

The Structure of Xanthoangelol, a New Chalcone from the Roots of *Angelica keiskei* KOIDZUMI (Umbelliferae)

A new chalcone, xanthoangelol was isolated from the roots of *Angelica keiskei* KOIDZUMI (Umbelliferae), and was elucidated as 2', 4', 4'-trihydroxy-3'-[(E)-3,7-dimethyl-2,6-octadienyl] chalcone.

Keywords—xanthoangelol; 4-hydroxyderricin; chalcone derivative; *Angelica keiskei* KOIDZUMI; CMR of xanthoangelol; CMR of geraniol; CMR of nerol

Angelica keiskei KOIDZUMI (Japanese name: ashitaba) (Umbelliferae) is as stout herb growing along the Pacific coast of the Kanto, Tokai and the Kansai districts, and is used as the folk remedy for a diuretics, laxative, analeptic and a lactagogue.

As already reported, the roots of this plant had been demonstrated to afford four furocoumarins,¹⁾ psoralen, angelicin, bergapten and xanthotoxin, on the other hand the yellow juice of the leaves had been shown to contain flavonoids,²⁾ luteorin-7-glucoside and isoquercitrin. In order to examine the yellow pigment of this plant more closely, the authors have re-investigated the constituents of this roots and have obtained two kinds of chalcone derivatives besides several coumarins. One of these chalcones was proved to be identical with 4-hydroxyderricin,³⁾ 2',4'-dihydroxy-3'-(γ,γ -dimethylallyl)-4'-methoxychalcone, on the basis of the spectral data and its chemical behaviour, and the other, named xanthoangelol, was elucidated as 2',4',4'-trihydroxy-3'-geranylchalcone.

This communication deals with the structure elucidation of xanthoangelol.

The dried roots were extracted with ethyl acetate after preextraction with hexane, and the extract was divided into neutral and phenolic portions by the use of aqueous sodium hydroxide. The phenolic portion upon chromatography over silica gel using a mixture of hexane and ethyl acetate as the solvent afforded 4-hydroxyderricin(I) and xanthoangelol(II), yellow needles of mp 114—115°, C₂₅H₂₈O₄, M⁺: 392. The compound (II) turns brown with ethanolic ferric chloride solution and gives a red coloration with magnesium and hydrochloric acid. The ethanolic solution of II gives a red coloration with concentrated sulfuric acid. The ultraviolet (UV) spectrum of II, being very similar to that of I, shows the absorption maxima at 225 and 368 nm.

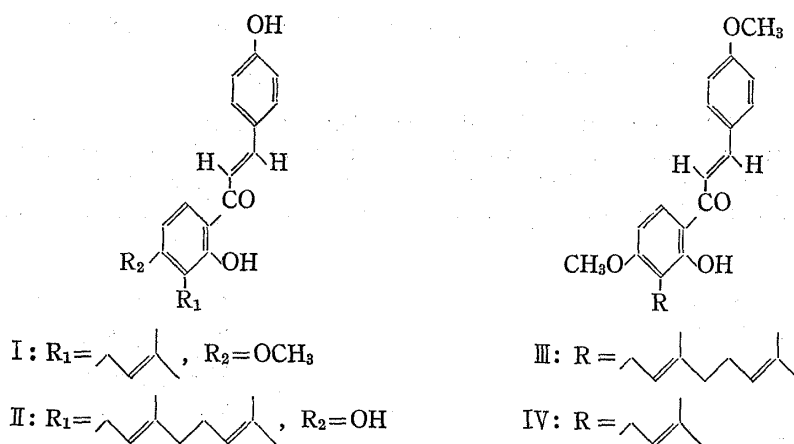


Chart 1

- 1) K. Hata and M. Kozawa, *J. Pharm. Soc.*, **81**, (11), 1647 (1961).
- 2) Y. Kimura and Y. Nishikawa, *Tokyo-to Laboratories for Medical Sciences*, **6**, 142 (1956).
- 3) Delle Monache, G., de Mello, J. F., Delle Monache, F., MariniBettólo, G.B., Gonçalves de Lima, O. and de Barros Coecheo, J. S., *Gazz. Chim. Ital.*, **104**, 861 (1975).

The infrared (IR) spectrum of II indicates the presence of hydroxyl and carbonyl groups and aromatic ring. In the proton magnetic resonance (PMR) spectrum (δ ppm, CDCl_3) of II the signals attributable to the protons of geranyl or neryl group are observed, *i. e.* singlets at 1.59, 1.67, and 1.82 ($3\text{H} \times 3$), a multiplet at 2.08 (4H), a doublet at 3.47 (2H, $J=6.5$ Hz), a multiplet at 5.05 (1H) and a triplet at 5.31 (1H, $J=6.5$ Hz). The doublet at 3.47 is apparently due to a benzylic methylene group, indicating that the geranyl or neryl group must be attached directly to the aromatic ring. Furthermore, II shows signals due to three hydroxyl protons at 6.06, 6.36 and 13.84 (1H \times 3), a pair of doublets due to the protons of *trans*-disubstituted olefinic system at 7.37 and 7.83 (1H \times 2, $J=16$ Hz), as well as two pairs of doublets due to six aromatic protons at 6.41 and 7.69 (1H \times 2, $J=9.2$ Hz), and 6.85 and 7.49 (2H \times 2, $J=9$ Hz).

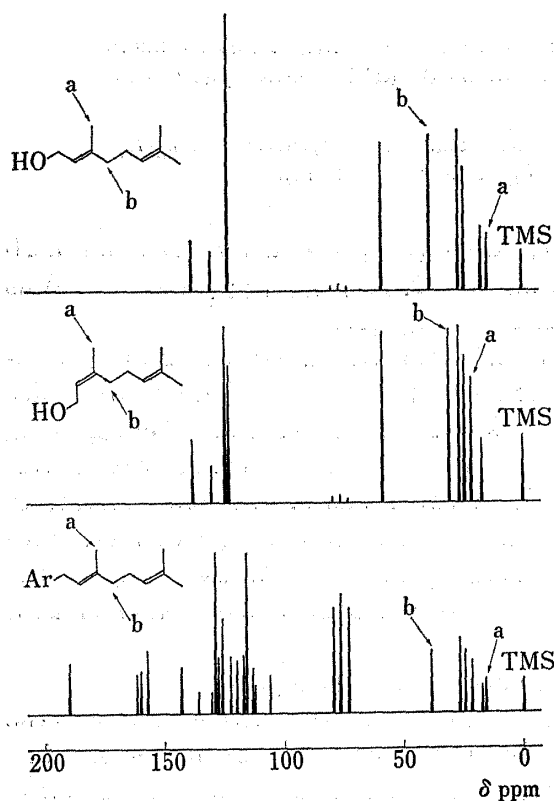


Fig. 1. The CMR Spectra of Geraniol, Nerol and II in CDCl_3

gave dimethyl ether(III), whose PNR spectrum is almost superimposable with that of 4-hydroxyderricin monomethyl ether(IV), except for the signals due to the protons of the side chains.

On the basis of these evidence the structure of II is represented as 2',4',4'-trihydroxy-3'-[(*E*)-3,7-dimethyl-2,6-octadienyl] chalcone.

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