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Synthesis of (*Z*)-5-[(5-(2-(Phenylsulfonyl-ethyl)-1*H*-indol-3-yl)methelene]-thiozolidine-2,4-dione of Potential Pharmacological Interest

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Formylation of 5-bromoindole (**1**) under Vilsmeier-Hack formylation conditions using $POCl_3$ and DMF as a reagents under cooling conditions (0-5 ºC) followed by simple processing gave a 5-bromoindole-3-carboxyaldehyde (**2**) and condensation of (**2**) with thiazolidine-2,4-dione (**3**) in toluene as a solvent in the presence of PTSA and TBAB as a phase transfer catalyst under stirring at room temperature for 10-30 min, then slowly raise the temperature to 105 ºC and maintained for 12-15 h, obtained a product(*Z*)-5-((5-bromo-1-alkyl-1*H*-indol-3-yl)methylene)thiazolidine-2,4-dione (**4**) later on condensation of (**4**) with phenylvinylsulfone (**5**) in the presence of palladium acetate as a catalyst in DMF as a solvent heating at 100-105 ºC for 16 h gave (5*Z*)-5-((1-alkyl-5-((*E*)-2(-(phenylsulfonyl)vinyl)-1*H*-indol-3-yl)methelene)thiozolidine-2,4-dione (**8**) and on reduction of (**8**) in the presence of hydrogen gas, palladium-carbon by using catalytic amount acetic acid medium in methanol as a solvent heating at 45-50 ºC for 8 h gave (*Z*)-5-((1-alkyl-5-(2-(-(phenylsulfonyl)ethyl)-1*H*-indol-3yl)methelene)thiozolidine-2,4-dione (**11**) and **11** could also be prepared by alternate methods structure of **11** has been established on the basis of its spectral and analytical data.

Key Words: (*Z*)-5-((5-Bromo-1-alkyl-1*H*-indol-3-yl)methylene)thiazolidine-2,4-dione, 1-Alkyl-5-((*E*)-2-(phenylsulfonyl)vinyl)-1*H*-indole, 1-Alkyl-5-bromo-((*E*)-2-(phenylsulfonyl)vinyl)-1*H*-indole-3-carbaldehyde, (5*Z*)-5-((1-Alkyl-5-((E)-2(-(phenylsulfonyl)vinyl)-1*H*-indol-3-yl)methelene)thiozolidine-2,4-dione, (Z)-5-((1-Alkyl-5-(2-(-(phenylsulfonyl)ethyl)-1*H*-indol-3-yl)methelene)thiazolidine-2,4-dione, DMF, $POCl_3$.

INTRODUCTION

Thiazolidinones are the derivatives of thiazolidine, which belong to an important group of heterocyclic compounds containing sulfur and nitrogen in a five member ring. Many thiazolidine dione and their derivatives serve as basic pharmacophore for various biological profiles *i.e.* antidiabetic[1], anticancer[2], antimalarial[3] and antiinflammatory[4]. Thiazolidine-2,4-dione analogues such as ciglitazone[5], troglitazone[6] and englitazone[7] are well known for their anti diabetic activity. The interesting chemistry and various pharmacological activities associated with thiazolidine-2,4-dione led to the discovery of various drugs such as rosiglitazone[8], pioglitazone[9] and netoglitazone[10]. These observations promoted us to synthesize a new series of thiazolidine dione with higher biological activity.

EXPERIMENTAL

Melting points are uncorrected and were determined in open capillary tubes in sulphuric acid bath. TLC was performed on silica gel-G and spotting was done using iodine or UV-light. IR spectra were recorded using Perkin-Elmer 1000 instrument in KBr phase. ^{1}H NMR spectra were recorded using a Varian 400 MHz instrument and Mass spectra on Agilent-LC-MS instrument giving only M^+ values using Q + 1 or Q-1 mode.

General procedure of formylation

General procedure for preparation of 2(2a, 2b), 7(7a, 7b), 10(10a, 10b) from 1(1a, 1b), 6(6a, 6b), 9(9a, 9b): To an ice cold solution of DMF (5 mL) was added $POCl_3$ (0.045 mol) at 0-5 ºC, over a period of 30-45min. The solution was maintained for 15 min at the same temperature until the reaction mass syrupy liquid was formed. To this, **1(1a, 1b), 6(6a, 6b), 9(9a, 9b)**: (0.05 mol, in 20.0 mL DMF) was added over period of 0.5-1.0 h at 0-5 ºC. Then maintained for 0.5 h at the same temperature. Then slowly raise the temperature to 45 ºC and maintained for 6-8 h at 45-50 ºC. The reaction was monitored by TLC. After completion of reaction cool to 20 ºC and stir for 15 min at 20-25 ºC and charge water (50.0 mL) at the same temperature, then adjust pH to 9-9.5 with 50 % sodium hydroxide solution at 20-30 ºC, then stir for 1.0 h at 20-25 ºC,

filter the mass and wash with water (50 mL) and obtained the crude material, which was recrystalized in ethanol to get pure compound **2(2a, 2b), 7(7a, 7b), 10(10a, 10b)**.

General procedure for condensation of thiazolidine-2,4-dione (3)

General procedure for preparation of 4(a-b), 8(a-b) and 11(a-b) from 2(a-b), 7(a-b), and 10(a-b): A mixture of toluene (10 vol.), **2(a-b) 7(a-b)** and **10(a-b)** (0.22 mol), 3 (1.2 eq.) and PTSA and TBAB (as catalysts) was stirred for 10 min at 25-30 ºC, then slowly raise the temperature to 105 ºC and maintained for 12-15 h at 105-110 ºC. Then monitored the reaction by TLC and cooled to 20-25 ºC and charged water (50.0 mL) and stir for 1.0 h at 20-25 ºC, filter the mass and wash with water (10.0 mL) and obtained the pure material **4(a-b), 8(a-b)** and **11(a-b)**.

General procedure for Heck reaction:

General procedure for preparation of 6(a-b), 7(a-b) and 8(a-b) from 1(a-b), 2(a-b) and 4(a-b): A mixture of DMF (10 vol.), palladium acetate (0.2 gm) and tri-orthotolylphosphine (0.06 mol) was stirred at 20-25 ºC and slowly add a mixture of **1(a-b)**, **2(a-b) (4a-b)** (1.2 eq), phenylvinylsulfone (**25**) (1.2 eq) and triethylamine (2.eq) at 20-25 ºC, stir the reaction mixture for 15.0 min at 20-25 ºC and raise the temperature to 100 ºC, then maintained for 16.0 h at 100-105 ºC, then monitored the reaction by TLC cool to 40 ºC and distilled the mass below 60 ºC, the obtained residue was run column chromatography and collect the pure compound **6(a-b)**, **7(a-b)** and **(8a-b)** by using solvent ratio hexane: ethyl acetate (7:3), but we collect the two major spots from residue and identified as monomer and dimmer by ^{1}H NMR and ^{13}C NMR of phenylvinylsulfone derivatives.

General procedure for reduction reaction

Preparation of 9(a-b), 10(a-b) and 11(a-b) from 6(a-b), 7(a-b), and 8(a-b): Reduction of **6(a-b)**, **7(a-b)** and **(8a-b)** (0.012 mol) in the presence of hydrogen gas, palladium-carbon by using catalytic amount of acetic acid medium in methanol as a solvent heating at 45-50 ºC for 8 h, reaction monitored by TLC, after completion of reaction cool to room temperature and filter the mass through hyflo bed, take filtrate and concentrated and obtained pure compound of **9(a-b)**, **10(a-b)** and **11(a-b)**.

Analytical results

2a: (*i.e.*, R = H) Yield 10.5 g (92.5 %) off white solid. m.p. = 200.5-203.5 ºC. IR (KBr): 3216.0 (strong -NH stretching) and 2838.0 (very strong, formyl); 1642.74 (strong, -C=O); ^{1}H NMR (DMSO d_6/TMS) δ 7.34-7.36 (d, 1H); 7.44-7.46 (d, 1H, benzene ring); 8.18 (s, 1H, benzene ring); 8.31 (s, 1H, indole ring); 9.89 (s, 1H, formyl proton); 12.3 (s, 1H, -NH, proton); MS *m/z* = 226 (M+2).

2b: (*i.e.*, R = CH_3) yield 10 g (94.96 %). White solid, m.p. > 260 ºC. IR (KBr): 2924 (strong -CH stretching); and 1660 (very strong-CHO, formyl carbonyl); 1535.0 (strong, $-CH_3$); ^{1}H NMR (DMSO d_6/TMS) δ 3.88 (s, 3H, $-CH_3$); 7.45-7.47 (d, 1H, benzene ring); 7.56-7.58 (d, 1H, benzene ring); 8.22 (s, 1H, benzene ring); 8.32 (s, 1H, indole ring); 9.88 (s, 1H, -CHO proton); MS *m/z* = 240 (M+2).

4a: (*i.e.*, R=H), yield 6.2 g (86.11 %) off white to light yellow colour solid m.p. >260 ºC, IR (KBr): 3134 (broad -NH stretching); 3025 (broad, -NH stretching, thiazolidine ring); 1736 (very strong, carbonyl); 1680 (very strong, carbonyl); ^{1}H NMR (DMSO d_6/TMS) δ 7.35 (d, 1H, benzene ring); 7.46 (d, 1H, benzene ring); 7.76 (s, 1H, -CH=); 8.05 (s, 1H, benzene ring); 8.14 (s, 1H, indole ring); 12.25 (s, 1H, -NH, indole ring); 12.37 (s, 1H, -NH proton, thiazolidine); MS *m/z* = 323 (M).

4b: (*i.e.*, R=CH_3) yield 7.0 g (95 %) off white solid, Pure **4b** (EtOAc) m.p. > 250-255 ºC. IR (KBr): 3435 (broad -NH stretching, thiazolidine ring); 1737 (very strong, carbonyl, stretching); 1680 (very strong, carbonyl, stretching); 1594.0 (strong, $-CH_3$); ^{1}H NMR (DMSO d_6/TMS) δ 3.86 (s, 3H, -N-CH_3); 7.36-7.38 (d, 1H, benzene ring); 7.47-7.49 (d, 1H, benzene ring); 7.76 (s, 1H, -CH=); 7.9 (s, 1H, benzene ring); 8.13 (s, 1H, indole ring); 12.27 (s, 1H, -NH); MS *m/z* = 338 (M+1).

6a: (*i.e.*, R=H) yield = 2.2 g (77 %) off white solid, m.p. > 260 ºC, off white solid; m.p. 126.7-129.8 ºC. IR (KBr): 3401 (strong -NH stretching); and 1604 (very strong, -C=C, sulfonyl vinyl); ^{1}H NMR (DMSO d_6/TMS) δ 6.45 (s, 1H, indole ring); 7.35 (d, 1H, indole ring); 7.37 (d, 1H, indole); 7.39 (d, 1H, indole ring); 7.47 (d, 1H, -CH=); 7.62 (d, 1H, SCH-); 7.66 (t, 1H, phenyl ring); 7.69 (t, 2H, phenyl ring); 7.88 d, 2H, phenyl ring); 7.90 (d, 1H, indole ring); 11.36 (s, -NH proton); MS *m/z* = 284 (M+1).

6b: (*i.e.*, R=CH_3) yield = 1.84 g (88 %), off white solid; m.p. 129.5-131.2 ºC. IR (KBr): 1446 (very strong $-CH_3$); ^{1}H NMR (DMSO d_6/TMS) δ 3.76 (s, 3H, $-CH_3$); 6.45 (s, 1H, indole ring); 7.35 (d, 1H, indole ring); 7.36 (d, 1H, indole ring); 7.39 (d, 1H, indole ring); 7.46 (d, 1H, -CH=); 7.62 (d, 1H, SCH); 7.66 (t, 1H, phenyl ring); 7.69 (t, 2H, phenyl ring); 7.88 (d, 2H, phenyl ring); 7.90 (d, 1H, indole ring); MS *m/z* = 298 (M+1).

7a: (*i.e.*, R=H), yield = 5.51 g (96 %) , off white solid m.p. > 260 ºC , IR (KBr): 3268 (broad -NH stretching), 2823 (very strong-6CHO, formyl stretching); and 1644 (very strong, -CHO, formyl carbonyl stretching); ^{1}H NMR (DMSO d_6/TMS) δ 7.51-7.60 (d, 1H, -CH=); 7.61 (d, 1H, indole ring proton); 7.66 (d, 1H, indole ring protons); 7.71 (t, 1H, phenyl ring); 7.73 (d, 1H, -SCH proton); 74 (t, 2H, phenyl ring); 7.93 (d, 2H, phenyl ring); 8.30 (s, 1H, indole ring); 8.36 (s, 1H, indole ring); 9.95 (s, 1H, formyl proton); 12.34 (s, 1H, -NH, proton); MS *m/z* = 311 (M+1).

7b: (*i.e.*, R=CH_3) yield = 5.51 g (96 %), off white solid, m.p. > 260 ºC IR (KBr): 3056.0 (strong -CH, vinyl stretching), 2821.39 (-CH, vinyl, stretching); 1651 (very strong, -CHO, formyl carbonyl) and 1535.32 (strong, methyl); ^{1}H NMR (DMSO d_6/TMS) δ 3.86 (s, 3H, $-CH_3$); 7.53-7.60 (d, 1H, -CH=); 7.61 (d, 1H, indole ring proton); 7.66 (d, 1H, indole ring protons); 7.71 (t,1H, phenyl ring); 7.73 (d, 1H, -SCH, proton); 7.74 (t, 2H, phenyl ring); 7.93 (d, 2H, phenyl ring); 8.30 (s, 1H, indole ring); 8.36 (s, 1H, indole ring); 9.8 (s, 1H, formyl proton); MS *m/z* = 326 (M+1).

8a: (*i.e.*, R=H) off white to light yellow colour solid m.p. >260 ºC, IR (KBr): 3197 (broad -NH stretching); 3044 (broad, -NH stretching, thiazolidine ring); 1723. (very strong, carbonyl, stretching); 1680.8 (very strong, carbonyl, stretching);

^{1}H NMR (DMSO d_6/TMS) δ 7.50 (s, 1H, indole ring); 7.60-7.78 (m, 7H, 5 proton in phenyl ring + 2 proton, -SCH=CH-); 7.93-7.95 (d, 2H, indole ring); 8.1 (s, 1H, indole ring); 8.49 (s, 1H, indole ring); 12.31 (ss, 2H, -NH, 1 proton indole ring + 1 proton in thiazolidine ring); MS *m/z* = 410.9 (M+1).

8b: (*i.e.*, R=CH_3); off white to light yellow colour solid m.p. > 260 ºC, IR (KBr): 3044 (broad, -NH stretching, thiazolidine ring); 1723. (very strong, carbonyl); 1680.8 (very strong, carbonyl); 1521 (very strong, -N-CH_3); ^{1}H NMR (DMSO d_6/TMS) δ 3.8 (s, 3H, -N-CH_3); 7.50(s, 1H, indole ring); 7.60-7.78 (m, 7H, 5 proton in phenyl ring + 2 proton, -SCH=CH-); 7.93-7.95 (d, 2H, indole ring); 8.1 (s, 1H, indole ring); 8.49 (s, 1H, indole ring); 12.31 (s, 1H, -NH, thiazolidine ring); MS *m/z* = 425 (M+1).

9a: (i.e., R=H) yield = 4.63 g (92 %) off white solid, m.p. =104-106 ºC , IR (KBr): 3361 (strong -NH, stretching); ^{1}H NMR (DMSO d_6/TMS) δ 2.86-2.90 (m, 2H, -CH_2, ethyl); 3.56-3.60 (m, 2H, -SCH_2); 6.28 (s, 1H, indole ring); 6.84-6.86 (d, 1H, indole ring); 7.22- (d, 1H, indole ring); 7.25 (d, 1H, indole ring); 7.28 (d, 1H, indole ring); 7.61-7.64, (t, 2H, phenyl ring); 7.73 (t, 1H, phenyl ring); 7.92-7.94 (d, 2H, phenyl ring); 10.97 (s, 1H, -NH proton); MS *m/z* = 286 (M+1).

9b: (*i.e.*, R=CH_3), yield = 4.96 g (95 %), off white solid, m.p. 78-80 ºC, IR (KBr): 1447 (very strong -CH_3); ^{1}H NMR (DMSO d_6/TMS) δ 2.87-2.90 (m, 2H, -CH_2, ethyl); 3.56-3.60 (m, 2H, -SCH_2); 3.69 (s, 3H, -CH_3); 6.27 (d, 1H, indole ring); 6.91-6.94 (d, 1H, indole ring); 7.23 (d, 1H indole ring); 7.25 (s, 1H, indole ring); 7.29 (d, 1H, indole ring); 7.6 (t, 2H, phenyl ring); 7.70 (t, 1H, phenyl ring); 7.93 (d, 2H, phenyl ring); MS *m/z* = 300 (M+1).

10a: (*i.e.*, R=H), yield = 5.25 g (96 %), off white solid, m.p.=130-135 ºC IR (KBr): 3434 (strong, -NH, stretching); 2830 (formyl stretching); and 1660 (very strong, -C=O, carbonyl); ^{1}H NMR (DMSO d_6/TMS) δ 2.85-2.95 (m, 2H, -CH_2, ethyl); 3.59-3.63 (m, 2H, -SCH_2); 7.05-7.08 (d, 1H, indole ring); 7.34-7.36 (d, 1H, indole ring); 7.60-7.64 (t, 2H, phenyl ring); 7.69-7.73 (t, 1H, phenyl ring); 7.83, (s, 1H, indole ring); 7.91-7.93 (d, 2H, phenyl ring); 8.2 (s, 1H, indole ring); 9.85 (s, 1H, formyl proton); 12.01 (s, 1H, -NH proton); MS *m/z* = 314 (M+1).

10b: (i.e., R=CH_3) yield = 4.96 g (96 %) off white solid, m.p. = 136.0-138.0 ºC. IR (KBr): 2926 (formyl Stretching); 1653 (very strong formyl carbonyl); and 1535 (very strong -CH_3); ^{1}H NMR (DMSO d_6/TMS) δ 2.96-2.99 (m, 2H, -CH_2, ethyl); 3.64-3.69 (m, 2H, -SCH_2); 3.85 (s, 3H, -CH_3); 7.19 (d, 1H, indole ring); 7.48 (d, 1H, indole ring); 7.6, (t, 1H, phenyl ring); 7.7 (t, 2H, phenyl ring); 7.8 (s, 1H, indole ring); 7.96 (d, 2H, phenyl ring); 8.2 (s, 1H, indole ring); 9.85 (s, 1H, formyl proton); MS *m/z* = 328 (M+1).

11a: (*i.e.*, R=H) yield = 4.3 g (86 %), yellow colour solid, m.p. > 260 ºC IR (KBr): 3299 (-NH, stretching, thiazolidine); 3149 (br, -NH, indole ring); 1718.7 (very strong, carbonyl); and 1675 (very strong, carbonyl); ^{1}H NMR (DMSO d_6/TMS) δ 2.93-2.98 (m, 2H, -CH_2, ethyl); 3.62-3.70 (m, 2H, -SCH_2); 7.02 (d, 1H, -indole ring); 7.33(d, 1H, indole ring); 7.60 (s, 1H, -CH=); 7.62, (s, 1H, indole ring); 7.64 (t, 1H, phenyl ring); 7.77 (t, 2H, phenyl ring); 7.93 (d, 2H, phenyl ring); 7.99 (s, 1H, indole ring); 12.01 (s, 1H, -NH, proton); 12.25 (s, 1H, -NH, thiazolidine, proton); MS *m/z* = 411 (M-1).

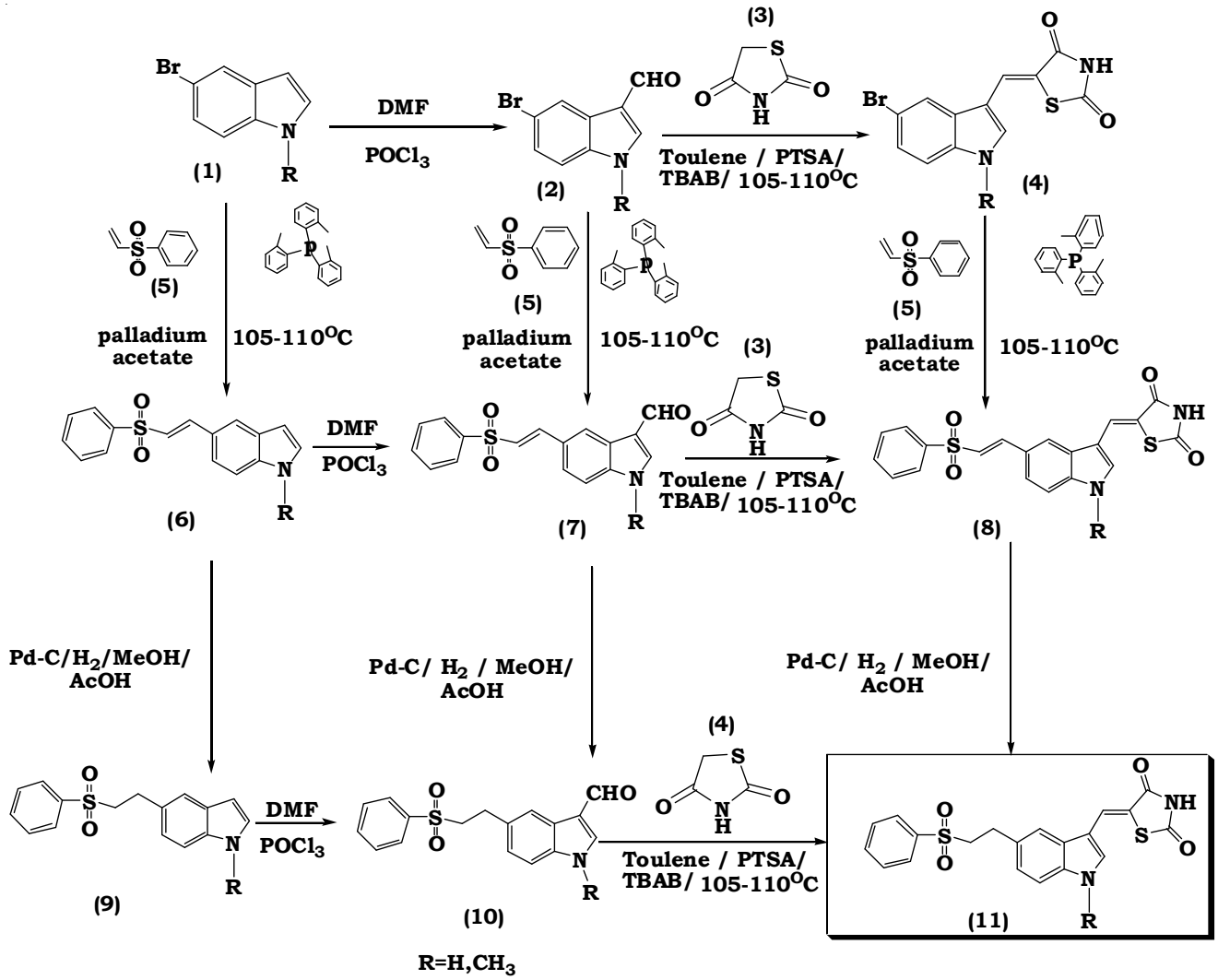
11b: (*i.e.*, R=CH_3) yield = 4.3 g (83 %) yellow colour solid, m.p. > 214-217 ºC IR (KBr): 3446.73 (-NH, stretching, thiazolidine); 1728.7 (very strong, carbonyl); and 1675.5 (very strong, carbonyl); ^{1}H NMR (DMSO d_6/TMS); δ 3.69-3.72 (m, 2H, -CH_2, ethyl); 3.86 (m, 2H, -SCH_2); 3.88 (s, 3H, -N-CH_3, indole ring); 7.39-7.41 (d, 1H, indole ring); 7.50-7.52 (d, 1H, indole ring); 7.64, (t, 2H, phenyl ring); 7.70 (t, 1H, phenyl ring); 7.82 (s, 1H, indole ring); 7.89 (d, 2H, phenyl ring); 8.09 (s, 1H, -CH=); 8.21 (s, 1H, indole ring); 12.25 (s, 1H, -NH, thiazolidine, proton); MS *m/z* = 427 (M+1).

RESULTS AND DISCUSSION

Formylation of 5-bromoindole (**1**) under Vilsmeier-Hack formylation conditions using $POCl_3$ and DMF as a reagents under cooling conditions (0-5 ºC) followed by simple processing gave a 5-bromoindole-3-carboxaldehyde (**2**). (**2a, 2b** *i.e.*, R=H, CH_3), which has been characterized on the basis of its spectral and analytical data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3220-3216 cm^{-1} assignable to -NH- stretching. Other absorptions were obtained in the IR spectrum at 1642 cm^{-1} as a strong peak and very sharp peak assignable to the carbonyl group as a diagnostic absorption. Its ^{1}H NMR spectrum (DMSO d_6/TMS) showed signals at δ 7.34-7.3 (d, 1H, indole ring proton), 9.89 (s, 1H, -CHO), 12.3 (s, 1H, -NH-, D_2O exchangeable NH). Its CI mass spectrum in Q+2 mode showed a molecular ion peak at 226 (base peak) corresponding to a molecular mass of 224.

Treatment of (**2**) with thiazolidine-2,4-dione (**3**) in toluene as a solvent in the presence of PTSA and TBAB as a phase transfer catalyst under stirring at room temperature for 10-30 min, then slowly raise the temperature to 105 ºC and maintained for 12-15 h, obtained a product (Z)-5-((5-bromo-1-alkyl-1*H*-indol-3-yl)methylene)thiazolidine-2,4-dione (**4**) (**4a**, **24b**, *i.e.*, R=H, -CH_3), which is homogeneous on TLC and has been characterized on the basis of spectral and analytical data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3134 cm^{-1} assignable to -NH- stretching vibrations indole ring, 3025 cm^{-1} assignable to -NH- stretching vibrations thiazolidine ring and a very strong, sharp peak in the region 1736 cm^{-1} assignable to the carbonyl group. Its ^{1}H NMR spectrum (DMSO d_6/TMS) showed signals at δ 7.35(d, 1H, benzene ring); 7.76 (s, 1H, -CH=C-); 12.25 (s, 1H, -NH- indole ring D_2O exchangeable NH); 12.37 (s, 1H, -NH-, thiazolidine D_2O exchangeable NH). Its CI mass spectrum in Q+1 mode showed a molecular ion peak at 338 (base peak) corresponding to a molecular mass of 337.

Later on condensation of (**4**) with phenylvinylsulfone (**5**) in the presence of palladium acetate as a catalyst in DMF as a solvent heating at 100-105 ºC for 16 h gave (5Z)-5-((1-alkyl-5-((E)-2-(-(phenylsulfonyl)vinyl)-1*H*-indol-3-yl)methelene)-thiozolidine-2,4-dione (**8**) (**8 a**, **8b** *i.e.*, R=H, CH_3), which has been characterized on the basis of spectral and analytical data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3197 cm^{-1} (broad -NH stretching, indole ring); 3044 cm^{-1} (broad, -NH stretching, thiazolidine ring); 1723 cm^{-1} (very strong, carbonyl, thiazolidine ring); 1680.8 (very strong, carbonyl, thiazolidine ring); showed signals at ^{1}H NMR (DMSO d_6/TMS) δ 7.50 (s, 1H, indole



Scheme-I

ring); 7.60-7.78 (m, 7H, 5 proton in phenyl ring + 2 proton, -SCH=CH-); 7.93-7.95 (d, 2H, indole ring); 8.1 (s, 1H, indole ring); 8.49 (s, 1H, indole ring); 12.31 (s, 2H, -NH, 1 proton indole ring +1 proton in thiazolidine ring); when recorded in the CI method, showed the molecular ion peak at 409.2 (M-1), corresponding to a molecular mass of 410.

On reduction of (**8**) in the presence of hydrogen gas, palladium-carbon by using catalytic amount acetic acid medium in methanol as a solvent heating at 45-50 ºC for 8 h gave (*Z*)-5-[(1-alkyl-5-(2-(phenylsulfonyl)ethyl)-1*H*-indol-3-yl)methelene]thiozolidine-2,4-dione (**11**) (**11a**, **11b**, *i.e.*, R= H, CH_3) (**Scheme-I**), which has been characterized on the basis of spectral and analytical data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3299 cm^{-1} assignable to -NH- thiazolidine stretching vibrations , 3149 cm^{-1} broad -NH-, indole ring and a very strong, sharp peak in the region 1675 cm^{-1} assignable to the carbonyl group. Its ^1H NMR spectrum (DMSO d_6/TMS) showed signals at δ 2.93-2.98 (m , 2H, $-CH_2-$); 3.62-3.70 (m, 2H, $-S-CH_2-$); 12.01 (s, 1H, -NH-, indole ring); 12.25 (s, 1H, thiazolidine proton); Its CI mass spectrum in Q^{-1} mode showed a molecular ion peak at 411 (base peak) corresponding to a molecular mass of 410.

Alternate preparation of target compound (11) (11a-b): Treatment of (**1**) with phenylvinylsulfone (**5**) in the presence of palladium acetate as a catalyst in DMF as a solvent heating at 100-105 ºC for 16 h gave 1-alkyl-5-((*E*)-2-(phenylsulfonyl)-vinyl)-1*H*-indole (**6**) (**6 a**, **6b**, *i.e.*, R= H, CH_3), which has been characterized on the basis of spectral and analytical data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3401 cm^{-1} assignable to -NH- stretching vibrations and a very strong, sharp peak in the region 1604 cm^{-1} assignable to the -C=C- group. Its ^1H NMR spectrum (DMSO d_6/TMS) showed signals at δ 6.45 (s, 1H, indole ring) , 7.37 (d, 1H, indole ring); 7.47 (d, 1H, -CH=); 7.37 (d, 1H, -SCH-); 11.36 (s, -NH-, proton); Its CI mass spectrum in Q+1 mode showed a molecular ion peak at 284 (base peak) corresponding to a molecular mass of 283.

Formylation of (**6**) under Vilsmeier-Hack formylation conditions using $POCl_3$ and DMF as a reagents under cooling conditions (0-5 ºC) followed by simple processing gave a 1-alkyl-5-((*E*)-2-(phenylsulfonyl)vinyl)-1*H*-indole-3-carboxy-aldehyde (**7**) (**7a**, **7b**, *i.e.*, R= H, CH_3), which has been characterized on the basis of its spectral data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3268 cm^{-1} assignable to -NH- stretching,

2823 cm^{-1} very strong -CHO other absorptions were obtained in the IR spectrum at 1644 cm^{-1} as a strong peak and very sharp peak assignable to the carbonyl group as a diagnostic absorption. Its ^1H NMR spectrum (DMSO d_6/TMS) showed signals at δ 7.51-7.60 (d, 1H, -CH=C), 7.61 (d, 1H, indole ring); 7.73 (d, 1H, -SCH=C); 9.95 (s, 1H,-CHO); 12.34 (s, 1H, -NH-, D_2O exchangeable NH). Its CI mass spectrum in Q+1 mode showed a molecular ion peak at 326 (base peak) corresponding to a molecular mass of 324.

Treatment of (**7**) with thiazolidine-2, 4-dione (**3**) in toluene as a solvent in the presence of PTSA and TBAB as a phase transfer catalyst stirring at room temperature for 10-30 min, then slowly raise the temperature to 105 ºC and maintained for 12-15 h, obtained a product (**8**) (**8a**, **8b**, *i.e.*, R=H, $-CH_3$), which has been characterized on the basis of spectral and analytical data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3299 cm^{-1} assignable to -NH- stretching vibrations thiazolidine ring, 3149 cm^{-1} assignable to -NH- stretching vibrations indole ring and a very strong, sharp peak in the region 1675 cm^{-1} assignable to the carbonyl group. Its ^1H NMR spectrum (DMSO d_6/TMS) showed signals at δ 7.51-7.60 (d, 1H, -CH=C), 7.61 (d, 1H, indole ring proton); 7.73 (d, 1H, -SCH=C); 12.25 (s, 1H, -NH-thiazolidine); 12.34 (s, 1H, -NH-, D_2O exchangeable NH). Its CI mass spectrum in Q-1 mode showed a molecular ion peak at 409 (base peak) corresponding to a molecular mass of 408.

On reduction of (**6**) in the presence of hydrogen gas, palladium-carbon by using catalytic amount acetic acid in methanol as a solvent heating at 45-50 ºC for 8 h gave (**9**) (**9a, 9b**, *i.e.* R= H, CH_3), which has been characterized on the basis of spectral and analytical data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3361 cm^{-1} assignable to -NH- indole ring. Its ^1H NMR spectrum (DMSO d_6/TMS) showed signals at δ 2.86-2.90 (m, 2H, $-CH_2-$); 3.56-3.60 (m, 2H, $-S-CH_2-$); 6.28 (s, 1H, indole ring); 10.97 (s, 1H,-NH- proton); Its CI mass spectrum in Q-1 mode showed a molecular ion peak at 286 (m).

Condensation of 5-(2-benzensulfonyl-ethyl-)-1*H*-indole (**9**) with $POCl_3$ in DMF as a solvent under cooling conditions (0-5 ºC) gave a 5-(2-benzensulfonyl-ethyl-) 1*H*-indole-3-carboxyalydehyde (**10**) (**10a**, **10b**, *i.e.*, R= H, CH_3), which has been characterized on the basis of its spectral data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3434 cm^{-1} assignable to -NH- stretching, 2830 cm^{-1} very strong -CHO other absorptions were obtained in the IR spectrum at 1660 cm^{-1} as a strong peak and very sharp peak assignable to the carbonyl group as a diagnostic absorption. Its ^1H NMR spectrum (DMSO d_6/TMS) showed signals at δ 2.85-2.95 (m, 2H, $-CH_2-$), 3.59-3.63 (m, 2H, $-SCH_2-$), 9.85 (s, 1H, -CHO); 12.01 (s, 1H, -NH-, D_2O exchangeable NH). Its CI mass spectrum in Q+1 mode showed a molecular ion peak at 314 (base peak) corresponding to a molecular mass of 313.

Treatment of (**10**) with thiazolidine-2, 4-dione (**3**) in toluene as a solvent in the presence of PTSA and TBAB as a phase transfer catalyst stirring at room temperature for 10-30 min, then slowly raise the temperature to 105 ºC and maintained for 12-15 h, obtained a product (**11**) (**11a**, **11b**, *i.e.*, R=Br, R1 = H, $-CH_3$) (**Scheme-I**), which has been characterized on the basis of spectral and analytical data. Thus, its IR (KBr) spectrum showed a very broad band of medium to strong intensity in the region 3299 cm^{-1} assignable to -NH- stretching vibrations thiazolidine ring, 3149 cm^{-1} assignable to -NH- stretching vibrations indole ring and a very strong, sharp peak in the region 1718 cm^{-1} assignable to the carbonyl group. Its ^1H NMR spectrum (DMSO *d*6/TMS) showed signals at δ 2.93-2.98 (m, 2H, $-CH_2-$, ethyl), 3.62-3.70 (m, 2H, $-SCH_2$,); 7.60 (s, 1H, -CH=C); 12.01 (s, 1H, -NH-indole, D_2O exchangeable NH); 12.25 (s, 1H, -NH-, D_2O exchangeable NH). Its CI mass spectrum in Q-1 mode showed a molecular ion peak at 411 (base peak) corresponding to a molecular mass of 410.

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