First Total Synthesis of the Benzotropolone/Bis(pulvinone) Natural Product Aurantricholone¹

Philip Koblischek, Reinhard Brückner

Dr. P. Koblischek, Prof. Dr. R. Brückner, Institut für Organische Chemie, Albert-Ludwigs-Universität Albertstraße 21, 79104 Freiburg (Germany), Philip.Koblischek@gmail.com

Aurantricholone as well as its calcium and lithium salts, all of which represent the coloring principle of the fungus Tricholoma aurantium,² were synthesized for the first time, namely in 15 steps, 10 of which were our longest linear sequence. We developed an access to benzotropolones after dibromocyclopropanating alkyl or silyl enol ethers of 1-tetralones. Successive treatments with DMAP-*N*-oxide and Ac₂O effected ring-enlargement, oxidation, and acetylation. *O*-acetyl-1-bromo-3,4-dimethoxybenzotropolone obtained thereby was brominated at C-8 in two steps by adopting our bromination protocol³ for otherwise unsubstituted *O*-acetylbenzotropolone. Thereafter, a double Suzuki-coupling with a newly introduced boronate established the *O*-methylated pulvinone moiety as well as the *O*-methylated "pulvinone-like" motif of what altogether equalled the completed aurantricholone scaffold. Its deprotection (two steps) furnished the title compound either as its protonated form or its calcium or lithium salt.



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