



Microwave Assisted Synthesis of Some Azo Disperse Dyes with Antibacterial Activities. Part 1

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THIS study aimed to synthesis a series of disperse dyes based on pyrazolopyrimidinones. Enaminones were used to prepare these dyes by reaction in acidic condition by using microwave irradiations. Their structures were established by using Elemental analysis, FTIR, Mass, UV and NMR spectroscopy. The antibacterial activities of these disperse dyes were also evaluated.

Introduction

The vitality of microwave photons is so low when it contrasted and the connection bond energies and, in this way, microwaves don't influence in a straightway on the molecular structure of a compound and they don't adjust the electronic setup of particles. At the point when materials are irradiated in microwave, they are influenced in an unexpected way. Microwave heating is an elective strategy to conventional heating for quick, compelling and uniform heating [1-4].

Azo disperse dyes are considered as organic colorants that consist of a conjugated chromospheres azo group in association with at least one aromatic or heteroaromatic ring system which have excellent technical properties. In continuation of our interest in synthesis of condensed pyrazolopyrimidinones new dyestuffs [5-9], the current study deals with efficient preparation of condensed disperse dyes by using microwave irradiation as an energy source and studying their antibacterial activities of the synthesized disperse dyes against Gram negative and Gram positive bacteria were investigated.

Material and Methods

All melting points were determined on an electrothermal digital melting point apparatus and are uncorrected. The infrared spectra were recorded on IR-470 infrared spectrophotometer, Shimadzu; and Pye Unicam SP3-100 spectrophotometer using KBr pellet technique at Assiut University. ¹H-NMR spectra were measured on a Varian 300 MHz in deuterated dimethylsulphoxide (DMSO-d₆) using tetramethylsilane (TMS) as internal reference and the chemical shifts are expressed in ppm at Cairo University. Mass spectra were performed on HP model MS-5988 at Cairo University. Microanalyses for C, H, N and halogen were performed on a Vario El Elemental analyzer at Cairo University.

General Procedure for the Synthesis of azo Disperse Dyes 3a-c, 5a-d and 7a,b.

Method A

A mixture of arylhydrazonopyrazolones (4.1, 0.02 M) and enaminones (3.5 g, 0.02 M) was dissolved in glacial acetic acid 5 mL and refluxed for 3 h. the formed solid was collected and crystallized from DMF/water to give dyes **3a-e**.

Method B

A mixture of arylhydrazonopyrazolones

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(0.02 M) and enaminones (g, 0.02 M) dissolved in glacial acetic acid 5 mL and irradiated in a microwave oven at power 420 watt for 5 min.

3-(2-Methoxy-phenylazo)-7-phenyl-pyrazolo[1,5-a]pyrimidin-2-one (3a).

Yield of method (A) (74.2%), Yield of method (B) (87.8%), m.p. 260-262 °C. IR (KBr): $\nu = 3493 \text{ cm}^{-1}$ (NH), 3035 cm^{-1} (CH-arom.), 2930 cm^{-1} (CH-aliph.), 1632 cm^{-1} (C=O of amid group), 1578 cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 425 \text{ nm}$. MS: $m/z = 345$ (M^+ , 65%), 238 (95%), 225 (46%), 182 (100%). $^1\text{H-NMR}$ (DMSO- d_6) 3.96 (s, 3H, OCH_3), 7.47 (d, 2H, $J = 4.8 \text{ MHz}$, arom-H), 7.61 (d, 2H, $J = 5.10 \text{ MHz}$, arom-H), 7.67-7.74 (m, 5H, arom-H), 8.05 (d, 2H, $J = 7.8 \text{ MHz}$, arom-H), 8.73 (d, 1H, $J = 4.8 \text{ MHz}$, NH). Anal. Calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}_2$ (345): C, 66.10; H, 4.35; N, 20.30. Found: C 65.91; H 4.24; N 20.19.

3-(4-Methoxyphenylazo)-7-phenyl-pyrazolo[1,5-a]pyrimidin-2-one (3b).

Yield of method (A) (84.3%), Yield of method (B) (92.8%), m.p. 222-224 °C. IR (KBr): $\nu = 3493 \text{ cm}^{-1}$ (NH), 3035 cm^{-1} (CH-arom.), 2930 cm^{-1} (CH-aliph.), 1632 cm^{-1} (C=O of amid group), 1578 cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 418 \text{ nm}$. MS: $m/z = 345$ (M^+ , 100%), 238 (52%), 210 (25%), 182 (57%). $^1\text{H-NMR}$ (DMSO- d_6) 3.84 (s, 3H, OCH_3), 7.46 (d, 2H, $J = 4.8 \text{ MHz}$, arom-H), 7.54-7.64 (m, 5H, arom-H), 7.79 (d, 2H, $J = 8.7 \text{ MHz}$, arom-H), 8.06 (d, 2H, $J = 8.4$, arom-H), 8.73 (d, 1H, $J = 4.8 \text{ MHz}$, NH). Anal. Calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}_2$ (345): C, 66.10; H, 4.35; N, 20.30. Found: C 65.90; H 4.30; N 20.24.

3-(2-Chlorophenylazo)-7-phenyl-pyrazolo[1,5-a]pyrimidin-2-one (3c)

Yield of method (A) (71 %), Yield of method (B) (90.1%), m.p. 280-282 °C. IR (KBr): $\nu = 3443 \text{ cm}^{-1}$ (NH), 3061 cm^{-1} (CH-arom.), 1633 cm^{-1} (C=O of amid group), 1601 cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 435 \text{ nm}$. MS: $m/z = 348.5$ (M^+ , 52%), 314 (25%), 238 (100%), 210 (25%). $^1\text{H-NMR}$ (DMSO- d_6) 7.67 (m, 5H, arom-H), 7.91 (d, 2H, $J = 8.70 \text{ MHz}$, arom-H), 8.07 (d, 2H, $J = 4.8 \text{ MHz}$, arom-H), 8.33 (d, 2H, $J = 7.8 \text{ MHz}$, arom-H), 7.78 (d, 1H, $J = 4.2 \text{ MHz}$, NH). Anal. Calcd. for $\text{C}_{18}\text{H}_{12}\text{N}_5\text{OCl}$ (349.5): C, 61.80; H, 3.43; N, 20.03. Found: C 62.00; H 3.71; N 20.07.

3-Phenylazo-7-p-tolyl-pyrazolo[1,5-a]pyrimidin-2-one (5a).

Yield of method (A) (65.7%), Yield of method (B) (86.4%), m.p. 200-202 °C. IR (KBr): $\nu = 3493 \text{ cm}^{-1}$ (NH), 3035 cm^{-1} (CH-arom.), 2930 cm^{-1} (CH-aliph.), 1632 cm^{-1} (C=O of amid group), 1578 cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 426 \text{ nm}$. MS: $m/z = 329$ (M^+ , 60%), 252 (59%), 224 (36%), 129 (54%). $^1\text{H-NMR}$ (DMSO- d_6) 2.35 (s, 3H, CH_3), 7.29 (d, 2H, $J = 8.1 \text{ MHz}$, arom-H), 7.45 (d, 2H, $J = 4.8 \text{ MHz}$, arom-H), 7.56-7.68 (m, 5H, arom-H), 8.05 (d, 2H, $J = 8.4 \text{ MHz}$, arom-H), 8.70 (d, 1H, $J = 4.8 \text{ MHz}$, NH). Anal. Calcd. For Chemical Formula: $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}$ (329): C, 69.29; H, 4.59; N, 21.26. Found: C 68.99; H 4.54; N 21.56.

Yield of method (A) (68.6%), Yield of method (B) (89.5%), m.p. 264-266 °C. IR (KBr): $\nu = 3446 \text{ cm}^{-1}$ (NH), 3050 cm^{-1} (CH-arom.), 2917 cm^{-1} (CH-aliph.), 1629 cm^{-1} (C=O of amid group), 1589 cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 446 \text{ nm}$. MS: $m/z = 359$ (M^+ , 72%), 252 (100%), 224 (30%), 196 (85%). $^1\text{H-NMR}$ (DMSO- d_6) 2.49 (s, 3H, CH_3), 3.96 (s, 3H, OCH_3), 7.47 (d, 2H, $J = 4.8 \text{ MHz}$, arom-H), 7.61 (d, 2H, $J = 5.10 \text{ MHz}$, arom-H), 7.67-7.74 (m, 5H, arom-H), 8.05 (d, 2H, $J = 7.8 \text{ MHz}$, arom-H), 8.73 (d, 1H, $J = 4.8 \text{ MHz}$, NH). Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_5\text{O}_2$ (359): C, 66.84; H, 4.74; N, 19.49. Found: C 66.56; H 4.45; N 19.70.

3-(2-Methoxyphenylazo)-7-p-tolyl-pyrazolo[1,5-a]pyrimidin-2-one (5b).

Yield of method (A) (64.3%), Yield of method (B) (88.4%), m.p. 215-217 °C. IR (KBr): $\nu = 3424 \text{ cm}^{-1}$ (NH), 3023 cm^{-1} (CH-arom.), 2960 cm^{-1} (CH-aliph.) 1632 cm^{-1} (C=O of amid group), 1589 cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 415 \text{ nm}$. MS: $m/z = 359$ (M^+ , 24%), 343 (100%), 252 (95%), 242 (45%). $^1\text{H-NMR}$ (DMSO- d_6) 2.42 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 7.07 (d, 2H, $J = 9 \text{ MHz}$, arom-H), 7.42 (d, 2H, $J = 4.5 \text{ MHz}$, arom-H), 7.79-7.86 (m, 4H, arom-H), 8.03 (d, 2H, $J = 8.7 \text{ MHz}$, arom-H), 8.71 (d, 1H, $J = 4.8 \text{ MHz}$, NH). Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_5\text{O}_2$ (359): C, 66.84; H, 4.77; N, 19.49. Found: C 70.26; H 4.86; N 19.55.

3-(4-Methoxyphenylazo)-7-p-tolyl-pyrazolo[1,5-a]pyrimidin-2-one (5c).

Yield of method (A) (58.6%), Yield of method (B) (87.4%), m.p. 246-248 °C. IR (KBr): $\nu = 3446 \text{ cm}^{-1}$ (NH), 3027 cm^{-1} (CH-arom.), 2965 cm^{-1} (CH-aliph.) 1629 cm^{-1} (C=O of amid group), 1586 cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 431 \text{ nm}$. MS: $m/z = 363.5$ (M^+ , 60%), 328 (30%), 252 (100%), 224 (34%). $^1\text{H-NMR}$ (DMSO- d_6) 3.35 (s, 3H, CH_3),

3-(2-Chlorophenylazo)-7-p-tolyl-pyrazolo[1,5-a]pyrimidin-2-one (5d).

Yield of method (A) (58.6%), Yield of method (B) (87.4%), m.p. 246-248 °C. IR (KBr): $\nu = 3446 \text{ cm}^{-1}$ (NH), 3027 cm^{-1} (CH-arom.), 2965 cm^{-1} (CH-aliph.) 1629 cm^{-1} (C=O of amid group), 1586 cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 431 \text{ nm}$. MS: $m/z = 363.5$ (M^+ , 60%), 328 (30%), 252 (100%), 224 (34%). $^1\text{H-NMR}$ (DMSO- d_6) 3.35 (s, 3H, CH_3),

7.41-7.48 (m, 4H, arom-H), 7.54 (d, 2H, $J=8.7$ MHz, arom-H), 7.78 (d, 2H, $J=8.7$ MHz, arom-H), 7.99 (d, 2H, $J=7.8$ MHz, arom-H), 8.70 (d, 1H, $J=4.8$ MHz, NH). Anal. Calcd. For $C_{19}H_{14}N_5OCl$ (363.5): C, 62.72; H, 3.86; N, 19.26. Found: C 62.57; H 3.63; N 19.39.

7-(4-Bromophenyl)-3-(2-methoxyphenylazo)-pyrazolo[1,5-a]pyrimidin-2-one (7a).

Yield of method (A) (78%), Yield of method (B) (89.8%), m.p. 292-294 °C. IR (KBr): $\nu = 3446\text{cm}^{-1}$ (NH), 3050cm^{-1} (CH-arom.), 2917cm^{-1} (CH-alph), 1629cm^{-1} (C=O of amid group), 1589cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 444\text{nm}$. MS: $m/z = 424$ (M^+ , 31%), 316 (30%), 262 (62%), 235 (14%). $^1\text{H-NMR}$ (DMSO- d_6) 3.84 (s, 3H, OCH_3), 7.49 (d, 2H, $J=4.5$ MHz, arom-H), 7.54 (d, 2H, $J=8.4$ MHz, arom-H), 7.79-7.85 (m, 4H, arom-H), 8.02 (d, 2H, $J=8.7$ MHz, arom-H), 8.73 (d, 1H, $J=4.5$ MHz, NH). Anal. Calcd. for $C_{19}H_{14}N_5O_2\text{Br}$ (423): C, 53.80; H, 3.30; N, 16.51. Found: C 53.55; H 3.60; N 16.85.

7-(4-Bromophenyl)-3-(2-chlorophenylazo)-pyrazolo[1,5-a]pyrimidin-2-one (7b).

Yield of method (A) (65.7%), Yield of method (B) (86.6%), m.p. > 300 °C. IR (KBr): $\nu = 3442\text{cm}^{-1}$ (NH), 3063cm^{-1} (CH-arom.), 1632cm^{-1} (C=O of amid group), 1602cm^{-1} (C=C). UV (DMSO) $\lambda_{\text{max}} = 446\text{nm}$. MS: $m/z = 472.5$ (M^+ , 51%), 292 (34%), 316 (100%), 262 (75%). $^1\text{H-NMR}$ (DMSO- d_6) 7.5 (d, 2H, $J=4.8$ MHz, arom-H), 7.67-7.75 (m, 4H, arom-H), 7.83 (d, 2H, $J=8.7$ MHz, arom-H), 8.02 (d, 2H, $J=8.7$ MHz, arom-H), 8.73 (d, 1H, $J=4.8$ MHz, NH). Anal. Calcd. For $C_{18}H_{11}N_5OClBr$ (426.5): C, 50.41; H, 2.57; N, 16.34. Found: C 49.77; H 2.02; N 16.14.

Antibacterial Activities Test

All prepared disperse dyes were screened in vitro for their antibacterial activities against *Pseudomonas aeruginosa* as Gram negative bacteria and *Bacillus cereus*, *Micrococcus luteus* and *Staphylococcus aureus* as Gram positive bacteria by the agar diffusion technique [10]. 1 mg/mL solution in dimethylformamide (DMF) was used. The bacteria are maintained on nutrient agar. DMF showed no inhibition zones. The agar media were inoculated with different microorganism's culture tested after 24 hours of inoculated at 37 °C for bacteria. The diameter of inhibition zone (mm) was measured. The data obtained are summarized in Table 1 (These tests conducted at Assiut University).

Results and Discussion

Synthesis and Characteristics

Our study was based on the preparation of dyes based on microwave technology. In our previous research[1], when using microwave radiation in the preparation of dyes or dye intermediates, we have shown that this technique provides saving of both energy and reaction time, as well as giving better yield. From this point of view aryl-5-Amino-4-(phenyl-hydrazono)-2,4-dihydro-pyrazol-3-one 1a-c react with 3-dimethylamino-1-phenyl-propenone 2 to give the corresponding disperse dyes 3a-c whose structures were elucidated by using elemental analysis, mass spectral data, $^1\text{H-NMR}$ spectroscopy as well as the IR, and UV (Scheme 1).

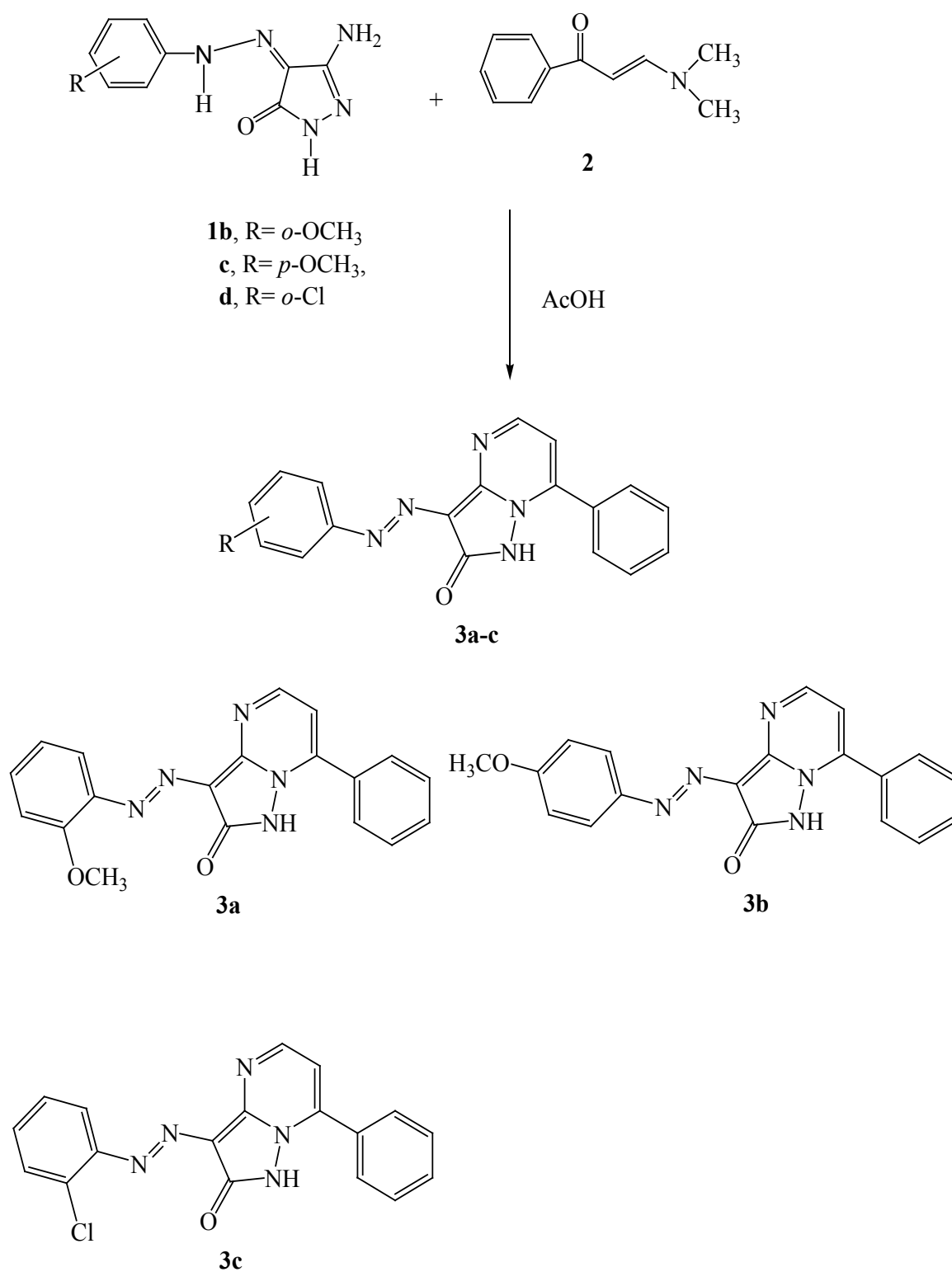
By the same way aryl-5-Amino-4-(phenyl-hydrazono)-2,4-dihydro-pyrazol-3-one 1a-d react with 3-dimethylamino-1-p-tolyl-propenone 4 by using microwave irradiation to yield the disperse dyes 5a-d whose identities were proved using elemental analysis, mass spectral data, $^1\text{H-NMR}$ spectroscopy as well as the IR, and UV (Scheme 2).

Summarily, by using microwave irradiation aryl-5-Amino-4-(phenylhydrazono)-2,4-dihydro-pyrazol-3-one 1a,b react with 1-(4-bromophenyl)-3-dimethylamino-propenone 6 to yield the disperse dyes 7a,b whose structures were conducted using elemental analysis, mass spectral data, $^1\text{H-NMR}$ spectroscopy as well as the IR, and UV (Scheme 3).

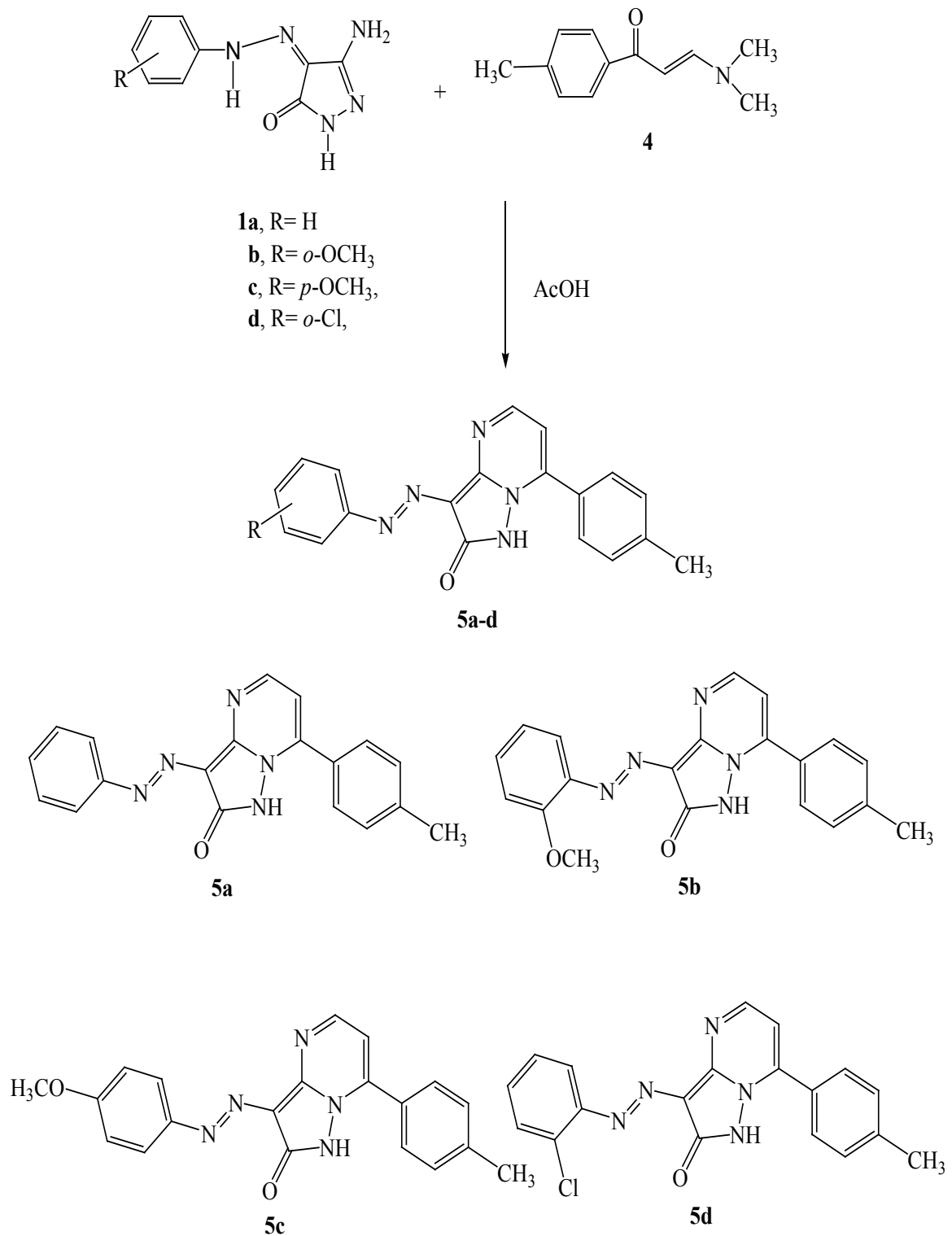
The obtained results revealed that the product yields of microwave irradiation were better than conventional heating and also save time from 3 hrs to 5 min.

Antibacterial Activity

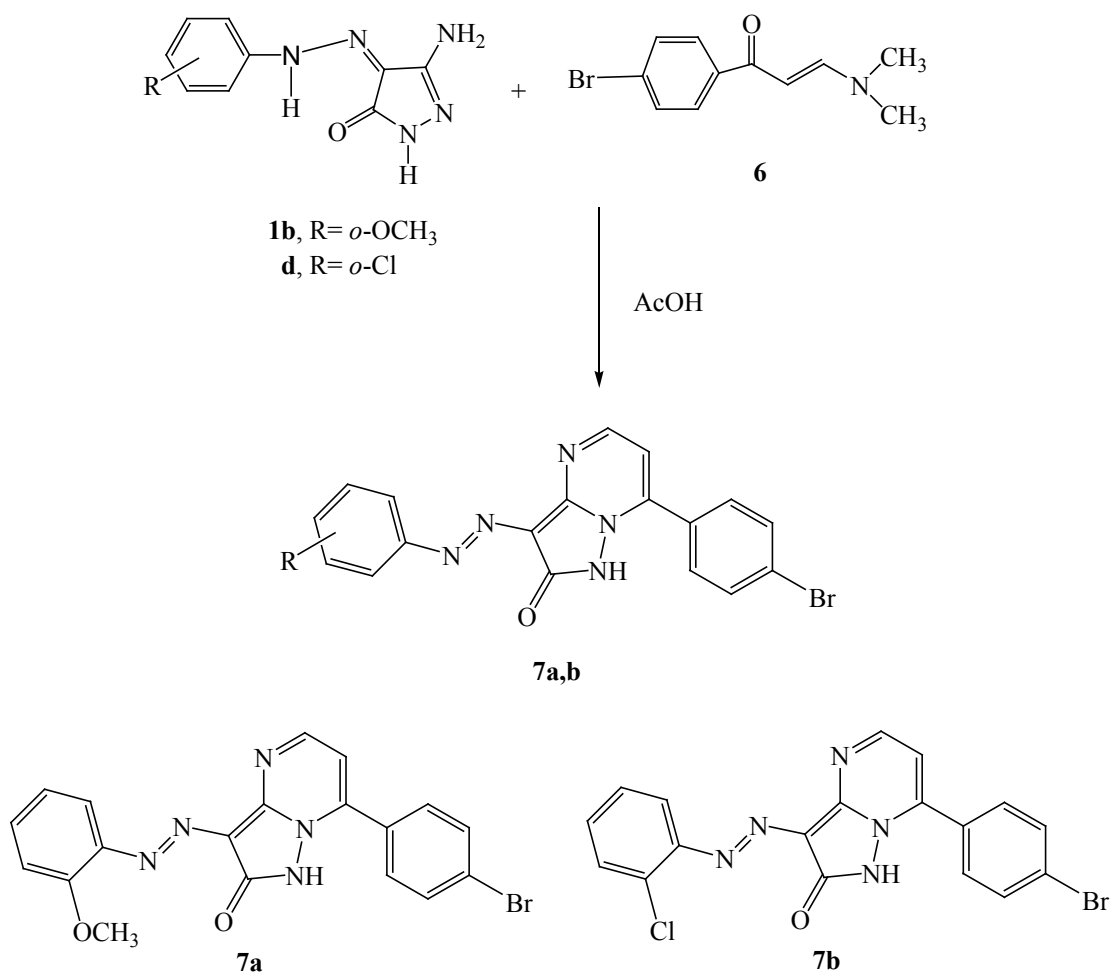
The obtained data that listed in Table 1 showed that the prepared dyes have yielded satisfactory and promising results and can therefore be used for various medical purposes whereas disperse dyes 3a-c, 5a-d and 7a,b showed positive antimicrobial activities against *Pseudomonas aeruginosa*, *Bacillus cereus*, *Micrococcus luteus* and *Staphylococcus aureus*. In contrast dyes 5a, 5d and 7b showed no activities against of *Bacillus cereus*. The same phenomena repeated



Scheme 1. Preparation of disperse dyes 3a-c.



Scheme 2. Preparation of disperse dyes 5a-d.



Scheme 3. Preparation of disperse dyes 7a,b.

TABLE 1. Antibacterial results of the synthetic disperse dyes.

Dye No	G ⁻ (inhibition zone in mm)		G ⁺ (inhibition zone in mm)	
	<i>Pseudomonas aeruginosa</i> (cont.42)	<i>Bacillus cereus</i> (cont.18)	<i>Micrococcus luteus</i> (cont.24)	<i>Staphylococcus aureus</i> (cont.34)
3a	10	10	10	15
3b	12	13	12	12
3c	12	14	10	12
5a	12	0	10	10
5b	10	15	0	15
5c	10	15	12	12
5d	15	0	0	10
7a	10	10	0	15
7b	15	0	10	10

with dyes 5b, 5d and 7a showed no activities against of *Micrococcus luteus*, respectively.

Conclusions

A series of disperse dyes were prepared by using both conventional and microwave heating. The obtained data indicated that the product yields of microwave irradiation were better than conventional heating. Finally, the antimicrobial activities of these dyes against Gram negative and Gram positive bacteria were evaluated.

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تشبيد بعض الصبغات الأزوية المنتشرة بمساعدة الميكروويف مع أنشطتها المضادة للبكتيريا الجزء الأول

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تم تشبيد فريد للصبغات الأزوية المنتشرة المعتمدة على مشتقات البيرازولوبيريمادينات باستخدام اشعة الميكروويف كطريقة خضراء و آمنة للبيئة و مقارنتها بطرق التحضير العادية و وجد أن استخدام هذه الطريقة موفرة للطاقة و وقت التفاعل كما انها تعطى ناتج تفاعل أعلى من الطرق العادية و تمت ايضا دراسة أنشطة هذه الصبغات المنتشرة ضد البكتيريا و وجد ان لها نشاط جيد.