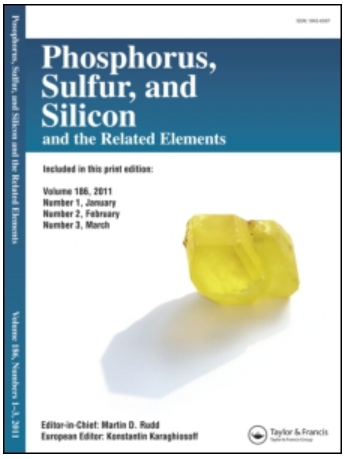

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STUDIES ON 2-MERCAPTO COUMARINOXAZOLE SYSTEMS: SYNTHESIS OF NOVEL TYPES OF 2-MERCAPTO-9-METHYL-7H-PYRANO-(3,2-e)BENZOXAZOLE-7-ONE DERIVATIVES—PART III

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STUDIES ON 2-MERCAPTO COUMARIN-OXAZOLE SYSTEMS: SYNTHESIS OF NOVEL TYPES OF 2-MERCAPTO-9-METHYL-7H-PYRANO-(3,2-e)BENZOXAZOLE-7-ONE DERIVATIVES—PART III

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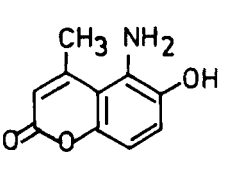
5-Amino-6-hydroxy-4-methylcoumarin (I) when treated with carbon disulphide in alkaline medium to furnish the novel and hitherto unknown 2-mercapto-9-methyl-7H-pyrano(3,2-e)benzoxazole-7-one (IIa). Treatment of IIa with alkyl halides and acid halides gives the corresponding thioethers (IIb–i) and thioesters (IIj–k) respectively. Oxidation of IIb, IIc, IId, IIf, IIh with hydrogenperoxide gives the corresponding sulfones (IIIa–e). These are characterised by elemental analysis, IR, PMR and mass spectral data.

In continuation of our earlier work on coumarin oxazole systems,[1,2] we now wish to report the synthesis of the hitherto unknown 2-mercapto-9-methyl-7H-pyrano-(3,2-e)benzoxazole-7-one derivatives with a view to evaluate their antibacterial and antifungal activities.

The starting compound, 5-amino-6-hydroxy-4-methyl-coumarin (I) is condensed with carbon disulphide in the presence of aqueous ethanolic potassium hydroxide to furnish 2-mercapto-9-methyl-6H-pyrano(3,2-e)benzoxazole-7-one (IIa). The structure of IIa is confirmed by elemental analysis and IR spectra.



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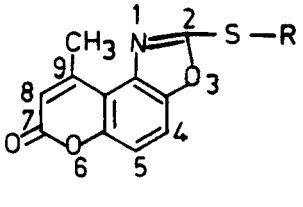
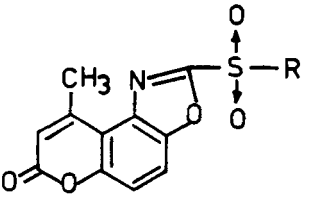


IIa : (R=H)

IIb–k : (R=alkyl/acyl)



IIIa–e : (R=alkyl)

The compound IIa exhibits IR bands at 1530–1520 cm^{-1} (N—C=S), 1075–1070 cm^{-1} (C=S).[3] The bands at 1655, 1580, 1365 and 1180 cm^{-1} are due to the vibrations arising from the heterocyclic oxazole system,[4] which are totally absent in the IR spectra of its precussor (I). The remaining compounds IIb–k reveal, the

TABLE I

Physical data of 2-mercapto-9-methyl-7H-pyrano(3,2-e)benzoxazole-7-one derivatives (II and III)

Compound[a]	R	m.p.[b] °C	Mol. formula	Found (Calc.)% N	S
IIa	—H	> 300	$C_{11}H_7NO_3S$	6.0 (6.01)	13.73 (13.75)
IIb	—CH_3	156	$C_{12}H_9NO_3S$	5.66 (5.69)	12.95 (12.92)
IIc	—CH_2—CH_3	203	$C_{13}H_{11}NO_3S$	5.36 (5.39)	11.63 (11.66)
IId	—$(CH_2)_2$—CH_3	145	$C_{14}H_{13}NO_3S$	5.09 (5.14)	11.63 (11.75)
IIe	—$(CH_2)_3$—CH_3	127	$C_{15}H_{15}NO_3S$	4.89 (4.90)	11.07 (11.14)
IIf	—CH_2—OH	215 (d)	$C_{12}H_9NO_4S$	5.32 (5.48)	12.16 (12.29)
IIg	—CH_2—CH=CH_2	158	$C_{14}H_{11}NO_3S$	5.12 (5.29)	11.72 (11.85)
IIh	—CH_2—C_6H_5	190	$C_{18}H_{13}NO_3S$	4.33 (4.36)	11.63 (11.17)
IIi	—CH_2—COOH	125	$C_{13}H_9NO_5S$	4.81 (4.87)	11.99 (12.05)
IIj	—C(=O)—CH_3	290	$C_{13}H_9NO_4S$	5.09 (5.16)	11.63 (11.77)
IIk	—C(=O)—C_6H_5	255 (d)	$C_{18}H_{11}NO_4S$	4.15 (4.19)	9.49 (9.56)
IIIa	—CH_3	> 300	$C_{12}H_9NO_5S$	5.01 (5.12)	11.46 (11.58)
IIIb	—CH_2—CH_3	> 300	$C_{13}H_{11}NO_5S$	4.77 (4.92)	10.92 (10.99)
IIIc	—$(CH_2)_2$—CH_3	> 300	$C_{14}H_{13}NO_5S$	4.56 (4.72)	10.42 (10.51)
IIId	—CH_2—OH	> 300	$C_{12}H_9NO_6S$	5.66 (5.80)	12.95 (12.98)
IIIe	—CH_2—C_6H_5	> 300	$C_{18}H_{13}NO_5S$	3.94 (3.98)	9.01 (9.12)

[a]Compounds were obtained in 60–70% yields, and satisfactory C and H analysis have been obtained for all the compounds.

[b]Compound IIa was crystallised from DMSO–Water. Compounds IIb–k were crystallised from ethanol–water and IIIa–e were crystallised from acetic acid.

absorption bands as expected, along with a band at 1730–1700 cm^{-1} characteristic of the lactonic carbonyl group.[5]

Treatment of IIa with alkyl halides and acid halides in the presence of ethanolic potassium hydroxide produces the corresponding thioethers IIb–i and thioesters IIj–k respectively (Table I).

The IR spectra of IIb–k indicate the absence of the C=S group. However strong absorption bands appear in each case, at 1730–1710 cm^{-1}, disclosing the lactonic carbonyl.[5] Bands appearing at 1635, 1610, 1380 and 1190 cm^{-1} are in agreement with heterocyclic oxazole ring systems.[4] In addition to those the compounds IIf and

IIi show absorption bands at 3500 and 3300 cm^{-1} due to the presence of —OH and —COOH groups respectively.

The mass spectrum of IIg contains peaks at m/z 273 (M^+) (80%), 258 (29.16%), 245 (14.58%), 232 (74.16%), 204 (79.16%) and 172 (100%). The base peak at m/z 172 is attributed to 8-methyl furo benzoxazolium ion.

The PMR spectrum of IIg in $CDCl_3$ (TMS internal reference) exhibits a singlet at δ 2.8 (3H, $—CH_3$) and a multiplet at δ 4.4–5 (5H, $—S—CH_2—CH=CH_2$). The aromatic protons appear in two regions, at δ 7.15–7.3 (1H) and δ 7.55 to 7.7 (1H).

Oxidation of the compounds IIb, IIc, IId, IIf and IIh with hydrogenperoxide converts them into the corresponding sulfones IIIa–e.

The structures IIIa–e are established on the basis of elemental analysis and spectral data. The IR spectra of these compounds contain an additional band at 1340–1320 cm^{-1} due to the sulfone group.[3]

The investigation upon the biological activity of these compounds is under progress. The results will be communicated later.

EXPERIMENTAL

Melting points were determined in open capillaries using sulphuric acid bath and are uncorrected. IR spectra (ν_{max} in cm^{-1}) were recorded in KBr disc on a Perkin-Elmer 283 instrument. 60 MHz PMR spectrum in $CDCl_3$ was recorded on a Varian spectrometer using TMS as internal standard (chemical shifts in δ ppm) and Mass spectrum on a JMS-D300 Mass spectrometer at 70 ev.

Preparation of 2-mercapto-9-methyl-7H-pyrano(3,2-e)benzoxazole-7-one (IIa)—General Procedure.[6] A mixture of 5-amino-6-hydroxy-4-methylcoumarin (0.1 mol), in carbon disulphide (10 ml), potassium hydroxide (0.02 mol), ethyl alcohol (40 ml) and water (10 ml) was refluxed for 48 hours and cooled. On acidification a solid precipitated. It was filtered and recrystallised from aqueous dimethyl sulfoxide.

Reaction of IIa with alkyl halides and acid halides. General procedure.[7] Compound IIa (0.005 mol) was dissolved in ethanol (20 ml) in presence of potassium hydroxide (0.005 mol) and the appropriate alkyl halide (0.005 mol) or acid halide (0.005 mol) was added, refluxed for 4 hours and after cooling poured into ice cold water. The compound precipitated was filtered and recrystallised from suitable solvent to give the corresponding thioethers IIb–i and thioesters IIj–k (Table I).

Oxidation of thioethers with hydrogen peroxide.[8] To a solution of thioether IIb, IIc, IId, IIf and IIh (0.002 mol) in acetic acid (20 ml) was added 5 ml of 30% (w/v) hydrogen peroxide and the reaction mixture warmed on a water bath for 1 hour, cooled and diluted with water. The separated sulfone (IIIa–e) was washed several times with cold water and recrystallised from ethanol.

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