Studies on the Reactivity of New Types of Tetracyclic-1,5-Benzoxazepines: Part V

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The syntheses of tetracyclic 1,5-benzoxazepines **3a-e** from heterocyclic β-chloroaldehydes **1a-e** and 2-aminophenol are reported herein (Scheme I). Attempted lithium aluminium hydride ($LiAlH_4$) reduction of the imine double bond in **3a-e** failed to furnish the corresponding saturated compounds **5a-e**. Attempted catalytic hydrogenation of **3a-e** in the presence of acetic acid and acetic anhydride gave surprisingly only the acetoxy derivatives **6a-e** in high yields (Scheme II). Base catalysed hydrolysis of acetoxy derivatives **6a-e** furnished, as expected, the corresponding phenolic derivatives **7a-e**, in moderate yields. Attempted cyclofunctionalization of **3a-e** either with mercaptoacetic acid or its methyl ester to obtain the new pentacyclic heterocycles **4a-e** was, however, not successful.

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Introduction.

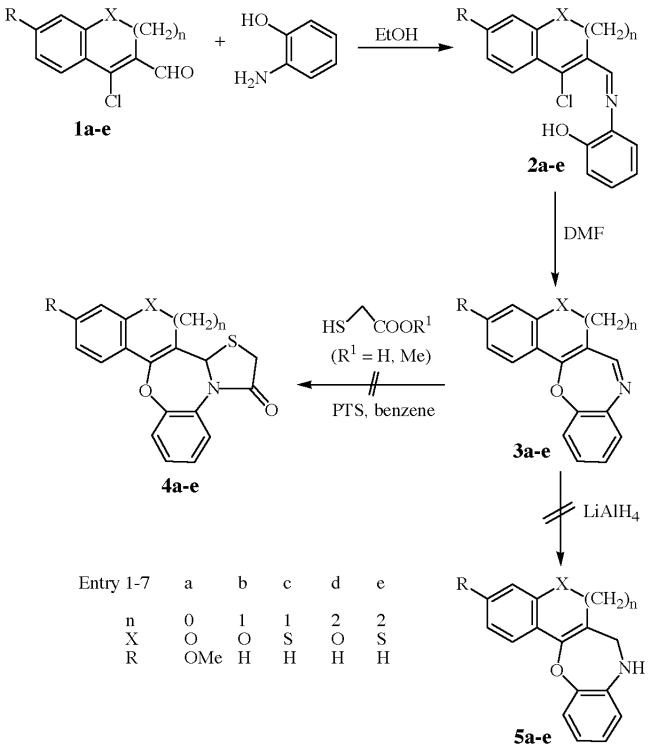
Although condensed seven membered heterocycles have been the subject of intensive study on their syntheses in the light of their antihelmentic [1] activity, surprisingly little work has been reported in the literature [1-8] on the preparation of such heterocycles. In a broad program to synthesize such polycyclic heterocycles, and in continuation of our studies [9-12] concerning the synthetic utility of heterocyclic β-chloroaldehydes, the syntheses of new tetracyclic 1,5-benzoxazepines have been achieved successfully in a simple way. This paper describes the synthesis and reactivity of these tetracyclic-1,5-benzoxazepines **3a-e** as detailed below.

Results and Discussion.

Heterocyclic β-chloroaldehydes [9-12] (**1a-e**) were condensed with 2-aminophenol to yield the intermediate imino derivatives (**2a-e**), as expected, in good yields. Cyclization of **2a-e** in refluxing DMF gave the anticipated 1,5-benzoxazepines (**3a-e**) in good yields (Scheme I).

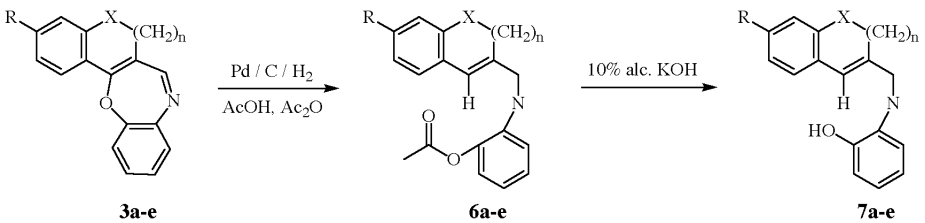
The structures assigned to these tetracyclic heterocycles (**3a-e**) were confirmed by spectroscopic and analytical data. An interesting feature of the ^{1}H-nmr spectra of these 1,5-benzoxazepines (**3a-e**) is the high field ^{1}H-nmr signal of the iminic protons in comparison with that shown by the corresponding aldimines (-CH=N-) in **2a-e**.

Scheme 1



Entry 1-7	a	b	c	d	e
n	0	1	1	2	2
X	O	O	S	O	S
R	OMe	H	H	H	H

Scheme 2



Paradisi and co-workers [3,4] have also made similar observations in 6*H*-quino[2,3-*b*][1,5]benzoxazepines. The attempted reduction of the imine double bond in **3a-e** using $LiAlH_4$ to generate the corresponding dihydro derivatives (**5a-e**), however, was unsuccessful. The attempted cyclofunctionalization of the imine double bond in **3a-e** with either mercaptoacetic acid, its methyl ester under the influence of *p*-toluene sulfonic acid (PTS), or Nafion H (super acid) as catalysts to furnish the expected pentacyclic heterocycles (**4a-e**) was also unsuccessful (Scheme I). Catalytic hydrogenation of **3a-e** in the presence of palladium on carbon (Pd/C) in acetic acid and acetic anhydride medium failed to give the desired products **5a-e**. Instead, hydrogenolysis occurred to yield the acetoxy derivatives (**6a-e**) (Scheme II). In order to confirm the structure of the acetoxy derivatives (**6a-e**), these were subjected to hydrolysis with 10% alcoholic KOH to obtain the expected phenolic derivatives (**7a-e**) in moderate yields. The presence of a singlet at δ 2.55 ppm in the ^{1}H nmr spectra of **6a-e** confirmed the presence of the acetoxy group (OCOMe) group. The typical absence of this signal in the ^{1}H nmr spectra of **7a-e** proved the assigned structure for **7a-e**.

EXPERIMENTAL

Melting points were determined with a Büchi 535 melting point apparatus and reported uncorrected. UV-Vis spectra were measured with a Shimadzu UV-2100S spectrophotometer. The ir spectra (potassium bromide) were recorded with a Perkin-Elmer 983 spectrophotometer. The ^{1}H nmr spectra were measured with a Varian EM-390 (90 MHz) spectrophotometer, and Bruker (400 MHz) using deuterochloroform as the solvent and tetramethylsilane as the internal standard. The mass spectra were recorded on a Varian MAT CH-7 and Finnigan MAT 8230 spectrometer operating in electron impact mode at 70 eV. ACME silica gel (60 - 120 mesh) was used for column chromatography. Anhydrous sodium sulphate was used as the drying agent.

Absolute ethanol and 2-aminophenol were purchased from Merck. The heterocylic chloroaldehydes **1a-e** were prepared according to literature procedures [9-12].

General Procedure for the Synthesis of Aldimines **2a-e**.

To a solution of heterocyclic β-chloroaldehydes [9-12] **1a-e** (5 mmoles) in absolute ethanol (25 ml) was added in small portions over a 10 minute period 2-aminophenol (5 mmoles) and the reaction mass was stirred at room temperature for 30 minutes. The aldimines (**2a-e**) that formed were collected by filtration and recrystallized from carbon tetrachloride. The following compounds were prepared by following the above-mentioned procedure with the appropriate reactants.

2-[[(3-Chloro-6-methoxy-2-benzofuranyl)methylene]amino]-phenol (**2a**).

This compound was obtained from 3-chloro-6-methoxybenzofuran-2-carboxaldehyde (**1a**), (1.05 g, 5 mmoles) and 2 aminophenol (0.54 g, 5 mmoles). Recrystallization of the crude product from carbon tetrachloride gave a yellow crystalline solid (1.2 g, 80%), mp 158-160°; ir: ν OH 3420, ν CN 1630, 1240 cm^{-1}; ^{1}H-NMR: δ 3.92 (s, 3H, Ar-OMe), 6.9 - 7.66 (m, 7H, aromatic), 8.73 (s, 1H, -C*H*=N-); ms: m/z 301 (M^+), 266 (M^+-Cl), 265 (M^+-Cl-H). UV-Vis: λ_{max} (methanol) (logε)/nm 204 (2.82), 241 (2.28), 337 (2.72) and 375 (2.83).

Anal. Calcd. for $C_{16}H_{12}ClNO_3$: C, 63.78; H, 3.98; N, 4.65. Found: C, 64.10; H, 3.51; N, 4.39.

2-[[(4-Chloro-2*H*-1-benzopyran-3-yl)methylene]amino]phenol (**2b**).

This compound was obtained from 4-chlorochromene-3-carboxaldehyde (**1b**), (0.97 g, 5 mmoles) and 2 aminophenol (0.54 g, 5 mmoles). Recrystallization of the crude product from carbon tetrachloride gave a yellow crystalline solid (1.11 g, 78%), mp 156-158°; ir: ν OH 3500, ν CN 1640, 1420 cm^{-1}; ^{1}H-NMR: δ 5.26 (s, 2H, -O-CH_2-), 6.68 - 7.76 (m, 8H, aromatic), 8.87 (s, 1H, -C*H*=N-); ms: m/z 285 (M^+), 268 (M^+-OH), 250 (M^+-Cl), 249 (M^+-Cl-H).). UV-Vis: λ_{max} (methanol) (logε)/nm 205 (3.00), 241 (2.52) and 424 (2.40).

Anal. Calcd. for $C_{16}H_{12}ClNO_2$: C, 67.36; H, 4.21; N, 4.91. Found: C, 66.93; H, 3.95; N, 4.71.

2-[[(4-Chloro-2*H*-1-benzothiopyran-3-yl)methylene]amino]-phenol (**2c**).

This compound was obtained from 4-chlorothiochromene-3-carboxaldehyde (**1c**), (1.05 g, 5 mmoles) and 2 aminophenol (0.54 g, 5 mmoles). Recrystallization of the crude product from carbon tetrachloride gave a light orange yellow solid (1.12 g, 75%), mp 151-152°; ir: ν OH 3350, ν CN 1620, 1430 cm^{-1}; ^{1}H-NMR: δ 4.05 (s, 2H, -S-CH_2-), 7.3 - 7.8 (m, 8H, aromatic), 9.4 (s, 1H, -C*H*=N-); ms: m/z 301 (M^+), 266 (M^+-Cl), 265 (M^+-Cl-H). UV-Vis: λ_{max} (methanol) (logε)/nm 206 (2.82), 244 (2.73) and 273 (2.56), 321 (2.55) and 394 (2.51).

Anal. Calcd. for $C_{16}H_{12}ClNOS$: C, 63.78; H, 3.98; N, 4.65. Found: C, 63.54; H, 3.79; N, 4.40.

2-[[(5-Chloro-2,3-dihydro-1-benzoxepin-4-yl)methylene]-amino]phenol (**2d**).

This compound was obtained from 5-chloro-2,3-dihydro-1-benzoxepin-4-carboxaldehyde (**1d**), (1.04 g, 5 mmoles) and 2 aminophenol (0.54 g, 5 mmoles). Recrystallization of the crude product from carbon tetrachloride gave a light orange crystalline solid (0.89 g, 60%), mp 162-164°; ir: ν OH 3300, ν CN 1620, 1400 cm^{-1}; ^{1}H-NMR: δ 2.8 (t, 2H, -O-CH$_2$-CH_2), 4.3 (t, 2H, -O-CH_2-CH$_2$-), 6.7 - 7.7 (m, 8H, aromatic), 8.27 (s, 1H, -b C*H*=N); ms: m/z 299 (M^+), 264 (M^+-Cl), 263 (M^+-Cl-H). UV-Vis: λ_{max} (methanol) (logε)/nm 206 (3.00), 247 (2.46) and 426 (2.58).

Anal. Calcd. for $C_{17}H_{14}ClNO_2$: C, 68.22; H, 4.68; N, 4.68. Found: C, 67.90; H, 4.93; N, 4.82.

2-[[(5-Chloro-2,3-dihydro-1-benzothiepin-4-yl)methylene]-amino]phenol (**2e**).

This compound was obtained from 5-chloro-2,3-dihydro-1-benzothiepin-4-carboxaldehyde (**1e**), (1.12 g, 5 mmoles) and 2 aminophenol (0.54 g, 5 mmoles). Recrystallization of the crude product from carbon tetrachloride gave a dark orange solid (1.26 g, 80%), mp 162-164°; ir: ν OH 3460, ν CN 1630, 1400 cm^{-1}; ^{1}H-NMR: δ 2.92 (t, 2H, -S-CH$_2$-CH_2), 3.52 (t, 2H, -S-CH_2-CH$_2$), 6.72 - 7.90 (m, 8H, aromatic), 9.64 (s, 1H, -C*H*=N-); ms: m/z 315 (M^+), 280 (M^+-Cl), 279 (M^+-Cl-H). UV-Vis: λ_{max} (methanol) (logε)/nm 206 (3.03), 253 (2.44) and 424 (2.45).

Anal. Calcd. for $C_{17}H_{14}ClNO_2$: C, 64.76; H, 4.44; N, 4.44. Found: C, 64.56; H, 4.22; N, 4.25.

Synthesis of Tetracyclic-1,5-benzoxazepines **3a-e**.

A solution of the aldimine **2a-e** (5 mmoles) in dry dimethylformamide (50 ml) was refluxed for 8 hours, after which the dimethylformamide was removed using a rotary evaporator. The residue was dissolved in ethyl acetate, washed with water, until the water layer became colorless. The organic phase was separated and dried. Evaporation of the dried organic extract gave a solid which was chromatographed on a column of silica (1:40). Elution with hexane/ethylacetate (9:1) afforded the titled compounds **3a-e** in a pure state.

3-Methoxybenzofuro[3,2-*b*][1,5]benzoxazepine (**3a**).

This compound was obtained from 2-[[(3-chloro-6-methoxy-2-benzofuranyl)methylene]amino]phenol (**2a**), (1.05 g, 5 mmoles). The crude product was purified by column chromatography which gave a pale yellow solid (0.53 g, 40%), mp 130-132°; ir: ν CN 1630, 1500, 1260 cm^{-1}; ^{1}H-NMR: δ 3.9 (s, 3H, Ar-O*Me*), 7.0 - 8.02 (m, 8H, aromatic); ms: m/z 265 (M^+), 250 (M^+-CH_3), 222 (M^+-CH_3CO). UV-Vis: λ_{max} (methanol) (logε)/nm 219 (2.99), 241 (2.73), 276 (3.04), 303 (2.52) and 347 (2.78).

Anal. Calcd. for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.15; N, 5.28. Found: C, 72.10; H, 4.56; N, 5.10.

6*H*-[1]Benzopyrano[4,3-*b*][1,5]benzoxazepine (**3b**).

This compound was obtained from 2-[[(4-chloro-2*H*-1-benzopyran-3-yl)methylene]amino]phenol (**2b**), (1.45 g, 5 mmoles). The crude product was purified by column chromatography which gave a white crystalline solid (0.622 g, 50%), mp 130-132°; ir: ν CN 1630, 1560, 1420 cm^{-1}; ^{1}H-NMR: δ 5.29 (s, 2H, -O-C*H*$_2$-), 6.87 - 8.41 (m, 8H, aromatic); ms: m/z 249 (M^+), 248 (M^+-H), 232 (M^+-OH), 222 (M^+-HCN). UV-Vis: λ_{max} (methanol) (logε)/nm 206 (2.82), 244 (2.73) and 273 (2.56), 321 (2.55) and 394 (2.51).

Anal. Calcd. for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.41; N, 5.62. Found: C, 76.87; H, 4.66; N, 5.48.

6*H*-[1]Benzothiopyrano[4,3-*b*][1,5]benzoxazepine (**3c**).

This compound was obtained from 2-[[(4-chloro-2*H*-1-benzothiopyran-3-yl)methylene]amino]phenol (**2c**), (1.5 g, 5 mmoles). The crude product was purified by column chromatography which gave a light yellow crystalline solid (0.68 g, 52%), mp 158-160°; ir: ν CN 1630, 1560, 1480 cm^{-1}; ^{1}H-NMR: δ 4.13 (s, 2H, -S-C*H*$_2$-), 7.40 - 8.81 (m, 9H, aromatic); ms: m/z 265 (M^+), 264 (M^+-H), 236 (M^+-H-CO). UV-Vis: λ_{max} (methanol) (logε)/nm 207 (3.03), 263 (3.07) and 277 (2.96) and 348 (2.35).

Anal. Calcd. for $C_{16}H_{11}NOS$: C, 72.45; H, 4.15; N, 5.28. Found: C, 72.18; H, 4.09; N, 5.01.

6,7-Dihydro[1]benzoxepino[5,4-*b*][1,5]benzoxazepine (**3d**).

This compound was obtained from 2-[[(5-chloro-2,3-dihydro-1-benzoxepin-4-yl)methylene]amino]phenol (**2d**) (1.5 g, 5 mmoles). The crude product was purified by column chromatography which gave a light yellow crystalline solid (0.78 g, 60%), mp 220-222°; ir: ν CN 1630, 1560, 1480 cm^{-1}; ^{1}H-NMR: δ 3.0 (t, 2H, -O-CH_2-C*H*$_2$-), 4.6 (t, 2H, -O-C*H*$_2$-CH_2-), 7.2 - 8.0 (m, 9H, aromatic); ms: m/z 263 (M^+), 262 (M^+-H), 234 (M^+-H-CO). UV-Vis: λ_{max} (methanol) (logε)/nm 207 (3.26), 266 (3.28) and 318 (2.29).

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.56; H, 4.94; N, 5.32. Found: C, 77.23; H, 4.66; N, 5.10.

6,7-Dihydro[1]benzothiepino[5,4-*b*][1,5]benzoxazepine (**3e**).

This compound was obtained from 2-[[(5-chloro-2,3-dihydro-1-benzothiepin-4-yl)methylene]amino]phenol (**2e**) (1.6 g, 5 mmoles). The crude product was purified by column chromatography which gave a white crystalline solid (0.767 g, 55%) as, mp 182-184°; ir: ν 1630, 1570, 1470 cm^{-1}; ^{1}H-NMR: 3.0 (t, 2H, -S-CH_2-C*H*$_2$-), 3.4 (t, 2H, -S-C*H*$_2$-CH_2-), 7.2 - 8.0 (m, 9H, aromatic); ms: m/z 279 (M^+), 278 (M^+-H), 252 (M^+-H-CN). UV-Vis: λ_{max} (methanol) (logε)/nm 207 (3.23) and 261 (3.20).

Anal. Calcd. for $C_{17}H_{13}NOS$: C, 73.11; H, 4.65; N, 5.01. Found: C, 73.00; H, 4.70; N, 4.89.

Procedure for the Preparation of Acetoxy Derivatives **6a-e**.

A well stirred solution of the tetracyclic-1,5-benzoxazepine **3a-e** (5 mmoles) in glacial acetic acid (25 ml) and acetic anhydride (0.5 g) was hydrogenated (110 ml hydrogen) using 10% palladium on activated carbon (100 mg) at atmospheric pressure. After stirring for 4 hours, the solid that was precipitated out was filtered, washed with water and dried. The impure solid was chromatographed on silica gel (1:40). Elution with hexane/ethyl acetate (9:1) gave pure samples of **6a-e**.

2-[[(6-Methoxy-2-benzofuranyl)methylene]amino]phenolacetate (**6a**).

This compound was obtained from 3-methoxybenzofuro-[3,2-*b*][1, 5]benzoxazepine (**3a**) (1.32 g, 5 mmoles) by hydrogenolysis. The crude product was purified by column chromatography which gave a light yellow solid (0.77 g, 50%), mp 146-148°; ir: ν CO 1750, ν CN 1630, 1260 cm^{-1}; ^{1}H-NMR: δ 2.7 (s, 3H, -OCO*Me*), 3.9 (s, 3H, Ar-O*Me*), 6.8 - 8.3 (m, 9H, aromatic); ms: m/z 309 (M^+, absent), 266 (M^+-CH_3CO), 265 (M^+-CH_3CO-H).

Anal. Calcd. for $C_{18}H_{15}NO_4$: C, 69.90; H, 4.85; N, 4.53. Found: C, 69.72; H, 4.63; N, 4.29.

2-[[(2*H*-1-Benzopyran-3-yl)methylene]amino]phenolacetate (**6b**).

This compound was obtained from 6*H*-[1]benzopyrano-[4,3-*b*][1,5]benzoxazepine (**3b**) (1.25 g, 5 mmoles) by hydrogenolysis. The crude product was purified by column chromatography which gave a white crystalline solid (0.879 g, 60%), mp 180-182°; ir: ν CO 1750, ν CN 1630, 1480 cm^{-1}; ^{1}H-NMR: δ 2.66 (s, 3H, -OCO*Me*), 5.31 (s, 2H, -OC*H*$_2$), 6.82 - 8.45 (m, 10H, aromatic); ms: m/z 293 (M^+, absent), 251 (M^+-CH_2CO), 250 (M^+-CH_2CO-H).

Anal. Calcd. for $C_{18}H_{15}NO_3$: C, 73.72; H, 5.11; N, 4.77. Found: C, 74.15; H, 5.52; N, 4.57.

2-[[(2*H*-1-Benzothiopyran-3-yl)methylene]amino]phenolacetate (**6c**).

This compound was obtained from 6*H*-[1]benzothio-pyrano[4,3-*b*][1,5]benzoxazepine (**3c**) (1.33 g, 5 mmoles) by hydrogenolysis. The crude product was purified by column chromatography which gave a white crystalline solid (0.81 g, 53%), mp 198-200°; ir: ν CO 1750, ν CN 1630, 1420 cm^{-1}; ^{1}H-NMR: δ 2.8 (s, 3H, -OCO*Me*), 4.0 (s, 2H, -SC*H*$_2$-), 7.0 - 8.3 (m, 10H, aromatic); ms: m/z 309 (M^+, absent), 267 (M^+-CH_2CO), 266 (M^+-CH_2CO-H).

Anal. Calcd. for $C_{18}H_{15}NO_2S$: C, 69.90; H, 4.85; N, 4.53. Found: C, 69.49; H, 4.97; N, 4.32.

2-[[(2,3-Dihydro-1-benzoxepin-4-yl)methylene]amino]phenol-acetate (**6d**).

This compound was obtained from 6,7-dihydro[1]benzoxepino[5,4-*b*][1,5]benzoxazepine (**3d**) (1.32 g, 5 mmoles) by hydrogenolysis. The crude product was purified by column chromatography which gave a white crystalline solid (0.92 g, 60%), mp 192-194°; ir: ν CO 1760, ν CN 1630, 1360 cm^{-1}; ^{1}H-NMR: δ 2.5 (s, 3H, -OCO*Me*), 3.02 (t, 2H, -OCH_2-CH_2), 4.58 (t, 2H, -OCH_2-CH_2), 7.0 - 8.3 (m, 10H, aromatic); ms: m/z 307 (M^+, absent), 265 (M^+-CH_2CO), 264 (M^+-CH_2CO-H).

Anal. Calcd. for $C_{19}H_{17}NO_3$: C, 74.26; H, 5.53; N, 4.56. Found: C, 74.01; H, 5.35; N, 4.28.

2-[[(2,3-Dihydro-1-benzothiepin-4-yl)methylene]amino]phenol-acetate (**6e**).

This compound was obtained from 6,7-dihydro[1]benzothiepino[5,4-*b*][1,5]benzoxazepine (**3e**) (1.6 g, 5 mmoles). The crude product was purified by column chromatography which gave a white crystalline solid (1.21 g, 75%), mp 186-188°; ir: ν CO 1760, ν CN 1630, 1360 cm^{-1}; ^{1}H-NMR: δ 2.5 (s, 3H, -OCO*Me*), 3.02 (t, 2H, -OCH_2-CH_2), 4.58 (t, 2H, OCH_2-CH_2), 7.72 - 8.04 (m, 10H, aromatic); ms: m/z 323 (M^+, absent), 281 (M^+-CH_2CO), 280 (M^+-CH_2CO-H).

Anal. Calcd. for $C_{19}H_{17}NO_3$: C, 70.58; H, 5.26; N, 4.33. Found: C, 70.72; H, 5.35; N, 4.21.

Procedure for the Preparation of Phenol Derivatives **7a-e**.

A solution of the acetoxy derivative **6a-e** (5 mmoles) in 10% ethanolic KOH (10 ml) was refluxed for 30 minutes and the solvent was evaporated by rotary evaporator under vacuum. The resulting mixture was cooled and dissolved in ethyl acetate. The organic layer was washed with water till the pH becomes neutral. The organic phase was dried and evaporated to give a solid residue, which was chromatographed on a column of silica (1:40). Elution with hexane/ethylacetate (9:1) gave pure samples of **7a-e**.

2-[[(6-Methoxy-2-benzofuranyl)methylene]amino]phenol (**7a**).

This compound was obtained from 2-[[(6-methoxy-2-benzofuranyl)methylene]amino]phenolacetate (**6a**) (1.54 g, 5 mmoles). The crude product was purified by column chromatography which gave a white crystalline solid (0.534 g, 40%), mp 126-128°; ir: ν OH 3450, ν CN 1640, 1240 cm^{-1}; ^{1}H-NMR: δ 3.9 (s, 3H, Ar-O*Me*), 6.80 - 8.30 (m, 9H, aromatic); ms: m/z 267 (M^+, absent), 266 (M^+-H), 265 (M^+-H-H).

Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.91; H, 4.86; N, 5.24. Found: C, 71.62; H, 4.59; N, 5.01.

2-[[(2*H*-1-Benzopyran-3-yl)methylene]amino]phenol (**7b**).

This compound was obtained from 2-[[(2*H*-1-benzopyran-3-yl)methylene]amino]phenolacetate (**6b**) (1.47 g, 5 mmoles). The crude product was purified by column chromatography which gave a white crystalline solid (0.50 g, 40%), mp 126-128°; ir: ν OH 3350, ν CN 1620, 1400 cm^{-1}; ^{1}H-NMR: δ 5.17 (s, 2H, -OCH_2), 6.77 - 8.45 (m, 10H, aromatic); ms: m/z 251 (M^+), 250 (M^+-H), 249 (M^+-H-H).

Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.49; H, 5.17; N, 5.57. Found: C, 76.82; H, 4.93; N, 5.28.

2-[[(2*H*-1-Benzothiopyran-3-yl)methylene]amino]phenol (**7c**).

This compound was obtained from 2-[[(2*H*-1-benzothiopyran-3-yl)methylene]amino]phenolacetate (**6c**) (1.55 g, 5 mmoles). The crude product was purified by column chromatography which gave a white crystalline solid (0.56 g, 42%), mp 156-158°; ir: ν OH 3350, ν CN 1630, 1566, 1480 cm^{-1}; ^{1}H-NMR: δ 4.0 (s, 2H, -SCH_2), 7.0 - 8.5 (m, 10H, aromatic); ms: m/z 267 (M^+), 266 (M^+-H), 265 (M^+-H-H).

Anal. Calcd. for $C_{16}H_{13}NOS$: C, 71.91; H, 4.86; N, 5.24. Found: C, 72.11; H, 4.48; N, 5.01.

2-[[(2,3-Dihydro-1-benzoxepin-4-yl)methylene]amino]phenol (**7d**).

This compound was obtained from 2-[[(2,3-dihydro-1-benzoxepin-4-yl)methylene]amino]phenolacetate (**6d**) (1.55 g, 5 mmoles). The crude product was purified by column chromatography which gave a white crystalline solid (0.66 g, 50%), mp 156-158°; ir: ν OH 3350, ν CN 1630, 1570, 1400 cm^{-1}; ^{1}H-NMR: δ 3.04 (t, 2H, -OCH_2-CH_2), 4.66 (t, 2H, -OCH_2CH_2), 7.01 - 8.04 (m, 10H, aromatic); ms: m/z 265 (M^+), 264 (M^+-H), 263 (M^+-H-H).

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.98; H, 5.66; N, 5.28. Found: C, 76.59; H, 5.21; N, 5.08.

2-[[(2,3-Dihydro-1-benzthiepin-4-yl)methylene]amino]phenol (**7e**).

This compound was obtained from 2-[[(2,3-dihydro-1-benzothiepin-4-yl)methylene]amino]phenolacetate (**6e**) (1.61 g, 5 mmoles). The crude product was purified by column chromatography which gave a white crystalline solid (0.77 g, 55%), mp 86 - 88°; ir: ν OH 3460, ν CN 1630, 1570 cm^{-1}; ^{1}H-NMR: 2.91 (t, 2H, -SCH_2-CH_2), 3.35 (t, 2H, -SCH_2-CH_2), 7.03 - 8.16 (m, 10H, aromatic); ms: m/z 281 (M^+), 280 (M^+-H), 279 (M^+-H-H).

Anal. Calcd. for $C_{17}H_{15}NOS$: C, 72.59; H, 5.33; N, 4.98. Found: C, 72.23; H, 5.41; N, 4.72.

REFERENCES AND NOTES

[1] E. F. Nielsen and E. B. Pedersen, *Chem. Scr.*, **26**, 343, (1986).

[2] N. Bhanumathi, K. R. Rao and P. B. Sattur, *Heterocycles*, **24**, 1683, (1986).

[3] G. P. Zecchini, I. Torrini and M. P. Paradisi, *Heterocycles*, **26**, 2443, (1987).

[4] I. Torrini, G. P. Zecchini and M. P. Paradisi, *Heterocycles*, **27**, 401, (1988).

[5] G. P. Zecchini, M. P. Paradisi and F. Scazzocchio, *Heterocycles*, **31**, 1687, (1990).

[6] G. R. Rao and K. R. Srinivasa, *Indian J. Pharm. Sci.*, **53**, 37, (1991).

[7] A. Jaya Shree and M. Darbarwar, *Org. Prep. Proced. Int.*, **25**, 65, (1993).

[8] N. J. Holman and G. B. Tometzki, WO 98,05,657 (1998); *Chem. Abstr.*, **128**, 16745a (1998).

[9] B. Chandra Sekhar, D. V. Ramana and S. R. Ramadas, *Sulfur Lett.*, **6**, 149, (1987).

[10] B. Chandra Sekhar, D. V. Ramana and S. R. Ramadas, *Sulfur Lett.*, **9**, 271, (1989).

[11] B. Chandra Sekhar, D. V. Ramana and S. R. Ramadas, *Sulfur Lett.*, **10**, 149, (1989).

[12] B. Chandra Sekhar, D. V. Ramana and S. R. Ramadas, *J. Indian. Chem. Soc.*, **67**, 493, (1990).