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PET waste recycling as chemical feedstock: Synthesis and antimicrobial activity of new compounds with anticipated industrial use

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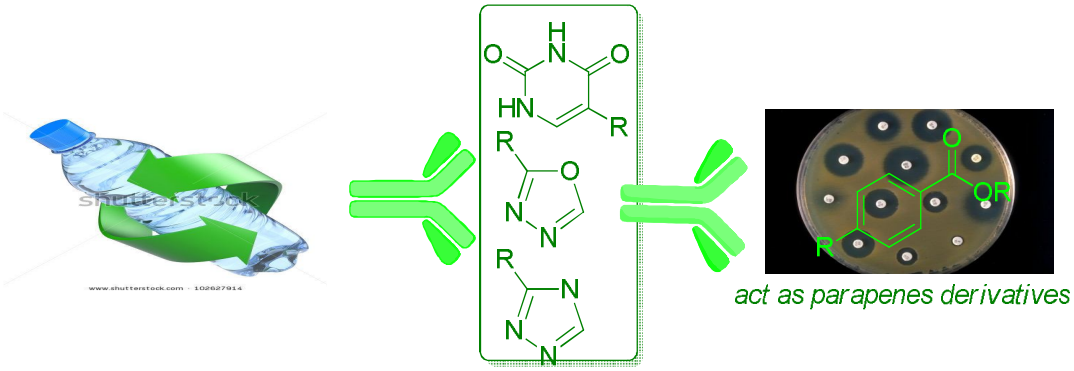
ABSTRACT

Successful solid waste management is a vital component of Egypt's sustainable (plastic waste). Synthesis of new uracil derivatives ***5a, b*** *and 1,3,4-Oxadiazols* ***8,11*** *along with triazoles****10a,b*** *were assayed to have high antimicrobial activity.*

Graphical Abstract:



Keywords: Plastic solid waste, heterocyclic, antimicrobial activity, recycling.

INTRODUCTION

During recent years, the microorganisms have developed increasing resistance against drugs. Therefore, there is a need to develop new, potent antimicrobial agents. Numerous reports have highlighted the chemistry, biological activity and use of Oxdiazoles[1–3]. Also 4-thiazolidine derivatives are also known to possess antibacterial and antifungal [4-8] activity. Meantime Plastic bottles (PET) waste is available and not properly used in Egypt.PET polymer as a feedstock for synthesis new antimicrobial agents especially for industrial uses will be a reasonable alternate of it is recycling. Our present study. Solar energy was used as thermal system for saponification of PET to it'sterepthalic acid monomer using NaOH to synthesis anew cheap 1,3,4-Oxadiazols, triazole derivatives which were assayed for antibacterial\antifungal activities.

MATERIALS AND METHODS

Antibacterial activity : (Fungus), Candida albicans (Fungus).the results were are recorded for each of the tested compound as the average diameter of the inhibition zone (IZ) of bacterial or fungal growth around the disks in mm. The results, depicted in Tables 1 revealed the most of the tested compounds displayed variable inhibitory effects on the growth of *G+* and *G-* bacterial strain and antifungal strains. In general, we could concluded that, the tested compounds showed moderate antibacterial activity when compared with the reference drug and low weak antifungal activity[20-21], when compared with the reference drug. It is worth to mention that, compound **5b** has higher antibacterial activity against *E.*coli and *S.* aureus than the compound containing uracil **5a** . Hydrazide**6** showed the higher activity in antibacterial and in antifungal than **Ampotericin .B** in *aspergilla flavus*, it is observed that oxadiazole moiety **8** has comparatively excellent activity against all bacterial strains, while triazole derivative **9** shows a good activity in all bacterial strains and the 1,2,4-triazole[3,4-b]-1,3,4-thiadiazole **10a,b** showed similar activities astriazole**9**. These bulky substituent deteriorate the antibacterial and antifungal activity of these triazole analogs. On the other hand the compounds **13, 14** shows activity in both bacterial and fungi strains as shown in Table [1].

All melting points were measured on a Gallenkamp melting point apparatus and uncorrected. The infrared spectra were recorded in potassium bromide disks on a Pye Unicam SP-3-300 and Shimadzu FT IR 8101 PC Infrared spectrophotometers. The NMR spectra were recorded on a Varian Mercury VX-500 NMR spectrometer. ^{1}HNMR spectra were run at 500 MHz and ^{13}CNMR spectra were run at 75.46 MHz in dimethyl sulphoxide (DMSO-d_6). Chemical shifts were related that of the solvents. Mass spectra were recorded on a Shimadzu GCMS-QP-1000EX mass spectrometer at 70 e.V.

Table 1 The antimicrobial activity screening of the prepared compounds at concentration 2mg disc^{-1} compared with tetracycline and Amphotericin B as a reference drug

Sample ID	**Antibacterial,*Antifungial activity*activity (in mm/conc1mg/ml $^{-1}$)**					
	Bacillus subtiles(G+)	**Escherichia coli (G-)**	**Neisseria gonrrhoeae (G-)**	**Staphylococcus aureus (G+)**	**Aspergillusflavus (Fungus)**	**Candida albicans (Fungus)**
5a	13	15	13	14	-	-
5b	15	21	13	18	-	-
6	16	16	18	15	21	15
8	17	15	16	22	-	-
9	17	20	18	16	-	-
10a	18	16	18	20	-	-
10b	15	14	15	15	0	12
11a	12	11	12	12	-	-
11b	-	-	-	-	13	12
13	12	13	12	13	0	10
14	13	13	13	14	0	10
tetracycline	**30**	**30**	**32**	**30**	**0**	**0**
Amphotericin B	**0**	**0**	**0**	**0**	**18**	**20**

Where: inhibition zone :High activity>12(mm), Moderate activity 9-11(mm),Slight activity 7-8(mm) and Non sensitive 0-6(mm)

General procedure

PET Hydrolysis: Plastic bottles (22g) were cut into a small strips and mixed with (12g) NaOH placed in sun light for one month to obtain the sodium salt of terepthalte and then dissolved in water then acidify by (5 mol/L) H_2SO_4 afforded of a white precipitate of terephthalicacid**(1),** Yield90 %; m.p. above 300 ° C.Then, terephthalic acid (10 g, 1.66mol) was refluxed in absolute butanol (30ml) and (5ml) H_2SO_4 for 6h to getamixture of**Dibutylterephthalat(2a)**, yellow oil, in 80% yield IR(KBr) ν_{max}/cm^{-1}: 1723 cm^{-1} (C=O);^{1}H NMR (DMSOd_6)**:** 0.853 (t, 6H, CH_3), 1.003 (m, 4H, CH_2) ,1.879 (m, 4H, CH_2), 4.19(t, 4H,CH_2), 8.102(s, 4H, ArH's);
MS*m/z*(%)278 M^+, 100.0%), 216 (27.5%); Anal calcd $C_{16}H_{22}O_4$ (278.15) C, 69.04 %; H, 7.97 %; Found C, 69.00%; H, 7.90%;and**4-(butoxycarbonyl) benzoic acid(2b)**; which could be separated by washing with 10%(Na_2CO_3) recrystallized from (EtOH) white solid in 10%yield ; m.p 116° C; IR(KBr) ν_{max}/cm^{-1}: 3066 (OH), 1722 (C=O), 1693 (C=O), 2961 (CH), 2872 (CH);^{1}H NMR (DMSOd_6)**:** 0.89 (t, 3H, CH_3), 1.3(m, 2H, CH_2) , 1.6 (m, 2H, CH_2),4.02 (s, 1H, OH D_2Oexchangeable), 4.13(t, 2H,CH_2) , aromatic CH at 7.95(dd, 2H, CH), 8.01(dd, 2H, CH); MS*m/z*(%) 206 (M^+, 100.0%), 191 (27.5%); Anal calcd $C_{12}H_{14}O_4$ (222.09) C,64.85%; H, 6.35 %; Found C, 64.80%; H, 6.83%;

Synthesis of nitro derivatives: In a 500- ml, three –necked, round –bottomed flask equipped with a magnetic stirrer, thermometer, decanter and condenser was charged with 20 g compound (**2a, b**). A mixture of 25 ml conc. H_2SO_4 and 75 ml fuming HNO_3 was added drop wise that caused that temperature raised to 80°C . After the addition was completed, the reaction was continued at 100°C for 3 h, then poured on to water / ice mixture, the precipitates were filtered and the filtrate was dissolved in hot water to be recrystalized (EtOH/DMF) (2:1) to afforded nitro derivatives
(**3a** and **3b**) **dibutyl 2-nitroterephthalate** (**3a**) yellowpowderin75% yield; mp 119°C IR(KBr) ν_{max}/cm^{-1}: 1599(C=O), 1466(CH_2), asymmetric 1313(N-O), symmetric 1120(N-O), ^{1}H NMR (DMSOd_6)**:** 0.89 (t, 6H, CH_3), 1.34 (m, 4H, CH_2), 1.61 (m, 4H, CH_2) 4.26 (t, 4H, CH_2), 7.94 (s, 1H,aromatic CH), 8.3 (dd, 1H,aromaticH) , 8.43 (dd, 1H, aromaticH) MS*m/z*(%) 323 (M^+, 100.0%);Anal calcd $C_{16}H_{21}NO_6$(323.14) C59.43 %; H, 6.55 %; N, 4.33%; Found C, 59.40%; H, 6.60%; N, 4.2% and **4-(butoxycarbonyl)-3-nitrobenzoic acid**(**3b**) whitein70% yield; mp 123°C IR(KBr) ν_{max}/cm^{-1}: 3025(OH),1675(C=O),1653(C=O), 1466(CH_2) asymmetric 1313(N-O), symmetric 1120(N-O), ^{1}H NMR (DMSOd_6)**:** .89 (t, 6H, CH_3), 1.30 (m, 4H, CH_2), 1.59 (m, 4H, CH_2) 4.25 (t, 4H, CH_2), 7.91 (s, 1H,aromatic CH), 8.25 (dd, 1H, aromatic H) , 8.39 (dd, 1H, aromatic H) ; MS*m/z*(%) 267 (M^+, 100.0%);Anal calcd $C_{12}H_{13}NO_6$ (267.23) C.53.93%; H, 4.90%; N, 5.24%; Found C, 53.90%; H, 5.00%; N, 5.00%.

Preparation of amino derivatives 4a, b: In 250 ml, three – necked, round – bottomed flask was fitted with a mechanical stirrer, containing 9g of Zn dust, 15 ml of acetic acid, 15 ml of water and 0.5 ml fuming HCl was heated to reflux with stirring for 10 min, then 3.2 of nitro derivatives **3a,b**were added drop wise for 20 min, then stirring was continued for another 10 min at reflux, then left to cooled down to room temperature and 0.3g of $NaHCO_3$ was added. After stirring for 3h, the mixture was filtered off and the filtrate was taken, concentrated and dissolved in EtOH (20ml) and 10ml HCl and the mixture was heated with stirring for 1h. The precipitates were filtered off to afford amino derivatives (4a,4b) and recrystallized from EtOHbutyl2-amino-4-pentanoylbenzoate(4a) yellow brown in 65% yield; mp 129°C IR(KBr) ν_{max}/cm^{-1}: 3423(NH_2), 1709(C=O), ^{1}H NMR (DMSOd_6)**:** 1.02 (t, 6H, CH_3), 1.382 (m, 4H, CH_2), 1.64 (m, 4H, CH_2) 4.24 (t, 4H, CH_2), 7.65 (s, 1H,aromatic CH), 8.03. (dd, 1H,aromaticCH) , 8.6 (dd, 1H, aromaticCH) , 10.45 (s, 2H, NH) ; MS*m/z*(%) 293 (M^+, 100.0%), 291(M-2, 21%); Anal calcd $C_{16}H_{23}NO_4$(293.36) C.65.51%; H, 7.90%; N, 4.77%; Found C, 65.54%; H, 7.92%; N, 4.73%. 3-amino-4-(butoxycarbonyl)benzoic acid (4b), yellow in 60%yield; mp 198; IR (KBr) ν_{max}/cm^{-1}: 3423 (NH_2), 1702 (C=O), 1623 (C=O); ^{1}H NMR (DMSOd_6)**:** 1.02(t, 3H, CH_3), 1.37 (m, 2H, CH_2), 1.73(m, 2H, CH_2), 4.05(s, 1H, OH, D_2Oexchangeable), 4.23 (t, 2H, CH_2) 6.64 (s, 2H, NH_2D_2O exchangeable) , 7.0 (s,1H,aromatic CH), 7.33 (dd, 1H, aromatic CH), 7.67 (dd, 1H, aromatic CH);MS*m/z*(%) 237(M^+, 100.0%), 219 (22%); Anal calcd $C_{12}H_{15}NO_4$(237.10) C, 60.75; H%, 6.37 %; N, 5.90 %; Found C, 60.70%; H, 6.45%; N, 5.88%.

Preparation of uracil derivatives: Compound **4a,b** (0.01mole) , triethylorthoformate (0.03 mole, 4.4 ml) and cyan acetyl urea (0.127g, .01mole) were refluxed in dioxane for 8 h (until the evolution of NH_3) .The solid product was formed on hot then filtered off and recrystallized from the proper solvent to obtain **5a,b** .dibutyl 2-(5-cyano-2-hydroxy-4-oxopyrimidin-1(4H)-yl)benzene-1,4-dioate(5a)recrystallized (EtOH/DMF)(2:1) brown in 62%; mp 198^oC ; IR (KBr) ν_{max}/cm^{-1} : 3348(OH), 2225(CN),1702(C=O), 1612 (C=O), ^1H NMR (DMSO d_6): δ1.02(t, 3H, CH_3), 1.3 (m,2H,CH_2), 1.7 (m,2H,CH_2), 7.38-7.45(d, 2H, CH), 7.99(s, 1H, CH), 9.95(s, 1H, CH), 12.5(s, 1H, OH D_2Oexchangeable); ^{13}C NMR (DMSO *d6*)13.8(CH_3), 18.9(CH_2), 31.1(CH_2), 64.5(CH_2), 114.1 (CH), 115.8(CN), 119.8(CH), 125.9(CH), 130.6 (CH), 135.2(CH), 142.6(CH), 163(CH), 165.4(C=O), 168.4(C=O); MS *m/z* (%) 413 (M^+, 100.0%),223 (6.28%);Anal calcd $C_{21}H_{23}N_3O_6$ (413.42); C, 61.01%; H, 5.61%; N, 10.16;% Found C, 61.05%; H,5.62%; N,10.62%; 4-(Butoxycarbonyl)-2-(5-cyano-2-hydroxy-4-oxopyrimidin-1(4H)-yl)benzoic acid 2243(CN), 1658(C=O) , 1602 (C=O);^1H NMR (DMSOd_6):1.02 (t, 3H, CH_3), 1.3 (m, 2H, CH_2), 1.7(m, 2H, CH_2), 2.05 (s, 1H, OH), 4.05 (s, 1H**,** OHD_2Oexchangeable), 4.23 (t, 2H, CH_2)**,** 7.47 (s, 1H, CH), 7.57 (s, 1H, CH), 7.85 (s, 1H, CH), 8.45 (s, 1H, CH); ^{13C} NMR (DMSO *d6*13.8(CH_3), 18.9 (CH_2), 31.1(CH_2), 64.5 (CH_2), 114.1 (CH), 115.8 (CN), 119.8 (CH), 127.8(CH), 131.1(CH), 136.1(CH), 143 (CH), 163 (CH) 165.4 (C=O), 166(C=O); MS *m/z* (%) 341 (M^+, 100.0%),320 (25%);Anal calcd $C_{17}H_{15}N_3O_6$ (357.32); C, 57.14%; H, 4.23;%; N, 11.76;% Found C, 57.12%; H,4.25%; N,11.70%;

Reactions of 4-butyrylbenzohydrazide*:*Dibutylterepthalate (10 ml) in hydrazine hydrate (1.4 ml) was refluxed in absolute ethanol (30ml) for 8 h to white solid which filtered off and washed with ether, dried and finally recrystallized from ethanol to afforded compound **6** with 87% yield ; m.p 300^o C; IR(KBr) ν_{max}/cm^{-1}: 3321(NH),1659 (C=O), 1612 (C=O), cm^{-1};^1H NMR (DMSOd_6**)**: 1.009 (t, 3H, CH_3), 1.379(m, 2H, CH_2) , 1.660(m, 2H, CH_2), 3.73(t, 2H,CH_2), 4.24 (dd, 2H, NH_2, D_2Oexchangeable), 7.81(dd, 2H, CH) 7.961(dd, 2H, CH), 9.83 (t,1H, NH, D_2Oexchangeable); ^{13}C NMR (DMSO *d6*):δ13.8 (CH_3), 18.9(CH_2), 31.1(CH_2), 64.5(OCH_2), 93.5 (C-CN), 114.1(CH), 115.8(CN), 119.8(CH), 125.9(CH),130.6(CH),135.5(CH), 142.6(CH), 163(C=O), 167.9(C=O);; MS*m/z*(%)236 (M^+, 100.0%), 191 (27.5%); Anal calcd $C_{12}H_{16}N_2O_3$ (236.27) C, 61.00%; H, 6.83%, N, 11.86%; Found C, 61.23%; H, 6.88%, N, 11.80%;.

Synthesis of potassium thiocarbazinate (7):Potassium hydroxide (3mmole) was dissolved in absolute ethanol (25 ml). The solution was cooled in ice bath and 4-butyrylbenzohydrazide (6) (1mmole) was added with stirring. To this carbon disulfide (5mmole) was added in small portion wise with constant stirring. The reaction mixture was agitated continuously for 12h at room temperature. The precipitated potassium thiocarbazinate was collected by filtration, washed with cold ethanol (50ml) and dried in vacuum. The potassium salt thus obtained was used in next step without further purification. 4-(5-mercapto-1,3,4-oxadiazol-2-yl)benzoic acid(8) Potassium salt of thiocarbazinate (1mmole) was treated with water and then filtered and the filtrate was cooled, neutralized to pH 6 using diluted HCl and the separated product was filtered , washed with water, dried and recrystallized from ethanol yellow crystals in 80% yield m.p>300^o C; IR (KBr) ν_{max}/cm^{-1}: 3259(OH), 1671(C=O) ;^1H NMR (DMSOd_6**)**:4.23(s, 1H, SH, D_2O exchangeable), 7.69(s,2H,CH), 8.19(s,2H,CH), 11.84(s, 1H,OH) ;^{13}C NMR (DMSO *d6*): 127.5(CH), 130.2(CH), 131.2(CH), 164.5(C-O),169.3(C=O); MS*m/z*(%)222 (M^+, 100.0%), 205 (7.11%), 180 (41.49%); Anal calcd $C_9H_6N_2O_3S$(222.22) C, 48.64%; H, 2.72%, N, 12.61%,S, 14.43%; Found C, 48.68%; H, 2.69%;N, 12.63%; S,14.40%.

4-(5-mercapto-4-amino-1,3,4-triazole)benzoic acid (9) : Suspension of potassium thiocarbazinate (1mmole) in water (5ml) and hydrazine hydrate (99%, 3mmole) was heated for 18h at 100^o C with occasional shaking. The color of the reaction was changed to green with evolution of hydrogen sulfide gas. A homogenous reaction mixture was obtained during reaction process. The reaction mixture was cooled to room temperature and diluted with cold water (20ml). On acidification with HCl the required triazole was precipitated out, which was recrystallized with DMF-H_2O(1:2) 80%yield, mp= 235^o C; IR (KBr) ν_{max}/cm^{-1}:3855(OH), 3434.6(NH_2), 1623(C=O);^1H NMR (DMSOd_6**)**: 4.2(s, 1H, SH), 7.99(s,2H, CH), 8.11(s,

2H,CH), 14.03(s, 2H, NH_2) ;^{13}C NMR (DMSO *d6*): δ127(CH),128(CH), 128.4(CH), 129.7(CH),142(C-SH), 155(CH–triazole), 167(C=O); MS*m/z*(%)236 (M^+, 100.0%), 180 (41.49%); Anal calcd $C_9H_8N_4O_2S$(236.25) C, 45.75%; H, 3.41%, N, 23.72%, S, 13.57%; Found C, 45.77%; H, 3.42%, N, 23.65%, S,13.59%.

Synthesis of 1,4 (6-substituted-[1,2,4]triazole[3,4-b][1,3,4]thiadiazoles (10 a,b]): An equimolar mixture of compound **8** with appropriate aromatic acid (1mmol) in phosphorous oxychloride (5ml) was refluxed for 5h. The reaction mixture was cooled to room temperature and then gradually poured on to crushed ice with stirring. The mixture was neutralized with $NaHCO_3$ solution and allowed to stand overnight. The solid separated out was filtered and washed thoroughly with cold water,4-(6-(3,5-dinitrophenyl)-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazol-3-yl)benzoic acid (10a) 65% yield, mp=260^o C ; IR (KBr) ν_{max}/cm^{-1} 3431(OH), 1638(C=O),symmetric1153(N-O);^{1}H NMR (DMSO*d$_6$***)**: 2.05 (s, 1H, OH D_2Oexchangeable), 7.69(s, 2H,CH), 8.19(s, 2H,CH), 8.80(s, 2H, CH), 9.08(s, 1H, CH) ;;^{13}C NMR (DMSO *d6*): 118.1(CH), 127.4(CH), 130.2(CH), 135.3(CH), 143.3(CH), 148(CH), 149.3(C-N),167.6(N-C-S), 169.3(C=O); MS*m/z*(%)412 (M^+, 100.0%), 180 (41.49%); Anal calcd $C_{16}H_8N_6O_6S$(412.02) C, 46.61%; H, 1.96%, N, 20.38%, S, 7.78%; Found C, 46.63%; H, 1.97%, N, 20.38%, S,7.80%; and 4-(6-*p*-caboxyl-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazol-3-yl)benzoic acid (10b) 77% yield, m.p= 280 ^{o} C ; IR (KBr) ν_{max}/cm^{-1}3580(OH), 1641(C=O); ^{1}H NMR (DMSO *d$_6$*): 7.69 (s, 4H,CH), 8.19(s, 4H, CH), 13.27(s, 2H, OH), ^{13}C NMR (DMSO *d$_6$*): δ 127.5(CH),130.2(C-C=O),135.8(CH|),138.7 (CH),CH(143.3),149 (CH),167.6 (CH), 170 (C=O); MS*m/z*(%)366 (M^+, 100.0%), 180 (41.49%); Anal calcd $C_{17}H_{10}N_4O_4S$(366.35) C, 55.73%; H, 2.75%, N, 15.29%, S, 8.75%; Found C, 55.74%; H, 2.75%, N, 15.30%, S,8.72%.

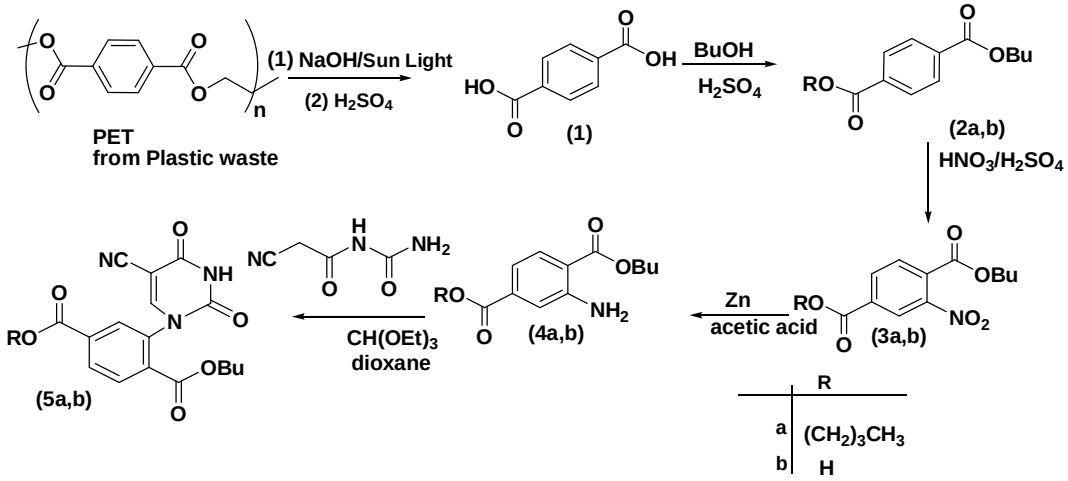
General procedure for the preparation of (5-aryl-1,3,4-oxaadiazole-2-yl)benzoate (11a,b) : A mixture of compound **6** (1mmol) and the appropriate aromatic acid (1mmol) in trifluroacetic acid (10ml) was refluxed for 4-6h. The reaction mixture was slowly poured over crushed ice and kept overnight. The solid thus separated out was neutralized with $NaHCO_3$. Filtered and washed with water and recrystallized from ethanol. **Butyl 4-(5-(3,5-dinitrophenyl)-1,3,4-oxadiazol-2-yl)benzoate (11a)** white m.p=220^o C ; IR (KBr) ν_{max}/cm^{-1} 3088(CH), 1719(C=O),asymmetric 1473(NO),symmetric 1348(NO); ^{1}H NMR (DMSO *d$_6$*): 0.897(t, 3H, CH_3), 1.38 (m, 2H,CH_2), 1.66(m, 2H, CH_2), 4.266(t,2H,CH_2), 7.9-8.32(d, 4H, ArH), 8.85-8.9 (d,2H,CH), 10.99(s, 1H, CH) ; ^{13}C NMR (DMSO *d6*)13.8(CH_3), 18.9(CH_2), 31.1(CH_2), 64.5(OCH_2), 118.1 (CH), 127.4(CH), 128.9(CH), 130.4(CH), 147.4(CH), 149.3CH), 164.5(C-O), 165.9 (C=O), MS *m/z* (%)412 (M^+, 100.0%), 395 (73.37%); Anal calcd $C_{19}H_{16}N_4O_7$ (412.35) C, 55.34%; H, 3.91%, N, 13.59%; Found C, 55.32%; H, 3.92%, N, 13.59%;**,4-(5-(4-(butoxycarbonyl)phenyl)-1,3,4-oxadiazol-2-yl)benzoic acid (11b)** In white m.p= 223 ^{o} C IR (KBr) ν_{max}/cm^{-1} 3248(OH), 1719(C=O), 1666(C=O); ^{1}H NMR (DMSO *d$_6$*): 0.96(t, 3H, CH_3), 1.33 (m, 2H,CH_2), 1.75(m, 2H, CH_2), 2.05(s, 1H, OH D_2Oexchangeable), 4.25(t,2H,CH_2), 7.59(d, 2H, CH), 7.69(d, 2H,CH), 8.03(d, 2H,CH), 8.19(d,2H,CH), ^{13}C NMR (DMSO *d$_6$*): δ13.8 (CH_3), 18.9(CH_2), 31.1(CH_2), 64.5(OCH_2), 127-130.5(CH), 147.4(CH), 164.5(CH), 65.9(C=O),170(C=O); MS *m/z* (%)367 (M^+, 100.0%), 349(18.01%), 310(10.18%); Anal calcd $C_{20}H_{18}N_2O_5$ (366.37) C, 65.57%; H, 4.95%, N, 7.65%; Found C, 65.58%; H, 4.96%, N, 7.66%.

Reaction with isothiocyanate derivatives: Compound **6** (0.01mol) was refluxed with an equimolar amount of ethylisothiocynate in dry dioxane (30ml) in presence NaOH for 3h .after the solution had been cooled, the solid formed was filtered off and crystallized from EtOH**4-(4-ethyl-5-mercapto-4H-1,2,4-triazol-3-yl)benzoic acid(13)** green in 75%; mp 198^{o}C **;** IR(KBr) ν_{max} cm^{-1} **:** 3428 (OH), 1689(C=O);^{1}H NMR (DMSO*d$_6$*):1.02(t, 3H, CH_3), 3.2(q, 2H, CH_2), 4.3 (s, 1H**,** SH), 7.69(dd, 2H, CH), 8.19(dd, 2H,CH), 11.9(s, 1H, OH); ^{13}C NMR (DMSO *d$_6$*): δ13.9 (CH_3), 19.11(CH_2), 126.7(CH), 129.8(CH), 130.6(CH), 134.1(CH), 165.6(CH), 167(CH), 178(C=O); MS *m/z* (%) 146 (M^+, 100.0%),219 (25%);Anal calcd $C_{11}H_{11}N_3O_2$ S (249.29); C, 53.00%; H, 4.45%; N, 16.86% ; S,12.86% Found C, 53.00%; H,4.43%; N,16.87%; S,12.83%.

General procedure: Compound **6** (0.01mol) was heated with phenylisothiocynate in dioxane and conc H_2SO_4 (3ml) at 100°C for 1h ; the solution was then cooled, and water was added drop wise till precipitation formed .the solid thus formed was filtered off, washed and crystallized from ethanol.**Butyl 4-(5-(phenylamino)-1,3,4-thiadiazol-2-yl)benzoate (14)** green in 71%; mp 225°C ;IR(KBr) ν_{max}/cm^{-1} **:** 3406 (OH), 1688(C=O);1H NMR (DMSOd_6):0.91(t, 3H, CH_3), 1.40 (m, 2H,CH_2), 1.68(m, 2H, CH_2), 4.05(s, 1H, NH, D_2Oexchangeable) 4.28(t,2H,CH_2), 6.46-7.01(m,5H, CH), 7.59 (dd,2H,CH) , 8.03 (d, 2H,CH), ;^{13}C NMR (DMSOd_6):δ13.9 (CH_3), 18.9 (CH_2), 31.1 (CH), 64.5 (OCH_2), 117.8 (CH),122.4 (CH), 127.4 (CH),129.5 (CH), 137.8 (CH), 147.4(CH), 152.7(CH),165.9(C=O); MS *m/z* (%)55 (M^+, 100.0%), 77 (82.22%), 242(34%); Anal calcd $C_{19}H_{19}N_3O_2S$(353.44) C, 64.57%; H, 5.42%, N, 11.89%, S, 9.07%; Found C, 64.77%; H, 5.40%, N, 11.86%, S, 9.06%.

RESULTS AND DISCUSSION

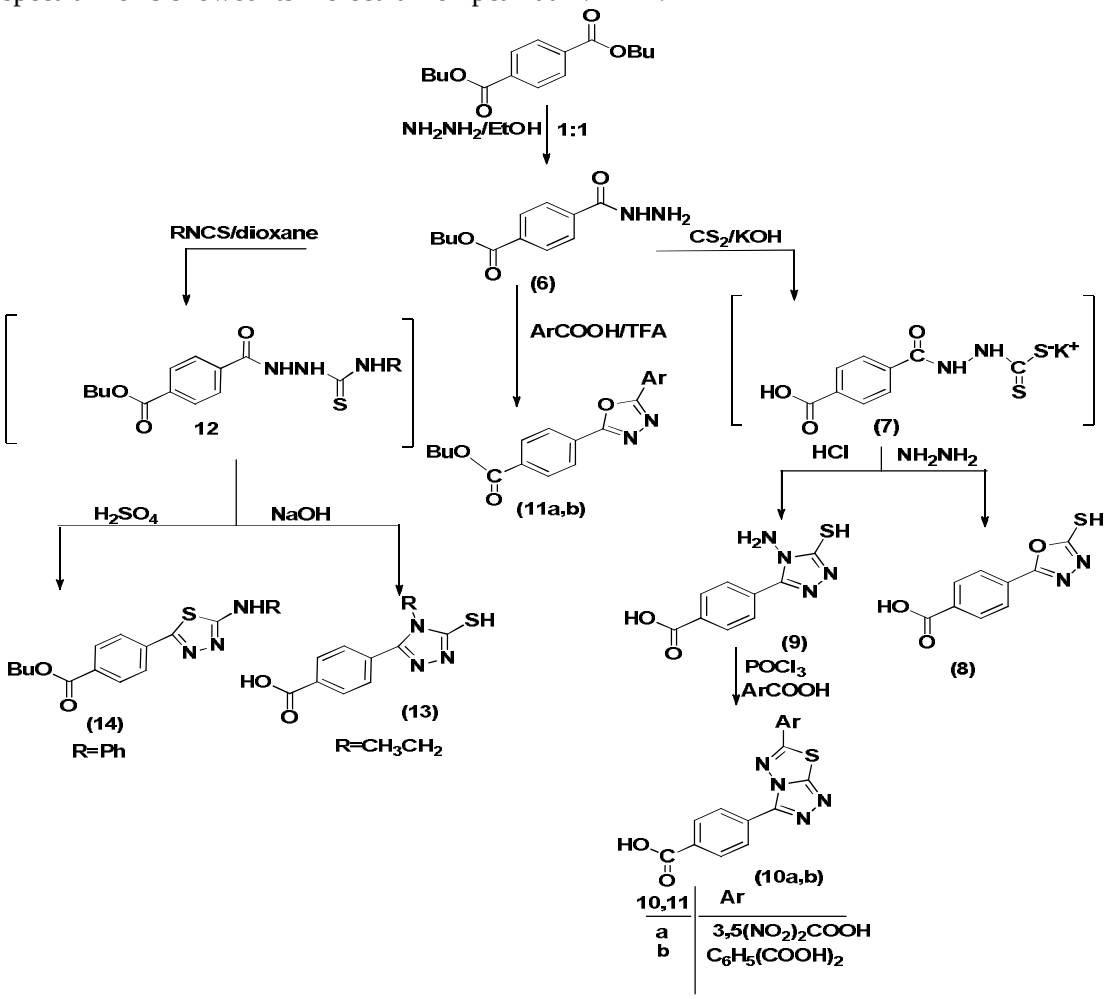
Saponification of PET plastic waste using sun light for 5 weeks afforded the corresponding terephthalic acid (**1**) in excellent yield. Estrification of terephthalicacid(**1**) in dry butanol containing H_2SO_4 [9-11] which afforded mixture of mono and di-butylterephthalate (**2a,b**) and separated very easily (cf.exp.). Up to our knowledge, the monoester not previously separated following the reported method [12]. It is worth to mention that, we could prepare the dieter as a sole product when using a solid acid catalyst (H_2SO_4 /charcoal) as a dehydrating agent instated of H_2SO_4. Conventional nitration of esters **2a, b** by (HNO_3/H_2SO_4) affording their corresponding nitro derivatives **3a,b**. The latter nitro derivatives **3a,b** have reduced in Zn dust and acetic acid affording anilines derivatives **4a,b,** Product **4b** for example showed IR strong absorption band at 3423cm^{-1} attributed to the formed NH_2 group, and its ^{1}HNMR of shows this group as D_2O exchangeable signal at 6.64 ppm ; these along with the expected protons pattern of the parent half ester **2b**[13,14]. Based on our previous reaction pathway [15]. Compounds **4a,b** was allowed to react with quantitative amount of cyanoacetyl urea and triethylorthoformate in refluxed dioxane to produce the uracil derivatives **5a,b** in a good yield . It assumed that the active methylene group in cyanoacetyl urea condense with triethylorthoformate to form the ethoxylidene derivatives which react with the corresponding amine 4**a,b**via loss of ethanol to afford uracil derivatives **5a,b** (c.f.Scheme1).The structures of obtained uracils were confirmed on the basis of their spectral data, their ^{1}HNMRreaveled absence of both of the phthalate ester amino group and the active methylene of the cyanoacetyl urea while showed instead the uracil-H-6 as singlet at δ 6.9ppm[15].



Scheme (1)

4-Butyrylbenzohydrazide (**6**) was prepared by the reaction of dibutylterephthalte (**2a**) with hydrazine hydrate in equal ratio amount in ethanol (scheme**2**). The obtained monohydrazide (**6**) was allowed to react with carbon disulfide in ethanol in presence of a catalytic amount of KOH, and subsequality treated with HCl to give 4-(5-mercapto-4-amino-1,3,4-oxadiazole)benzoic acid (**8**) it is assumed that **8** formed via

the intermediate of thiocarbazinate salt (7)[2,16-19]. The IR spectrum of compound **8,** exhibited a strong carbonyl band at ∂ 1671cm^{-1}and hydroxyl band at ∂ 3259cm^{-1}. The ^{1}HNMR spectrum of compound **8**revealed signals at δ 14.2ppm and δ 11.84ppm attributed to SH and OH protons respectively. Mass spectrum of **8** showed its molecular ion peak at m/z 222.



Scheme (2)

Repeated the above mention reaction using NH_2NH_2 instead of HCl affording the**4-**(5-mercapto-4-amino-1,3,4-triazole)benzoic acid **(9)** was the sole product. It showed an additional (D_2O)exchangeable NH_2protonsto the previously detected SH and carboxyl group in **8**. Structure of triazole**9** was further confirmed by its chemical transformation to the bicycle compounds **10a, b** via condensation with aromatic acids in presence of $POCl_3$[2,16]. In this context, product**11a, b** were prepared by treating hydrazide**6** with appropriate aromatic acids in presence of trifluroacetic acid Structures of **11a,b** were established on the basis of their spectral data an previous reported [2].Moreover, it was found that 4-butylrylbenzohydrazide (**6**) reacts with isothiocyanate derivatives affording product **13** and **14** based on the reaction PH. Thus in presence of NaOH compound **13** obtained as sole product, while in the presence of H_2SO_4 compound **14** was formed in good yield [18]. It seems that both product **13** and **14** were formed via 1:1 adduct **12**. Compound **13** showed carbonyl band at ∂1689 cm^{-1}, OH and SH bands at ∂ 3428, 3220 cm^{-1} respectively, The ^{1}H NMR spectrum revealed two signals at δ 11.9 and δ 14.3 for OH and SH(D_2O-exchangable) respectively. In addition, the mass spectrum showed molecular ion base peak m/e at 249 (scheme **2**), this interpretation is in accordance with previous report [18]. Its worth to mention that,

compound **14**[1]HNMR spectral data ,reaveled the characterstics of butrateres due which was absent due to base–hydrolysis in the corresponding triazole**13**.

APPLICATIONS

PET waste which utilized as chemical feed stock for preparing new cheap compounds with antibacterial/antifungal activity

CONCLUSION

The preparation and characterization of novel 1,3,4- Oxadiazol,triazoles and uracil moiety has been detailed from plastic bottle waste utilizing the renewable source of safe energy (Sun energy). PET waste which utilized as chemical feed stock for preparing new cheap compounds with antibacterial/antifungal activity. In this report, an easy and useful method to synthesize antibacterial activity of benzoic acid hydrazide**6** resembling that of the known parapenes preservative [20-21] which are useful in industrial application. On the other hand the activity of the 1,3,4- Oxadiazol**8** show higher activity against all types of strains. It can be concluded that this class of compounds certainly holds great promise towards pursuit to discover novel class of antimicrobial agents. Further studies are being conducted to acquire more information about quantitative structure–activity relations.

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REFERENCES

[1] A.Z. Mamdouh, E.Abu-Zaied, M.ElTelbanie, G H .Elgemhie, Galal A. M. Nawwar, *European Journal of Medicinal Chemistry*, **2011,** 46, 229-235
[2] S. Vikrant, Palekar, Amey J. Damle, S.R. Shukla;*European Journal of Medicinal Chemistry*, **2009,** 44, 5112–5116.
[3] M.R. Shiradkar, K.K.Murahari, H.R.Gangadasu, T.Suresh, C.C.Kalyan, D.Panchal, R.Kaur, P.Burange, J.Ghogare, V.Mokale, M.Raut, *Bioorg. Med. Chem.* **2007**, *15*, 3997-4008.
[4] A. Gürsoy, Karali, *Eur. J. Med. Chem.* **2003**, *38*,633-634.
[5] P. Vicini, M.Incerti, I.Doytchinova, P.La Colla, B.Busonera, R.Loddo, *Eur. J.Med. Chem.* **2006**, *41*,624-632.
[6] M. E. Abd EI-Fattah; *Arch. Pharm. Res.***1998,** 21(6), 723-728.
[7] R. VenkatRagavan; V. Vijayakumar; N. SuchethaKumari *European Journal of Medicinal Chemistry,* **2010,** 45, 1173–1180.
[8] MiroslavSoural; Jan Hlaváč; PavelHradil; IvetaFryšová; MariánHajdúch; Valerio Bertolasi; Michal Maloň; *European Journal of Medicinal Chemistry* **2006,** 41, 467–474.
[9] Daniel Paszun and TadeuszSpycha**j**, *Ind. Eng. Chem. Res.* **1997,** *36*, 1373.
[10] A. Oku, L.-C.Hu, E. Yamada; *J. Appl. Polym.Sci.*, **1997,** 63, 595.
[11] S.M. Al-Salem; P. Lettieri, J. Baeyens,*Waste Management* , **2009,**29 , 2625–2643
[12] Elodie-Denise Chenot, *Synthetic Communications*, **2007,** 37, 483–490.
[13] Chikara Kaamura; Kei Ito, Reijiro Nishida; Ichiro Yoshihara; Nobushige Numa *Progress in Organic Coatings,* **2002,** 45 , 185–191.
[14] Krzysztof Wojciechowski; AgnieszkaWyrc˛cebak; Joanna Gumula*Dyes and Pigments* **2003**, 6, 99–109.

[15] Bo-RenZhuang, Gien-Jow Hsu and Kuangsen Sung; *Bioorganic & Medicinal Chemistry*, 2006, 14, 3399–3409.
[16] Kamal M. Dawood; Ahmad M. Farag; Hatem A. Abdel-Aziz; *Heteroatom Chemistry* 2005, 16(7).
[17] M.G.Soni, S.L.Taylor, N.A.Greenberg, G.A.Burdock; Food chemical toxicology 2002, 40, 1335-1373.
[18] El-Sayed M..A .Yakout,Yahia A. Allam, GalalA.M.Nawwar; *Heteroatom Chemistry*,1998 ,10.
[19] AsifHusain, Md. ArifNaseer,*MedChem Res* **2011**, 20,47–54.
[20] Bansod S. and Rai M, *World Journal of Medical Sciences*, **2008**, 93 (2), 81-88.
[21] Andrews J. M, *Journal of Antimicrobial Chemotherapy***, 2001**, 48, 5-16