

$^2\Pi_{3/2}-^2\Sigma$  sublevel and have also been identified but their number is too small to form suitable combination differences.

Efforts are being made to obtain more intense spectra after which a detailed analysis would be published elsewhere.

Laser and Spectroscopy Laboratory,  
Department of Physics,  
Banaras Hindu University,  
Varanasi 221 005,  
June 24, 1981.

A. K. RAI.  
S. B. RAI.  
D. K. RAI.

1. Fabry et al., *Astrophys. J.*, 1905, **21**, 356.
2. Datta, S., *Proc. R. Soc. (London)*, 1921, **A99**, 436.
3. Hulthén, E., *Z. Phys.* 1928, **50**, 319.
4. Johnson, R. C., *Proc. R. Soc. (London)*, 1929, **A122**, 161.
5. Harvey, A., *Ibid.*, 1931, **A133**, 336.
6. Folwer, C. A., *Phys. Rev.*, 1941, **59**, 645.
7. Mohanty, B. S., and Upadhyaya, K. N., *Ind. J. Pure Appl. Phys.*, 1967, **5**, 523.
8. Nanda, D. P. and Mohanty, B. S., *Curr. Sci.*, 1970, **39**, 300.
9. Field, R. W., Harris, D. O. and Tanaka, T., *J. Mol. Spec.*, 1975, **57**, 107.
10. Nakagawa, J., Domaille, P. J., Steimle, T. C. and Harris, D. O., *J. Mol. Spec.*, 1978, **70**, 374.
11. Ram, R. S., Rai, S. B. and Upadhyaya, K. N., *Pramāṇa*, 1979, **13**, 149.
12. Singh, J. and Mohan, H., *Spect. Letters*, 1973, **6**, 139.

### SYNTHESIS OF 2H, 4H, 5H-SULPHONYL-PYRANO (3.2-c) (1)-BENZOPYRAN-4.5-DIONES

In the course of our attempts to synthesise new sulphones derived from different heterocyclic nuclei which might possess definite antituberculous activity we studied the reaction of 3-bromocoumarin<sup>1</sup> derivatives (1 mol) with  $\beta$ -mercaptopropionic acid (1.1 mol) in excess of pyridine (5 mol) and refluxing the mixture for 4-5 hr at 40° to yield the corresponding coumarinomercaptopropionic acids as crystalline solids from ethyl acetate in about 60% yield (Table I). The propionic acid (IA) showed a singlet for one proton corresponding to the C<sub>3</sub> proton at  $\delta$  5.7, which generally appears around  $\delta$  6.5 in coumarin and at  $\delta$  6.23 in 7-methoxycoumarin. The upfield shift of the C<sub>3</sub> proton indicates that the reaction has probably occurred at the '4' position instead of the expected '3' position according to the following mechanism.

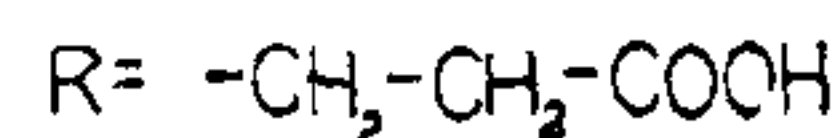
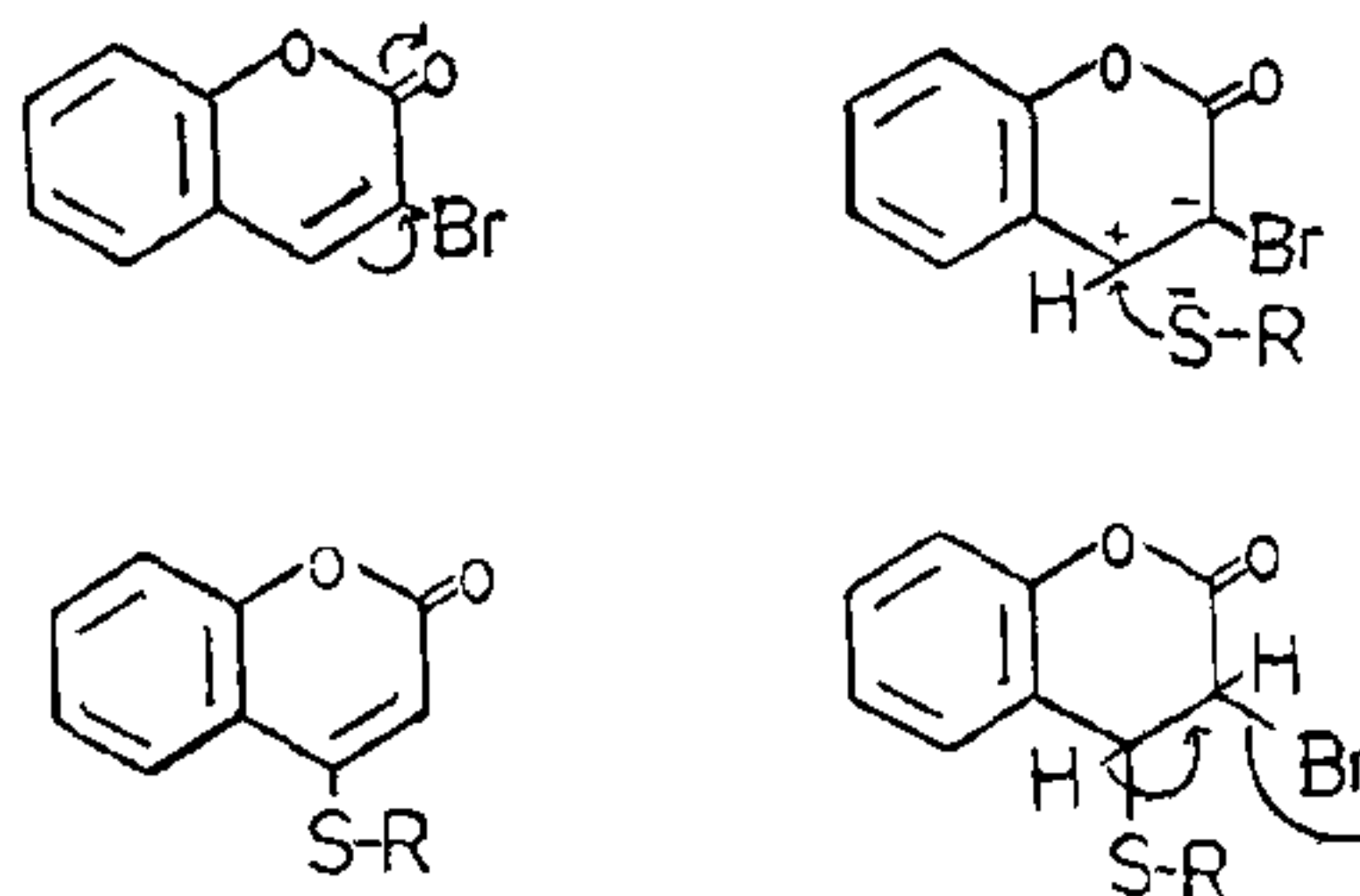
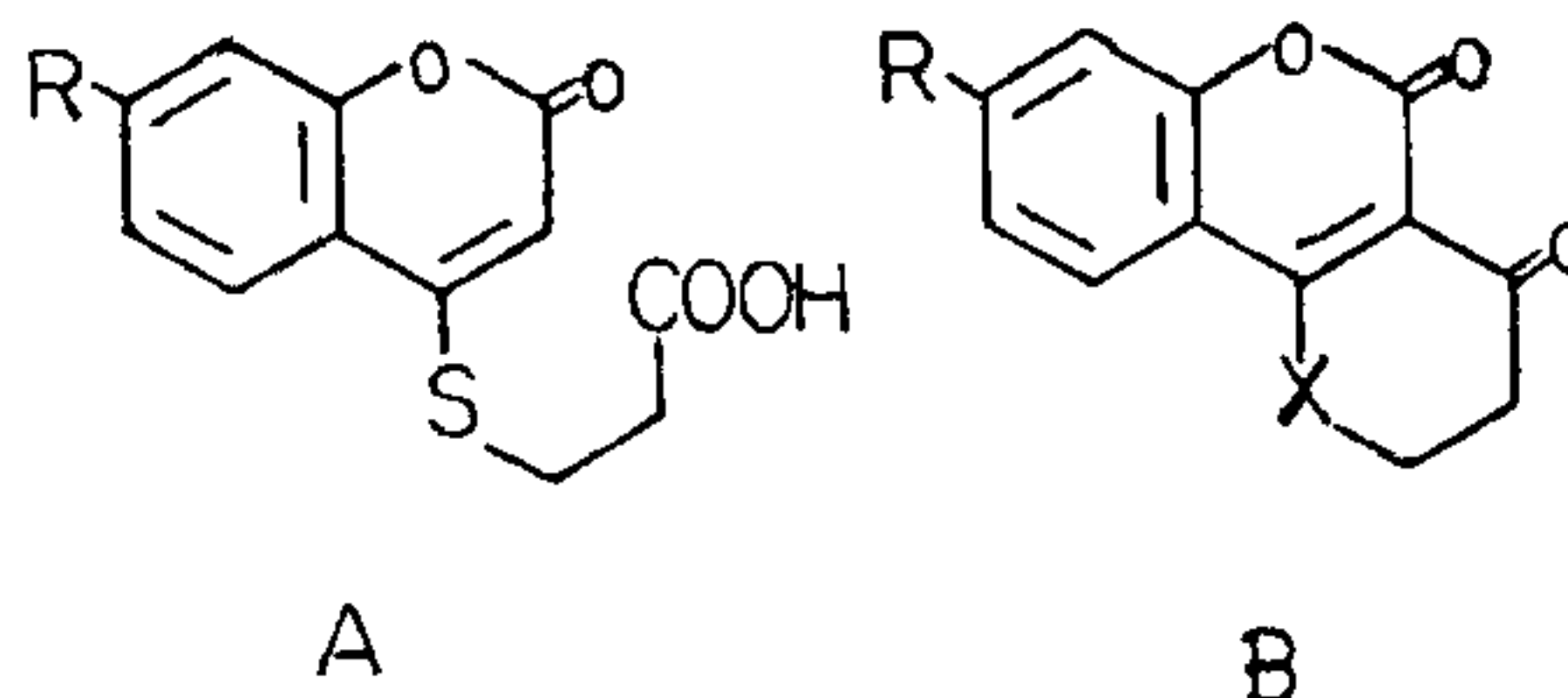


TABLE I



No.	R	M.P.	X=S			Anti-T.B. activity of sulphones ( $\mu$ g/cm <sup>3</sup> )
			M.P. (°C)	2,4-DNP M.P. (°C)	X=SO <sub>2</sub> M.P. (°C)	
I	H	187-88	243-44	279-80	175	20
II	OCH <sub>3</sub>	228	232-33	282-83	176-77	50
III	OC <sub>2</sub> H <sub>5</sub>	211-12	289-90	270-71	180	40

The structure of the acid IA was confirmed by synthesising it by reacting 4-chlorocoumarin<sup>2</sup> (1 mol) with  $\beta$ -mercaptopropionic acid (1 mol) in excess of pyridine containing a few drops of piperidine at 140° for 4–5 hr in about 40% yield.

The coumarinomercaptopropionic acids (0.1 mol) were cyclised by heating them with concentrated sulphuric acid (2 ml) on a boiling water-bath for 2 hr to afford the corresponding 2H, 4H, 5H-thiopyrano-3,2-*c* (1)-benzopyran 4,5-diones which crystallised from ethanol as yellowish plates in 50% yield. The diones also gave 2,4-DNP derivatives which crystallised from acetic acid.

The above diones were oxidised with hydrogen peroxide (30%) in acetic acid at room temperature to yield the appropriate sulphones in 45% yields. IR (KBr) of IB showed bands at 1720 (lactone CO), 1610 (C=O); 1325, 1130 ( $-\text{SO}_2$ )  $\text{cm}^{-1}$ .

The screening for the antitubercular activity of the above sulphones was carried out against highly virulent  $\text{H}_3\text{R}_0$  *Mycobacterium tuberculosis* var. *hominis*. As compared to that of streptomycin taken as 1 and INH as 0.04, the sulphones possessed the activity as shown in Table I.

All the compounds were found to be single substances (by t.l.c.) and gave the anticipated elemental analysis. All melting points were taken in open capillary and they are uncorrected.

Thanks are due to Haffkine Institute, Bombay, for the screening of the sulphones for their anti-TB activity and to Mrs. J. A. Patankar and D. S. More for microanalysis.

Department of Organic  
Chemistry,  
Institute of Science,  
Madame Cama Road,  
Bombay 400 032, June 14, 1980.

J. R. MERCHANT.  
N. M. KOSHTI.  
P. J. SHAH.

1. Marathe, M. G. and Ghia, B. J., *J. Sci. Ind. Res.*, 1962, 21B, 28.
2. David, P. Spalding, Harry, S. Mosher and Frank, C. Whitemore, *J. Am. Chem. Soc.*, 1950, 72, 5338.

### SPOILAGE OF MANGO BY *ASPERGILLUS FLAVUS*

DURING prolonged storage and ripening, mangoes become more susceptible to microbial infection<sup>1-3</sup>. Most of the severe post-harvest deteriorations of mango fruits are due to fungal rots, like soft rot<sup>4</sup>, anthracnose<sup>5</sup> and stem end rot<sup>6</sup>, caused by *Rhizopus arrhizus*, *Gleosporium mangiferae* and *Diplodia natalensis* respectively.

Black spot formation due to the infection of *Rhizoctonia bataticola* has been reported by Chhatpar *et al.*<sup>7</sup>. Development of such abnormalities results in the wastage and low marketing value of the fruits. Present communication deals with the study of biochemical changes associated with the spoilage of mango by *A. flavus*.

#### Methods and Materials

Fungal culture was isolated from the naturally infected mango and was identified as *Aspergillus flavus*.

Spore suspension of the mold ( $10^8$  spores) in normal saline was injected into healthy mangoes by sterilized syringe and the mangoes were incubated at 30° C, till the development of black spots.

The various stages of the mango during ripening were marked by the colour development and appearance (a) unripe-hard green peel, (b) Partly ripe-slightly soft, green to yellow peel, (c) ripe-soft, golden yellow peel.

A 30% extract was prepared in tris HCl buffer (0.05 M) pH 7.0 containing polyvinyl polypyrrolidone (1g/g tissue) from the healthy and infected part of the mango tissues. The extract was centrifuged at 10,000 g for 10 minutes and the supernatant was used for the biochemical analysis.

Total reducing sugar and sucrose was estimated by Nelson's method<sup>8</sup> after the hydrolysis with 1 N hydrochloric acid. Citric acid was estimated by pentabromoacetic acid method<sup>9</sup>. Determination of amylase and invertase activities were essentially the same as described by Mattoo and Modi<sup>10</sup>.

TABLE I  
Comparison of the degree of infection by *A. flavus* at three different stages of ripening mango

Stages of mango ripening	Incubation period (days)					
	1	2	3	4	5	6
Unripe	—	—	—	—	+	++
Partly ripe	—	—	—	+	++	+++
Ripe	—	—	+	++	+++	++++

— shows no infection; + shows mild infection; ++ shows good infection; +++ shows very good infection.

#### Results and Discussion

The degree of infection of the fungi was studied by artificially infecting the healthy fruits with a spore suspension. Three different stages of ripening were taken into consideration, viz., mature unripe, partly