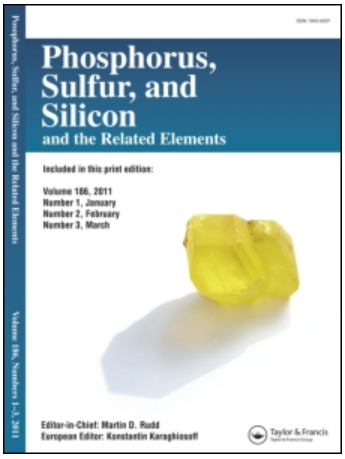


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# 5-Chromonylidene-hydantoins, 2-Thiohydantoins, Synthesis and Reaction with Some Alkylhalides, Some Amines and Some Diazoalkanes

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# 5-Chromonylidene-hydantoins, 2-Thiohydantoins, Synthesis and Reaction with Some Alkylhalides, Some Amines and Some Diazoalkanes

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*5-Chromonylidene-hydantoin, 2-thiohydantoin derivatives 2a–g, 3a,b were prepared by condensation of 3-formylchromones 1a,b with hydantoin, 2-thiohydantoin derivatives. Compounds 2a,b undergo Mannich reaction with formaldehyde and morpholine to give the corresponding Mannich prouducts 5a,b respectively. Reaction of 2a,b with alkylhalides namely Methyl iodide, Phenacly bromide, and Chloroacetic acid afforded the corresponding compounds 6a,b, 7a,b, 9a,b and 10a,b respectively. Reaction of 5-Chromonylidene-2-methylthio-hydantoin 6a,b with secondry and primary amines such as morpholine, piprazine, anthranilic acid, and glycine afforded the Glycocyamidine derivatives 11a,b, 12a,b, 13a,b and 15a,b. On reacting 2a,b with dazoalkanes afforded 16a,b and 17a,b respectively.*

**Keywords** 2-Thiohydantoin; alkylthiohydantoin; chromones; diazoalkanes; glycocyamidines; hydantoin



## INTRODUCTION

5-Chromonylidene-hydantoin, 2-thiohydantoin derivatives were prepared by condensation of 3-formylchromone with hydantoin, 2-thiohydantoin. 3-Formylchromones were chosen as being synthetically versatile molecules with reactive carbonyl group. They have considerable significance for their biological activities[1–3] and for their reactivity towards nucleophiles which allows the synthesis of wide variety of heterocyclic. In the course of biological investigation 3-formalychromone derivatives has a hereditary bleaching effect on the plastid system of Euglena gracilis[4] and antimycobacterial activity similar to effect of isonicotin acid hydrazide (INH).[4,5] Hydantoin derivatives have found

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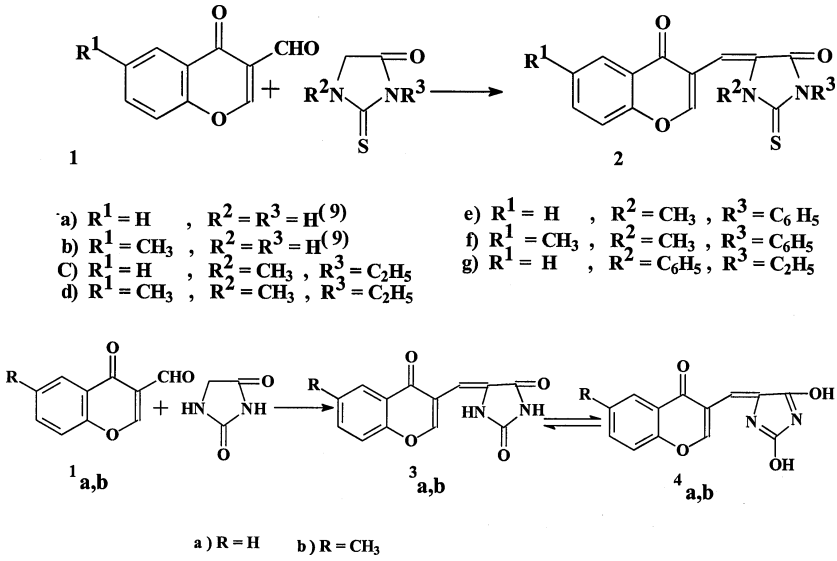
use in medicine, they have mainly been considered as anticonvulsant agent,[6] 5,5-Disubstituted hydantoins were used as drugs in which penetrated the blood-brain in significant concentration,[7] 2-deoxyuridine with 5-methyl-2-thiohydantoin as the heterocycle in the 5-position showed cytotoxicity against MT-4 cell at 100 mM.[8] Those results are interesting and prompted us to prepare some new chromonylidene-hydantoin, 2-thiohydantoin derivatives.

## RESULTS AND DISCUSSION

Condensation of formylchromones 1a,b with 2-thiohydantoin derivatives in acetic acid in the presence of fused sodium acetate yielded 2-thioxoimidazolidinones 2a–g in good yield (68–85%), while its reaction with hydantoin afforded 3a,b in low yield (38–52%). Infrared spectra of compounds 2a–g and 3a,b exhibited bands in the region 1740 $cm^{-1}$ and 1645 $cm^{-1}$ corresponding to carbonyl groups of hydantoin and benzopyran ring respectively, $H^1$-NMR spectra of 3a,b confirmed existence of the two isomers 3a,b and 4a,b (Scheme 1).

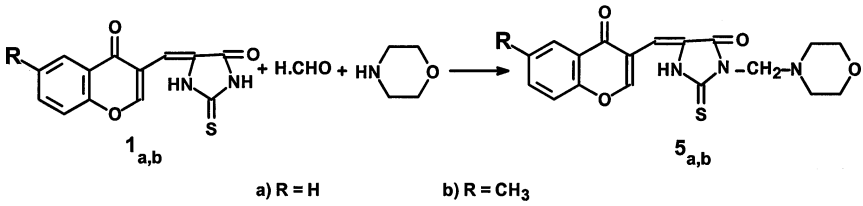



**SCHEME 1**

The structure of compounds 2a–g and 3a,b were established by correct analytical and spectral data (*cf.* Experimental).

Synthesis of Mannich bases derived from 5-substituted 2-thiohydantoin was previously studied and the site of attack was reported to be only at position three.[10,12] Thus, when 6-substituted

chromonylidene-2-thiohydantoin 2a,b were allowed to react with formaldehyde and morpholin in ethanol, it yielded the corresponding 2-thioxo-$N^3$-morphlinomethyl-imidazolidinones 5a,b, $H^1$-NMR spectra of compounds 5a,b showed N—C$H_2$—N as a singlet at 4.67 and 4.68 ppm respectively (Scheme 2).



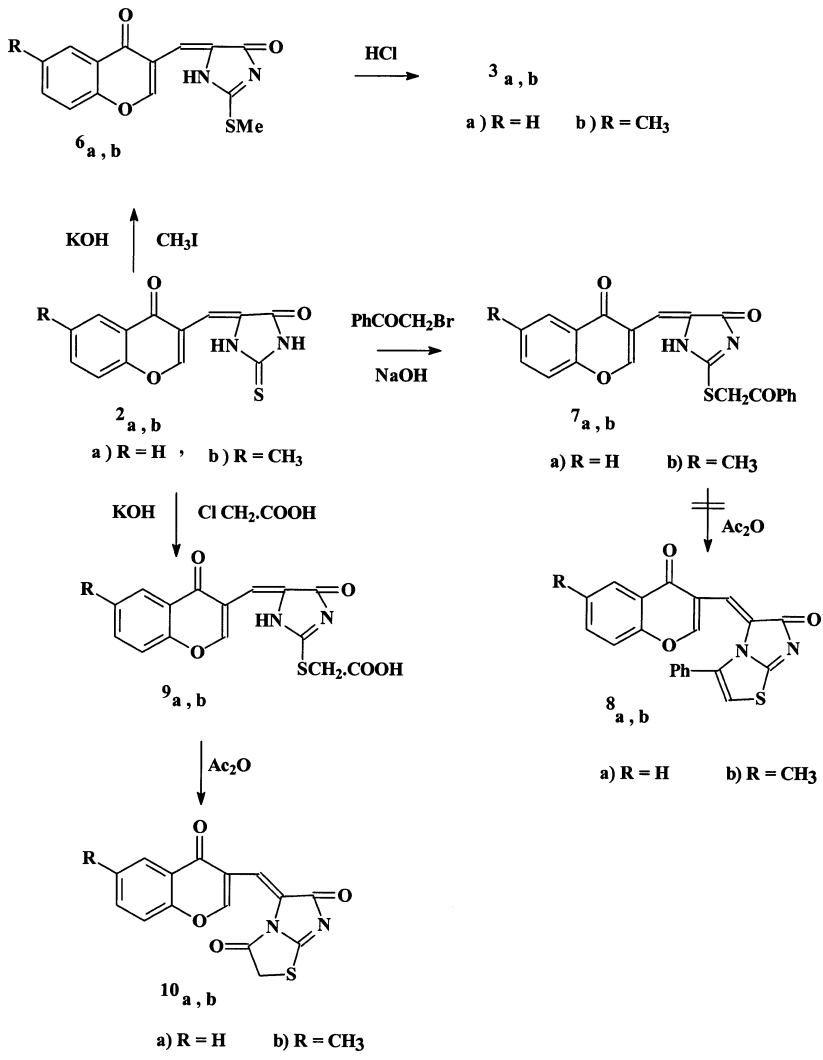

**SCHEME 2**

Microanalytical and spectral data of compounds 5a,b were fully consistent with the assigned structure (*cf.* Experimental).

Reaction of 6-substituted 5-chromonylidene-2-thiohydantoin 2a,b with various alkylhalides namely methyl iodide, phenacyl bromide, and chloroacetic acid in ethanol in the presence of aqueous KOH gave the corresponding 2-methylthio- 6a,b, 2-benzoylmethylthio- 7a,b and 2-carboxymethylthio-imidazolidinones 9a,b respectively. The structure of 6a,b, 7a,b, and 9a,b were established by $H^1$-NMR, $C^{13}$-NMR, IR and mass spectroscopy, which were found in agreement with proposed structurs (*cf.* Experimental). $H^1$-NMR spectra of compounds 6a,b and 7a,b showed a singlet at 2.72, 2.67, 4.94 and 4.93 ppm corresponding to S—$CH_3$ for 6a, 6b and S—$CH_2$—CO for 7a and 7b respectively, moreover $C^{13}$-NMR spectrum of 7a showed signals at 177.202 ppm (C=O of hydantoin), 179.11 ppm (C=O of benzopyrane) and 194.75 ppm (C=O of benzoyl group). Acid hydrolysis of compounds 6a,b afforded the products which proved to be identical with 3a,b or 4a,b.

Cyclization of 9a,b in acetic anhydride yielded the imidazothiazol derivatives 10a,b, while several attempts for cyclization of compounds 7a,b to yield 8a,b were failed, this may be attributed to the steric hindrance of the bulky aryl group (Scheme 3). $H^1$-NMR spectra of 10a,b showed a singlet at 4.12 and 4.01 ppm corresponding to $CH_2$ of thiazol ring for 10a and 10b respectively, in addition the IR spectra of 10a,b showed appearance of strong stretching vibration frequency of carbonyl group of thiazol ring at 1755–1760 $cm^{-1}$.

Reaction of 6-substituted 5-chromonylidene-2-methylthiohydantoin 6a,b with primary and secondary amines was also investigated. It was reported that 5-benzylidene-2-alkylthiohydantoins react with primary and secondary amines to gave glycocymidine derivatives.[10,11] Treating 6a,b with morpholine and piprazine (mole: mole) in boiling

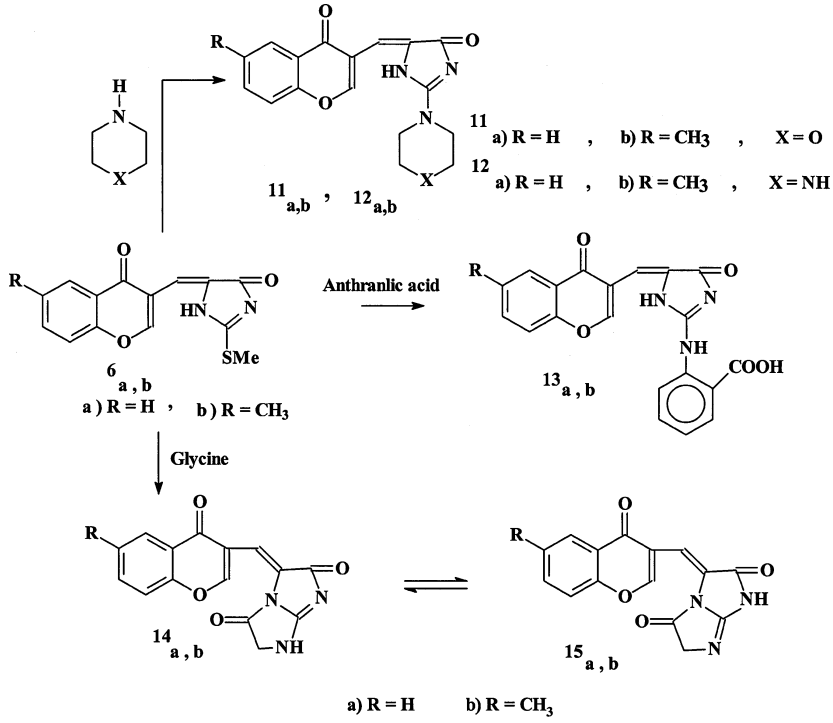



**SCHEME 3**

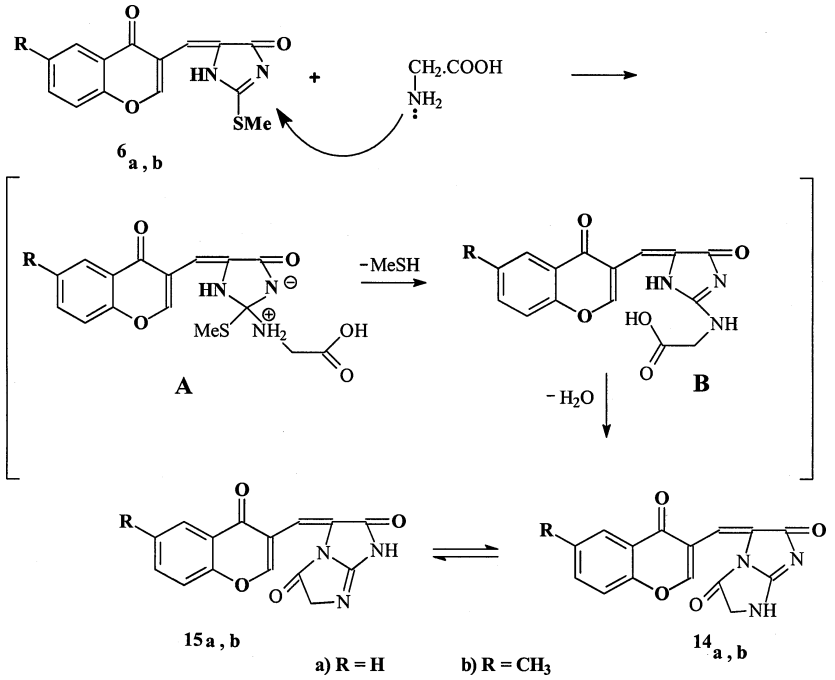
ethanol afforded the corresponding 2-morpholino-glycocyamidines 11a,b and 2-piprazeno-glycocyamidines 12a,b respectively. On reacting 6a,b with anthranlic acid in ethanol afforded $N^2$-(o-carboxyphenyl)-glycocyamidines 13a,b. IR spectra of 13a,b exhibited a new band in the region 1680–1695 $cm^{-1}$ corresponding to carbonyl of carboxylic group, $C^{13}$-NMR spectrum of 13b showed signals at 177.31 (C=O of COOH), 177.36 (C=O of hydantoin) and 179.01 (C=O of benzopyrane). On heating 6a,b with glycine under the fusion

condition afforded 1,6-dihydroimidazo[1,2-a]-imidazole-2,5-diones derivatives 14a,b (Scheme 4). $H^1$-NMR spectra showed two isomer 14a,b and 15a,b, the formation of those two isomer obtained through the elimination of alkyl thiol followed by cyclization with elimination of water as proposed by the following mechanism. As to the formation of 14a,b and 15a,b a nucleophilic attack of 5-chromonylidene-2-methylthiohydantoin 6a,b by the amino group of glycine to afford the intermediate A, the elimination methylthiol from compound A afforded the intermediate B which eleminated a molecule of water to give the final product 14a,b or 15a,b respectively (Scheme 5). The structure of compounds 11a,b, 12a,b, 13a,b and 14a,b were proved by microanalytical and spectral data (*cf.* experimental).

The reaction of 5-substituted 2-thiohydantoin with diazoalkanes was reported by Aly et al.[12,13] On reacting 2a,b with diazomethane in ice bath afforded 2-methylthio-imidazolidinones 6a,b and 2-thioxo-$N^3$-methyl-imidazolidinones 16a,b. Heating 2a,b with diphenyldiazomethane in boiling dry benzene yielded 2-thioxo-$N^3$-diphenylmethyl-imidazolidinones 17a,b. Acid hydrolysis of 17a,b furnished the product




**SCHEME 4**

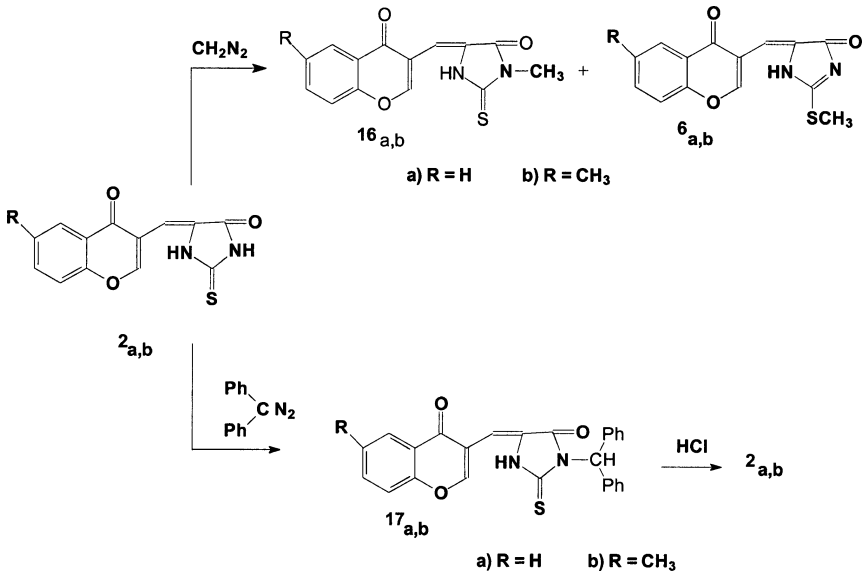



**SCHEME 5**

which proved to be identical with 2a,b. The structure of 16a,b and 17a,b was established on the basis of analytical and spectral data (*cf.* Experimental). $H^1$-NMR spectra of 16a,b and 17a,b showed a singlet at 4.22, 4.18, 5.82, and 5.78 corresponding to $N^3$—$CH_3$ for compounds 16a, 16b, and $N^3$—CH for compounds 17a and 17b, respectively (Scheme 6).

## EXPERIMENTAL

All melting points are uncorrected. IR were recorded on Perkin-Elmer 1420 spectrophotometer using KBr Wafer Technique. The $^1$H-NMR spectra were recorded using a Bruecker 200 MHz spectrophotometer using DMSO as solvents and TMS as internal standard. Chemical shift values are expressed in $\delta$ ppm units. $^{13}$C-NMR spectra were recorded on a Bruecker 200 MHz spectrophotometer. TMS was used to determine the carbon chemical shifts and expressed in ppm. All analytical samples were homogeneous by thin-layer chromatography, which was performed on EM silica gel 60 F sheet (0.2 mm) with $C_6H_6/CH_3 \cdot COOC_2H_5$ (2:5, V/V) and in ether/benzene (2:1, V/V) as the developing solvents. The spots were detected with UVModel UVGL-58.




**SCHEME 6**

## Reaction of 1a or 1b with 2-Thiohydantoin Derivatives (Synthesis of 2 a–g)

### *General Procedure*

A mixture of 1a or 1b (0.01 mole) and 2-thiohydantoin derivatives (0.01 mole) in glical acetic acid (40 ml) in presence of fused sodium acetate (2 gm) was refluxed for 2–3 h. The solid formed on hot was filtered off and recrystallized from the proper solvent to give 2-thioxo-5-[(4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]imidazolidin-4-one 2a,[9] 2-thioxo-5-[(6-methyl-4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]imidazolidin-4-one 2b,[9] 2-thioxo-5-[(4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-$N^1$-methyl-$N^3$-ethyl-imidazolidin-4-one 2c, 2-thioxo-5-[(6-methyl-4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-$N^1$-methyl-$N^3$-ethyl-imidazolidin-4-one 2d, 2-thioxo-5-[(4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-$N^1$-methyl-$N^3$-phenyl-imidazolidin-4-one 2e, 2-thioxo-5-[(6-methyl-4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-$N^1$-methyl-$N^3$-phenyl) imidazolidin-4-one 2f and 2-thioxo-5-[(4-oxo-4*H*-[1]-benzopyran-3-yl) methylidene]-$N^1$-phenyl-$N^3$-ethyl-imidazolidin-4-one 2g.

*For compound 2c.* m.p.: 228–230°C, yield 83%; calc. for $C_{16}$ $H_{14}$ $N_2$ $O_3S$(314): C, 61.14; H, 4.45; N 8.92; S, 10.19; found: C, 61.18; H, 4.41; N, 8.81; S, 10.12; IR ($cm^{-1}$); 1730 (CO of hydantoin), 1650 (CO of

benzopyrane), 1325 (C=S). $H^1$-NMR (DMSO): $\delta$ (ppm) = 1.28 (3H, t, $CH_3$ of ethyl group); 2.48 (3H, s, $N^1$-$CH_3$); 4.01 (2H, q, $N^3$-$CH_2$); 6.23 (1H, s, CH chromonylidene); 7.28–8.72 (4H, m, aromatic protons); 9.07 (1H, s, CH-2 of benzopyran).

*For compound 2d.* m.p.: 258–260°C; yield: 71%; calc. for $C_{17}H_{16}N_2O_3S$ (328): C, 62.22; H, 4.88; N 8.53; S, 9.75; found: C, 62.30; H, 4.81; N, 8.62; S, 9.68; IR ($cm^{-1}$) 1740(CO of hydantoin), 1645 (CO of benzopyrane ring), 1320 (C=S); $H^1$-NMR (DMSO): $\delta$ (ppm) = 1.32 (3H, t, $CH_3$ of ethyl group); 2.38 (3H, s, $CH_3$ of benzopyran); 2.51 (3H, s, $N^1$-$CH_3$); 4.12(2H, q, $N^3$-$CH_2$); 6.31(1H, s, CH chromonylidene); 7.35–8.02 (2H, d, aromatic protons); 8.76(1H, s, CH-5 of benzopyrane); 9.12 (1H, s, CH-2 of benzopyran ring).

*For compound 2e.* m.p.; 294–296°C; yield: 68%; calc. for $C_{20}H_{14}N_2O_3S$ (362): C, 66.30; H, 3.86; N 7.73; S, 8.83; found: C, 66.35; H, 3.86; N, 7.68; S, 8.85; IR ($cm^{-1}$) 1725 (CO hydantoin), 1640 (CO of benzopyrane ring), 1320 (C=S); $H^1$-NMR(DMSO): $\delta$ (ppm) = 2.50(3H, s, $N^1$-$CH_3$); 6.57(1H, s, CH chromonylidene); 7.38–8.73 (8H, m, aromatic protons of $N^3$-ph and benzopyrane ring); 9.36 (1H, s, CH-2 of benzopyran ring).

*For compound 2f.* m.p.: 280–282°C; yield: 72%; calc. for $C_{21}H_{16}N_2O_3S$ (376): C, 67.02; H, 4.25; N 7.44; S, 8.51; found: C, 67.11; H, 4.18; N, 7.41; S, 8.48; IR ($cm^{-1}$) 1720 (CO of hydantoin), 1640 (CO of benzopyrane), 1315 (C=S); $H^1$-NMR(DMSO): $\delta$ (ppm) = 2.38 (3H, s, $CH_3$ of benzopyrane ring), 2.49 (3H, s, $N^1$-$CH_3$; 6.27 (1H, s, CH chromonylidene); 7.30–8.03 (7H, m, aromatic protons of $N^3$-ph and benzopyrane ring); 8.71 (1H, s, CH-5 of benzopyrane); 9.07 (1H, s, CH-2 of benzopyran ring).

*For compound 2g.* m.p.: 312–314°C; yield: 66%; calc. for $C_{21}H_{16}N_2O_3S$ (376): C, 67.02; H, 4.25; N 7.44; S, 8.51; found: C, 67.15; H, 4.27; N, 7.38; S, 8.42; IR ($cm^{-1}$) 1730 (CO of hydantoin), 1650 (CO of benzopyrane), 1325 (C=S); $H^1$-NMR (DMSO): $\delta$ (ppm) = 1.28 (3H, t, $CH_3$ of ethyl group); 3.92–3.95 (2H, q, $N^3$-$CH_2$); 6.23 (1H, s, CH chromonylidene); 7.28–8.03 (9H, m, aromatic protons of $N^1$-ph and benzopyrane ring); 9.59 (1H, s, CH-2 of benzopyran ring).

### *Reaction of 1a or 1b with Hydantoin (Synthesis of 3a,b)*

To a mixture of 1 a,b (0.01 mole) and hydantoin (0.01 mole) in glical acetic acid a fused sodium acetate (2 gm) was added. The reaction mixture was refluxed for 24 h for 3a and 38 h for 3b. The solid

formed on hot was filtered off, washed with ethanol and recrystallized from acetic acid to give 5-[(4-oxo-4-*H*-[1]-benzopyrane-3-yl)methylidene] imidazolidin-2,4-diones 3a or 4a and 5-[(6-methyl-4-oxo-4-*H*-[1]-benzopyrane-3-yl)methylidene]imidazolidin-2,4-diones 3b or 4b.

*For compound 3a or 4a.* m.p.; 345–348°C, yield: 38%; calc. for $C_{13}H_8N_2O_4$ (256): C, 60.94; H, 3.15; N 10.93; found: C, 61.01; H, 3.09; N, 10.89; IR ($cm^{-1}$) 3230, 3120 (2 NH); 1700, 1620 (CO at C-4 and C-2 of hydantoin), 1645 (CO of benzopyrane ring); 1610 (C=C); $H^1$-NMR (DMSO): $\delta$ (ppm) = 6.35, 6.38 (1H, 2s, CH chromonylidene structure 3a or 4a); 7.58–8.20 (8H, m, aromatic protons structure 3a or 4a); 8.78, 8.94 (2H, 2s, CH-2 of benzopyran ring structure 3a or 4a); 10.52, 11.32 (1H, 2s, 2 OH structure 3a or 4a); 11.79, 12.40 (1H, 2s, 2 NH structure 3a or 4a).

*For compound 3b or 4b.* m.p.; 310–312°C, yield: 58%; calc. for $C_{14}H_{10}N_2O_4$ (270): C, 62.22; H, 3.73; N 10.37; found: C, 62.31; H, 3.68; N, 10.29; IR ($cm^{-1}$) 3250, 3130 (2 NH); 1710, 1630 (CO at C-4 and C-2 of hydantoin), 1650 (CO of benzopyrane ring); 1620 (C=C); $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.51, 2.53 (3H, 2s, 2 $CH_3$ structure 3b or 4b); 6.33, 6.36(1H, 2s, CH chromonylidene structure 3b or 4b); 7.53–7.88 (4H, 2d, aromatic protons structure 3b or 4b); 8.14, 8.18 (1H, 2s, CH-5 of benzopyrane structure 3b or 4b); 8.74, 8.91 (2H, 2s, CH-2 of benzopyran ring structure 3b or 4b); 10.31, 11.29 (1H, 2s, 2 OH structure 3b or 4b); 11.77, 12.38 (1H, 2s, 2 NH structure 3b or 4b). MS: m/z = 272, ($M^+ + 2$, 100%, $C_{14}H_{10}N_2O_4^+$); 271($M^+ + 1$, 7.8%); 270($M^+$, 1.9%, $C_{14}H_{10}N_2O_4$); 186(13.7%, $C_{12}H_{10}O_2^+$); 185 (95.5%, $C_{12}H_9O_2^+$); 159 (3.7%, $C_{10}H_7O_2^+$).



## *Reaction of 2a or 2b with Formaldehyde and Morpholin (Synthesis of 5a,b)*

A mixture of 2a or 2b (0.01 mole), formaldehyde (1.0 mole, 40% solution) and morpholine (0.01 mole) in ethanol (30 ml) was stirred at room temperature for 48 h (TLC), the solid formed filtered off washed with ethanol and recrystallized from acetic acid to give 2-thioxo-5-[(4-oxo-4-*H*-[1]-benzopyrane-3-yl)methylidene]-$N^3$-morpholinomethyl-imidazolidin-4-one 5a and 2-thioxo-5-[(6-methyl-4-oxo-4-*H*-[1]-benzopyrane-3-yl)methylidene]-$N^3$-morpholinomethyl-imidazolidin-4-one 5b.

*For compound 5a.* m.p.: 298–300°C; yield 73%, calc. for $C_{18}H_{17}N_3O_4S$(371): C, 58.22; H, 4.16; N 11.31; S, 8.63; found: C, 58.18; H, 4.28; N, 11.40; S, 8.59; IR ($cm^{-1}$) 3110 (NH); 2980 (CH aliphatic); 1730(CO hydantoin), 1650 (CO of benzopyrane ring), 1330 (C=S). $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.61 (4H, t, 2 C—$CH_2$-N); 3.24–3.58 (4H, t,

2 C—$CH_2$-O); 4.67 (2H, s, N—$CH_2$-N); 6.32(1H, s, CH chromonylidene); 7.55–8.16 (4H, m, aromatic protons); 8.91 (1H, s, CH-2 of benzopyran ring); 12.15 (1H, s, $N^1$-H).

*For compound 5b.* m.p.: 284–286°C; yield 75%, calc. for $C_{19}H_{19}N_3O_4S$ (385): C, 59.22; H, 4.93; N 10.91; S, 8.31; found: C, 59.31; H, 4.87; N, 10.86; S, 8.22; IR ($cm^{-1}$) 3120 (NH); 2950 (CH aliphatic); 1725 (CO hydantoin), 1640 (CO of benzopyrane ring), 1325 (C=S). $H^1$-NMR(DMSO): $\delta$ (ppm) = 2.45 (3H, s, $CH_3$ of benzopyrane); 2.61 (4H, t, 2 C—$CH_2$—N); 3.53–3.56 (4H, t, 2 C—$CH_2$—O); 4.68 (2H, s, N—$CH_2$—N); 6.35 (1H, s, CH chromonylidene); 7.60–7.71(2H, d, aromatic protons of benzopyrane ring); 7.94 (1H, s, CH-5 of benzopyran ring) 8.88 (1H, s, CH-2 of benzopyran ring); 12.012 (1H, s, $N^1$-H).

### *Reaction of 2a or 2b with Methyl Iodide (Synthesis of 6a, b)*

Potassium hydroxide solution (0.01 mole in 10 ml water) was added to suspended solution of compound 2a or 2b in 30 ml ethanol. The reaction mixture become dark brown. Methyl iodide (0.03 mole) in 10 ml ethanol was added dropewise, the reaction mixture was kept under stirring for 3h (TLC), the solid formed filtered off, washed with water and ethyl alcohol, recrystallized from acetic acid to give 2-methylthio-5-[(4-oxo-4-*H*-[1]-benzopyrane-3-yl)methylidene] imidazolidin-4-one 6a and 2-methylthio-5-[(6-methyl-4-oxo-4-*H*-[1]-benzopyrane-3-yl)methylidene]imidazolidin-4-one 6b.

*For compound 6a.* m.p.: 200–202°C, yiled 82%; calc. for $C_{14}H_{10}N_2O_3S$ (286): C, 58.74; H, 3.49; N 9.79; S, 11.19; found: C, 58.71; H, 3.42; N, 9.81; S, 11.25; IR ($cm^{-1}$); 1725 (CO hydantoin), 1655 (CO of benzopyrane ring), 1595 (C=N). $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.72 (3H, s, S—Me); 6.93 (1H, s, CH chromonylidene); 7.62–8.01 (4H, m, aromatic protons of benzopyrane ring); 8.22 (1H, s, CH-2 of benzopyran ring); 12.01 (1H, s, $N^1$-H).

*For compound 6b.* m.p.: 212–214°C, yield 85%; reaction time 3 h.; calc. for $C_{15}H_{12}N_2O_3S$(300): C, 60.00; H, 4.00; N 9.33; S, 10.66; found: C, 59.94; H, 4.15; N, 9.28; S, 10.71; IR ($cm^{-1}$); 1710 (CO hydantoin), 1650 (CO of benzopyrane ring), 1590 (C=N). $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.50 (3H, s, $CH_3$ of benzopyrane); 2.67 (3H, s, S-Me); 6.90(1H, s, CH chromonylidene); 7.57–7.85 (2H, d, aromatic protons of benzopyrane ring); 8.16 (1H, s, CH-5 of benzopyrane ring); 8.61 (1H, s, CH-2 of benzopyran ring); 11.91 (1H, s, $N^1$-H). Ms: m/z = 300 ($M^+$, 38.6, $C_{15}H_{12}N_2O_3S^+$), 286 (100%, $C_{14}H_{10}N_2O_3S$); 253 (17.9%, $C_{14}H_9N_2O_3$); 199 (52.2%, $C_{12}H_9NO_2$); 185 (12%, $C_{12}H_9O_2$).

### *Acid Hydrolysis of Compound 6a and 6b*

A mixture of each of compound 6a or 6b (0.01 mole) in ethanol (30 ml) and concentrated hydrochloric acid (10 ml) was refluxed for 3 h. The reaction mixture was concentrated to half its volume, cooled, and filtered off by washing with water several times and recrystallized from acetic acid. M.p. and mixed m.p. with compounds 3a,b gave no depression.

### *Reaction of Compounds 2a or 2b with Phenacyl Bromide (Synthesis of 7a,b)*

A mixture of compound 2a or 2b (0.01 mole) in ethanol (30 ml), potassium hydroxid solution (0.01 mole in 10 ml water), and phenacyl bromide (0.011 mole, 2.2 g) was stirred at room temerature for 3 h (TLC), the reaction mixture was triturated with water. The sloid product was filtered off, washed with water, and recrystallized from DMF to give 2-benzoylmethylthio-5-[(4-oxo-4*H*-[1]-benzopyran-3-yl)-methylidene]imidazolidin-4-one 7a and 2-benzoylmethylthio-5-[(6-methyl-4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]imidazolidin-4-one 7b.

*For compound 7a.* m.p.: 296–298°C, yield 74%; calc. for $C_{21}H_{14}N_2O_4S$ (390): C, 64.61; H, 3.59; N 7.18; S, 8.20; found: C, 64.65; H, 3.48; N, 7.22; S, 8.26; IR ($cm^{-1}$); 3230 (NH); 1730 (CO of hydantoin), 1695 (CO of benzoyl); 1645 (CO of benzopyrane), 1590 (C=N); $H^1$-NMR (DMSO): $\delta$ (ppm) = 4.94 (2H, s, S—$CH_2 \cdot$ CO); 6.31 (1H, s, CH chromonylidene); 7.45–8.85 (8H, m, aromatic protons of benzopyrane and phenyl group); 8.97(1H, s, CH-2 of benzopyran ring); 12.35 (1H, s, $N^1$–H); $^{13}$C-NMR (DMSO) $\delta$ (ppm) = 40.52 ($CH_2$ of benzoylmethyl); 103.98 (C of chromonylidene); 111.29; 119.77; 120.202; 124.52; 127.23; 127.95; 130.039; 135.59; 136.26; 140.63; 15 6.84; 157.12(aromatic carbon atoms); 161.03; 161.71 ($C_2$, $C_3$ of benzopyrane); 166.65 ($C_2$ of hydantoin); 166.75 (C=N); 171.30 ($C_4$ of hydantoin); 177.202 (CO of hydantoin); 179.11(CO of benzopyrane); 194.76(CO of benzyol ring). Ms: m/z = 390 ($M^+$, 3%, $C_{21}H_{14}N_2O_4S^+$), 272 (100%, $C_{13}H_8N_2O_3S^+$); 185 (53%, $C_{11}H_7NO_2$); 120 (52.9 $C_8H_8O$); 105(58%, $Ph.CO.^+$); 77 (39.5%, $C_6H_5^+$).

*For compound 7b.* m.p.: 310–312°C, yield 76%; calc. for $C_{22}H_{16}N_2O_4S$ (404): C, 65.34; H, 3.96; N 6.93; S, 7.96; found: C, 65.28; H, 3.89; N, 6.88; S, 7.94; IR ($cm^{-1}$); 3225 (NH); 1725 (CO hydantoin), 1690 (CO of benzoyl); 1645 (CO of benzopyrane ring), 1590 (C=N). $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.48 (3H, s, $CH_3$ of benzopyrane) 4.93 (2H, s, S—$CH_2 \cdot$ CO); 6.096 (1H, s, CH chromonylidene); 7.49–8.095 (7H,m,aromatic protons of benzopyrane and phenyl group); 8.88 (1H, s, CH-5 of benzopyrane); 9.54(1H, s, CH-2 of benzopyran ring); 11.92 (1H, s, $N^1$-H); Ms:

m/z = 404 ($M^+$, 2.1%, $C_{22}H_{16}N_2O_4S^+$), 286 (100%, $C_{14}H_{10}N_2O_3S$); 200 (10.2%, $C_{12}H_{10}NO_2$); 119(4.7%, $Ph.CO \cdot CH_2^+$); 105 (50.7%, $Ph.CO^+$); 77 (39.5%, $C_6H_5^+$).

### *Reaction of Compound 2a or 2b with Chloroacetic Acid (Synthesis of 9a,b)*

Potassium hydroxide solution (0.01 mole, .56 g in 10 ml water) was added to suspended solution of compound 2a or 2b (0.01 mole in 40 ml ethanol). The reaction mixture become dark brown, chloroacetic acid solution (0.01 mole in 10 ml. ethanol) was added dropwise to the reaction mixture. The reaction mixture was stirred over neight at room temperature (TLC), the solid formed filtered off washed with water and recrystallized from acetic acid to give 2-carboxymethyl-5-[(4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]imidazolidin-4one 9a and 2-carboxymethyl-5-[(6methyl-4-oxo-4*H*-[1]benzopyran-3-yl)methylidene]imidazolidin-4-one 9b.



*For compound 9a.* m.p.: above 350°C; yield 82%, reaction time 14 h.; IR ($cm^{-1}$); 3340(brode band OH); 3240(NH); 1745 (CO of COOH); 1725 (CO hydantoin); 1645(CO of benzopyrane ring), 1590 (C=N); $H^1$-NMR (DMSO): $\delta$ (ppm) = 4.74 (2H, s, $S{-}CH_2 \cdot COOH$); 6.25 (1H, s, CH chromonylidene); 7.42–7.83 (4H,m,aromatic protons of benzopyrane ring); 8.92 (1H, s, CH-2 of benzopyran ring); 11.83 (1H, s, $N^1$-H); 12.32 (1H, s, OH).

*For compound 9b.* m.p.: above 350°C; yield 85%, reaction time 13 h.; solvent of crystallization acetic acid, IR ($cm^{-1}$): 3320 (brode band OH); 3230 (NH); 1740(CO of carboxylic group); 1730 (CO hydantoin); 1640 (CO of benzopyrane ring), 1595 (C=N). $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.43 (3H, s, $CH_3$ of benzopyrane), 4.85 (2H, s, $S{-}CH_2 \cdot COOH$); 6.29 (1H, s, CH chromonylidene); 7.56–7.63 (2H, d, aromatic protons of benzopyrane ring); 7.89 (1H, s, CH-5 of benzopyrane); 9.83 (1H, s, CH-2 of benzopyran ring); 11.71 (1H, s, $N^1$-H); 12.37 (1H, s, OH).

### *Reaction of 9a or 9b with Acetic Anhydride (Synthesis of 10a,b)*

Compound 9a or 9b (0.01 mole) in acetic anhydride (30 ml) was refluxed for 6–8 h until the starting material was consumed (TLC). The reaction mixture was coold and poured on ice cold water, the solid formed filterd off and recrystallised from acetic acid to give 5-[(4-oxo-4*H*-[1]-benzopyrane-3-yl)methylidene]imidazo-[2,1-b]thiazole-3,6-diones 10a and 5-[(6-methyl-4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-imidazo-[2,1-b]thiazole-3,6-diones 10b.

*For compound 10a.* m.p.: 258–260°C; yield 52%, reaction time 8 hours, calc. for $C_{15}H_8N_2O_4S$(312): C, 57.69; H, 2.56; N 8.97; S, 10.25; found: C, 57.72; H, 2.53; N, 9.02; S, 10.15; IR ($cm^{-1}$); 1760 (CO of thiazol ring); 1730 (CO hydantoin); 1650 (CO of benzopyrane ring), 1600 (C=N). $H^1$-NMR (DMSO): $\delta$ (ppm) = 4.12 (2H, s, S—$CH_2$); 6.22 (1H, s, CH chromonylidene); 7.28–7.82 (4H,m,aromatic protons of benzopyrane ring); 9.11 (1H, s, CH-2 of benzopyran ring).

*For compound 10b.* m.p.: 272–274°C, yield 58%, reaction time 6 hours, calc. for $C_{16}H_{10}N_2O_4S$ (326): C, 58.90; H, 3.06; N 8.58; S, 9.81; found: C, 58.87; H, 3.10; N, 8.51; S, 9.84; IR ($cm^{-1}$); 1755 (CO of thiazol ring); 1725 (CO hydantoin); 1650 (CO of benzopyrane ring), 1595 (C=N). $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.38 (3H, s, $CH_3$ of benzopyrane), 4.01(2H, s, S—$CH_2$); 6.18 ((1H, s, CH chromonylidene); 7.12–7.28 (2H, d, aromatic protons of benzopyrane ring); 7.78 (1H, s, CH-5 of benzopyrane); 8.92 (1H, s, CH-2 of benzopyrane).



## *Reaction of 6a or 6b with Morpholine (Synthesis of 11a,b)*

A mixture of 6a or 6b (0.01 mole) in 30 ml. ethyl alcohol and morpholine (0.015 mole) was refluxed until the starting matrial was consumed (TLC). The reaction mixture was evaporated to dryness under vacum, the residue was crystallized from acetic acid to give 2-morpholino-5-[(4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-glycocyamidine 11a and 2-morpholino-5-[(6-methyl-4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-glycocyamidine 11b.

*For compound 11a.* m.p.: above 350°C, yield 76%, reaction time 5 h, calc. for $C_{17}H_{15}N_3O_4$ (325): C, 62.77; H, 4.61; N 12.92; found: C, 62.81; H, 4.56; N, 12.88; IR ($cm^{-1}$); 3220 (NH); 1710 (CO hydantoin); 1650 (CO of benzopyrane ring), 1595 (C=N); $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.51(4H, t, 2 $CH_2$-N), 3.22 (4H, t, 2 $CH_2$-O); 6.35 ((1H, s, CH chromonylidene); 7.60–7.94 (4H,m,aromatic protons of benzopyrane ring); 8.88 (1H, s, CH-2 of benzopyrane); 12.10 (1H, s, $N^1$-H).

*For compound 11b.* m.p.: above 350°C, yield 78%, reaction time 6 h., calc. for $C_{18}H_{17}N_3O_4$ (339): C, 63.71; H, 5.01; N 12.39; found: C, 63.77; H, 4.94; N, 12.28; IR ($cm^{-1}$); 3230 (NH); 1720 (CO hydantoin); 1655 (CO of benzopyrane ring), 1590 (C=N); $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.41 (3H, s, $CH_3$ of benzopyrane), 2.62(4H, t, 2 $CH_2$-N), 3.45(4H, t, 2 $CH_2$-O); 6.45 ((1H, s, CH chromonylidene); 7.68–7.96 (2H, d, aromatic protons of benzopyrane ring); 8.86 (1H, s, CH-5 of benzopyrane); 8.93 (1H, s, CH-2 of benzopyrane); 11.96 (1H, s, $N^1$-H).

### *Reaction of 6a or 6b with Piprazene (Synthesis of 12a,b)*

A mixture of 6a or 6b (0.01 mole) in 40 ml. ethanol and piprazene (0.01 mole) was refluxed until the starting material was conusumed (TLC), the reaction mixture was evaporated to dryness under vacuum, the residue was crystallized from DMF to give 2-piprazeno-5-[(4-oxo-4*H*-benzopyran-3-yl)methylidene]-glycocyamidine 12a and 2-piprazeno-5-[(6-methyl-4-oxo-4*H*-benzopyran-3-yl)methylidene]-glycocyamidine 12b.

*For compound 12a.* m.p.: 318–320°C, yield 67%, reaction time 8 h.; calc. for $C_{17}H_{16}N_4O_3$ (324): C, 62.69; H, 4.94; N 17.28; found: C, 63.02.; H, 4.91; N, 17.31; IR ($cm^{-1}$); 3245 (NH hydantoin); 3210 (NH piprazene); 1710 (CO hydantoin); 1645 (CO of benzopyrane ring), 1595 (C=N); $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.51 (4H, t, 2 $CH_2$-N); 2.85 (4H, t, 2 $CH_2$-N); 6.31 ((1H, s, CH chromonylidene); 7.48–7.87 (4H,m,aromatic protons of benzopyrane ring); 8.76 (1H, s, CH-2 of benzopyrane); 10.25(1H, s, NH piprazene); 11.23 (1H, s, $N^1$-H of hydantoin); Ms: m/z = 324 ($M^+$,2.2%, $C_{17}H_{16}N_4O_3^+$), 286 (19.4%, $C_{15}H_{15}$ $N_3$ $O_3$); 256 (100%, $C_{13}H_{10}N_3O_3$); 185(65%, $C_{11}H_7NO_2$); 86 (14%, $C_4H_{10}N_2^+$).

*For compound 12b.* m.p.: 305–307°C, yield 71%, reaction time 10 h.; calc. for $C_{18}H_{18}N_4O_3$ (338): C, 63.90; H, 5.32; N16.57; found: C, 63.94; H, 5.29; N, 16.53; IR ($cm^{-1}$); 3250 (NH hydantoin); 3200 (NH piprazene); 1710(CO hydantoin); 1650 (CO of benzopyrane ring), 1595 (C=N). $H^1$-NMR(DMSO): $\delta$ (ppm) = 2.401 (3H, s, $CH_3$ of benzopyrane); 2.49(4H, t, 2 $CH_2$-N); 2.67 (4H, t, 2 $CH_2$-N); 6.87 ((1H, s, CH chromonylidene); 7.51–7.61 (2H, d, aromatic protons of benzopyrane ring); 7.89(1H, s, CH-5 of benzopyrane); 9.51 (1H, s, CH-2 of benzopyrane); 11.69 (2H, brode band, 2NH piprazene, and hydantoin); Ms: m/z = 338 ($M^+$, 2%, $C_{18}H_{18}N_4O_3^+$), 253 (48%, $C_{14}H_9$ $N^2$ $O_3$); 199 (97%, $C_{12}H_9$ $NO_2$); 86 (15.7%, $C_4H_{10}N_2^+$).

### *Reaction of 6a or 6b with Anthranilic Acid (Synthesis of 13a,b)*

A mixture of 6a or 6b (0.01 mole) and anthranilic acid (0.011 mole) was heated under reflux in absolute ethanol until the starting material was consumed (TLC). The reaction mixture was coold the sloid filtered off and recrystallized from acetic acid to give $N^2$-(o-carboxyphenyl)-5-[(4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-glycocyamidine 13a and $N^2$-(o-carboxyphenyl)-5-[(6-methyl-4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]–glycocyamidine 13b.

*For compound 13a.* m.p.: above 350°C, yield 48%, reaction time 72 h; calc. for $C_{20}H_{13}N_3O_5$ (375): C, 64.00; H, 3.46; N 11.20; found: C, 64.12.; H, 3.38; N, 11.28; IR ($cm^{-1}$); 3350 (OH); 3150 (NH hydantoin);

1715 (CO hydantoin); 1680 (CO of carboxylic group); 1645 (CO of benzopyrane ring), 1585 (C=N). $H^1$-NMR (DMSO): $\delta$ (ppm) = 6.34, ((1H, 2s, CH chromonylidene); 7.50–7.81 (8H, m, aromatic protons of benzopyrane ring and anthranlic acid); 8.74, (1H, 2s, CH-2 of benzopyrane); 10.32, (1H, s, OH); 11.87, (1H, s, NH); 12.13, ((1H, s, $N^1$-H of hydantoin).

*For compound 13b.* m.p.: above 350°C; yield 54%, reaction time 78 h.; calc. for $C_{21}H_{15}N_3O_5$ (389): C, 64.78; H, 3.86; N 10.79; found: C, 64.82.; H, 3.81; N, 10.71; IR ($cm^{-1}$); 3360 (OH); 3165 (NH hydantoin); 1720 (CO hydantoin); 1695 (CO of carboxylic group); 1640 (CO of benzopyrane ring), 1590 (C=N). $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.41, (3H, s, $CH_3$ of benzopyrane), 6.32 (1H, s, CH chromonylidene); 7.50–7.86 (6H, m, aromatic protons); 8.74 (1H, s, CH-5 of benzopyrane); 8.91 (1H, 2s, CH-2 of benzopyrane); 11.57 (1H, s, OH); 12.01 (H, s, NH); 12.13 (1H, 2s, $N^1$-H of hydantoin). $^{13}$C-NMR (DMSO) $\delta$ (ppm) = 22.25 ($CH_3$ of benzopyrane); 104.15(C of chromonylidene); 110.95; 119.58; 119.98; 120.08; 120.39; 124.32; 126.54; 130.55; 137.29; 137.35; 155.33; 155.43; (aromatic carbon atoms); 137.69 ($C_5$ of hydantoin); 161.01; 161.63 ($C_2$, $C_3$ of benzopyrane); 166.73 ($C_2$ of hydantoin); 177.31 (CO of carboxylic group); 177.36 ($C_4$ of hydantoin); 179.01 (CO of benzopyrane).



### *Reaction of 6a or 6b with Glycine (Synthesis of 14a,b or 15a,b)*

A mixture of 6a or 6b (0.01 mole) and glycine (0.011 mole) was grinded together and fused in an oil bath at 140–150°C for 2–3 h. The reaction mixture was allowed to cool to room temperature, the obtained solid was dissolved in a solution of 5% NaOH and then acidified by dilute HCl (10%), the solid formed was filtered off and crystallized from acetic acid to give 3-[(4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-1,6-dihydro-imidazo[1,2-a]-imidazole-2,5-diones 14a or 15a and 3-[(6-methyl-4-oxo-4*H*-[1]-benzopyran-3-yl)methylidene]-1,6-dihydro-imidazo[1,2-a]-imidazole-2,5-diones 14b or 15b.

*For compound 14a or 15a.* m.p.: 260–262°C, yield 68%, reaction time 2 h.; calc. for $C_{15}H_9N_3O_4$ (295): C, 61.01; H, 3.05; N 14.23; found: C, 60.92.; H, 3.01; N, 14.32; IR ($cm^{-1}$); 3230 (NH); 1760 (CO of amino acid moity); 1720 (CO hydantoin); 1655 (CO of benzopyrane ring); 1600 (C=N). $H^1$-NMR (DMSO): $\delta$ (ppm) = 4.10, 4.23(2H, 2s, $CH_2$ of amino acid structure 15a or 16a); 6.35, 6.38 ((1H, 2s, CH chromonylidene structure 15a or 16a); 7.55–7.94 (8H, m, aromatic protons of benzopyrane ring 15a or 16a); 8.89, 8.92 (1H, 2s, CH-2 of benzopyrane structure 15a or 16a); 11.07, 11.78 (1H, 2s, NH structure 15a or 16a).

*For compound 14b or 15b.* m.p.: 242–244°C, yield 72%, reaction time 2 h; calc. for $C_{16}H_{11}N_3O_4$ (309): C, 62.13; H, 3.55; N 13.59; found: C, 62.19; H, 3.51; N, 13.52; IR ($cm^{-1}$); 3225 (NH); 1750 (CO of amino acid moity); 1715 (CO hydantoin); 1645 (CO of benzopyrane ring); 1600 (C=N); $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.51, 2.53 (3H, 2s, $CH_3$ of benzopyrane ring structure 15b or 16b); 4.10,4.15 (2H, 2s, $CH_2$ of amino acid structure 15b or 16b); 6.38, 6.39 ((1H, 2s, CH chromonylidene structure 15b or 16b); 7.54–7.90 (4H, m, aromatic protons of benzopyrane ring 15b or 16b); 8.17, 8.21 (1H, 2s, CH-5 of benzopyrane structure 15b or 16b); 8.83, 8.93 (1H, 2s, CH-2 of benzopyrane structure 15a or 16a); 11.78, 12.41 (1H, 2s, NH structure 15b or 16b).

### *Reaction of 2a or 2b with Diazomethane: (Synthesis of 6a,b and 16a,b)*

An ethereal diazomethane solution (prepared from 10 g. nitrosomethylurea) was added to 0.01 mole of 1a or 1b suspended in 30 ml of dry ether. The reaction mixture was kept in ice bath with vigorous stirring until the starting material was consumed (TLC). The solvent was evaporated to dryness under vacuum and the solid product was chromatographed on silica gel (100/200 mech) by using ethylacetate/petroleum ether 60–80 (1: 3, v/v) as an eluent to yield 6a,b (yield 26%) and 2-tioxo-5-[(-4-oxo-4*H*-[1]-benzopyrane-3-yl)methylidene]-$N^3$-methyl-imidazolidin-4-one 16a and 2-thioxo-5-[(6-methyl-4-oxo-4*H*-[1]-benzopyrane-3-yl)methylidene]-$N^3$-methyl-imidazolidin-4-one 16b (yield 52%).

*For compound 16a.* m.p.: 210–212°C; yield 52%; calc. for $C_{14}H_{10}N_2O_3S$ (286) C, 58.74; H, 3.49; N 9.79 S, 11.18; found: C, 58.69; H, 3.52; N, 9.71; S, 11.12; IR ($cm^{-1}$); 3205 (NH), 1735 (CO hydantoin), 1645 (CO of benzopyrane ring), 1340 (C=S). $H^1$-NMR (DMSO): $\delta$ (ppm) = 4.22 (3H, s, $N^3$-$CH_3$), 6.35 (1H, s, CH chromonylidene), 7.52–8.22 (4H, m, aromatic protons), 8.67 (1H, s, CH-2 of benzopyrane ring); 11.82 (1H, s, N–H).

*For compound 16b.* m.p.: 224–226°C; yield 47%; calc. for $C_{15}H_{12}N_2O_3S$ (300) C, 60.00; H, 4.00; N 9.33; S, 10.66; found: C, 59.86; H, 4.08; N, 9.25; S, 10.58; IR ($cm^{-1}$); 3195 (NH), 1740 (CO hydantoin), 1650 (CO of benzopyrane ring), 1350 (C=S). $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.48 (3H, s, $CH_3$ of benzopyrane), 4.18 (3H, s, $N^3$-$CH_3$), 6.28 (1H, s, CH chromonylidene), 7.56–7.65 (2H, d, aromatic protons), 8.07 (1H, s, CH-5 of benzopyrane), 8.72 (1H, s, CH-2 of benzopyrane ring); 11.15 (1H, s, N–H).

### *Reaction of 2a or 2b with Diphenylaiazomethane (Synthesis of 17a,b)*

Diphenyldiazomethane (0.011 mole) in dry benzene (20 ml) was added to a suspension of each compound, 2a or 2b, in 50 ml dry benzene. The reaction mixture was refluxed until the starting material was consumed (TLC). The solvent was evaporated to dryness under vacuum and the obtained solid was purified by silica gel and crystallized from acetic acid to give 2-thioxo-5-[(4-oxo-4-*H*-[1]-benzopyrane-3-yl)methylidene]-$N^3$-diphenylmethyl-imidazolidin-4-one 17a and 2-thioxo-5-[(6-methyl-4-oxo-4-*H*-[1]-benzopyrane-3-yl)methylidene]-$N^3$-diphenylmethyl-imidazolidin-4-one 17b.

*For compound 17a.* m.p.: 285–287°C; yield 46%; calc. for $C_{26}H_{18}N_2O_3S$ (348) C, 71.23; H, 4.11; N 6.39; S, 7.30; found: C, 71.31; H, 4.02; N, 6.32; S, 7.42; IR ($cm^{-1}$); 3210 (NH), 1735 (CO hydantoin), 1640 (CO of benzopyrane ring), 1335 (C=S). $H^1$-NMR (DMSO): $\delta$ (ppm) = 5.82 (3H, s, $N^3$-CH), 6.38 (1H, s, CH chromonylidene), 7.44–8.12 (14H, m, aromatic protons), 8.72 (1H, s, CH-2 of benzopyrane ring); 11.87 (1H, s, N—H).

*For compound 17b.* m.p.: 298–300°C; yield 43%; calc. for $C_{27}H_{20}N_2O_3S$ (452) C, 71.68; H, 4.42; N 6.19; S, 7.08; found: C, 71.82; H, 4.38; N, 6.22; S, 6.93; IR ($cm^{-1}$); 3215 (NH), 1730 (CO hydantoin), 1640 (CO of benzopyrane ring), 1350 (C=S). $H^1$-NMR (DMSO): $\delta$ (ppm) = 2.52 (3H, s, $CH_3$ of benzopyrane), 5.78 (1H, s, $N^3$-CH), 6.33 (1H, s, CH chromonylidene), 7.32–8.14 (13H, m, aromatic protons), 8.12 (1H, s, CH-5 of benzopyrane), 8.63 (1H, s, CH-2 of benzopyrane ring); 12.13 (1H, s, N—H).



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