2-methylbuta-1,3-diene (4)[3] were consistent with that found for (2) and the coupling constant of 12Hz measured for the AcO-CH=CH-$\overset{|}{C}$- group established that the double bond had the E-configuration (*cf.* the E,E-isomer of (4), J 13Hz; Z,Z isomer of (4), J 7Hz). Thus structure (2) was supported for flexilin.

Diels-Alder reaction of (2) with benzoquinone in benzene afforded the expected product (5) a pale yellow oil which had an ^1H n.m.r. spectrum entirely in accord with the proposed structure [δ(CCl_4) 7.88(1H, d, J 7.5Hz), 7.79(1H, s), 7.48(1H, d, J 7.5Hz), 6.86(2H, bs), 5.05(2H, m), 2.77 (2H, t, J 7Hz), 2.37(2H, m), 1.95(4H, m), 1.66(3H, s), 1.58(3H, s) and 1.53(3H, s)]. Reduction of (2) with sodium borohydride gave a 1:1 mixture of the two diols (6) and (8) which could be separated as their acetates (7) and (9). The ^1H n.m.r. spectrum of (7) showed a four proton multiplet at δ4.02 due to two AcO-CH_2-groups whilst that of (9) gave two signals due to allylic AcO-CH_2- groups at δ4.55(2H, d, J 7Hz) and 4.47(2H, s) consistent with the proposed structure.

The hexane extract of *C. trifaria*[2b] gave trifarin (3), $C_{24}H_{38}O_4$, as colourless oil in 0.3% dry algal yield after silica gel chromatography. The m.s., ^1H n.m.r. and ^{13}C n.m.r. spectra of (3) showed it to be almost identical to (2) but with an additional terminal isopentyl unit. The i.r. spectra of (2) and (3) were almost superimposable above 1400 cm^{-1}. The ^1H n.m.r. spectrum of (3) showed signals at δ7.33(1H, d, J 12Hz), 7.09(1H, s), 5.83(1H, d, J 12Hz), coupled to 7.33 doublet), 5.17(2H, m), 2.10(6H, s), c 2.1(10H, m), 1.64(3H, bs), 1.59(3H, bs), c 1.3(3H, m) and 0.88(6H, d, J 7Hz) and the ^{13}C n.m.r. had the following resonances:- δ167.7(s), 167.3(s), 136.7(s, 2 carbons), 135.6(d), .34(d), 123.0(d), 121.2(s), 119.8(d), 113.3(d), 49.0(d), 40.6(t), 32.6, 31.7, 29.8, 27.5(2C), 26.6, 25.4, 23.4, 23.0, 20.6(2C) and 16.1.

ACKNOWLEDGEMENTS

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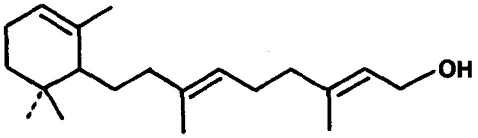

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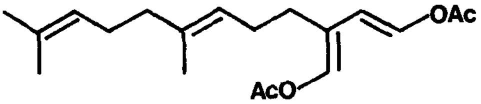

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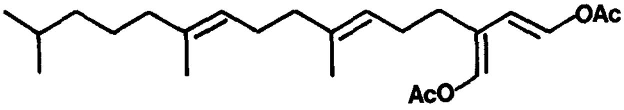

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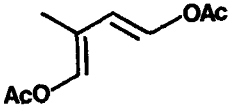

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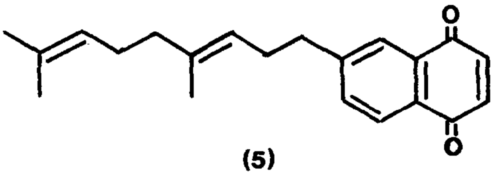

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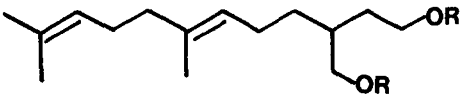
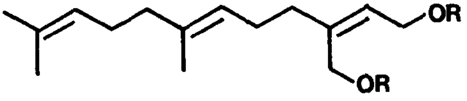


(6) R=H (7) R=Ac



(8) R=H (9) R=Ac

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