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FREELINGNITE, A NEW FURANOSESQUITERPENE FROM EREMOPHILA FREELINGII

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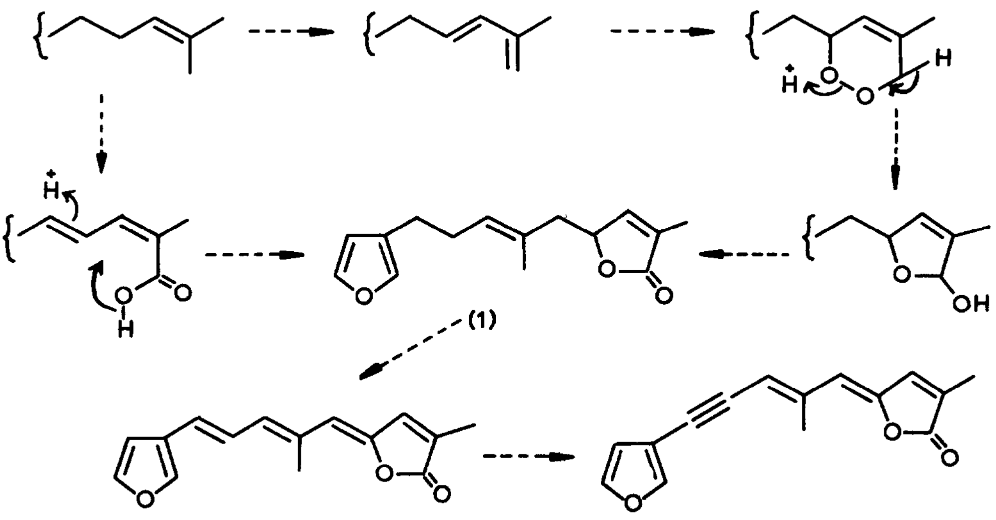
Freelingyne (3) from Eremophila freelingii was the first acetylenic terpenoid to be isolated from Nature.[1] Its biosynthesis poses several interesting problems. Here we report the presence of a new furanosesquiterpene, freelingnite, in E. freelingii whose structure (1) has a direct bearing on considerations of the biosynthesis of (3). Freelingnite represents the first example of a furanosesquiterpene containing a 4-alkylbut-2-enolide moiety.

Chromatography of the acetone extract of the ground twig-wood of E. freelingii (silica gel - chloroform, then 1:1 pentane-ether) gave freelingnite (~0.01%) as an oil, $[\alpha]_D^{25}$ + 11.5°(dioxan,c 1.3). The infrared spectrum showed the presence of an α,β-unsaturated γ-lactone (ν_{max} 1755cm^{-1}), and the ultraviolet spectrum indicated that the molecule was essentially transparent between 220-360nm. The mass spectrum displayed a prominent molecular ion at $^m/e$ 246 corresponding to $C_{15}H_{18}O_3$, and showed main fragmentation ions at $^m/e$ 149 ($C_{10}H_{13}O$), $^m/e$ 97 ($C_5H_5O_2$), $^m/e$ 81 (C_5H_5O; parent ion) and $^m/e$ 53 (C_4H_5).[2] Five olefinic protons, between τ 2.74-4.78, were observed in the p.m.r. spectrum, three of which at τ 2.74, 2.86 and τ 3.78 were associated with the protons of a 3-substituted furan ring.[2] Spin decoupling experiments established that the olefinic proton at τ 3.11 was coupled to a vinyl methyl resonance at τ 8.11 and also to a methine proton (-C<u>H</u>.O) at τ 5.1. The remaining olefinic proton, a triplet at τ 4.78, showed coupling to a second vinyl methyl resonance at τ 8.36. The foregoing data supported structure (1) for freelingnite.

Although several furanosesquiterpenes have been isolated from higher plants, freelingnite represents the first example containing a 4-alkylbut-2-enolide moiety. Bohlmann and co-workers[3] have recently identified a coumarin



(2) (3)

derivative from Capnophyllum peregrinum which contains a similarly substituted butenolide end-grouping. It is possible that the butenolide moiety in freelingnite is formed in Nature from a sesquiterpenoid hydrocarbon precursor *via* several stages of oxidation as outlined in the Scheme. Alternatively, a terminal Z-α-unsaturated carboxylic acid precursor might be implicated in its biosynthesis (see Scheme). Freelingyne is then probably formed from freelingnite *via* the dihydro analogue (2)[4] by step-wise dehydrogenation.

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References.

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