SYNTHESIS OF (±)-1-HYDROXY-2,6-DIARYL-3,7-DIOXABICYCLO[3,3,0]-OCTANE LIGNANS

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The perhydrofurofuran-type lignans from the insecticidal plant, Phryma leptostachya L. subsp. asiatica (Hara) Kitam., are characerized by highly oxygenated phenyl groups (hexa-, hepta-, octaalkoxy) and a tertiary acetoxy group on C-1 of 3,7-dioxabicyclo[3,3,0]octane skeleton[1]. Gmelinol and paulownin are also rare examples of 1-hydroxy-2,6-diaryl-3,7-dioxabicyclo[3,3,0]octane lignan, which has not been synthesized yet.

Our strategy for the synthesis of the title compound is : a) furnishing the hydroxy group on C-1 along with co-formation of an oxolane ring by intramolecular cyclization of a 4-aryl-3,4-epoxybutan-1-ol, b) incorporating each aryl group (Ar_1, Ar_2) stepwise into the lignan skeleton, since this is necessary for preparing asymmetric lignans with different aryl groups, c) fixing the aryl groups at their proper positions without racemization, d) easy separation of the intermediary diastereomeric products, e) optical resolution of the title compound.

First of all, the skeleton compound of the naturally-occurring lignans, 1-hydroxy-2,6-diphenyl-3,7-dioxabicyclo[3,3,0]octane was synthesized from phenylparaconate ; the γ-lactone was transformed to oxolane according to the Kraus' reduction[2]. Then, (±)-paulownin and (±)-isopaulownin were synthesized from methylenedioxybenzylidenesuccinic acid monoester.

1) E.Taniguchi and Y.Oshima, 8th International Symposium on the Chemistry of Natural Products (New Dehli), 124 (1972)

2) G.A.Kraus, K.A.Frazier, B.D.Roth, M.J.Tashner, and K.Neuenschwander, J. Org. Chem. 46, 2417 (1981).