Isolation and Synthesis of (±)-Obtusafuran

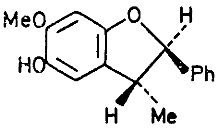
By L. Jurd,* G. Manners, and K. Stevens

(*Western Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Berkeley, California 94710*)

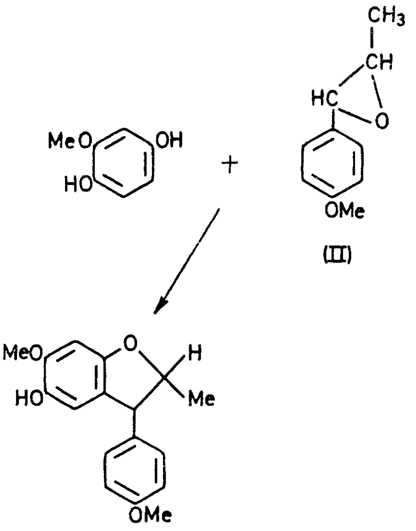
Summary (±)-Obtusafuran from *Dalbergia retusa* is synthesized by a model, biogenetic-type alkylation reaction.

The heartwood of the Panamanian tree, *Dalbergia retusa* Hemsley (cocobolo), contains obtusaquinone, (±)-obtusaquinol, and (±)-4-methoxydalbergione.[1] Petroleum ether extracts of the wood also yield an optically inactive, colourless, crystalline, monohydric phenol, $C_{16}H_{16}O_3$, m.p. 123° (acetate, m.p. 119—120°). The 100 MHz n.m.r. spectrum of the phenol in $CDCl_3$ closely matches the published[2] spectrum of (+)-obtusafuran (m.p. 110—113°) from *Dalbergia obtusa* Lecomte. For this reason, the *D. retusa* compound is considered to be the racemic form of obtusafuran (I).

This identification is supported by a simple synthesis of (I) by alkylation of methoxyquinol with protonated cinnamyl alcohol in warm 1% aqueous citric acid and ascorbic acid. This condensation yields substantial quantities of obtusafuran (*ca.* 10%), in addition to the previously recognized[3,4] 2-cinnamyl-5-methoxyquinol (43%) and obtusaquinol (25%). Similar condensations with cinnamyl alcohol in aqueous formic or propionic acids, and with (±)-1-phenylallyl alcohol in aqueous propionic acid also yield obtusafuran. The synthetic product (m.p. 123°; acetate, m.p. 119—120°) is identical in all respects with the natural compound. The synthetic sequence is analogous to that recently suggested for the biosynthesis of obtusafuran,[5] and it provides significant support for the mechanistic feasibility of the proposed biogenetic origin of dihydrobenzofurans, neoflavanoids, and cinnamylphenols.



(I)



(II)

(III)

Iso-obtusafuran and similar 2-methyl-3-phenyldihydrobenzofurans have not yet been found in plants. However, Seshadri recently suggested[6] that they are related to known neoflavanoids and may be synthesized[7] from 4-phenylcoumarins *via* coumarilic acids. These iso-compounds are formed directly from phenols and epoxy-propenylbenzene derivatives in aqueous media, *e.g.* in dilute acetic acid methoxyquinol condenses readily with anethole oxide (II) or the corresponding glycol to yield (III) (m.p. 138°; acetate, m.p. 88°). Since the natural occurrence of these benzofurans has not been established, it is not known at this time whether this type of ready condensation has any biosynthetic significance.

All the above compounds were fully characterized by elemental and spectroscopic analyses.

(*Received*, 12*th* *June* 1972; *Com.* 994.)

[1] L. Jurd, K. Stevens, and G. Manners, *Tetrahedron Letters*, 1972, 2149.
[2] M. Gregson, W. D. Ollis, B. T. Redman, I. O. Sutherland, and H. H. Dietrichs, *Chem. Comm.*, 1968, 1394.
[3] L. Jurd, *Tetrahedron Letters*, 1969, 2863.
[4] S. Mageswaran, W. D. Ollis, R. J. Roberts, and I. O. Sutherland, *Tetrahedron Letters*, 1969 ,2897.
[5] W. D. Ollis and O. R. Gottlieb, *Chem. Comm.*, 1968, 1396.
[6] T. R. Seshadri, *Phytochem.*, 1972, **11**, 881.
[7] T. Saroja, T. R. Seshadri, and S. K. Mukerjee, *Indian J. Chem.*, 1971, **9**, 1316.