

The authors are grateful to Professor P. C. Vaidya for many useful suggestions.

January 31, 1981.

1. Krishna Rao, J., *Ph.D. Thesis*, Gujarat University, 1966.
2. —, *Progress of Mathematics*, 1969, 3, 167.
3. Bondarenko, N. P. and Kohashkih, P. K., *Soviet Physics, Dcklady*, 1972, 17, 48.

AB-INITIO STUDIES OF ANOMERIC EFFECT IN THIOSUGARS

SARASWATHI VISHVESHWARA AND V. S. R. RAO

Molecular Biophysics Unit, Indian Institute of Science Bangalore 560 012, India

It is well known that anomeric effect¹ plays an important role in carbohydrate chemistry. This effect influences the conformational equilibria in solution and the preferred conformation in solid state. This phenomenon has been well characterized for oxygen systems both theoretically and experimentally. However, recently it has been reported that the replacement of O-5 and O-1 oxygens by sulfur in pyranose sugars affect the conformational equilibria in solution² and the observed conformations in the solid state³. This has been attributed to the reduced anomeric effect in sulfur systems²⁻⁴. In this note we report the *ab-initio* quantum chemical studies on $X-C-X$ system when $X = O$ or S , and discuss the anomeric effect in sulfur-containing systems.

The Hartree-Fock theory⁵ at STO-3G level⁶ is used in this study. The calculations were carried out using GAUSSIAN 74 programme, which was adopted to DEC-10 computer. The studies are done using standard bond lengths and angles⁷ for methanediol and the geometry given in reference 8 is used for methanedithiol. The conformational energies were computed as functions of two dihedral angles θ and ϕ (Fig. 1). The calculated relative energies plotted as a function of the dihedral angle θ , for $\phi = 180^\circ$ or -60° are shown in Fig. 2 and in Table I. The noteworthy features between the methanediol and the methanedithiol systems are (1) the energy difference, ΔE_1 between $(-60^\circ, -60^\circ)$ and $(180^\circ, -60^\circ)$ conformations is very much reduced in case of methanedithiol, (2) the energy difference, ΔE_2 , between $(180^\circ, -60^\circ)$ and $(180^\circ, 180^\circ)$ conformations is also reduced considerably in the $S-C-S$ system and finally (3) the $(180^\circ, 180^\circ)$ conformation which has the maximum potential energy in methanediol becomes one of the local minima in methanedithiol. The same features are

reproduced at 4-31G level and after geometry optimization at STO-3G level¹¹.

The above results bring out a few interesting points. The second and third features mentioned in the previous paragraph explain the observed conformation corresponding to (ap, ap) in 1,5, dithio- α -D-ribo-pyranoside³ for the fragment $C-S-C-S-C$, a confor-

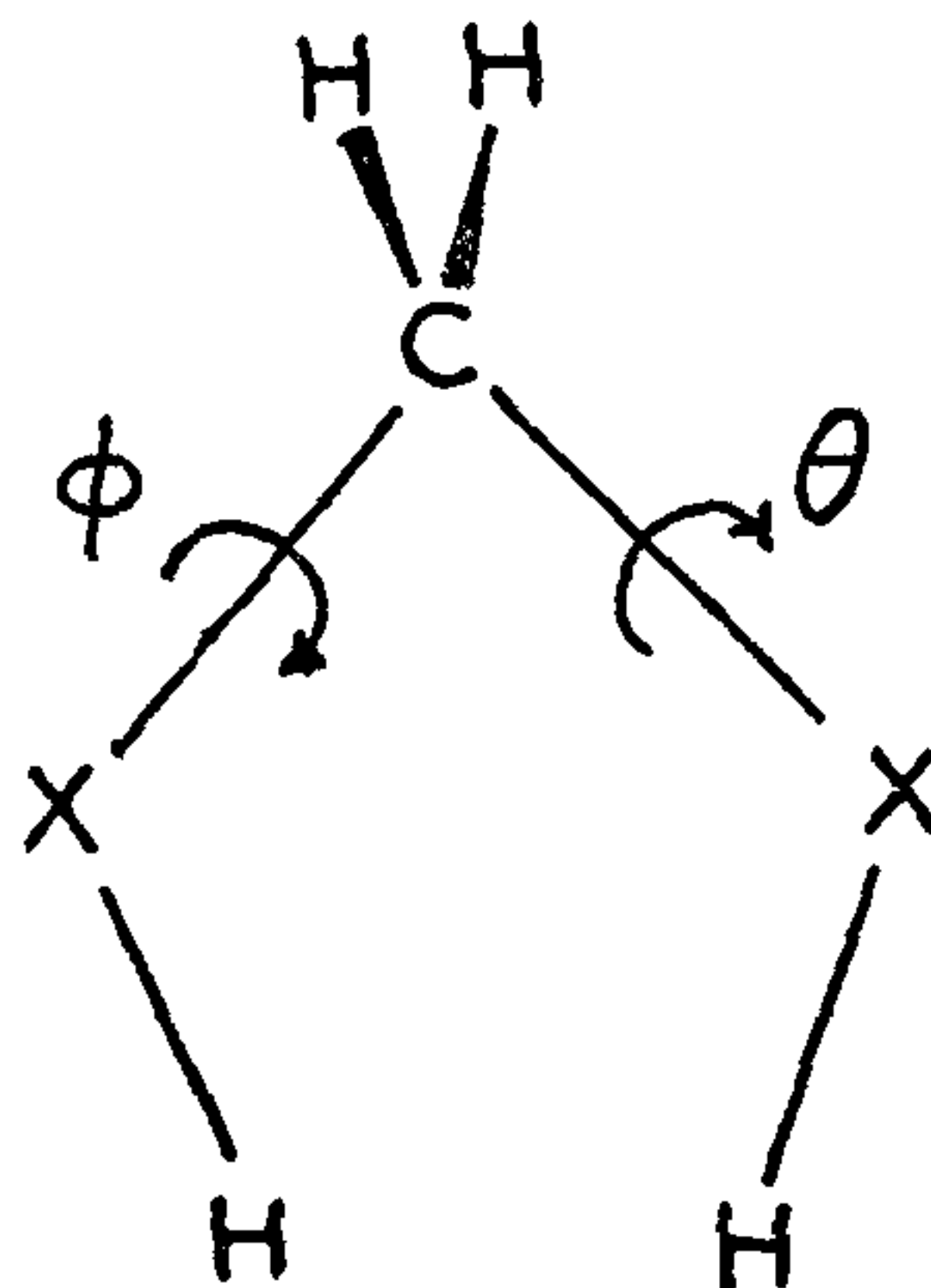


FIG. 1. Schematic representation of the dihedral angles ϕ and θ in $X-C-X$ systems. X is oxygen in methanediol and sulfur in methanedithiol ($\theta = \phi = 0^\circ$).

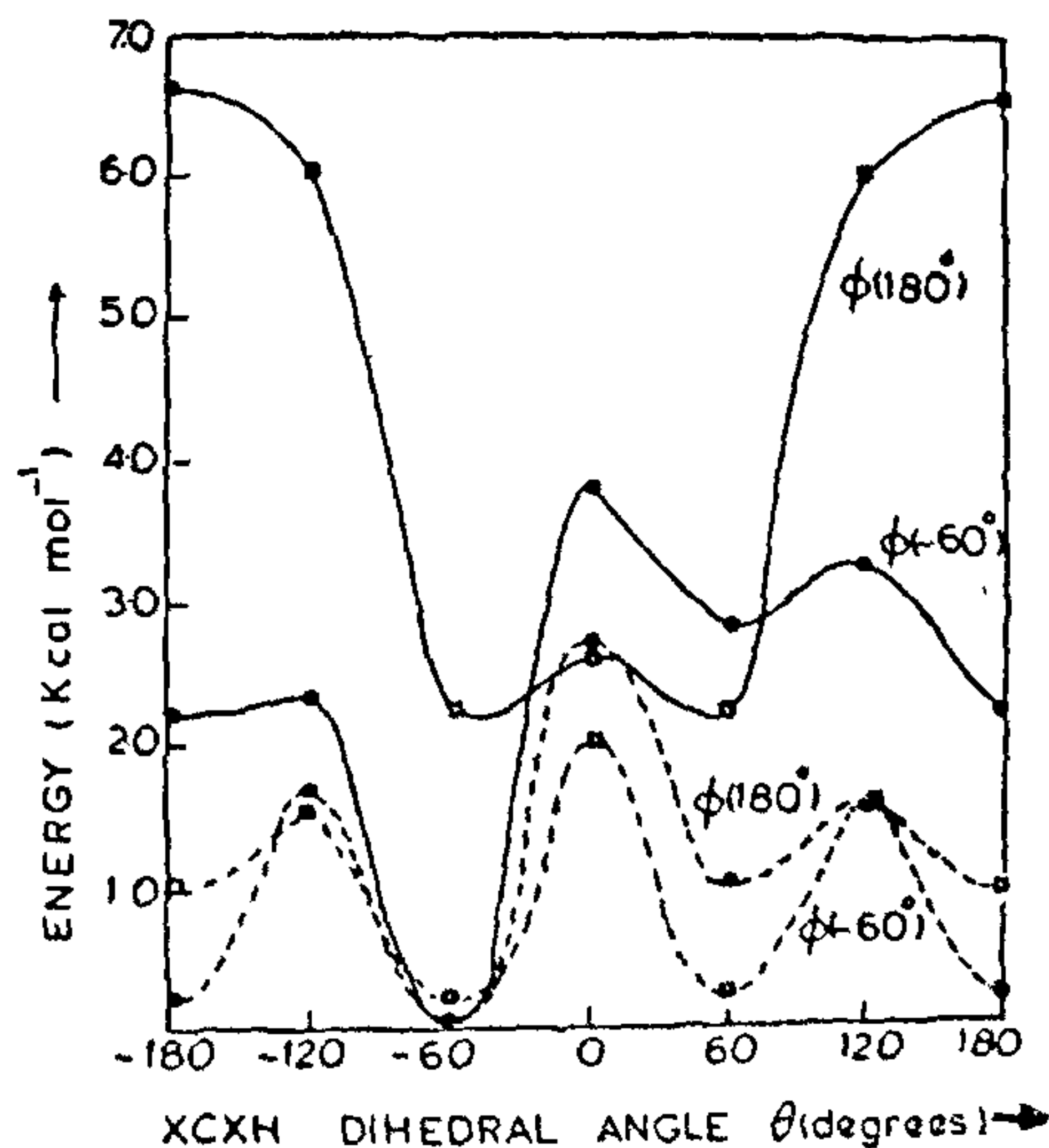


FIG. 2. Sections, $V(\theta)$ of the potential surface for internal rotation in $X-C-X$ systems for fixed values of ϕ . The solid lines refer to methanediol and the dotted lines are for methanedithiol.

TABLE I

STO-3G energy differences for various conformations in methanediol and methanedithiol (in Kcal mol⁻¹) using standard bond lengths and bond angles

Conformation	Methanediol ^a	Methanedithiol
(sc, sc)	0 ^b	0 ^c
(sc ap)	2.24	0.18
(ap, ap)	6.60	0.97

^a 4-31G and 6-31G* calculations on methanediol are reported in reference 9 and reference 10 respectively. STO-3G calculations on methanediol were done in this study, to carry out the comparison of methanediol and methanedithiol at the same level of approximation.

^b Total energy for this conformation is -187.38249 a.u.

^c Total energy is -834.223984 a.u.

mation which is never observed and is known to be least favoured due to exoanomeric effect in the oxygen systems.

The results can also be applied to the preferences of ring conformations. Though the ring conformation depends on the environment^{12,13} and the nature of hydrogen bonds involved¹⁴, some features are apparent from the present study. In β -D-ribose, the ⁴C₁ conformation has only one axially oriented OH group (at C3) and ¹C₄ conformation has three axially oriented hydroxyl groups (two of the hydroxyl groups are involved in 1-3 diaxial interactions). Hence non-bonded interaction energies favour ⁴C₁ conformation for β -D-pyranoside¹⁵. However, because of predominance of anomeric effect (ΔE_1), ¹C₄ conformation becomes more favoured for β -D-ribose. This is in agreement with the observed conformation of β -D-ribose both in solution² and solid state³. The present calculation suggests that the anomeric energy (ΔE_1) is reduced considerably in S-C-S system and hence the resulting ring conformation in β -1,5 dithio-D-ribose may be decided mainly by non-bonded interactions. This explains the existence of this molecule in ⁴C₁(D) conformation in solid state and its predominance in solution.

In the case of α -D-ribose, ¹C₄ conformation is slightly more favoured from non-bonded energy calculations. Since the anomeric effect (ΔE_1) is small for S-C-S system, theory predicts that α -1,5 (d) dithioribopyranoside exist in ⁴C₁ \rightleftharpoons ¹C₄ equilibrium in solution and either of them in solid state depending on the lattice energy. This is in agreement with the experimental studies in solution² and solid state³.

July 23, 1981,

1. (a) Lemieux, R. U., In P. De Mayo (Ed), *Molecular Rearrangements*, Part 2, Interscience, New York, 1964, p. 709; (b) Romers, C., Altona, C., Buys, H. R. and Havinga, E., *Topics Stereochem.*, 1969, 4, 39; (c) Edward, J. T., *Chem. Ind. (London)*, 1955, p. 1102.
2. Hughes, N. A., *Carbohydr. Res.*, 1973, 27, 97 and references therein.
3. Girling, R. L. Jeffrey, G. A., *Acta Crystallogr.*, Sect. B, 1974, 30, 327 and references therein.
4. Wolfe, S., Whangho, M. H. and Mitchell, D. J., *Carbohydr. Res.*, 1979, 69, 1.
5. Roothaan, C. C. J., *Rev. Mod. Phys.*, 1951, 23, 69.
6. Hehre, W. H., Stewart, R. F. and Pople, J. A., *J. Chem. Phys.*, 1969, 51, 2657.
7. Pople, J. A. and Gordon, M., *J. Am. Chem. Soc.*, 1967, 89, 4253.
8. Kojima, T., *J. Phys. Soc. Japan*, 1960, 15, 1284.
9. Jeffrey, G. A., Pople, J. A. and Radom, L., *Carbohydr. Res.*, 1972, 25, 117.
10. —, —, Binkley, J. S. and Vishveshwara, S., *J. Am. Chem. Soc.*, 1978, 100, 373.
11. To be published.
12. Stoddart, J. F., In *Stereochemistry of Carbohydrates*, Wiley Interscience, New York, N.Y., 1971, Chapter 3.
13. Angyal, S. J., *Aust. J. Chem.*, 1968, 21, 2737.
14. Girling, R. L. and Jeffrey, G. A., *Carbohydrate Res.*, 1971, 18, 339.
15. Vijayalakshmi, K. S. and Rao, V. S. R., *Ibid.*, 1972, 22, 413.

EMBRYOLOGY OF ACANTHOSPERMUM HISPIDUM DC

T. PULLAIAH

Department of Bio-Sciences
Sri Krishnadevaraya University
Anantapur 515 003, India

ALTHOUGH considerable literature is available on the embryology of the tribe Heliantheae of the family Compositae (see Pullaiah¹), information on the genus *Acanthospermum* is inadequate. Vaidya² studied a few aspects of embryology of *Acanthospermum hispidum*, but no detailed information is available regarding fertilisation, endosperm and embryo development. The present investigation on *Acanthospermum hispidum* DC was undertaken to bridge the gap in our present knowledge of the embryology of the genus.

Pollen grains in *Acanthospermum hispidum* at the time of shedding are three-celled with thick spinous