N-Quaternary Compounds

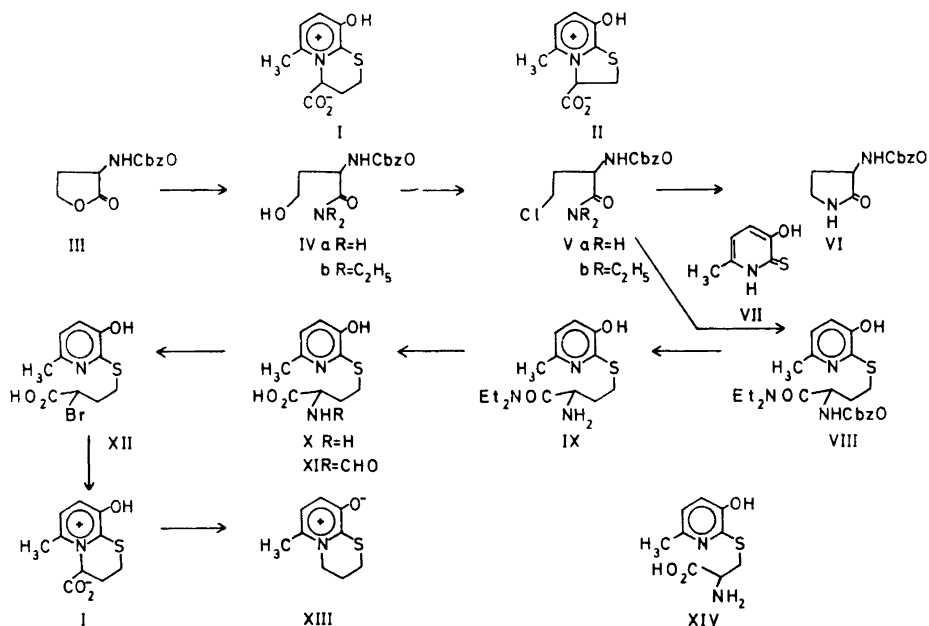## Part XXX.[1] Synthesis and Configurational Assignments of Chiral Pyridine Derivatives

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A synthesis of 9-hydroxy-6-methyldihydro[1,3]thiazino[3,2-a]
pyridinium-4-carboxylate is described. An intermediate S-α-pyridyl-
homocysteine was optically resolved, the isolated enantiomer α-bro-
minated and cyclised. Configurational correlations using circular
dichroism show that the cyclisation goes with configurational in-
version. Modes of racemisation and optical stability have been in-
vestigated.

Configurational inversion on the chiral carbon takes place in the Men-
schutkin reaction between 3-hydroxypyridine and α-bromo-carboxylic
acids except when the alkylating agent is branched at the β-carbon.[2] Depending
on relative position, sulphur present in the alkylating agent may affect the
stereochemical course of the reaction by neighbouring group participation.[2]
In this work the sulphur in the alkylating agent is present in a thioether with
pyridine in the α-position in which case the Menschutkin reaction leads to
cyclisation. The α-pyridyl thioether from 2-bromo-4-mercaptobutyric acid
thus yields the corresponding dihydro[1,3]thiazino[3,2 − a]pyridinium-4-
carboxylate illustrated by I. The latter is a homologue of 8-hydroxy-5-methyl-
dihydrothiazolo[3,2-a]pyridinium-3-carboxylate (II) whose absolute con-
figuration has been established by synthesis.[3] The chiroptical properties of
II have been determined[4] and are thus available for comparative purposes.
The synthesis of I was achieved as shown in Scheme 1.

The S-pyridyl homocysteine (X) is the key substance in the synthetic
scheme. Its racemic modification was first synthesized and then optically
resolved for the stereochemical cyclisation studies. The synthesis of X was
originally attempted by the reaction of the sodium salt of 3-hydroxy-6-
methylpyrid-2-thione (VII) with 2-amino-4-butyrolactone in the same way
as methione is synthesized by means of sodium methiolate.[5] The latter reaction
involves nucleophilic attack by the sulphur on the sp^3-carbon of the lactone
group. The reaction between the butyrolactone and VII failed to yield pre-

paratively useful yields of the *S*-pyridyl homocysteine X. The latter was there-fore synthesized over several steps. For this purpose *N*-carbobenzoxy-2-amino-4-butyrolactone (III) was prepared.[6,7] Ammonia will attack the sp^2-carbon of the lactone (III) under formation of the hydroxy-amide IVa.[8] The latter was converted to the 4-chloro compound Va with thionyl chloride. Treatment of Va with the sodium salt of the thione VII resulted in selective cyclisation of Va with formation of a pyrrolidone (VI). Intramolecular reaction such as in Va was prevented by removal of the acidic amido hydrogens. The same series of reactions from III using diethylamine was therefore repeated and yielded Vb. The latter was successfully reacted with the thione (VII) using potassium carbonate as base. The carbobenzoxy group in VIII was removed using HBr in cold acetic acid. Stereospecific replacement of the amino group by bromine by means of diazotisation requires the holding effect of an α-carboxyl group. The amide IX was therefore further hydrolyzed to the acid (X). The reaction was run in 6N HCl at 100°C. Direct hydrolysis of the carbobenzoxy derivative (VIII) to X was also possible. For optical resolution the amino acid was formylated (XI) and resolved as brucine salt by fractional crystallisation from dilute methanol. The *N*-formyl acid (XI), isolated after ammonia decompo-sition of the brucine salt, had specific rotation $[\alpha]_D^{25} = +11.5°$ (N HCl). The formyl group was removed by acid hydrolysis; $[\alpha]_D^{25} = -18.0°$ (N HCl).

Optically active 2-bromocarboxylic acids are most conveniently prepared from the corresponding amino acids by diazotisation in the precence of bromide ions.[9] The reaction goes with retention of configuration and the optical purity is of the order of 90 % somewhat dependent on the nature of the substituents.[9] The diazotisation of X was carried out with nitrosyl bromide generated *in situ*

to yield the bromo derivative XII, specific rotation $[\alpha]_D^{25} = +17.5°$ (N HCl). Cyclisation of XII, by heating in an organic solvent such as acetontrile with and without added organic base, led largely to decarboxylation (XIII) of the cyclisation product (I) due to the activating effect of the α-pyridinium nitrogen. Decarboxylation was avoided by cyclisation at 60°C in aqueous solution. The reaction required several hours for completion. The relatively low reactivity of XII is in marked contrast to the high reactivity of simple 3-α-pyridylthio-2-bromopropionic acids.[10] The latter can only be isolated with difficulty as HBr salt and are cyclised immediately to dihydrothiazolo[3,2-a]-pyridinium derivatives (II) on neutralisation.[10] Besides the normally higher rate of 5- rather than 6-ring formation, sulphur group participation is invoked in the 5-ring formation to explain the relatively large rate difference.

The cyclisation reaction of the optically active bromo acid (XII) was stopped when the reaction was only partially completed due to increasing racemisation with time as discussed below. The product which crystallized from the reaction solution was racemic. Optically active acid I was isolated by phenol extraction of the filtrate after removal of the precipitated racemate, $[\alpha]_D^{25} = +73.6°$ (H$_2$O). From the CD curves, as discussed below, the amino and bromo compounds have the (R)-configuration. The bicyclic product I has the (S)-configuration in agreement with net inversion of configuration in the cyclisation step. The optical rotation observed, however, cannot be used as a measure of the stereochemical homogeneity of the cyclisation due to extensive racemisations occurring which do not involve the actual cyclisation step. Thus optically inactive bromo compound (XII) was isolated from the reaction solution after the reaction had been stopped. Previously we have also found that it is racemisation by bromine interchange in the alkylating agent which is mainly responsible for the low optical yield in reactions which requires a long time for completion.[2] Racemisation caused by proton abstraction from the activated chiral carbon in I was excluded since the racemic acid I from reactions in deuterium oxide showed no deuterium incorporation. This also follows from the optical stability studies below. Thus the quaternary acid I in acid solution is optically quite stable. Information on the stability in alkaline solution was obtained by studies in 0.4 N NaOD at 40°C. NMR was used to study the deuterium incorporation on the chiral carbon while the racemisation was followed by means of the sodium D-line rotation. Fifty percent deuteriation was observed in I after 60 min and in the case of the thiazolo analogue (II) after 30 min. The optical rotation for either compound was practically the same after 2.5 h at which time compound I was fully deuteriated.

The chemical shifts in trifluoroacetic acid for the methine protons are at 4.0 and 3.7 τ for I and II, respectively, and in 0.4 N NaOD at 4.7 and 4.3 τ. The chemical shift thus reflects the relative acidity as measured by the rate of deuteriation. The explanation advanced[11] for the optical stability of II is equally applicable to I. Since proton exchange occurs rapidly, while the optical rotation remains virtually constant, the intermediate pyramidal carbanion must recapture a proton from the solvent faster than inversion can occur. The increased energy barrier to inversion arises because of non-bonded interaction between the 4-carboxyl group and the 6-methyl group in a planar or nearly planar inversion intermediate.

For configurational correlations the CD curves of the optically active compounds have been recorded. α-Amino acids of the L-series in acid solution have a strong positive Cotton effect in the 210-220 nm region.[12,13] For aliphatic amino acids this has been ascribed to $n \rightarrow \pi^*$ transitions of the carboxyl group. [12,14] In neutral or alkaline solution a weaker band with opposite sign is seen in the 230 – 245 nm region ascribed to the same optical transition but due to a
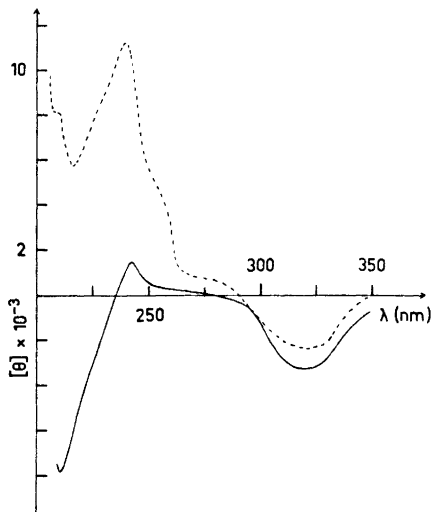

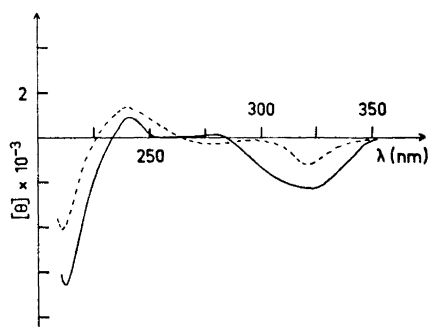Fig. 1. CD curves recorded in 1 N HCl for (R)-X (———) and (R)-XIV (– – –).

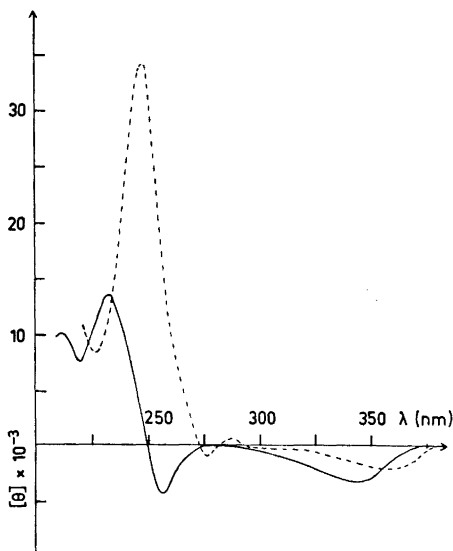Fig. 2. CD curves recorded in 1 N HCl for (R)-XI (———) and (R)-XII (– – –).

Fig. 3. CD curves for (S)-I recorded in 1 N HCl (———) and in 1 N NaOH (– – –).

different rotamer.[12,14] In the aromatic amino acids the observed Cotton effect is near 220 nm but the assignment of the 220 nm band is difficult due to the proximity of the $n \to \pi^*$ transition of the carboxyl group and the ^1L_a transition of the aromatic ring. Otherwise a weak Cotton effect, with considerable fine structure, is observed at $260-280$ nm due to weak ^1L_b transitions of the aromatic chromophore.[13]

Table 1. UV absorption maxima in N HCl.

Compound:	X		XIV		XI		XII		I		I in N NaOH	
λ nm, log ε	321	3.96	318	3.97	323	3.83	322	3.96	342	4.06	360	4.07
λ nm, log ε	237	3.59	237	3.59	238	3.47	238	3.61	239	3.70	247	3.94
λ nm, log ε									211	4.00		

The pyridyl chromophore gives rise to intense dichroic absorption near and below 220 nm [15] which corresponds to the region for the $n \to \pi^*$ transition of the carboxyl group. The observed dichroic absorption in the low wavelength region therefore results from superposition of group dichroic bands. The isolated enantiomer of the amino acid X has a strong negative CD band at 211 nm in acid solution (Fig. 1). In accordance with the dichroic absorption of aromatic amino acids, the enantiomer of X is assigned the (R)-configuration. Support for this assignment follows from the CD absorption of the cysteine derived amino acid XIV, a lower homologue of X. The acid XIV has the (R)-configuration [10] and shows positive dichroic absorption near 210 nm (Fig. 1). In this connection it is pointed out that (R)-X belongs to the amino acid D-series while (R)-XIV belongs to the L-series. The formylated derivative XI has closely similar dichroic absorption to that of the amino acid X (Fig. 2). Further support for the (R)-configurational assignment is found in the spectrum of the bromo acid XII (Fig. 2), which is prepared from X with configurational retention as discussed above. Thus α-bromo acids of the (S)-configuration have been reported [16] to have a positive Cotton effect at $205-220$ nm and a negative Cotton effect at $235-263$ nm. The strong negative band at 210 nm for XII is in accordance with (R)-configurational assignment. The dichroic bands at higher wavelengths (Figs. 1 and 2) correspond well to the respective UV-maxima (Table 1). The pyridyl absorption near 240 nm will interfere with the otherwise observed $n \to \pi^*$ transition from the carboxyl group in alternative conformational rotamers. In all cases the highest wavelength dichroic bands near 320 nm, due to the pyridyl chromophore, are negative even for the configurationally opposite cysteine derived amino acid XIV.

Fig. 3 shows CD curves for the quaternary acid I in acid and alkaline solution. The spectrum in acid solution has positive bands at 212 and 233 nm and negative bands at 257 and 345 nm with observed UV maxima at 342, 239 and 211 nm. At least the former two bands are associated with the aromatic chromophore. In alkaline solution a bathochromic shift has occurred because

of dissociation of the phenolic group. Positive dichroic absorption is indicated below 220 nm but the maximum was not reached because of strong absorption. UV maxima at 360 and 247 nm correspond to the negative CD maximum at 360 nm and the positive maximum at 247 nm. The CD curves in Fig. 3, both in acid and alkaline solution, have closely similar positional maxima and signs for the dichroic bands as reported [4] for the dihydrothiazolo analogue II of the (R)-configuration. The dihydro[1,3]thiazino acid I is therefore assigned the (S)-configuration. Since the dichroic absorption requires assignment of the (R)-configuration to the (+)-amino acid enantiomer X and the derived (+)-bromo acid, but (S)-configuration to the quaternary acid I, the intramolecular Menschutkin reaction must proceed by inversion of ⌊the configuration.

EXPERIMENTAL

The CD and UV spectra were recorded on a Jasco model J − 10 spectropolarimeter. The cell length was 1 mm and the temperature 27°C. NMR data were recorded on a Varian A − 60A instrument.

*2-Carbobenzoxyamino-4-hydroxy-*N,N-*diethylbutyramide (IVb)*. A solution of 2-carbobenzoxyamino-4-butyrolactone [6,7] (105 g, 0.52 mol) and diethylamine (300 ml) in benzene (600 ml) was kept at 45°C for 4 days before evaporation. The residual oil crystallized on drying. The product appeared homogeneous on chromatography and was used as such in the next step. The yield was 131 g (95 %). The analytical sample in benzene was filtered through a short column of aluminium oxide and recrystallized from carbon tetrachloride, m.p. 73°C. (Found: C 62.69; H.7.88; N 9.15. Calc. for $C_{16}H_{24}N_2O_4$: C 62.31; H 7.85; N 9.09.) NMR in CDCl₃: 8.8 − 8.9 and 6.3 − 6.8 τ (N − Et); 8.2 τ (2H³); 7.2 τ (2H⁴); 5.2 τ (H²); 4.9 τ (benzyl-CH₂) and 2.7 τ (benzyl-C₆H₅).

*2-Carbobenzoxyamino-4-chloro-*N,N-*diethylbutyramide (Vb)*. 2-Carbobenzoxyamino-4-hydroxy-N,N-diethylbutyramide (131 g, 0.43 mol) was added gradually with stirring to ice-cold thionyl chloride (300 ml). To minimize loss of the carbobenzoxy group the volatile acids liberated were removed as formed at reduced pressure. The excess thionyl chloride was evaporated at reduced pressure after 2 ½ h and the residual oil triturated with water before crystallisation from dilute ethanol. Recrystallisation from benzene/carbon tetrachloride gave the white title compound in 72 % yield (100 g); m.p. 86°C. (Found: C 58.97; H 6.79; N 8.29. Calc. for $C_{16}H_{23}ClN_2O_3$: C 58.77; H 7.07; N 8.57.) NMR in CDCl₃: 8.8 − 8.9 and 6.3 − 6.9 τ (N − Et); 8.0 τ (2H³); 6.3 − 6.9 τ (2H⁴); 5.2 τ (H²); 4.9 τ (benzyl-CH₂) and 2.7 τ (benzyl-C₆H₅).

2-Carbobenzoxyamino-4-chlorobutyramide (Va). This compound was prepared and crystallized as Vb; yield 70 %, m.p. 121°C. (Found: C 53.38; H 5.52; N 10.17. Calc. for $C_{12}H_{15}ClN_2O_3$: C 53.19; H 5.58; N 10.34.)

3-Carbobenzoxyamino-2-pyrrolidinone (VI). The title compound was formed when 2-carbobenzoxyamino-4-chlorobutyramide was heated for 1 h in methanolic sodium methylate. The product was isolated by evaporation of the solution, trituration with water followed by crystallisation from ethyl acetate/ethanol; m.p. 168°C. An attempt to carry out S-alkylation of 3-hydroxy-6-methylpyrid-2-thione (VII) using Va gave only the title compound. (Found: C 61.34; H 5.70; N 11.73. Calc. for $C_{12}H_{14}N_2O_3$: C 61.52; H 6.00; N 11.96.) NMR in TFA: 7.5 τ (2H⁴); 6.4 τ (2H⁵); 5.2 τ (H³); 4.7 τ (benzyl-CH₂); 2.6 τ (benzyl-C₆H₅).

*2-Carbobenzoxyamino-4-(3-hydroxy-6-methyl-2-pyridylthio)-*N,N-*diethylbutyramide (VIII)*. 2-Carbobenzoxyamino-4-chloro-N,N-diethylbutyramide (100 g, 0.30 mol), anhydrous potassium carbonate (45.6 g, 0.33 mol), and 3-hydroxy-6-methylpyrid-2-thione (42.3 g, 0.30 mol) in dimethylformamide (600 ml) were stirred for 4 days at 40°C. The reaction mixture was then diluted with water, pH adjusted to 5 and the solution extracted with chloroform. The chloroform extract was dried, decolorized with charcoal, the solution evaporated and the residual material crystallized from carbon tetrachloride; yield 77 g (60 %). The analytical sample was recrystallized once from carbon tetrachloride/benzene; m.p. 140°C. (Found: C 61.32; H 6.72; N 9.81. Calc. for $C_{22}H_{29}N_3O_4S$: C 61.24;

H 6.77; N 9.74.) NMR in CDCl$_3$: 8.8 − 9.1 and 6.4 − 7.2 τ (*N*-Et); 8.0 τ (2H^3); 7.6 τ (pyridyl-CH$_3$); 6.4 − 7.2 τ (2H^4); 5.3 τ (H^2); 4.9 τ (benzyl-CH$_2$); 2.7 τ (benzyl-C$_6$H$_5$); 3.0 and 3.2 τ (pyridyl-H^4, H^5).

*2-Amino-4-(3-hydroxy-6-methyl-2-pyridylthio)-*N,N-*diethyl-butyramide (IX)*. A solution of 2-carbobenzoxyamino-4-(3-hydroxy-6-methyl-2-pyridylthio)-*N,N*-diethylbutyramide (4.3 g, 0.01 mol) in 40 % HBr in acetic acid (40 ml) was left in the cold for 2 h, excess ether added, the supernatant solution decanted from the oily precipitate, the residue dissolved in water, the aqueous solution washed with ether to remove any residual benzyl bromide before the solution was neutralized with sodium bicarbonate. The precipitated title compound was recrystallized from dilute ethanol; yield 2.1 g (71 %), m.p. 170°C. (Found: C 56.61; H 7.44; N 14.18. Calc. for C$_{14}$H$_{23}$N$_3$O$_2$S: C 56.55; H 7.80; N 14.13.) NMR in TFA: 8.4 − 8.9 and 6.0 − 6.7 |τ (*N*-Et); 7.4 τ (2H^3); 7.1 τ (pyridyl-CH$_3$); 6.0 − 6.7 τ (2H^4); 1.9 and 2.3 τ (pyridyl-H^4, H^5.)

2-Amino-4-(3-hydroxy-6-methyl-2-pyridylthio)butyric acid (X). 2-Amino-4-(3-hydroxy-6-methyl-2-pyridylthio)-*N,N*-diethylbutyramide or 2-carbobenzoxyamino-4-(3-hydroxy-6-methyl-2-pyridylthio)-*N,N*-diethylbutyramide were hydrolyzed to the title compound by heating in 6 N HCl at 100°C for 12 days. The cold solution was then extracted with ethyl acetate, the aqueous solution evaporated, the residual oil redissolved in water, the aqueous solution treated with a little charcoal and filtered before the pH was adjusted to 5. The solid precipitate was recrystallized from dilute ethanol; yield 60 − 65 %, m.p. 265°C (decomp.). (Found: C 49.21; H 6.04; N 11.48. Calc. for C$_{10}$H$_{14}$N$_2$O$_3$S: C 49.47; H 5.83; N 11.57.) NMR in TFA: 7.4 τ (2H^3); 7.2 τ (pyridyl-CH$_3$); 6.4 τ (2H^4); 5.3 τ (H^2); 2.0 and 2.3 τ (pyridyl-H^4, H^5).

2-Formylamino-4-(3-hydroxy-6-methyl-2-pyridylthio)butyric acid (XI). Acetic anhydride (21 ml) was added dropwise with stirring to an ice-cold solution of 2-amino-4-(3-hydroxy-6-methyl-2-pyridylthio) butyric acid (7.26 g, 0.3 mol) in formic acid (100 ml). The resultant solution was left at room temperature overnight, evaporated at reduced pressure, redissolved in boiling ethanol and treated with charcoal. A hygroscopic solid was obtained which was recrystallized from ethanol; yield 7.0 g (86 %), m.p. *ca*. 98°C. The molecular ion (C$_{11}$H$_{14}$N$_2$O$_4$S) on mass spectrometry corresponds to the title compound. The hygroscopic nature of the substance made elementary analyses difficult but chromatography shows a homogeneous product. NMR in TFA: 7.6 τ (2H^3); 7.2 τ (pyridyl-CH$_3$); 6.5 τ (2H^4); 4.9 τ (H^2); 2.0 and 2.3 τ (pyridyl-H^4, H^5).

Optical resolution of the 2-formylamino derivative (XI). XI (8.1 g, 0.03 mol) was dissolved in methanol (20 ml) and added to a solution of brucine. 4H$_2$O (14.0 g, 0.03 mol) in methanol (30 ml) and water (3 ml). On cooling the warm solution, 14.3 g of salt was precipitated, [α]$_D$^{25} = − 15.4°. The specific sodium D-line rotation for the racemic salt was − 18°. All the rotations were measured as 1 % solution in N HCl at 25°C. The salt was redissolved in methanol (50 ml) and water (9.5 ml) by heating. Two well defined crystal modifications were formed which were separated mechanically. The major part consisted of fine needles (7.3 g), [α]$_D$^{25} = − 14.3°. The cubic crystals (1.8 g) had [α]$_D$ = − 21.5°. The major product was recrystallized from methanol (65 ml) and water (15 ml) which gave [α]$_D$^{25} = − 12.8°. Two more recrystallisations hardly changed the rotation which was − 12.7°; final yield 4.4 g. This salt was dissolved in 1 N ammonia (130 ml), the brucine extracted into chloroform, and the solution evaporated to yield 2.0 g of the title compound shown to be homogeneous by chromatography; [α]$_D$^{25} = + 11.5° (*c* = 1 in N HCl).

(R)-2-Amino-4-(3-hydroxy-6-methyl-2-pyridylthio)butyric acid (X). The *N*-formyl derivative (XI) (2.0 g) was heated in 1 N HCl for 2 h and the pH of the cold solution adjusted to 5.5 with sodium bicarbonate. The title compound was slowly precipitated; yield 1.3 g (73 %), [α]$_D$^{25} = − 18.0° (*c* = 1 in N HCl).

(R)-2-Bromo-4-(3-hydroxy-6-methyl-2-pyridylthio)butyric acid (XII) as HBr salt. Sodium nitrite (1.60 g, 0.02 mol) in water (10 ml) was added over 1 h to an ice-cold solution of the *(R)*-amino acid (X) (1.08 g, 0.0045 mol) in 5 N HBr (70 ml). The resultant solution was left at 5°C overnight, evaporated at reduced pressure, the hygroscopic solid redissolved in water and the pH brought to 2.5. The bromo compound was extracted into ethyl acetate, the solution washed, dried and a few drops of HBr added before the solution was evaporated. A crystalline product was obtained in this way; yield 1.36 g, (79 %), m.p. 175°C, [α]$_D$^{25} = 17.5 (*c* = 1 in N HCl). (Found: C 31.10; H 3.40; N 3.83. Calc. for C$_{10}$H$_{12}$BrNO$_3$S. HBr: C 31.04; H 3.39; N 3.62.) NMR in TFA: 7.6 τ (2H^3); 7.2 τ (pyridyl-CH$_3$); 6.5 τ (2H^4); 5.3 τ (H^2); 2.0 and 2.3 τ (pyridyl-H^4, H^5).

9-Hydroxy-6-methyldihydro[1,3]thiazino[3,2-a]pyridinium-4-carboxylate (I). 2-Bromo-4-(3-hydroxy-6-methyl-2-pyridylthio)butyric acid HBr salt (1.0 g, 0.0033 mol) was dissolved in water (60 ml), the pH adjusted to 4.5 with sodium bicarbonate, the solution heated at 60°C for 12 h, concentrated to a small volume and left in the cold. The title compound was slowly precipitated and was recrystallized from water; yield 0.45 g (78 %), m.p. 177° (decomp.). (Found: C 53.09; H 5.27; N 6.06. Calc. for $C_{10}H_{11}NO_3S$: C 53.33; H 4.92; N 6.22.) NMR in TFA: 7.2 τ (6-CH₃); 6.4 – 6.8 τ (2H², H³); 7.2 – 7.7 τ (H³); 4.0 τ (H⁴); 2.3 and 2.6 τ (H⁷, H⁸).

(S)-9-Hydroxy-6-methyldihydro[1,3]thiazino[3,2-a]pyridinium-4-carboxylate (I). The (R)-bromo compound (XII) as hydrobromide (0.75 g) was dissolved in a small volume of water, the pH adjusted to 2.5 and the bromo compound extracted into ethyl acetate to remove the bromide ions. The ethyl acetate was evaporated and the bromo compound dissolved in water (40 ml) which gave pH 4.5. The solution was then heated at 60°C for 4 h, and the pH readjusted to 4.5 before concentration to a small volume. The zwitterion precipitated (0.2 g) was optically inactive. The filtrate was brought to pH 2.5 and un-reacted bromo acid (XII) extracted into ethyl acetate. XII was optically inactive. The aqueous solution was extracted with aqueous phenol (90 %, 3 × 10 ml), the phenol extract washed with water (10 ml), ether (150 ml) added to the phenol, the separated water layer collected, the phenol/ether phase extracted with water (4 × 10 ml), the combined aqueous solutions washed with ether (2 × 10 ml) and the aqueous phase acidified with HCl before evaporation. The residue was the hydrochloride of the title compound which after tri-turation with acetone and ethyl acetate was a white solid (39 mg), $[\alpha]_D^{25} = +73.6°$ ($c = 0.7$ in H_2O).

6-Methyldihydro[1,3]thiazino[3,2-a]pyridinium-9-oxide (XIII). 2-Bromo-4-(3-hydroxy-6-methyl-2-pyridylthio)butyric acid hydrobromide (1.0 g, 0.0033 mol) was dissolved in acetonitrile (50 ml) containing triethylamine (1 ml). The resultant solution was heated at 80°C overnight, evaporated, the residue triturated with a little water and recrystallized from ethanol; yield 0.3 g (50 %). M.p. 167°C (decomp.). The product had spectral properties as previously described.[17]

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