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Green synthesis: Antimicrobial activity of novel benzothiazole-bearing coumarin derivatives and their fluorescence properties

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Abstract

A new benzothiazole derivatives **4a-f** were prepared by the reaction of 2-cyanomethylbenzothiazole **1** with 2-hydroxy-5-(aryldiazenyl)benzaldehyde derivatives **2a-f** under thermal method in ethanol containing few drops of triethylamine. The previous reaction was reinvestigated at room temperature using grindstone technique using sodium hydroxide. The compounds **4a-f** were transformed into benzothiazole-bearing coumarin derivatives **5a-f** by refluxing in dioxane with few drops of conc. hydrochloric acid. The structure of the newly synthesized compounds **4a-f** and **5a-f** was established by spectral data. The compounds **5a-f** showed fluorescence properties as well as antimicrobial activity.

Keywords: 2-cyanomethylbenzothiazole; grindstone method; coumarin derivatives; antimicrobial activity; fluorescence properties.

Introduction

Benzothiazole derivatives have a number of biological effects, including antibacterial [1], antimicrobial [2], anti-inflammatory [3], antiviral [4], and anticancer activity [5]. Ethoxzolamide (I), a commercial drug containing the benzothiazole moiety, is also used to treat glaucoma and duodenal ulcers, as well as a diuretic. Furthermore, Frentizole (II) is an immunosuppressive drug approved by the FDA, while Riluzole (III) is a medication used to treat amyotrophic lateral sclerosis. Also, Zopolrestat (IV) is a novel carboxylic acid aldose reductase inhibitor as shown in Figure 1.

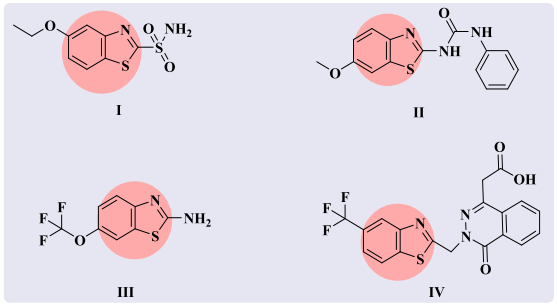

Fig.1. Some commercial drugs containing benzothiazole moiety

Coumarins, (known as benzopyran-2-ones) can be found within various natural sources for instance, fruits, essence, green tea, and other foods [6-8]. Coumarins are good class of naturally occurring compounds with promising therapeutic applications. Also, some substituted coumarins and polycyclic coumarins have gotten a lot of attention due to their broad range of biological activity like amino-coumarins (novobiocin and coumermycin) are antibiotics because they can inhibit DNA gyrase (Fig 2) [9]. Warfarin, a coumarin analogue, is an anticoagulant and a vitamin K antagonist [10, 11] and coumaphos is used as insecticide which kills insect and mites as shown in Figure 2 [12].

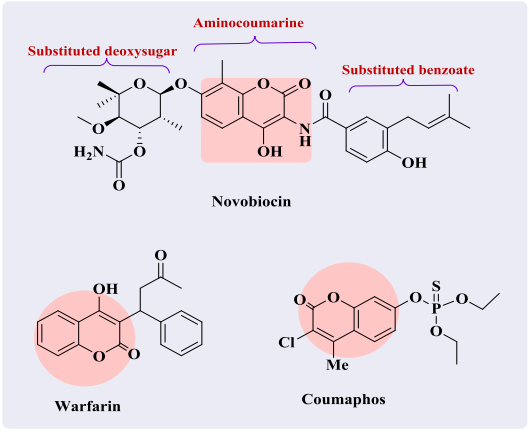

Fig. 2. Biological activity of coumarin analogs

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We recently published diverse synthetic approaches for the preparation of benzothiazole and coumarine derivatives using nitriles as starting materials [13,14].In light of these finding and as part of our program aimed at the preparation of possible antimetabolites [15-20], which showed biologically important antimetabolic agents in many biochemical reactions [21,22] and in accordance of these reports and based on our previous results in the preparation of biologically active heterocycles [23-28], the current study reports a new grindstone method synthesis of some novel benzothiazoles bearing a coumarin moiety **5a-f** and investigate their antimicrobial activity as well as fluorescence properties.

2. Material and methods

2.1 Measurements

All melting points were determined using Electrothermal (9100) apparatus. At Ain Shams, the ^{1}H NMR spectra were recorded in DMSO-d_6 using $Si(Me)_4$ as an internal norm on a Bruker Avance (III)-400 Spectrometer (400 MHz). At 70 eV, mass spectra were collected on a Shimadzu GCMS-QP 1000 Ex mass spectrometer. Elemental analyses were carried out at Cairo University's Microanalyses Center using a Vario EL III Elemental CHNS analyzer. At Cairo University, electronic absorption spectra were obtained using a UV-3101 pc spectrophotometer. A 700 V biassed face form photomultiplier was used at Cairo University to test fluorescent absorption. The laser device, monochromator, and photomultiplier tube, as well as the Spectra-Physics-Laser model 183-C0201 and the Instrument Group amplifier model AD110, are all manufactured in the United States. The Biological Center at Cairo University conducted antimicrobial assessments. The preparation of compounds **1** and **2** was prepared according to the previous methods [29,30].

2.2. Synthesis procedures

2.2.1.General procedures for the synthesis of compounds 4a-f

Method A

In 10 ml absolute ethanol containing triethylamine, compound **1** (0.01 mol) and arylazosalicylaldehydes **2a-f** (0.01 mol) were refluxed for 3 hours. The precipitated solid that formed by cooling was filtered off and recrystallized from ethanol / dioxane mixture.

Method B

Compound **1** (0.01 mol), arylazosalicylaldehydes **2a-f** (0.01 mol), and solid sodium hydroxide (0.01 mol) were ground in a mortar for 30 minutes at room temperature, the reaction mixture was triturated with water, filtered off, and recrystallized to give the respective products **4a-f**, which were identical to those obtained by method **A** in all aspects.

2.2.1.1. 3-(Benzo[*d*]thiazol-2-yl)-6-(phenyldiazenyl)-2*H*-chromen-2-imine (4a)

Pale orange, yield 62% (A), 70% (B); m.p. 222 ℃; ν_{max} / cm^{-1} (KBr) 3191 (NH), 1650 (C=N), 1602 (N=N); ^{1}H NMR (DMSO-d_6) δ = 7.49 (d, 2H, *J* = 7.6 Hz, Ar), 7.70-7.79 (m, 5H, Ar and CH), 7.95 (d, 2H, *J* = 9.2 Hz, Ar), 8.08 (d, 2H, *J* = 8.0 Hz, Ar), 8.06 (d, 2H, *J* = 8.4 Hz, Ar), 9.45 (s, 1H, NH); Anal. Calcd. for $C_{22}H_{14}N_4OS$: C, 69.09; H, 3.69; N, 14.65; S, 8.38. Found: C, 69.27; H, 3.51; N, 14.43; S, 8.56%.

2.2.1.2. 3-(Benzo[*d*]thiazol-2-yl)-6-(*p*-tolyldiazenyl)-2*H*-chromen-2-imine (4b)

Brown crystals, yield 66% (A), 76% (B); m.p. 204 ℃; ν_{max} / cm^{-1} (KBr) 3221 (NH), 1648 (C=N), 1603 (N=N); ^{1}H NMR (DMSO-d_6) δ = 2.41 (s, 3H, CH_3), 7.40 (d, 2H, *J* = 8.4 Hz, Ar), 7.66-7.78 (m, 4H, Ar and CH), 7.97 (d, 2H, *J* = 7.2 Hz, Ar), 8.02-8.06 (m, 2H, Ar), 8.11-8.22 (m, 2H, Ar), 9.42 (s, 1H, NH); Anal. Calcd. for $C_{23}H_{16}N_4OS$: C, 69.68; H, 4.07; N, 14.13; S, 8.09. Found: C, 69.50; H, 4.26; N, 14.34; S, 8.28%.

2.2.1.3. 3-(Benzo[*d*]thiazol-2-yl)-6-((4-methoxyphenyl)diazenyl)-2*H*-chromen-2-imine (4c)

Brown crystals, yield 60% (A), 71% (B); m.p. 210 ℃; ν_{max} / cm^{-1} (KBr) 3227 (NH), 1654 (C=N), 1606 (N=N); ^{1}H NMR (DMSO-d_6) δ = 3.83 (s, 3H, OCH_3), 6.50 (d, 2H, *J* = 8.4 Hz, Ar), 7.39-7.58 (m, 3H, Ar), 7.90 (s, 1H, CH), 7.95 (d, 2H, *J* = 8.4, Ar), 8.0-8.04 (m, 2H, Ar), 8.72-8.88 (m, 2H , Ar), 9.45 (s, 1H, NH); Anal. Calcd. for $C_{23}H_{16}N_4O_2S$: C, 66.98; H, 3.91; N, 13.58; S, 7.77. Found: C, 66.79; H, 3.73; N, 13.35; S, 7.59%.

2.2.1.4. 3-(Benzo[*d*]thiazol-2-yl)-6-[(4-chlorophenyl)diazenyl]-2*H*-chromen-2-imine (4d)

Yellowish brown crystals, yield 71% (A), 80% (B), m.p. 242 ℃, υ_{max}/ cm^{-1} (KBr) 3211 (NH), 1649 (C=N), 1603 (N=N); ^{1}H NMR (DMSO-d_6) δ = 7.39 (d, 2H, *J* = 7.6 Hz, Ar), 7.39-7.58 (m, 3H, Ar), 7.90 (s, 1H, CH), 7.95 (d, 2H, *J* = 8.4, Ar), 8.0 -8.04 (m, 2H, Ar), 8.72-8.88 (m, 2H , Ar), 9.45 (s, 1H, NH); m/z = 416 (M^+, 33.2%), 417 (M^++1, 10.4), 399 (13.9%), 290 (12.6%), 277 (25.9%), 248 (25.0%), 222 (10.8%), 139 (12.9%), 111 (100%), 75 (48.7%), 69 (18.6%); Anal. Calcd. for $C_{22}H_{13}ClN_4OS$: C, 63.39; H, 3.14; Cl, 8.50; N, 13.44; S, 7.69. Found: C, 63.57; H, 3.31; N, 13.68; S, 7.86%.

2.2.1.5. 3-(Benzo[*d*]thiazol-2-yl)-6-((4-chloro-2-methylphenyl)diazenyl)-2*H*-chromen-2-imine (4e)

Reddish brown crystals, yield 64% (A), 68% (B), m.p. 216 ℃, υ_{max}/ cm^{-1} (KBr) 3235 (NH), 1663 (C=N), 1600 (N=N); ^{1}H NMR (DMSO-d_6) δ = 2.33 (s, 3H, CH_3), 6.39-6.52 (m, 3H, Ar), 7.29 (d, 2H, *J* = 6.8 Hz,

Ar), 7.52-7.58 (m, 3H, Ar), 7.96 (s, 1H, CH), 8.0-8.04 (m, 2H, Ar), 9.43 (s, 1H, NH); m/z = 430 (M^+, 58.7%), 431 (M^++1, 20%), 413 (15.5%), 385 (3.2%), 290 (16.7%), 277 (34.9%), 248 (33.4%), 222 (14.1%), 153 (11.4%), 127 (32.0%), 125 (100%), 99 (18.6%), 89 (52.9%), 77 (8.9%), 63 (25.2%); Anal. Calcd. for $C_{23}H_{15}ClN_4OS$: C, 64.11; H, 3.51; Cl, 8.23; N, 13.00; S, 7.44. Found: C, 64.29; H, 3.34; N, 13.23; S, 7.61%.

2.2.1.6. 3-(Benzo[*d*]thiazol-2-yl)-6-((2,4-dichlorophenyl)diazenyl)-2*H*-chromen-2-imine (4f)

Brown crystals, yield 61% (A), 73% (B); m.p. 208 ℃; υ_{max}/ cm^{-1} (KBr) 3235 (NH), 1663 (C=N), 1600 (N=N); ^{1}H NMR (DMSO-d_6) δ = 7.51-6.52 (m, 3H, Ar), 7.29 (d, 2H, *J* = 6.8 Hz, Ar), 7.52-7.58 (m, 3H, Ar), 7.96 (s, 1H, CH), 8.0-8.04 (m, 2H, Ar), 9.47 (s, 1H, NH); Anal. Calcd. for $C_{22}H_{12}Cl_2N_4OS$: C, 58.55; H, 2.68; Cl, 15.71; N, 12.41; S, 7.10. Found: C, 58.76; H, 2.87; N, 12.65; S, 7.29%.

2.2.2. Synthesis of compounds 5a-f.

Compounds **4a-f** are dissolved in dioxane with the addition of few drops of hydrochloric acid. The mixture was refluxed for 30 minutes, and the solid thus precipitated as a result of cooling was filtered out and recrystallized from a mixture of ethanol and dioxane.

2.2.2.1. 3-(Benzo[*d*]thiazol-2-yl)-6-(phenyldiazenyl)-2*H*-chromen-2-one (5a)

Orange crystals, yield 65%, m.p. 254 ˚C, ν_{max} / cm^{-1} (KBr) 1731 (CO), 1599 (N=N); ^{1}H NMR (DMSO-d_6) δ = 7.49 (d, 2H, *J* = 7.6 Hz, Ar), 7.70-7.79 (m, 5H, Ar and CH), 7.95 (d, 2H, *J* = 9.2 Hz, Ar), 8.06 (d, 2H, *J* = 8.4 Hz, Ar), 8.08 (d, 2H, *J* = 8.0 Hz, Ar); m/z = 383 (M^+, 20.0%), 278 (40.7%), 250 (5.6%), 222 (13.0%), 196 (5.0%), 105 (14.3%), 77 (100%), 69 (8.6%), 51 (26.7%); Anal. Calcd. for $C_{22}H_{13}N_3O_2S$: C, 68.92; H, 3.42; N, 10.96; S, 8.36. Found: C, 68.73; H, 3.61; N, 10.74; S, 8.54%.

2.2.2.2. 3-(Benzo[*d*]thiazol-2-yl)-6-(*p*-tolyldiazenyl)-2*H*-chromen-2-one (5b)

Reddish brown crystals, yield 53%, m.p. 246 ℃, υ_{max} / cm^{-1} (KBr) 1717 (CO), 1607 (N=N); ^{1}H NMR (DMSO-d_6) δ = 2.41 (s, 3H, CH_3), 7.40 (d, 2H, *J* = 8.4 Hz, Ar), 7.66-7.78 (m, 3H, Ar and CH), 7.97 (d, 2H, *J* = 7.2 Hz, Ar), 8.02-8.06 (m, 2H, Ar), 8.11-8.22 (m, 2H, Ar); m/z = 397 (M^+, 80.4%), 278 (71.8%), 250 (10.4%), 222 (24.9%), 196 (8.0%), 178 (5.5%), 119 (22.1%), 91 (100%), 65 (32.5%); Anal. Calcd. for $C_{23}H_{15}N_3O_2S$: C, 69.51; H, 3.80; N, 10.57; S, 8.07. Found: C, 69.32; H, 3.63; N, 10.79; S, 8.26%.

2.2.2.3. 3-(Benzo[*d*]thiazol-2-yl)-6-((4-methoxyphenyl)diazenyl)-2*H*-chromen-2-one (5c)

Reddish brown crystals, yield 69% , m.p. 258 ℃, υ_{max}/ cm^{-1} (KBr) 1718 (CO), 1605 (N=N); ^{1}H NMR (DMSO-d_6) δ = 3.79 (s, 3H, OCH_3), 7.39 (d, 2H, *J* = 7.6 Hz, Ar), 7.40-7.58 (m, 3H, Ar), 7.90 (s, 1H, CH), 7.95 (d, 2H, *J* = 8.4, Ar), 8.0-8.04 (m, 2H, Ar), 8.72-8.88 (m, 2H, Ar), m/z = 413 (M^+, 24.3%), 278 (15.6%), 250 (3.6%), 222 (9.3%), 135 (28.5%), 107 (100%), 92 (32.9%), 77 (48.5%), 64 (16.1%); Anal. Calcd. for $C_{23}H_{15}N_3O_3S$: C, 66.82; H, 3.66; N, 10.16; S, 7.75. Found: C, 66.99; H, 3.84; N, 10.39; S, 7.92%.

2.2.2.4. (3-(Benzo[*d*]thiazol-2-yl)-6-((4-chlorophenyl)diazenyl)-2*H*-chromen-2-one (5d)

Reddish brown crystals, yield 65%, m.p. 282 ℃, υ_{max} / cm^{-1} (KBr) 1725 (CO), 1603 (N=N); ^{1}H NMR (DMSO-d_6) δ = 7.39-7.60 (m, 5H, Ar), 7.90 (s, 1H, CH), 7.98 (d, 2H, *J* = 8.4, Ar), 8.05-8.09 (m, 2H, Ar), 8.72-8.91 (m, 2H, Ar); m/z = 417 (M^+, 34.3%), 418 (M^++1, 11.4%), 278 (74.5%), 250 (10.4%), 222 (22.7%), 196 (9.1%), 139 (20.1%), 111 (100%), 75 (38.5%), 69 (15.7%); Anal. Calcd. for $C_{22}H_{12}ClN_3O_2S$: C, 63.24; H, 2.89; Cl, 8.48; N, 10.06; S, 7.67. Found: C, 63.43; H, 2.72; N, 10.30; S, 7.86%.

2.2.2.5. 3-(Benzo[*d*]thiazol-2-yl)-6-((4-chloro-2-methylphenyl)diazenyl)-2*H*-chromen-2-one (5e)

Brown crystals, yield 59%, m.p. 274 ℃, υ_{max}/ cm^{-1} (KBr) 1741 (CO), 1596 (N=N); ^{1}H NMR (DMSO-d_6) δ = 2.36 (s, 3H, CH_3), 6.39-6.52 (m, 3H, Ar), 7.29 (d, 2H, *J* = 6.8 Hz, Ar), 7.52-7.58 (m, 3H, Ar), 7.96 (s, 1H, CH), 8.01-8.05 (m, 2H, Ar); m/z = 431 (M^+, 38.2%), 432 (M^++1, 13.1%), 403 (3.1%), 278 (55.0%), 250 (10.1%), 222 (26.4%), 196 (9.4%), 153 (12.9%), 127 (30.9%), 125 (100%), 99 (15.2%), 89 (43.3%), 69 (11.9%), 63 (21.7%); Anal. Calcd. for $C_{23}H_{14}ClN_3O_2S$: C, 63.96; H, 3.27; Cl, 8.21; N, 9.73; S, 7.42. Found: C, 63.78; H, 3.46; N, 9.95; S, 7.63%.

2.2.2.6. 3-(Benzo[*d*]thiazol-2-yl)-6-((2,4-dichlorophenyl)diazenyl)-2*H*-chromen-2-one (5f)

Reddish brown crystals, yield 63%, m.p. 262 ℃, υ_{max}/ cm^{-1} (KBr) 1717 (CO), 1605 (N=N); ^{1}H NMR (DMSO-d_6) δ = 6.52-7.11 (m, 3H, Ar), 7.32 (d, 2H, *J* = 6.4 Hz, Ar), 7.56-7.62 (m, 3H, Ar), 7.96 (s, 1H, CH), 8.02-8.07 (m, 2H, Ar); m/z = 450 (M^+, 30.0%), 451 (M^++1, 9.2%), 452 (M^++2, 14.5%), 306 (2.3%), 278 (100%), 250 (12.0%), 222 (26.5%), 196 (8.4%), 173 (8.5%), 145 (22.4%), 109 (10.5%), 69 (6.0%); Anal. Calcd. for $C_{22}H_{11}Cl_2N_3O_2S$: C, 58.42; H, 2.45; Cl, 15.68; N, 9.29; S, 7.09. Found: C, 58.60; H, 2.66; N, 9.51; S, 7.27%.

2.3. Biological evaluation

2.3.1. Antimicrobial assay

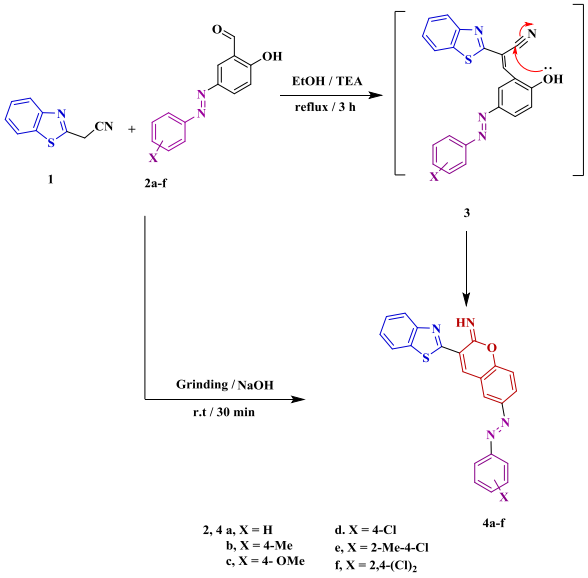
Using the agar well diffusion process, the coumarin derivatives **5a-f** were tested against bacteria such as *staphylococcus aureus* and *Streptococcus mutans* (Gram positive bacteria), *Escherichia coli*, *Pseudomonas aeruginosa*, and *Klebsiella pneumonia* (Gram negative bacteria) [31]. The compounds were measured against bacterial and fungal strains at a concentration of 15 mg/ml, with DMSO as the control.

2.3.2. Method of testing

The following steps were followed in order to assess antimicrobial activity:
i- Preparing the sterilized Petri dishes (20-25 ml, each petri dish) and add on it the sterilized media and take of at room temperature till solidified.
ii- Making a microbial suspension in sterilised saline proportionate to McFarland 0.5 standard solution (1.5x 105 CFU ml^{-1}) and adjusting the turbidity to OD = 0.13 using a spectrophotometer at 625 nm.
iii- A sterile cotton swab was plunged into the modified suspension and overflowed on the dried agar surface within 15 minutes of changing the turbidity of the inoculum suspension. This was then allowed to dry for 15 minutes with the lid in place.
iv- Wells of 6 mm diameter was made within the solidified media with the assistance of sterile borer.
v- By micropipette 100 µl of tested compound solution was added to each well.
vi- In the antibacterial activity, the plates were incubated at 37 °C for 24 hrs.
vii- This experiment was performed in triplicate and zones of inhibition were measured in mm scale.

3. Results and Discussion

The isolated products **4a-f** were obtained by the condensation of 2-cyanomethylbenzothiazole **1** with various arylazosalicylaldehdes **2a-f** under reflux in ethanol in the presence of triethylamine (Scheme 1). The above reaction was reinvestigated using the grindstone process as a green method with a better yield and short time. So compound **1** was grand with arylazosalicylaldehdes **2a-f** in a mortar for 30 minutes using solid sodium hydroxide. Based on melting points and mixed melting points of the obtained products as well as their spectral data and elemental analyses, both protocols (A or B) afforded the same products **4a-f** (see Scheme 1, Table 1 and Figure 3). The structures of **4a-f** were proved using spectroscopic techniques. For example the IR spectrum of **4d** revealed absorption bands at 3211 cm^{-1} (NH) and 1649 cm^{-1} (C=N). The ^1H NMR spectrum of **4d** showed two singlets at δ = 7.90 and 9.45 ppm which were assigned to NH and CH protons, respectively, besides, the signals corresponding to aryl protons. The mass spectrum revealed molecular ion peaks at m/z = 416 (M^+) and 417 (M^++1), which corresponds to the molecular formula of the assigned structure.



Scheme 1

Table 1. Comparison between the yield % of 4a-f by methods A and B

Compound no.	EtOH / TEA/ reflux (Yield %)	NaOH / Grinding (Yield %)
4a	62	70
4b	66	76
4c	60	71
4d	71	80
4e	64	68
4f	61	73

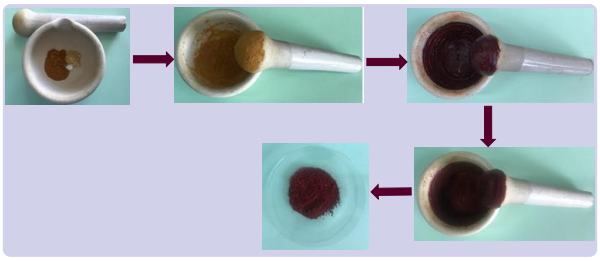
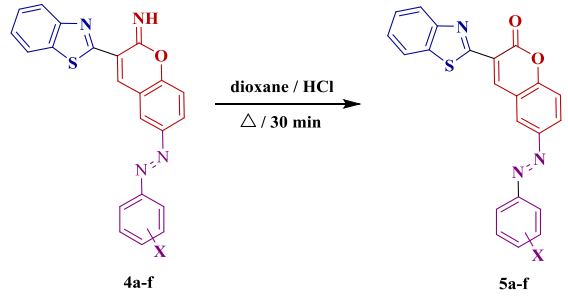


Fig. 3. Reaction sequence of formation of compound **4c**

Compounds **4a-f** were refluxed in dioxane in the presence of few drops of concentrated hydrochloric acid to afford the products **5a-f** (Scheme 2). The structure of the products was proved by spectroscopic data. Thus, compound **5c** appeared absorption band at 1718 cm^{-1} which corresponding to the CO group in its IR spectrum. Its ^1H NMR

spectrum exhibited two singlet signals at δ = 3.79 and 7.90 ppm due to the OCH_3 and CH protons, respectively, in addition to signals corresponding to aryl protons. In addition, its mass spectrum revealed a molecular ion peak at m/z = 413 (M^+), confirmed the molecular formula $C_{23}H_{15}N_3O_3S$.



Scheme 2

Antimicrobial activity

The prepared coumarins **5a-f** were investigated toward Gram positive bacteria like *Staphylococcus* aureus (ATCC:13565), and *Streptococcus mutans* (ATCC:25175). Also, they investigated against Gram negative bacteria such as *Escherichia coli* (ATCC:10536), *Klebsiella pneumonia* (ATCC:10031) and *Pseudomonas aeruginosa* (ATCC:27853), additionally against fungi as example *Candida albicans* (ATCC:10231) and *Asperagillus Nigar* (ATCC:16404). The data summarized in Table 2, indicated that all the tested compounds have antibacterial effect toward *Staphylococcus aureus* (ATCC:13565) using ampicillin as standard drug and they exhibited antifungal activity toward Candida albicans (ATCC:10231) using Nystatin as reference drug.

Table 2. Antimicrobial activity of compounds 5a-f

Sample	5a	5b	5c	5d	5e	5f	Ref.
Gram -ve							**Gent.**
E. coli	*E. coli*	NA	14.3±0.5	NA	11.3±0.5	NA	NA
K.pneum.	*K.pneum.*	NA	12.3±0.5	NA	NA	NA	NA
P. aerug.	*P. aerug.*	NA	14.3±0.5	NA	NA	NA	NA
Gram +ve							**Amp.**
S. aureus	14.6	25.3±0.5	20.3±0.5	10.6±0.5	15.3±0.5	20.3	22±0.1
S. mutans	14.3	12.6±0.6	11.6±0.5	NA	NA	NA	30±0.5
Fungi							**Nyst.**
C.alb.	12.3	12.3±0.5	12.3±0.5	12.3±0.5	NA	13.3	21±0.5
A. Nigar	NA	NA	NA	NA	NA	NA	19±0.5

Compound **5b** showed moderate potency against the four types of bacteria than the other tested compounds. On the other hand, **5b** showed strong activity (25.3 ±0.6) towards *Staphylococcus aureus* than the reference drug ampicillin (22±0.1). Also, **5b** showed a moderate activity against the *Candida albicans* (ATCC:10231).

UV and fluorescence Determination

It have been reported that fluorescent natural chromophores derived from coumarin utilized as fluorescent brighteners, laser colors, and natural nonlinear optical constituents [32,33]. Thus, the UV-visible spectra was measured for the newly coumarin derivatives **5a-f** as shown in figure 4 and Table 3. The results showed compounds **5c, 5e** and **5f** exhibited strong absorption bands at 366, 358 and 360 nm.

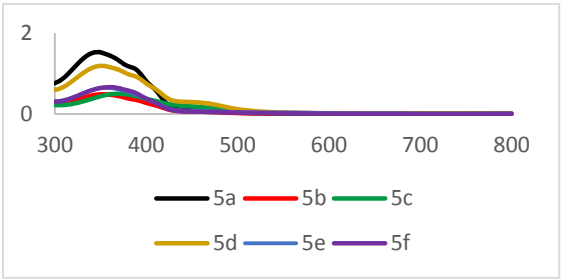


Fig. 4. UV-visible spectra of compounds **5a-f** in DMF

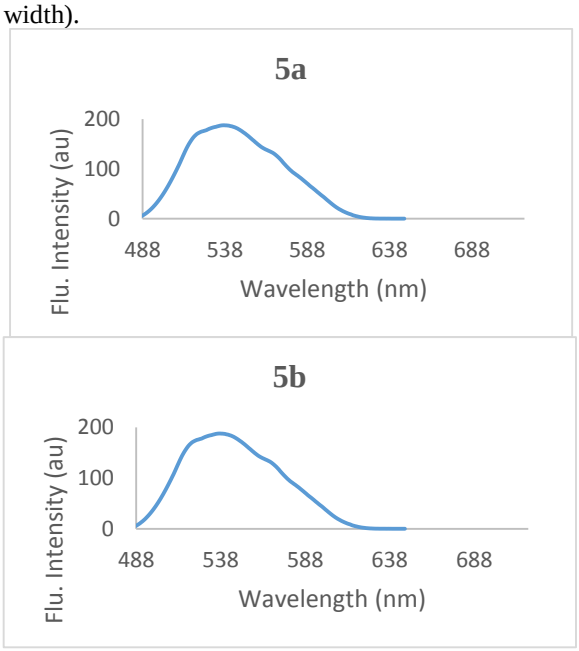
In addition, the fluorescence quantum yields of the newly prepared compounds **5a-f** were measured in order to see whether they could be used as fluorescent materials in laser devices.

The quantum yield of photo-excited fluorescence (QY) is the ratio of the number of photons emitted and the number of photons absorbed. Rhodamine 6G used as a standard (η_{ref} = 0.94, DMF) in this determination

in DMF, the QY was determined using the following equation below.

$$QY = QY_{ref} \frac{\eta^2}{\eta^2_{ref}} \frac{I}{I_{ref}} \frac{A_{ref}}{A}$$

QY: The sample which have emission quantum yield.
QY_{ref} : Reference`s quantum yield.
A_{ref} and A: The absorbance of the reference and sample at the excitation wavelength, respectively.
I_{ref} and I: The calculated integrated emission band areas of the reference and sample, respectively.
η_{ref} and η: The refractive index of the reference and sample.
This approach is based on the fact that the unknowns of the equation must be the same quantitatively for different fluorescent solutions when compared under equal excitation conditions, such as acquisition of excitation wavelength and aperture settings (slit width).



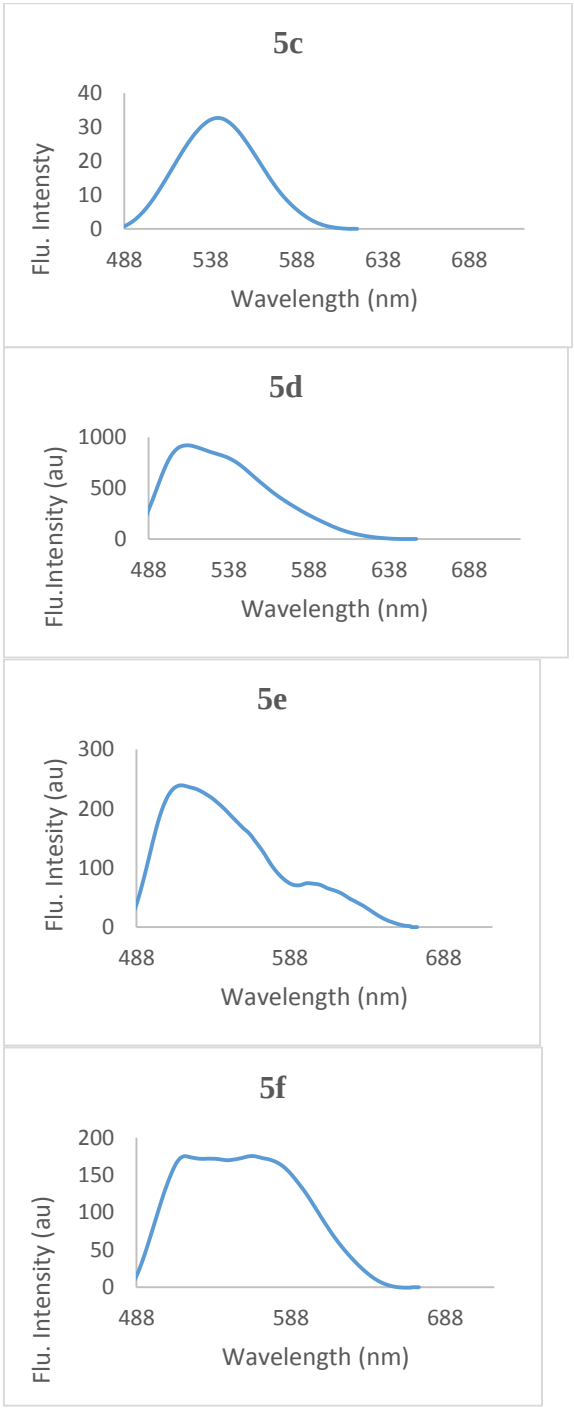


Fig. 5. Florescence spectra of compounds **5a-f** in DMF; λ_{max} = 488 nm

Table 3. Fluorescent properties of synthesized compounds **5a-f**

Compound no.	λ_{max}^{abs}	λ_{max}^{flu}	QY
5a	347	540	0.034
5b	352	538	0.028
5c	366	546	0.091
5d	350	515	0.001
5e	358	517	0.002
5f	360	522	0.004

Fluorescence quantum yields of compounds **5a-c** were determined to be 0.034, 0.028 and 0.091, respectively. The calculated fluorescence quantum yield values are computable with the fluorescent images (resulted from irradiation at 448 nm) as shown in figure 5. From this present study it concluded that coumarin derivatives **5a-f** showed remarkably moderate quantum yields. Such relatively moderate fluorescence quantum yields of coumarin containing benzothiazole moiety can be used as fluorescent tests in different optoelectronic applications.

4. Conclusion

In conclusion, a novel compounds of benzothiazoles contained coumarin moiety **5a-f** was synthesized *via* the reaction of 2-cyanomethylbenzthiazole **1** with 2-hydroxy-5-(aryldiazenyl)benzaldehyde derivatives **2a-f** under grindstone method in the presence of sodium hydroxide at room temperature. The structures of all the newly prepared compounds were proved by ^{1}H NMR, IR, MS and elemental analyses. The fluorescence properties of the coumarin derivatives revealed high absorption bands ranging from 347 to 366 nm, which are caused by the π-π* electronic transition. Fluorescence quantum yields of coumarin derivatives were also found to be in the 0.034-0.091 range. In addition, the antimicrobial activities against *Escherichia coli*, *Klebsiella pneumonia*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Streptococcus mutans* and *Candida albicans* strains have been also screened and some of the examined compounds showed activities against the tested bacterial and fungal strains.

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