GROUP REORIENTATION IN SOLID MANDELIC ACID—A N.M.R. INVESTIGATION

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ABSTRACT

Low resolution N.M.R. investigations were carried out on solid mandelic acid (a, hydroxy-phenyl acetic acid) at $7 \cdot 5$ MHz in the temperature region 77–391 K. The lattice was found rigid and non-rotating at 77 K. In the region 77–215 K, the gradual fall of second moment from rigid lattice value ($25 \cdot 22$ G^2) is attributed to the oscillations of hydroxy and carboxylic protons. The sudden drop of second moment in range 215–285 K is explained as due to the hindered reorientation of OH and COOH groups about the bond connecting them to asymmetric carbon. The second moment data in the region 285–390 K suggest some kind of motion of the phenyl group which possibly is slow reorientational in nature. The activation energy for the motion was computed to be $6 \cdot 03$ K.cal/mole.

THE N.M.R. experiments were performed on poly-crystalline mandelic acid to study the molecular motions present in the crystal lattice. The study affords a check of the proposed molecular structure and shows that the intramolecular space near the asymmetric centre of the molecule is constantly agitated as regards the charged particle density due to the protonic formal oscillations of the hydroxy group and the carboxylic resonance, still maintaining an equilibrium. The input of thermal energy provides for group reorientation, of course, hindered in nature and style.

MOLECULAR STRUCTURE AND HYDROGEN BONDING

In the absence of any precise data regarding the molecular and crystal structure of the sample, the molecular model (Fig. 1) of the compound was constructed assuming the standard values of the bond distances and bond angles. The space co-ordinates of the constituent protons are given in Table I. The model was found fairly accurate for the calculation of intramolecular second moment. IR and UV studies[1] of some salts of mandelic acid complexes suggest an octahedral configuration. N.M.R. exami-

nation[2] of methyl mandelate indicates that carboxyl resonance occurs at a higher field than that of their mirror images[3] as regards their stereo-chemical structure[4].

EXPERIMENTAL

The experiments were performed at T.I.F.R., Bombay. The experimental second moment was calculated from the derivative traces by means of trapezium rule, $S = \Sigma h^3 f(h)/3\Sigma hf(h)$. The accuracy in the measurement was about ± 1 G^2 as measured from standard results. The variation of second moment with temperature is shown in Fig. 2.
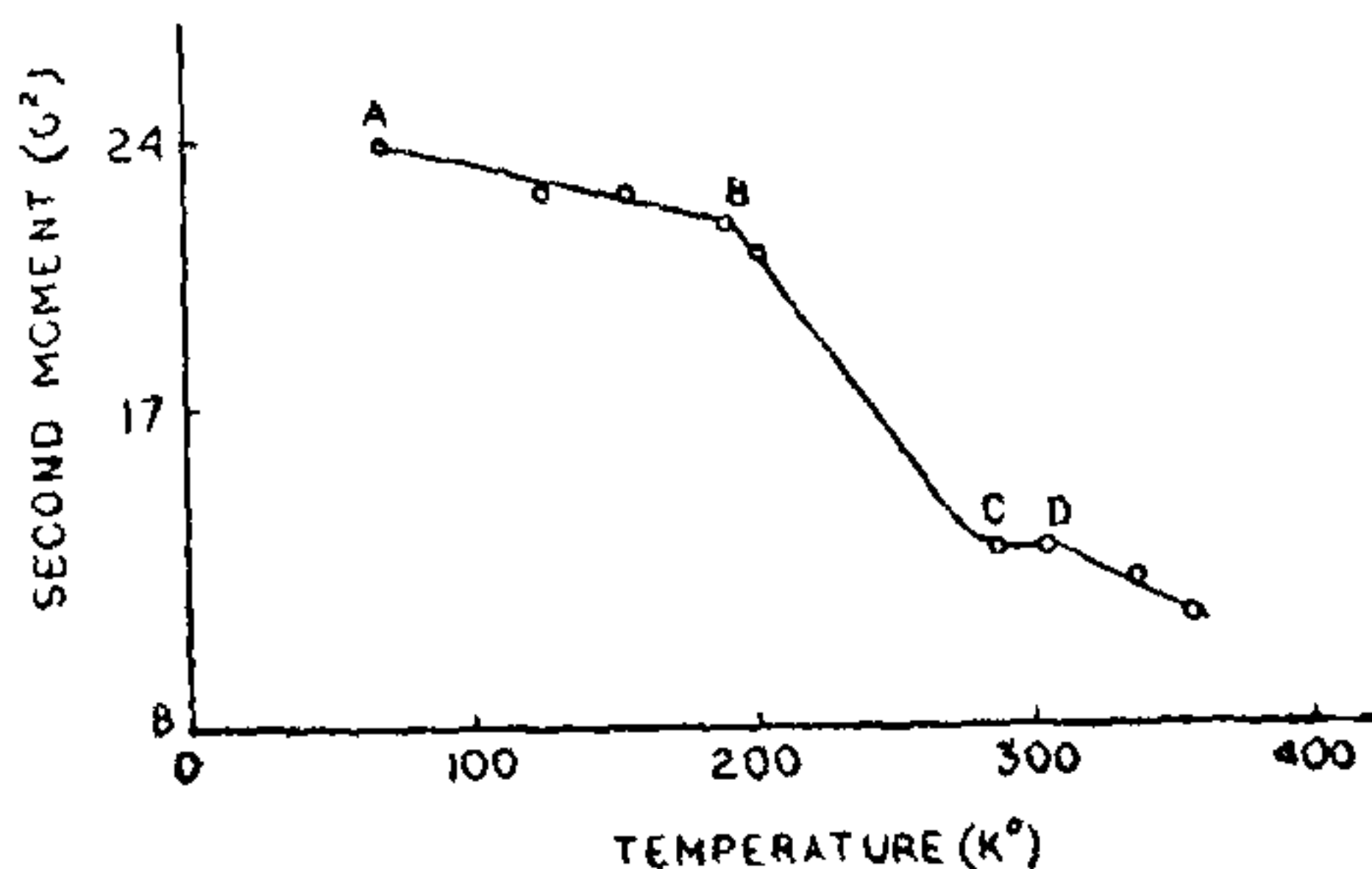

FIG. 2. Variation of second moment with temperature.

CALCULATIONS

Rigid Lattice Second Moment

The rigid lattice second moment (S) consists of two parts S_i and S_a. The intramolecular contribution S_i was calculated using Van Vleck's formula[5]. The value of Σr_{jk}^{-6} in the formula was calculated with the help of the model and Table I. S_i, thus, came out to be $20 \cdot 59$ G^2.
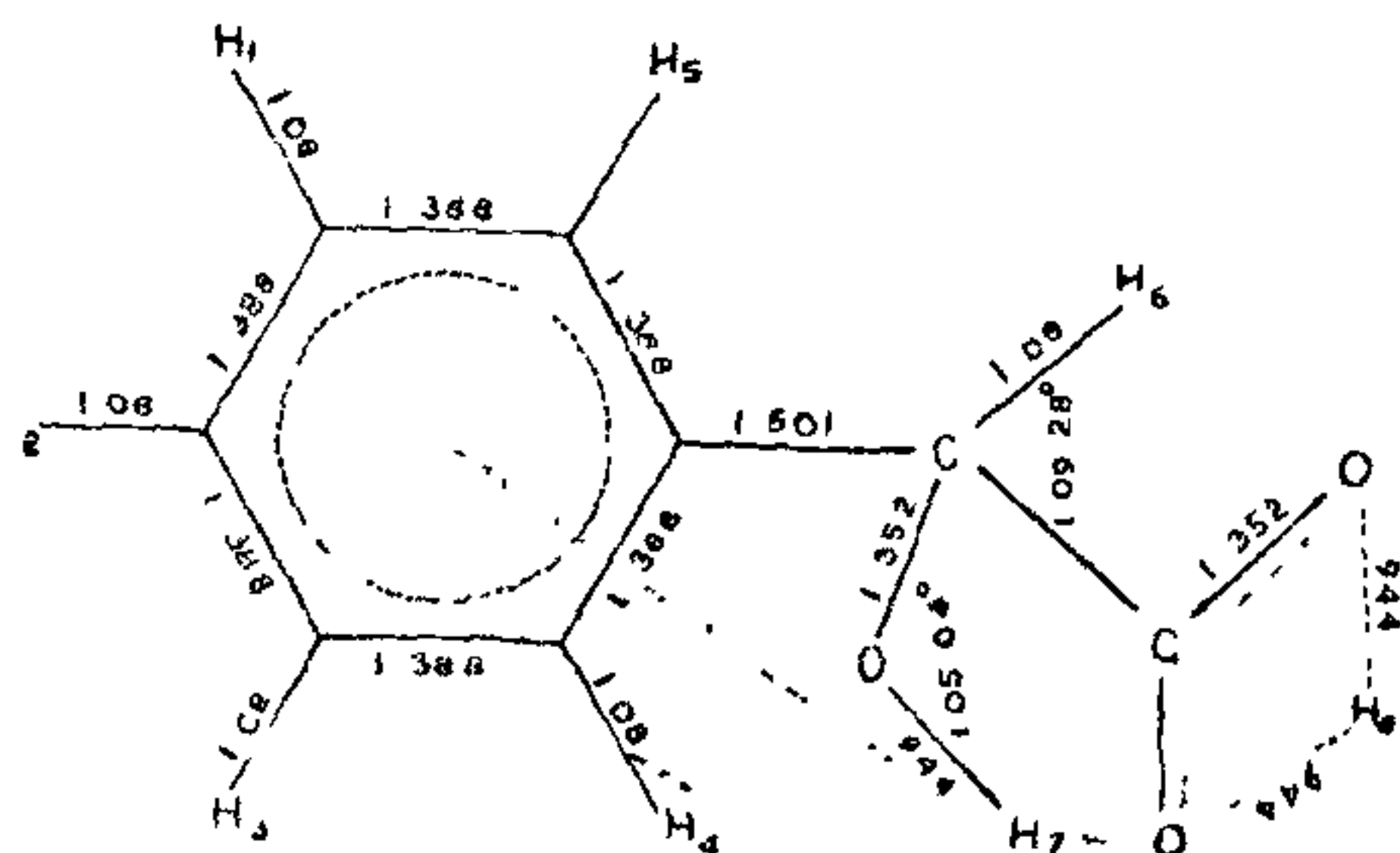

FIG. 1. Molecular model of mandelic acid with intramolecular *Cis* and *Trans* hydroxy bonding.

TABLE I

The final position co-ordinates of the protons in mandelic acid : A 2-D Analysis (Z = 0)

Protons	X	Y
H_1	−0·7391	2·1224
H_2	−2·468	0
H_3	−0·7342	−2·1224
H_4	0·7341	−2·1224
H_5	0·7341	2·1224
H_6	3·5138	0·8847
H_7	2·8009	−1·5953
H_8	5·333	−0·7482

The inter-part S_2 was found 4·73 G^2 approx. (Andrew and Eades[6]) which differs reasonably from L-glutamic acid for which authors found a S_2 value of 6·0 G^2.

The total rigid lattice second moment is, thus,

$$S = S_1 + S_2 = 20·49 + 4·73 = 25·22 \ G^2.$$

REORIENTATIONAL SECOND MOMENT WHEN OH AND COOH GROUPS REORIENT

The reduction in S_1 brought about by group rotation can be calculated from the theory of Gutowsky and Pake[7]. The reduction in S_1 due to the reorientation of OH group about C–O axis was calculated to be 7·23 G^2 and that due to the rotation of COOH group about C–C bond, the reduction was 8·11 G^2. The reduced second moment, for the assumption of free and simultaneous rotation of both groups, was in the range 7·98–8·70 G^2 using Smith's reduction factor[8]. For the case of hydroxy group stationary and carboxyl group rotating, the reduced second moment was found in the range 14·04–14·75 G^2 and for a *vice versa* case, *i.e.*, carboxyl group stationary and hydroxy rotating, it was in the range 14·92–15·63 G^2.

DISCUSSION

A reasonable agreement in the theoretical rigid lattice second moment (25·22 G^2) and the experimental second moment at 77 K (23·68 G^2) is seen to exist. This justifies our assumed model and shows that the hydrogen position co-ordinates are consistent and all sorts of molecular motions are virtually frozen at 77 K. The second moment gradually falls from the rigid lattice value upto 215 K. This may perhaps be due to torsional oscillations of the hydroxy and carbo-

xylic protons. These oscillations seem reasonable because at the asymmetric carbon there are associated four groups which distort the regular tetrahedron and render optical activity to the molecule. The alcoholic OH group is capable (Fig. 1) of involving itself in chelation forming potential formal bond with both COOH and phenyl groups. Similarly the proton of COOH group may associate with either of its oxygen.

After 215 K, abrupt fall in the second moment suggests the onset of intramolecular motion. The possibility of molecular rotation as a whole may safely be ruled out considering the large size, nature of substituent, symmetry and intramolecular linking of the molecule. To account for the observed reduction, the calculations were made for the reduced second moments. For the hypothesis of free and simultaneous rotation of OH and COOH groups (as stated earlier) reduced second moment was in the range 7·98–8·70 G^2 which is too low even lower than the minimum observed second moment (12·78 G^2 at 285 K) and as such rules out the possibility of free and simultaneous rotation of the groups. For the case of OH stationary and COOH rotating and *vice versa* cases, second moments were found in the ranges 14·04–14·75 G^2 and 14·92–15·63 G^2 respectively. Both values tally satisfactorily with the observed second moment. We thus regard that both groups reorient but their rotation is hindered instead of free, the hindrance being offered by intra and inter-group bonding. Mori *et al.*[9] have shown that the title compound exists in an internally bonded conformation and Schmid[10] has observed the existence of intramolecular H-bond formation. The hindered reorientation of OH and COOH groups is supported by the studies of Lehman *et al*[11] and Lawrence[12] has also suggested the presence of several rotational isomers.

The activation energy was found from B.P P* Theory[13] using

$$(\Delta H)^2 = \beta^2 + (2/\pi) \ C^2 \tan^{-1}\left[\frac{a \ \gamma \ \Delta H}{2\pi \ v_0}\right]$$

where symbols have their usual meaning. From the line width transition data, the activation energy was obtained to be 6·03 K.cal/mole. Waugh and Fedin[14] method (E = 37 T cal/mole) yielded a value 7·81 K cal./mole.

The second moment remains practically constant in the range 285–325 K. After 325 K, it further decreases which may be attributed to slow rotational motion of the phenyl ring, although torsional motion may also be a mode but studies[15] support a greater possibility of the former case. Phenyl ring inversion in phenyl substituted systems[16] has been studied and Mishra *et al.*[17] have also observed such a slow rotational motion of ring in benzil.

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STUDIES ON KAWA-PYRONES : SYNTHESIS OF 5,6-DEHYDROKAWAIN

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ABSTRACT

A convenient synthesis of 5,6-dehydrokawain(I) is reported. The ^{13}C-NMR study of the key intermediate(IV) was also carried out. The preparation of 7,8-dihydroyangonin and its spectroscopical properties are also described.

DURING the course of our studies on the ^{13}C-NMR of kawa-pyrones[1] we needed the compounds 5,6-dehydrokawain (I), 7,8-dihydro-5,6-dehydrokawain (II) and 7,8-dihydroyangonin (III). A convenient synthesis of 5,6-dehydrokawain (I) was achieved by adopting the process Bu'Lock *et al.*[2] used for yangonin(V). The ^{13}C-NMR spectrum of the key synthetic intermediate 3-acetyl-4-hydroxy-6-methyl-2-pyrone (enol form of IV, Scheme I) was also investigated. Compounds(II) and (III) were obtained by the catalytic hydrogenation of (I) and yangonin(V) respectively and characterised by their spectroscopic properties.

5,6-dehydrokawain(I) was synthesised from ethylacetoacetate according to Scheme I. The yields in the final condensation step utilising magnesium methoxide, the base that Bu'Lock used, are fairly low (19%). In an attempt to improve the yield the condensation was carried out in benzene in the presence of sodium hydride but with no significant improvement. (I) was characterised from its spectral properties which are similar to those reported earlier[3] as a constituent of *Aniba firmula*.
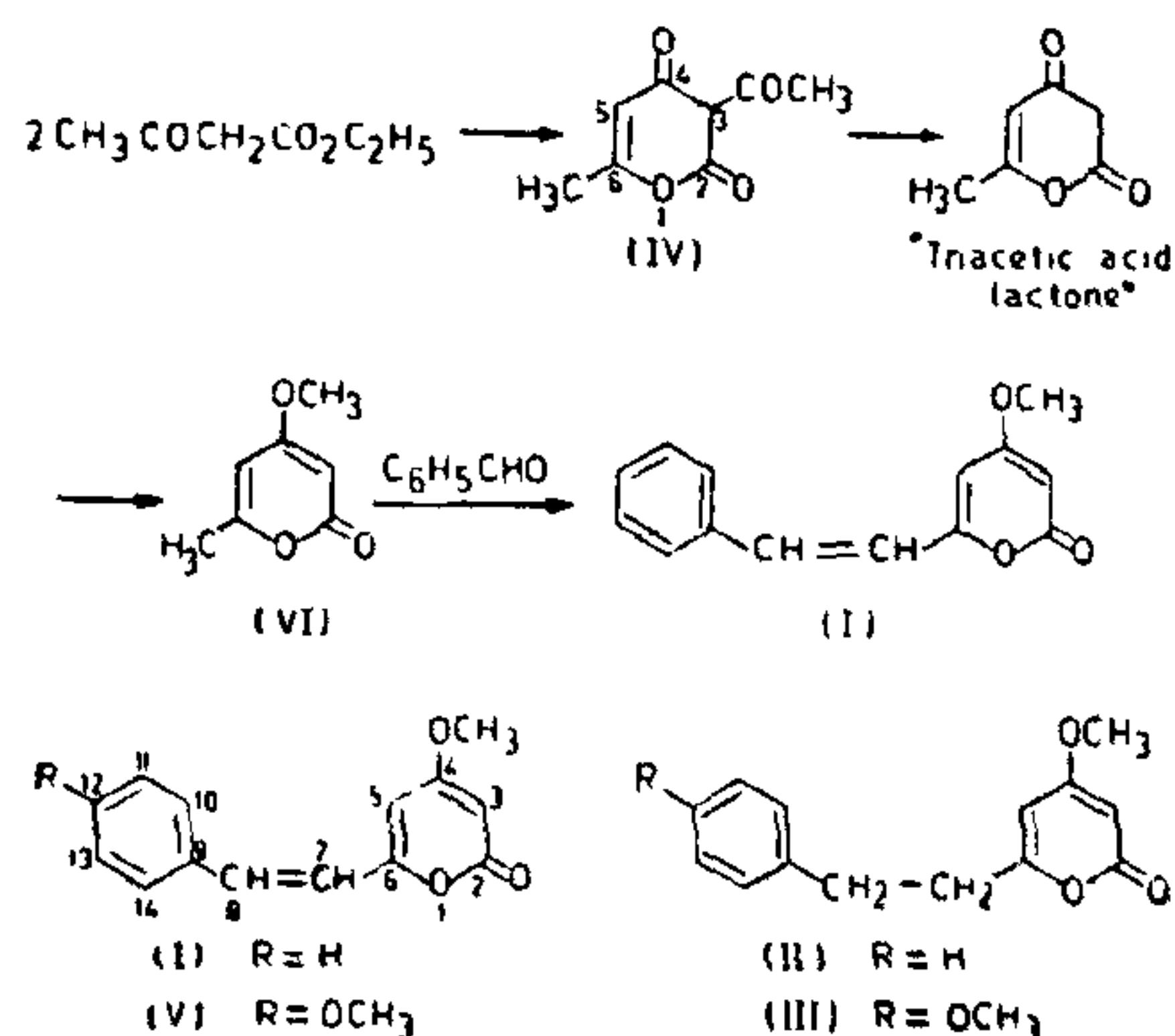
SCHEME I. Synthesis of 5,6-dehydrokawain

Catalytic hydrogenation of (I) gave 7,8-dihydro-5,6 dehydrokawain(II). The IR and ^{1}H-NMR spectra of the dihydro derivative(II) were similar to those described earlier[3]. Similarly, 7,8-dihydroyangonin(III) which was obtained by the catalytic hydrogenation