ABSTRACT

SYNTHESSES EMPLOYING (2S,3S)- AND (2S,3R)-TETRAHYDRO-3-HYDROXY-5-OXO-2,3-FURANDICARBOXYLIC ACIDS:- SYNTHESSES OF THE ANALOGUES OF QUARARIBEA METABOLITE CHIRAL ENOLIC-γ-LACTONE.

(2S,3S)- and (2S,3R)-tetrahydro-3-hydroxy-5-oxo-2,3-furandicarboxylic acids (Garcinia and Hibiscus acids) have been isolated in large amounts from cheap natural sources and the optical purity of the molecules were asserted by VCD analysis. A systematic literature survey for biologically potent γ-butyrolactone based natural products has been conducted. The study revealed that there are several γ-butyrolactone based molecules which have matching structure and stereochemistry with that of the title compounds. Attempts were made to synthesize analogues of the Quararibea metabolite chiral enolic-γ-lactone (2,5-dihydro-2,3-furandicarboxylates) from (2S,3S)- and (2S,3R)-tetrahydro-3-hydroxy-5-oxo-2,3-furandicarboxylic acids. Reaction of Dialkyl (2S,3S)- and (2S,3R)-tetrahydro-3-hydroxy-5-oxo-2,3-furandicarboxylates with POCl₃ in pyridine followed by treatment with diazomethane resulted in the isolation of 2S-Dialkyl 4-methoxy-5-oxo-2,5-dihydro-2,3-furandicarboxylates, analogues of the Quararibea metabolite chiral enolic-γ-lactone (3-hydroxy-4,5-(R)-dimethyl-2(5H)-furanone). Certainly an unusual α-hydroxylation of γ-butyrolactone (dialkyl tetrahydro-3-hydroxy-5-oxo-2,3-furandicarboxylates) is involving with POCl₃. The feasibility of α-hydroxylation with methanesulfonyl chloride failed instead resulted in the formation of aromatic dialkyl 5-[(methylsulfonyl)oxy]-2,3-furandicarboxylates. This clearly indicates the involvement of a (2,3)-sigmatropic rearrangement leading to α-hydroxylation of dialkyl tetrahydro-3-hydroxy-5-oxo-2,3-furandicarboxylates. Trialkyl (1S,2S)- and (1S,2R)-1,2-dihydroxy-1,2,3-propane tricarboxylates was converted to (4S,5S)-4-(2-Hydroxy-2,2-diarylethyl)-2,2-Dimethyl-α,α',α'-tetraaryl-1,3-dioxalane-4,5-dimethanols. This TADDOL analogue was found to be effective chiral dopants for the phase transformation of nematic liquid crystal into cholesteric liquid crystal.