CHAPTER II

EXPERIMENTAL

1. Chemicals and Equipment

Acid chlorides were obtained from Fluka and were used as received.

S-(2-Aminoethyl) isothiouronium bromide hydrobromide was obtained from Aldrich Chemical Company and used without further purification.

Melting points were measured with cover glass sample holder electrothermal melting point apparatus.

Microanalyses were carried out by AMDEL (Austalia) and by technical staffs at the Scientific and Technological Research Equipment Centre (STREC) of Chulalongkorn University using the elemental analyser, Perkin Elmer, model 240C.

Spectroscopic measurements were obtained by Technical staffs at the (STREC).

The following machines were used to obtain the UV, IR, NMR and Mass spectrometer respectively:-

UV-visible spectrophotometer, Hitachi, model UV-220A.

Infrared spectrophotometer, Shimadzu, model IR-440.

Fourier transform NMR spectrometer, Jeol, model JNM-FX90Q. at 21.1 Tesla.

GC/MS spectrometer, Jeol, model JMS-DX 300/JMA 2000, with electron ionization source.

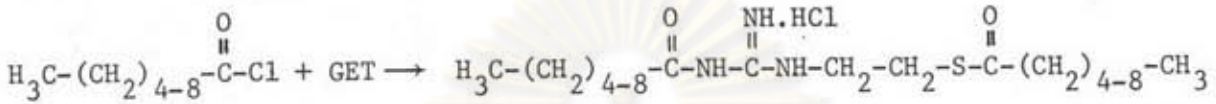
2. Preparation of 2-Guanidinoethyltrithiocarbonate zwitterion

S-(2-Aminoethyl) isothiouronium bromide hydrobromide 1.4 g. (0.005 mole) was dissolved in water 3.75 ml. and treated with concentrated ammonium hydroxide 0.75 ml. Carbon disulfide 1 ml.was added dropwise with stirring into the resulting solution of 2-mercaptoethylguanidine which was placed in an ice bath. A bright yellow precipitate was isolated and was recrystallized from water and ethanol [1]. The yield was 0.7 g. (72%) m.p. 138-139°C.

3. General Preparation of N,S-Diacyl-2-mercaptoethylguanidine hydrochlorides (S-series compounds)

A mixture of the acyl chlorides (5.5 mole) and 2-guanidinoethyltrithiocarbonate zwitterion (1 mole) and pyridine (1-2 drop) was heated on a steam bath for 1 hour. The reaction mixture was cooled, ether was added, then kept refrigerated for 24-48 hours. The resulting crystals were then filtered and washed with cold ether. The product was recrystallized from ethanol [1]. The yield and melting points are shown in Table I.

Table I The preparation of N,S-diacyl-2-mercaptoethylguanidine hydrochlorides (S-series compounds)



Compound No.	Acid chlorides used			*GET		Yield	m.p.(°C)	
	Structure	ml.	Mole	Mole	wt. (g.)	(%)	Found	Lit.
S-6	$H_3C-(CH_2)_4-C(=O)-Cl$	1.0	0.007	0.0012	0.23	46	81-82	83-86 (1)
S-7	$H_3C-(CH_2)_5-C(=O)-Cl$	0.5	0.003	0.0005	0.10	71	83-84	87-89 (1)
S-8	$H_3C-(CH_2)_6-C(=O)-Cl$	0.8	0.005	0.0009	0.18	84	92-93	94-95 (1)
S-9	$H_3C-(CH_2)_7-C(=O)-Cl$	0.7	0.004	0.0009	0.18	82	94-95	95-96 (2)
S-10	$H_3C-(CH_2)_8-C(=O)-Cl$	0.8	0.004	0.0009	0.18	92	99-100	99-100 (2)
S-11	$H_2C=HC-(CH_2)_8-C(=O)-Cl$	5.4	0.025	0.0064	1.25	69	85-86	85-86 (2)

*GET = 2-guanidinoethyltrithiocarbonate zwitterion; 

4. Optimization of the Thermal Reaction of N,S-Diacyl-2-mercapto-ethylguanidine hydrochlorides (S-series compounds)

For this purpose a previously dried (6 hours at 56°C) sample of N,S-diacyl-2-mercaptoethylguanidine hydrochlorides kept at various temperatures (room temperature -200°C) for various times (1-10 hours) in air or under N_2 atmosphere. The solvent was also varied (DMF or DMSO + pyridine) but experiments were also carried out without a solvent. At the end of the experiment, the reaction mixture was examined by TLC using alumina and, as the eluent, 80% hexane and 20% acetone. The conditions and results are displayed in Table II. The reaction products were designated as S (starting material), A, B, C in the order of R_f values from lower to higher and U (unidentified product). Their relative amounts were estimated, by taking the initial as 10, from the densities of the I_2-complex colour on TLC plates whenever trace amount was obtained it was designated as T.

Table II The investigation of thermal reaction products from N,S-diacyl-2-mercaptoethylguanidine hydrochlorides

under various conditions

Compound No.	R	Conditions and Products															R_f
		Temp. (°C)	Heating Time in hr(s)	In Air					Under N_2					Reduced Pressure					
				Rel. Amount					Rel. Amount					Rel. Amount					
				S	A	B	C	U	S	A	B	C	U	S	A	B	C	U	
S-6	C_5H_{11}	160	1						<9	1	-	T	-						S-6 = 0.57
			2						5	2	<1	1	>1						
			3						1	<3	1	2	>3						
S-7	C_6H_{13}	160	1						9	<1	T	-	-	>9	T	T	T	-	S-7 = 0.59
			2						>>7	1	<1	<1	-	>>7	<1	<1	<1	T	A = 0.04
			3						<<7	>1	1	1	T	>>6	1	<1	<1	1	B = 0.46
			4						>4	<2	<2	>1	1	<5	>1	1	1	2	C = 0.61
			5						3	2	2	<2	>1	3	2	1	1	3	
			6						<2	>2	>2	2	<2	>>1	3	<1	<1	4	
			7						<1	<3	>2	>2	2	T	3	<1	<1	>5	
			8						T	3	<<3	2	>2						
			9						-	3	<3	<2	>>2						
			10						-	>3	<3	>1	<3						
		170	1						8	<1	1	T	-						
			2						>5	<2	2	<1	T						
		180	1						<5	2	>2	<1	T						
			2	<1	2	>1	1	5	>1	3	3	2	<1						
		190	1						3	2	2	2	1						
			2						1	3	<3	1	>2						
		200	1						2	2	1	1	4						
			2						T	1	<1	<1	>7						

Table II Continued

Compound No.	R	Conditions and Products															R_f
		Temp. (°C)	Heating Time in hr(s)	In Air					Under N_2					Reduced Pressure					
				Rel. Amount					Rel. Amount					Rel. Amount					
				S	A	B	C	U	S	A	B	C	U	S	A	B	C	U	
S-8	C_7H_{15}	RT.	48	10	-	-	-	-											S-8 = 0.61
			72	10	-	-	-	-											A = 0.04
		80	1	10	-	-	-	-											B = 0.54
		110	1	10	-	-	-	-											C = 0.65
		140	1	10	-	-	-	-											
		160	1	>9	T	T	T	T	>9	T	T	T	-	>9	-	T	T	-	
			2	>>7	<1	T	<<1	1	>>7	1	<1	<1	-	8	T	<1	<1	1	
			3	>6	1	<1	<1	>1	<7	>1	1	1	-	<6	>1	1	1	1	
			4	<5	>1	1	1	2	<5	<2	2	>1	T	<<5	1	>1	>1	2	
			5	<<4	>>1	>1	>1	<<3	4	2	>2	>>1	<<1	3	2	1	1	3	
			6	<<2	<<2	>>1	>>1	4	3	>2	>>2	<<2	<1	>2	>2	<1	<1	4	
			7	T	2	<2	<2	>>4	<2	>>2	3	<2	1	T	3	<1	<1	5	
			8						<1	<3	>3	2	>1						
			9						<<1	3	3	2	>>1						
			10						T	3	<3	<2	2						
		170	1						<8	1	1	T	-						
			2						5	<2	2	1	T						
		180	1						5	2	2	<1	T						
			2	1	2	1	1	5	2	3	3	<2	T						
		190	1						4	2	2	<2	T						
			2						>1	3	3	1	<2						
		200	1						2	2	2	1	3						
			2						T	1	1	<1	7						

Table II Continued

Compound No.	R	Conditions and Products															R_f
		Temp. (°C)	Heating Time in hr(s)	In Air					Under N_2					Reduced Pressure					
				Rel. Amount					Rel. Amount					Rel. Amount					
				S	A	B	C	U	S	A	B	C	U	S	A	B	C	U	
S-9	C_8H_{17}	RT	48	10	-	-	-	-											S-9 = 0.62
			72	10	-	-	-	-											A = 0.04
		80	1	10	-	-	-	-											B = 0.59
		110	1	10	-	-	-	-											C = 0.66
		140	1	10	-	-	-	-											
		160	1	>9	T	T	T	T	>9	T	T	T	-	>9	-	T	-	-	
			2	>7	<1	T	<<1	1	>>7	1	<1	<1	-	>>8	T	<1	<1	T	
			3	>>6	1	<<1	<1	>1	<7	>1	1	1	-	>6	<1	1	1	1	
			4	5	>1	<1	1	2	5	2	<2	>1	T	<5	1	>1	>1	<2	
			5	4	<<2	1	>1	>2	<4	>2	2	>>1	<<1	<3	<2	>1	>1	3	
			6	>2	2	>1	<<2	3	3	>>2	>2	<<2	<1	<2	>2	1	1	4	
			7	T	>2	<2	<2	4	2	<3	>>2	<2	1	T	3	<1	<1	5	
			8						1	3	<3	2	>1						
			9						<1	>3	3	<2	>>1						
			10						T	>>3	<3	<<2	2						
		170	1						<8	1	1	T	-						
			2						>5	<2	2	<1	T						
		180	1						>>5	<2	<2	<1	T						
			2	1	2	1	>1	<5	>>2	<3	<3	<2	T						
		190	1						4	2	2	<2	T						
			2						>1	3	3	1	<2						
		200	1						2	2	2	1	3						
			2						T	1	1	<1	7						

Table II Continued

Compound No.	R	Conditions and Products															
		Temp. (°C)	Heating Time in hr(s)	In Air					Under N_2					Reduced Pressure					R_f
				Rel. Amount					Rel. Amount					Rel. Amount					
				S	A	B	C	U	S	A	B	C	U	S	A	B	C	U	
S-10	C_9H_{19}	RT	48	10	-	-	-	-											S-10 = 0.65
			72	10	-	-	-	-											A = 0.04
		80	1	10	-	-	-	-											B = 0.61
		110	1	10	-	-	-	-											C = 0.72
		120	1	10	-	-	-	-											
		140	1	10	-	-	-	-											
		152	1	10	-	-	-	-											
			2	10	-	-	-	-											
		160	1	>9	T	T	T	T	>9	T	T	T	-	9	-	T	T	-	
			2	>7	<1	T	<<1	1	>>7	1	<1	<1	-	<7	T	1	1	1	
			3	6	1	<1	1	>1	<7	>1	1	1	-						
			4	5	>1	1	>1	2	5	2	<2	>1	T						
			5	<<4	<2	>1	>>1	2	<4	>2	2	>>1	<<1						
			6	<2	2	>>1	<2	3	<3	>>2	>2	<2	<1						
			7	T	>2	>2	<2	<4	2	<<3	>>2	2	1						
			8						1	<3	<3	>2	>1						
			9						<<1	3	3	2	>>1						
			10						T	3	3	2	<2						
		170	1						8	1	<1	T	-						
			2						5	2	<2	1	T						
		180	1						>5	2	<2	<1	T	<5	1	T	T	4	
			2	1	2	>1	1	<5	<2	3	3	2	T	T	T	T	T	>9	

Table II Continued

Compound No.	R	Conditions and Products															R_f
		Temp. (°C)	Heating Time in hr(s).	In Air					Under N_2					Reduced Pressure					
				Rel. Amount					Rel. Amount					Rel. Amount					
				S	A	B	C	U	S	A	B	C	U	S	A	B	C	U	
S-10		190	1						4	2	2	<2	T						
			2						>1	3	<3	>1	<2						
		200	1						2	2	2	1	3						
			2						T	1	1	<1	7						
S-11	H_2C = CH-$(CH_2)_8$	RT	48	10	-	-	-	-											S-11 = 0.57
			72	10	-	-	-	-											A = 0.04
		80	1	10	-	-	-	-											B = 0.61
		110	1	10	-	-	-	-											C = 0.68
		140	1	10	-	-	-	-											
		160	1	>9	T	T	T	T	>9	T	T	T	-						
			2	>>7	<1	T	T	<1	>>7	1	<1	<1	-						
			3	>>6	1	<1	<1	1	7	>1	1	1	T						
			4	5	>1	1	1	<2	5	2	>1	>1	<1						
			5	<4	<2	>1	>1	2	<4	>2	<<2	>>1	1						
			6	2	>2	<2	<2	>2											
			7	1	>>2	2	2	3											
			8	T	<2	<2	>2	>4											
		170	1						8	<1	<1	T	T						
			2						>>6	1	1	<1	<1						
			3						>>4	<2	<2	1	1						
			4						3	2	2	<2	>1						
			5						1	<3	<3	2	>>1						

Table II Continued

Compound No.	R	Conditions and Products																R_f
		Temp. (°C)	Heating Time in hr(s)	In Air					Under N_2					Reduced Pressure					
				Rel. Amount					Rel. Amount					Rel. Amount					
				S	A	B	C	U	S	A	B	C	U	S	A	B	C	U	
S-11		180	1						>5	2	<2	<1	T						
			2	<<1	>2	1	1	>5	<4	>2	2	1	1						
			3						2	<3	>2	<2	>1						
			4						1	3	<<3	2	>>1						
			5						T	>3	3	>2	<<2						
S-12	$C_{10}H_{21}$	160	1						>9	T	T	T	-						S-12 = 0.67
			2						>8	<1	<1	T	-						A = 0.04
			3						>7	1	1	<1	-						B = 0.64
			4						>5	2	<2	1	T						C = 0.74
			5						<4	>2	2	>1	<1						
		170	1						>8	<1	<1	T	-						
			2						>>6	2	1	<<1	T						
			3						4	>2	<2	>1	<1						
			4						<3	>>2	2	<2	1						
			5						1	3	<3	2	>1						
		180	1						>5	2	2	<1	T						
			2	T	>2	<2	<2	4	4	<3	>2	1	T						
			3						>2	3	<3	>1	<1						
			4						1	3	3	<2	1						
			5						T	>3	3	2	<<2						

5. Preparation of 2-Amino-2-thiazoline hydrochloride (A-series compound) by Thermal Reaction of N,S-Diacyl-2-mercaptoethylguanidine hydrochlorides (S-series compounds)

A previously dried sample of N,S-diacyl-2-mercaptoethylguanidine hydrochlorides (0.05-3.26 g.) were heated at 180°C for various periods of 2-7 hours either under ordinary condition in air or under nitrogen. The cooled reaction mixture was then added with acetone to precipitate a crystalline product which was separated from the solution by rinsing. The separated liquid was repeatedly added with acetone to obtain more cyrstalline product. While the liquid was kept for further separation of other compounds, the crystalline product was collected, dissolved in methanol, and treated with activated carbon for 30 minutes. After filtration of the solution, the solvent was almost completely evaporated then some more acetone was added to yield white needles of 2-amino-2-thiazoline hydrochloride m.p. 194-203°C R_f = 0.04. It is soluble in methanol and water but insoluble in carbontetrachloride. The results and elemental analysis are shown in Table III.

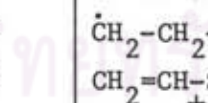
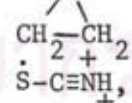
The spectroscopic data of 2-amino-2-thiazoline hydrochloride (A-series compound) are shown in Table IV.

Table III The preparation of 2-amino-2-thiazoline hydrochloride (A-series compound) by thermal reaction of N,S-diacyl-2-mercaptoethylguanidine hydrochlorides (S-series compounds) at 180°C.

Compound No.	Weight (g.)		Heating Time (hrs.)		Product										
					Yield (%)		m.p.*	Elemental Analysis (%)							
	In Air	Under N_2	In Air	Under N_2	In Air	Under N_2	(°C)	Found					Calcd for $C_3H_7N_2SCl$				
								C	H	N	Cl	S	C	H	N	Cl	S
S-7	0.05	2.79	2	3	94	92	200-202	25.98	5.07	20.20	-	21.7					
S-8	0.05	2.67	2	3	89	92	200-202	24.19	5.54	20.07	28.4	-					
S-9	0.05	3.26	2	3	86	90	200-203	24.74	5.17	20.44			25.99	5.09	20.21	25.58	23.13
S-10	0.06	3.05	2	7	89	98	198-201	24.43	5.13	20.11	-						
S-11	0.05	0.66	2	5	88	90	199-201	-	-	-	-						
S-12	0.06	1.06	2	5	89	92	194-196										

*The m.p. of this compound was previously reported as 196-198[15] and 198°C[19].

Table IV Spectroscopic data of 2-amino-2-thiazoline hydrochloride (A-series compound)

Spectra from	Signals	Assignments
IR $\lambda_{max}^{(KBr)}$ (cm^{-1})	3260	N-H stretching
	3000-3100	C-H stretching coupling with N-H streching
	1660	C=N stretching
	1400-1440	C-N stretching and N-H bending
	660-700	N-H bending
UV λ_{max} (nm)	240.5	double bond
^{13}C NMR (DMSO) (ppm)	172.73	-C=N-
	48.38	$-\underline{C}H_2-N-$
	30.83	$-\underline{C}H_2-S-$
^{1}H NMR (DMSO) δ(ppm)	t 3.46-3.63	$-C\underline{H}_2-S-$
	t 3.82-3.98	$-C\underline{H}_2-N-$
	br 9.76	$-NH_2$
MS (m/e)	103	M^+-Cl
	102	M^+-HCl
	101	$M^+-HCl,-H^{\cdot}$
	60	$\dot{C}H_2-CH_2-S^+$,  
	59	$CH_2=CH-S^+$, $\dot{S}-C\equiv NH$, CH_2-CH
	56	$\dot{C}H_2-N=C-NH_2$, $\dot{C}H_2-N\equiv C-NH_2$
	55	$CH_2=N-C\equiv NH$
	45	$CH=S$, $NH=CH-NH_3$
	44	$NH=CH-NH_2$, $HN=\dot{C}-NH_3$
	43	$N\equiv C-NH_3$
	42	$N\equiv C-NH_2$

6. The Preparation of Aliphatic primary amides (B-series compounds) and of N,N'-Diacyl-cystamines (C-series compounds) by the Thermal Reaction of N,S-Diacyl-2-mercaptoethylguanidine hydrochlorides (S-series compounds)

Procedure 6.1 (in air)

N,S-Diacyl-2-mercaptoethylguanidine hydrochlorides (0.05 g.-0.06 g.) were heated for 2 hours at 180°C. The cooled reaction mixture was then added 2 ml.of acetone to separate the crystalline product of 2-amino-2-thiazoline hydrochloride from the solution. The components in the liquid was further separated by preparative layer chromatography (alumina, eluent, 80% hexane: 20% acetone). The bands with R_f = 0.46-0.64 (for B-series compounds) and R_f = 0.61-0.74 (for C-series compounds) were separately collected and extracted with chloroform, then the volume of each collected solvent was evaporated on water bath and some hexane was added to crystallize the resulting white needles (for B-series compounds) and white amorphous precipitates (for C-series compounds). The products of both series are shown in Table V and VI respectively.

Procedure 6.2 (under N_2)

In those experiments which were carried out in the absence of air (under N_2). After the addition of acetone to separate the cyrstalline product of 2-amino-2-thiazoline hydrochloride the liquid portion was further separated to obtain the desired products of aliphatic primary amides (B-series compounds) and N,N'-diacyl-cystamines (C-series compounds) by column chromatography on alumina and using mixed hexane: acetone as eluent. Conditions for the preparation are also shown in Table V and VI. Details of the separation are shown in Table VII.

All of the products are soluble in chloroform and slightly soluble in hexane. However, the products of B-series compounds are slightly soluble

in hexane and water while the products of C-series compounds are slightly soluble in hexane and insoluble in water.

The elemental analysis of both aliphatic primary amides (B-series compounds) and N,N-diacyl-cystamines (C-series compounds) are shown in Table VIII and Table XIV respectively. Those spectroscopic data of UV, IR, ^{13}C NMR, ^{1}H NMR, MS for the B-series compounds are displayed in Table IX to Table XIII. While those for the C-series compounds are shown in Table XV to Table XIX.

Table V The preparation of aliphatic primary amides (B-series compounds) by the thermal reaction of N,S-diacyl-2-mercaptoethylguanidine hydrochlorides (S-series compounds) at 180°C

Starting Materials			Heating Time (hrs)		Products				
Compound No.	Weight (g.)				Designated	Yield (%)		m.p. (°C)	
	In Air	Under N_2	In Air	Under N_2	B-Series Compounds	In Air	Under N_2	Found	Lit.
S-7	0.05	2.79	2	3	B-7	13	57	90-92	93-94[151,152] 95-96[57]
S-8	0.05	2.67	2	3	B-8	14	49	100-102	105-106[152] 106.5-107.5[153] 107-108[90] 104-105[154]
S-9	0.05	3.26	2	3	B-9	14	49	93-95	98.7-99.1[155] 92-94[156]
S-10	0.06	3.05	2	7	B-10	36	51	93-95	97.6-98.2[155] 99.5-100[75] 103[157]
S-11	0.05	0.66	2	5	B-11	34	46	81-83	87.0-87.5[153] 87[158] 85-86[72]
S-12	0.06	1.06	2	5	B-12	32	49	91-93	98.0-98.7[155] 97.5-99[75]

Table VI The preparation of N,N´-diacyl-cystamines (C-series compounds) by the thermal reaction of N,S-diacyl-2-mercaptoethylguanidine hydrochlorides (S-series compounds) at 180°C

Starting Materials			Heating Time (hrs.)		Products				
Compound No.	Weight (g.)				Designated	Yield (%)		m.p. (°C)	
	In Air	Under N_2	In Air	Under N_2	C-Series Compounds	In Air	Under N_2	Found	Lit.
S-7	0.05	2.79	2	3	C-7	28	14	108-110	-
S-8	0.05	2.67	2	3	C-8	18	22	114-116	-
S-9	0.05	3.26	2	3	C-9	18	16	115-117	-
S-10	0.06	3.05	2	7	C-10	20	46	119-121	-
S-11	0.05	0.66	2	5	C-11	30	12	101-103	-
S-12	0.06	1.06	2	5	C-12	22	10	98-100	-

Table VII The separations of aliphatic primary amides (B-series compounds) and N,N'-diacyl-cystamines (C-series compounds) by column chromatography

Starting Materials		Heating Time (hrs.)	Separation for those Under N_2 (Procedure 6.2)				
Compound No.	Weight(g.)		Eluent Hexane:Acetone	Separated Fractions	Flow Rates ml./min.	Total Volume (ml.)	Fractions obtaining the products
S-7	2.79	3	100:0	1-9	1.7	900	-
			90:10	10-14	1.4	500	15-18 (C-7)
			90:10	15-70	1.4	2800	21-70 (B-7)
S-8	2.67	3	100:0	1-9	2.3	900	-
			90:10	10-13	1.5	400	14-20 (C-8)
			90:10	14-71	1.5	2850	22-71 (B-8)
S-9	3.26	3	100:0	1-9	3.5	900	-
			90:10	10-13	3.7	400	14-17 (C-9)
			75:25	14-24	3.9	550	18-23 (B-9)
S-10	3.05	7	100:0	1-3	2.3	1300	-
			90:10	4-7	2.5	800	8 (C-10)
			75:25	8-12	2.5	1380	9-10 (B-10)
			0:100	13	2.5	1600	-
S-11	0.66	5	100:0	1	2.7	300	4-6 (C-11)
			90:10	1-26	3.0	1250	9-25 (B-11)
S-12	1.06	5	100:0	1	1.8	300	3 (C-12)
			90:10	2-12	1.0	550	4-11 (B-12)

Table VIII The elemental analysis of aliphatic primary amides (B-series compounds)

Compound No.	Calcd. and Found	C (%)	H (%)	N (%)	O (%)
B-7	Calcd. for $C_7H_{15}NO$	65.07	11.70	10.84	12.38
	Found	65.08	11.77	10.83	12.10
B-8	Calcd. for $C_8H_{17}NO$	67.07	11.96	9.78	11.17
	Found	67.45	11.96	9.84	11.04
B-9	Calcd. for $C_9H_{19}NO$	68.74	12.18	8.91	10.17
	Found	68.68	12.18	8.96	10.25
B-10	Calcd. for $C_{10}H_{21}NO$	70.12	12.33	8.18	9.34
	Found	70.02	12.42	8.01	9.51
B-11	Calcd. for $C_{11}H_{21}NO$	72.08	11.54	7.64	8.73
	Found	71.34	11.45	7.57	9.03
B-12	Calcd. for $C_{11}H_{23}NO$	71.29	12.51	7.56	8.63
	Found	71.21	12.45	7.66	8.59

Table IX The UV spectra of aliphatic primary amides (B-series compounds)

Compound No.	λ_{max} (nm)	Assignments
B-7	239.5	double bond
B-8	240.0	
B-9	239.5	
B-10	239.5	
B-11	239.5	
B-12	240.0	

Table X The IR spectra of aliphatic primary amides (B-series compounds)

Absorption peaks ν_{max}^{KBr} (cm^{-1}) / Compound No.	3398-3198	2950-2850	1668-1618	1428-1410	705-695	645-630
B-7	3365, 3199	2920, 2880	1660, 1630	1420-1410	695	635
B-8	3360, 3198	2910, 2850	1660, 1630	1425-1415	702	640
B-9	3350, 3198	2905, 2850	1660, 1635	1415-1410	698	638
B-10	3360, 3199	2905, 2850	1665, 1635	1425-1415	705	645
B-11	3360, 3199	2920, 2850	1630, 1618	1422-1416	700	630
B-12	3398, 3205	2950, 2895	1668, 1640	1428-1419	701	639
Assignments	antisymmetric N-H stretching, and symmetric N-H stretching	antisymmetric C-H stretching, and symmetric C-H stretching	C=O stretching (amide I band) was coupling with N-H bending (amide II band), and N-H in plane bending (amide II band)	C-N stretching, N-H bending (amide III band)	N-H out of-plane bending (amide V band)	O-C-N bending (amide IV, VI band)

Table XI The ^{13}C NMR spectra in ppm of aliphatic primary amides (B-series compounds) in $CDCl_3$

Compound No. \ Carbon positions	C-1	C-2	C-3	C-4	C-5	C_{t-4}	C_{t-3}	C_{t-2}	C_{t-1}	C_t
B-7	175.87	36.03	25.57	28.99	-	-	-	31.59	22.49	13.92
B-8 Found	175.70	36.03	25.63	29.26	29.09	-	-	31.75	22.59	13.98
B-8 Lit.(159)	175.93	35.87	25.48	29.10	28.87	-	-	31.55	22.48	13.93
B-9	175.92	36.03	25.63	29.31	29.15	-	29.15	31.86	22.65	13.98
B-10	175.79	36.03	25.59	29.31	29.31	29.31	29.31	31.92	22.72	14.10

Table XII The ^{1}H NMR spectra of aliphatic primary amides (B-series compounds) in $CDCl_3$

Signals (δ) / Compound No.	0.88 (br t)	1.27-1.30 (br s)	1.61-1.79	2.14-2.31 (t)	5.60-6.11 (br)
B-7	0.88	1.30	1.62	2.14-2.31	6.11
B-8	0.88	1.30	1.61	2.14-2.31	6.10
B-9	0.88	1.27	1.63	2.14-2.31	5.60
B-10	0.88	1.27	1.79	2.14-2.30	5.60
Assignments	$-C\underline{H}_3$	$-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-(C\underline{H}_2)_n-CH_3$ n = 3-6 respectively	$-\overset{O}{\overset{\|}{C}}-CH_2-C\underline{H}_2-$	$-\overset{O}{\overset{\|}{C}}-C\underline{H}_2-$	$-N\underline{H}_2$

Table XIII The MS spectra aliphatic primary amides (B-series compounds)

Compound No.	peaks (m/e)	Assignments
	43	$CH_3-CH_2-\overset{+}{C}H_2$
	44	$\overset{O+}{\overset{\|\|}{C}}-NH_2$
B-7,B-8,B-9,B-10,B-11,B-12	59 (base peak)	$CH_2=\underset{\|}{C}-NH_2$ with $:\dot{\overset{+}{O}}-H$
	72	$\overset{+}{C}H_2-CH_2-\overset{O}{\overset{\|\|}{C}}-NH_2$
	73	$\dot{C}H_2-CH_2-\underset{+}{\overset{OH}{\underset{\|}{C}}}-NH_2$
	86	$H_2\overset{+}{N}-CH_2-CH_2-CH_2-C=O$
B-8,B-9,B-10,B-11,B-12	114	$\left[-(CH_2)_5-\overset{O}{\overset{\|\|}{C}}-NH_2\right]^+$
B-7	129 (M^+)	$\left[CH_3-(CH_2)_5-\overset{O}{\overset{\|\|}{C}}-NH_2\right]^{+\cdot}$
B-8	143 (M^+)	$\left[CH_3-(CH_2)_6-\overset{O}{\overset{\|\|}{C}}-NH_2\right]^{+\cdot}$
B-9	157 (M^+)	$\left[CH_3-(CH_2)_7-\overset{O}{\overset{\|\|}{C}}-NH_2\right]^{+\cdot}$
B-10	128	$(M^+)-\dot{C}_3H_7$
	171 (M^+)	$\left[CH_3-(CH_2)_8-\overset{O}{\overset{\|\|}{C}}-NH_2\right]^{+\cdot}$
B-11	140	$(M^+)-\dot{C}_3H_7$
	183 (M^+)	$\left[CH_2=CH-(CH_2)_8-\overset{O}{\overset{\|\|}{C}}-NH_2\right]^{+\cdot}$
B-12	142	$(M^+)-\dot{C}_3H_7$
	185 (M^+)	$\left[CH_3-(CH_2)_9-\overset{O}{\overset{\|\|}{C}}-NH_2\right]^{+\cdot}$

Table XIV The elemental analysis of N,N'-diacyl-cystamines (C-series compounds)

Compound No.	Calcd. and Found	C (%)	H (%)	N (%)	O (%)	S (%)
C-7	Calcd. for $C_{18}H_{36}N_2O_2S_2$	57.40	9.63	7.44	8.50	17.03
	Found	57.59	9.90	7.90		22.50
C-8	Calcd. for $C_{20}H_{40}N_2O_2S_2$	59.36	9.96	6.92	7.91	15.85
	Found	59.11	10.08	6.82		15.60
C-9	Calcd. for $C_{22}H_{44}N_2O_2S_2$	61.06	10.25	6.47	7.39	14.82
	Found	60.89	10.24	6.77		
C-10	Calcd. for $C_{24}H_{48}N_2O_2S_2$	62.56	10.50	6.08	6.94	13.94
	Found	62.77	10.40	5.99		
C-11	Calcd. for $C_{26}H_{48}N_2O_2S_2$	64.42	9.98	5.78	6.60	13.23
	Found	63.84	9.95	5.53		
C-12	Calcd for $C_{26}H_{52}N_2O_2S_2$	63.88	10.72	5.73	6.55	13.12
	Found	63.06	10.29	6.48		

Table XV The UV spectra of N,N'-diacyl-cystamines (C-series compounds)

Compound No.	λ_{max} (nm)	Assignments
C-7	248.5	double bond
C-8	241.5	
C-9	242.5	
C-10	241.0	

Table XVI The IR spectra of N,N´-diacyl-cystamines (C-series compounds)

Absorption peaks ν_{max}^{KBr} (cm^{-1}) / Compound No.	3320-3300	2940-2845	1640-1635	1545-1540	1205-1198	705-675	585-425
C-7	3301	2920, 2850	1638	1542	1205	700, 682	580
C-8	3300	2910, 2845	1638	1540	1201	702, 678	580, 425
C-9	3305	2920, 2885	1638	1545	1200	705, 680	585
C-10	3301	2920, 2850	1635	1545	1198	700, 675	578, 445
C-11	3320	2940, 2880	1640	1545	1199	705, 680	585
C-12	3310	2930, 2870	1639	1545	1199	705, 680	585
Assignments	N-H stretching of secondary amine group	antisymmetric C-H stretching and symmetric C-H stretching	C=O stretching (amide I band)	N-H in-plane bending (amide II band)	C-N stretching and N-H bending (amide III band)	N-H out of-plane bending (amide V band), and O-C-N bending (amide IV, VI band)	C-S stretching and S-S stretching of disulfide

Table XVII The ^{13}C NMR spectra in ppm of N,N´-diacyl-cystamines (C-series compounds)

Carbon positions / Compound No.	C-1 C-1´	C-2 C-2´	C-3 C-3´	C-4 C-4´	C-5 C-5´	C_{t-4} C_{t-4}´	C_{t-3} C_{t-3}´	C_{t-2} C_{t-2}´	C_{t-1} C_{t-1}´	C_t C_t´	C-N C-N´	C-S C-S´
C-7	173.65	36.73	25.74	29.08	-	-	-	31.64	22.54	13.98	38.58	38.31
C-8	173.54	36.68	25.74	29.31	29.04	-	-	31.75	22.59	13.98	38.52	38.25
C-9	173.48	36.73	25.79	29.42	29.20	-	29.20	31.91	22.70	14.03	38.58	38.31
C-10	173.65	36.73	25.79	29.42	29.42	29.42	29.42	31.91	22.70	14.03	38.58	38.25

Table XVIII The ^{1}H NMR spectra of N,N'-diacyl-cystamines (C-series compounds) in $CDCl_3$

Signals δ (ppm) / Compound No.	0.88(br t)	1.26-1.29 (br s)	1.61-1.72	2.13-2.31(t)	2.75-2.90(t)	3.46-3.68(q)	6.29-6.81(br)
C-7	0.88	1.29	1.62	2.14-2.31	2.76-2.90	3.46-3.68	6.47
C-8	0.88	1.28	1.61	2.13-2.30	2.75-2.90	3.46-3.67	6.37
C-9	0.88	1.27	1.69	2.13-2.28	2.76-2.90	3.46-3.67	6.29
C-10	0.88	1.26	1.72	2.13-2.29	2.75-2.90	3.46-3.67	6.81
Assignments	$-\underline{CH}_3$	$-C(=O)-CH_2-\underline{CH}_2-(\underline{CH}_2)_n-CH_3$ n = 3-6 respectively	$-C(=O)-CH_2-\underline{CH}_2-$	$-C(=O)-\underline{CH}_2-$	$-S-\underline{CH}_2-$	$-NH-\underline{CH}_2-$	$-\underline{NH}-$

Table XIX The MS spectra of N,N-diacyl-cystamines (C-series compounds)

Compound No.	peaks (m/e)	Assignments
C-7,C-8,C-9,C-10 C-11,C-12	43	$\overset{+}{\underset{\|\|}{O}}\cdot$ $C-NH$, $CH_3-CH_2-\overset{+}{C}H_2$
	44	$NH=C=\overset{+}{O}-H$
	55	$CH_3-\overset{+}{C}H-CH=CH_2$
	57	$HN-\overset{+}{\underset{\|\|}{C}}-\overset{O}{\cdot}CH_2$, $CH_3-CH_2-CH_2-\overset{+}{C}H_2$
	119	$\cdot CH_2-\overset{\overset{+}{:O-H}}{\underset{\|\|}{C}}-NH-CH_2-CH_2-SH$
C-7	156 (base peak)	$CH_3-(CH_2)_5-\overset{O}{\underset{\|\|}{C}}-NH-CH_2-\overset{+}{C}H_2$
	188 (½ M)	$CH_3-(CH_2)_5-\overset{O}{\underset{\|\|}{C}}-NH-CH_2-CH_2-\overset{+}{S}$
	189 (½ M + H)	$CH_3-(CH_2)_5-\overset{O}{\underset{\|\|}{C}}-NH-CH_2-CH_2-\overset{+.}{S}H$
	376 (M^+)	$\left[CH_3-(CH_2)_5-\overset{O}{\underset{\|\|}{C}}-NH-CH_2-CH_2-S-\right]_2^{\overset{+}{\cdot}}$
C-8	170 (base peak)	$CH_3-(CH_2)_6-\overset{O}{\underset{\|\|}{C}}-NH-CH_2-\overset{+}{C}H_2$
	202 (½ M)	$CH_3-(CH_2)_6-\overset{O}{\underset{\|\|}{C}}-NH_2-CH_2-CH_2-\overset{+}{S}$
	203 (½ M + H)	$CH_3-(CH_2)_6-\overset{O}{\underset{\|\|}{C}}-NH-CH_2-CH_2-\overset{+.}{S}H$
	404 (M^+)	$\left[CH_3-(CH_2)_6-\overset{O}{\underset{\|\|}{C}}-NH-CH_2-CH_2-S-\right]_2^{\overset{+}{\cdot}}$

Table XIX Continued

Compound No.	peaks (m/e)	Assignments
C-9	184 (base peak)	$CH_3-(CH_2)_7-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{+}{C}H_2$
	216 (½ M)	$CH_3-(CH_2)_7-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{+}{S}$
	217 (½ M + H)	$CH_3-(CH_2)_7-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{+\cdot}{S}H$
	432 (M^+)	$\left[CH_3-(CH_2)_7-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-S-\right]_2^{\overset{+}{\cdot}}$
C-10	198 (base peak)	$CH_3-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{+}{C}H_2$
	230 (½ M)	$CH_3-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{+}{S}$
	231 (½ M + H)	$CH_3-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{+\cdot}{S}H$
	460 (M^+)	$\left[CH_3-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-S-\right]_2^{\overset{+}{\cdot}}$
C-11	210 (base peak)	$CH_2=CH-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{+}{C}H_2$
	242 (½ M)	$CH_2=CH-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{+}{S}$
	243 (½ M + H)	$CH_2=CH-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{+\cdot}{S}H$
	484 (M^+)	$\left[CH_2=CH-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-S-\right]_2^{\overset{+}{\cdot}}$

Table XIX Continued

Compound No.	peaks (m/e)	Assignments
C-12	212 (base peak)	$CH_3-(CH_2)_9-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{+}{C}H_2$
	244 (½ M)	$CH_3-(CH_2)_9-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{+}{S}$
	245 (½ M + H)	$CH_3-(CH_2)_9-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{+.}{S}H$
	488 (M^+)	$\left[CH_3-(CH_2)_9-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-S-\right]_2^{\cdot+}$