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Synthesis of Nucleophilic Adducts of Thiols (I). Addition of Cysteine to β-Nitrostyrene Derivatives

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The addition reactions of cysteine without blocking amino and carboxyl groups to substituted and unsubstituted β-nitrostyrene derivatives were investigated. β-Nitrostyrene(1a), *p*-methyl-β-nitrostyrene(1b), 3,4,5-trimethoxy-β-nitrostyrene (1c), ω-3,4-methylendeioxy-β-nitrostyrene(1d), *o*-, *m*- and *p*-chloro-β-nitrostyrene (1e, 1f, 1g) and *o*-, *m*- and *p*-methoxy-β-nitro-styrene (1h, 1i, 1j) easily undergo addition reactions with cysteine to form S-(2-nitro-1-phenylethyl)-*L*-cysteine(3a), S-[2-nitro-1-(*p*-methyl)phenyl-ethyl]-*L*-cysteine(3b), S-[2-nitro-1-(3′, 4′, 5′- trimethoxy) phenylethyl]-*L*-cysteine(3c), S-[2-nitro-1-(ω-3′, 4′-methylenedioxy)phenylethyl]-*L*-cysteine(3d), S-[2-nitro-1-(*o*-chloro)phenylethyl]-*L*-cysteine(3e), S-[2-nitro-1-(m-chloro)-phenylethyl]-*L*- cysteine(3f), S-[2-nitro-1-(*p*-chloro)phenylethyl]-*L*-cysteine(3g), S-[2-nitro-1-(o-methoxy)phenyl-ethyl]-*L*-cysteine(3h), S-[2-nitro-1-(*m*-methoxy)phenylethyl]-*L*-cysteine(3i) and S-[2-nitro-1-(*p*-methoxy)phenylethyl]-*L*-cysteine(3j), respectively. The structure of adducts were confirmed by means of UV-spectrum, IR-spectrum, molecular weight measurement and elemental analysis. The various factors effecting the yeild of cysteine adducts to β-nitrostyrene derivatives were also studied.

1. Introduction

In recent years, there has been a growing interest in the synthesis of cysteinyl peptides in conjunction with the studies of many other peptides and proteins of biological importance[1-5].

It was well known that the reaction of cysteine with conjugated aldehydes and 4-hydroxy conjugated aldehydes leads to the formation of 2-substituted thiazolidine-4-carboxylic acids[6,7] and these compounds exert their antitumor[8], antimicrobial[9] and anticancer[10] activity.

But due to the sensitivity of the cysteine molecule toward oxidation and elimination, it usually is necessary to protect β-sulfhydryl function and all the other reactive functional group such as amino group and carboxyl group during synthesis. Customarily this is accomplished by transformation of the β-sulfhydryl group to a S-benzylthioether[11] or oxidation to the cysteinyl derivative[12,13] with the amino group usually blocked with the carbobenzoxy group.

In 1948, Schöberl[14] studied the addition reaction of cysteine to unsaturated compounds forming thioetherbinding amino acids, which have biochemical importance.

Sheehan[1] reported a new protective system for sulfhydryl and amino groups of cysteine. Cysteine was converted to a thiazolidine derivatives by reaction with acetone, the amino group may be blocked by formylation, which were removed by acid-catalyzed solvolysis and mild acid hydrolysis or by mercuric chloride treatment[15].

Yong[16] and Camble[17] reported sulfhydryl group protection by using S-benzylthiomethyl group which eliminated easily with mercuric acetate in 80 % formic acid solution instead of S-benzyl group accompaning side reaction during elimination.

Jung, *et al.*, obtained the N-methylmorpholinium salt of N-*t*-butoxycarbonyl-S-(2-nitro-1-phenylethyl)-*L*-cysteine by the addition reaction of N-methylmorpholinium N-*t*-butoxycarbonyl-*L*-cysteinate with β-nitrostyrene and aplied this method for the synthesis of adduct.[18]

However, no study has been undertaken on the addition reaction of cysteine without protection of amino and carboxyl groups to β-nitrostyrene derivatives. Such adducts would exhibit great synthetic utility as biochemical and pharmaceutical products and may undergo a number of interesting peptide synthesis.

Accordingly, the main purpose of this study was to synthesize the addition products of cysteine without

TABLE 1: Analytical Data of β-Nitrostyrene Derivatives

Compound	R_1	R_2	R_3	R_4	R_5	Yield (%)	mp (°C. dec)	Analytical data of elements (%) Calculated C	H	N	Found C	H	N
1a	H	H	H	H	H	80.5	56–58[a]	64.42	4.73	9.39	64.70	4.60	9.50
1b	H	H	CH_3	H	H	57.0	99–100[b]	66.25	5.52	8.59	66.10	5.90	8.20
1c	H	OCH_3	OCH_3	OCH_3	H	67.3	123–124[c]	55.23	5.44	5.90	55.40	5.66	6.10
1d	H	$-OCH_2O-$		H	H	57.0	162–163	55.97	3.62	7.25	55.40	3.40	7.40
1e	Cl	H	H	H	H	53.0	46–48	52.34	3.30	7.63	52.10	3.10	7.43
1f	H	Cl	H	H	H	51.0	48–49	52.34	3.30	7.63	52.63	3.45	7.75
1g	H	H	Cl	H	H	68.0	111–112[d]	52.34	3.30	7.63	52.26	3.60	7.41
1h	OCH_3	H	H	H	H	70.0	47–48	60.33	5.06	7.82	60.15	4.81	7.60
1i	H	OCH_3	H	H	H	77.2	93–95	60.33	5.06	7.82	60.55	5.23	7.95
1j	H	H	OCH_3	H	H	59.0	120–121[e]	60.33	5.06	7.82	60.47	5.21	7.74

[a] 57–58 °C (47); [b] 102 °C (48); [c] 123 °C (49); [d] 113–114°C (50); [e] 120–121 °C (50)

protection of amino and carboxyl groups to various β-substituted styrene derivatives. The factors effecting the yield and the structure of adducts were studied and confirmed.

2. Experimental

2. 1 General

Melting points(uncorrected) were determined by the Fisher Johne's melting point apparatus. Ultraviolet spectra were obtained on a Beckman Model 26 spectrophotometer. Infrared spectra were taken with JASCO IRA-2 spectrophotometer, and elemental analysis was conducted with a MOO-1106 Model carlo Erba, Italy. Optical rotation was measured with a JASCO DIP-181(Japan) polarimeter. Thin-layer chromatography were run on Merck HF-254 silica gel plates, and spots on chromatograms were detected by their ultraviolet absorption or by spraying ninhydrin reagent. *L*-cysteine and *L*-cysteine hydrochloride monohydrate were purchased from Nakarai Chemicals, Ltd., Japan. Various substituted benzaldehydes, nitromethane, N-methylmorpholine and triethylamine were obtained from Merck and Kyoei Chemical Cooperation and used without further purification. Unless otherwise indicated, all other reagents were used as received.

β-Nitrostyrene derivatives were prepared according to Worrall's method.[19]

2. 2 Preparation of Adducts

S-(2-Nitro-1-phenylethyl)-L-cysteine[3a]. *L*-Cysteine hydrochloride monohydrate (25 g, 0.143 mole) was dissolved in 300 m*l* of distilled water. Potassium acetate (22 g, 0.224 mole) and 22 g (0.147 mole) of β-nitrostyrene in methanol (600 m*l*) were added to the solution. The reaction mixture was allowed to be stirred at room temperature for 12 hours. the resulting precipitates were collected by filtration and washed with methanol. Recrystallization was performed in 50 % methanol solution (28 g, 72.5 %); m.p 182-184° C dec.; ir (KBr) cm^{-1}; 3400(NH), 3260 (intra H-bond chelation), 3200-2800($-NH^+_3$,$-COO^-$) 1555, 1370 ($C-NO_2$), 1450(sulfide), 1420 ($S-CH_2-$), 1307(CH), 700(sulfide); UV (0.1 *N* NaOH) nm; λ_{max}=251 (ε=13700).

Analysis: Calculated from $C_{11}H_{14}N_2O_4S$; C, 48.88; H, 5.22; N, 10.36; S, 11.86. Found; C,48.70; H, 4.98; N, 10.17; S, 12.01.

Other Adducts of β-Nitrostyrene Derivatives. *L*-Cysteine hydrochloride, monohydrate (25 g, 143 mmole) was dissolved in 900 m*l* of 62 % aquous acetonitrile or methanol.

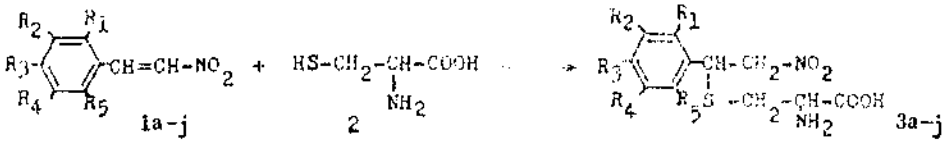
Potassium acetate (147 m mole) or N-methylorpholine (145 m mole) was added and β-nitrostyrene derivatives (142 m mole) were added and stirred for 12 hrs at 25° C. The each precipitated product, S-[2-nitro-1-(*p*-methyl) phenylethyl]-*L*-cysteine[3b], S-[2-nitro-1-(3′, 4′, 5′-trimethoxy) phenylethyl]-*L*-cysteine[3c], S-[2-nitro-1-(ω-3′, 4′-methylenedioxy)phenylethyl]-*L*-cysteine[3d], S-[2-nitro-1-(*o*-chloro)phenylethyl]-*L*-cysteine[3e], S-[2-nitro-1-(*m*-chloro)-phenylethyl]-*L*-cysteine[3f], S-[2-nitro-1-(*p*-chloro) phenylethyl]-*L*-cysteine[3g], S-[2-nitro-1-(*o*-methoxy) phenylethyl]-*L*-cysteine[3h], S-[2-nitro-1-(*m*-methoxy)-phenylethyl]-*L*-cysteine[3i], and S-[2-nitro-1-(*p*-methoxy) phenylethyl]-*L*-cysteine[3j], was collected by filtration, washed with water and methanol. Recrystallization from 50 % aquous methanol. Analytical data of S-(2-nitro-1-phenylethyl)-*L*-cysteine derivatives are recorded in Table 1.

3. Results and Discussions

3. 1 Identification of Adducts

The cysteine adducts of β-nitrostyrene derivatives were identified by measuring melting point, specific rotation and elemental analysis, confirmed by thin-layer chromatography, IR-spectrum and UV-spectrum and molecular weight was determined by nonaqueous amine titration method. Nonaqueous amine titrations were carried out to determine molecular weight. One m*l* of 0.1 *N*-$HClO_4$ is equivalent to 0.027033 g of S-(2-nitro-1-phenylethyl)-*L*-cysteine. The data of yield, melting point and elemental analysis are recorded in Table 2. Specific rotation of adducts

TABLE 2: Analytical Data of S-(2-Nitro-1-phenylethyl)-*L*-Cysteine Derivatives



Compound	R_1	R_2	R_3	R_4	R_5	Yield (%)	mp[a] (°C. dec)	Analytical data of elements (%) Calculated C	H	N	S	Found C	H	N	S	
3a	H	H	H	H	H	72.5	182–184	48.88	5.22	10.36	11.86	48.70	4.98	10.17	12.01	
3b	H	H	CH_3	H	H	76.2	195–197	50.71	5.63	9. 86	11.27	50.28	5.91	10 11	11.40	
3c	H	OCH–	OCH_3	OCH_3	H	75.0	191–192	46.68	5.55	7.77	8.91	46.80	6.01	7.41	9.04	
3d	H	–OCH	O–	H	H	77.0	210–213	45.86	4.49	8.91	10.20	45.65	4.73	8.76	9.92	
3e	Cl	H	H	H	H	72.6	174–175	43.35	4.30	9.19	10.52	43.40	4.51	9.10	10.42	11.4[b]
3f	H	Cl	H	H	H	79.2	174–175	43.35	4.30	9.19	10.52	43.15	4.21	9.01	10.32	11.43
3g	H	H	Cl	H	H	72.6	181–182	43.35	4.30	9.19	10.52	43.20	4.43	9.30	10.49	11.46
3h	OCH_3	H	H	H	H	56.2	179–180	47.97	5.39	9.33	10.67	47.81	5.51	9.20	10.48	
3i	H	OCH_3	H	H	H	66.7	170–172	47.97	5.39	9.33	10.67	47.85	5.21	9.21	10.43	
3j	H	H	OCH_3	H	H	86.7	180–182	47.97	5.39	9.33	10.67	47.95	5.43	9.30	10.57	

[a] Determined after recrystalization in acetonitrile and methanol. [b] Calculated content Cl: 11.63 %.

TABLE 3: Spectral Data of β-Nitrostyrene Derivatives and Their Cysteine Adducts.

Comp.	λ_{max}(mn); (extinction coef.)	Characteristic absorption peak of IR-spectrum (cm^{-1})
1a	230(5900), 311(11500)	3140, 1640, 1605, 1580, 1520, 1475, 1350
3a	251(13700)	3400, 3260, 3200–2800, 1555, 1450, 1420, 1370, 1307, 700
2b	236(5900), 326(12500) f	3140, 2960, 1640, 1615, 1570, 1510, 1245, 1040, 975, 790, 730
3b	248(11000)	3400, 3000, 1620, 1555, 1420, 1370, 1310, 675
1c	244(9400), 350(16200)	3140, 2560, 2860, 1635, 1590, 1510, 1470, 1335, 1005, 975, 790
3c	229(17400)	3400, 3000–2900, 2820, 1620, 1550, 1450, 1420, 1375, 665
1d	260(6600), 360(12500)	3100, 3060, 2900, 1640, 1600, 1495, 1335, 1255, 1030, 975
3d	243(5500), 279(5100)	3400, 3000, 2840, 1620, 1550, 1450, 1420, 1370, 670
1e	292(6600), 300(10700)	3140, 1640, 1595, 1520, 1475, 1350, 1060, 1045, 975, 775
3e	236(11800)	3400, 3000, 1620, 1550, 1460, 1420, 1380, 755, 670
1f	244(8200), 295(11700)	3140, 2640, 1575, 1520, 1485, 1350, 1085, 1005, 980, 770, 720,
3f	234(12100)	3400, 3000, 1620, 1550, 1460, 1420, 1380, 770, 670l.
1g	228(8300), 313(11900)	3140, 1640, 1600, 1525, 1510, 1500, 1350, 1096, 975, 755
3g	244(14300)	3400, 3000, 1620, 1550, 1380, 790, 650
1h	302(10000), 351(9800)	3140, 1980, 2880, 1635, 1605, 1580, 1515, 1470, 1350, 1030, 970. 785
3h	238(13700)	3400, 3000, 2880, 1620, 1555, 1645, 1425, 1385, 670
1i	248(8800), 307(13300)	3140, 2980, 2880, 1645, 1600, 1575, 1520, 1470, 1355, 1050, 970, 790
3i	240(13600)	3400, 3000, 2880, 1615, 1560, 1460, 1420, 1375, 670
1j	226(1320) 350(10300)	3140, 3000, 2960, 2940, 2880, 1635, 1610, 1585, 1525, 1475, 1340, 790
3j	277(13700)	3400, 3000, 2880, 1610, 1550, 1460, 1420, 1380, 675

were determined in 1*N* HCl solution and others in dimethylsulfoxide. The results of specific rotation are recorded in Table 4.

The purity of the adducts of cysteine to β-nitrostyrene derivatives was tested by thin-layer chromatography on silica gel G plate. The R_f-values of the adducts were 0.66–0.83 compared with that (0.29) of cysteine. The results are recorded in Table 4.

The structure of cysteine adducts to β-nitrostyrene derivatives was confirmed by IR and UV spectra and their results are recorded in Table 3. The characteristic peaks of adducts correspond to NH streching vibration at 3400 cm^{-1}, intra H-bond chelation at 3260 cm^{-1}, $-NH^+_3$ and $-CH_2-$ streching vibration of cysteine portion at 3200–2800 cm^{-1}, assymmetric bending of $-NH^+_3$ and assymetric streching vibration of $-COO^-$ at 1620 cm^{-1}, $-CH_2NO_2$ at 1555 cm^{-1}, $-S-CH_2-$at 1420 cm^{-1}, CH bending vibration at 1370 cm^{-1} and sulfide at 600–700 cm^{-1}. The synthesis of cysteine adducts to β-nitrostyrene derivatives could be easily ascertained by comparing IR-spectra of β-nitrostyrene and those of their adducts. The conjugated system of β-nitrostyrene derivatives ($-CH-CHNO_2$) disappeared in case of cysteine. adducts. We could confirm characteristic peak of $-CH=CH-NO_2$ at 1510 cm^{-4} and of $-CH-CH_2-NO_2$ of adduct at higher frequency, 1555 cm^{-1}.

The formation of adducts was also confirmed by the change of UV-absorptions in methanol and 0.1 *N* NaOH solution at 10^{-4} *M* concentration. Maximum UV-

TABLE 4: Analytical Data of Cysteine Adducts of β-Nitrostyrene Derivatives

Compound	$[\alpha]_D^{20}$	R_f-value	Amine content(%)	Molecular weight	
				Calculated	Found
3a	+20[b]	0.82–0.83	99.85–100.10	270.33	270.06–270.74
3b	+31.8[b]	0.82	99.80–100.40	284.33	283.20–284.90
3c	+84.0[b]	0.81	99.20–100.56	360.16	358.15–363.06
3d	[c]	0.80	99.10	314.33	317.18
3e	+3.5	0.69	102.20	304.74	298.18
3f	−3.2	0.70	101.90	304.74	299.06
3g	+5.2(12.4)[b]	0.70	102.50	304.74	297.30
3h	−5.4	0.66	99.7	300.33	301.23
3i	−5.4	0.66	100.60	300.33	298.54
3j	−5.5	0.66	100.50	300.33	298.83
Cysteine	+5.7[d]	0.29	99.80	121.16	121.40

[a] Determined in DMSO; [b] determined in 1*N* HCl; [c] not determined; [d] determined in 5*N* HCl.

absorption peak of β-nitrostyrene appeared at 311 nm and of its adduct at 251 nm with disappearance of conjugated system of β-nitrostyrene.

The absorption characteristics of β-nitrostyrene derivatives containing chromophoric nitro groups which conjugated with double bond absorbed strongly in the region of 295 nm and 350 nm. β-Nitrostyrene derivatives containing both π-and *n*-electrons can undergo 3 transitions; $n\rightarrow\sigma^*$, $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$. The cysteine adducts of β-nitrostyrene derivatives moves the absorption to shorter wavelength with disappearance of conjugated double bond.

3. 2 The Effects of pH and Base on the Addition of Cysteine to β-Nitrostyrene Derivatives

The additions of cysteine to β-nitrostyrene derivatives were sensitive to change in pH of reaction media. At too low pH, the yield of adducts was very low, on the other hand, at high pH, β-nitrostyrene derivatives readily hydrolyzed to benzaldehyde and nitromethane to afford thiazolidine derivatives.[20] The effects of pH and base on the addition reaction are shown in Figure 1.

At a fixed pH, the yield of adducts depended on the base used for neutralization of cysteine hydrochloride. S-[2-Nitro-1-(3′, 4′, 5′-trimethoxy) phenylethyl]-*L*-cysteine was obtained in maximum yield at pH 5.8–5.9 and 25 °C with *N*-methylmorpholine.

However, the maximum yield was obtained at pH 5.4–5.5 at temperature 45 °C. In general, the higher the temperature, the .lower the yield.

S-(2-Nitro-1-phenylethyl)-*L*-cysteine was obtained in maximum yield at pH 4.8–4.9 with N-methylmorpholine, but in maximum yield at pH 5.2–5.3 with potassium acetate as nase.

S-[2-Nitro-1-(*p*-methyl)phenylethyl]-*L*-cysteine was obtained in maximum yield at pH 5.6–5.7 with N-methylmorpholine, but at pH 4.6–4.7 with potassium acetate.

The addition reaction was carried out in aqueous methanol but the yield was differ in aqueous acetonitrile solution.

S-(2-nitro-1-phenylethyl)-*L*-cysteine was obtained in maximum yield of 26.3 % with *N*-methylmorpholine or potassium acetate in aqueous acetonitrile but the adduct was contaminated with thiazoline derivatives.

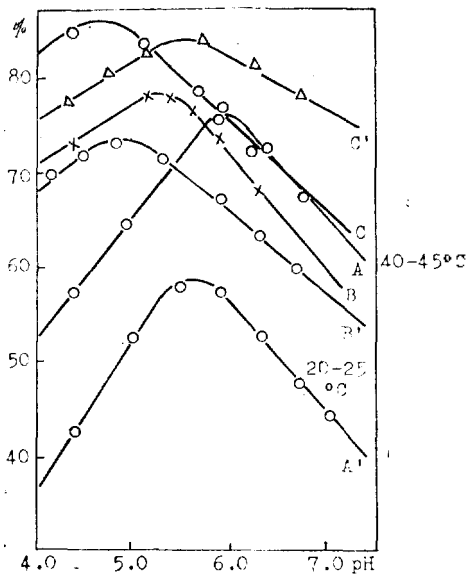


Figure 1. The Changes of yield of adducts with pH and base. A,A′: Adduct 3c A; 20–25°C A′; 40–45°C. B,B′:Adduct 3a B; CH_3COOK B′: N-methylmorpholine. C,C′: Adduct 3b C; CH_3 COOK C′; N-methylmorpholine.

S-[2-nitro-1-(*p*-methyl)phenylethyl]-*L*-cysteine was obtained in maximum yield of 57.3 % at pH 6.3 with N-methylmorpholine and 69.1 % at pH 5.85 with potassium acetate in aqueous acetonitrile solution.

The yield of adducts depends on the pH of the reaction media, and on the bases used as neutralizing agent and reaction solvent.

So it is necessary to find out suitable reaction pH, selection of base and reaction solvent for the better synthesis of various cysteine adducts with β-nitrostyrene derivatives. These adducts which protect β-sulfhydryl group of cysteine without protection of amino and carboxyl groups are applicable for the synthesis of cysteinyl peptides which derived from amino and carboxyl group of cysteine.

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Rheological Properties of Polystyrene Degraded by Mechanical Forces

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Polystyrene was degraded by using a vibrating ball mill. The viscosities and molecular weights of the degraded products were measured, and the decrease of viscosity η with $\dot{s}$ (rate of shear) observed for the degraded products were analyzed by applying the Ree-Eyring equation for viscous flow. The variation of the parameters $x_2/\alpha_2, \beta_2$ and $x_1\beta_1/\alpha_1$ in the equation were explained by the fracture of polymer molecules by mechanical force. The electron paramagnetic resonance spectrum of the degraded sample was taken, and it was confirmed that free radicals were produced by the chain-scission of polystyrene.

Introduction

It is well known that degradation occurs when mechanical force is applied to polymers[1]. That is, lower grade polymers are formed because of chain scission by mechanical force; as a result, the molecular weight decreases and the rheological properties change[2].

In this study, after degrading solid state polystyrene by using a vibrating ball mill, the viscosity η of degraded products was measured and the flow curves of η *vs.* shear rates were determined. The experimental results where analyzed by using the Ree-Eyring generalized viscosity equation. The results showed that the chain scission occurs by the mechanical degradation as expected. We also confirmed the free radical formation during degradation by using electron paramagnetic resonance (EPR). These results are reported and discussed in this paper.

Theory

The Ree-Eyring generalized viscosity equation based on absolute reaction rate theory is given by:[3]

$$\eta = \sum_{i=1}^{n} \frac{x_i \beta_i}{\alpha_i} \frac{\sinh^{-1} \beta_i \dot{s}}{\beta_i \dot{s}} \tag{1}$$

where η is viscosity, $\dot{s}$ is shear rate, x_i is the fraction of area occupied by flow units of the ith group, and α_i and β_i are defined, respectively, by the following equations:

$$\alpha_i = (\lambda\lambda_2\lambda_3)_i / 2kT \tag{2}$$

and

$$\beta_i = 1/(\lambda/\lambda_1)_i 2k_i' \tag{3}$$

In the above, α_i^{-1} is the quantity proportional to the shear modulus of the ith flow group unit, β_i is proportional to the relaxation time, k is Boltzmann constant, T is absolute