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Novel Photochemical Conversion of Pulvinic Acid to Leprapinic acid

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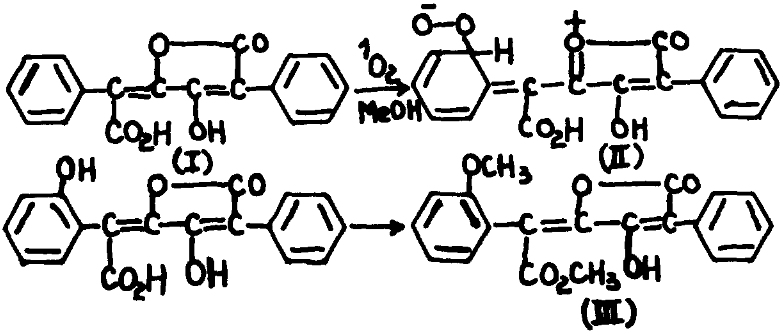
Abstract: Pulvinic acid, an important Lichen acid from the lower variety of lichens has been converted to leprapinic acid in good yields. The conversion has a significance in the biogenesis of lichen acids.

Recently singlet oxygen has been suggested as a nonenzymatic model for dioxygenases and its involvement in several biosystems and biogeneses of plant phenolics has been postulated.[2-5] As a part of our continuing studies on the reactions of singlet oxygen with naturally occurring plant products we have carried out the dye sensitized photooxygenation of a lichen acid, pulvinic acid (1) with the hope to understand the connection between such photo-oxygenations and enzymic reactions in the lichen series. The present communication deals with the convenient conversion of pulvinic acid to another lichen acid, leprapinic acid (III).

Pulvinic acid (200 mg) was dissolved in methanol (100 ml) with 10^{-2} times its molar concentration of the sensitizer, rose bengal. The solution was irradiated with 100 watt tungsten filament lamp (60 hr) while oxygen was passed through the solution continuously. To avoid side reactions, a potassium chromate screen was placed between the lamp and the solution to arrest u.v. radiations, quite common in tungsten lamps while progress of the reaction was monitored by TLC. The involvement of $^1O_2$ was confirmed by carrying out the reaction in the presence of well known free radical and singlet oxygen quenchers like quinol and β-carotene respectively, when no reaction was observed. After about 75% of the reaction, the solvent was removed under pressure and the residue extracted with ether, ethyl acetate and chloroform. The organic extracts were evaporated and subjected to column chromatography (silica gel) using petroleum ether-benzene (1:1) as the eluent to yield a yellow compound, m.p. 160-1°, R_f 0.83 (Benzene-Acetic acid; 100:1), ν_{max}^{KBr} 3500 (broad, OH), 2960, 2920, 1765, 1725, 1680, 1610 cm^{-1}; $_{max}^{MeOH}$ 270, 316 (inf) nm; NMR (δ, $CDCl_3$), 3.72 (s, 3H, $-OCOC\underline{H}_3$), 3.8 (s, 3H, $-OC\underline{H}_3$), 4.1 (s, 1H, $-O\underline{H}$), 7.13-8.0 (9H, Aromatic protons) in good yield (30%). It could be identified as leprapinic acid by comparison with an authentic sample (m.m.p., Co-IR and Co-TLC)[6].

The reaction can be considered to take place by an electrophilic attack of singlet oxygen at the electron rich ortho position to yield a hydroperoxide (II) which gets converted to leprapinic acid under the conditions of the experiment as depicted below:



This is the first report of a one step conversion of pulvinic acid to leprapinic acid which otherwise is obtained by a lengthy and low yield route.[6] This reaction illustrates the case of oxygen incorporation in the o-position and indicates this reaction as a non-enzymatic model for the genesis of lichen acids because both pulvinic and leprapinic acids co-occur quite often. The earlier known example of such participation of singlet oxygen is that of hydroxy phenyl pyruvic acid which is converted to hemogentisic acid where the reaction exclusively takes place at the p-position.[7]

Further work on the mechanism and reactions of singlet oxygen with other lichen acids is in progress.

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