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Synthesis of Some New Substituted 1,2,4-Triazole and 1,3,4-Thiadiazole and Their Derivatives

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Several 5-(isomeric pyridyl)-4-aryl-1,2,4-triazole-3-thiol/yl-thiomethyl/yl-thioethyl/yl-thiobenzyl and yl-thioglycolic acids were prepared as possible biologically active agents. The infrared, nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR), mass spectra and elemental analysis of these compounds are reported.

Introduction

1,2,4-Triazole and their derivatives constitute an important class of organic compounds with diverse agricultural, industrial and biological activities [1-3], including anti-microbial [4-5], sedative, anti-convulsant [6-7] and anti-inflammatory [8]. The synthesis of these heterocycles has received considerable attention in recent years [9-12]. As part of our program aimed at developing new biologically active compounds, in this work we report the synthesis of some new 3,5-disubstituted-1,2,4-triazole, substituted 1,3,4-thiadiazole and their derivatives through the intramolecular cyclization of 1,4-disubstituted thiosemicarbazides as shown in the Scheme.

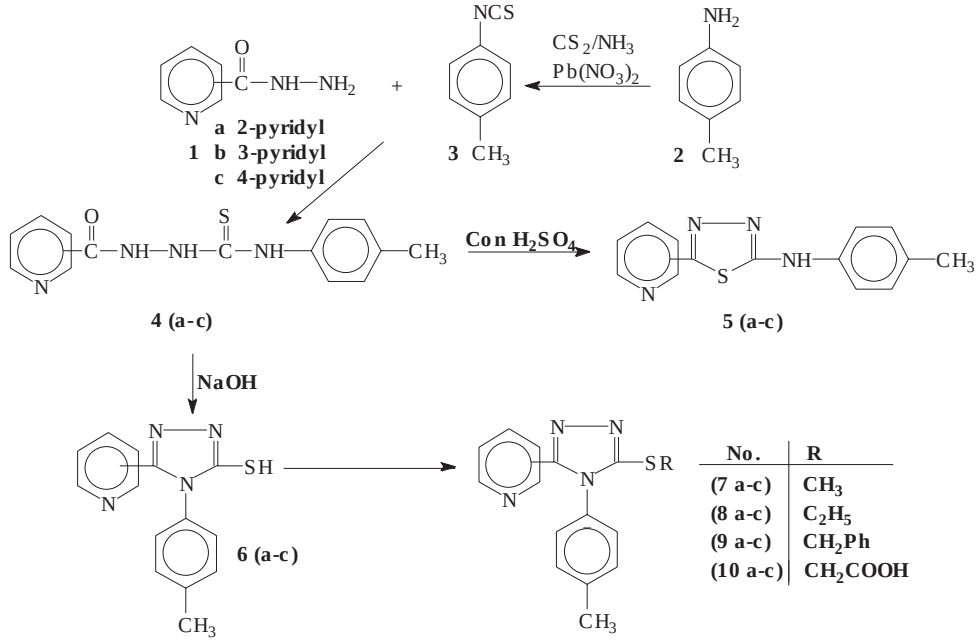
Experimental

Melting points was determined using an electrothermal digital melting point apparatus and are uncorrected. FTIR spectra were recorded on a UNICAM Galaxy Series FTIR 5000 spectrophotometer using KBr disk. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian 500 MHz instrument. The EIMS were recorded on a MAT-112-s-machine.

Preparation of 4-methylphenyl isothiocyanate (3)

A mixture of 4-methylphenyl amine (0.25 mol, 26.75 g), carbon disulfide (0.39 mol, 37.4 ml) and methanol (95%, 60 ml) was cooled to about 10°C. Ammonia (33%, 0.32 mol) was added dropwise to the reaction mixture with continuous stirring. The mixture was allowed to stand overnight. Water was added to the mixture (400 ml). An aqueous solution of lead nitrate (0.25 mol, 82.7 g) was slowly added to the solution.

The mixture was then steam distilled to yield 4-methylphenyl isothiocyanate **(3)** as a low melting point solid. The infrared (KBr) of the isolated isothiocyanate indicates a prominent characteristic absorption band at 2070 cm^{-1} attributed to an N=C=S group (yield 52%).



Scheme

Preparation of 1-(4-methylphenyl)-4-(isomeric pyridoyl)thiosemicarbazides (4a-c)

General procedure: Respective substituted pyridine carboxylic acid hydrazides **(1a-c)** (0.004 mol) were dissolved in absolute ethanol (50-80 ml), depending upon the solubility of the compounds. The 4-methylphenyl isothiocyanate **(3)** (0.004 mol) was separately dissolved in absolute ethanol (30 ml). Then the solution of the isothiocyanate was poured into the solution of hydrazide with continuous stirring. The reaction mixture was then refluxed. Each reaction required different times determined by TLC. After the completion of the reaction, the mixture cooled to room temperature. As a result a white solid crystal appeared. The crude solid was then filtered and recrystallized from appropriate solvent to yield the compounds **(4a-c)**.

Preparation of 2-(4-methylphenylamino)-5-(isomeric pyridyl)-1,3,4-thiadiazole (5a-c)

General procedure: Each thiosemicarbazide **(4a-c)**(7 x 10^{-4} mol, 0.2 g) was added portionwise to 25 ml of concentrated sulfuric acid at 0°C with continuous stirring. The reaction mixture was stirred further for 3 h at room temperature and then allowed to stand overnight. Neutralization with diluted sodium hydroxide precipitated a crude solid, which was filtered, and washed with water. The crude product was then recrystallized from a mixture of acetic acid and water (1:1 or 1:2) to furnish disubstituted 1,3,4-thiadiazole **(5a-c)**.

Preparation of 2,4-Dihydro-4-(4-methylphenyl)-5-(isomeric pyridyl)-3H-1,2,4-triazole (6a-c)

General procedure: Solid thiosemicarbazides **(4a-c)**(4 x 10^{-4} mole) were added portionwise to 15 ml of 2M sodium hydroxide solution. The reaction mixture was refluxed and completion of the reaction checked by using TLC. After the completion of the reaction, the mixture was allowed to cool and then filtered. The filtrate was acidified with 2M hydrochloric acid. The precipitated solid was filtered, washed thoroughly with water, dried and recrystallized from ethanol/water.

Preparation of 3-methyl-, 3-ethyl-, 3-benzyl-4-(4-methylphenyl)-5-(isomeric pyridyl)-1,2,4-triazoles (7-9a-c)

A mixture of suitable substitute-*s*-triazole-3-thiol**(6a-c)**(1.48 x 10^{-3} mol, 0.4 g), corresponding alkyl halide (1.48 x 10^{-3} mol) in ethanolic alkali (0.08 g KOH in 20 ml aqueous EtOH) refluxed for 2 h. On the cooling of the reaction mixture, a crude precipitate was obtained, which was recrystallized, from water-ethanol (2:8).

Preparation of 3-carboxymethylthio-4-(4-methylphenyl)-5-(isomeric pyridyl)-1,2,4-triazoles (10a-c)

A mixture of suitable substitute-1,2,4-triazole-3-thiol (7.4 x 10^{-4} mol), monochloroacetic acid (7.4 x 10^{-4} mol) and 20 ml of aqueous potassium hydroxide solution (7.4 x 10^{-4} mol) was refluxed for 3 h. The hot reaction mixture was filtered and the filtrate was acidified with 2M hydrochloric acid. The various substituted 1,2,4-triazol-3-yl-thioglycolic acids were thus precipitated out, filtered, washed with water and recrystallized from an appropriate solvent.

Results and Discussion

In the present work 1-(4-methylphenyl)-4-(isomeric pyridoyl)thiosemicarbazides **(4a-c)** were used as the key intermediates for the synthesis of heterocyclic compounds. Various thiosemicarbazides were synthesized by condensing 4-methylphenyl isothiocyanate **(3)** with isomeric pyridine carboxylic acid hydrazides **(1a-c)**. The required isothiocyanate was prepared from the treatment of 4-methyl aniline with carbon disulfide and ammonia in methanol and then reacted with lead nitrate. The acid or base catalyzed intramolecular dehydrative cyclization of the thiosemicarbazides **(4a-c)** furnished the corresponding substituted 1,3,4-thiadiazole **(5a-c)** and 1,2,4-triazole **(6a-c)** respectively.

Compounds **(6a-c)**, when treated with methyl iodide, ethyl iodide, benzyl chloride and mono chloroacetic acid in the presence of potassium hydroxide, yielded methylthio **(7a-c)**, ethylthio **(8a-c)**, benzylthio **(9a-c)** and thioglycolic acid derivatives of 1,2,4-triazole **(10a-c)**. In Table 1 the observed melting points, % yields, formula and elemental analysis of the products are listed and all the products were obtained in good yields (56-95%).

The infrared spectra of compounds **(4a-c)** (Table 2) exhibited a characteristic strong absorption at 1240-1258 cm^{-1} attributable to the C=S of the thiourea residue. The carbonyl absorption in these compounds was observed at 1655-1682 cm^{-1}. The dehydrative cyclization of **(4a-c)** in sodium hydroxide or concentrated sulfuric acid afforded corresponding substituted 1,2,4-triazole **(6a-c)** and substituted 1,3,4-thiadiazole **(5a-c)** respectively. In the IR spectra of compounds **(5-6a-c)** the absence of signals in the region

1655-1682 cm^{-1} established the lack of a C=O group. The refluxing of compounds **(6a-c)** with methyl iodide, ethyl iodide, benzyl chloride and mono chloroacetic acid in alkaline ethanol yielded corresponding methylthio **(7a-c)**, ethylthio **(8a-c)**, benzylthio **(9a-c)** and carboxymethylthio **(10a-c)** derivatives of 1,2,4-triazole respectively.

Table 1. Yields, Melting points, Formulas and Elemental Analysis for Compounds.

Compd.	R	R′	Yield (%)	M.p. °C	Formula	Found (required) (%)		
						C	H	N
4a	2-Pyridyl	4-CH_3Ph	85	192	$C_{14}H_{14}N_4SO$			
4b	3-Pyridyl	4-CH_3Ph	75	188	$C_{14}H_{14}N_4SO$			
4c	4-Pyridyl	4-CH_3Ph	82	202	$C_{14}H_{14}N_4SO$	58.27(58.72)	5.02(4.93)	19.49(19.57)
5a	2-Pyridyl	4-CH_3Ph	71	251	$C_{14}H_{12}N_4S$			
5b	3-Pyridyl	4-CH_3Ph	56	223	$C_{14}H_{12}N_4S$			
5c	4-Pyridyl	4-CH_3Ph	64	280	$C_{14}H_{12}N_4S$	62.38(62.66)	4.47(4.51)	11.70(11.93)
6a	2-Pyridyl	4-CH_3Ph	89	232	$C_{14}H_{12}N_4S$			
6b	3-Pyridyl	4-CH_3Ph	72	263	$C_{14}H_{12}N_4S$			
6c	4-Pyridyl	4-CH_3Ph	87	276	$C_{14}H_{12}N_4S$	62.48(62.66)	4.62(4.51)	11.78(11.93)
7a	2-Pyridyl	4-CH_3Ph	89	287	$C_{15}H_{14}N_4S$			
7b	3-Pyridyl	4-CH_3Ph	73	248	$C_{15}H_{14}N_4S$			
7c	4-Pyridyl	4-CH_3Ph	85	219	$C_{15}H_{14}N_4S$	63.93(63.81)	5.05(5.00)	19.13(19.85)
8a	2-Pyridyl	4-CH_3Ph	89	284	$C_{16}H_{16}N_4S$			
8b	3-Pyridyl	4-CH_3Ph	81	142	$C_{16}H_{16}N_4S$			
8c	4-Pyridyl	4-CH_3Ph	94	189	$C_{16}H_{16}N_4S$	64.61(64.84)	5.22(5.45)	18.92(18.92)
9a	2-Pyridyl	4-CH_3Ph	67	268	$C_{21}H_{18}N_4S$			
9b	3-Pyridyl	4-CH_3Ph	73	242	$C_{21}H_{18}N_4S$			
9c	4-Pyridyl	4-CH_3Ph	95	209	$C_{21}H_{18}N_4S$	70.08(70.37)	5.18(5.06)	15.50(15.64)
10a	2-Pyridyl	4-CH_3Ph	69	210	$C_{16}H_{14}N_4SO_2$			
10b	3-Pyridyl	4-CH_3Ph	57	208	$C_{16}H_{14}N_4SO_2$			
10c	4-Pyridyl	4-CH_3Ph	63	278	$C_{16}H_{14}N_4SO_2$	58.53(58.88)	4.47(4.33)	17.32(17.18)

Table 2. Infra red (KBr, cm^{-1}) Spectral Data for Compounds.

No.	C=O	C=N,C=C	C=S	NH	No.	C=O	C=N, C=C	C=S	NH	No.	C=O	C=N, C=C
4a	1655	1584	1240	3250	**6a**	—-	1541	1248	2885	**8a**	—-	1560
4b	1658	1595	1258	3300	**6b**	—-	1543	1275	2730	**8b**	—-	1520
4c	1682	1570	1255	3200	**6c**	—-	1606	1265	3430	**8c**	—-	1570
5a	—-	1556	—-	2890	**7a**	—-	1550	—-	—-	**9a**	—-	1560
5b	—-	1540	—-	2764	**7b**	—-	1580	—-	—-	**9b**	—-	1587
5c	—-	1541	—-	2885	**7c**	—-	1540	—-	—-	**9c**	—-	1570
10a	1728	1571	—-	—-	**10b**	1736	1560	—-	—-	**10c**	1720	1565

In each of the synthesized derivatives **(7-10a-c)** the absence of signals in the region 1240-1275 cm^{-1} and above 3200 cm^{-1} in IR spectral data established the absence of C=S and NH respectively. ^{1}H-NMR, ^{13}C-NMR, mass spectral data and elemental analysis of the compounds supported this.

In the ^{1}H-NMR data of compounds **(7a-c)** the addition of a singlet peak in the region 2.62-2.63 ppm was observed due to S-CH_3protons. In the NMR spectra of **(8a-c)** the protons of the ethyl group gave triplet signals in the region of 1.32-1.33 for $\underline{CH_3}$- CH_2 and quartet for CH_3-$\underline{CH_2}$ in the region 3.15-3.16 ppm. The methylene proton of benzylthio **(9a-c)** derivatives exhibited a signal in the 4.02-4.43 ppm region while the methylene protons of the thioglycolic acid group in **(10a-c)** gave a signal in the region 3.92-4.08 ppm. The ^{1}H-NMR spectral data of the synthesized compounds are depicted in Table 3.

In the ^{13}C-NMR spectrum of the compounds **(7a-c)** the signal of the carbon of S-CH_3 was observed in the region 14.24-14.36 ppm. For the ethyl group of ethylthio derivatives **(8a-c)** the CH_3 appeared in

the region 14.74-14.81 ppm, while the methylene carbon attached to the sulfur atom exhibited a signal in the region 26.24-26.42 ppm. In the ^{13}C-NMR of compounds **(9a and c)** the methylene carbon bridge between sulfur and phenyl appeared in the region 35.95-36.02 ppm. The methylene carbon of thioglycolic acid derivative **(10a and c)** appeared in the region 34.06-34.14 ppm. The ^{13}C-NMR spectral data of most of the synthesized compounds are tabulated in Table 4.

Table 3. ^{1}H-NMR Spectral Data for Compounds.

No.	^{1}H-NMR (DMSO-d^{6} δ ppm)
4a	2.23 (s, 3H, CH_3), 7.16 (d, 2H, Ar-H), 7.33 (d, 2H, Ar-H), 7.64(m, 1H, Py-H), 8.00-8.08 (m, 2H, Py-H), 8.68 (m, 1H, Py-H), 9.71 (bs, 1H, NH), 10.69 (bs, 1H, NH).
4b	2.25 (s, 3H, CH_3), 7.15 (d, 2H, Ar-H), 7.41 (d, 2H, Ar-H), 7.55(m, 1H, Py-H), 8.27 (m, 1H, Py-H), 8.75 (m, 1H, Py-H), 9.10 (m, 1H, Py-H), 9.71, 9.82, 10.72 (3bs, 3H, 3NH).
4c	2.28 (s, 3H, CH_3), 7.13 (d, 2H, Ar-H), 7.29 (d, 2H, Ar-H), 7.84(m, 2H, Py-H), 8.76 (m, 2H, Py-H), 8.77 (m, 2H, Py-H), 9.74 (bs, 1H, NH), 9.79 (bs, 1H, NH), 10.83 (bs, 1H, NH).
5a	2.35 (s, 3H, CH_3), 7.25 (m, 2H, Ar-H), 7.29 (m, 2H, Ar-H), 7.39(m, 1H, Py-H), 7.68 (m, 1H, Py-H),8.49 (m, 1H, Py-H), 8.58 (m, 1H, Py-H), 14.23 (bs, 1H, NH).
5b	2.33 (s, 3H, CH_3), 7.21 (d, 2H, Ar-H), 7.32 (d, 2H, Ar-H), 7.39(m, 1H, Py-H), 7.77 (m, 1H, Py-H), 7.89 (m, 1H, Py-H), 8.37 (m, 1H, Py-H), 14.81 (bs, 1H, NH).
5c	2.37 (s, 3H, CH_3), 7.24 (m, 2H, Ar-H), 7.26 (m, 2H, Ar-H), 7.32(m, 2H, Py-H), 8.56 (m, 2H, Py-H), 14.35 (bs, 1H, NH).
6a	2.33 (s, 3H, CH_3), 3.37 (bs, 1H, SH), 7.14 (m, 2H, Ar-H), 7.22 (m, 2H, Ar-H), 7.38(m, 1H, Py-H), 7.77 (m, 1H, Py-H), 7.88 (m, 1H, Py-H), 8.36 (m, 1H, Py-H).
6b	2.35 (s, 3H, CH_3), 3.25 (bs, 1H, SH), 7.21 (d, 2H, Ar-H), 7.28 (d, 2H, Ar-H), 7.37(m, 1H, Py-H), 7.63 (m, 1H, Py-H), 8.46 (dd, 1H, Py-H), 8.54 (dd, 1H, Py-H).
6c	2.29 (s, 3H, CH_3), 6.43 (bs, 1H, SH), 7.08 (d, 2H, Ar-H), 7.32 (d, 2H, Ar-H), 7.66(m, 2H, Py-H), 8.81 (m, 2H, Py-H).
7a	2.34 (s, 3H, $PhCH_3$), 2.62 (s, 3H, S-CH_3), 7.20 (d, 2H, Ar-H), 7.21 (d, 2H, Ar-H), 7.36(m, 1H, Py-H), 7.90 (m, 1H, Py-H), 7.95 (m, 1H, Py-H), 8.33 (m, 1H, Py-H).
7b	2.38 (s, 3H, $PhCH_3$), 2.63 (s, 3H, S-CH_3), 7.33 (m, 2H, Ar-H), 7.36 (m, 2H, Ar-H), 7.41(m, 1H, Py-H),7.73 (m, 1H, Py-H), 8.55 (m, 1H, Py-H), 8.58 (m, 1H, Py-H).
7c	2.39 (s, 3H, $PhCH_3$), 2.63 (s, 3H, S-CH_3), 7.30 (m, 2H, Ar-H), 7.35 (m, 2H, Ar-H), 7.38(m, 2H, Py-H), 8.56 (m, 2H, Py-H).
8a	1.32 (t, 3H, $CH_2\underline{CH_3}$ 2.39 (s, 3H, $PhCH_3$), 3.16 (q, 2H, $\underline{CH_2}$ CH_3), 7.32 (d, 2H, Ar-H), 7.31 (dd, 2H, Ar-H), 7.37(m, 1H, Py-H), 7.38 (m, 1H, Py-H), 8.55 (d, 1H, Py-H), 8.57 (d, 1H, Py-H).
8b	1.33 (t, 3H, $CH_2\underline{CH_3}$), 2.37 (s, 3H, $PhCH_3$), 3.15 (q, 2H, $\underline{CH_2}$ CH_3), 7.31 (m, 2H, Ar-H), 7.35 (m, 2H, Ar-H), 7.40(m, 1H, Py-H), 7.73 (m, 1H, Py-H), 8.54 (m, 1H, Py-H), 8.56 (m, 1H, Py-H).
8c	1.32 (t, 3H, $CH_2\underline{CH_3}$), 2.36 (s, 3H, $PhCH_3$), 3.15 (q, 2H, $\underline{CH_2}$ CH_3), 7.19 (m, 2H, Ar-H), 7.34 (m, 2H, Ar-H), 7.90(m, 2H, Py-H), 8.33 (m, 2H, Py-H).
9a	2.34 (s, 3H, $PhCH_3$), 4.43 (m, 2H, CH_2), 7.10 (d, 2H, Ar-H), 7.25 (m, 2H, Ar-H), 7.30 (m, 2H, Ar-H), 7.35 (m, 3H, Ar-H, Py-H), 7.90(ddd, 1H, Py-H), 7.95 (d, 1H, Py-H), 8.32 (d, 1H, Py-H), 8.56 (m, 1H, Py-H).
9b	2.38 (s, 3H, $PhCH_3$), 4.04 (m, 2H, CH_2), 7.01 (d, 1H, Py-H), 7.20 (d, 2H, Ar-H), 7.38 (m, 2H, Ar-H), 7.40 (m, 2H, Ar-H), 7.45 (m, 3H, Ar-H, Py-H), 7.90(ddd, 1H, Py-H), 8.54 (d, 1H, Py-H), 9.1 (m, 1H, Py-H).
9c	2.37 (s, 3H, $PhCH_3$), 4.43 (m, 2H, CH_2), 7.21-7.37 (m, 11H, Ar-H, Py-H), 8.55 (dd, 1H, Py-H).
10a	2.37 (s, 3H, CH_3), 4.06 (s, 2H, CH_2), 7.21 (m, 2H, Ar-H), 7.30 (m, 2H, Ar-H), 7.36 (m, 1H, Py-H), 7.90 (ddd, 1H, Py-H), 7.95(m, 1H, Py-H), 8.34 (m, 1H, Py-H), 12.95(bs, 1H, OH).
10b	2.39 (s, 3H, CH_3), 3.92 (s, 2H, CH_2), 7.08 (m, 1H, Py-H), 7.32 (m, 2H, Ar-H), 7.45 (m, 2H, Ar-H), 7.90 (ddd, 1H, Py-H), 8.05(m, 1H, Py-H), 8.54 (m, 1H, Py-H), 12.95(bs, 1H, OH).
10c	2.38 (s, 3H, CH_3), 4.08 (s, 2H, CH_2), 7.19-7.51 (m, 6H, Ar-H, Py-H), 8.66 (m, 2H, Py-H), 12.85(bs, 1H, OH).

The mass spectra of the compounds **(4-10a)** were studied. The molecular ion peak was found to be present in all the compounds, although their relative intensities varied from 2 to 100%. One of the major fragmentation patterns was found to be similar to the one described earlier by Potts *et al.* [13], and shown in the Figure. Thus, the cleavage of bonds between N_1-N_2 and N_4-C_5 resulted in the (pyridyl-CN)$^+$ ion radical, which was observed in compounds **(6-10a)** at m/e 104. This ion lost CN radical to give (pyridyl)$^+$ ion at m/e 78. The cleavage of N_1-N_2 and C_3-N_4 bonds was also observed in 1,2,4-triazole and its thio-derivatives. Thus in the thiol series, the (CNSR)$^+$ was seen at m/e 59 (R=H), 73 (R=CH_3), 87 (R=C_2H_5), 149 (R=CH_2Ph) and 117 (R=CH_2COOH). The mass spectral data of these compounds are given in Table 5.

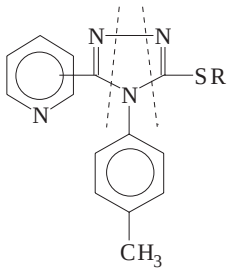


Figure. Fragmentation pattern of the s-triazole and its derivatives.

Table 4. ^{13}C-NMR Spectral Data for Compounds.

No.	^{13}C-NMR (DMSO-d^6 δ ppm)
4a	0.49, 122.39, 122.41, 126.86, 128.27, 128.42, 133.93, 136.62, 137.63, 148.44, 149.25, 181.32.
4b	20.52, 122.33, 123.37, 128.44, 129.86, 135.54, 136.52, 139.20, 148.62, 152.31, 168.86, 181.10.
4c	20.54, 121.67, 126.01, 128.52, 134.34, 136.52, 139.60, 150.158, 164.45, 181.14.
5a	20.73, 124.00, 124.83, 128.04, 129.16, 132.58, 137.22, 138.06, 145.31, 149.17, 149.60, 169.09.
5b	20.72, 123.09, 123.40, 128.41, 129.67, 132.41, 135.25, 138.56, 148.22, 148.26, 150.26, 169.08.
5c	20.83, 123.59, 127.32, 128.27, 130.14, 131.25, 139.63, 145.42, 147.19, 169.79.
6a	20.73, 122.36, 123.45, 128.43, 129.85, 131.58, 135.78, 139.17, 148.49, 148.60, 150.91, 168.86.
6b	20.73, 124.06, 124.92, 128.04, 129.19, 132.46, 137.24, 138.16, 145.20, 149.20, 149.61, 169.10.
6c	20.78, 121.83, 128.31, 129.96, 131.57, 133.23, 139.34, 148.40, 150.06, 169.31.
7a	14.24, 20.72, 123.47, 124.27, 127.01, 129.74, 131.94, 137.15, 138.89, 146.32, 149.00, 153.61, 153.94.
7b	14.36, 20.72, 123.07, 123.55, 127.36, 130.50, 130.80, 135.29, 140.04, 148.20, 150.39, 152.24, 153.52.
7c	14.30, 20.76, 121.38, 127.23, 130.60, 130.79, 133.94, 140.23, 150.07, 152.22, 154.36.
8a	14.78, 20.77, 26.39, 121.38, 121.42, 127.28, 127.33, 130.55, 130.89, 133.97, 140.16, 150.06, 152.12, 153.39.
8b	14.81, 20.71, 26.42, 123.11, 123.53, 127.45, 130.42, 130.91, 135.30, 139.96, 148.23, 150.37, 152.14, 152.50.
8c	14.74, 20.72, 26.24, 123.51, 127.11, 129.69, 132.02, 137.14, 138.83, 149.01, 152.96, 153.51.
9a	20.70, 35.95, 123.53, 124.33, 127.04, 127.49, 128.43, 128.98, 129.67, 131.91, 136.94, 137.17, 138.89, 148.29, 149.02, 152.63, 153.58.
9c	20.75, 36.02, 121.40, 127.23, 127.48, 128.44, 128.98, 130.52, 130.74, 133.88, 136.90, 140.19, 150.08, 152.22, 153.06.
10a	20.73, 34.06, 123.51, 124.34, 126.97, 129.80, 131.79, 137.19, 139.01, 146.23, 149.03, 152.54, 153.59, 169.19.
10c	20.80, 34.14, 122.09, 122.81, 125.96, 127.16, 130.35, 130.48, 130.75, 148.01, 148.08, 169.09.

Table 5. MS Spectral Data for Compounds.

No.	MS (EI , 70ev) MS(%)
4c	286 (10.4), 252 (18.3), 179 (43.5), 148 (94.1), 107 (100), 78 (98.3).
5c	268 (100), 267 (99.1), 263 (37.2), 105 (28.9), 97 (98.0).
6c	268 (63.0), 266 (100), 207 (8.6), 162 (7.3), 104 (13.8), 91 (20.6), 78 (13.1), 59 (2.0).
7c	282 (30.7), 195 (12.3), 131 (37.1), 104 (100), 91 (24.7), 78 (7.2), 73 (4.3).
8c	296 (13.3), 294 (18.6), 267 (57.3), 130 (37.6), 119 (95.7), 104 (19.0), 91 (53.1), 87(24.6), 78 (12.8).
9c	358 (2.0), 236 (13.6), 181 (6.1), 149 (4.2), 104 (7.1), 91 (18.8), 78 (3.5).
10c	326 (100), 309 (18.3), 282 (99.1), 266 (98.0), 248 (39.0), 235 (34.1), 195 (87.1), 191 (18.0), 124 (97.11), 117 (18.4), 104 (89.2), 91 (98.1), 78 (56.3).

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