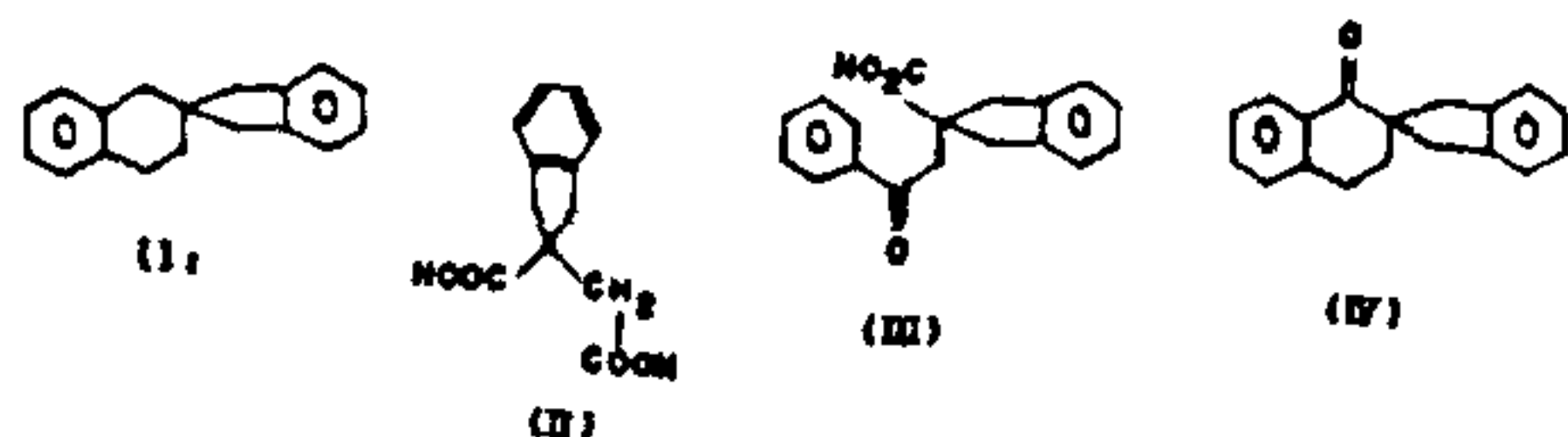


dehydrogenation<sup>1</sup>. With a view to studying the effect of an aromatic ring on the mode and manner of ring fission of a spirocyclopentane ring, we have synthesised the spirane, 1', 2', 3', 4',-tetrahydro-spiro-[3,4-benzo-cyclopentane-1,2'- naphthalene] (I) and studied its rearrangement on catalytic dehydrogenation.

The hydrocarbon (I) was prepared starting from indane which on reaction with formic acid and hydrogen peroxide followed by cyclisation of the resulting monoformate of indane-1, 2-diol yielded 2-indanone<sup>2</sup>, m.p. 58°. Condensation of this ketone with ethyl cyanoacetate in the presence of piperidine at low temperature<sup>3</sup> furnished ethyl indenyl-2-cyanoacetate in 55% yield, m.p. 116° along with anhydro bis- $\beta$ -hydrindone, m.p. 176°. The former on addition of potassium cyanide in aqueous alcoholic solution followed by hydrolysis by hydrochloric acid gave 3, 4-benzocyclopentane-1-carboxy-1-acetic acid (II), m.p. 168°, anhydride, m.p. 165°, anilic acid, m.p. 187°.



The anhydride of the acid (II) on catalysed condensation with benzene in the presence of aluminium chloride gave  $\alpha\alpha$  (3, 4-benzocyclopentane)- $\beta$ -benzoyl propionic acid (III), m.p. 220°, 2,4-DNP derivative, m.p. 211°, which on Clemmensen reduction furnished  $\alpha\alpha$ -(3, 4-benzocyclopentane)- $\gamma$ -phenyl butyric acid, m.p. 155°, along with a neutral compound, m.p. 255°, which is believed to be a lactone derived from bimolecular reduction of the keto acid. Cyclisation of the butyric acid derivative with PPA yielded 3', 4' - dihydrospiro - [3, 4-benzocyclopentane-1, 2' (1', 'H)-naphthalene]-1'-one (IV), m.p. 93°, which gave the desired spirane on Clemmensen reduction.

The hydrocarbon underwent smooth rearrangement on dehydrogenation with 10% Pd-C catalyst at 320°, by fission of the spiro-cyclopentane ring adjacent to the aromatic ring, followed by angular cyclisation and dehydrogenation, yielding 1, 2-benzanthracene, m.p. 160°, picrate, m.p. 141°, TNB complex, m.p. 156°. No other hydrocarbon could be isolated from the reaction mixture.

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## HYDROGEN BONDING INTERACTION OF $\alpha$ -TOCOPHEROL

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TOCOPHEROL has important biological functions<sup>1,2</sup> and its antioxidant properties have received considerable attention. Efforts have been made recently to determine the polarity of the environment around  $\alpha$ -tocopherol and its binding with lipids<sup>3</sup>. Hydrogen donating capability of  $\alpha$ -tocopherol to free radicals has also been examined<sup>4</sup>. We considered it important to obtain quantitative information on the hydrogen bonding interaction of  $\alpha$ -tocopherol with electron donors and also on its self-association. We report results of such a study in this communication.

Self-association of  $\alpha$ -tocopherol was studied in  $\text{CCl}_4$  solution by employing the O-H overtone band in the near IR region following the procedure of Singh and Rao<sup>5</sup>. Hydrogen bonding interaction of  $\alpha$ -tocopherol with electron donor molecules was studied in  $\text{CCl}_4$  solution<sup>6</sup>. Equilibrium constants (1:1) were determined at several temperatures, but only the value at 298 K is given here for the sake of brevity. The  $\Delta H$  value reported here agrees to within  $\pm 2 \text{ kJ mol}^{-1}$ .

The 1:1 equilibrium constant for the dimerization of  $\alpha$ -tocopherol at 298 K ( $0.32 \text{ lit mol}^{-1}$ ) is much lower than that of phenol, but is comparable to that in sterically hindered phenols<sup>7</sup>. The  $\Delta\nu(\text{OH})$  due to dimerization of  $\alpha$ -tocopherol is  $140 \text{ cm}^{-1}$ . The enthalpy change which is directly related to the hydrogen bond energy is also low ( $13.8 \text{ kJ mol}^{-1}$ ) in  $\alpha$ -tocopherol compared to  $\sim 20 \text{ kJ mol}^{-1}$  in the case of phenol.

Data on the hydrogen bonding interaction of  $\alpha$ -tocopherol with electron donors are shown in table 1. The 1:1 equilibrium constants are generally lower than those with phenol<sup>8</sup>, but are comparable to those with sterically hindered phenols<sup>7,8</sup>. Thus, with ethylacetate and DMF, 2, 6-dimethyl phenol shows  $K$  values of 0.8 and  $7.2 \text{ lit mol}^{-1}$  respectively. Enthalpy changes for the hydrogen bonding of electron donors with  $\alpha$ -tocopherol are also lower than those with phenol. Thus, with ethyl acetate, DMF and DMSO, phenol shows  $\Delta H$  values of 19.3, 26.4 and  $29.3 \text{ kJ mol}^{-1}$  respectively. Even 2,6-dimethyl phenol shows higher  $\Delta H$  values than  $\alpha$ -tocopherol (15 and  $31 \text{ kJ mol}^{-1}$  with ethyl acetate and DMF respectively). It,

TABLE I  
Hydrogen bonding of  $\alpha$ -tocopherol with electron-donors<sup>a</sup>

Donor	$K$ (298 K)	$\Delta\nu(\text{OH})$	$\Delta H$
	in lit. mol <sup>-1</sup>	in cm <sup>-1</sup>	in kJ mol <sup>-1</sup>
Ethyl acetate	0.69	110	11.7
Ethyl caprylate	1.00	110	11.7
Acetone	1.03	155	12.1
DMF	5.50	270	18.0
DMSO	11.80	350	26.8

<sup>a</sup>in CCl<sub>4</sub>

therefore, appears that  $\alpha$ -tocopherol is a poorer acid than phenol or hindered phenols. Accordingly, we find that the  $\Delta\nu(\text{OH})$  values are generally much lower in the case of  $\alpha$ -tocopherol (table 1). We, however, see that  $\Delta\nu(\text{OH})$  varies roughly proportionally with  $\Delta H$  since in the case of oxygen donors studied here, we are in the linear range where Badger-Baner rule is applicable<sup>9</sup>.

Recently, interaction of  $\alpha$ -tocopherol with fatty acid derivatives like ethyl caprylate has been investigated<sup>3</sup> by studying the effect of these derivatives on the kinetics of hydrogen abstraction by DPPH. The 1:1 binding constant between ethyl caprylate and  $\alpha$ -tocopherol in alcoholic solution is very large (6,500 lit mol<sup>-1</sup>). We see that this association is distinctly different from hydrogen bonding interaction examined here. The 1:1 equilibrium constant for hydrogen bonding interaction is only 1.0 lit mol<sup>-1</sup> (table 1).

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## INDUCED MUTAGENESIS IN *CAPSICUM* L. II. EFFECTS OF SINGLE AND COMBINED MUTAGENIC TREATMENTS ON HABIT AND FRUIT

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BOTH physical as well as chemical mutagens have been employed considerably for experimental induction of mutations in chillies<sup>1,2</sup>. Information is, however, lacking on the efficiency of these mutagens when used in combinations. The present report deals with some mutations obtained after single and combined treatments of various mutagens.

Seeds of *Capsicum annum* L. cv. N.P. 46 A, obtained from National Seeds Corporation, Jaipur, were subjected to mutagens\* namely  $\gamma$ -rays (5, 10, 15, 20 Kr), DMS (0.25, 0.5, 1, 2, 3%), EMS (0.1, 0.3, 0.5, 0.6%), MES (0.1, 0.3, 0.5%), HA (0.05, 0.1, 0.15%), HZ (0.1, 0.15, 0.2%) for the present investigation. Genetically pure seeds were used for treatments. Dry seeds (moisture content 6.08%) were irradiated with gamma-rays at the above dosages at IARI, New Delhi. Seeds used for chemical treatment were presoaked in distilled-water for 12 hr and then treated with freshly prepared solution of the mutagen for 12 hr at room temperature. Seeds were immersed in solution, three times more in volume than that of the seed. For combination treatments, gamma-ray-irradiated seeds for the above dosages were presoaked in distilled-water for 12 hr and then treated with 2 and 3% of DMS solution. A control was maintained with seeds soaked in distilled-water only. Chemically treated seeds were thoroughly washed with water and sown in petriplates for measuring germination and seedling injury and pots simultaneously. Seedlings at 6-leaf stage were later on transplanted in garden beds to raise  $M_1$  population. Mutants isolated were established by raising them in subsequent generations for mutated characters. Viable mutations affecting plant habit and fruit characteristics were recorded in  $M_1$  and  $M_2$  generations derived from individual

\* $\gamma$ -rays, Gamma rays; DMS, dimethyl sulphate; EMS, ethyl methane sulphonate; MES, methyl ethane sulphonate; HA, hydroxyl ammonium chloride; HZ, hydrazine sulphate.