

storage of prawns at 4 and -18°C agree with that of ice stored shrimps^{6,11,13,14}. Dominance and pre-dominance of *Vibrio* sp at a few instances at reduced temperature were similar to the observations made with ice-stored paraben-treated sardines (*Sardinella longiceps*) where *Vibrio* sp dominated among the late spoilers.⁷

Spoilage of fish and prawn commences immediately after rigormorties, progresses rapidly at higher temperatures and perishes within a short period before the harvested commodity goes to the fish processors. The dominant flora at the time of catch have ample chance to invade the flesh, progress rapidly and form a part of dominant flora or fully command spoilage. Reports on ice-stored and frozen prawn and fish, confirm *Pseudomonas* and *Achromobacter* as kings of spoilers. But the present study strongly suggests the possible association of *Vibrio* as spoilage flora of fresh tropical white prawns.

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SYNTHESIS AND PHYSIOLOGICAL ACTIVITY OF SOME NEW PYRANO-BENZOXAZOLES

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PYRANOBENZOXAZOLES have been reported to possess antibacterial activity^{1,2}. It was therefore considered interesting to synthesise some new pyranobenzoxazoles from hydroxyaminocoumarins and hydroxyaminochromones.

The starting materials were 5-amino-6-hydroxy-, 6-amino-7-hydroxy-4-methyl-, 8-amino-7-hydroxy-4-methyl- coumarins and 6-amino-7-hydroxy-8-bromo-2-methyl-, and 8-amino-7-hydroxy-2-methyl-chromones. These were prepared by hydrogenation of the known nitro compounds³⁻⁶ in the presence of palladium/charcoal catalyst.

Refluxing the amino hydroxy compounds with acetic anhydride for 1 hr and then decomposing over crushed ice, directly afforded the pyrano-2-methylbenzoxazole derivatives as crystalline solids in 80–85% yield.

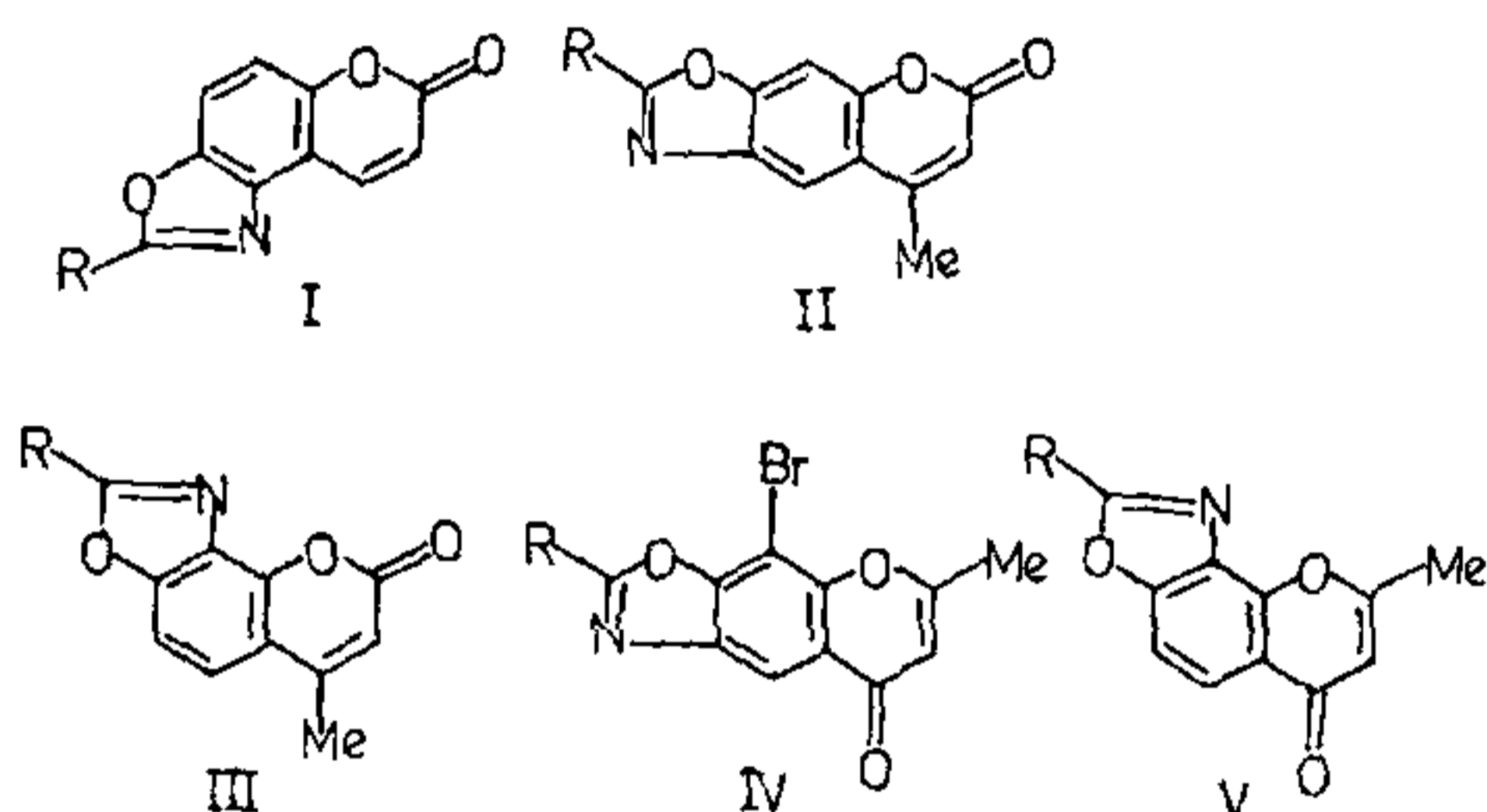
Similarly, when equimolecular quantities of the amino-hydroxy compounds and aromatic or heterocyclic acids were heated with PPA at $150-60^{\circ}$ for 1.5 hr and later at $200-205^{\circ}$ for a further period of 3 hr the corresponding 2-substituted oxazoles were isolated as crystalline solids in 60–70% yields.

The pyranobenzoxazoles are listed in table 1. A typical pyranobenzoxazole (IIIa) showed $\lambda_{\text{max}}^{\text{MeOH}}$ (log ϵ): 225 (4.57) and 275 (4.11) nm. Its IR (nujol) spectrum showed bands at 1710 ($> \text{C}=\text{O}$), 1570, 1350, 1050 (characteristic of oxazole ring system) cm^{-1} . Its NMR spectrum (TFA) showed δ 2.76 (3H, s, $-\text{CH}_3$); 6.8 (1H, s, $\text{C}_7\text{-H}$); 7.8–8.7 (7H, m, C_4H , C_5H and C_{2-6}H). The benzoxazole (V-d) showed $\lambda_{\text{max}}^{\text{MeOH}}$ (log ϵ): 224 (4.62) and 273 (4.13) nm. Its IR (nujol) spectrum showed bands at 1655 cm^{-1} ($> \text{C}=\text{O}$), 1570 cm^{-1} , 1350 cm^{-1} , 1050 (characteristic of oxazole ring system) cm^{-1} . Its NMR spectrum (CDCl_3) showed δ 2.5 (3H, s, $-\text{CH}_3$); 2.75 (3H, s, $-\text{CH}_3$); 6.15 (1H, s, C_2H); 7.1–8.03 (6H, m, ArH). All the above compounds were

Table 1 Structures and m.ps. of Pyranobenzoxazoles

Compd.	R	M.P. (°C)		Compd.	R	M.P. (°C)	
Ia	Phenyl	237	a*	IIIc	1-Naphthyl	235	a
Ib	<i>p</i> -Chlorophenyl	274-75	a	IIId	Methyl	163-64	b
Ic	<i>m</i> -Toluyyl	220-21	a	IVa	Phenyl	238-40	b
Id	Methyl	182	b	IVb	<i>p</i> -Chlorophenyl	> 300	b
IIa	Phenyl	230-31	a	IVc	1-Naphthyl	298-300	b
IIb	<i>p</i> -Toluyyl	267-68	a	IVd	Methyl	253-54	b
IIc	3-Pyridyl	269-70	a	Va	<i>o</i> -Chlorophenyl	226-27	b
IId	Methyl	205	a	Vb	<i>p</i> -Chlorophenyl	249-50	b
IIIa	Phenyl	235-36	a	Vc	Benzyl	198-200	b
IIIb	<i>o</i> -Chlorophenyl	225-26	a	Vd	<i>p</i> -Toluyyl	260	b

*Crystallised from: a = benzene, b = ethyl acetate.



tested for antibacterial activity using *Staphylococcus aureus*, *E. coli* and *Pseudomonas aerogenosa* as representative species employing the tube dilution method. However, none of the compounds exhibited any appreciable antibacterial activity.

Melting points are uncorrected. All the compounds gave satisfactory elemental analysis.

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ISOLATION AND ANTIALLERGIC ACTIVITY OF- γ -PYRONES FROM THE FLOWERS OF *CASSIA SPECTABILIS*

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CASSIA spectabilis is a tall, well-branched, shaded and ornamental plant with beautiful golden yellow flowers. From the leaves of this plant a few piperidine-3-ol alkaloids were isolated¹⁻⁵. From the aerial parts of the plant piperidine alkaloids, β -sitosterol, stigmaterol and an anthraquinone were isolated⁵. We report here the isolation of two γ -pyrones from the flowers of this plant; the anti-allergic activity of these γ -pyrones are also reported.

The ethanol extract of the freshly collected flowers yielded two γ -pyrones—compound-A and B. Compound A, mp 265° (dec), is analysed for C₇H₄O₆, M⁺; 184. The compound is acidic and dibasic in nature by volumetric titration against standard barium hydroxide solution. The IR spectrum recorded in KBr revealed ν_{\max} (C=O) 1670 cm⁻¹ (carboxylic acid carbonyl) and another at 1645 cm⁻¹ (γ -pyrone carbonyl)⁶. The UV absorption $\lambda_{\max}^{\text{MeOH}}$ 265 nm (log ϵ 4) is characteristic of γ -pyrones⁷. The NMR of compound-A recorded in D₂O revealed only one sharp signal at δ 7. In the mass spectrum of compound-A prominent ions due to M-CO, M-OH-CO, M-CO-OH-CO and retro Diels-Alder fragments m/e 114 (60%) and m/e 70 (10%) were observed. The mass spectral fragmentation pattern is similar to that of γ -pyrones⁸. Alkaline hydrogen peroxide oxidation of compound-A yielded oxalic acid. Compound-A on esterification with methanol in the presence of few drops of concentrated