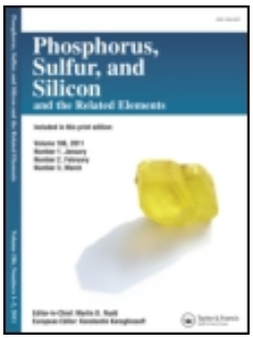

Phosphorus, Sulfur, and Silicon

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: www.tandfonline.com/journals/gpss20

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To cite this article: V. Rajeswar Rao & V. Ravinder Reddy (2006) Heterocyclic Systems Containing a Bridge Head Nitrogen Atom: Reaction of 5-Pyrimidine Carboxylic Acid 1,2,3,4-Tetrahydro-6-Methyl-4-Aryl-2-Thioxoethyl Ester with 3-(2-Bromoacetyl)coumarins, Phosphorus, Sulfur, and Silicon, 181:1, 147-158, DOI: 10.1080/104265090969252

To link to this article: https://doi.org/10.1080/104265090969252

Published online: 01 Feb 2007.

Phosphorus, Sulfur, and Silicon, 181:147–158, 2006

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090969252

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Heterocyclic Systems Containing a Bridge Head Nitrogen Atom: Reaction of 5-Pyrimidine Carboxylic Acid 1,2,3,4-Tetrahydro-6-Methyl-4-Aryl-2-Thioxoethyl Ester with 3-(2-Bromoacetyl)coumarins

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*Condensation of 5-pyrimidine carboxylic acid 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxoethyl ester II with various 3-(2-bromoacetyl)coumarins I, followed by the PPA cyclization of the intermediate ketones III, yielded 3-(2-oxo-*2H*-chromen-3-yl)-7-methyl-5-phenyl-*5H*-thiazolo[3,2-a]pyrimidine-6-carboxylicacid ethyl esters IV. The structures of newly synthesized compounds have been confirmed from analytical and spectral data.*

Keywords 3-(2-bromoacetyl)coumarin; dihydropyrimidine; thioazolopyrimidine

INTRODUCTION

Benzopyran-2-ones exhibit significant biological activities.[1] Coumarins bearing a heterocyclic moiety at the 3rd position are spasmolytic, uricosuric,[2] and CNS active.[3] Furthermore, thiazole[4] and also heterocyclic systems at the 3rd position of coumarin exhibit promising biological activities.[5] In view of these data and in continuation of our earlier work on the synthesis of heterocyclic systems from coumarin derivatives,[6–9] we report herein the synthesis of some new heterocyclic systems, namely chromen-3-yl thiazolopyrimidinecarboxylic acid ethyl esters (Scheme 1).

RESULTS AND DISCUSSION

The reaction of 3-(2-bromoacetyl)coumarins I with 5-pyrimidinecarboxylic acid 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxoethyl esters

Received September 7, 2004; in final form January 24, 2005.
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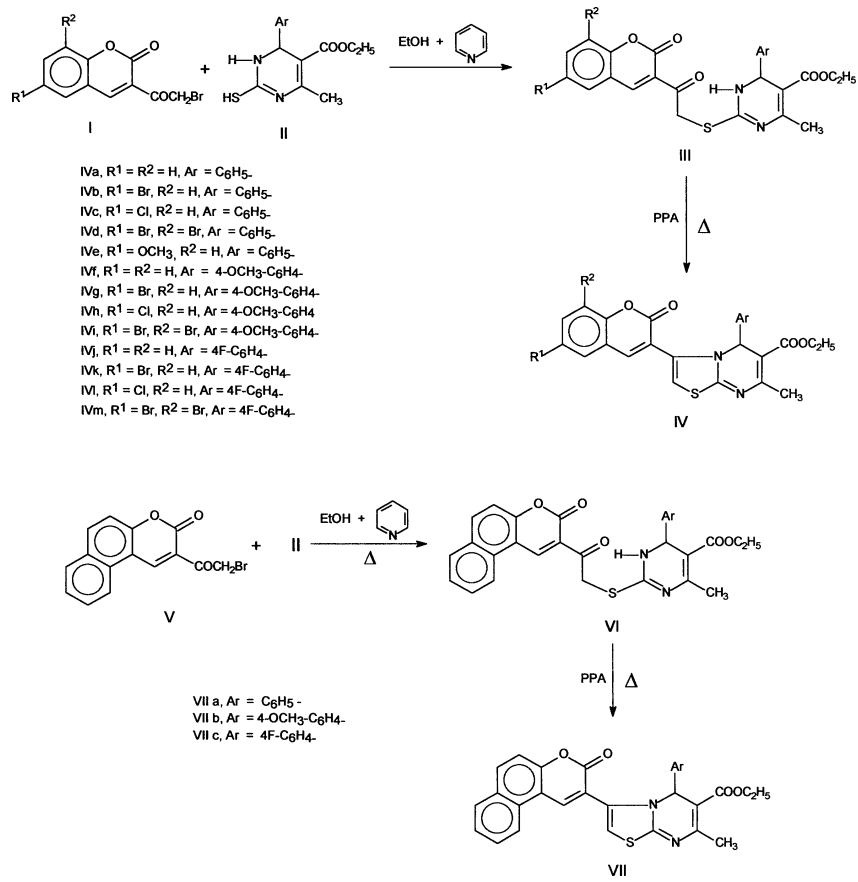

SCHEME 1

II in ethanol containing pyridine resulted in the formation of uncyclized ketones 2-[2-(2-oxo-*2H*-chromen-3-yl)-2-oxoethyl-sulphanyl]-4-methyl-6-phenyl-1-6-dihydropyrimidine-5-carboxylic acid ethyl esters III. The latter, on the cyclodehydration with polyphosphoric acid, afforded a series of 3-(2-oxo-*2H*-chromen-3-yl)-7-methyl-5-phenyl-*5H*-thiazolo[3,2-*a*]pyrimidine-6-carboxylic acid ethyl esters IV. Similarly 5,6-benzo-3-(2-bromo acetyl) coumarins on reaction with 5-pyrimidine carboxylic acid 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxoester in ethanol containing pyridine gave uncyclized ketone VI, which on cyclodehydration with PPA, resulted in the formation of 3-(2-oxo-5,6-benzo-*2H*-chromen-3-yl)-7-methyl-5-phenyl-*5H*-1-thiazolo[3,2-*a*]pyridine-6-carboxylic acid ethyl ester VII. 3-(2-bromoacetyl) coumarins were prepared from 3-(2-bromoacetyl) coumarin following the literature procedure.[10] Other

5-pyrimidine carboxylic acids 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxo ethyl ester II intermediates were prepared from an aldehyde, β-ketoesters, and thiourea using TMSI in acetonitrile.[11]

The ultraviolet spectra of 2-(2-(2-oxo-*2H*-chromen-3-yl)-2-oxoethyl-sulphanyl)-4-methyl-6-phenyl-1,6-dihydropyrimidine-5-carboxylic acid ethyl ester III show four bands:

1. an intense absorption at 320 ± 15 nm.
2. two bands around 285 and 270 nm, and
3. a band at 235 ± 15 nm.

Simple unsubstituted coumarin shows absorption at 315 nm and the large bathochromic shift from 310 to 335 nm was observed when electron-donating halogens or a methoxyl group is placed in a benzene ring of coumarin moiety. The similar increase in the bathochromic shift is observed when electron-donating groups are placed in 6-aryl moiety of III.

From the UV spectral data of the cyclized compounds IV, it can be seen that the substituents on the coumarin ring are more effective than on the pyrimidine ring. Simple unsubstituted coumarin shows absorption at 333 nm, while electron-donating groups such as 'X' or OCH_3, when placed in a benzene ring of coumarin moiety, show a large bathochromic shift from 333 to 378 nm. This is explained on the basis of extended conjugation in the cyclized systems.

Further examination of UV spectral data of VII, i.e., cyclized compounds (360 ± 3 nm), clearly shows that they have greater absorption values compared to corresponding uncyclized compounds VI (356 ± 3 nm). These values clearly indicate the presence of extended conjugation in cyclized compounds VII.

All the 2-[2-(2-oxo-*2H*-chromen-3-yl)-2-oxoethylsulphanyl)-4-methyl-6-phenyl-1,6-dihydropyrimidine-5-carboxylic acid ethyl esters III displayed strong absorption bands due to −C=N, lactone −C=O and ester −C=O at 1600–1610 cm^{-1}, 1717 cm^{-1}, and 1740 cm^{-1}, respectively. The ^{1}H-NMR of IIIa exhibited a characteristic singlet at δ 5.67 for the pyrimidine C_4 proton. All the cyclized compounds IV and VII in their IR (cm^{-1}) spectra displayed strong absorption bands due to C=N (1600 ± 11), lactone −C=O (1686–1695), and ester −C=O (1694–1740). The examination of IR spectra of cyclized compounds IV and VII have shown that there is a slight decrease in the wave number values of lactone −C=O when compared to wave numbers of lactone −C=O of the uncyclized compounds III and VI. The decrease may be attributed due to the conjugation in IV and VII. This is supported further by an earlier observation on similar type of compounds.[12,13]

TABLE I Spectral Data of Compounds III and VI

Compound	C═N	C═O	C═O (Ketone)	C═O (Ester)	—NH— (Str)	^{1}H-NMR (δ ppm) Solvent DMSO d_6	Mass Spectrum	UV Spectrum* Wave Length (nm)	UV Spectrum* Absorbance (A^0)
IIIa	1607	1687	1716	1730 (br, merged)	3418	0.99–1.03 (t,3H, CH_3 ethyl), 2.40 (s, 3H, CH_3), 3.56–3.60 (d, 1H of, S—CH_2), 4.09–4.13(d, 1H of, S—CH_2), 3.95–3.97(q, 2H, CH_2), 5.67 (s, 1H of Pyrimidine), 4.09–4.13 (d, 1H of, S—CH_2), 6.84–6.86 (m, 1H, Phenyl), 7.02 (m, 1H, Ar—H), 7.15–7.18 (d, 1H, Ar—H), 7.39–7.66 (m, 1H, Ar—H), 7.90–7.92 (d, 1H, Ar—H), 8.44 (s,1H,C-4H of Coumarin), 8.90 (s,1H, —NH—, D_2O exchangeable)	186 (10) 265 (15) 462 (100) 484 (5%)	315.5 285 205	0.474 0.583 1.456
IIIb	1602	1690 (merged)	1715	1730 (br, merged)	3426	0.98–1.03 (t, 3H, CH_3 ethyl), 2.37 (s, 3H, CH_3 pyrimidine), 3.50–3.54 (d, 1H of SCH_2), 3.93–4.0 (q, 2H, CH_2), 4.05–4.09 (d, 1H of SCH_2), 5.63 (s, 1H, pyrimidine), 6.86–6.88 (m, 4H, Ar—H), 7.01–7.04 (m, 1H, Ar—H), 7.13–7.16 (d, 1H, Ar—H), 8.17–8.18 (d, 1H, Ar—H), 8.39 (d, 1H, Ar—H), 8.84 (s, 1H, C-4H of coumarin) 8.96 (s, 1H, —NH—, D_2O exchangeable)	—	332.5 293 259.5	0.176 0.191 0.051
IIIc	1605	1690 (merged)	1718	1740 (br, merged)	3426	0.99–1.04 (t,3H, CH_3 ethyl), 2.39 (s, 3H, CH_3 pyrimidine), 3.53–3.57 (d, 1H of, S—CH_2), 3.86(s, 3H, —OCH_3), 3.95–4.02(q, 2H, CH_2), 4.06–4.10 (d, 1H of, S—CH_2), 5.64 (s, 1H, Pyrimidine), 6.86 (s, 5H, Phenyl), 7.60–7.33 (m, 2H, Ar-H), 7.81–7.84 (d, 1H, Ar—H), 8.37 (s,1H,C-4H of Coumarin), 8.81 (s,1H, —NH—, D_2O exchangeable)	—	331.5 293 259.5	0.197 0.184 0.093

IIId	—	—	—	—	—	0.98–1.03 (t, 3H, CH_3 ethyl), 2.37 (s, 3H, CH_3 pyrimidine), 3.52–3.56 (d, 1H of S—CH_2), 3.92–3.96 (q, 2H, CH_2), 4.06–4.11 (d, 1H of S—CH_2), 5.63 (s, 1H, pyrimidine) 6.87–7.35 (m, 5H, Ar—H), 8.19 (s, 2H, Ar—H), 8.37 (s, 1H, C-4H of coumarin), 8.91 (s, 1H, —NH—, D_2O exchangeable).	—	331 285 207	0.259 0.482 1.140
IIIe	—	—	—	—	—	—	—	335 206	0.790 1.770
IIIf	1609	1690 (merged)	1717	1740 (br, merged)	3419	1.00–1.04 (t,3H, CH_3 ethyl), 2.39 (s, 3H, CH_3Pyrimidine), 3.51(s, 3H, —OCH_3), 3.56–3.60 (d, 1H of, S—CH_2), 3.94-3.99(q, 2H, CH_2), 4.05-4.09(d, 1H of, S—CH_2), 5.65 (s, 1H of Pyrimidine), 6.33-6.36(d, 2H, Ar—H), 6.75-6.78 (d, 2H, Ar—H), 7.18-7.20(d, 1H, Ar—H), 7.4-7.45 (m, 1H, Ar—H),7.64-7.7 (m, 1H, Ar—H), 7.89-7.92 (d, 1H, Ar—H), 8.39 (s, 1H, C-4H of Coumarin), 8.86 (s,1H, —NH—, D_2O exchangeable)	186 (5) 265 (10) 428 (2) 492 (100) 514 (5%)	287 205	0.680 1.390
IIIh	—	—	—	—	—	—	—	207 221 278 326	1.461 1.493 0.802 0.476
III j	1607	1688	1717	1740 (br, merged)	3417	0.99–1.03 (t,3H, CH_3 ethyl), 2.39–2.50 (s, 3H, CH_3Pyrimidine), 3.55–3.59(d, 1H of, S—CH_2), 3.95–4.00(s, 2H, CH_2), 4.07–4.12 (d, 1H of, S—CH_2), 5.69 (s, 1H of Pyrimidine), 6.63–6.68(m, 2H, Ar—H), 6.91–6.95 (m, 2H, Ar—H), 7.20-7.23(d, 1H, Ar—H), 7.43-7.45 (m, 1H, Ar—H), 7.65-7.68(d, 2H, Ar—H), 7.89-7.92(d, 2H, Ar—H), 8.43 (s, 1H, C-4H of Coumarin), 8.90 (s,1H, —NH—, D_2O exchangeable)	—	212 244 281 305 320	2.739 0.921 1.755 1.280 1.353

(Continued on next page)

TABLE I Spectral Data of Compounds III and VI

Compound	C=N	C=O	C=O (Ketone)	C=O (Ester)	—NH— (Str)	^{1}H-NMR (δ ppm) Solvent DMSO d_6	Mass Spectrum	UV Spectrum* Wave Length (nm)	UV Spectrum* Absorbance (A^0)
IIIk	—	—	—	—	—	—	—	207	1.406
								225	1.160
								278	0.594
								334	0.468
IIIm	—	—	—	—	—	—	—	210	1.443
								227	1.116
								285	0.569
								338	0.409
VIa	1590	1672	1721.8	1740 (br, merged)	3428	0.93–0.98 (t, 3H, CH_3 ethyl), 2.41 (s, 3H, CH_3 pyrimidine), 3.61–3.66 (d, 1H, S—CH_2), 3.90–3.97 (m, 2H, CH_2 ethyl), 4.13–4.17 (d, 1H, S—CH_2), 5.76 (s, 1H of pyrimidine), 6.80–6.88 (m, 4H, Ar—H), 7.00–7.02 (d, 1H, Ar—H), 7.33–7.36 (t, 1H, Ar—H), 7.7–7.72 (t, 1H, Ar—H), 7.81–7.83 (d, 1H, Ar—H), 8.1–8.13 (d, 1H, Ar—H), 8.61–8.64 (d, 1H, Ar—H), 9.04–9.09 (d, 1H, Ar—H and C_4—H of coumarin), 9.04 (s, 1H, —NH—,D_2O exchangeable)	512 (100%), 535 (30%) (Na adduct), 237 (10%)	358.5	0.528
								323.5	0.495
								253.5	0.648
								232	2.107
								211	1.484
VIb	1604	1673	1721.8	—	3427	—	—	356	0.699
								324	0.602
								250	0.660
								232	2.317
								210.5	1.624
VIc	1609	1670	1717.9	1740 (br, merged)	3425	0.93–0.98 (t, 3H, CH_3 ethyl), 2.39 (s, 3H, CH_3 pyrimidine), 3.59–3.63 (d, 1H of SCH_2), 3.87–4.02 (q, 2H, CH_2), 4.12–4.16 (d, 1H of SCH_2), 5.78 (s, 1H of pyrimidine), 6.61–6.66 (t, 2H, Ar—H), 6.94 (m, 2H, Ar—H), 7.38–7.41 (d, 1H, Ar—H), 7.68–7.86 (m, 2H, Ar—H), 8.11–8.14 (d, 1H, Ar—H), 8.26–8.29 (d, 1H, Ar—H), 8.6–8.63 (d, 1H, Ar—H), 9.02 (s, 1H, —NH—, D_2O exchangeable), 9.09 (s, 1H, C-4H of coumarin).	—	358.5	0.470
								322.5	0.474
								352	0.570
								227	1.832

TABLE II Spectral Data of Compounds IV and VII

Compound	O=C–O (Lactone)	O=C–O (Ester)	–C=N–	^{1}H-NMR (δ ppm) Solvent DMSO d_6	Mass Spectrum	UV Spectrum* Wave Length (nm)	UV Spectrum* Absorbance A^0
IVa	1695	1715	1607	1.09 (t, 3H, CH_3 of ethyl), 2.38 (s, 3H, CH_3), 4.01 (q, 2H, CH_2), 6.30 (s, 1H, C_5 of thiazolo pyrimidine), 6.84–7.98 (m, 10H, 9 Ar–H and 1H of thiazole), 8.55 (s, 1H,C_4 of coumarin)	244 (100), 266 (30), 282 (20), 370 (20), 444 (6%)	210 294 333	1.575 0.539 0.686
IVb	—	1722	1601	1.06–1.10 (t, 3H, CH_3 of ethyl), 2.37 (s, 3H, CH_3), 4.02 (q, 2H, –CH_2–), 6.23 (s, 1H, C_5 of thiazolo pyrimidine), 7.03–7.56 (m, 7H, 6 Ar–H and 1H of thiazole), 7.87–7.93 (m, 3H, 2 Ar–H and 1H of C_4 of coumarin)	200 (2), 322 (5), 324 (6), 450 (5), 452 (2), 476 (7), 478 (8), 482 (9), 484 (10), 522 (96), 524 (100%)	211 285 339	1.818 0.575 0.672
IVc	1690	1722	1605	1.06–1.11 (t, 3H, CH_3 of ethyl), 2.35 (s, 3H, CH_3), 4.01–4.04 (q, 2H, –CH_2–), 6.18 (s, 1H, C_5 of thiazolo pyrimidine), 6.99–7.21 (m, 6H, Ar–H), 7.76–7.81 (m, 2H, Ar–H), 7.91(s, 1H, C_4 of coumarin)	—	375.5 285 220 206.5	0.385 0.473 1.260 1.420
IVd	1694	1740	1589	1.07–1.11 (t, 3H, CH_3 of ethyl), 2.37 (s, 3H, CH_3), 4.00-4.05 (q, 2H, –CH_2–), 6.19 (s, 1H, C_5 of thiazolo pyrimidine), 7.04–7.25 (m, 6H, Ar–H), 7.92-7.96 (d, 2H, Ar–H and 1H of thiazole), 8.28 (s, 1H, C_4 of coumarin)	—	213 298 341	1.976 0.575 0.585
IVf	1696	1723	1608	1.01–1.11 (t, 3H, CH_3 of ethyl), 2.36 (s, 3H, CH_3), 3.63 (s, 3H,–OCH_3), 3.97-4.04 (q, 2H, –CH_2–), 6.17 (s, 1H, C_5 of thiazolo pyrimidine), 6.67-6.95 (m, 6H, Ar–H), 7.28 (s, 1H, thiazole, 7.41–7.77 (m, 4H, Ar–H), 8.00(s, 1H, C_4 of coumarin)	—	378 329.5 283 204.5	0.513 0.433 0.636 1.770

(Continued on next page)

TABLE II Spectral Data of Compounds IV and VII

Compound	O=C–O (Lactone)	O=C–O (Ester)	–C=N–	^{1}H-NMR (δ ppm) Solvent DMSO d_6	Mass Spectrum	UV Spectrum* Wave Length (nm)	UV Spectrum* Absorbance A^0
IVh	1690	1732	1607	1.07–1.10 (t, 3H, CH_3 of ethyl), 2.32 (s, 3H, CH_3), 3.60 (s, 3H,–OCH_3), 3.98–4.02 (q, 2H, –CH_2–), 6.05 (s, 1H, C_5 of thiazolo pyrimidine), 6.68–7.00 (m, 5H, 4H, Ar–H and 1H of thiazole), 7.57–7.92 (m, 4H, 3Ar–H andC_4 of coumarin)	—	—	—
IVI	1695	1739	1608	1.06–1.10 (t, 3H, CH_3 of ethyl), 2.30 (s, 3H, CH_3 of thiazolo pyrimidine), 3.55 (s, 3H,–OCH_3), 3.96–4.00 (q, 2H, –CH_2–), 5.99 (s, 1H, C_5 of thiazolo pyrimidine), 6.69–7.05 (m, 5H Ar–H), 7.90 (s, 1H, C_2 of thiazole), 7.98 (s, 1H, Ar–H), 8.26 (s, 1H,C_4 of coumarin)	—	—	—
IVj	—	—	—	1.06–1.10 (t, 3H, CH_3 of ethyl), 2.34 (s, 3H, CH_3 of thiazolo pyrimidine), 3.98–4.02 (q, 2H, –CH_2–), 6.16 (s, 1H, C_5 of thiazolo pyrimidine), 6.99–7.02 (m, 4H, Ar–H), 7.15 (s, 1H, C_2 of thiazole), 7.34–7.77 (m, 4H, Ar–H), 8.00 (s, 1H,C_4 of coumarin)	—	209 287	1.801 0.685
IVk	1686	1729	1602	1.05–1.12 (t, 3H, CH_3 of ethyl), 2.32 (s, 3H, CH_3 of thiazolo pyrimidine), 3.96–4.04 (q, 2H, –CH_2–), 6.12 (s, 1H, C_5 of thiazolo pyrimidine), 6.98-7.11 (m, 5H, 4 Ar–H and 1H of thiazole), 7.52–7.53 (d, 1H, Ar–H), 7.84–7.98 (m, 4H, 3Ar–H and 1H,C_4 of coumarin)	—	209 284	1.362 0.506
IVl	—	—	—	—	—	218	2.192
IVm	1740	1694	1604	1.06–1.11 (t, 3H, CH_3 of ethyl), 2.33 (s, 3H, CH_3 of thiazolo pyrimidine), 3.98–4.03 (q, 2H, –CH_2–), 6.08 (s, 1H, C_5 of thiazolo pyrimidine), 6.99–7.11 (m, 5H, 4 Ar–H and 1H of thiazole), 7.93-7.99 (d, 2H, Ar–H), 8.28 (s, 1H, C_4 of coumarin)	—	281	0.731

(Continued on next page)

VIIa	1694 merged	1721	1603.4	1.01–1.05 (t, 3H, CH_3 of ethyl), 2.41 (s, 3H, CH_3 of pyrimidine), 3.94–4.01 (q, 2H, $-CH_2-$), 6.25 (s, 1H, C_5 of thiazolo pyrimidine), 7.01–7.19 (d, 2H, Ar—H and 1H C-2 of thiazole), 7.39–7.48 (m, 2H, Ar—H), 7.67–7.74 (m, 3H, Ar—H), 8.09–8.12 (d, 1H, Ar—H), 8.30–8.33 (d, 1H, Ar—H), 8.8 (s, 1H, C_4 of coumarin)	494 (100%) 477 (15%) 448 (20%)	364.5 227.0 209.5	0.606 1.639 1.419
VIIb	1695.6	1725.0	1609	1.03–1.06 (t, 3H, CH_3 of ethyl), 2.42 (s, 3H, CH_3 pyrimidine), 3.41 (s, 3H, $-OCH_3$), 3.80-4.00 (q, 2H, $-CH_2-$), 6.20 (s, 1H, C_5 of thiazolo pyrimidine), 6.59–6.62 (d, 2H, Ar—H), 6.85-6.87 (d, 2H, Ar—H), 7.2 (s, 1H, C-2 of thiazole), 7.63-7.74 (m, 4H, Ar—H), 8.1-8.12 (d, 1H, Ar—H), 8.31–8.34 (d, 1H, Ar—H), 8.45-8.48 (d, 1H, Ar—H) 8.78 (s, 1H, C_4 of coumarin)	—	369.0 256.0 227.0	0.674 0.567 2.16
VIIc	1687.4	1717.6	1605	1.00–1.05 (t, 3H, CH_3 of ethyl), 2.50 (s, 3H, CH_3 pyrimidine), 3.92–4.0 (q, 2H, CH_2), 6.19 (s, 1H, C_5 of thiazolo pyrimidine), 6.89–6.98 (m, 4H, Ar—H), 7.13 (s, 1H, C-2 of thiazole), 8.09–8.12 (d, 1H, Ar—H), 8.30–8.32 (d, 1H, Ar—H), 8.85 (s, 1H, C_4—H of coumarin)	—	370.5 227.0 209.0	0.532 1.56 1.15

*UV spectrum of all the compounds were recorded in a 20 ppm solution in methanol, except for IIIb and IIIc, which were recorded in a 10 ppm solution in methanol, and for IVm, which was recorded in a 20 ppm solution in DMF.

The ^{1}H-NMR spectrum of IVa exhibited a characteristic singlet at δ 6.30 for the C_5-H of thiazolopyrimidine, a triplet at δ 1.09, a quartet at δ 4.01 for ethyl CH_2 protons, a singlet at δ 2.38 for methyl protions, and a characteristic singlet for the C_4-H of coumarin at δ 8.55. The remaining protons were observed in the expected regions (Table I and II).

EXPERIMENTAL

All melting points were determined by a POLMAN-MP apparatus (Model No. MP-96). IR spectra (ν_{max} cm^{-1}) were recorded on Perkin-Elmer spectrophotometer. The ^{1}H-NMR spectra was recorded on a

TABLE III Analytical Data of Compounds III–V, and VII

Compound	R^1	R^2	Ar	m.p* (°C)	Formula (M.W.)	Calc. (Found) % N	S
IIIa	H	H	C_6H_5	212–214	$C_{25}H_{22}N_2O_5S$ (462)	6.06 (6.04)	6.92 (6.88)
IIIb	Br	H	C_6H_5	214–216	$C_{25}H_{21}BrN_2O_5S$ (541)	5.17 (5.20)	5.91 (5.95)
IIIc	Cl	H	C_6H_5	212–214	$C_{25}H_{21}ClN_2O_5S$ (496.5)	5.63 (5.60)	6.44 (6.40)
IIId	Br	Br	C_6H_5	198–200	$C_{25}H_{20}Br_2N_2O_5S$ (620)	4.51 (4.55)	5.16 (5.20)
IIIe	OCH_3	H	C_6H_5	222–224	$C_{26}H_{24}N_2O_6S$ (492)	5.69 (5.66)	6.50 (6.56)
IIIf	H	H	4-OCH_3 C_6H_5	210–212	$C_{26}H_{24}N_2O_6S$ (492)	5.69 (5.64)	6.50 (6.54)
IIIg	Br	H	4-OCH_3 C_6H_5	214–216	$C_{26}H_{23}BrN_2O_6S$ (571)	4.90 (4.94)	5.60 (5.64)
IIIh	Cl	H	4-OCH_3 C_6H_5	220–222	$C_{26}H_{23}ClN_2O_6S$ (526.5)	5.31 (5.34)	6.07 (6.09)
IIIi	Br	Br	4-OCH_3 C_6H_5	190–192	$C_{26}H_{22}Br_2N_2O_6S$ (650)	4.30 (4.34)	4.92 (4.94)
IIIj	H	H	4-F C_6H_5	210–212	$C_{25}H_{21}FN_2O_5S$ (480)	5.83 (5.86)	6.66 (6.69)
IIIk	Br	H	4-F C_6H_5	209–211	$C_{25}H_{20}BrF\ N_2O_5S$ (559)	5.00 (5.04)	5.72 (5.75)
IIIl	Cl	H	4-F C_6H_5	208–210	$C_{25}H_{20}ClFN_2O_5S$ (514.5)	5.44 (5.46)	6.21 (6.25)
IIIm	Br	Br	4-F C_6H_5	183–185	$C_{25}H_{19}Br_2FN_2O_5S$ (638)	4.38 (4.40)	5.01 (5.06)
Va	—	—	C_6H_5	208–210	$C_{29}H_{24}N_2O_5S$ (512)	5.46 (5.50)	6.25 (6.21)
Vb	—	—	4-OCH_3 C_6H_5	190–192	$C_{30}H_{26}N_2O_6S$ (542)	5.16 (5.14)	5.90 (5.93)
Vc	—	—	4-OCH_3 C_6H_5	208–210	$C_{29}H_{23}FN_2O_5S$ (530)	5.28 (5.30)	6.03 (6.09)
IVa	H	H	C_6H_5	200–202	$C_{25}H_{20}N_2O_4S$ (444)	6.30 (6.27)	7.20 (7.23)
IVb	Br	H	C_6H_5	196–198	$C_{25}H_{19}BrN_2O_4S$ (523)	5.35 (5.31)	6.11 (6.15)
IVc	Cl	H	C_6H_5	198–200	$C_{25}H_{19}ClN_2O_4S$ (478.5)	5.85 (5.81)	6.68 (6.71)
IVd	Br	Br	C_6H_5	200–202	$C_{25}H_{18}Br_2N_2O_4S$ (602)	5.31 (5.35)	4.65 (4.70)
IVe	OCH_3	H	C_6H_5	194–196	$C_{26}H_{22}N_2O_6S$ (474)	5.90 (5.92)	6.75 (6.74)
IVf	H	H	4-OCH_3 C_6H_4	128–130	$C_{26}H_{22}N_2O_5S$ (474)	5.90 (5.93)	6.75 (6.71)
IVg	Br	H	4-OCH_3 C_6H_4	164–166	$C_{26}H_{21}BrN_2O_5S$ (553)	5.06 (5.03)	5.79 (5.81)
IVh	Cl	H	4-OCH_3 C_6H_4	170–172	$C_{26}H_{21}ClN_2O_5S$ (508.5)	5.50 (5.52)	6.30 (6.32)
IVi	Br	Br	4-OCH_3 C_6H_4	142–144	$C_{26}H_{20}Br_2N_2O_5S$ (632)	4.43 (4.46)	5.07 (5.09)
IVj	H	H	4-F C_6H_4	140–142	$C_{25}H_{19}FN_2O_4S$ (462)	6.04 (6.02)	6.91 (6.88)
IVk	Br	H	4-F C_6H_5	182–184	$C_{25}H_{18}BrF\ N_2O_4S$ (541)	5.16 (5.13)	5.90 (5.92)
IVl	Cl	Br	4-F C_6H_5	244-246	$C_{25}H_{18}ClFN_2O_4S$ (496.5)	5.62 (5.59)	6.43 (6.44)
IVm	Br	Br	4-F C_6H_5	204–206	$C_{25}H_{17}Br_2FN_2O_4S$ (620)	4.50 (4.52)	5.15 (5.13)
VIIa	—	—	C_6H_5	224–226	$C_{29}H_{22}N_2O_4S$ (494)	5.65 (5.62)	6.46 (6.40)
VIIb	—	—	4-OCH_3 C_6H_4	220–222	$C_{30}H_{24}N_2O_5S$ (524)	5.33 (5.30)	6.46 (6.10)
VIIc	—	—	4-OCH_3 C_6H_4	230–232	$C_{29}H_{21}FN_2O_4S$ (512)	5.45 (5.42)	6.09 (6.10)

Bruker Avance 300 MHz instrument using TMS as an internal standard. The mass spectra were scanned on a Perkin-Elmer SCIEX API-2000 instrument.

2-(2-(2-Oxo-*2H*-chromen-3-yl)-2-oxoethylsulphanyl)-4-methyl-6-phenyl-l,6-dihydropyrimidine-5-carboxylicacid ethyl ester (III and VI): General Procedure

A mixture of 3-(2-bromoacetyl)coumarin (0.01 mol) and 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ester (0.01 mol) was refluxed in ethanol (20 mL) containing pyridine (0.001 mol) for 4 h. The reaction mixture was cooled to room temperature. The solid obtained was filtered, dried, and recrystallised from ethanol (Table III).

3-(2-Oxo-*2H*-chromen-3-yl)-7-methyl-5-phenyl-*5H*-thiazolo[3,*2-a*]pyrimidine-6-carboxylic acid ethyl ester (IV–VII): General Procedure

A mixture of 3-(2-oxo-*2H*-chromen-3-yl)-7-methyl-5-phenyl-*5H*-thiazolo[3,2-*a*] pyrimidine-6-carboxylic acid ethyl ester (0.01 mol) and freshly prepared polyphosphoric acid (0.2 mol) was heated at 95–100° C for 1 h. The reaction mixture then was cooled to room temperature. The solid obtained was treated with aqueous sodium bicarbonate, filtered, dried, and recrystallised from methanol (Table III).

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