

ZEYLOXANTHONONE, A NEW TETRAHYDROXANTHONE FROM
CALOPHYLLUM ZEYLANICUM¹ (GUTTIFERAE)

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Summary: Zeyloxanthone, a triprenylated tetrahydroxanthone isolated from C.zeylanicum has been shown to be 6,8-dihydroxy-1,1,7-tri(3-methylbut-2-enyl)-2-oxo-1,2,3,4-tetrahydroxanthone-9-one (I) by chemical and spectroscopic methods.

The bark benzene extractives of Calophyllum zeylanicum Kosterm.,² gave a new tetrahydroxanthone named zeyloxanthone (0.04%), m.p. 137°, which has been shown to be 6,8-dihydroxy-1,1,7-tri(3-methylbut-2-enyl)-2-oxo-1,2,3,4-tetrahydroxanthone-9-one (I). This communication deals with its structure elucidation.

A molecular formula of C₂₈H₃₄O₅ was assigned to zeyloxanthone, based on the C, H microanalysis data and high resolution mass spectral data of the M⁺ ion. In addition to the xanthone type conjugated carbonyl group, the IR spectrum showed the presence of a six membered ring carbonyl group (ν_{\max} 1702 cm⁻¹). This was further confirmed by the ¹³C-NMR spectrum of the compound (Fig.1), which had a signal at 212 ppm. Diazomethane methylation of zeyloxanthone gave a monomethyl derivative (m.p. 118°), whilst acetic anhydride-pyridine acetylation at room temperature gave a mono-acetate (m.p. 115°). The ¹H-NMR spectra of both these derivatives and the parent compound all showed the presence of a chelated hydroxy group. The acetic anhydride-pyridine acetylation at 100° for 6 hr gave a diacetate (m.p. 120°) in which the chelated hydroxy group was also found to be acetylated. These data indicated the presence of two phenolic hydroxy groups one of which was chelated. The ¹H-NMR spectra of zeyloxanthone, its monomethyl ether and its mono-acetate all had two types of vinylic protons in the ratio (1:2), methyl proton signals at 8.52 τ (2 x CH₂), 8.44 τ (2 x CH₂), 8.3 τ (1 x CH₂) and 8.2 τ (1 x CH₂). These indicated the presence of three isoprenyl groups. The presence of two benzylic protons at 6.6 τ (d, J = 6Hz) in the ¹H-NMR spectrum of zeyloxanthone indicated that one of the isoprenyl chains was attached to an aromatic ring. This isoprenyl chain should be adjacent to the non-chelated hydroxy group since it underwent easy DDQ cyclisation³ to give a chromene (m.p. 78°), which had a chelated hydroxy group.

Zeyloxanthone gave a positive Gibbs test,⁴ and had only one aromatic proton at 3.75 τ (s). The doublet at 93.4 ppm in the off-resonance decoupled ¹³C-NMR spectrum of zeyloxanthone confirmed that the only unsubstituted aromatic carbon atom was C-5 (Fig. 1).

Significant peaks were present at m/e 69 in the mass spectra of zeyloxanthone and its derivatives. High resolution of this peak showed it to be due to C₅H₉⁺. The ready

removal of this isoprenyl group from the molecular ion indicated that it was either attached to a quaternary carbon atom or placed adjacent to a C=O group or both factors were present.⁵ This, with the presence of a singlet at 54.9 ppm in the off-resonance decoupled ¹³C-NMR spectrum of zeyloxanthone, indicated that two of the isoprenyl groups were attached to the same carbon atom C-1.

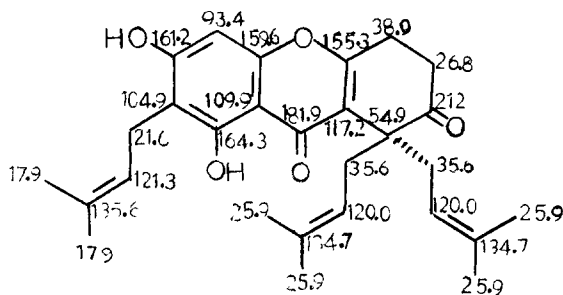


Figure 1. ¹³C-NMR (25.15 MHz) data (ppm) of zeyloxanthone in CDCl₃

The multiplet around 7.1τ - 7.6τ in the ¹H-NMR spectrum of zeyloxanthone indicated that two methylene groups were attached to adjacent carbon atoms as in Structure I. The allylic methylene protons of the two isopentenyl chains appeared at 6.95τ (d) and under the methylene envelope (7.1τ - 7.6τ). Structure I has been assigned to zeyloxanthone based on these data. Figure 1 gives the ¹³C-NMR assignments of zeyloxanthone.

This is the first report of the isolation of a triprenylated tetrahydroxanthone as a natural product. Hostettmann *et al.*⁶ have recently reported the isolation of a tetrahydroxanthone glucoside from *Gentiana campestris*. The isolation of a tetrahydroxanthone should be of biogenetic and chemotaxonomic interest.

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