# X-Ray Structure of Two Naturally Occuring Cinnamylidene-butenolides

R. Reinhardt

Institut für Kristallographie der Freien Universität Berlin

R. Hänsel

Institut für Pharmakognosie und Phytochemie der Freien Universität Berlin

(Z. Naturforsch. **32 c**, 290–291 [1977]; received December 10, 1976)

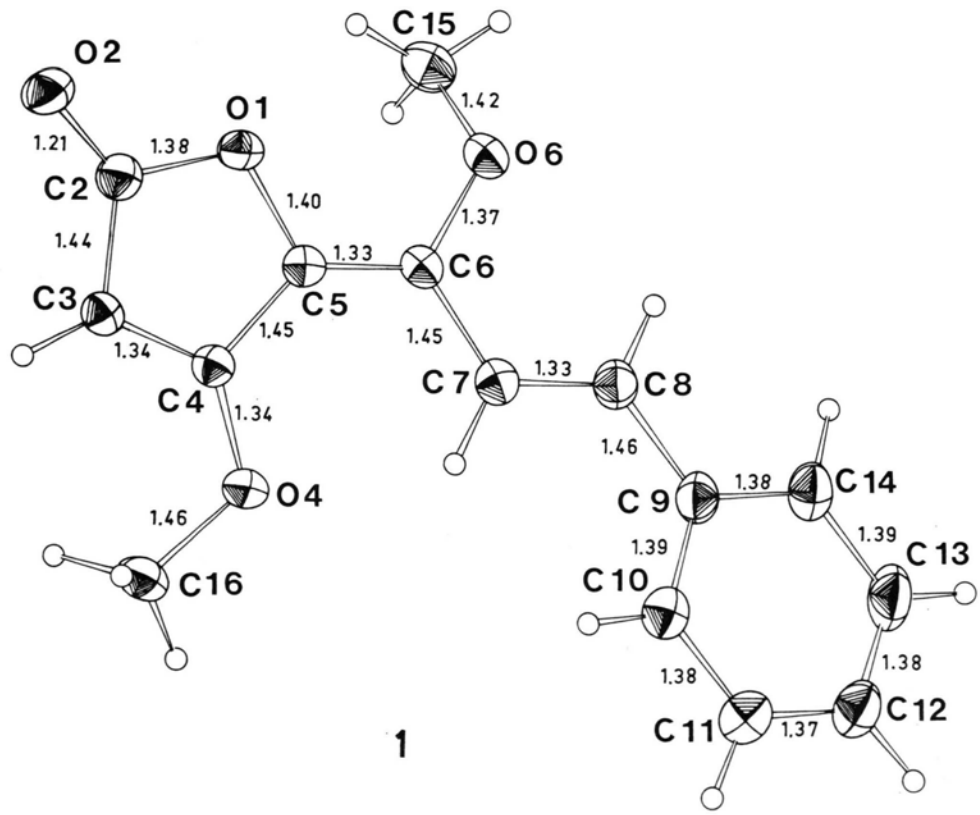
Piperaceae, Cinnamylidene-butenolides, Piperolide, X-Ray

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)-$\beta$-$\gamma$ epoxy-$\alpha$-methoxy-cinnamyliden]-4-methoxy-2(5H)-furanon (= epoxypiperolide [**2**]). The stereochemistry of the semicyclic double bond is in favour of the Z-isomeres.

Requests for reprints should be sent to Prof. Dr. R. Hänsel, Institut für Pharmakognosie und Phytochemie der Freien Universität Berlin, Königin-Luise-Str. 2–4, *D-1000 Berlin 33*.

From the subterranean parts of *Piper sanctum* Schlecht, three cinnamyliden-butenolidderivatives 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/aceton and **2** (Fig. 1) from methanol. For compound **1** ($C_{15}O_4H_{14}$) the space group is Pbca with cell dimensions of: $a = 44.174(3)$, $b = 8.056(3)$, $c = 7.515(4)$ Å, $D_{cal} = 1.28\,g\cdot cm^{-3}\cdot 2523$ independent reflexions ($\Theta \leqq 70^\circ$) were measured with Cu-$K_\alpha$ radiation ($\Theta/2\,\Theta$ scan), 537 were coded unobserved ($I < 2\,\sigma$). Compound **2** ($C_{15}O_5H_{14}$) crystallises in $P2_1/c$ with cell dimensions of: $a = 11.351(4)$, $b = 8.292(5)$, $c = 14.292(4)$ Å, $\beta = 96.28^\circ$, $D_{cal} = 1.36\,g\cdot cm^{-3}$. With Mo-$K_\alpha$ radiation 2329 independent reflexions ($\Theta \leqq 25$) were measured as above, 658 coded unobserved. These structures were solved by direct methods (MULTAN [3], X-RAY 72 [4]) 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




1

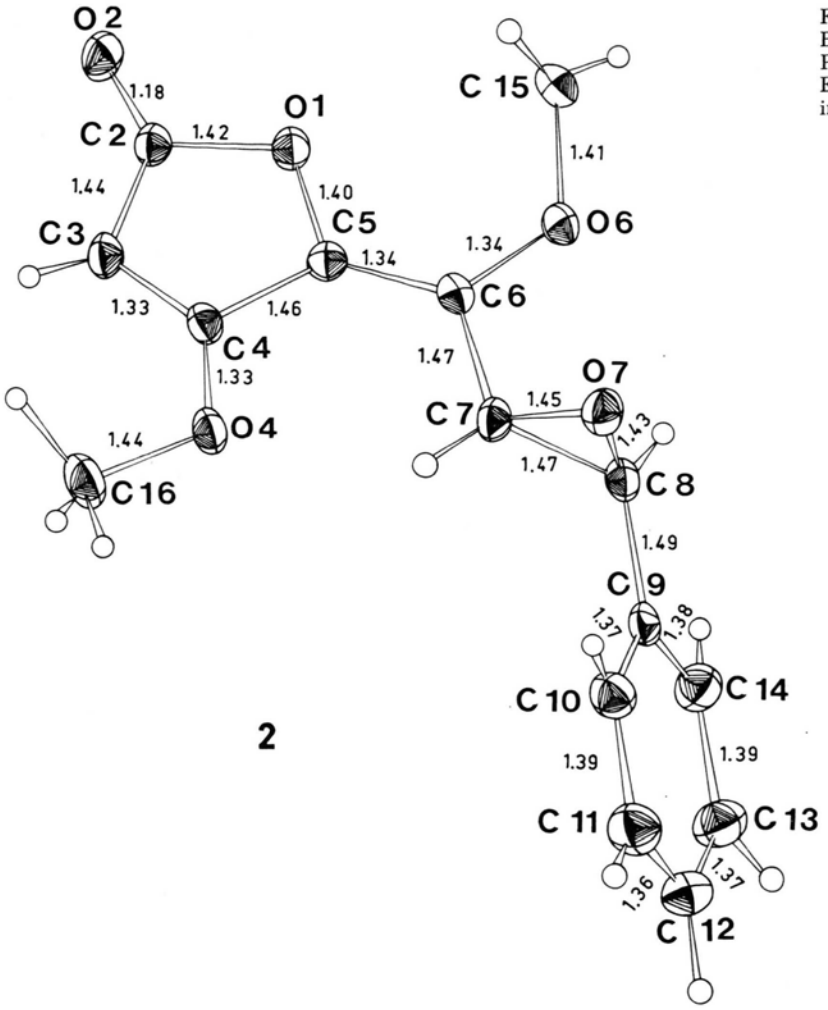



Fig. 1.
Bond distances of Piperolide (**1**) and Epoxypiperolide (**2**) in Å.

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 calculations [5] 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, indecating 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.

We like to thank the Deutsche Forschungsgemeinschaft for financial supports.

[1] R. Hänsel and A. Pelter, Phytochemistry **10,** 1627, 1634 [1971].
[2] A. Pelter and R. Hänsel, Z. Naturforsch. **27 b,** 1186—1190 [1972].
[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).