NOVEL IMIDES AMINO ACIDS AND DIPEPTIDE DERIVATIVES

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Abstract

Some novel imides derivatives condensed with different amino acids using **THF-Et_3N** method, afforded an excellent yield of compounds **3-8**, **20-23b, 32-35b**. some of these compounds react with **CH_3OH-$SOCl_2$** mixture to give corresponding methyl esters **9-11, 24-25, 36-37** Hydrazinolysis of some methyl esters give hydrazides **12-14, 26-27** some dipeptides derivatives **15-17, 28-29, 38-40** were prepared using Dicyclohexylcarbodiimide **DCC** method, some spectra data were briefly discussed.

Key Words: Amino acid and Dipeptide Derivatives of: N-Phenylmaleimide, N-phenylsuccinimde and N-Phenylcamphorimide

Introduction And Discussion

The work reported here is a continuation of our general program on the chemistry and reactivity of aryl sulfonyl derivatives as candidate pesticides, which are found to possess hypoglycemic, antipyretic, analgesic diuretic, bacteriastatic, and other pharmacological activities.[1-14c].

Sulfonamides are well-established antibactrial agents[15], and several are also fungicidal[16], several cyclic imides display antifungal properties, probably associated with their ability to acylate enzymes by nucleophilic ring-opening[17].

Previous workers[18-19] have demonstrated that N-arylmaleimides are fungicidal against a wide spectrum of phytopathogenic fungi and damping of diseases. In addition. Sulfonyl derivatives have well established antibacterial[20] and antifungal properties[21].

We decided to synthesis some sulfonylmaleimamide amino acid and dipeptide derivatives as candidate fungicides.

Compound **18** by heating with chlorosulfanic acid (6 mol. equivalent) at 80°C give an excellent yield of N-(P-Chlorosulfonylphenyl) succinimide **19**[22-23].

In succinimdes **(20-29)** the bands appeared at approximately 1780 and 1720 cm^{-1}, whereas in the camphorimide derivatives **(32-40)**, the carbonyl bands were at slightly lower frequency 1740 and 1700 cm^{-1}.

PMR spectra were especially valuable in structural elucidation and aromatic protons resonated as singlet indicating that all the aromatic protons are magnetically equivalent, and gave the correct aliphatic and aromatic protons, while the mass spectra **23b** showed the molecular ion **(M^+ : 310),** and fragment ions **(238, 174)** corresponding to successive loss of the diethylamino and sulfonyl group.

Spectroscopy was therefore of special importance in confirming the structures. The IR spectra of succinimde compounds showed the normal stretching absorption bands associated with NH, C = O, SO_2, and amino acid residue. Mass spectra show the molecular ions (M^+), and extensive fragmentation was observed in agreement with Various results obtained with the anologous amino acid derivatives.

Compounds **20-23b** were obtained by reaction of 19 with the appropriate amino acids or amines at room temperature using THF-Et_3N method.

The relative difficulty in forming six membered ring imides is well known[24a].

Cyclization of camphoric acid with aniline gave N-phenylcamphorimide comp **30**[24a], SCHEME 3.

Camphoric acid with acetyl chloride and aniline gave the amic acid, which by refluxing with acetyl chloride, in glacial acetic acid afforded N-phenyl camphorimide (84%) yield.

The excellent yield is due to the presence of gem dimethyl bridge bond which holds the two reactions sites in a favourable conformation for cyclisation.

The imide **30**, by heating with chlorosulfonic acid gave sulfonyl chloride **31** (55%) yied[24a], which underwent subsequent condensation with amino acids affording amino acid derivatives **32-40**.

The IR spectrum of the imides showed two absorption bands corresponding to the symmetric and antisymmetric stretching vibrations of the carbonyl group[25-26].

Camphor is known[27-29], to form different sulfonic acids depending on the reagents used. Acetyl sulfonate yields the 10-sulfonic acid, the chlorosulfonic acid or fuming sulfuric acid yields the 8-sulfonic acid and methyl chlorosulfonate followed by hydrolysis yields the 3-sulfonic acid.

The 10-acid has been confirmed by X-ray crystallography[30-31]. The 8-acid has been studied both by X-ray crystallography[32] and by two dimensional NMR[33], both techniques indicate that sulfonation accurs on the gem-methyl group remote from the carbonyl group. The formation of the 8-and 10-acids is considered[34-35] to involve **Wagener and Nemetkin rearrangements**.

N-Phenylmaleimide was obtained in good yield (77%) by reaction of maleic anhydride with aniline and subsequent dehydration with acetic anhydride-sodium acetate as previously described[35]. Refluxing maleic anhydride and aniline in glacial acetic acid gave a very poor yield (10%) of N-phenylmaleimide together with acetanilide and N-Phyenylmaleamic acid in agreement with other workers[37a]. SCHEME 1.

N-phenylmaleimide react with chlorosulfonic acid (6-mol) to give sulfonyl chloride as cream Powder **2** [37b].

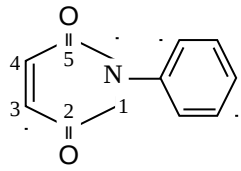
Compound **2** react with amino acid and amines at room temeprautre using THF-Et_3N medium.

The IR spectra of maleimide amino acid derivatives showed two carbonyl absorptions (1780, 1730cm^{-1}) and indicating that the imide ring was present.

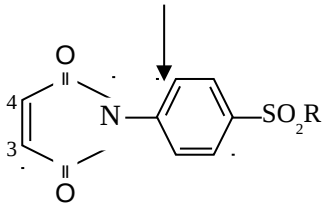
N-phenylsuccinimide **18** was prepared as previously described[24a], by reaction of succinic anhydride with aniline and dehydration with acetic anhydride – sod. acetate[24b] SCHENE 2.

Attempts to obtain **18** by boiling succinic anhydride and aniline in glacial acetic acid were unsuccessful, although the procedure worked well for the synthesis of N-phenylphthalimide[38c].

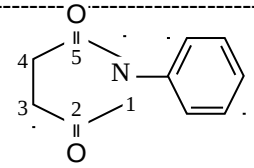
SCHEME 1



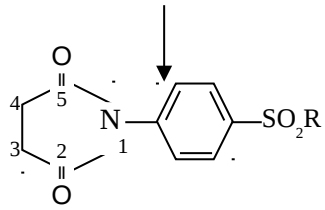
Comp (1)



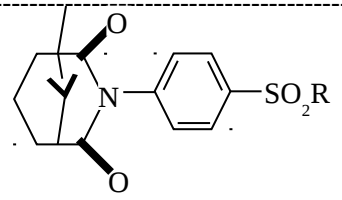
* Comp **(2)** , R = Cl
* Comp **(3-17)** , R = amino acid residue



Comp (18)



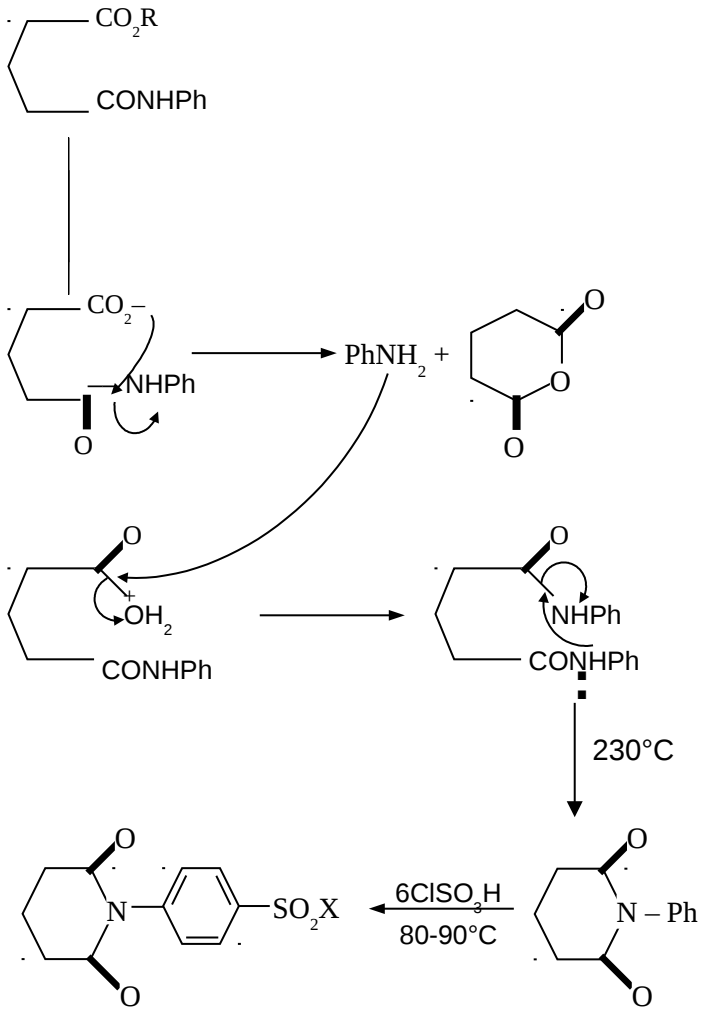
* Comp **(19)** , R = Cl
* Comp **(20-29)**, R = amino acid residue



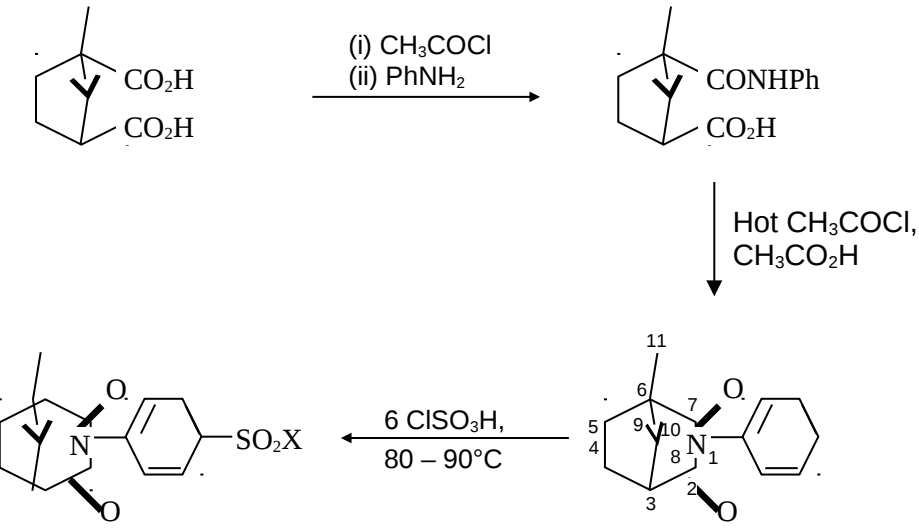
Comp (30) N-Phenyl campharimide
* Comp **(31)** , R = Cl

* Comp **(32-40)**, R = amino acid residue

SCHEME 2


CO2R
CONHPh
CO2–
NHPh
O
PhNH2 +
O
O
O
O
+
OH2
CONHPh
O
NHPh
CONHPh
230°C
O
N – Ph
O
6ClSO3H
80-90°C
O
N
SO2X
O

SCHEME 3



Experimental

Melting points were taken on a Griffin melting point apparatus and are uncorrected, Infrared of solid samples were run as KBr disc on a Schimadzu model 440 spectrophotometer, 1H-NMR spectra were measured in DMSO-d_6 as solvent unless otherwise stated using Fx 90 Q Furier Transform 1H-NMR. Mass spectra were obtained using a Schimadzu. GC. M.S. QP 1000 Ex spectrometer using the direct inlet system. TLC analyses were carried out on Merck silica gel plates and developed with n-butanol acetic acid-water (4:1:1) using iodine, ninhydrin, and benzidine as spraying agents.

Compounds **2, 19, 31** were prepared according to the procedure described earlier[37b, 27a, 22, 23].

Coupling Reactions (3-8), (20-23b) and (32-35)

General procedure:

To an amino acid (0.1 mol) in a water (25 ml) THF (15 ml) mixture, was added triethylamine (5 ml), followed by protionwise addition of sulfonyl chloride (0.1 mol) during 30 min. The temperature of the reaction mixture during the process of

addition was kept at 10°C. Stirring continued for 4 hr at 20°C. Tetrahydrofuran was removed by concentration of the reaction mixture under reduced pressure, water (50ml) was added and acidified with 2M HCl to pH_5. The crude products were filtered and recrystalized (ethanol - water). All the products **(3-8), (20-23b) and (32-35)**, were chromatographically homogeneous by iodine and benzidine development cf **SCHEME (1,2,3). TABLE 1.**

IR of 8 : ν 1780, 1720 cm^{-1} (C = O), ν 1600cm^{-1} (ArC = C), ν 1340, 1160 cm^{-1} (SO_2). **IR of 22** : ν 3360, 3280cm^{-1} (NH), ν 1780, 1710 cm^{-1} (C = O), ν 1600 cm^{-1} Ar(C = C), ν 1340, 1160cm^{-1} (SO_2). **IR of 23b**: ν 1780, 1720 cm^{-1} (C = O), ν 1605 cm^{-1} Ar(C = C), ν 1345, 1165 cm^{-1} (SO_2). **IR of 35b** : ν 1745, 1700 cm^{-1} (C = O), ν 1600 cm^{-1} Ar(C = C), ν 1340, 1160 cm^{-1} (SO_2). **^{1}H-NMR of 23b**: (DMSO – d_6): δ 8.0 – 7.2 (s, 4H, Ar – H), δ 3.4 – 3.1 (s, 4H, 2N – CH_2), δ 2.92 (s, 4H, 2 – CH_2O), δ 1.3 – 1.1 (s, 6H, 2CH_3) **MS of 23b: m/z 310 (M^+) 238 (M – NEt_2), 174 (M – SO_2 Net_2), 118 (C_6H_4NCO), 56 (CH_2 – CH_2 – CO), 28 (CO)**. **^{1}H-NMR of 20** : (DMSO – d_6): δ 1.6 [s, 6H, $(CH_3)_2$], 1.91 (s, H, β CH valyl), δ 4.31 (s, H, α CH Valyl), δ 2.9 (s, 4H, 2CH_2O), δ 8.0 – 7.0 (s, 4H, ArH), δ 8.6 (s, H, SO_2NH), δ 11.1 (s, H, COOH). **^{1}H-NMR of 8** : (DMSO – d_6): δ 8.00 – 7.20 (S, 4H, Ar – H), δ 6.90 (s, 2H, CH = CH), δ 3.40 – 3.15 (s, 4H, 2N CH_2), δ 1.30 – 1.00 (s, 6H, 2N CH_2 CH_3). **MS of 8: m/z 308(M^+) 293 (M – Me), 236 (M – NEt_2), 172 (M – SO_2 NEt_2), 144, 118 (C_6H_4NCO). ^{1}H-NMR of 35b** : (DMSO – d_6): δ 7.90 – 7.25 (s, 4H, Ar – H), δ 2.9–2.8 (s, H, CH, C_3), δ 2.70 (s, 6H, 2CH_3) δ 2.22 – 2.20 (s, 4H, 2CH_2, C_4, C_5), δ 1.30 (s, 3H, CH_3, C_{11}), δ 1.2 – 1.1 (s, 6H, 2CH_3)

Synthesis of sulfanilylamino acid methyl esters (9-11), (24-25) and (36-37) General procedure

A suspension of coupling reaction products **(9-11), 24, 25, 36, 37** (0.2 mole) in absolute methanol (100 ml) was cooled to – 10°C and pure thionyl chloride (2.2 ml) was added dropwise during one hour. The reaction mixture was stirred for an additional 3-4 h at room temperature. Kept overnight and the solvent was removed by vacuum distillation. The residual solid material was recrystallized (methanol-water). **(Table 1).**

IR of 9 : ν 1760, 1720 cm^{-1} (C = O), ν 1730, cm^{-1} ($COOCH_3$) **IR of 36** : ν 3400 cm^{-1} (NH), ν 1750 cm^{-1} ($COOCH_3$), **^{1}H-NMR of 10**: (DMSO – d_6): δ 3.75 (3H, $COOC\underline{H}_3$) and disappear of OH protons.

Synthesis of sulfanilyamion acid hydrazides (12-14), (26-27), General procedure

The methyl esters **(12-14) and (26-27)** (0.2 mol) were dissolved in ethanol (100 ml) and hydrazine hydrate 85% (0.2 mol) was added. The reaction mixture was stirred for 3h at 20°C and left 24 h at room temperature. The crystalline products **(12-14) and (26-27)** were filtered off, washed with water and recrystallized (ethanol-water).

The hydrazides **(12-14)** and **(26-27)** were shown to be chromatographically to be homogeneous (Table 1).

IR of 13 : ν 3430, 3300 cm^{-1} (NH, NH_2), ν 1550 cm^{-1} (CONH), ν 3300, 1160 cm^{-1} (SO_2NH). **^{1}H-NMR of 27**: (DMSO – d_6): δ 9 (1H, $SO_2N\underline{H}$) δ: 5.50 ($H.N\underline{H}$), δ 5.60 (2H, $N\underline{H}_2$)

Synthesis of sulfanilyl dipeptide methyl esters (15-17),(28-29) and (38-40) General procedure

To a solution of amino acid methyl ester hydrochloride (0.11 mol) in **THF** (100 ml) was added triethylamine (5 ml), the solution was stirred at 20°C for 30 min. and cooled to 0°C, where the sulfanilyl amino acid (0.005 mol), and **dicyclohexylcarbodiimide DCC** (1.62 g) were added to the above mixture. The reaction mixture was stirred for 2 h at 0°C and for another 2 h at room temperature. The precipitated dicyclohexylurea was filtered off, acetic acid (2 ml), was added to the solution and left standing overnight. The precipitated was filtered off and the remaining solution was distilled under vacuum. The remaining solid was recrystallized from (ethanol-water). The products were to be chromatographically homogeneous.

IR of 16 : ν 3300, 3100 cm^{-1} (NH, CONH), ν 1750 cm^{-1} (C = O), ν 1320 cm^{-1} ($COOC\underline{H}_3$). **^{1}H-NMR of 38**: (DMSO – d_6): δ 3.5 3H, ($COOC\underline{H}_3$) δ 9.2 (1H, $CON\underline{H}$) and other bands supporting the structure of dipeptide. **MS of 16 : m/z 423 (M^+)**, **MS of 28 : m/z 425 (M^+)**

TABLE (1): Physical Data for Various Imido Amino Acid Derivatives (3-17), (20-29) and (32-40).

Comp No.	R	m.p. °C	Yield %	R_f	Molecular formula	Elemental Analysis calculated / found			
						%C	%H	%N	%S
3	**Gly**	195-97	60	0.94	$C_{12}H_{10}N_2O_6S$	46.45 46.44	3.23 3.21	9.03 9.01	10.32 10.30
4	**DL-Ala**	172-74	65	0.56	$C_{13}H_{12}N_2O_6S$	48.15 48.13	3.70 3.68	8.64 8.61	9.88 9.86
5	**L-Val**	181-83	63	0.79	$C_{15}H_{16}N_2O_6S$	51.44 51.11	4.55 4.53	7.95 7.93	9.09 9.06
6	**L-Leu**	137-39	66	0.78	$C_{16}H_{18}N_2O_6S$	52.64 52.61	4.92 4.90	7.65 7.62	8.74 8.71
7	**L-Ph-Ala**	165-67	58	0.71	$C_{19}H_{16}N_2O_6S$	57.00 56.98	4.00 3.97	7.00 6.96	8.00 7.97
8	**N-Et_2**	199-20	80	0.60	$C_{14}H_{16}N_2O_4S$	54.53 54.51	5.19 5.11	9.09 9.05	10.39 10.36
9	**DL-Ala-OMe**	225-27	78	0.64	$C_{14}H_{14}N_2O_4S$	49.70 49.66	4.14 4.11	8.28 8.26	9.47 9.43
10	**L-Val-OMe**	200-02	80	0.86	$C_{16}H_{18}N_2O_6S$	52.46 52.43	4.92 4.90	7.65 7.63	8.74 8.71
11	**L-Leu-OMe**	210-12	82	0.82	$C_{17}H_{20}N_2O_6S$	53.68 53.66	5.26 5.21	7.37 7.33	8.42 8.40
12	**DL-Ala-N_2H_3**	140-42	71	0.48	$C_{13}H_{14}N_2O_6S$	46.15 46.10	4.14 4.10	16.57 16.53	9.47 9.47
13	**L-Val-N_2H_3**	164-66	68	0.44	$C_{15}H_{18}N_4O_5S$	49.18 49.15	4.92 4.90	15.30 15.26	8.74 8.71
14	**L-leu-N_2H_3**	232-34	73	0.62	$C_{16}H_{20}N_4O_5S$	50.53 50.50	5.26 5.23	14.74 14.71	8.42 8.40
15	**Gly-Gly-OMe**	290-92	63	0.65	$C_{15}H_{15}N_3O_7S$	47.24 47.21	3.94 3.91	11.02 11.00	8.40 8.38
16	**L-Val-Gly-OMe**	193-92	88	0.50	$C_{18}H_{21}N_3O_7S$	51.06 51.03	4.96 4.94	9.93 9.91	7.56 7.53
17	**L-leu-Gly-OMe**	200-02	77	0.76	$C_{19}H_{23}N_3O_7S$	52.17 52.13	5.26 5.23	9.61 9.58	7.32 7.30
20	**L-Val**	168-70	71	0.83	$C_{15}H_{18}N_2O_6S$	50.85 50.81	5.08 5.04	7.91 7.90	9.04 9.01
21	**L-leu**	154-56	68	0.74	$C_{16}H_{20}N_2O_6S$	52.17 52.10	5.43 5.40	7.61 7.59	8.69 8.66
22	**NH.NH_2**	163-65	70	0.88	$C_{10}H_{11}N_3O_4S$	44.61 44.50	4.09 4.05	15.61 15.58	11.89 11.86
23a	**NH ‖ N=C.$(CH_3)_2$**	188-90	75	0.75	$C_{13}H_{15}N_3O_4S$	50.49 50.46	5.85 5.83	13.59 13.56	10.36 10.33
23b	**N.Et_2**	250-52	72	0.88	$C_{14}H_{18}N_2O_4S$	54.19 54.11	5.81 5.80	9.03 9.00	10.32 10.30
24	**L-Val-OMe**	216-18	74	0.77	$C_{10}H_{20}N_2O_6S$	52.17 52.10	5.43 5.41	7.61 7.59	8.69 8.66
25	**L-leu-OMe**	234-36	78	0.79	$C_{17}H_{22}N_2O_6S$	53.10 53.00	5.76 5.73	7.33 7.31	8.38 8.35

26	**L-Val-N_2H_3**	104-06	79	0.69	$C_{15}H_{20}N_4O_5S$	48.91 48.81	5.43 5.41	15.22 15.11	8.70 8.68

Cont. TABLE (1)

27	**L-leu-N_2H_3**	180-82	83	0.53	$C_{16}H_{22}N_4O_5S$	50.26 50.21	5.76 5.73	14.66 14.61	8.37 8.33
28	**L-Val-Gly-OMe**	284-86	65	0.61	$C_{18}H_{23}N_3O_7S$	50.82 50.81	5.41 5.37	9.88 9.83	7.53 7.51
29	**L-leu-Gly-OMe**	217-19	75	0.37	$C_{19}H_{25}N_2O_7S$	51.94 51.91	5.69 5.63	9.57 9.51	7.29 7.21
32	**Gly**	204-06	61	0.87	$C_{18}H_{22}N_2O_6S$	54.82 54.81	5.58 5.53	7.11 7.00	8.12 8.10
33	**DL-Ala**	196-98	66	0.69	$C_{19}H_{24}N_2O_6S$	55.88 55.83	5.88 5.83	6.86 6.83	7.84 7.81
34	**L-Val**	179-81	70	0.62	$C_{21}H_{28}N_2O_6S$	57.80 57.78	6.42 6.40	6.42 6.40	7.34 7.31
35a	**L-leu**	185-87	74	0.59	$C_{22}H_{30}N_2O_6S$	58.67 58.61	6.67 6.63	6.22 6.21	7.11 7.98
35b	**N.Me_2**	155-57	62	0.75	$C_{18}H_{24}N_2O_4S$	59.34 59.31	6.59 6.56	7.69 7.67	8.67 8.64
36	**L-Val-OMe**	230-32	81	0.72	$C_{22}H_{30}N_2O_6S$	58.67 58.63	6.67 6.63	6.22 6.21	7.11 7.98
37	**L-leu-OMe**	240-42	77	0.68	$C_{23}H_{32}N_2O_6S$	59.48 59.46	6.90 6.88	6.03 6.01	6.90 6.88
38	**Gly-Gly-OMe**	292-94	71	0.51	$C_{21}H_{27}N_3O_7S$	54.19 54.11	5.81 5.78	9.03 9.00	6.88 6.83
39	**L-Val-Gly-OMe**	207-09	76	0.54	$C_{24}H_{33}N_3O_7S$	56.80 56.77	6.51 6.49	8.28 8.26	6.31 6.26
40	**L-leu-GlyOMe**	270-72	78	0.60	$C_{25}H_{35}N_3O_7S$	57.58 57.51	6.72 6.70	8.06 8.00	6.14 6.11

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