compound was prepared by silanolysis of the low R_f carbamate **5b** as previously described.[5] The (−)-**4b** was obtained as a clear, colorless oil (93% yield): $[\alpha]^{24}_D$ −6.7° (*c* 3.5, $CHCl_3$); NMR and IR spectra were identical to those of racemic **4b**.

(+)-*cis*-7(*R*),8(*S*)-Epoxy-2-methyloctadecane (1a). This compound was prepared by methylation of (−)-**4b** (200 mg, 0.5 mmol) with $(CH_3)_3OBF_4$ (80 mg, 0.54 mmol) in dry CH_2Cl_2, followed by treatment with NaOH (10%, aqueous). The crude product was purified by GLC (3% SE-30 on Chromosorb W, ⅛ in. × 12 in. column, 170 °C).

A clear colorless liquid was obtained (129 mg, 90%): $[\alpha]^{24}_D$ +0.8 ± 0.1° (*c* 10, CCl_4); NMR (CCl_4) δ 2.65 (m, 1 H, $\overline{CHCHO}$), 1.1–1.6 (m, 27 H, CH_2's and $CH(CH_3)_2$), 0.86 (d and t, 9 H, CH_2CH_3 and $CH(CH_3)_2$); IR (CCl_4) 2960, 2940, 2860, 1470, 1385, 1370, and 1250 cm^{-1}; MS, *m/e* 282.

1-Decyl-2-phenylthio-6-methylheptyl *N*-[1-(1-Naphthyl)-ethyl]carbamates Derived from 4a. These carbamates were prepared from *erythro*-**4a** and resolved in a manner identical to that used for the preparation of the threo derived **5a** and **5b**. After chromatographic separation of the two diastereomeric carbamates (α = 1.5), the NMR, IR, and MS of these erythro compounds were found to be essentially indistinguishable from those of the threo analogues, **5a** and **5b**.

(−)-*erythro*-2-Methyl-7-phenylthio-8-octadecanol (4a). This compound was obtained by a procedure identical to the one used for the resolution of **4b**. It was obtained by silanolysis of the low R_f carbamate derived from (*R*)-(+)-1-(1-naphthyl)ethylamine: NMR, IR, MS, identical to those of racemic **4a**; $[\alpha]^{24}_D$ −7.5° (*c* 3.5, $CHCl_3$).

(−)-*trans*-7(*S*),8(*S*)-Epoxy-2-methyloctadecane (1b). This compound was prepared from (−)-**4a** by a procedure identical to that used to obtain **1a**.

A clear colorless liquid was obtained: $[\alpha]^{24}_D$ −23.6 (*c* 1, CCl_4); NMR (CCl_4) δ 2.43 (t, 2 H, $\overline{CHCHO}$), 1.1–1.6 (m, 27 H, CH_2's and $CH(CH_3)_2$), 0.86 (d and t, 9 H, $CH(CH_3)_2$ and CH_3); IR (CCl_4) 2960, 2930, 2860, 1470, 1390, 1370, 1250, 860, and 800 cm^{-1}; MS, *m/e* 282.

Preparation of 4a from 4b. Methanesulfonyl chloride (0.03 mL, 0.5 mmol) was added to a solution of **4b** (137 mg, 0.35 mmol) in CH_2Cl_2 and pyridine (0.04 mL, 0.5 mmol) at −20 °C. The mixture was stirred for 1 h; the organic solution was extracted with dilute HCl and 5% $NaHCO_3$ and then dried (K_2CO_3). Solvent removal at reduced pressure afforded crude mesylate which was used without further purification.

The mesylate from **4b** was dissolved in a mixture of dry solvents (DMF–DME–Me_2SO 1:1:1) and 18-crown-6 (100 mg). The mixture was cooled (0 °C) and KO_2 (170 mg) was added in small portions over 5 min. The mixture was stirred for 30 min, then extracted with 10% Na_2SO_3, and dried (K_2CO_3). Solvent removal at reduced pressure afforded a clear oil, the NMR and IR of which were identical to those of authentic **4a**; yield 100 mg (73%).

Acknowledgment. This work was partially supported by grants from the National Science Foundation and the National Institutes of Health.

Registry No.—**1a,** 54910-51-9; **1b,** 54910-54-2; **2,** 1653-40-3; **3,** 68900-43-6; **4a,** 68900-44-7; (−)-**4a,** 68927-72-7; **4b,** 68900-45-8; (−)-**4b,** 68926-73-8; **4b** mesylate, 68900-47-0; **5a,** 68900-46-9; **5b,** 68926-74-9; undecanal, 112-44-7.

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(8) The initial elution of *erythro*-hydroxy sulfide, **4a,** is not expected on the basis of the model previously proposed for such separations.[6] Possibly, the large alkyl chains do not permit the weak OH–S hydrogen bonding interaction to determine the conformation about the C_7–C_8 bond.
(9) W. H. Pirkle and J. R. Hauske, *J. Org. Chem.*, **42,** 2779 (1977).
(10) The overall yield of 12% (including the resolution step; i.e., yield is actually 24% of theoretical) is to be compared to the overall yield of 13.8% (excluding resolution) attained by Farnum et al.[4] If allowance is made for the recovery of 30% of **3**, the yield is raised to 17.2% (or 34.4% theory). Epimerization of **4a** to **4b** (a refinement that could be similarly applied to Farnum's sequence)[4] further raises the overall yield to 29.8% (or 58.6% of theory). However, the recycling of **2** and the epimerization of **4a** would be of significance only during production of large quantities of disparlure.
(11) E. J. Corey, K. C. Nicolaou, M. Shibasaki, Y. Machida, and C. S. Shiner, *Tetrahedron Lett.*, 3183 (1975).
(12) Although numerous procedures for the synthesis of **2** have been reported, we have found it convenient to prepare **2** by conjugate addition of lithium diisoamyl cuprate to methyl acrylate (75%),[11,12] followed by $LiAlH_4$ reduction of the product ester (95%).[12]
(13) G. H. Posner, *Org. React.*, **19,** 1 (1972).
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Synthesis of *C*-Nucleosides. 17.[1] *s*-Triazolo[4,3-*a*]pyrazines[2]

Tam Huynh-Dinh, R. Simon Sarfati,[3] Catherine Gouyette, and Jean Igolen*

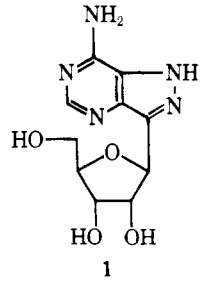
Laboratoire de Chimie Organique, Unité de Chimie des Protéines, Institut Pasteur, 75024 Paris Cédex 15, France

Emile Bisagni,* Jean-Marc Lhoste, and Alain Civier

Institut Curie, Section de Biologie, Bâtiments 110-112, 91405 Orsay, France

8-Substituted-3-alkyl- and -glycosyl-*s*-triazolo[4,3-*a*]pyrazines, closely related to the *C*-nucleoside formycin, have been prepared from 3-chloro-2-hydrazinopyrazine and thioimidates. Their spectroscopic properties, especially ^1H and ^{13}C NMR, are discussed.

We report further development of synthetic routes to *C*-nucleosides containing a nitrogen bridgehead atom such as the *s*-triazolo[4,3-*a*]pyrazine cycle. A nucleoside of type **2** or **3** is of special interest since it has a structure closely related to that of adenosine and formycin **1**. Such fused heterocycles are not well known; although some substituted *s*-triazolo[4,3-*a*]pyrazines have been obtained by Nelson and Potts[4] and Mallet and Rose[5] by reaction of 2-hydrazinopyrazines with ortho esters or carboxylic acid derivatives, no *s*-triazolo[4,3-*a*]pyrazine functionalized on carbon 8 (i.e., atom 6 of the purine ring) has been described to our best knowledge.



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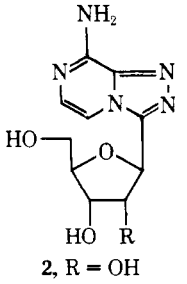
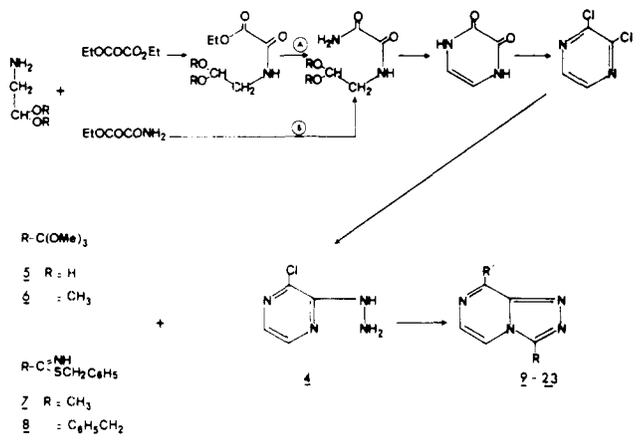


2, R = OH
3, R = H

0022-3263/79/1944-1028$01.00/0

Scheme I



9, R = H; R′ = Cl
10, R = H; R′ = SH
11, R = H; R′ = $SCH_2C_6H_5$
12, R = H; R′ = $NHCH_2C_6H_5$
13, R = CH_3; R′ = Cl
14, R = CH_3; R′ = SH
15, R = CH_3; R′ = $SCH_2C_6H_5$
16, R = CH_3; R′ = $NHCH_2C_6H_5$
17, R = CH_3; R′ = OH
18, R = CH_3; R′ = NH_2
19, R = CH_3; R′ = $NHCH_2CH{=}C(CH_3)_2$
20, R = CH_3; R′ = SNO_2CH_3Im
21, R = $C_6H_5CH_2$; R′ = $SCH_2C_6H_5$
22, R = $C_6H_5CH_2$; R′ = OH
23, R = $C_6H_5CH_2$; R′ = Cl

So a general synthetic procedure for these compounds had first to be worked out for 3-alkyl substituents before it could be extended to glycosyl derivatives.

Results

The main heterocyclic component for the synthesis outlined on Scheme I is 2-hydrazino-3-chloropyrazine (**4**): it is prepared by reaction of hyrazine on 2,3-dichloropyrazine,[6] which is obtained in good yield by a modification (pathway B) of a procedure already described (pathway A).[7]

We started by condensing pyrazine **4** with ortho esters **5** (R = H) and **6** (R = CH_3), which gave a high yield (>80%) of 8-chloro-*s*-triazolo[4,3-*a*]pyrazines **9** (R = H) and **13** (R = CH_3). These two chloro derivatives were very reactive with thiourea, benzyl mercaptan, and benzylamine to give, respectively, the 8-mercapto- (**10, 14**), 8-(benzylthio)- (**11, 15**) and 8-(benzylamino)pyrazines (**12, 16**).

A second route to the 8-chloro-*s*-triazolo[4,3-*a*]pyrazines would be to condense the same 3-chloropyrazine **4** with alkylthioimidates such as benzyl thioacetimidate (**7**, R = CH_3). With pyridine in reflux, the reaction gave directly 3-methyl-8-(benzylthio)-*s*-triazolo[4,3-*a*]pyrazine (**15**; 90%) instead of the expected 3-methyl-8-chloro-*s*-triazolo[4,3-*a*]pyrazine (**13**): the displacement of 8-Cl by the benzyl mercaptan liberated in situ was not surprising, since we have already obtained in the same experimental conditions the 8-(benzylthio) compound **15** (80%) from the 8-chloro compound **13**. The isolation of the 8-(benzylthio) derivative **21** occurred also (93%) with the benzyl(phenylthio)acetimidate **8** (R = $C_6H_5CH_2$).

These preliminary experiments showed clearly the two possible ways which could lead to the obtention of 3-glycosyl-8-amino-*s*-triazolo[4,3-*a*]pyrazines **2** and **3**. (a) To develop the preparation of the yet unknown glycosyl ortho esters, which will give by condensation with chlorohydrazine **4** the 8-chloropyrazines. Then, the 8-chlorotriazolopyrazine will be easily transformed into the 8-amino compounds. (b) To use the already known[8] glycosylthioformimidates for the access to the 8-(benzylthio)pyrazines and to transform them into the more reactive 8-chloro derivatives. We chose the second way, which permits us to carry out inexpensively the model reactions with the 3-alkylpyrazines using classical methods of heterocyclic chemistry. We tried first but unsuccessfully the direct displacement reaction with benzylamine on the *S*-benzyl compounds **11, 15,** and **21**. We tried also with no more success to isolate the sulfones after oxidization of the same compounds with *m*-chloroperbenzoic acid. Finally, the *S*-(benzylthio) compounds **15** and **21** were easily oxidized with hydrogen peroxide in formic acid into the 8-oxo compounds **17** and **22,** which were chlorinated afterwards with phosphorus oxychloride into the desired 8-chloro compounds **13** and **23.** Treatment of **13** with ammonia and 3-methyl-2-butenylamine afforded the 8-amino-*s*-triazolo[4,3-*a*]pyrazines **18** and **19.** Alkylation of the 8-mercapto compound **14** with 5-chloro-4-nitro-1-methylimidazole gave the 3-methyl analogue (**20**) of Imuran.

In the carbohydrate series, condensation of ribofuranosylthioimidate[8] (**24**) (R_1 = Bz; R_2 = H; R_3 = OH) with 3-chloro-2-hydrazinopyrazine (**4**) in pyridine at reflux gave 52% of 3-(5′-*O*-benzoyl-β-D-ribofuranosyl)-8-(benzylthio)-*s*-triazolo[4,3-*a*]pyrazine (**26**). Oxidation with hydrogen peroxide afforded the 8-oxo compound **27** (R_1 = Bz; R_2 = H; R_3 = OH), which had to be acetylated into **28** (R_1 = Bz; R_2 = H; R_3 = OAc) before the chlorination into the 8-chloro compound **29.** As in the 3-alkyl series, nucleophilic displacements of **29** with thiourea and 3-methyl-2-butenylamine[9] gave the protected 8-mercapto compound **30** and 8-(3-methyl-2-butenylamino) compound **31,** whereas in methanolic ammonia at 120 °C it yielded directly the *C*-nucleoside 3-β-D-ribofuranosyl)-8-amino-*s*-triazolo[4,3-*a*]pyrazine (**2**). Debenzoylation of the protected nucleosides provided the 8-benzylthio (**32**), 8-oxo (**33**), 8-mercapto (**34**), and 8-(3-methyl-2-butenylamino) (**36**) compounds. Alkylation of the 8-mercapto compound **34** converted it into the *C*-nucleoside analogue of Imuran (**35**) (Scheme II).

With the 2′-deoxyribofuranosylthioimidate[8] **25** (R_1 = R_2 = Tol; R_3 = H), the condensation gave a mixture of anomers ($\beta/\alpha \simeq 4$) of 2′-deoxy *C*-nucleosides **37**, which were separated by column chromatography. The further syntheses have been carried out only with the more abundant β anomer. The sequences were more straightforward than in the ribose series, since the two glycosyl hydroxy groups were already protected: oxidation of **37** into 8-oxo compound **38,** chlorination into 8-Cl compound **39,** and displacement into 8-mercapto (**40**), 8-(3-methyl-2-butenylamino) (**41**), and 8-amino (**3**; R_1 = R_2 = R_3 = H) compounds. The deprotection of the toluyl groups gave the *C*-nucleosides **42** (R′ = $SCH_2C_6H_5$), **43** (R′ = OH), **44** (R′ = SH), and **46** (R′ = $NHCH_2CH{=}C(CH_3)_2$). The 2′-deoxy analogue of Imuran (**45**) was also obtained (40%) from **44.**

Discussion

The structural assignment of the heterocycles and of the nucleosides is based mainly on spectral evidence: UV spectra, ^1H and ^{13}C NMR, mass spectra, and circular dichroism.

1. Structure of the Heterocycles. The various series of *s*-triazoles fused with another nitrogen heterocycle in position [4,3-*x*] are known[10-13] to give frequently Dimroth-like transpositions into their isomeric [1,5-*x*] derivatives.

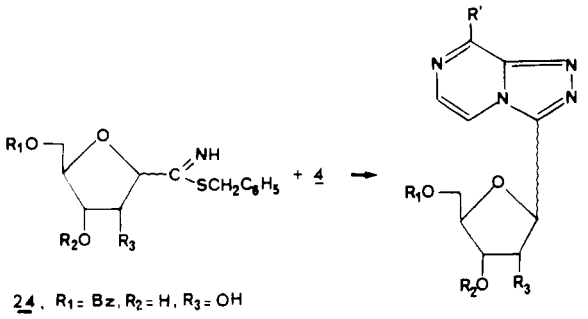
The fact that the model 3-methyl-8-chloro compound **13** was obtained from two different routes [(a) chlorination of **17** isolated in two steps from thioimidate **7,** and (b) condensation of orthoacetate **6** with 3-chloro-2-hydrazinopyrazine (**4**)] is the first chemical evidence that our synthetic sequences afford the *s*-triazolo[4,3-*a*]pyrazine and not the transposed *s*-triazolo[1,5-*a*]pyrazines. It also has been demonstrated that the condensation of ortho esters with a hydrazino heterocycle leads exclusively to the *s*-triazolo[4,3,-*a*] derivatives, even in the presence of an electron-withdrawing substituent in the

Table I. ^{13}C Chemical Shifts [b] of the *s*-Triazolo[4,3-*a*]pyrazine and -furanosyl Carbons in Me_2SO-d_6 at 34 °C [c]

	R	R′	C-3	C-8	C-8a	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′
9	H	Cl	138.9	142.4	141.0	118.4	127.7					
13	CH_3	Cl	146.7	142.7	141.0	117.3	127.1					
23	$CH_2C_6H_5$	Cl	148.6	142.9	141.4	117.0	127.6					
29	β-2′3′-Ac-5′-Bz-rib.	Cl	146.4	143.7	141.4	117.7	128.1	(70.5,	72.7,	74.1)[a]	79.28	62.56
16	CH_3	$NHCH_2C_6H_5$	145.3	147.3	138.89	106.1	128.5					
19	CH_3	$NHCH_2CH{=}C(CH_3)_2$	145.2	147.2	138.9	105.7	128.7					
46	β-D-rib.	$NHCH_2CH{=}C(CH_3)_2$	147.8	147.3	139.7	106.8	129.0	71.0	38.5	71.6	88.4	61.7
15	CH_3	$SCH_2C_6H_5$	145.5	151.6	142.7	113.2	128.2					
21	$CH_2C_6H_5$	$SCH_2C_6H_5$	147.5	152.0	142.8	112.9	128.3					
20	CH_3	SNO_2CH_3Im	146.0	148.4	142.5	115.1	128.1					
14	CH_3	S(H)	147.2	172.2	148.8	108.9	118.3					
17	CH_3	O(H)	147.2	152.7	144.1	103.7	117.5					
33	β-rib.	O(H)	148.5	152.5	145.1	104.3	117.6	75.6	73.3	70.9	85.9	61.3
43	β-D-rib.	O(H)	149.4	152.5	145.1	104.3	117.6	70.8	38.6	71.4	88.4	61.6

[a] Assignments not certain for these three carbons. All other assignments are based on proton-coupled spectra and off-resonance proton-decoupling experiments. [b] In ppm with respect to Me_4Si. [c] The carbon resonances of the R and R′ substituents other than furanoses have been omitted for clarity although they have been observed and assigned.

Scheme II



24, R_1 = Bz, R_2 = H, R_3 = OH

25, $R_1 = R_2$ = Tol, R_3 = H

2, **3**, **26**–**40**

Ribose

26, R′ = $SCH_2C_6H_5$; R_1 = Bz; R_2 = H; R_3 = OH
27, R′ = OH; R_1 = Bz; R_2 = H; R_3 = OH
28, R′ = OH; R_1 = Bz; R_2 = Ac; R_3 = OAc
29, R′ = Cl; R_1 = Bz; R_2 = Ac; R_3 = OAc
30, R′ = SH; R_1 = Bz; R_2 = Ac; R_3 = OAc
31, R′ = $NHCH_2CH{=}C(CH_3)_2$; R_1 = Bz; R_2 = Ac; R_3 = OAc
32, R′ = $SCH_2C_6H_5$; $R_1 = R_2$ = H; R_3 = OH
33, R′ = OH; $R_1 = R_2$ = H; R_3 = OH
2, R′ = NH_2; $R_1 = R_2$ = H; R_3 = OH
34, R′ = SH; $R_1 = R_2$ = H; R_3 = OH
35, R′ = SNO_2CH_3Im; $R_1 = R_2$ = H; R_3 = OH
36, R′ = $NHCH_2CH{=}C(CH_3)_2$; $R_1 = R_2$ = H; R_3 = OH

2′-Deoxyribose

37, R′ = $SCH_2C_6H_5$; $R_1 = R_2$ = Tol; R_3 = H
38, R′ = OH; $R_1 = R_2$ = Tol; R_3 = H
39, R′ = Cl; $R_1 = R_2$ = Tol; R_3 = H
40, R′ = SH; $R_1 = R_2$ = Tol; R_3 = H
41, R′ = $NHCH_2CH{=}C(CH_3)_2$; $R_1 = R_2$ = Tol; R_3 = H
42, R′ = $SCH_2C_6H_5$; $R_1 = R_2 = R_3$ = H
43, R′ = OH; $R_1 = R_2 = R_3$ = H
3, R′ = NH_2; $R_1 = R_2 = R_3$ = H
44, R′ = SH; $R_1 = R_2 = R_3$ = H
45, R′ = SNO_2CH_3Im; $R_1 = R_2 = R_3$ = H
46, R′ = $NHCH_2CH{=}C(CH_3)_2$; $R_1 = R_2 = R_3$ = H

heterocycle, which could favor the transposition into the [1,5-*a*] structure.

A direct evidence for the [4,3-*a*] structure is provided by the carbon-13 NMR spectra. There is indeed a large difference in chemical shift value for the carbon at position 2 or 3 in the two isomers, respectively. Due to the π-electron donor character of the neighboring bridgehead nitrogen atom at position 4 as compared to a nitrogen atom bearing a nonbonding pair of electrons, the C-3 resonance in the [4,3-*a*] isomers appears 15–20 ppm upfield as compared to the corresponding C-2 resonance in the transposed [1,5-*a*] isomers.[13-14] In the series of compounds investigated by ^{13}C NMR (Table I) this resonance appeared in a range of chemical shift values extending from 138.9 (unsubstituted **9**) to 149.4 ppm (2′-deoxy *C*-nucleoside **43**) characteristic of the [4,3-*a*] isomers. The structure was further confirmed by ^1H NMR (Table II) observing a noticeable (up to 20%) nuclear Overhauser enhancement of the integrated intensity of the H-5 resonance upon irradiation of the methyl group substituted on the carbon under consideration (**13**, **20**). Due to the r^{-6} distance dependence of the dipole–dipole interactions responsible for such effects, these measurements can be interpreted only if the substituted carbon is at position 3, allowing a close proximity of the observed proton and the saturated methyl group.[15]

2. Structure and Configuration of the Nucleosides. The ultraviolet spectra of *C*-nucleosides are quite similar to those of their alkyl analogues (Table III).

The structure of the nucleosides is confirmed by their mass spectra: all the compounds show the molecular ion $M^{+\cdot}$ except in the case of the Imuran analogues **35** and **45**, which exhibit a different fragmentation pattern due to the lability of the *S*-nitromethylimidazole moiety. In the same way, the 8-thiobenzyl derivatives **32** and **42** present the main fragment at 91 ($C_6H_5CH_2^{+\cdot}$). As observed previously,[8,13] the peaks at B + 1 are very small and the major peaks appear at B + 30 or B + 44 for the *C*-ribonucleosides (**2**, **32**–**36**) and at B + 28 for the 2′-deoxy *C*-nucleosides (**3**, **42**–**46**).

The α and β isomers are easily distinguished by ^1H NMR whenever the pair of anomers is available (Table IV). In the nonsubstituted 2′-deoxynucleosides the H-2′ resonances in the β anomer exhibit a larger difference in their relative chemical shift values, larger average downfield shifts, and more different coupling constants with the H-1′ proton than in the corresponding α anomer. The similarity of the NMR data for the related 2′-deoxynucleosides for which only one anomer was isolated (Table IV) permits assignment of a β anomeric conformation to the whole series of compounds. The synthetic route which was followed for the preparation of the ribonucleosides leads almost exclusively to a single anomeric form which has been assigned to the β conformation.[13] This does not permit, however, a straightforward assignment by comparison of the NMR spectra of the pairs of corresponding anomers. In fact, vicinal couplings in the ribose moiety are in favor of the β assignment,[16] considering for example the great constancy of the value of $J_{1'2'} + J_{3'4'}$ (10.3 ± 0.4 Hz) in the whole series. Spin–lattice relaxation times T_1 were measured in the formycin-like compound **2**, using the inversion–recovery technique with a [180°–*t*–90°] pulse sequence,[17] in order to

Table II. Proton NMR Characteristics of the s-Triazolo[4,3-a]pyrazine Bases in Me_2-SO-d_6 at 34 °C [c]

	R	R′	base H-5	base H-6	base NH-7	R	R′ NH	R′ CH_2	R′ C_6H_5
9	H	Cl	8.63[a] (4.7)	7.77		9.54			
11	H	$SCH_2C_6H_5$	8.36 (4.7)	7.80		9.39		4.60	7.30–7.50
12	H	$NHCH_2C_6H_5$	7.76 (4.8)	7.25		9.20	8.65 (6.2)	4.69	~7.30
13	CH_3	Cl	8.52 (4.7)	7.77		2.75			
14	CH_3	S(H)	7.79 (5.6)	7.05 (4.9)	13.09	2.62			
15	CH_3	$SCH_2C_6H_5$	8.21 (4.8)	7.79		2.70		4.60	7.30–7.50
16	CH_3	$NHCH_2C_6H_5$	7.59[a] (4.7)	7.25		2.63	8.56 (6.3)	4.69	~7.30
17	CH_3	O(H)	7.37 (5.8)	6.89 (exch[b])	11.28	2.60			
18	CH_3	NH_2	7.59 (4.7)	7.21		2.62	7.32		
19	CH_3	$NHCH_2CH=C(CH_3)_2$	7.56 (4.8)	7.27		2.61	7.98 (5.7)	CH_2, 4.05 (6.6)	CH, 5.33 (1.4) CH_3, 1.69, 1.67
20	CH_3	SNO_2CH_3Im	8.32[a] (4.7)	7.64		2.73		CH, 8.26	NCH_3, 3.72
21	$CH_2C_6H_5$	$SCH_2C_6H_5$	8.22 (4.8)	7.78		4.54, 7.30		4.59	7.30–7.50
22	$CH_2C_6H_5$	O(H)	7.36 (5.9)	6.87 (5.2)	11.34	4.45, 7.30			
23	$CH_2C_6H_5$	Cl	8.54 (4.7)	7.77		4.61, 7.30			

[a] Assigned by nuclear Overhauser enhancement (15–35%) upon saturation of the R group. [b] Coupling not observed because of proton exchange with water. [c] The chemical shifts are in ppm with respect to Me_4Si. The coupling constants, in hertz, between vicinal protons are given in parentheses.

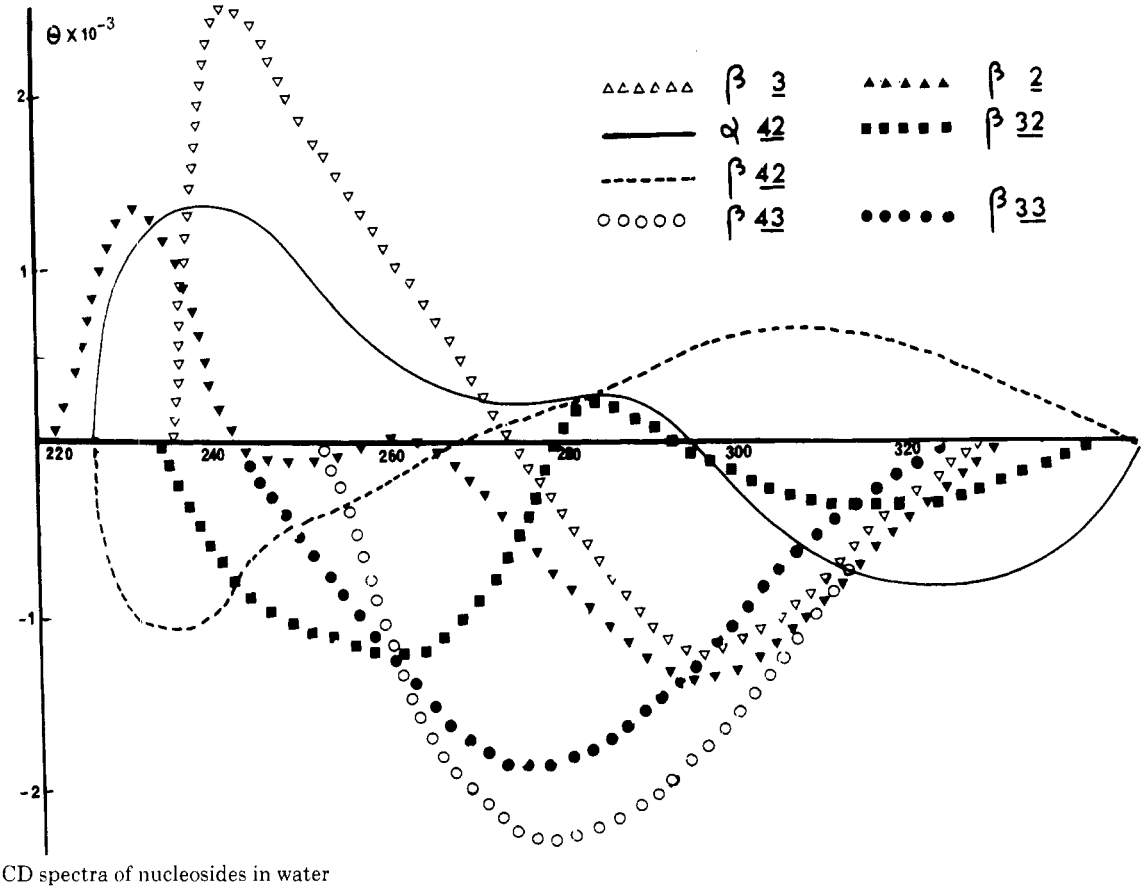


Figure 1. CD spectra of nucleosides in water

analyze its structure and conformation. It has been shown previously[18] in formycin and other analogues devoid of protons at position 2 and 5 of the base that the relaxation of the H-1′ proton of the ribose is dominated by its dipole–dipole interaction with the H-2′ proton. Then, the T_1 value of H-1′ depends critically upon its distance to H-2′ and is at least twice as long in the β anomer as compared to the α anomer or compared to the T_1 values of the H-2′ and H-3′ protons in both anomers. For compound **2** dissolved in thoroughly degassed Me_2-SO-d_6 we measured at 34 °C T_1 values of 1.15 s for H-1′ and 0.6 s for H-2′ and H-3′. We also observed a large difference between the T_1 values of the base H-5 (0.75 s) and H-6 (1.5 s) protons. The latter difference indicates that the dipolar interaction of H-5 and H-1′ contributes to their reciprocal relaxation. The T_1 value measured for H-1′ is therefore no longer governed only by its interaction with H-2′, but should be shortened due to the presence of the H-5 proton. The ratio of H-1′ over H-2′ relaxation times is, however, still large, confirming the β-anomeric configuration of compound **2**. Furthermore, the noticeable H-1′/H-5 interaction should correspond to a major trans conformation of the glycosidic bond.

The configuration of the nucleosides determined by NMR is further confirmed by the circular dichroism spectra: the ribo- and 2′-deoxyribonucleosides having a β configuration

Table III. Ultraviolet Absorption Spectral Data

compd	R′	λ_{max} (ϵ) in 96% EtOH		
11	$SCH_2C_6H_5$	257 (9 600)	312 (11 800)	
15	$SCH_2C_6H_5$	258 (10 200)	315 (8 800)	
26	$SCH_2C_6H_5$	258 (10 200)	312 (10 100)	
α-42	$SCH_2C_6H_5$	256 (15 100)	312 (13 800)	
β-42	$SCH_2C_6H_5$	257 (14 700)	312 (14 200)	
9	Cl		296 (4 100)	
13	Cl		305 (4 100)	
29	Cl	280 (9 000)	305 (6 300)	
39	Cl	280 (11 300)	305 (6 800)	
17	OH	280 (4 700)		
33	OH	280 (7 600)		
43	OH	280 (6 300)		
14	SH	272 (7 300)	356 (12 900)	
34	SH	268 (12 700)	351 (17 600)	
44	SH	268 (11 000)	351 (16 000)	
18	NH_2	229 (12 100)	297 (6 200)	
2	NH_2	228 (15 100)	290 (7 300)	
3	NH_2	227 (14 100)	290 (6 400)	
20	SNO_2Im	245 (16 400)	300 (10 600)	
35	SNO_2Im	242 (16 400)	300 (13 000)	
45	SNO_2Im	236 (17 100)	298 (13 500)	
19	$NHCH_2CH{=}CH(CH_3)_2$	237 (13 900)		296 (9 300)
36	$NHCH_2CH{=}CH(CH_3)_2$	235 (19 400)	244 (16 100)	280 (13 000)
46	$NHCH_2CH{=}CH(CH_3)_2$	235 (20 700)	244 (17 300)	280 (14 000)

present a negative Cotton effect, with the maxima of absorption spread from 280 to 320 nm. In addition to the general rules which stated that β anomers of purine nucleosides with a trans conformation gave negative Cotton effects, the noticeable interaction H-1′–H-5 observed by NMR suggests the same trans conformation around the glycosidic bond.

Experimental Section

Melting points were determined with a Kofler microscope and were uncorrected. Ultraviolet spectra were recorded with a Perkin-Elmer 237 or a Cary 118C. NMR spectra were obtained using a Varian XL-100 with tetramethylsilane as internal reference. Mass spectra were obtained with a Varian CH-7 or MS-9. Optical activities were measured with a Perkin-Elmer 241 MC polarimeter and circular dichroism spectra were recorded with a Roussel-Jouan II-185 dichrograph. Chromatographic columns were packed with Silicar 100 mesh grade I; 0.25-mm thick TLC plates were prepared with Merck Kieselgel $HF_{254+366}$ and visualized with a UV light at 254 nm.

***N*-(β,β-Dimethoxyethyl)oxamide.** Aminoacetaldehyde dimethyl acetal (105 g, 1 mol) was added to a boiling solution of ethyl oxamate (117 g, 1 mol) in ethanol (800 mL). The mixture was heated 5 min more and cooled. After filtration, the compound was recrystallized with ethanol to give colorless needles (135 g, 79.5%), mp 146 °C.

Anal. Calcd for $C_6H_{12}N_2O_4$ (176): C, 40.90; H, 6.87; N, 15.90. Found: C, 41.24; H, 6.86; N, 15.74.

3-Chloro-2-hydrazinopyrazine (4). 2,3-Dichloropyrazine (30 g, 0.2 mol), obtained according to ref 6 and 13, was heated at reflux for 1.5 h with a solution of hydrazine hydrate (20 mL, 0.4 mol) in ethanol (600 mL). The solvent was evaporated and the residue was taken up in water, filtered, and recrystallized twice with ethanol to yield 25 g of **4** (87%), mp 154 °C.

Anal. Calcd for $C_4H_4ClN_4$ (144.5): C, 33.22; H, 3.46; N, 38.75; Cl, 24.57. Found: C, 33.43; H, 3.56; N, 38.50; Cl, 24.59.

8-Chloro-*s*-triazolo[4,3-*a*]pyrazine (9). A suspension of pyrazine **4** (10 g, 6.9 mmol) in ethyl orthoformate (**5**; 40 mL) was heated at reflux for 4 h. After cooling, the compound was filtered and recrystallized with ethanol, giving yellow needles (9 g, 84%), mp 205 °C.

Anal. Calcd for $C_5H_3ClN_4$ (154.5): C, 38.83; H, 1.94; N, 36.24; Cl, 22.98. Found: C, 38.57; H, 2.0; N, 36.43; Cl, 22.91.

8-Chloro-3-methyl-*s*-triazolo[4,3-*a*]pyrazine (13). (a) From 4. As above, methyl orthoacetate (**6**; 40 mL) and **4** (8 g, 5.5 mmol) gave 87% (8 g) of **13**, mp 226 °C (EtOH).

Anal. Calcd for $C_6H_5ClN_4$ (168.5): C, 42.73; H, 2.97; N, 33.23; Cl, 21.06. Found: C, 42.61; H, 3.05; N, 33.17; Cl, 20.94.

(b) From 17. **17** (1 g, 6.6 mmol) and diethylaniline (1 g, 6.6 mmol) were heated at reflux in phosphorus oxychloride (20 mL) for 2 h. After evaporation of the excess oxychloride, the residue was dissolved with CH_2Cl_2 and the organic layer was washed with a solution of potassium hydrogen carbonate. The organic solution was dried and evaporated to yield **13** (0.49 g, 45%).

8-Mercapto-3-methyl-*s*-triazolo[4,3-*a*]pyrazine (14). The 8-chloro compound **13** (0.50 g, 3 mmol) was heated with thiourea (0.44 g, 6 mmol) in ethanol (10 mL) at reflux for 3 h. The mixture was cooled, 20 mL of H_2O was added, and the precipitate was filtered and recrystallized with ethanol, giving 361 mg (65.4%) of **14**, mp 280–330 °C dec.

Anal. Calcd for $C_6H_6N_4S$, H_2O (184): C, 39.13; H, 4.34; N, 30.43; S, 17.39. Found: C, 39.51; H, 4.39; N, 30.90; S, 16.88.

8-Mercapto-*s*-triazolo[4,3-*a*]pyrazine (10). The same reaction as above with **9** (1 g, 6.5 mmol), thiourea (1 g, 13 mmol), and ethanol (15 mL) for 0.5 h gave 200 mg of **10** (20.3%), mp 235 °C.

Anal. Calcd for $C_5H_4N_4S$ (152): C, 39.47; H, 2.64; N, 36.84; S, 21.05. Found: C, 39.24; H, 2.44; N, 36.97; S, 21.32.

8-(Benzylthio)-3-methyl-*s*-triazolo[4,3-*a*]pyrazine (15). (a) From 13. In pyridine (10 mL) and benzyl mercaptan (0.5 g, 4 mmol) at reflux for 1 h, **13** (0.5 g, 3 mmol) gave after evaporation 0.61 g of **15** (80.2%), mp 181 °C (EtOH).

Anal. Calcd for $C_{13}H_{12}N_4S$ (256): C, 60.94; H, 4.69; N, 21.87; S, 12.50. Found: C, 60.89; H, 4.85; N, 21.58; S, 12.76.

(b) From 4. A solution of **4** (2.5 g, 20 mmol) and benzylthioacetimidate (**7**; 4 g, 20 mmol) in pyridine (50 mL) was stirred at room temperature for 3 h and heated at reflux for 1.5 h. After evaporation of the solvent, the residue was treated with charcoal and recrystallized in ethanol to yield 4.6 g (90%).

8-(Benzylthio)-*s*-triazolo[4,3-*a*]pyrazine (11). As above, the reaction from **9** (1 g, 6.5 mmol), benzyl mercaptan (1.61 g, 13 mmol), and 10 mL of pyridine gave 800 mg of **11** (47.5%), mp 114 °C.

Anal. Calcd for $C_{12}H_{10}N_4S$, H_2O (260): C, 55.36; H, 4.65; N, 21.52; S, 12.31. Found: C, 55.61; H, 4.50; N, 21.82; S, 12.73.

8-(Benzylthio)-3-benzyl-*s*-triazolo[4,3-*a*]pyrazine (21). The reaction of **4** (2.89 g, 20 mmol) and benzyl phenylthioacetimidate (**8**; 5.55 g, 20 mmol) in pyridine (100 mL) at reflux for 1 h gave after evaporation a residue which was recrystallized with benzene: 6.2 g (93.3%); mp 181 °C.

Anal. Calcd for $C_{19}H_{16}N_4S$ (332): C, 68.67; H, 4.82; N, 16.86; S, 9.63. Found: C, 68.58; H, 4.85; N, 16.18; S, 9.79.

8-(Benzylamino)-*s*-triazolo[4,3-*a*]pyrazine (12). **9** (1 g, 6.5 mmol) was heated for 1 h with benzylamine (2.8 g, 26 mmol) in methyl cellosolve (10 mL) at reflux. The solvent was evaporated, water was added, and the residue was filtered and recrystallized with benzene–cyclohexane (9:1) into colorless needles: 500 mg (34%); mp 204 °C.

Anal. Calcd for $C_{12}H_{11}N_5$ (225): C, 63.98; H, 4.92; N, 31.09. Found: C, 64.15; H, 5.20; N, 30.90.

8-(Benzylamino)-3-methyl-*s*-triazolo[4,3-*a*]pyrazine (16). As above, **16** (900 mg, 75%) was obtained from **13** (0.85 g, 5 mmol), benzylamine (2.14 g, 20 mmol), and 25 mL of methyl cellosolve at reflux

Table IV. Proton NMR Characteristics of the *C*-Nucleosides in Me_2SO-d_6 at 34 °C [e]

	H-5		H-6		NH-7	H-1′		H-2′		H-2″		H-3′	H-4″		H-5′		H-5″ [a]
A. Ribonucleosides																	
26	8.17		7.64			5.38		4.84					[4.20–4.30] [c]				4.59
		(4.8)					(3.2)									(12)	
27	7.37		6.73		11.33	5.24		4.84					[4.20–4.30]				4.55
		(5.6)		(ex) [b]			(3.5)										
28	7.44		6.83		11.38	5.67		6.08				5.57	4.51		4.33		4.53
		(5.6)		(5.4)			(3.9)		(5.1)				(6.7)				
29	8.53		7.72			5.84		6.17				5.60	4.58		4.32		4.60
		(4.8)					(3.6)		(5.1)				(6.6)				
30	7.84		7.00		13.17	5.71		6.10				5.57	4.50		4.35		4.55
		(5.6)		(5.3)			(3.8)		(5.2)				(6.3)				
31	7.63		7.20			5.69		6.14				5.59	4.55		4.34		4.55
		(4.7)					(3.7)		(5.3)				(6.3)			(13.5)	
32	8.52		7.79			5.23		4.49				4.09	3.96			[3.57]	
		(4.8)					(6.7)		(5.1)				(3.8)	(3.6)			
33	7.68		6.86		11.42	5.09		4.43				4.06	3.93			[3.54]	
		(5.8)		(ex)			(6.7)		(5.0)				(4.1)	(3.5–4.0)		(12.3)	
2	7.92		7.20			5.13		4.48				4.08	3.93			[3.55]	
		(4.7)					(6.9)		(5.0)				(3.4)	(3.8)			
34	8.07		7.02		13.18	5.14		4.45				4.06	3.93			[3.54]	
		(5.7)		(ex)			(6.5)		(5.0)				(4.0)	(3.8)			
35	8.61		7.64			5.26		4.50				4.09	3.97			[3.56]	
		(4.8)					(6.8)		(5.6)				(3.5)	(3.6)			
36	7.89		7.27			5.13		4.46				4.00	3.93			[3.55]	
		(4.8)					(7.0)										
B. 2′-Deoxyribonucleosides [d]																	
α-**37**	8.32		7.80			5.96		2.06		2.00		5.62				[4.55]	
		(4.8)					(7.3,5.5)										
β-**37**	8.34		7.72			5.87		3.21		2.72		5.68	4.60			[4.44]	
		(4.9)					(9.0,6.3)		(14.0)		(6.5,2.4)		(3)				
38	7.52		6.81		11.40	5.74		3.16		2.68		5.67	4.57			[4.43]	
		(5.6)		(5.6)			(9.0,6.1)		(14.0)		(6.3,2.2)		(3.2)				
39	8.63		7.70			5.92		3.25		2.76		5.70	4.61		4.40		4.49
		(4.9)					(8.8,6.5)		(14.1)		(6.3,2.2)		(3.5)	(5.6,3)		(12.2)	
40	7.92		6.96		13.18	5.78		3.18		2.69		5.63	4.58			[4.43]	
		(5.7)		(ex)			(9.0,6.3)		(13.9)		(6.5,2.2)		(3.2)	(4)			
41	7.72		7.19			5.78		3.18		2.67		5.67	4.56			[4.44]	
		(4.7)					(9.7,6.4)		(14.0)		(6.8,2.5)		(3)	(4)			
α-**42**	8.43		7.83			5.62		2.70		2.45		4.31	3.84			[3.52]	
		(4.8)					(8.2,7.2)		(13.3)		(7.2,5.0)		(4.3)	(4.2)			
β-**42**	8.47		7.79			5.62		2.61		2.20		4.35	3.91			[3.45]	
		(4.8)					(9.5,6.2)		(13.0)		(5.8,2.3)		(2.7)	(4.2)			
43	7.62		6.86		11.35	5.48		2.56		2.17		4.31	3.88			[3.40]	
		(5.8)		(ex)			(9.8,6.2)		(12.9)		(6.0,2.3)		(2.6)	(4.5)			
3	7.86		7.20			5.51		2.61		2.17		4.34	3.88			[3.42]	
		(4.8)					(9.8,6.2)		(13.1)		(6.0,2.1)		(2.7)	(4.3)			
44	8.02		7.02		13.18	5.52		2.59		2.19		4.32	3.89			[3.44]	
		(5.6)		(ex)			(9.4,6.3)		(12.9)		(5.8,2.3)		(2.5)	(4.5)			
45	8.56		7.64			5.65		2.61		2.23		4.35	3.92			[3.47]	
		(4.8)					(9.6,6.2)		(13.2)		(6.0,2.3)		(2.6)	(4.4)			
46	7.83		7.27			5.52		2.60		2.16		5.33	3.89			[3.45]	
		(4.8)					(9.6,6.1)		(12.9)		(6.0,2.4)		(2.6)	(4.3)			

[a] The resonances of the sugar hydroxylic groups and of the base and sugar substituents have been analyzed but have not been included in the table for clarity. [b] Proton exchange resulting in the loss of observable coupling. [c] Unresolved protons. [d] Coupling constants of the 2′-deoxyriboses are given in the order ($J_{1'2'}$, $J_{1'2''}$) ($J_{2'2''}$) ($J_{2'3'}$, $J_{2''3'}$) ($J_{3'4'}$) ($J_{4'5'}$, $J_{4'5''}$) ($J_{5'5''}$). [e] The chemical shifts, in ppm, are referenced to Me_4Si. The coupling constants, in hertz, for vicinal or geminal protons are given in parentheses.

for 4 h, mp 211 °C (EtOH).

Anal. Calcd for $C_{13}H_{13}N_5$ (239): C, 65.25; H, 5.48; N, 29.27. Found: C, 65.48; H, 5.61; N, 29.26.

8-Oxo-7,8-dihydro-3-methyl-*s*-triazolo[4,3-*a*]pyrazine (17). Hydrogen peroxide (6.35 g, 30%) was added gradually to a solution of **15** (5.1 g, 20 mmol) in 45 mL of formic acid at 35 °C. The solution was heated to 50 °C after the end of the addition and continued to be stirred at room temperature for 15 h. The solvent was evaporated and the residue was dissolved in 20 mL of water and neutralized with sodium hydrogen carbonate. The solid was filtered and recrystallized in water: 1.3 g (43.5%); mp >335 °C.

Anal. Calcd for $C_6H_6N_4O$ (150): C, 48.00; H, 4.03; N, 37.32. Found: C, 47.90; H, 4.04; N, 37.12.

8-Oxo-7,8-dihydro-3-benzyl-*s*-triazolo[4,3-*a*]pyrazine (22). The reaction as above from **21** (6.2 g, 18.6 mmol) gave after recrystallization in ethanol 3.6 g of **22** (85%), mp 285–310 °C dec.

Anal. Calcd for $C_{12}H_{10}N_4O$ (226): C, 63.70; H, 4.46; N, 24.77. Found: C, 63.43; H, 4.43; N, 24.50.

8-Chloro-3 benzyl-*s*-triazolo[4,3-*a*]pyrazine (23). The reaction as for **13**, from **22** (2 g, 8.85 mmol), 40 mL of phosphorus oxychloride, and diethylaniline (1.3 g, 8.85 mmol), gave 1.3 g of **23** (60%), mp 158 °C (EtOH).

Anal. Calcd for $C_{12}H_9ClN_4$ (244.5): C, 58.90; H, 3.71; N, 22.90; Cl, 14.49. Found: C, 58.88; H, 3.73; N, 22.65; Cl, 14.33.

8-Amino-3-methyl-*s*-triazolo[4,3-*a*-]pyrazine (18). **13** (1.7 g) was heated at 120 °C for 13 h with 120 mL of a solution of ethanol

saturated at 0 °C with ammonia, in a steel vessel. The solvent was evaporated and the residue was recrystallized with ethanol to yield 1.1 g of **18** (73%), mp 316 °C.

Anal. Calcd for $C_6H_7N_5$ (149): C, 48.31; H, 4.73; N, 46.96. Found: C, 48.17; H, 4.57; N, 47.10.

8-(3-Methyl-2-butenylamino)-3-methyl-*s*-triazolo[4,3-*a*]pyrazine (19). As for **16**, the reaction from **13** with 3-methyl-2-butenylamine[9] gave 1.05 g (98%) of **19**, mp 148 °C.

Anal. Calcd for $C_{11}H_{15}N_5$ (217): C, 60.80; H, 6.96; N, 32.24. Found: C, 60.79; H, 6.87; N, 31.95.

8-[(1-Methyl-4-nitroimidazol-5-yl)thio]-3-methyl-*s*-triazolo[4,3-*a*]pyrazine (20). **14** (400 mg, 2.6 mmol), 1-methyl-4-nitro-5-chloroimidazole (419 mg, 2.6 mmol), and sodium acetate (460 mg, 5.6 mmol) in anhydrous ethanol (25 mL) were heated at reflux for 4 h. After evaporation of the solvent, water was added and the residue was filtered: 473 mg (61%); mp 236 °C (acetone).

Anal. Calcd for $C_{10}H_9N_7O_2S$ (291): C, 41.23; H, 3.09; N, 33.68. Found: C, 41.28; N, 3.13; N, 33.72.

8-(Benzylthio)-3-(5′-*O*-benzoyl-β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (26). A solution of thioimidate **24**[8] (13.3 g, 31.4 mmol) and **4** (4.54 g, 31.4 mmol) in pyridine (120 mL) was stirred at room temperature for 3 h and heated at reflux for 2 h. After evaporation of the solvent, the residue was dissolved with ethanol and the solution was neutralized with 1 N NaOH. The solvent was removed and the residue was chromatographed (400 g, 50 × 5 cm) ($CHCl_3$–EtOH 96:4) to yield 7.9 g of **26** (52.5%): mp 170 °C; R_f 0.68 ($CHCl_3$–EtOH 9:1); MS *m/e* 478 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −91 (*c* 0.11, DMF).

Anal. Calcd for $C_{24}H_{22}N_4O_5S$ (478): C, 60.24; H, 4.63; N, 11.71. Found: C, 60.07; H, 4.91; N, 12.13.

8-Oxo-7,8-dihydro-3-(5′-*O*-benzoyl-β-D-ribofuranosyl)-*s*-triazolo[4,3,-*a*]pyrazine (27). The reaction as for **17** on 2.4 g of **26** with hydrogen peroxide (30%, 1.8 mL) in 20 mL of formic acid at room temperature for 15 h gave after evaporation a residue which was dissolved in water. The neutralization at pH 7 precipitates a white solid which was recrystallized in methanol: 1037 mg (55%); mp 238 °C; R_f 0.4 ($CHCl_3$–EtOH 4:1); MS *m/e* 372 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −96.5° (*c* 0.09, DMF).

Anal. Calcd for $C_{17}H_{16}N_4O_6$ (372); C, 54.84; H, 4.33; N, 15.05. Found: C, 54.24; H, 4.90; N, 15.56.

8-Oxo-7,8-dihydro-3-(5′-*O*-benzoyl-2′,3′-di-*O*-acetyl-β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (28). A solution of **27** (503 mg, 1.35 mmol) in acetic anhydride (8 mL) and pyridine (8 mL) was stirred at room temperature for 24 h. After addition on ice, the precipitate was filtered and washed with cold water: 465 mg (72%); mp 182 °C; R_f 0.77 ($CHCl_3$–EtOH, 10:1); MS *m/e* 456 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −70° (*c* 0.10, DMF).

Anal. Calcd for $C_{21}H_{20}N_4O_8$ (456): C, 55.26; H, 4.42; N, 12.28. Found: C, 54.90; H, 4.82; N, 12.49.

8-Chloro-3-(5′-*O*-benzoyl-2′,3′-di-*O*-acetyl-β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (29). A solution of **28** (4.5 g, 9.8 mmol), chloroform (50 mL), thionyl chloride (2.8 mL, 38 mmol), and DMF (0.7 mL) was heated at reflux for 4.5 h. After cooling, 200 mL of chloroform was added and the solution was washed with a cold solution of sodium hydrogen carbonate and water and dried. Evaporation to dryness gave 2.2 g (47%) of **29**: mp 189 °C ($CHCl_3$–AcOEt); R_f 0.69 ($CHCl_3$–EtOH 100:3); MS *m/e* 474 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −93° (*c* 0.08, DMF).

Anal. Calcd for $C_{21}H_{19}N_4ClO_7$ (474.5): C, 53.10; H, 4.00; N, 11.80. Found: C, 53.16; H, 4.25; N, 12.30.

8-Mercapto-3-(5′-*O*-benzoyl-2′,3′-di-*O*-acetyl-β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (30). The mercapto compound was obtained from **29** with the same procedure as for **14**, with 90% yield: mp 218 °C; R_f 0.78 ($CHCl_3$–EtOH, 10:1); MS *m/e* 472 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −67° (*c* 0.09, DMF).

Anal. Calcd for $C_{21}H_{20}N_4O_7S$ (472): C, 53.38; H, 4.23; N, 11.86. Found: C, 53.81; N, 4.49; N, 12.07.

8-(3-Methyl-2-butenylamino)-3-(5′-*O*-benzoyl-2′,3′-di-*O*-acetyl-β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (31). A solution of **29** (1 g, 2 mmol) and 3-methyl-2 butenylamine (0.7 g, 8.2 mmol) in 25 mL of ethanol was heated to reflux for 24 h. After evaporation of the solvent, the residue was chromatographed (25 g, 30 × 1 cm) ($CHCl_3$–EtOH, 100:1) to yield 400 mg (36%) of **31**: mp 128 °C; R_f 0.81 ($CHCl_3$–EtOH, 100:5); MS *m/e* 523 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −66 ° (*c* 0.10, DMF).

Anal. Calcd for $C_{26}H_{29}N_5O_7$ (523): C, 59.65; H, 5.58; N, 13.38. Found: C, 60.20; H, 6.02; N, 13.67.

8-(Benzylthio)-3-(β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (32). A solution of **26** in methanolic ammonia gave after 24 h at room temperature a quantitative yield of **32**: mp 180 °C (MeOH); R_f 0.64 ($CHCl_3$–EtOH 4:1); MS *m/e* 374 (39%, $M^{+\cdot}$), 285 (9%, B + 44), 194 (9%, B − $CH_2C_6H_5$ + 44), 180 (10%, B − $CH_2C_6H_5$ + 30), 91 (100%, $C_6H_5CH_2$); $[\alpha]^{25}_D$ −63° (*c* 0.08, DMF); CD $[\theta]_{227}$ −1200, $[\theta]_{257}$ −1700, $[\theta]_{280}$ 0, $[\theta]_{282}$ +200, $[\theta]_{291}$ 0, $[\theta]_{315}$ −300, $[\theta]_{340}$ 0.

Anal. Calcd for $C_{17}H_{18}N_4O_4S$ (374): C, 54.54; H, 4.85; N, 14.97. Found: C, 54.65; N, 5.23; N, 14.72.

8-Oxo-7,8-dihydro-3-(β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (33). The debenzoylation as for **32** gave after 72 h **33**: mp 244 °C: R_f 0.38 ($CHCl_3$–EtOH 1:1); MS *m/e* 268 (3%, $M^{+\cdot}$), 250 (4%, M − 18), 179 (100%, B + 44), 165 (60%, B + 30), 136 (20%, BH); $[\alpha]^{25}_D$ −63° (*c* 0.07, H_2O); CD $[\theta]_{244}$ 0, $[\theta]_{277}$ −1900, $[\theta]_{305}$ −700, $[\theta]_{325}$ 0.

Anal. Calcd for $C_{10}H_{12}N_4O_5$ (268): C, 44.78; H, 4.51 N, 20.89. Found: C, 44.58; N, 4.72; N, 20.85.

8-Amino-3-(β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (2). A suspension of **29** (830 mg, 1.75 mmol) in methanol (100 mL) was saturated at 0 °C with ammonia and heated in a steel vessel at 120 °C for 8 h. After cooling, the solvent was removed and the residue was chromatographed on Sephadex G-10 (90 × 2 cm) (H_2O) to yield 271 mg of **2** (58%): mp 207 °C; R_f 0.38 ($CHCl_3$–EtOH 1:1); MS *m/e* 267 (12%, $M^{+\cdot}$), 236 (2%, M − 31), 178 (98%, B + 44), 164 (100%, B + 30), 149 (17%, B + 15), 135 (12%, BH); $[\alpha]^{25}_D$ −61° (*c* 0.08, H_2O); CD $[\theta]_{223}$ 0, $[\theta]_{232}$ + 1400, $[\theta]_{243}$ 0, $[\theta]_{252}$ −100, $[\theta]_{262}$ 0, $[\theta]_{295}$ −1500, $[\theta]_{330}$ 0.

Anal. Calcd for $C_{10}H_{13}N_5O_4$ (267): C, 44.94; H, 4.86; N, 26.21. Found: C, 44.89; H, 5.33; N, 26.55.

8-Mercapto-3-(β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (34). The same procedure as for **2** gave **34**: mp 283 °C (EtOH–H_2O); R_f 0.28 ($CHCl_3$–EtOH, 10:3); MS *m/e* 284 (22%, $M^{+\cdot}$), 266 (3%, M − 18), 217 (77%, MH − $2H_2O$ − S), 195 (100%, B + 44), 181 (94%, B + 30), 166 (19%, B + 15), 152 (25%, BH); $[\alpha]^{25}_D$ −54° (*c* 0.08, H_2O); CD $[\theta]_{225}$ −5800, $[\theta]_{242}$ 0, $[\theta]_{245}$ +1400, $[\theta]_{263}$ 0, $[\theta]_{286}$ −2000, $[\theta]_{310}$ 0, $[\theta]_{345}$ +1100, $[\theta]_{380}$ 0.

Anal. Calcd for $C_{10}H_{12}N_4O_4S$ (284): C, 42.25; H, 4.26; N, 19.71. Found: C, 42.74; H, 4.64; N, 20.20.

8-[(1-Methyl-4-nitroimidazol-5-yl)thio]-3-(β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (35). The same procedure as for **20** on 320 mg of **34** (1.12 mmol) gave after a reflux of 16 h **35** (229 mg, 50%): mp 249–252 °C; R_f 0.21 ($CHCl_3$–EtOH 4:1);MS *m/e* 391 (1%, M − 18), 379 (2%, M − 30), 363 (23%, M − NO_2), 284 (5%, MH − NO_2Im), 195 (9%, B − NO_2Im + 44), 158 (100%, SNO_2Im − CH_3); $[\alpha]^{25}_D$ −70° (*c* 0.08, H_2O); CD $[\theta]_{235}$ −2200, $[\theta]_{246}$ −2400, $[\theta]_{280}$ −200, $[\theta]_{304}$ −900, $[\theta]_{340}$ 0.

Anal. Calcd for $C_{14}H_{15}N_7O_6S$ (409): C, 41.07; H, 3.66; N, 23.96. Found: C, 40.84; H, 3.84; N, 24.06.

8-(3-Methyl-2-butenylamino)-3-(β-D-ribofuranosyl)-*s*-triazolo[4,3-*a*] pyrazine (36). The debenzoylation of **31** for 5 days gave 86% of **36**: mp 183 °C; R_f 0.5 ($CHCl_3$–EtOH 5:1); MS *m/e* 335 (100%, $M^{+\cdot}$), 320 (50%, M − CH_3), 292 (93%, M − $CH(CH_3)_2$), 202 (10%, B), 178 (79%, B − C_5H_8 + 44), 164 (86%, B − C_5H_8 + 30); $[\alpha]^{25}_D$ −58° (*c* 0.10; H_2O); CD $[\theta]_{230}$ −1000, $[\theta]_{257}$ 0, $[\theta]_{267}$ +300, $[\theta]_{278}$ 0, $[\theta]_{302}$ −1200, $[\theta]_{336}$ 0.

Anal. Calcd for $C_{15}H_{21}N_5O_4$ (335): C, 53.72; H, 6.31; N, 20.89. Found: C, 53.03; H, 6.49; N, 21.12.

8-(Benzylthio)-3-(2′-deoxy-3′,5′-di-*O*-p-toluoyl-α- and -β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (37). A solution of **4** (0.867 g, 6 mmol) and thioimidate **25**[8] (3.3 g, 6 mmol) in 60 mL of pyridine was heated to reflux for 18 h. The treatment as for **26** gave after chromatography (220 g, 37 × 4.5 cm) ($CHCl_3$–EtOH 100:1) α- and β-**37**. **β-37:** 1.85 g (52%); mp 65 °C; R_f 0.91 ($CHCl_3$–EtOH 100:1); MS *m/e* 594 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −58° (*c* 0.10, DMF).

Anal. Calcd for $C_{33}H_{30}N_4O_5S$ (594): C, 66.66; H, 5.00; N, 9.42. Found: C, 66.00; H, 5.27; N, 9.90.

α-37: 0.427 g (12%); mp 142 °C (MeOH); R_f 0.75 ($CHCl_3$–EtOH 100:1); MS *m/e* 594 ($M^{+\cdot}$); $[\alpha]^{25}_D$ + 78° (*c* 0.11, DMF).

Anal. Calcd for $C_{33}H_{30}N_4O_5S$ (594): C, 66.66; H, 5.00; N, 9.42. Found: C, 66.08; H, 5.15; N, 8.91.

8-Oxo-7,8-dihydro-3-(2′-deoxy-3′,5′-di-*O*-p-toluoyl-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (38). Oxidation of β-**37** (1.2 g, 2.02 mmol) in 10 mL of formic acid with 30% hydrogen peroxide (0.8 mL) gave after 20 h at room temperature 0.278 g (64%) of **38**: mp 198 °C (EtOH); R_f 0.76 (AcOEt–EtOH 9:1); MS *m/e* 488 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −41° (*c* 0.09, DMF).

Anal. Calcd for $C_{26}H_{24}N_4O_6$ (488): C, 63.93; H, 4.91; N, 11.47. Found: C, 63.57; H, 4.99; N, 12.0.

8-Chloro-3-(2′-deoxy-3′,5′-di-*O*-p-toluoyl-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (39). A solution of **38** (0.5 g, 1 mmol), thionyl chloride (0.22 mL, 3 mmol), DMF (0.1 mL), and chloroform (6 mL) was heated to reflux for 5 h. After cooling, 40 mL of dichloromethane was added and the organic layer was washed with a cold solution of sodium hydrogen carbonate and cold water and dried over sodium sulfate. After evaporation, the residue was chromatographed (6 g, $CHCl_3$–AcOEt 1:1) to yield 425 mg of **39** (81%): mp

192 °C ($CHCl_3$–AcOEt); R_f 0.84 ($CHCl_3$–AcOEt 1:1); MS *m/e* 506 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −63° (*c* 0.09, DMF).

Anal. Calcd for $C_{26}H_{23}N_4O_5Cl$ (506.5): C, 61.59; H, 4.54; N, 11.05. Found: C, 61.15; H, 4.80; N, 11.56.

8-Mercapto-3-(2′-deoxy-3′,5′-di-*O*-*p*-toluoyl-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (40). As for **30, 39** (0.83, 1.63 mmol) gave 760 mg of **40** (92%): mp 125–127 °C; R_f 0.69 ($CHCl_3$–AcOEt (5:6); MS *m/e* 504 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −61° (*c* 0.10, DMF).

Anal. Calcd for $C_{26}H_{24}N_4O_5S$ (504): C, 61.90; H, 4.76; N, 11.11. Found: C, 61.87; H, 5.25; H, 11.56.

8-(3-Methyl-2-butenylamino)-3-(2′-deoxy-3′,5′-di-*O*-*p*-toluyl-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (41). A solution of **39** (1.6 g, 3 mmol) and 3-methyl-2-butenylamine (1.4 g, 4 mmol) in ethanol (25 mL) was heated to reflux for 18 h. After evaporation, the residue was recrystallized with ethanol to yield 1.10 g (63%) of **41**: mp 109 °C; R_f 0.63 (C_6H_6–AcOEt, 1:1); MS *m/e* 555 ($M^{+\cdot}$); $[\alpha]^{25}_D$ −44° (*c* 0.10, DMF).

Anal. Calcd for $C_{32}H_{33}N_5O_5$ (555): C, 67.01; H, 5.99; N, 12.61. Found: C, 66.62; H, 6.17; N, 12.68.

8-(Benzylthio)-3-(2′-deoxy-α-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (α-42). The detoluoylation of α-**37** with methanolic ammonia at room temperature for 10 days gave after evaporation to dryness α-**42**: mp 136 °C (MeOH); R_f 0.40 ($CHCl_3$–EtOH 25:3); MS *m/e* 358 (47%, $M^{+\cdot}$), 178 (3%, B − $CH_2C_6H_5$ + 28), 269 (8%, B + 28), 91 (100%, $CH_2C_6H_5$); $[\alpha]^{25}_D$ + 65° (*c* 0.08, H_2O); CD $[\theta]_{226}$ 0, $[\theta]_{232}$ −1000, $[\theta]_{266}$ 0, $[\theta]_{312}$ +600, $[\theta]_{345}$ 0.

Anal. Calcd for $C_{17}H_{18}N_4O_3S$ (358): C, 56.98; H, 5.02; N, 15.64. Found: C, 56.34; H, 5.40; N, 16.22.

8-(Benzylthio)-3-(2′-deoxy-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (β-42). As above, methanolic ammonia on β-**37** gave after 7 days 67% of β-**42**: mp 143 °C (EtOH); R_f 0.40 ($CHCl_3$–EtOH 25:3); MS *m/e* 358 (100%, $M^{+\cdot}$), 178 (4%, B − $CH_2C_6H_5$ + 28), 269 (7%, B + 28), 91 (64%, $CH_2C_6H_5$); $[\alpha]^{25}_D$ −43° (*c* 0.10, DMF); CD $[\theta]_{227}$ 0, $[\theta]_{234}$ +1500; $[\theta]_{292}$ 0, $[\theta]_{315}$ −800, $[\theta]_{345}$ 0.

Anal. Calcd for $C_{17}H_{18}N_4O_3S$ (358): C, 56.98; H, 5.02; N, 15.64. Found: C, 56.97; H, 5.13; N, 15.89.

8-Oxo-7,8-dihydro-3-(2′-deoxy-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (43). The detoluoylation as above gave after evaporation a residue which was chromatographed on Sephadex G-10 (90 × 2 cm) (H_2O): mp 231 °C (EtOH); R_f 0.64 ($CHCl_3$–EtOH 1:1); MS *m/e* 252 (1%, $M^{+\cdot}$), 222 (1%, M − 30), 179 (3%, B + 44), 165 (6%, B + 30), 163 (100%, B + 28), 150 (4%, B + 15), 136 (1%, BH); $[\alpha]^{25}_D$ −49° (*c* 0.08, H_2O); CD $[\theta]_{253}$ 0, $[\theta]_{278}$ −2200, $[\theta]_{324}$ 0.

Anal. Calcd for $C_{10}H_{12}N_4O_4$ (252): C, 47.61; H, 4.76; N, 22.22. Found: C, 47.35; H, 5.00; N, 22.44.

8-Amino-3-(2′-deoxy-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (3). The same procedure as for **2** gave 170 mg (83%) of **3** from **39** (410 mg, 1.97 mmol): mp 241 °C (EtOH); R_f 0.62 ($CHCl_3$–EtOH 1:1); MS *m/e* 251 (13%, $M^{+\cdot}$), 220 (9%, M − 31), 164 (24%, B + 30), 162 (100%, B + 28), 149 (10%, B + 15), 135 (6%, BH); $[\alpha]^{25}_D$ −46° (*c* 0.10, H_2O); CD $[\theta]_{237}$ 0, $[\theta]_{242}$ 2600, $[\theta]_{275}$ 0, $[\theta]_{295}$ −1200, $[\theta]_{330}$ 0.

Anal. Calcd for $C_{10}H_{13}N_5O_3$ (251): C, 47.80; H, 5.17; N, 27.88. Found: C, 47.65; H, 5.46; N, 27.71.

8-Mercapto-3-(2′-deoxy-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (44). The same procedure as for **42** gave **44**: mp 278 °C; R_f 0.43 ($CHCl_3$–EtOH 7:3); MS *m/e* 268 (26%, $M^{+\cdot}$), 238 (2%, M − 30), 237 (2%, M − 31), 195 (2%, B + 44), 179 (100%, B + 28); $[\alpha]^{25}_D$ −19° (*c* 0.09, H_2O); CD $[\theta]_{225}$ −3000, $[\theta]_{235}$ 0, $[\theta]_{257}$ +1900, $[\theta]_{276}$ 0, $[\theta]_{287}$ −1700, $[\theta]_{309}$ 0, $[\theta]_{345}$ +1400, $[\theta]_{383}$ 0.

Anal. Calcd for $C_{10}H_{12}N_4O_3S$ (268): C, 44.77; H, 4.47; N, 20.89. Found: C, 44.87; H, 4.81; N, 21.34.

8-[(1-Methyl-4-nitroimidazol-5-yl)thio]-3-(2′-deoxy-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (45). As for **35, 44** gave 40% of **45**: mp 241 °C; R_f 0.28 ($CHCl_3$–EtOH 4:1); MS *m/e* 375 (1%, M − 18), 363 (15%, M − 30), 347 (100%, M − NO_2), 268 (10%, MH − NO_2Im), 179 (27%, B + 28); $[\alpha]^{25}_D$ −62° (*c* 0.09, H_2O); CD$[\theta]_{241}$ 0, $[\theta]_{255}$ −400, $[\theta]_{260}$ −300, $[\theta]_{300}$ −1300, $[\theta]_{340}$ 0.

Anal. Calcd for $C_{14}H_{15}N_7O_5S$ (393): C, 42.75; H, 3.84; N, 24.93. Found: C, 43.11; H, 4.19; N, 24.56.

8-(3-Methyl-2-butenylamino)-3-(2′-deoxy-β-D-*erythro*-pentofuranosyl)-*s*-triazolo[4,3-*a*]pyrazine (46). Debenzoylation as for **43** gave 71% of **46** from **41**: mp 103 °C; R_f 0.58 ($CHCl_3$–EtOH 5:1); MS *m/e* 319 (34%, $M^{+\cdot}$), 304 (17%, M − CH_3), 276 (8%, M − $CH(CH_3)_2$), 231 (14%, B + 44), 162 (100%, B − C_5H_8 + 28); $[\alpha]^{25}_D$ −27° (*c* 0.01, H_2O); CD $[\theta]_{222}$ 0, $[\theta]_{236}$ 3000, $[\theta]_{267}$ 1700, $[\theta]_{282}$ 0, $[\theta]_{302}$ −1800, $[\theta]_{334}$ 0.

Anal. Calcd for $C_{15}H_{21}N_5O_3$ (319): C, 56.41; H, 6.63; N, 21.93. Found: C, 56.41; H, 6.83; N, 21.45.

Registry No.—**2,** 68797-11-5; **3,** 68797-19-3; **4,** 63286-28-2; **5,** 149-73-5; **6,** 1445-45-0; **7,** 59696-97-8; **8,** 54331-09-2; **9,** 68774-77-6; **10,** 68774-83-4; **11,** 68796-94-1; **12,** 68796-95-2; **13,** 68774-78-7; **14,** 68774-84-5; **15,** 68796-96-3; **16,** 68796-97-4; **17,** 68774-82-3; **18,** 68774-80-1; **19,** 68796-98-5; **20,** 68796-99-6; **21,** 68797-00-2; **22,** 68797-01-3; **23,** 68797-02-4; **24,** 50908-31-1; **25** (isomer 1), 50908-34-4; **25** (isomer 2), 50908-33-3; **26,** 68797-03-5; **27,** 68797-04-6; **28,** 68797-05-7; **29,** 68797-06-8; **30,** 68797-07-9; **31,** 68797-08-0; **32,** 68797-09-1; **33,** 68797-10-4; **34,** 68797-12-6; **35,** 68797-13-7; **36,** 68813-53-6; β-**37,** 68797-23-9; α-**37,** 68797-24-0; **38,** 68797-14-8; **39,** 68797-15-9; **40,** 68797-16-0; **41,** 68797-17-1; α-**42,** 68797-25-1; β-**42,** 68797-26-2; **43,** 68797-18-2; **44,** 68797-20-6; **45,** 68797-21-7; **46,** 68797-22-8; *N*-(β,β-dimethoxyethyl)oxamide, 68797-27-3; aminoacetaldehyde dimethyl acetal, 22483-09-6; ethyl oxamate, 617-36-7; 2,3-dichloropyrazine, 4858-85-9; benzyl mercaptan, 100-53-8; benzylamine, 100-46-9; 3-methyl-2-butenylamine, 13822-06-5; 1-methyl-4-nitro-5-chloroimidazole, 4897-25-0.

References and Notes

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