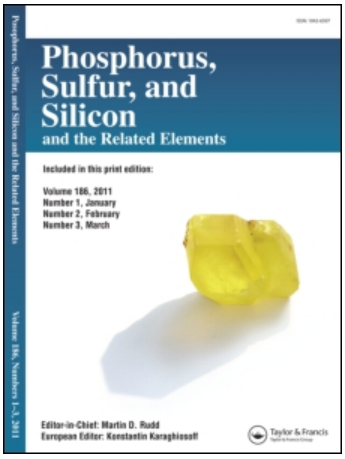

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Efficient Synthesis and Plant-Growth Regulating Activities of 1-Aryloxyacetyl-4-(2-benzofuroyl)- semicarbazides

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Under grinding and solvent-free conditions via a one-pot procedure, the reaction of 2-benzofuroyl chloride with ammonium thiocyanate and aryloxyacetetic acid hydrazide afforded 1-aryloxyacetyl-4-(2-benzofuroyl)-thiosemicarbazide. Not isolating, the resulting thiosemicarbazides were further ground with $HIO_4{\cdot}H_2O$ to give a series of new 1-aryloxyacetyl-4-(2-benzofuroyl)-semicarbazides in high yields. Structures of compounds are confirmed by elemental analyses and IR and ^1H NMR spectra.

Keywords Grinding; semicarbazides; solvent-free; synthesis; thiosemicarbazides

INTRODUCTION

The development of solvent-free organic synthesis is of current interest because of the many advantages, such as reduced pollution, low cost, simplicity in process and handling, and potential applications in combinatorial chemistry and the chemical industry.[1]

Substituted semicarbazides can be used as herbicides[2,3] and plant growth regulators.[4] Despite the importance of these compounds, the efficient synthetic methods are still very scarce. The synthetic

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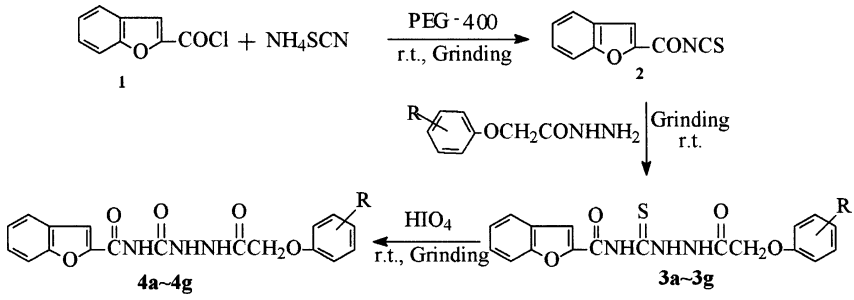
methods of 1,4-diacylthiosemicarbazides have been established. They can be readily prepared by reactions of acyl chloride with ammonium thiocyanate and acid hydrazides under the condition of phase transfer catalysis in high yields.[5,6] However, the analogous species, 1,4-diacylsemicarbazides, cannot be obtained using similar methods because of the instability of intermediate acyl isocyanate.

Recently, we have reported the synthesis of some 1,4-diacyl semicarbazides using easily made 1,4-diacyl thiosemicarbazides in a water suspension.[7] In continuation of our interest on biologically active compounds such as thiosemicarbazides and their derivatives[8,9] and on developing a benign and rapid strategy for organic transformation,[10] we herein wish to report an expeditious, one-pot and solvent-free method for the preparation of a series of new 1,4-diacylsemicarbazides. This method offers a reduction in reaction time, operational simplicity, a cleaner reaction, an easy work-up, and better yields over conventional methods.

RESULTS AND DISCUSSION

2-benzofuroyl chloride (**1**) was ground with ammonium thiocyanate in the presence of poly(ethylene glycol)-400 (PEG-400) in a mortar at r.t., giving 2-benzofuroyl isothiocyanate (**2**). Compound **2** did not need to be isolated; **2** was further reacted with an equivalent of aryloxyacetic acid hydrazides affording 1-aryloxyacetyl-4-(2-benzofuroyl)-thiosemicarbazides (**3a–g**). With need to be isolated, compounds **3a–g** were further ground with $HIO_4 \cdot 2H_2O$, giving the products 1-aryloxyacetyl-4-(2-benzofuroyl)-semicarbazides (**4a–g**) (Scheme 1). It was interesting to note that $HIO_4 \cdot 2H_2O$ was a quite efficient reagent for the transformation of C=S to C=O to afford 1-aryloxyacetyl-4-(2-benzofuroyl)-semicarbazides **4**.



SCHEME 1

TABLE I Preparation of Compounds 4a–g in Solvent-Free and R.T. Conditions

		Total reaction time (min)		Yield (%)	
Compound	R	a	b	a	b
4a	H	12	120	97	90
4b	2-CH_3	12	120	90	88
4c	3-CH_3	12	120	90	85
4d	4-CH_3	12	120	95	89
4e	4-CH_3O	12	120	93	90
4f	4-Cl	12	120	94	89
4g	4-NO_2	12	120	94	85

a: Reaction conditions: grinding at r.t. for a total time of 12 min.

b: Reaction conditions: According to reference 7, **3a–g** were prepared in CH_2Cl_2 for a total time of 1.5 h; it further reacted with $HIO_4 \cdot 2H_2O$ in a water suspension for 0.5 h to give **4a–g**.

We also carried out these reactions in solvent media according to the literature method.[7] The results are listed in Table I. It indicates that the described method has the advantages of no solvent, mild reaction conditions, and a shorter period with higher yields compared to traditional methods in solvent and water suspension.

The plant-growth regulating activities of **4a–g** were tested on wheat growth, and the average length of seedlings and roots are recorded. The data of compounds **4a–g** are compared with the known plant-growth regulator, α-NAA. All compounds **4a–g** efficiently promote the growth of wheat seedling and root. Maximum lengths of seedling obtained were 11.72 cm at 0.0001 ppm for **4a–g** and 11.45 cm at 0.01 ppm for α-NAA. Furthermore, maximum lengths of roots were 13.48 cm at 0.0001 ppm for **4a–g** and 12.96 cm at 0.0001 ppm for α-NAA (see Table II).

In conclusion, title compounds can be expeditiously synthesized by a one-pot procedure under solvent-free conditions in excellent yields. The method is relevant in the context of green chemistry and also provides better prospects in terms of a yield, short reaction period, and simplicity in performance. All products were screened for wheat growth regulating activity. Some compounds, such as **4b** and **4d**, have significant effects on wheat growth.

EXPERIMENTAL SECTION

IR spectra were recorded using KBr pellets on a Nicolet AVATAR 360 FT-IR spectrophotometer, and ^{1}H NMR spectra were recorded on a Avanci-D2X-200 instrument using $(CD_3)_2SO$ as solvent and Me_4Si as

TABLE II Effect at Various Concentrations (ppm) of Compounds 4a–g on Wheat Seeds (Gansu 602) After 7 Days

	Length of Seedlings (cm)						Length of Roots (cm)					
Compound	10	1	0.1	0.01	0.001	0.0001	10	1	0.1	0.01	0.001	0.0001
4a	5.76	11.90	11.80	11.70	10.50	11.30	1.49	7.20	10.10	10.80	11.40	11.50
4b	6.20	11.59	11.35	11.49	10.11	11.72	3.20	10.95	12.26	11.03	11.08	11.58
4c	5.77	11.37	11.64	11.21	11.05	11.10	3.25	10.13	11.25	10.58	11.71	11.20
4d	2.48	10.72	10.46	10.99	11.31	11.53	0.41	9.66	11.20	11.15	11.85	13.48
4e	6.21	10.73	10.96	11.19	11.54	11.01	4.99	10.79	11.44	11.90	10.57	11.75
4f	6.06	11.28	10.76	10.99	11.58	11.11	4.48	10.04	10.61	10.66	11.05	11.14
4g	5.55	11.41	11.12	11.24	11.26	11.37	3.80	10.39	10.74	12.14	11.37	12.90
α-NAA	2.49	8.46	10.87	11.45	11.01	11.08	0.00	0.70	3.95	9.73	11.36	12.96

internal standard. Elemental analyses were performed on a Vario El Elemental Analysis instrument. Melting points were observed in an open capillary tube and are uncorrected. 2-benzofuroyl chloride[11] and aryloxyacetic acid hydrazides[12] were prepared according to literature procedures.

General Procedure for the Preparation of 4a–g

The mixture of 2-benzofuroyl chloride chloride (**1**) (1 mmol), ammonium thiocyanate (1.5 mmol), and PEG-400 (0.02 mmol) was ground in an agate mortar with a pestle for 2 min until a yellow solid was formed, and TLC (ethyl acetate:benzene: ethyl ether 2:1:1 as an eluent) indicated the disappearance of **1** and the formation of a new compound. Then aryloxyacetic acid hydrazide (0.95 mmol) was added in situ, and the mixture was further ground for 5 min. After the reaction completion, $HIO_4 \cdot 2H_2O$ (1.5 mmol) was added to the mixture and ground for another 5 min to complete the reaction (monitored by TLC using acetone as an eluent). Then the resulting solid was washed with water (3 × 10 mL), and the product isolated as a solid. The analytic sample was obtained by the recrystallization from DMF-EtOH-H_2O (6:4:1).

1-Phenyloxyacetyl-4-(2-benzofuroyl)-semicarbazides (4a)

M.p. 202–203°C, IR(KBr) υ: 3341, 3153 (NH), 1690, 1664 (C=O) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ11.83 (s, 1H, NH), 11.13 (s, 2H, NH), 7.21∼8.13 (m, 10H, Ar—H & Fu—H), 4.73 (s, 4H, CH_2); anal. calcd. for $C_{18}H_{15}N_3O_5$: C, 61.19; H, 4.28; N, 11.89; found: C, 61.22; H, 4.34; N, 11.82.

1-(2-Methylphenyloxyacety)l-4-(2-benzofuroyl)-semicarbazides (4b)

M.p. 157–158°C, IR(KBr) υ: 3346, 3170 (NH), 1696, 1663(C=O); ^{1}H NMR (DMSO-d_6): δ 11.80 (s, 1H, NH), 10.98 (s, 2H, NH), 7.10∼8.11 (m,

9H, Ar-H & Fu-H), 4.78 (s, 4H, CH_2), 2.23 (s, 3H, CH_3); anal. calcd. for $C_{19}H_{17}N_3O_5$: C, 62.12; H, 4.66; N, 11.44; found: C, 62.01; H, 4.54; N, 11.56.

1-(3-Methylphenyloxyacety)l-4-(2-benzofuroyl)-semicarbazides (4c)

M.p. 180–181°C, IR(KBr) υ: 3336, 3166 (NH), 1702, 1670 (C=O); ^{1}H NMR (DMSO-d_6): δ11.84 (s, 1H, NH), 10.96 (s, 2H, NH), 7.11~8.14 (m, 9H, Ar—H & Fu—H), 4.71 (s, 4H, CH_2), 2.25 (s, 3H, CH_3); anal. calcd. for $C_{19}H_{17}N_3O_5$: C, 62.12; H, 4.66; N, 11.44; found: C, 62.19; H, 4.52; N, 11.50.

1-(4-Methylphenyloxyacety)l-4-(2-benzofuroyl)-semicarbazides (4d)

M.p. 204–205°C, IR(KBr) υ: 3349, 3132 (NH), 1669, 1673 (C=O); ^{1}H NMR (DMSO-d_6): δ11.81 (s, 1H, NH), 10.92 (s, 2H, NH), 7.09~8.06 (m, 9H, Ar—H & Fu—H), 4.74 (s, 4H, CH_2), 2.22 (s, 3H, CH_3); anal. calcd. for $C_{19}H_{17}N_3O_5$: C, 62.12; H, 4.66; N, 11.44; found: C, 62.06; H, 4.53; N, 11.39.

1-(4-Methoxylphenyloxyacety)l-4-(2-benzofuroyl)-semicarbazides (4e)

M.p. 172–173°C, IR(KBr) υ: 3341, 3156 (NH), 1688, 1675 (C=O); ^{1}H NMR (DMSO-d_6): δ11.84(s, 1H, NH), 10.90 (s, 2H, NH), 7.01~8.10 (m, 9H, Ar-H & Fu-H), 4.76 (s, 4H, CH_2), 3.40 (s, 3H, CH_3); anal. calcd. for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N ,10.96; found: C, 59.59; H, 4.53; N, 10.89.

1-(4-Chlorophenyloxyacety)l-4-(2-benzofuroyl)-semicarbazides (4f)

M.p. 210–211°C, IR (KBr) υ: 3361, 3162 (NH), 1698, 1673 (C=O); ^{1}H NMR (DMSO-d_6): δ11.87 (s, 1H, NH), 10.89 (s, 2H, NH), 6.99~8.09 (m, 9H, Ar—H & Fu—H), 4.72 (s, 4H, CH_2); anal. calcd. for $C_{18}H_{14}ClN_3O_5$: C, 55.75; H, 3.64; N, 10.84; found: C, 55.81; H, 3.68; N, 10.77.

1-(4-Nitrophenyloxyacety)l-4-(2-benzofuroyl)-semicarbazides (4g)

M.p. 262–263°C, IR(KBr) υ: 3352, 3108 (NH), 1708, 1674 (C=O); ^{1}H NMR (DMSO-d_6): δ11.86 (s, 1H, NH), 10.84 (s, 2H, NH), 7.18~8.20 (m, 9H, Ar-H & Fu-H), 4.76 (s, 4H, CH_2); anal. calcd. for $C_{18}H_{14}N_4O_7$: C, 54.28; H, 3.54; N, 14.07; found: C, 54.22; H, 3.61; N, 14.02.

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