

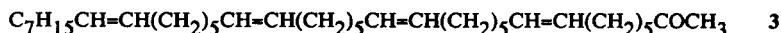
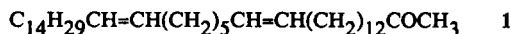
Unusual Long Chain Ketones of Algal Origin.

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Abstract: Recent reports have suggested the use of the relative abundances of long chain (n - C_{37}) alken-2-ones (1,2, and 3) in Quaternary marine sediments as a palaeoclimate indicator¹. Here we report the synthesis of these ketones with all-*E* and all-*Z* stereochemistry. Use of the synthesised compounds has shown that the natural counterparts in the alga *Emiliania huxleyi* and in marine sediments have the unusual and unexpected *E* configuration.

Series (n - C_{37} - C_{39}) of long chain alken-2- and 3-ones and esters occur, often as abundant components, in certain members of the *Prymnesiophyceae* and in Quaternary marine sediments where the extent of unsaturation has been used to infer water column palaeotemperatures¹. The gross structures of the C_{37} alkenones have been assigned previously by degradation and mass spectral studies². The position of the double bonds has only been elucidated in the case of the dienone (1); the positions in the other C_{37} alkenones were assumed to be analogous to the dienone and to other long chain ketones in the series which were assigned in the same way. The double bond geometry was assumed to be *Z* on biogenetic grounds³.



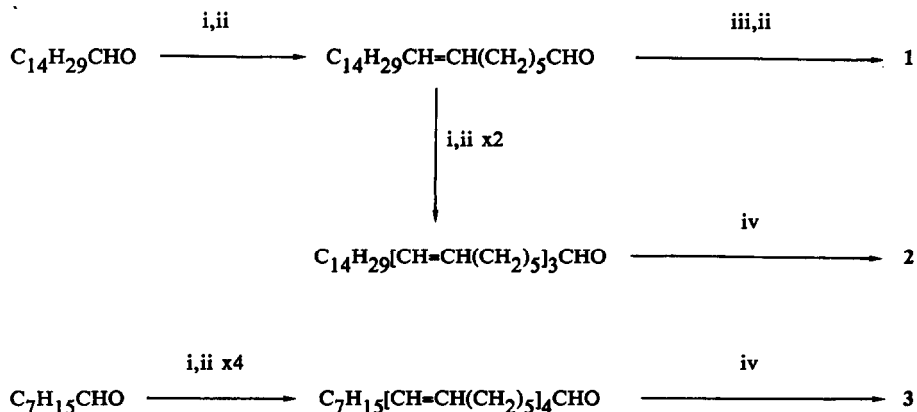
We therefore undertook the synthesis of these compounds to confirm the structures and to provide standards for further studies.

The compounds all have a common C_7 skeletal unit by way of five methylene groups separating the double bonds, with one such unit in the dienone, three in the trienone and four in the tetraenone. The use of this skeletal unit with suitable functionality at the terminal positions allowed stepwise construction of intermediate aldehydes which were then converted to the required product either by addition of a C_{15} unit in the case of the dienone, or by a Grignard reaction followed by oxidation, for the tri- and tetraenone (Scheme 1.)

In the case of the all-*Z* compounds the sub-units were coupled using the "salt free" Wittig reaction⁴ to obtain the appropriate geometry at each double bond, (Scheme 1 R= PPH_3). For the all *E* compounds the *E* configuration was obtained at each stage using a new olefination reaction⁵, involving the coupling of a 1,1-diodide in the presence of chromium(II) chloride, (Scheme 1 R= $(Cr[III])_2$).

Comparison of the synthesised compounds with the natural compounds in the prymnesiophyte alga *E. huxleyi* and in marine sediments showed that the latter have the all-*E* configuration⁶. By analogy, it is inferred that the other members of the series (alkenones and esters) also have the same configuration. This configuration is unexpected among non-conjugated polyunsaturated lipids and points to an unusual biosynthetic pathway, and raises questions about the biochemical role of the compounds.

Full details of syntheses and physical characteristics of the natural compounds will be described elsewhere⁷.



i) $\text{R}=\text{CH}(\text{CH}_2)_5\text{CH}(\text{OCH}_3)_2$; ii) $\text{H}^+, \text{H}_2\text{O}$; iii) $\text{R}=\text{CH}(\text{CH}_2)_{12}\text{C}(\text{OCH}_2\text{CH}_2\text{O})\text{CH}_3$; iv) MeMgBr then pyridinium chlorochromate

$\text{R} = \text{PPh}_3$ or $(\text{Cr}[\text{III}])_2$, see text

Scheme 1

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