

6. Bapat, M. N. and Sivaraman, S., *Indian J. Pure Appl. Phys.*, 1983, **21**, 247.
7. Kyarner, T. N., *Eesti NSV Tead Akad Fuus Inst Uurim USSR*, 1974, **49**, 172.
8. Hoogenstraaten, W., *Philips Tech. Rep.*, 1958, **13**, 515.
9. Kyarner, T. N. and Sorkin, B. A., *Sov. Phys. Solid State*, 1978, **20**, 1557.
10. Kyarner, T. N., Malyasheva, A. F., Maaros, A. A., *Eesti NSV Tead Akad Inst Uurim USSR*, 1979, **50**, 35.
11. Bapat, M. N., *Indian J. Pure Appl. Phys.*, 1984, **22**, 318.
12. Harris, E. F. and Crawford, Jr, J. H., *Phys. Stat. Solidi*, 1975, **A30**, 223.
13. Leszczynski, R., Wysoki, S. and Sugier, H., *Radiochem. Radioanal. Lett.*, 1981, **46**, 27.

## DYSENSITIZED PHOTO-OXYGENATION OF $\alpha$ -KETOGLUTARIC ACID

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ALTHOUGH moderate attention has been paid in studying the dyesensitized photo-oxygenation of  $\alpha$ -keto acids by singlet oxygen<sup>1-4</sup>, still the mechanism of the photo-oxygenation is not certain. In the present study  $\alpha$ -ketoglutaric acid has been oxidized by singlet oxygen. Succinic acid and carbon dioxide have been isolated as the end products. A mechanism has been proposed involving peracid intermediate.

All the solvents were dried and distilled before use. Purity of the  $\alpha$ -ketoglutaric acid was judged by its melting point.

### (i) Eosin-Y sensitized photo-oxygenation of $\alpha$ -ketoglutaric acid by singlet oxygen in aqueous medium

$\alpha$ -ketoglutaric acid (Romali Austrian Praparate Co., 0.25 g) was taken in reaction vessel and dissolved in distilled water (200 ml) and eosin-Y solution (5 ml,  $4 \times 10^{-3}$  M) was added. The solution was irradiated with a tungsten filament lamp with simultaneous passage of air through the solution. Continuous 'tlc'

analysis indicated the formation of a new spot on the tlc plate above the spot of  $\alpha$ -ketoglutaric acid after about 7 hr and after about 12 hr the spot corresponding to the starting compound completely disappeared. At this point irradiation was stopped. Solution was decolorized by activated animal charcoal and dried to a solid mass. This solid was again crystallized (m.p. 187°C). The product was identified as succinic acid by physical, chemical and spectral methods.

### (ii) Photo-oxygenation in presence of different solvents

(A) *Water*: The solution of  $\alpha$ -ketoglutaric acid was irradiated under similar conditions as given above. After 7½ hr, 25 ml of solution was withdrawn and spotted on tlc plate meant for preparative tlc. The product was separated, purified and identified as succinic acid. The percentage yield of the product was calculated.

(B) *Methanol*: Under similar conditions, methanol (200 ml) was used as the solvent in place of water. Solution was irradiated. Reaction initiated after 5½ hr. Percentage yield of the product (succinic acid) after 6 hr was calculated.

(C) *Acetone*: Acetone was used as solvent in place of either water or methanol. Reaction was found to initiate after 3½ hr. After 4 hr, the percentage yield of the product was calculated.

### (iii) Methylene blue sensitized photo-oxygenation of $\alpha$ -ketoglutaric acid

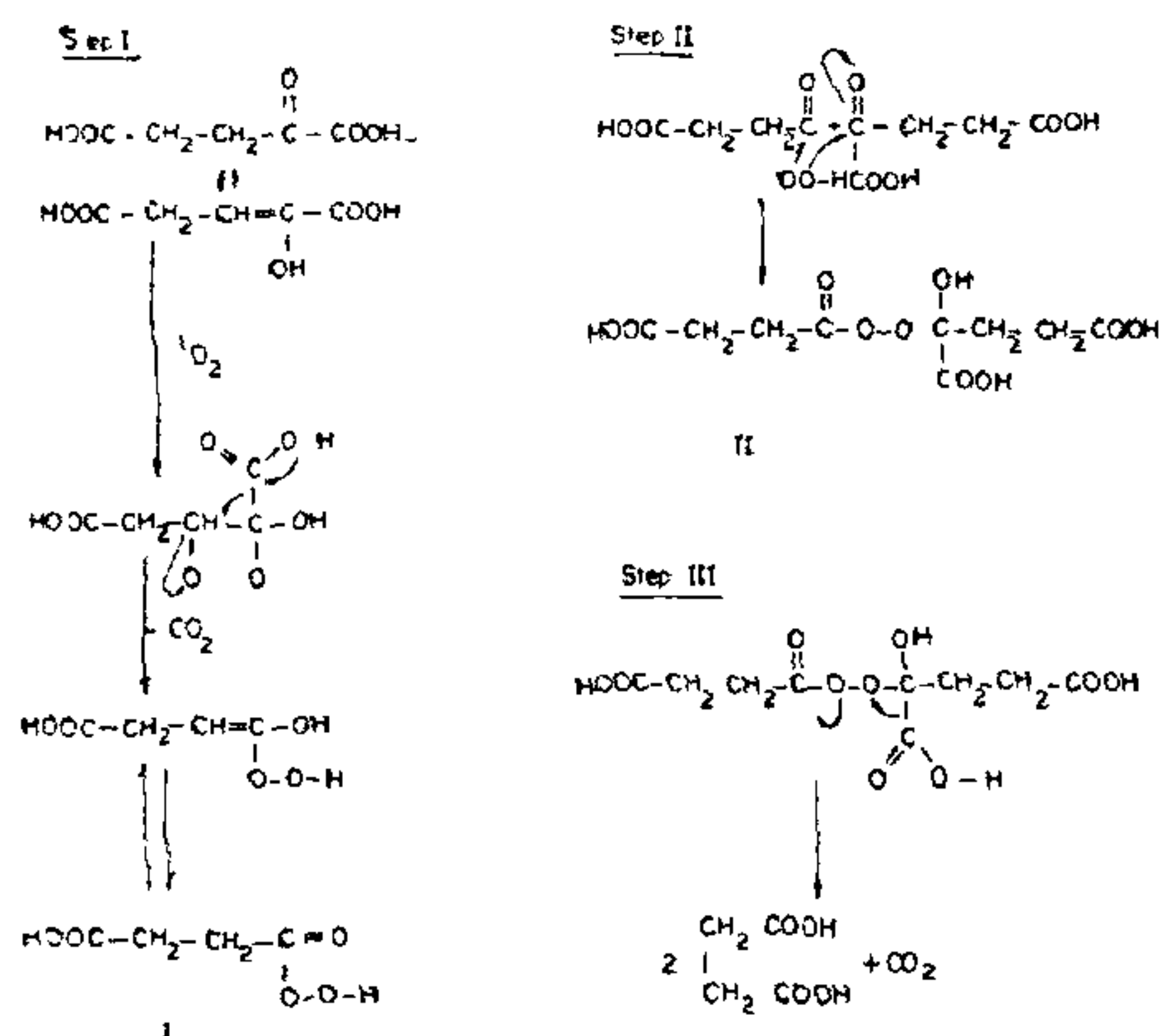
Under exactly similar conditions of substrate and dye concentration as given above, methylene blue was used in place of eosin-Y and percentage yield of the product (succinic acid) was calculated in water, methanol and acetone media by similar methods.

The experiments (i) and (ii) have also been carried out in presence of nickel chloride and cobalt chloride as singlet oxygen quenchers. Yield of the product decreased.

Dyesensitized photo-oxygenation of  $\alpha$ -ketoglutaric acid has been carried out using eosin-Y and methylene blue sensitizers in aqueous, methanolic and acetone media. In all the cases succinic acid and carbon dioxide have been identified as the end products by fluorescein and lime water test respectively. Infrared spectrum of the succinic acid was superimposable on that of authentic sample of succinic acid. The tentative mechanism of the reaction may be explained as follows:

The first step of the reaction involves the formation of  $\alpha$ -ketoglutaric peracid (I) in an oxidative decarboxy-

lative step. In the formation of I, the enol form of  $\alpha$ -ketoglutaric acid probably undergoes reaction with singlet oxygen. In the next step, I adds on to the unreacted  $\alpha$ -ketoglutaric acid to give adduct II. The formation of this type of adduct has already been reported in the literature<sup>5</sup>. In the last step, II cleaves to two molecules of succinic acid and carbon dioxide (see scheme).



Percent yield of the succinic acid has been noted in water, methanol and acetone media using eosin-Y and methylene blue (table 1). It has been found that the yield is maximum in acetone medium and minimum in aqueous medium for both sensitizers. This has been attributed to the greater life time of singlet oxygen in acetone medium (26  $\mu\text{s}$ ) and comparatively short life time in water (2  $\mu\text{s}$ ). Methanol occupies mid position (10  $\mu\text{s}$ )<sup>6</sup>.

Effect of scavengers has also been studied and it has been found that the yield of product decreases highly by their use and thereby confirming the participation of singlet oxygen in the reaction.

**Table 1** Time of reaction half an hour from the initiation of reaction as shown by tlc.

Media used	Percent yield of succinic acid in presence of eosin-Y	Percent yield of succinic acid in presence of methylene blue
Water	11	14
Methanol	13	17
Acetone	16	20

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1. Jefford, C. W., Boschung, A. F., Bolsman, T. A. B. M., Moriarty, R. M. and Melnick, B., *J. Am. Chem. Soc.*, 1976, **98**, 1017.
2. Jefford, C. W., Exarchon, A. and Cadby, P. A., *Tetrahedron Lett.*, 1978, 2053.
3. Moriarty, R. M., Chin, A. and Tucker, M. P., *J. Am. Chem. Soc.*, 1978, **100**, 5578.
4. Davidson, R. S., Goodwin, D. and Smith, G., *J. C. S. Chem. Commun.*, 1979, 463.
5. Jefford, C. W., Boschung, A. F. and Cadby, P. A., *Singlet Oxygen (Reactions with organic compounds and polymers)* edited by B. Ranbey and J. F. Rabek, (John Wiley and Sons), 1978, p. 193.
6. Merkel, P. B. and Kearns, D. R., *J. Am. Chem. Soc.*, 1972, **94**, 1029.

## NEW GLYCOSIDES FROM THE STEM BARK OF *APHANAMIXIS POLYSTACHYA*

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THE plant *Aphanamixis polystachya* is a medicinal plant employed locally as astringent, spleen, liver, tumors and abdominal diseases and in rheumatism<sup>1,2</sup>. Our earlier studies on the stem bark of *A. polystachya* disclosed the presence of (24R)-24-ethylcholestra-5, 22-diene-3-O-rhamnoside<sup>3</sup>,  $\beta$ -sitosterol, stigmasterol and aglailol-3-O-rhamnosyl-xyloside<sup>4</sup>. Further examination led to the isolation and characterization of two new glycosides which are assigned as 1,5-dihydroxy-6, 7, 8-trimethoxy-2-methyl-anthraquinone-3-O- $\beta$ -D-xylopyranoside (A) and naringenin 7, 4'-dimethyl ether-5-O- $\alpha$ -L-rhamnopyranoside (B) respectively by physico-chemical data.

Compound-A, reddish brown amorphous solid,  $\text{C}_{23}\text{H}_{24}\text{O}_{12}$  m.p. 158–62° gave positive tests for an anthraquinone glycoside. Acid hydrolysis (7%  $\text{H}_2\text{SO}_4$ ) gave an aglycone,  $\text{C}_{18}\text{H}_{16}\text{O}_8$  ( $M^+$  360), m.p. 140–45° and D-xylose (Co-paper chromatography and osazone). The aglycone on Zn dust distillation gave 2-methyl anthracene showing thereby that the compound is related to 2-methyl-anthraquinone. The