

CARBOXYLIC GROUP REORIENTATION AND HYDROGEN BONDS IN GALLIC ACID

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ABSTRACT

Broad line PMR spectra of solid gallic acid (3, 4, 5 trihydroxy benzoic acid) were recorded in the temperature range 77–526 K at 7.5 MHz. The crystal lattice is found to be effectively rigid up to 340 K. The analysis of the second moment data suggested the onset of reorientation of carboxyl group at 348 K. The activation energy for the motion is found to be 10.8 Kcal/mole. In the temperature range 410–526 K, p-OH group is found to exhibit remarkable motion. No change in crystalline structure was observed at or above the transition temperature.

THE present PMR study was undertaken to investigate the reorientational status of the COOH group and the kinetics of the three OH groups at adjacent sites of the ring in the gallic acid, a compound of high medicinal and Industrial importance.

CRYSTALLOGRAPHIC DETAILS

Harry¹ reported the X-ray diffraction patterns of gallic acid which reveals the strong hydrogen bonding in the molecule. The proton positions in the molecule are tabulated in Table I. Fig. 1 shows the structure and bond lengths. The structure of the carboxyl group and the three hydroxy groups facilitates the intermolecular H-bonding and formal protonic oscillations. The free radical of ethyl derivative of the sample exists in close association with the protein structure² in biological tissues and reduces their concentrations in cancer cells³. There are interactions between hydroxyl groups⁴ and the hindrances due to the vicinal position of the H-bonding groups are observed⁵⁻⁶. The tanning property results⁷ from the ability to form strong H-bonds with the peptide linkage which is promoted by quinonoid structure resonance in the benzhydroxy with a para OH.

TABLE I

Positional co-ordinates of the protons in the gallic acid, a 2D analysis

Sl. No.	Protons	Y	Z
1.	H ₁	2.1217	1.2650
2.	H ₂	2.1266	-2.2271
3.	H ₃	-0.8177	-2.0243
4.	H ₄	-3.1095	-0.7012
5.	H ₅	-2.1909	1.2250
6.	H ₆	1.8625	2.9212

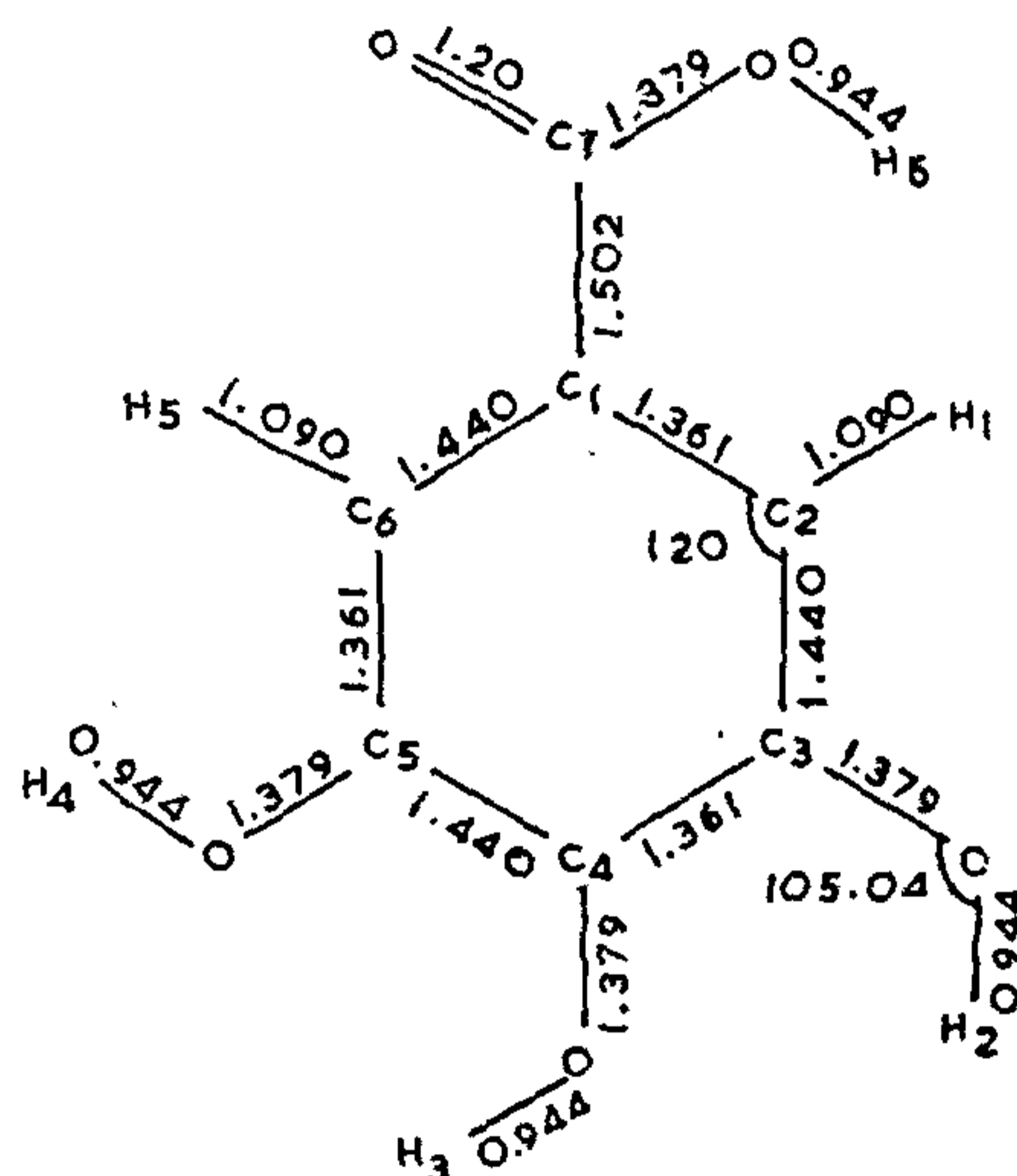


FIG. 1. Molecular Model of gallic acid; bond lengths (Å) and bond angles (°).

CALCULATIONS

Rigid lattice proton second moment

Modified Van Vleck's⁸ relation was used to compute the intramolecular $S_2^{(1)}$ contribution to proton second moment (S_2). This value was found to be 7.37 G². $S_2^{(2)}$, the intermolecular contribution, has been calculated using the method of Andrew and Eades⁹, which gave a value 6.60 G². This seems reasonable in the light of studies of Agarwal *et al.*¹⁰. Thus, the rigid lattice proton second moment S_2 is $S_2^{(1)} + S_2^{(2)}$, i.e., 13.97 G².

Rotational second moment for the reorientation of COOH group

The formula of Slichter¹¹ provides for the estimation of rotational second moment. Reduction in

total rigid lattice proton second moment for the intramolecular motion of substituent group was obtained using equation

$$\langle \Delta W^2 \rangle_{\text{rot}} = \langle \Delta W^2 \rangle_{\text{R.L.}} \left[\frac{3 \cos^2 \gamma_{jk-1}}{2} \right]^2$$

where γ_{jk} is the angle between the radius j and k rotation axis. $\langle \Delta W^2 \rangle_{\text{rot}}$ is the rotational second moment and $\langle \Delta W^2 \rangle_{\text{R.L.}}$ represents rigid lattice psm. For the various modes of interaction, the value of the term $\left[\frac{3 \cos^2 \gamma_{jk-1}}{2} \right]^2$ was calculated to be 0.53. The rotational (reduced) second moment, thus, comes out to be 7.41 G² and the theoretical reduction for group reorientation should then be 13.97 - 7.41 = 6.56 G².

Activation Energy

Modified B.P.P. theory¹²⁻¹⁴ that relates the line width with reorientation frequency can be used for estimation of activation energy. The equation used is

$$(\Delta H)^2 = \beta^2 + (2/\pi) C^2 \tan^{-1} \left(\frac{a\gamma \Delta H}{2\pi\nu_0} \right)$$

The Arrhenius equation used had the form $\nu_0 = \nu_0 \exp(-E_a/RT)$ and the activation energy was thus obtained to be 10.8 Kcal/mole.

EXPERIMENT AND RESULT

Broad line FMR spectra were recorded using Varian's variable frequency spectrometer having a 12" magnet system at TIFR, Bombay, at fixed resonant frequency 7.5 MHz. Modulation amplitude was kept small. The accuracy in the measurements is about ± 1 G². Proton second moment was obtained from the derivative traces using the trapezium rule mentioned elsewhere¹⁵. The variation of the second moment with temperature is shown in Fig. 2.

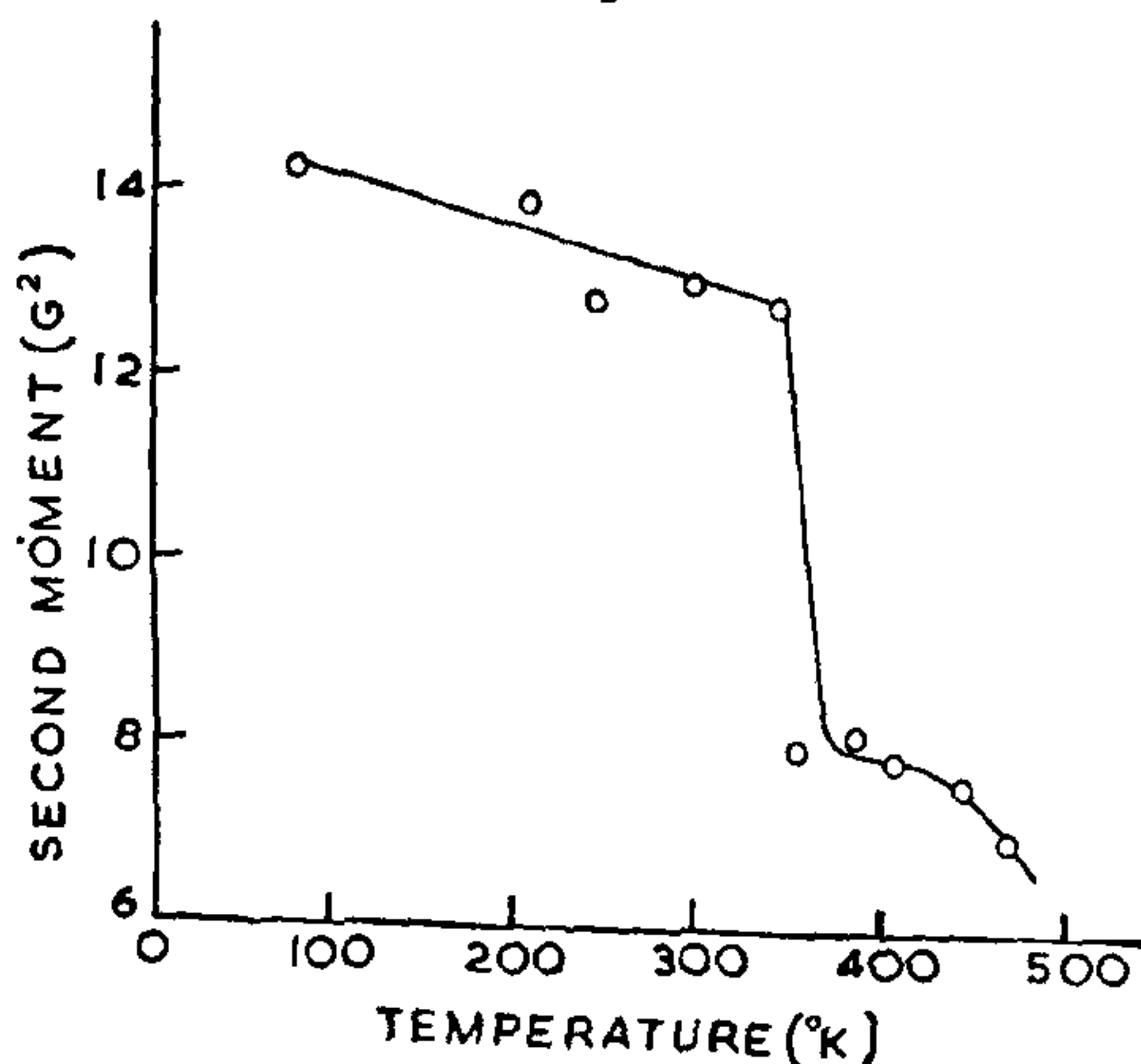


FIG. 2. Variation of second moment with temperature.

DISCUSSION

The theoretical rigid lattice psm (13.97 G²) agrees satisfactorily with the experimental second moment at 77 K (14.30 \pm 1 G²). This supports the assumed model and suggests that the lattice is rigid and non-rotating. Second moment gradually falls upto 340 K. This indicates some sort of oscillation before actual group rotation sets in. This is attributed to the intramolecular motion of the hydroxyl group involved in prototropy. Several workers have indicated the possibility of such motions¹⁶⁻¹⁹. Jaroslav²⁰ has shown that the position of functional group on the aromatic nucleus does not influence the final mobility. The COOH group is unaffected by steric and structural influence of the hydroxyl groups and a bond moment type of desmotropic resonance goes on with formation of potential formal bonds involving para OH group which, as a result, highly restricts the group mobility. The second moment abruptly drops to 8.02 G² from rigid lattice value in the range 340-352 K. This abrupt fall suggests the onset of reorientational motion^{21,18}. The possibility of molecular reorientation as a whole about the crystallographic symmetry axis can be ruled out on account of size and linear packing (parallel layers) of the molecules. Calculations for the reduction in $S_2^{(1)}$ due to the molecular reorientation as a whole may be calculated from the theory of Gutowsky and Pake¹³ and Andrew and Eades²². They have shown that the molecular rotation about a symmetry axis reduces $S_2^{(1)}$ by a factor 0.24. The value of reduced intra and inter-contributions from these calculations come out to be 2.51 and 1.58 G² respectively and the presence of molecular reorientation must reduce the rigid lattice psm to 2.51 + 1.58 = 4.09 G². This does not show an agreement with the observed second moment of 8.02 G². Thus, the possibility of molecular rotation can be safely ruled out. The other probability is that of reorientation of COOH group about C-C bond. The effect of COOH group rotation on second moment was calculated using the expression of Slichter¹¹ (discussed earlier in this note). The theoretical rotational second moment was obtained there to be 7.41 G², which is quite consistent with the experimentally observed second moment of 8.02 G² and supports the hypothesis of COOH group reorientation.

The studies of Ramaiah²³ in the range 303-353 K and the UV spectroscopy also suggests for the decrease in Pka values with the rising temperatures in the above range. The rotational probabilities are also pointed out by Sedlack²⁴ and Adams *et al.*²⁵. The psm further falls in the range (400-500 K). This may be due to restricted reorientation of OH groups. The activation energy available in this range is 12.0 Kcal/mol approximately (Waugh and Fedin²⁶). The steric

effects due to vicinal position of the H-bonding groups are demonstrated by Roberts *et al.*²⁷. Since the groups in the gallic acid are strongly internally H-bonded, so free reorientation appears inadequate.

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FLORAL BIOLOGY AND STIGMA-POLLEN MATURATION SCHEDULE IN ISABGUL *PLANTAGO OVATA* F.

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ABSTRACT

Stigma-pollen maturation schedule and their interrelationship in diploid and tetraploid isabgul (*Plantago ovata* F.) revealed that anthesis in maximum number of florets occurred during early morning hours and stigma maturity was distributed to both morning and evening hours. Effective artificial crossing can be achieved by pollinating the matured stigmata daily till anthesis in the lowest floret of that spike takes place when the immature florets are clipped off. Protogyny was confirmed. In diploid and tetraploid, 14 and 5 florets, respectively, had matured stigmata before anthesis started in the spike. Minimum time-gap between stigma receptivity and anthesis was 14 hours. Stigma receptivity and hair development on the stigma and the style were simultaneous.

PROTOGYNY prevails in almost all the species of Plantaginaceae¹. In *Plantago ovata* protogyny can be confirmed by the protruding stigmata, through the tip of the buds. The detailed morphology of spike and floret has been studied by Osol *et al.*². The results of an experiment conducted to study stigma-pollen

maturation schedule, in diploid and tetraploid isabgul, are presented here.

Time of anthesis and stigma receptivity were studied using ten spikes from ten plants each of diploid variety Gujarat Isabgul-I and tetraploid strain FC-411181-37. Every floret with receptive stigma (*i.e.*, when style