

X-Ray Structure of Two Naturally Occurring Cinnamylidene-butenolides

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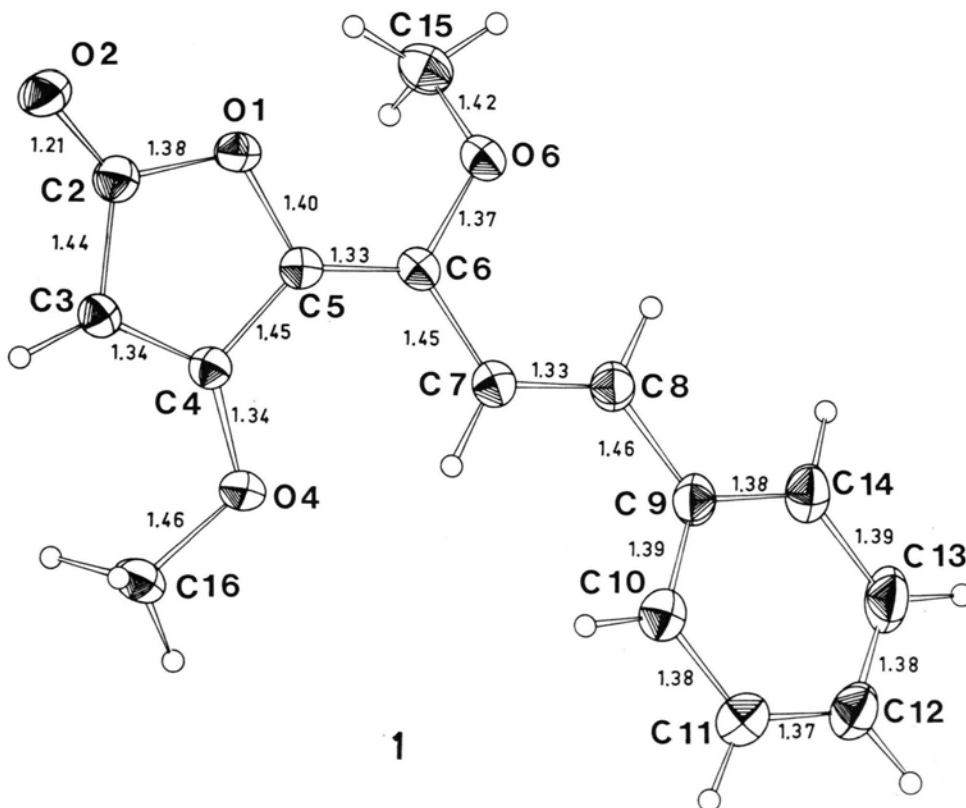
Piperaceae, Cinnamylidene-butenolides, Piperolide, X-Ray

An X-ray analysis of two compounds isolated from *Piper sanctum* confirmed the *trans* configuration for 5-(methoxy)-cinnamyliden-4-methoxy-but-3-enolide (= piperolide [1]) and for 5-[*trans*-(2)- β - γ epoxy- α -methoxy-cinnamyliden]-4-methoxy-2(5H)-furanon (= epoxypiperolide [2]). The stereochemistry of the semicyclic double bond is in favour of the *Z*-isomers.

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From the subterranean parts of *Piper sanctum* Schlecht, three cinnamyliden-butenolide derivatives were isolated by Hänsel *et al.*^{1,2}, but it was impossible to get definitive information about the configuration with respect to the semicyclic double bond.

Single crystals were obtained by recrystallisation of **1** (Fig. 1) from methanol/acetone and **2** (Fig. 1) from methanol. For compound **1** (C₁₅O₄H₁₄) the space group is *Pbca* with cell dimensions of: $a = 44.174(3)$, $b = 8.056(3)$, $c = 7.515(4)$ Å, $D_{\text{cal}} = 1.28 \text{ g} \cdot \text{cm}^{-3}$. 2523 independent reflexions ($\theta \leq 70^\circ$) were measured with Cu-K α radiation ($\theta/2\theta$ scan), 537 were coded unobserved ($I < 2\sigma$). Compound **2** (C₁₅O₅H₁₄) crystallises in *P2₁/c* with cell dimensions of: $a = 11.351(4)$, $b = 8.292(5)$, $c = 14.292(4)$ Å, $\beta = 96.28^\circ$, $D_{\text{cal}} = 1.36 \text{ g} \cdot \text{cm}^{-3}$. With Mo-K α radiation 2329 independent reflexions ($\theta \leq 25^\circ$) were measured as above, 658 coded unobserved. These structures were solved by direct methods (MULTAN³, X-RAY 72⁴) and refined to $R = 4.8\%$ (compound **1**) and 7.5% (compound **2**) respectively. Fig. 1 shows the configuration of the methoxy groups to be *trans* with respect to the semicyclic



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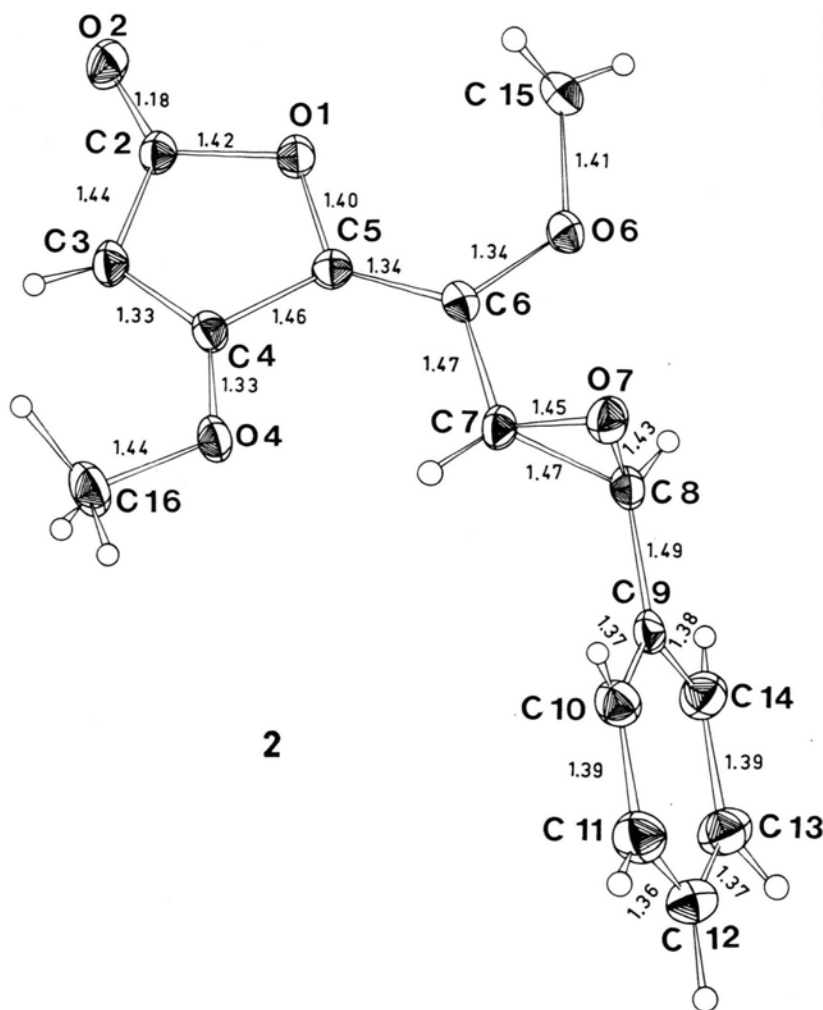


Fig. 1.
Bond distances of
Piperolide (1) and
Epoxypiperolide (2)
in Å.

double bond. Contact distances of O(6) are 2.78 to C(8), 2.78 to O(7) and 2.88 Å to O(1). Model calculations⁵ for the *cis*-configuration showed additional small distances for O(6) to O(4) with 2.98, C(15) to O(4) 2.43 and O(6) to O(1) being increased to 3.67 Å, indicating the *cis*-configuration as stereochemically less favourable. The phenyl- and

lactone rings are planar with angles of 22.0° for **1** and 67.8° for **2** between their least-squares planes.

Full crystallographic details will be given in J. Christ. Mol. Struct.

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³ P. Main, M. M. Woolfson, and G. Germain, MULTAN Univ. of York Printing Unit, York, Version 1975.

⁴ X-Ray System 72, Univ. of Maryland (1972).

⁵ H. J. Hecht, MPOT, Thesis, Free University Berlin (1976).