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Spectroscopic Identification of 3-Substituted 4-Methoxycarbonyl-1,3-thiazolidine (or -oxazolidine)-2-thiones and 2-Substituted Thio-4-methoxycarbonyl-Δ^2-1,3-thiazolines (or -oxazolines)[1)]

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rac-4-Methoxycarbonyl-Δ^2-1,3-thiazolines **2a**—**z** and *rac*-4-methoxycarbonyl-1,3-thiazoline-2-thiones **3a**,**d**—**t** were examined by carbon-13 and proton nuclear magnetic resonance and ultraviolet spectroscopic methods to provide a basis for spectroscopic identification of Δ^2-1,3-oxazolines and 1,3-oxazolidine-2-thiones. X-Ray structural analysis of 3-(4′-bromobenzyl)-2-thioxo-1,3-thiazolidine-4-carboxylic acid **4n** was also carried out.

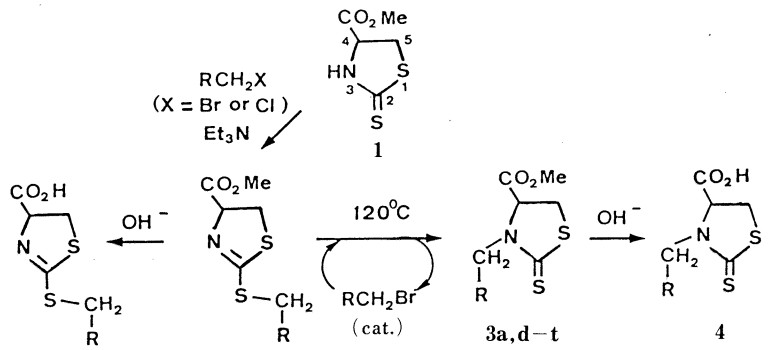
Keywords——2-substituted thio-4-methoxycarbonyl-Δ^2-1,3-thiazoline; 3-substituted 4-methoxycarbonyl-1,3-thiazolidine-2-thione; spectroscopy; ambident nature; Δ^2-1,3-oxazoline; 1,3-oxazolidine-2-thione; X-ray analysis; imine; thiocarbonyl

In order to develop new inhibitors of aldose reductase, various *rac*-2-substituted thio-4-methoxycarbonyl-Δ^2-1,3-thiazolines **2a**—**z** and *rac*-3-substituted 4-methoxycarbonyl-1,3-thiazolidine-2-thiones **3a**, **d**—**t** were synthesized in our previous work (Chart 1).[2-4)] Carboxylic acids **4** and **5** were also prepared by saponification of **2** and **3**, respectively.[5)]

We were also able to show that structural differentiation between *exo*-S-substituted Δ^2-1,3-thiazolines (**2**) and N(3)-substituted-1,3-thiazolidines (**3**) can be done unequivocally on the basis of the spectroscopic data, especially carbon-13 and proton nuclear magnetic resonance (^{13}C- and ^{1}H-NMR) and ultraviolet (UV) spectra.

Previously, two (EF and YN)[6)] of the authors reported the utility of ^{13}C-NMR spectral data for the structure confirmation of N(3)-acyl derivatives **6** and *exo*-S-phenacyl derivatives **7** of 1,3-thiazolidine-2-thione which showed an ambident nature (N or *exo*-S)[7-12)] toward electrophiles. However, there have been no systematic studies on the spectral data of 4-methoxycarbonyl-1,3-thiazolidine (or -oxazolidine)-2-thione derivatives. We present here detailed spectral data for Δ^2-1,3-thiazoline (or -oxazoline) and 1,3-thiazolidine (or -oxazolidine) derivatives.

Chemical shifts (δ ppm) on the ^{13}C-NMR chart of 2-benzylthio-Δ^2-1,3-thiazoline (**8**) and 3-benzyl-1,3-thiazolidine-2-thione (**9**) are summarized in Table I. On the basis of the ^{13}C-NMR data of **8** and **9**, assignments of the signals of various 4-methoxycarbonyl-Δ^2-1,3-thiazolines **2** and 1,3-thiazolidine-2-thiones **3** were made. These are also included in Table I. Thus, in the cases of 4-methoxycarbonyl derivatives, the ^{13}C-NMR signals due to the imine



5 2a–z 3a,d–t 4

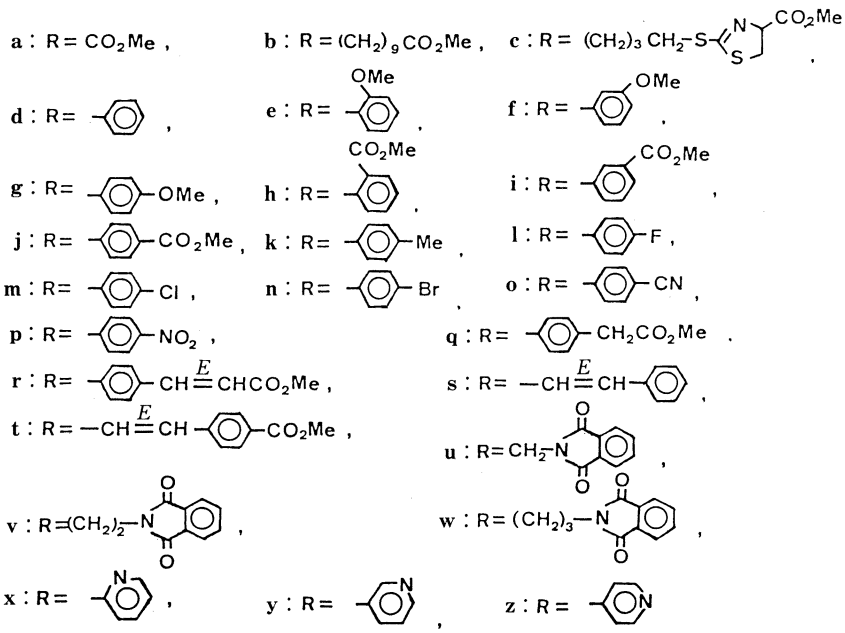
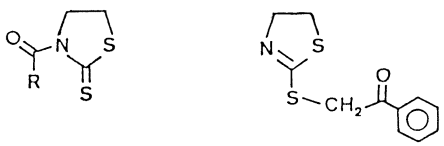


Chart 1



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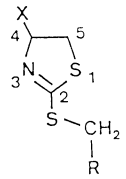
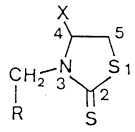
carbon and the thiocarbonyl carbon were always observed in the regions of δ 170.7—174.2 and δ 197.5—199.3 ppm, respectively. Interestingly, ^{13}C-chemical shift values of the Δ^2-1,3-thiazoline nucleus **2** having a 4-methoxycarbonyl group are generally lower than those of the 4-unsubstituted Δ^2-1,3-thiazolines (*e.g.*, compound **8**). A similar phenomenon was seen in the case of the 1,3-thiazolidine nucleus **3** having a 4-methoxycarbonyl group, in comparison with **9**. These lower magnetic field shifts in the cases of **2** and **3** are presumably due to the electron-withdrawing effect of the 4-methoxycarbonyl group.

^{1}H-NMR spectroscopy is also an effective method for the assignment of the structures **2**

TABLE I. ^{13}C-NMR (50.10 MHz) Spectral Data for Δ^2-1,3-Thiazolines and 1,3-Thiazolidines in $CDCl_3$ (TMS)



Δ^2-1,3-thiazolines
8: X=H, R=Ph
2: X=CO_2Me, R=alkyl and aromatic group



1,3-thiazolidines
9: X=H, R=Ph
3: X=CO_2Me, R=alkyl and aromatic group

Compound	C(2) (δ ppm)	C(4) (δ ppm)	C(5) (δ ppm)
8	165.2	64.2	35.6
2	170.7—174.2	76.9—77.6	37.1—37.9
9	197.1	52.6	27.0
3	197.5—199.3	66.7—67.6	30.8—31.2

and **3**, as illustrated by the ^{1}H-NMR spectra of **2d** and **3d** (Fig. 1). In the ^{1}H-NMR chart of **2d**, one set of AB-type signals due to benzyl protons can be recognized at δ 4.36 and δ 4.44 (J_{DC} = 13.2 Hz). Signals of H_C and H_D are adjacent, as shown in Fig. 1. The corresponding AB-type signals of **3d** are observed at δ 4.30 and δ 5.89 (J_{DC} = 14.9 Hz). Signals of H_C and H_D in the case of **3d** are located apart from each other because of the quite different environments of H_C and H_D in the molecule. Namely, one of the benzyl protons lying close to the thiocarbonyl group may be deshielded, while the other proton may be shielded by the methoxycarbonyl group. This is clear from an inspection of the molecular model of **3d**, and also from the perspective views obtained from X-ray analysis of the carboxylic acid **4n** (*vide infra*). Coupling patterns of ABX-type seen for the C(4) and C(5) proton signals in **3d** are dramatically different from those in **2d**. In the former, the coupling constants are as follows: J_{AX} = 8.8 Hz, J_{BX} = 8.1 Hz, and J_{AB} = 11.0 Hz. In the latter, the coupling constants J_{AX} = 2.9 Hz, J_{BX} = 8.8 Hz, and J_{AB} = 11.5 Hz are observed. Such characteristic coupling patterns should be common in the ^{1}H-NMR spectra of **2** and **3**. However, this feature can not be used for the identification of compounds **8** and **9** because of their lack of substitution at the C(4) position in the thiazolidine moiety.

Structural assignments of 2-substituted thio-Δ^2-1,3-thiazolines and 1,3-thiazolidine-2-thiones can also be done on the basis of UV spectral data. In the UV spectra of the former, the absorption due to the imine moiety is observed around λ_{max} 220 nm. For the latter, the absorption due to the thiocarbonyl moiety is observed around λ_{max} 280 nm.

Crystalline **4n** obtained by alkaline hydrolysis of **3n** was subjected to X-ray analysis. The details are presented in the experimental section. Interestingly, it was found that four atoms, C(2), N(3), C(4), and the benzylic carbon in the carboxylic acid **4n** exist on the same plane (Figs. 2 and 4). Thus, the N(3) atom in the N(3)-*p*-bromobenzyl derivative **4n** is sp^2-hybridized, as in the case of N(3)-acyl-1,3-thiazolidine-2-thiones (*e.g.*, compound **6**).[13,14]

Subsequently, we prepared 2-benzylthio-Δ^2-1,3-oxazoline (**12a**) and its *rac*-4-methoxycarbonyl derivative **12b** according to the usual method (Chart 2).[15,16] These compound were converted to the corresponding 1,3-oxazolidine-2-thiones **13a** and **13b** *via* the same catalytic thermal rearrangement as in the case of the Δ^2-1,3-thiazolines **2**.

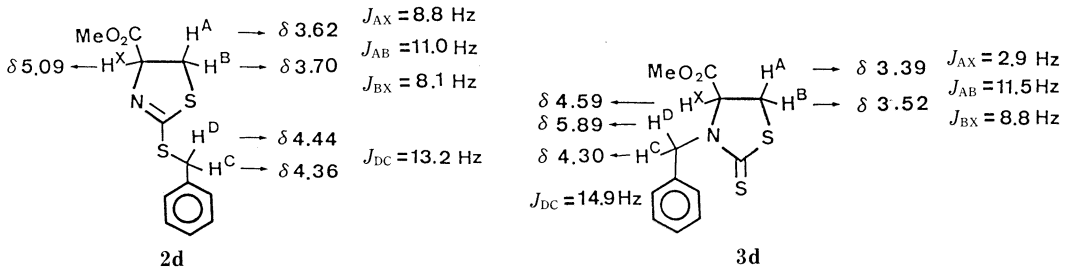


Fig. 1. ^{1}H-NMR (199.50 MHz) Spectral Data for Compounds **2d** and **3d** in $CDCl_3$ (δ ppm from TMS)

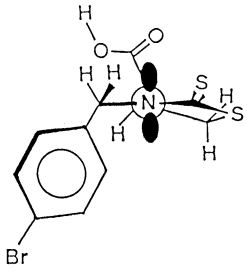


Fig. 2. Illustration of the Crystallographic Structure of Compound **4n**

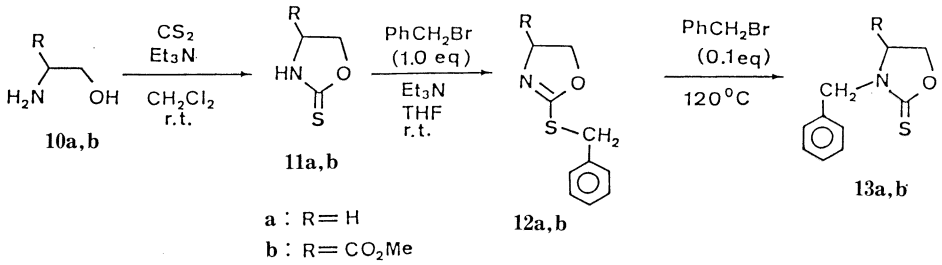
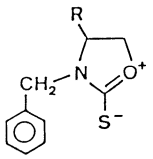


Chart 2

TABLE II. ^{13}C-NMR (50.10 MHz) Spectral Data for Δ^2-1,3-Oxazolines **12a, b** and 1,3-Oxazolidine-2-thiones **13a, b** in $CDCl_3$ (TMS)

Compound	C=N (δ ppm)	C=S (δ ppm)	C=O (δ ppm)
12a	165.8		
12b		167.5	
13a	171.2		168.7
13b		171.5	170.2



14a : R=H
14b : R=CO_2Me

The ^{13}C-NMR chemical shifts of imine, carbonyl, and thiocarbonyl carbons of **12a, b** and/or **13a, b** are summarized in Table II. Unfortunately, ^{13}C-NMR analysis could not clearly differentiate between the **12** type structure and the **13** type one. The absence of a distinct δ value of the thiocarbonyl carbon of **13a, b** from that of the imine carbon of **12a, b** may be explained in terms of a dipolar structure, **14a, b**.[17]

The ^{1}H-NMR spectra of **12b** and **13b** provided useful data, as in the cases of **2d** and **3d**. Assignments of the ^{1}H-NMR signals are summarized in Fig. 3. Thus, we can readily

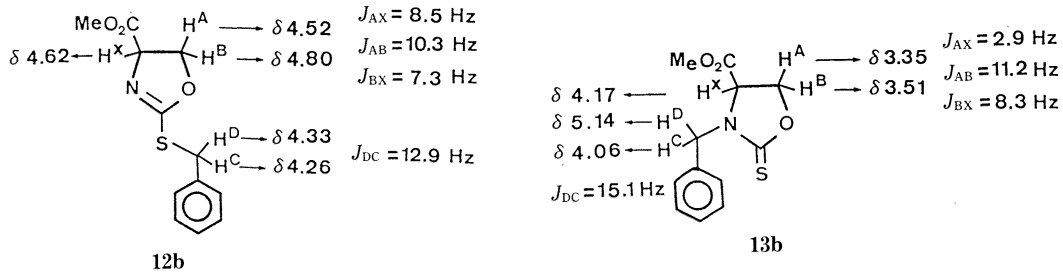


Fig. 3. ^{1}H-NMR (199.50 MHz) Spectral Data for Compounds **12b** and **13b** in $CDCl_3$ (δ ppm from TMS)

distinguish the 2-substituted thio-4-methoxycarbonyl-Δ^2-1,3-oxazoline structure from the 4-methoxycarbonyl-1,3-oxazolidine-2-thione structure by comparing the coupling patterns and coupling constants due to the AB-type signals of benzyl CH_2 and the ABX-type signals of the C(4) and C(5) protons. The reasons for the differences described above are presumably similar to those in the case of compounds **2d** and **3d**.

Experimental

Infrared (IR) spectra were run on a Shimadzu IR 420 spectrophotometer. UV spectra were recorded on a Hitachi 323 spectrophotometer. The ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL FX-200 spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in δ values (ppm) with tetramethylsilane (TMS) as an internal standard. Mass spectra (MS) were determined with a Hitachi RMU-6M mass spectrometer. Extracts were dried over anhydrous Na_2SO_4. Kiesel gel 60 (70—230 mesh) (Merck) was employed for column chromatography. Detailed spectroscopic data for the *rac*-4-methoxycarbonyl-Δ^2-1,3-thiazolines **2a**—**z**, *rac*-4-methoxycarbonyl-1,3-thiazolidines **3a**, **d**—**t**, and the carboxylic acid **4n** have been reported by us.[3-5]

X-Ray Analysis of 3-(4′-Bromobenzyl)-2-thioxo-1,3-thiazolidine-4-carboxylic Acid (4n)——Crystal data: $C_{11}H_{10}BrNO_2S_2$, $M_r = 332.2$, monoclinic, space group $P2_1/c$, $a = 14.957$ (3), $b = 7.204$ (1), $c = 13.272$ (4) Å, $\beta = 109.70$ (2)°, $V = 1346.4$ (6) Å^3, $D_x = 1.639$ g cm^{-3}, $Z = 4$, crystal dimensions $= 0.2 \times 0.2 \times 0.1$ mm.

A Rigaku AFC-5 diffractometer employing graphite-monochromated CuK_α radiation ($\lambda = 1.54178$ Å) was used. Lattice parameters were refined by least-squares analysis of 2θ values of 20 reflections measured in the region of $35° \leq 2\theta \leq 40°$. Intensity data of 2290 independent reflections with $\theta \leq 65°$ were collected by using the ω–2θ scanning technique and 2088 were observed with $|F_o| > 3\sigma(F_o)$. Lorentz and polarization corrections were applied, but not absorption corrections.

The structure was solved by use of the program MULTAN84[18] and refined by a block-diagonal least-squares method to $R = 0.055$ for 2020 reflections. The hydrogen atoms were located on a difference electron density map, and the positional parameters were refined at the last stage of the least-squares refinement. The temperature factor of each hydrogen atom was assumed to be isotropic and equal to B_{eq} of the atom to which it was bound. The mean C–H bond length is 1.06 Å. No peaks higher than those due to the hydrogen atoms were found in the difference electron density map. Calculations were performed by a FACOM M-340R computer at Shionogi Research Laboratories using the programs of XPACK86 SHIONOGI.[19]

Atomic coordinates, thermal parameters, bond lengths and bond angles are presented in Tables III, IV, V and VI, respectively.

1,3-Oxazolidine-2-thione (11a)——Triethylamine (55.6 g, 0.55 mol) was added to a solution of ethanolamine (12.2 g, 0.2 mol) and CS_2 (22.8 g, 0.3 mol) in CH_2Cl_2 (300 ml) under ice-cooling with stirring. After being stirred at room temperature for 6 h, the reaction mixture was washed with saturated aqueous ammonium sulfate, dried, and evaporated *in vacuo* to give an oily residue. The residue was purified on a silica gel column by using CH_2Cl_2–AcOEt to afford compound **11a** (6.5 g, 32% yield) as colorless needles from CH_2Cl_2. mp 98 °C [lit.[20] mp 99 °C (cyclohexane–benzene)]. ^{1}H-NMR δ: 3.84 (2H, t, $J = 8.3$ Hz), 4.73 (2H, t, $J = 8.3$ Hz). ^{13}C-NMR δ: 44.2 (t), 70.4 (t), 190.5 (s). IR (KBr): 1680 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 246 (4.25). *Anal.* Calcd for C_3H_5NOS: C, 34.89; H, 4.91; N, 13.40. Found: C, 34.95; H, 4.85; N, 13.59.

***rac*-4-Methoxycarbonyl-1,3-oxazolidine-2-thione (11b)**——Triethylamine (27.9 ml, 0.2 mol) was added to a solution of *rac*-serine methyl ester hydrochloride (15.6 g, 0.1 mol) and CS_2 (11.4 g, 0.15 mol) in CH_2Cl_2 (150 ml). After being stirred at room temperature for 6 h, the reaction mixture was subjected to treatment as mentioned above to give compound **11b** (5 g, 31% yield) as a colorless oil. ^{1}H-NMR δ: 3.85 (3H, s), 4.63—4.71 (1H, m), 4.85—4.94 (2H, m),

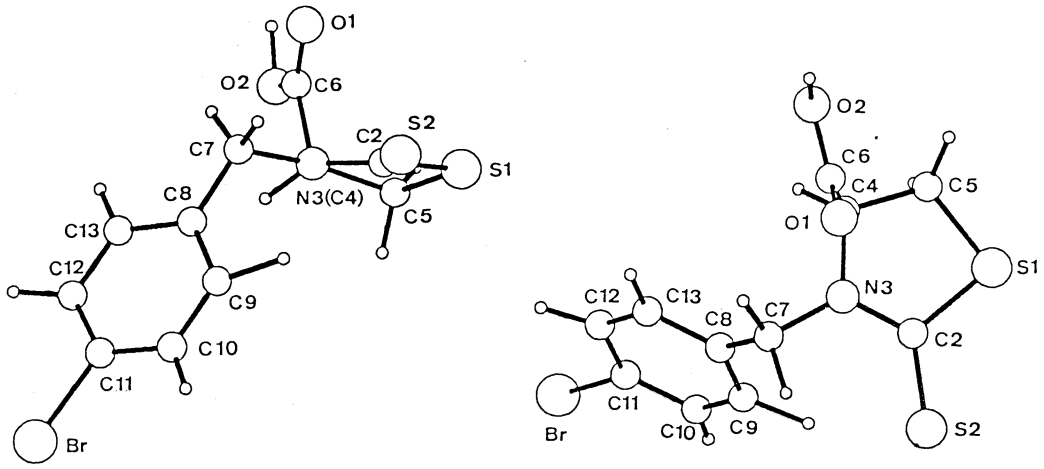


Fig. 4. Perspective View of the Crystallographic Structure of Compound **4n**

TABLE III. Atomic Coordinates ($\times 10^4$; $\times 10^3$ for H) and Equivalent Isotropic Temperature Factors ($\times 10^2$ Å^2) with e.s.d. Values in Parentheses, for Compound **4n**

Atom	*x*	*y*	*z*	B_{eq} [a)]
S(1)	−4088 (1)	−131 (1)	3982 (1)	515 (3)
C(2)	−3371 (2)	−1848 (4)	3730 (2)	367 (8)
N(3)	−3006 (2)	−1336 (3)	2984 (2)	339 (7)
C(4)	−3330 (2)	445 (4)	2459 (2)	385 (8)
C(5)	−3720 (3)	1558 (5)	3211 (3)	529 (11)
C(6)	−4081 (2)	178 (4)	1377 (2)	367 (8)
C(7)	−2473 (2)	−2592 (5)	2530 (2)	400 (8)
C(8)	−1433 (2)	−2205 (4)	2921 (2)	374 (8)
C(9)	−971 (2)	−1625 (5)	2215 (3)	439 (10)
C(10)	−7 (3)	−1359 (5)	2558 (3)	484 (11)
C(11)	517 (3)	−1670 (4)	3608 (3)	433 (9)
C(12)	95 (3)	−2208 (8)	4332 (3)	592 (13)
C(13)	−870 (2)	−2495 (8)	3982 (3)	580 (13)
Br	1863.0 (3)	−1376.7 (7)	4074.5 (4)	635 (2)
S(2)	−3196 (1)	−3864 (1)	4379 (1)	511 (3)
O(1)	−4546 (2)	−1256 (3)	1123 (2)	396 (6)
O(2)	−4194 (2)	1668 (3)	785 (2)	440 (7)
H(C4)	−274 (4)	108 (6)	231 (4)	385
H(C5)	−422 (4)	229 (9)	273 (4)	529
H′(C5)	−314 (3)	231 (9)	374 (4)	529
H(C7)	−280 (3)	−242 (7)	168 (3)	400
H′(C7)	−259 (4)	−396 (6)	272 (4)	400
H(C9)	−133 (4)	−139 (6)	145 (4)	439
H(C10)	29 (4)	−121 (6)	192 (4)	484
H(C12)	55 (4)	−242 (9)	507 (4)	592
H(C13)	−141 (4)	−310 (8)	442 (4)	580
H(O2)	−477 (3)	163 (6)	23 (4)	440

e.s.d., estimated standard deviation. *a)* $B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} \boldsymbol{a}_i \boldsymbol{a}_j$.

7.99 (1H, br). ^{13}C-NMR δ: 53.4 (q), 57.3 (d), 72.2 (t), 168.9 (s), 190.0 (s). IR (film): 1740 cm^{-1}. Mol. wt. Calcd for $C_5H_7NO_3S$: 161. Found: MS *m/z*: 161 (M^+).

General Preparation Method for 2-Benzylthio-Δ^2-1,3-oxazolines (12)——Triethylamine (2.02 g, 20 mmol) was

TABLE IV. Anisotropic Thermal Parameters ($\times 10^4$) with e.s.d. Values in Parentheses, for Compound **4n**

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	57 (1)	241 (2)	105 (1)	0 (1)	39 (1)	−57 (1)
C(2)	45 (2)	152 (5)	70 (2)	−19 (2)	20 (1)	−23 (2)
N(3)	36 (1)	156 (5)	65 (2)	11 (1)	16 (1)	0 (2)
C(4)	38 (1)	153 (5)	77 (2)	0 (2)	10 (1)	6 (2)
C(5)	77 (3)	166 (6)	86 (3)	23 (3)	10 (2)	−20 (3)
C(6)	39 (1)	158 (5)	76 (2)	10 (2)	20 (1)	19 (2)
C(7)	40 (1)	213 (6)	68 (2)	19 (2)	15 (1)	−13 (3)
C(8)	37 (1)	192 (6)	67 (2)	16 (2)	14 (1)	−4 (2)
C(9)	48 (2)	231 (7)	69 (2)	−2 (2)	14 (1)	21 (3)
C(10)	49 (2)	240 (8)	90 (3)	−4 (3)	23 (2)	27 (3)
C(11)	44 (2)	183 (6)	83 (2)	2 (2)	11 (1)	0 (3)
C(12)	48 (2)	430 (13)	71 (2)	12 (4)	7 (1)	9 (4)
C(13)	47 (2)	466 (14)	63 (2)	13 (4)	17 (1)	20 (4)
Br	44 (1)	332 (1)	126 (1)	−10 (1)	11 (1)	24 (1)
S(2)	86 (1)	174 (2)	84 (1)	−26 (1)	36 (1)	3 (1)
O(1)	43 (1)	170 (4)	71 (1)	−13 (1)	9 (1)	16 (2)
O(2)	55 (1)	158 (4)	84 (2)	−2 (2)	17 (1)	23 (2)

The temperature factor is of the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

TABLE V. Bond Lengths (Å) with e.s.d. Values in Parentheses, for Compound **4n**

S(1)–C(2)	1.742 (3)	S(1)–C(5)	1.792 (5)
C(2)–N(3)	1.334 (4)	C(2)–S(2)	1.664 (3)
N(3)–C(4)	1.462 (4)	N(3)–C(7)	1.463 (5)
C(4)–C(5)	1.540 (5)	C(4)–C(6)	1.508 (4)
C(6)–O(1)	1.227 (4)	C(6)–O(2)	1.307 (4)
C(7)–C(8)	1.491 (5)	C(8)–C(9)	1.402 (5)
C(8)–C(13)	1.391 (6)	C(9)–C(10)	1.371 (6)
C(10)–C(11)	1.368 (6)	C(11)–C(12)	1.371 (7)
C(11)–Br	1.908 (5)	C(12)–C(13)	1.375 (8)

TABLE VI. Bond Angles (°) with e.s.d. Values in Parentheses, for Compound **4n**

C(2)–S(1)–C(5)	92.6 (2)	S(1)–C(2)–N(3)	112.3 (2)
S(1)–C(2)–S(2)	121.3 (2)	N(3)–C(2)–S(2)	126.4 (2)
C(2)–N(3)–C(4)	116.3 (3)	C(2)–N(3)–C(7)	123.4 (3)
C(4)–N(3)–C(7)	119.0 (3)	N(3)–C(4)–C(5)	106.6 (3)
N(3)–C(4)–C(6)	111.3 (3)	C(5)–C(4)–C(6)	111.1 (3)
S(1)–C(5)–C(4)	105.8 (3)	C(4)–C(6)–O(1)	122.7 (3)
C(4)–C(6)–O(2)	111.8 (3)	O(1)–C(6)–O(2)	125.4 (3)
N(3)–C(7)–C(8)	113.0 (3)	C(7)–C(8)–C(9)	121.0 (3)
C(7)–C(8)–C(13)	121.9 (3)	C(9)–C(8)–C(13)	117.0 (4)
C(8)–C(9)–C(10)	121.3 (4)	C(9)–C(10)–C(11)	119.5 (4)
C(10)–C(11)–C(12)	121.3 (4)	C(10)–C(11)–Br	119.5 (3)
C(12)–C(11)–Br	119.2 (4)	C(11)–C(12)–C(13)	119.0 (5)
C(8)–C(13)–C(12)	121.8 (5)		

added to a solution of 1,3-oxazolidine-2-thione (**11a**) (2.06 g, 20 mmol) in tetrahydrofuran (THF) (15 ml). After addition of benzyl bromide (3.42 g, 20 mmol), the mixture was stirred at room temperature for 16 h. Insoluble materials were filtered off and the filtrate was evaporated *in vacuo* to give an oily residue. The residue was

chromatographed on a silica gel column with CH_2Cl_2 to afford 2-benzylthio-Δ^2-1,3-oxazoline (**12a**) (1.7 g, 44% yield) as a colorless oil. Compound **12b** was similarly prepared.

2-Benzylthio-Δ^2-1,3-oxazoline (12a)——^{1}H-NMR δ: 3.19 (2H, t, J=9.0 Hz), 4.26 (2H, s), 4.36 (2H, t, J=9.0 Hz), 7.26—7.37 (5H, m). ^{13}C-NMR δ: 36.4 (t), 54.9 (t), 69.2 (t), 127.5 (d), 128.6 (d), 129.0 (d), 136.8 (s), 165.8 (s). IR (film): 1760 cm^{-1}. Mol. wt. Calcd for $C_{10}H_{11}NOS$: 193. Found: MS m/z: 193 (M^+).

***rac*-2-Benzylthio-4-methoxycarbonyl-Δ^2-1,3-oxazoline (12b)**——39% yield. Colorless oil. ^{1}H-NMR δ: 3.81 (3H, s), 4.26, 4.33 (each 1H, AB type J_{AB}=12.9 Hz), 4.52 (1H, ABX type, J_{AB}=10.3 Hz, J_{AX}=8.5 Hz), 4.62 (1H, ABX type, J_{XA}=8.5 Hz, J_{XB}=7.3 Hz), 4.80 (1H, ABX type, J_{BA}=10.3 Hz, J_{BX}=7.3 Hz), 7.28—7.41 (5H, m). ^{13}C-NMR δ: 36.5 (t), 52.6 (q), 68.3 (d), 71.2 (t), 127.7 (s), 128.7 (d), 129.1 (d), 136.4 (s), 168.7 (s), 171.2 (s). IR (film): 1740 cm^{-1}. Mol. wt. Calcd for $C_{12}H_{13}NO_3S$: 251. Found: MS m/z: 251 (M^+).

General Preparation Method for 3-Benzyl-1,3-oxazolidine-2-thiones (13)——A mixture of 2-benzylthio-Δ^2-1,3-thiazoline (**12a**) (386 mg, 2 mmol) and benzyl bromide (34.2 mg, 0.2 mmol) was heated at 120 °C under N_2 for 1.5 h. The reaction mixture was chromatographed on a silica gel column with benzene to give compound **13a** (150 mg, 39% yield) as a colorless amorphous powder. Compound **13b** was similarly prepared.

3-Benzyl-1,3-oxazolidine-2-thione (13a)——^{1}H-NMR δ: 3.22 (2H, t, J=7.1 Hz), 3.51 (2H, t, J=7.1 Hz), 4.49 (2H, s), 7.24—7.40 (5H, m). ^{13}C-NMR δ: 31.7 (t), 34.4 (t), 42.9 (t), 127.3 (s), 128.6 (d), 128.8 (d), 138.0 (s), 167.4 (s). IR ($CHCl_3$): 1670 cm^{-1}. Mol. wt. Calcd for $C_{10}H_{11}NOS$: 193. Found: MS m/z: 193 (M^+).

***rac*-3-Benzyl-4-methoxycarbonyl-1,3-oxazolidine-2-thione (13b)**——40% yield. Colorless amorphous powder. ^{1}H-NMR δ: 3.35 (1H, ABX type, J_{AB}=11.2 Hz, J_{AX}=2.9 Hz), 3.51 (1H, ABX type, J_{BA}=11.2 Hz, J_{BX}=8.3 Hz), 3.70 (3H, s), 4.17 (1H, ABX type, J_{XB}=8.3 Hz, J_{XA}=2.9 Hz), 4.06, 5.14 (each 1H, AB type, J_{AB}=15.1 Hz), 7.21—7.40 (5H, m). ^{13}C-NMR δ: 29.0 (t), 47.9 (t), 52.8 (q), 59.4 (d), 128.0 (d), 128.3 (d), 128.9 (d), 135.7 (s), 170.3 (s), 171.5 (s). IR ($CHCl_3$): 1750, 1670 cm^{-1}. Mol. wt. Calcd for $C_{12}H_{13}NO_3S$: 251. Found: MS m/z: 251 (M^+).

References and Notes

1) This paper forms Part III of the series "New Aldose Reductase Inhibitors." For Part II of this series, see ref. 4.
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