

COMPARISON OF THE CATALYTIC ACTIVITIES BETWEEN ISOPROPYL ALCOHOL DECOMPOSITION AND NITROUS OXIDE DECOMPOSITION OVER  $\text{La}_2\text{TiMO}_6$  (WHERE M=Ni, Cu AND Zn)

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MULTIPLE ion substituted perovskites of the type  $\text{A}_2\text{BB}'\text{O}_6$  with transition metal ions at B sites, have gained considerable attention because of their interesting solid state and useful catalytic properties. The preparation and characterization of perovskites of the formula  $\text{La}_2\text{TiMO}_6$  (where M = Ni, Cu, Zn, Co and Mn) have been reported from our laboratories<sup>1, 2</sup> and some of them have been tested for the activity for nitrous oxide decomposition<sup>3, 4</sup>. The present communication deals with the comparison of the activities of the above catalysts towards isopropyl alcohol and nitrous oxide decompositions.

The compounds  $\text{La}_2\text{TiMO}_6$  (where M = Ni, Cu and Zn) were prepared by the solid state reactions between the individual oxides of lanthanum, titanium and M ions (all of A.R. grade). The synthesis and characterization of the compounds by x-ray electrical conductivity, magnetic moments and the measurement of B.E.T. surface areas have already been reported<sup>2, 4</sup>.

Double distilled isopropyl alcohol (A.R. grade) was employed throughout the present investigation. Decomposition studies were carried out in a fixed bed flow type integral reactor using 2 ml of the catalyst each time and standard techniques were employed for following the reaction and analysis of the products<sup>5</sup>. The regeneration of the catalyst after each reaction was effected by passing dry air through the reactor at 400°C for 4 hours to restore the activity. The reaction was carried out at various contact times and at each contact time kinetics of decomposition was followed at several temperatures.

The products of the reaction were found to be exclusively acetone and hydrogen with no traces of either ethers or olefins. From the plots made between contact time and mole per cent conversion of alcohol on all these catalysts, initial rates were calculated and these values were utilised for the evaluation of activation energies.

Table I incorporates the kinetic parameters of the present decomposition reaction and also the activation energies for nitrous oxide decomposition<sup>3, 4</sup>. This series of catalysts did not exhibit any compensation effect (evidenced from a plot between activation energy and logarithmic frequency factor). Hence the comparison of the activities was made on the basis of activation energies alone, rather than on the basis of rate constant values at a particular temperature. It is seen from Table I that the observed activity pattern is as :



A similar activity pattern was observed for the decomposition of nitrous oxide over these catalysts<sup>4</sup>.

Product inhibition studies\* showed that desorption of acetone is the rate limiting step in the alcohol decomposition reaction. Measurement of electrical conductivity\* of the catalysts in ambient atmospheres revealed that desorption of acetone involves donation of electrons from the substrate to the catalyst.

During the studies on the kinetics of decomposition of nitrous oxide it was reported<sup>4</sup> that on all the catalysts employed in the present investigation, desorption of oxygen involving transfer of electrons from oxygen to the catalyst surface constitutes the rate limiting step.

From the above observations, it is clear that the rate limiting steps, in both the reactions, involve electron transfer from the substrate to the catalyst. In other words, both the decomposition reactions are facilitated on the catalyst having relatively high tendency to accept electrons ( $\text{La}_2\text{TiNiO}_6$  in the present series). Thus a positive correlation as shown in Fig. 1 between activation energy for isopropyl alcohol and activation energy for nitrous oxide decomposition seems reasonable.

TABLE I

Catalyst	Surface area $\text{m}^2/\text{g}$	Temperature range of study °C	$E_a$ for alcohol decomposition k. cal/mole	Frequency factor moles $\text{m}^{-2} \cdot \text{min}^{-1}$	$E_a$ for $\text{N}_2\text{O}$ decomposition k. cal/mole
$\text{La}_2\text{TiNiO}_6$	2.8	250-290	5.3	7.3	3.5
$\text{La}_2\text{TiCuO}_6$	0.9	250-290	9.3	$5.9 \times 10^3$	21.5
$\text{La}_2\text{TiZnO}_6$	1.2	270-310	13.0	$1.5 \times 10^4$	40.7

\* Under communication.

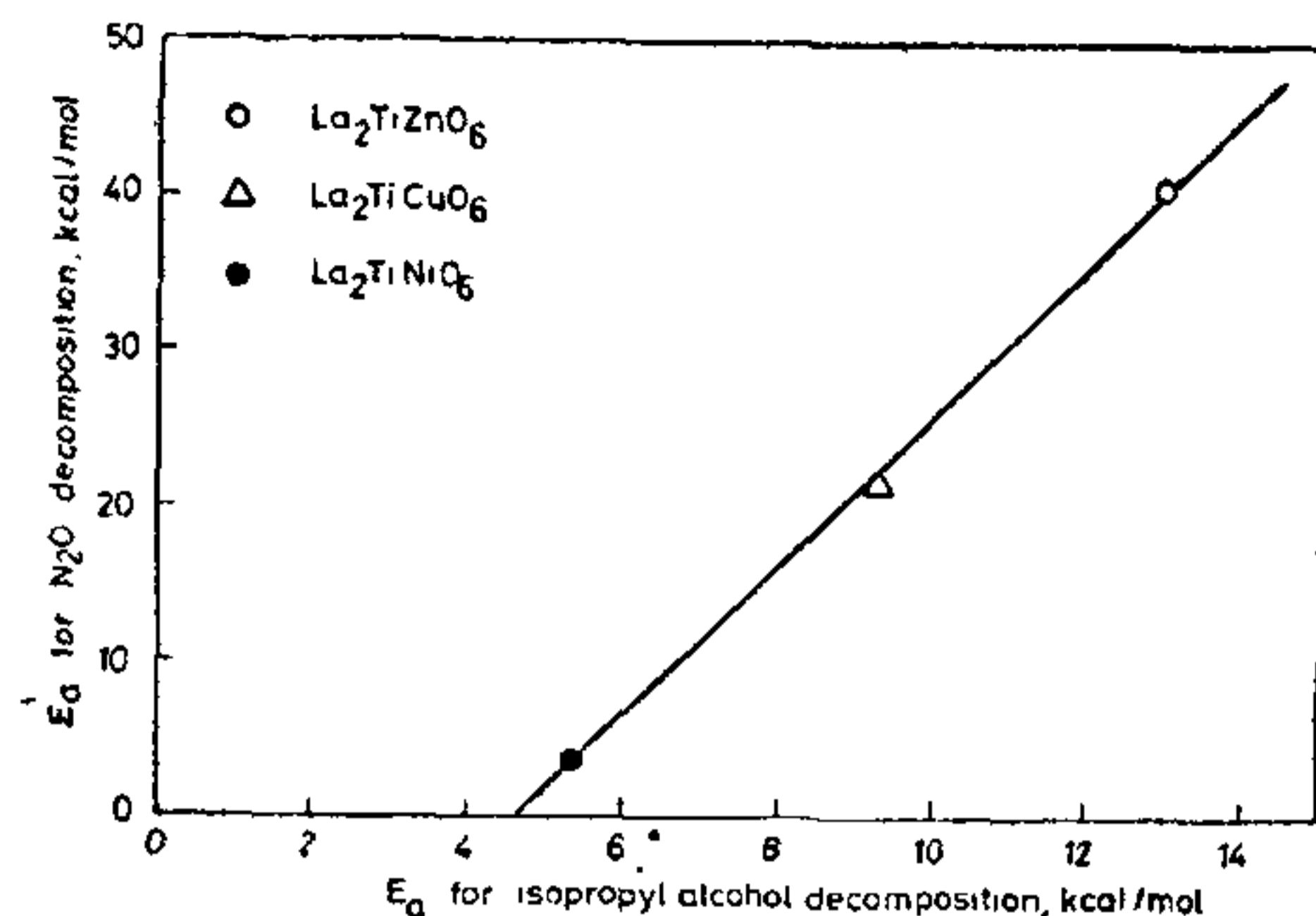


FIG. 1. Correlation between  $E_a$  for  $N_2O$  decomposition and isopropyl-alcohol decomposition.

Financial support from Department of Atomic Energy for one of the authors (KVR) is gratefully acknowledged.

July 10, 1980.

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## CONFIRMATION OF THE STRUCTURE OF SEMECARPUS BIFLAVANONE B

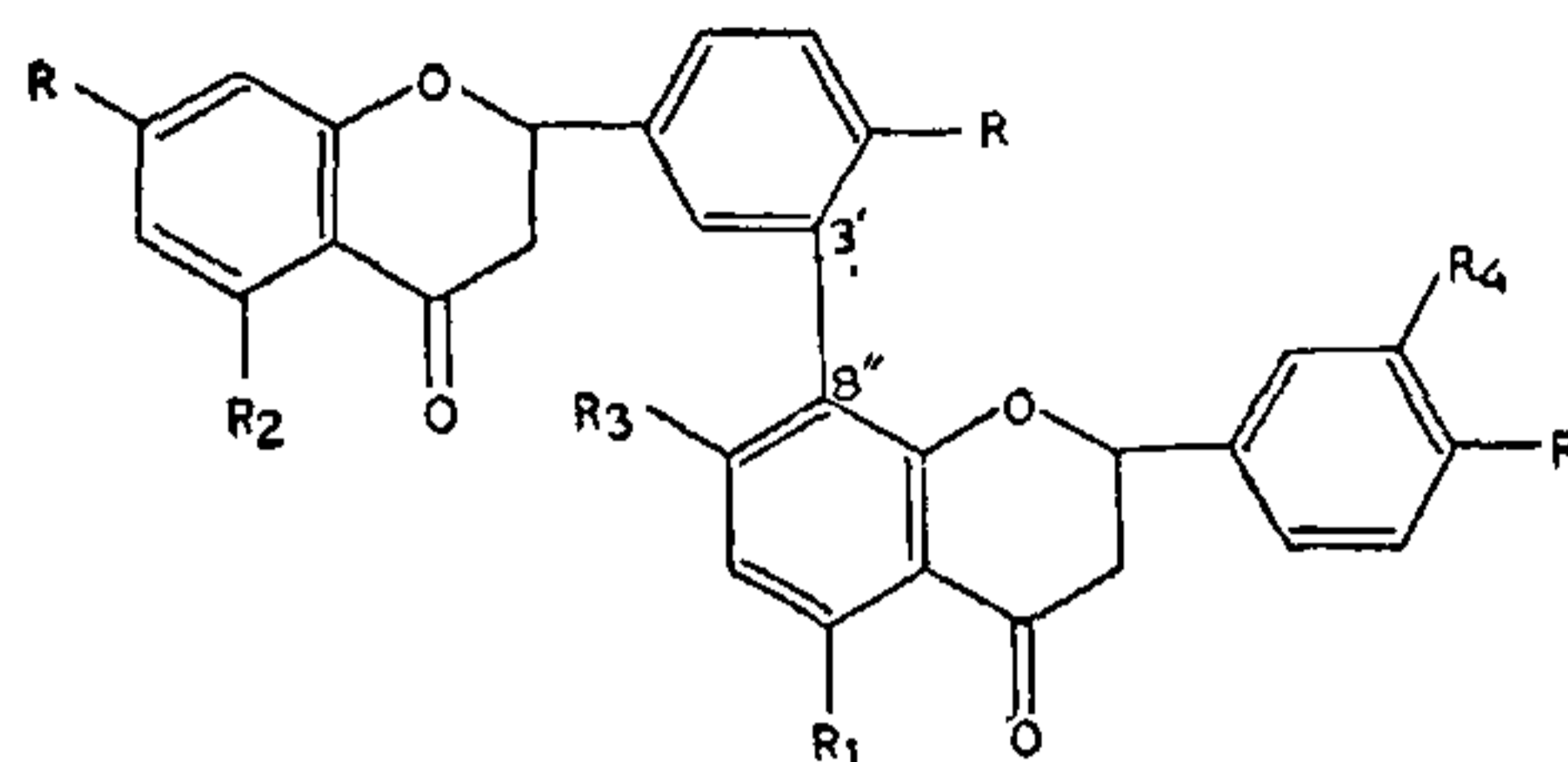
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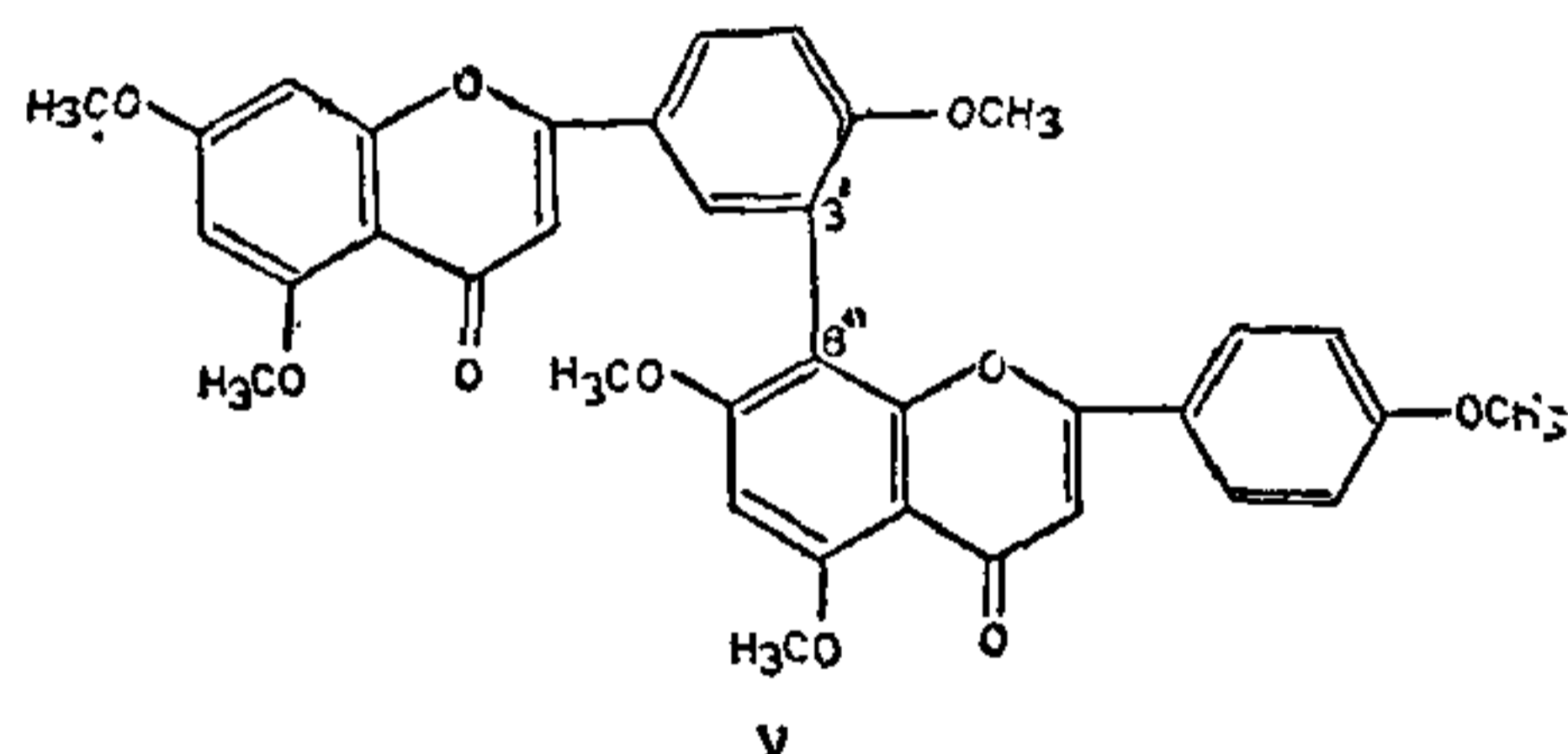
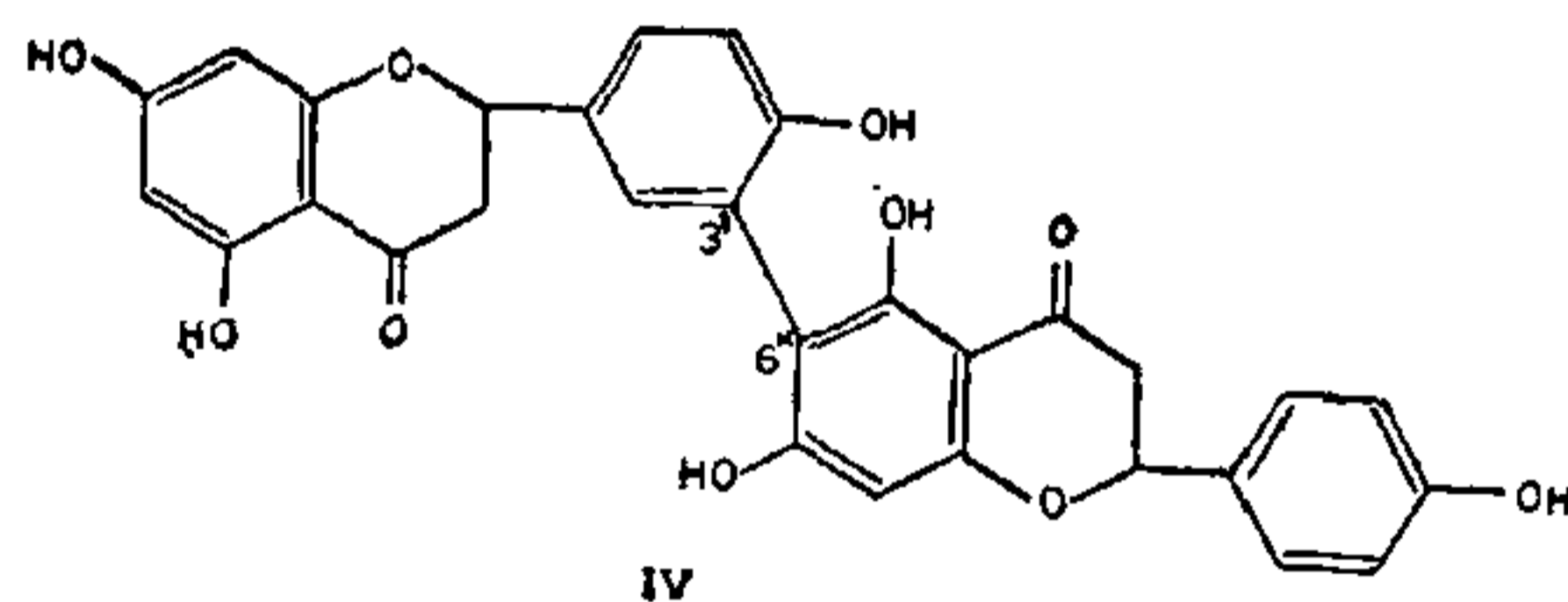
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THREE new semecarpus biflavones, A (I), B (II), and C (III) were reported from the ether soluble fraction of the methanolic extract of the defatted nut shells of *Semecarpus anacardium* Linn. by Row *et al.*<sup>1</sup>. Biflavone B [tetrahydroamentoflavone, (II)] and tetrahydr. robustaflavone (IV) were isolated<sup>2</sup> from the nut shells of the same plant. The structures of the three biflavones (I), (II) and (III) were assigned based mainly on spectral data. Hence it is proposed

to provide further chemical evidence by converting them into the corresponding stabler biflavones<sup>3</sup>. The present study deals with the confirmation of the structure of semecarpus biflavone B (II).



- I.  $R=R_1=R_2=R_4=OH, R_3=H$   
 II.  $R=R_1=R_2=R_3=OH, R_4=H$   
 III.  $R=R_3=OH, R_1=R_2=R_4=H$



Adopting the procedure of Row *et al.*<sup>1</sup>, the yellow biflavonoid mixture (40 mg) was reisolated and dehydrogenated with iodine (0.80 g) and potassium acetate (3.50 g) in acetic acid<sup>3,4</sup> (20 ml) at reflux temperature for 3 hours to give the biflavone mixture which also showed a single spot like the parent compound. The dehydrogenated product (20 mg) was methylated with dimethyl sulphate (1 ml), potassium carbonate (3.0 g) in dry acetone (20 ml) under reflux for several hours till the product gave a negative ferric reaction. The reaction product showed a number of trailing spots on TLC. It was chromatographed over a small column of silica gel (finer than 20 mesh) and eluted with benzene; chloroform mixture and chloroform. The chloroform eluate afforded a single component (compound A) which was crystallised from chloroform; methanol mixture as needles,  $C_{26}H_{20}O_{10}$