C-Nucleoside Studies. Part 22.[1] *cine*-Substitution in 1,4-Dinitropyrazoles: Further Model Studies, an Improved Synthesis of Formycin and Pyrazofurin and the Synthesis of some 3(5)-Alkylsulphonyl-4-amino-5(3)-β-D-ribofuranosylpyrazoles

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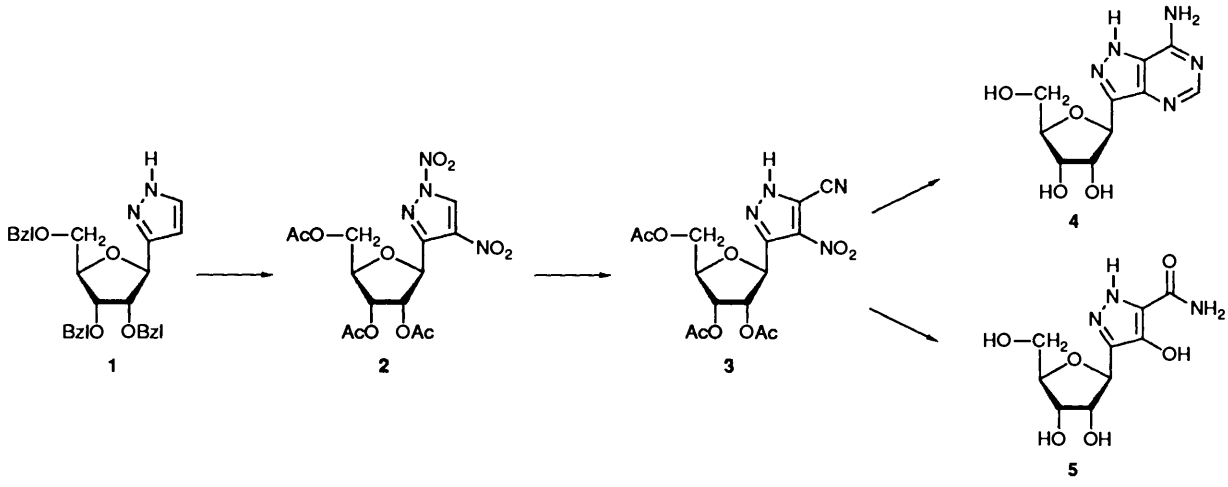
Reaction of 3-methyl-1,4-dinitropyrazole **6** with ethyl 2-mercaptoacetate gave, by *cine*-substitution, ethyl [5(3)-methyl-4-nitropyrazol-3(5)-ylthio]acetate **8**, which could be oxidised to the corresponding sulphoxide **11** or sulphone **12**. Reduction and cyclisation of **8** and **12** gave respectively, 3-methyl-1,6-dihydropyrazolo[3,4-*b*]-1,4-thiazin-5(4*H*)-one **14** and the 5,7,7-trioxo analogue **15**. Similarly treatment of **6** with glycine ethyl ester and sarcosine ethyl ester gave respectively ethyl 3(5)-methyl-4-nitropyrazol-5(3)-ylaminoacetate **16**, and its *N*-methyl analogue **17**; cyclisation of **17** gave 3,7-dimethyl-6,7-dihydro-1*H*-pyrazolo[3,4-*b*]pyrazin-5(4*H*)-one **18**. Reaction of **6** with various stabilized carbanions gave rise to a number of 3(5)-methyl-4-nitro-5(3)-(2-oxoalkyl)pyrazoles.

3(5)-(2,3,5-Tri-*O*-benzyl-β-D-ribofuranosyl)pyrazole **1** was subjected to transfer hydrogenation followed by acetylation, to give 1-acetyl-3-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)pyrazole **23** in 95% yield. Treatment of **23** with ammonium nitrate and trifluoroacetic anhydride in trifluoroacetic acid gave 1,4-dinitro-3-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)pyrazole **2** (95%). This sequence gives a much improved route to formycin **4** and pyrazofurin **5** as compared to the previously-reported route involving **1** and **2** as intermediates.

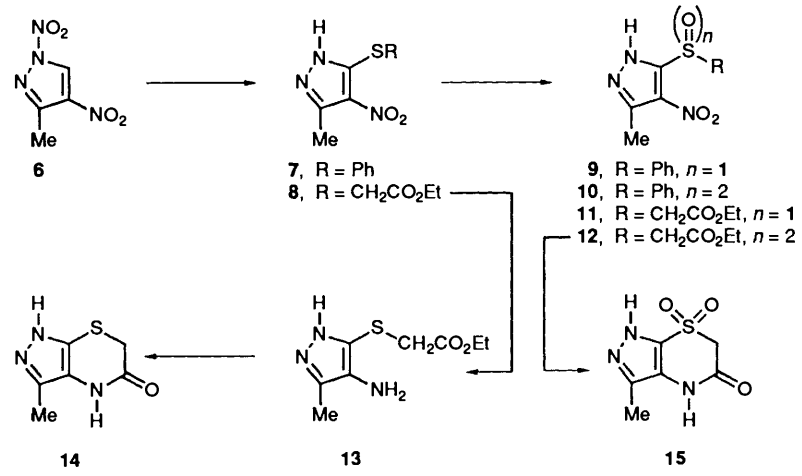
cine-Substitution of **2** with sulphur nucleophiles, and subsequent manipulation led to the synthesis of 4-amino-3(5)-methylsulphonyl-5(3)-(β-D-ribofuranosyl)pyrazole **29** and 4-amino-3(5)-[(carbamoyl)methyl]sulphonyl-5(3)-(β-D-ribofuranosyl)pyrazole **33**.

In earlier work we have described syntheses of the *C*-nucleoside antibiotics[2] formycin **4**[3] and pyrazofurin **5**.[4] Our approach to these targets (Scheme 1) has been to develop an efficient route to the protected ribofuranosylpyrazole **1**,[5] which could be converted into the 1,4-dinitropyrazole **2** in a number of steps.[3,5] This dinitro compound **2** could then undergo *cine*-substitution[6] with cyanide ion to generate the key nitro nitrile intermediate **3**,[3] which is convertible[3,4] into the natural products **4** and **5**. A disadvantage of the synthetic route as previously reported is, however, the need for six steps to convert the first-formed pyrazole **1** into the 1,4-dinitro compound **2**. In this paper we report; (a) further investigations in a simple model system, in addition to those we have noted earlier,[3] into the scope of *cine*-substitution for the production of functionalised pyrazoles, including the use of some more complex nucleophiles with the potential for subsequent elaboration into bicyclic heterocycles; (b) a much improved procedure for the preparation of **2** from **1** in two high-yielding steps, and (c) the use of **2** for the synthesis of some 3(5)-alkylsulphonyl-4-aminopyrazole *C*-nucleosides of potential interest as enzyme inhibitors.

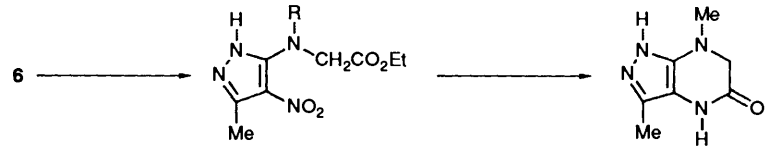
(*a*) *Further Examples of* cine-*Substitution Reactions on* 3-*methyl*-1,4-*dinitropyrazole*.—We have previously described the reaction of 3-methyl-1,4-dinitropyrazole **6** in *cine*-substitutions with ammonia, ethoxide, ethanethiolate and, in an Arbusov-type reaction, with trimethyl phosphite, as well as with cyanide.[3]



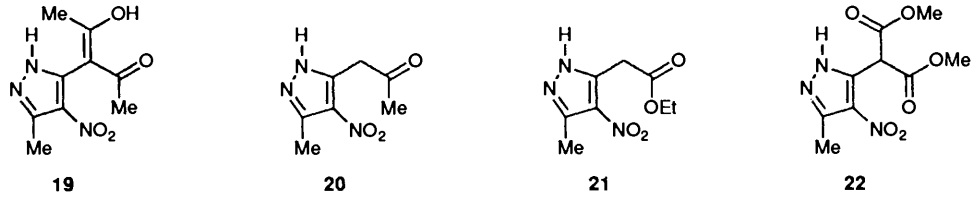
Scheme 1



Scheme 2



Scheme 3



Habraken and Poels had earlier demonstrated this type of reactivity with secondary amines as nucleophiles.[6] In our present work we showed firstly that treatment of 3-methyl-1,4-dinitropyrazole **6**[7] with thiophenoxide in ethanol gave (Scheme 2) thioether **7** in 94% yield. The thioether **7** could be oxidised to the sulphoxide **9** using 1.5 equiv. of 30% hydrogen peroxide in acetic acid, or, in rather higher yield, by means of sodium periodate. Oxidation of **7** to the sulphone **10** was also possible in high yield using potassium permanganate in aqueous acetic acid.

In a similar manner, a functionalised side-chain could be introduced by reaction of the dinitropyrazole **6** with the anion of ethyl 2-mercaptoacetate, giving the sulphide **8** in 92% yield. Again oxidation to the sulphoxide **11** was readily accomplished with sodium periodate, or, in somewhat higher yield, by hydrogen peroxide in aqueous acetic acid, whilst the sulphone **12** was accessible by oxidation with excess of hydrogen peroxide in acetic acid at higher temperatures, or better, by use of potassium permanganate (77% yield). In this series of compounds, the oxidation state was clearly indicated, in addition to mass spectrometric and IR spectroscopic evidence, by the progressive downfield shift of the methylene group in the ^{1}H NMR spectra, from δ 3.8 in sulphide **8** to δ *ca.* 4.4 in sulphoxide **11**, where the signal appeared as an AB system, and δ 4.7 in the sulphone **12**.

When nitro sulphide **8** was hydrogenated, an intermediate amino sulphide **13** was produced and identified spectroscopically, although its instability to oxidation precluded full characterisation. Treatment of the amino compound **13** in toluene plus a few drops of dilute hydrochloric acid at reflux[8] induced cyclisation to pyrazolo[3,4-*b*]1,4-thiazine derivative **14** in 72% overall yield from **8**. Similarly, reduction of the nitro sulphone **12**, best accomplished with zinc in acetic acid, gave an intermediate amino sulphone, which could be cyclised to the bicyclic heterocycle **15**, again using refluxing toluene plus a little dilute hydrochloric acid. Our methods seem to offer a direct entry to this rare heterocyclic system; additionally, the chemistry involved in the formation of the cyclic sulphone **15** could, if applied to nucleoside systems, give rise to analogues of the purine nucleosides of interest as potential inhibitors of enzymes catalysing reactions at C-6 of such purine nucleosides and nucleotides.[9]

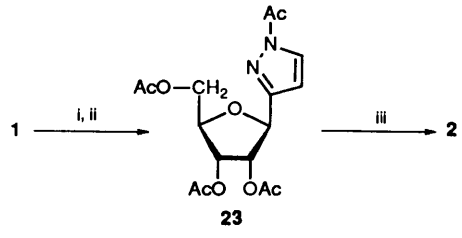
Introduction of a functionalised amine was also possible; reaction of 3-methyl-1,4-dinitropyrazole **6** with the ethyl esters of glycine and sarcosine giving the *cine*-substitution products **16** and **17** respectively (Scheme 3). When the sarcosine derivative **17** was hydrogenated in ethanol, cyclization of the presumed 4-amino intermediate occurred spontaneously, and the pyrazolo[3,4-*b*]pyrazine **18** could be isolated in 78% yield.[10] However this method failed to give any isolable product when applied to **16**. After work-up the reaction mixture darkened rapidly to give a complex mixture.

The direct introduction of functionalised carbon chains was also possible by reaction of **6** with carbanions derived from 1,3-dicarbonyl compounds. Reaction of the dinitro compound **6** with the anion of acetylacetone in methanol at room temperature gave two products. By conducting the reaction at 0 °C, one of these products was dominant. It could be isolated as a crystalline material in 70% yield, and identifed as the enolised

β-diketone **19**. On the other hand, from a reaction carried out at room temperature, followed by brief heating under reflux, the acetonylpyrazole **20** could be isolated as the only major product. In a similar reaction with the anion of ethyl acetoacetate, two products were detectable (TLC) at room temperature but from a reaction carried out at 40 °C only the deacetylated material **21** was isolated. Alternatively, reaction of **6** with the anion of dimethyl malonate in methanol at 10 °C gave the substituted malonate **22**. Surprisingly, given the similarity in acidity of nitromethane with the active methylene compounds above, a reaction of **6** with the anion of nitromethane in excess of methanol gave 3(5)-methoxy-5(3)-methyl-4-nitropyrazole[11] (63%) as the only isolable product.

(*b*) *An Improved Route to Formycin* **4** *and Pyrazofurin* **5**.—As noted above, our present routes to formycin **4**[3] and pyrazofurin **5**[4] suffer from the disadvantage of a six-step conversion of pyrazole **1** into the key 1,4-dinitro compound **2**, involving *inter alia*, protection of the pyrazole ring as the 1-(2,4-dinitrophenyl) derivative, and sequential introduction of the *C*- and *N*-nitro groups, the introduction of the *C*-nitro group involving the action of copper(II) nitrate–acetic anhydride on a 1-(2,4-dinitrophenyl)pyrazole.[5] We have recently shown, however, that treatment of 3(5)-methylpyrazole with ammonium nitrate and trifluoroacetic anhydride (TFAA) in trifluoroacetic acid (TFA) leads directly in one step to 3-methyl-1,4-dinitropyrazole **6**,[12] and we expected that these reagents could be used to effect a much more direct conversion of **1** into **2**.

Accordingly, the tri-*O*-benzyl derivative **1** was subjected to transfer hydrogenation with cyclohexene as hydrogen donor, and the resultant triol was directly acetylated to give the *N*,*O*,*O*,*O*-tetraacetyl derivative **23** (Scheme 4) in 95% yield after chromatography. The location of the *N*-acetyl group on N^1 is



Scheme 4 *Reagents:* i, $Pd(OH)_2/C$, cyclohexene, EtOH; ii, Ac_2O, C_5H_5N; iii, NH_4NO_3, trifluoroacetic acid, trifluoroacetic anhydride

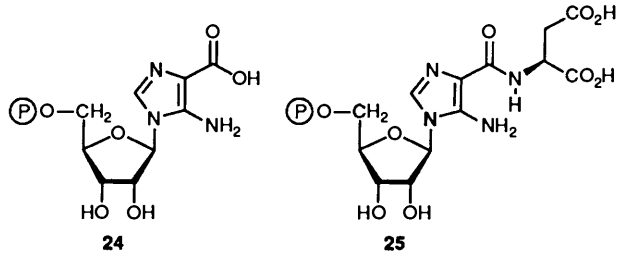
strongly supported by the lowfield signal (δ 8.23) seen for the signal of 5-H in the ^1H NMR spectrum of **23**, as compared with the equivalent signal in the spectrum of **1** (δ *ca.* 7.3). Although **23** could be cleanly deacetylated at nitrogen on treatment with triethylamine in methanol, this was not necessary, since treatment of **23** with ammonium nitrate–TFAA–TFA, led directly to the 1,4-dinitro compound **2** in 95% yield. Clearly the *N*-acetyl group is labile under the reaction conditions, as might be expected.

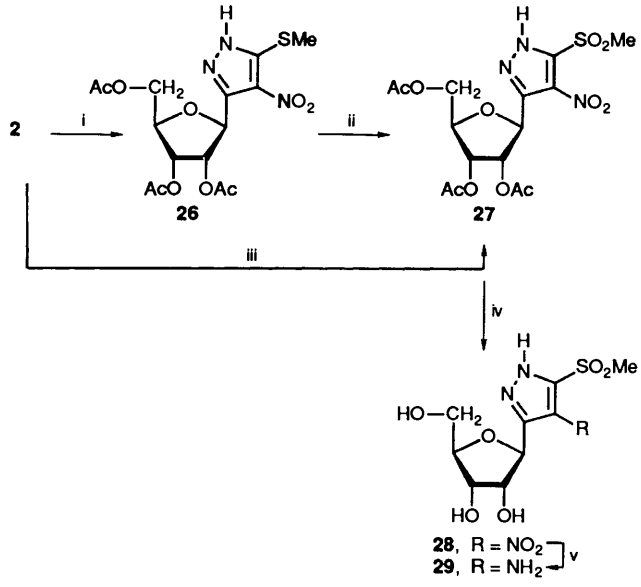
The use of these two high-yielding steps thus provides a considerable improvement on our previous methods, both with regard to experimental convenience and overall yield.

(*c*) *Synthesis of Some Potential Inhibitors of Purine Nucleoside Biosynthesis*.—As part of an interest in the synthesis of inhibitors of the *de novo* biosynthesis of purine nucleotides as possible antitumour agents, we have been concerned with the preparation of potential inhibitors of the enzyme SAICAR kinosynthetase (E.C. 6.3.2.6),[13] which catalyses the ATP-dependent conversion of the 4-carboxyimidazole nucleotide **24** (CAIR) and aspartate into the amide **25** (SAICAR). In an earlier paper,[14] we have outlined our rationale for believing that imidazole nucleotides related to **24** and **25**, but carrying a tetrahedral centre adjacent to C-4 of the imidazole, might act as inhibitors of SAICAR kinosynthetase, and we reported the synthesis of some imidazole nucleosides of this type.

We have also been interested in developing in parallel routes to similar pyrazole *C*-nucleosides, and we report here the synthesis of two 5-alkylsulphonyl-4-aminopyrazole *C*-nucleosides, **29** and **33**. As regards the presence of a pyrazole ring rather than an imidazole, it is noteworthy that the pyrazolopyrimidine formycin **4** is able to replace adenosine in a number of biochemical processes,[15] and that pyrazofurin **5** acts as an inhibitor of a later stage in purine biosynthesis.[16] It has also been shown that 4-amino-3-β-D-ribofuranosylpyrazole-5′-phosphate is an inhibitor (albeit weakly) of the carboxylase which interconverts CAIR **24** and its decarboxylated precursor.[17]

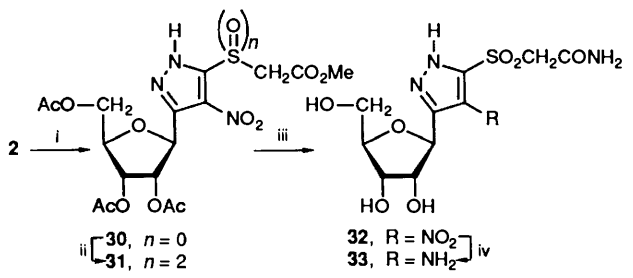
Thus, for the synthesis of the simpler analogue **29** (Scheme 5), the 1,4-dinitro compound **2**, prepared by the abbreviated procedure described above, was treated with sodium methanethiolate in methanol to give the *cine*-substitution product **26** in 76% yield. This sulphide could be oxidised to the corresponding





Scheme 5 *Reagents:* i, MeSNa, MeOH; ii, *m*-chloroperbenzoic acid, CH_2Cl_2; iii, MsCl, $NaHCO_3$, Na_2SO_3, $MeOH/H_2O$; iv, NH_3, MeOH; v, H_2, Pd/C, MeOH

sulphone **27** in high yield using *m*-chloroperbenzoic acid. The same sulphone **27** was also accessible directly from the dinitro compound **2** in 65% yield by substitution using methanesulphinate ion, generated *in situ* from methanesulphonyl chloride and sodium sulphite–sodium hydrogen carbonate.[18] Subsequent treatment of **27** with methanolic ammonia led to the triol **28**, which on catalytic reduction led to amino sulphone **29** isolated as a crystalline hydrochloride in high yield. Surpris-



Scheme 6 *Reagents:* i, $HSCH_2CO_2Me$, NaOMe, MeOH; ii, *m*-chloroperbenzoic acid, CH_2Cl_2; iii; NH_3, MeOH; iv, H_2, Pd/C, MeOH

ingly, however, this hydrochloride and its corresponding free base **29** were unstable to prolonged storage in air.

In a similar way, for the synthesis of the more complex analogue **33** (Scheme 6), the 1,4-dinitropyrazole **2** was treated with the sodium salt of methyl mercaptoacetate in methanol to give the thioether **30** as a crystalline compound in 70% yield. This sulphide could be oxidised to the corresponding sulphone **31** in high yield by *m*-chloroperbenzoic acid. The structure of the sulphone **31** was fully supported by spectroscopic data; in the ^1H NMR spectrum of **31**, the methylene group adjacent to the sulphone resonated at δ 4.61, as compared with the equivalent signal at δ 3.90 in the precursor **30**. When **31** was treated with methanolic ammonia, the amido triol **32** was readily obtained, and this, on catalytic hydrogenation, gave the 4-amino compound **33** as a crystalline solid. It is perhaps noteworthy that in the ^1H NMR spectra of both the triols **32** and **33**, recorded in D_2O, no signal was observed for the methylene group adjacent to the sulphone, due presumably to rapid exchange with the solvent; all other spectroscopic data fully supported the structures.

The amino amide **33** did not show significant cytotoxicity against either mouse L1210 leukaemia or Walker rat carcinoma cell lines *in vitro*. The instability of **29** precluded its testing. Studies on the enzymic phosphorylation[19] of **33** and the effects of the 5′-phosphate on SAICAR kinosynthetase[13] will be reported elsewhere.

Experimental

IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer; UV spectra were obtained on a Shimadzu 160 spectrophotometer. Mass spectrometry was performed using VG updated MS 9 and VG ZAB-E high resolution EI/CI/FAB instruments. NMR spectra were recorded on Perkin-Elmer R12B, JEOL MH100 and Bruker WP 200 SY spectrometers with $CDCl_3$ as solvent unless otherwise stated. *J* values are given in Hz. Specific rotations were measured at room temperature using a Bendix-NPL 143D automatic polarimeter (path length 1 cm). M.p.s were determined using an Electrothermal MKII apparatus and are uncorrected.

Reactions were monitored by TLC on pre-coated aluminium-backed plates [Kieselgel HF_{254} type 60 (Merck)]. Column chromatography was carried out using Kieselgel H type 60 (Merck 7734); an external pressure was applied to the top of the columns. Light petroleum refers to the fraction of boiling range 40–60 °C. Ether refers to diethyl ether. Organic extracts were dried over anhydrous sodium sulphate.

3(5)-*Methyl*-4-*nitro*-5(3)-(*phenylthio*)*pyrazole* **7**.—3-Methyl-1,4-dinitropyrazole **6** (0.344 g) in ether (2 cm^3) was added dropwise to a solution of sodium (69 mg) and thiophenol (0.61 cm^3) in ethanol (5 cm^3). After 1 h at room temperature, the solvent was evaporated, and the residue in water (10 cm^3) was neutralised with acetic acid. Extraction with ethyl acetate and evaporation of the dried organic layers gave a solid which was crystallised from dichloromethane–light petroleum to give the *sulphide* **7** (0.43 g, 94%), m.p. 200 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1480 and 1380 (NO_2) and 1330 (S); δ_H(60 MHz) 2.6 (3 H, s, Me) and 7.5–7.9 (5 H, m, Ph) (Found: C, 51.1; H, 3.85; N, 17.75; S, 13.5. $C_{10}H_9N_3O_2S$ requires C, 51.06; H, 3.82; N, 17.87; S, 13.61%).

3(5)-*Methyl*-4-*nitro*-5(3)-(*phenylsulphinyl*)*pyrazole* **9**.—A solution of sodium periodate (0.13 g) in water (1 cm^3) was added to a solution of sulphide **7** (0.1 g) in acetic acid (3 cm^3). The mixture was maintained at 70 °C for 2 h, and then poured into ice–water (50 cm^3). The precipitate was collected and recrystallised from water to give *sulphoxide* **9** (0.07 g, 66%), m.p. 220 °C; ν_{max}(KBr)/cm^{-1} 1485 and 1380 (NO_2) and 1050 (S=O); δ_H[60 MHz, $(CD_3)_2CO$] 2.6 (3 H, s, Me) and 7.5–8.0 (5 H, m, Ph) (Found: M^+ 251.034. $C_{10}H_9N_3O_3S$ requires *M*, 251.036).

3(5)-*Methyl*-4-*nitro*-5(3)-(*phenylsulphonyl*)*pyrazole* **10**.—Potassium permanganate (0.118 g) was added to a solution of the sulphide **7** (0.117 g) in acetic acid (8 cm^3) and water (2 cm^3). After 2 h at room temperature, evaporation and chromatography of the residue on silica, eluting with ethyl acetate–light petroleum (1:1) gave *sulphone* **10** (0.12 g, 92%), m.p. 200–203 °C; ν_{max}(KBr)/cm^{-1} 1340 and 1140 (SO_2); δ_H[60 MHz, $(CD_3)_2CO$] 2.6 (3 H, s, Me) and 7.4–8.2 (5 H, m, Ph) (Found: M^+, 267.030. $C_{10}H_9N_3O_4S$ requires *M*, 267.031).

Ethyl [3(5)-*Methyl*-4-*nitropyrazol*-5(3)-*ylthio*]*acetate* **8**.—To a solution of sodium (69 mg) in ethanol (5 cm^3) was added ethyl 2-mercaptoacetate (0.65 cm^3) followed by 3-methyl-1,4-dinitropyrazole (0.344 g) in ether (3 cm^3). After 2 h, the mixture was neutralised with acetic acid and evaporated. The residue was partioned between ethyl acetate and water. Evaporation of the dried organic layer gave colourless crystals which were washed with dichloromethane–light petroleum (1:1) to give *title compound* **8** (0.45 g, 92%), m.p. 114–116 °C; ν_{max}(KBr)/cm^{-1} 1700 (C=O), 1550 and 1350 (NO_2); δ_H(60 MHz) 1.25 (3 H, t, CH_2CH_3), 2.55 (3 H, s, Me), 3.8 (2 H, s, $S-CH_2$) and 4.2 (2 H, q, CH_2CH_3) (Found: C, 39.1; H, 4.4; N, 17.25; S, 12.95. $C_8H_{11}N_3O_4S$ requires C, 39.15; H, 4.48; N, 17.13; S, 13.05%).

Ethyl 3(5)-*Methyl*-4-*nitropyrazol*-5(3)-*ylsulphinylacetate* **11**.—Aqueous hydrogen peroxide (30%, 2 cm^3) was added to a solution of the sulphide **8** (0.2 g) in acetic acid (3 cm^3). After 18 h at room temperature, the mixture was poured onto ice (100 cm^3), and the precipitate was recrystallised from water to give the *sulphoxide* **11** (0.18 g, 84%) as needles, m.p. 178–181 °C; ν_{max}(KBr)/cm^{-1} 1730 (C=O), 1500 and 1330 (NO_2) and 1050 (S=O); δ_H[60 MHz, $(CD_3)_2CO$] 1.3 (3 H, t, CH_2CH_3), 2.75 (3 H, s, Me), 4.1–4.7 (4 H, m, 2 × CH_2) (Found: MH^+ 262.052. $C_8H_{12}N_3O_5S$ requires *M*H, 262.052).

Ethyl 5(3)-*Methyl*-4-*nitropyrazol*-3(5)-*ylsulphonylacetate* **12**.—Potassium permanganate (0.237 g) was added with stirring to a solution of the sulphide **8** (0.247 g) in acetic acid–water (4:1, 5 cm^3). After 2 h, evaporation and chromatography of the residue on silica, eluting with ethyl acetate–light petroleum (1:1) gave the *sulphone* **12** (0.21 g, 77%), m.p. 121–122 °C; ν_{max}(KBr)/cm^{-1} 1725 (C=O), 1310 and 1150 (SO_2); δ_H[60 MHz, $(CD_3)_2CO$] 1.2 (3 H, t, CH_2CH_3), 2.78 (3 H, s, Me), 4.15 (2 H, q, CH_2CH_3) and 4.7 (2 H, s, CH_2) (Found: C, 34.6, H, 4.0; N, 15.15; S, 11.45. $C_8H_{11}H_3O_6S$ requires C, 34.65; H, 3.97; N, 15.16; S, 11.55%).

3-*Methyl*-1,6-*dihydropyrazolo*[3,4-b]-1,4-*thiazin*-5(4H)-*one* **14**.—The nitro ester **8** (0.26 g) in ethanol (25 cm^3) was hydrogenated for 48 h using palladium-on-charcoal (5%, 0.15 g) as catalyst. Filtration, evaporation and chromatography of the residue on silica gel, eluting with ethyl acetate–light petroleum

(1:1) gave the amino ester **13** (0.18 g), as a syrup; ν_{max}(film)/cm^{-1} 3420–3300 (NH) and 1720 (C=O); δ_H(100 MHz) 1.2 (3 H, t, CH_2CH_3), 2.17 (3 H, s, CH_3), 3.36 (2 H, s, CH_2) and 3.8–4.2 (4 H, m, CH_2CH_3, NH_2); *m/z* 215 (M^+). This material in toluene (30 cm^3) and aqueous hydrochloric acid (3 mol dm^{-3}; 3 drops) was heated under reflux for 6 h. The precipitate which formed on cooling was filtered and recrystallised from water to give the *pyrazolothiazine* **14** (0.13 g, 72%), m.p. 277 °C; ν_{max}(KBr)/cm^{-1} 1650 (amide); δ_H[100 MHz, $(CD_3)_2SO$] 2.15 (3 H, s, Me) and 3.43 (2 H, s, CH_2) (Found: M^+ 169.030. $C_6H_7N_3OS$ requires *M*, 169.031).

3-*Methyl*-1,6-*dihydropyrazolo*[3,4-b]-1,4-*thiazine*-5(4H)-*one* S,S-*Dioxide* **15**.—To a stirred suspension of zinc (0.78 g) in acetic acid (11 cm^3) was added the nitro sulphone **12** (0.4 g) in acetic acid (1.5 cm^3). After 1 h, a further portion of zinc (0.3 g) was added. After 6 h, the residue after evaporation was partitioned between ethyl acetate and water, residual solids being removed by filtration. The washed ($NaHCO_3$ aq.), dried organic layer was evaporated and the residue chromatographed on silica, eluting with ethyl acetate–light petroleum (9:1) to give the amino sulphone (0.3 g) as an oil; ν_{max}(film)/cm^{-1} 3300 (NH), 1725 (C=O), 1320 and 1120 (SO_2); δ_H[60 MHz, $(CD_3)_2CO$] 1.23 (3 H, t), 2.3 (3 H, s) and 4.0–4.5 (6 H, m); *m/z* 247 (M^+). This material in toluene (25 cm^3) and dil. HCl (3 mol dm^{-3}; 3 drops) was heated under reflux overnight. The solid obtained on cooling was filtered and crystallised from ethanol to give the *cyclic sulphone* **15** (0.1 g, 34%), m.p. 225 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1670 (C=O) and 1320 and 1130 (SO_2); δ_H[60 MHz, $(CD_3)_2CO$] 2.5 (3 H, s, Me) and 4.5 (2 H, s, CH_2) (Found: C, 35.9; H, 3.65; N, 20.85; S, 15.8. $C_6H_7N_3O_3S$ requires C, 35.82; H, 3.48; N, 20.89; S, 15.92%).

Ethyl 3(5)-*Methyl*-4-*nitropyrazol*-5(3)-*ylaminoacetate* **16**.—Glycine ethyl ester hydrochloride (0.13 g) in ethanol (1.5 cm^3) was added to a solution of sodium (18 mg) in ethanol (1.5 cm^3). The filtered solution was treated with 3-methyl-1,4-dinitropyrazole **6** (0.1 g) in ether (1 cm^3) at 10 °C. After 1 h at 10 °C, the mixture was neutralised with acetic acid and evaporated. The residue was chromatographed on silica, eluting with ethyl acetate–light petroleum (1:3) to give the *glycine derivative* **16** (0.09 g, 68%), m.p. 125–127 °C; ν_{max}(KBr)/cm^{-1} 3330 and 3290 (NH) and 1740 (C=O); δ_H(100 MHz) 1.23 (3 H, t, CH_2CH_3), 2.43 (3 H, s, Me) and 3.83–4.26 (4 H, m, 2 × CH_2) (Found: C, 42.1; H, 5.3; N, 24.7. $C_8H_{12}N_4O_4$ requires C, 42.10; H, 5.26; N, 24.56%).

Ethyl 3(5)-*Methyl*-4-*nitropyrazol*-5(3)-*yl*-N-*methylaminoacetate* **17**.—Sarcosine ethyl ester hydrochloride (0.307 g) in ethanol (1.5 cm^3) was added to a solution of sodium (46 mg) in ethanol (3.5 cm^3). The filtered solution was treated with 3-methyl-1,4-dinitropyrazole **6** (0.344 g) in ether (1.5 cm^3) at room temperature. After 2 h, solvents were evaporated and the residue was partitioned between ethyl acetate and water. The dried organic layer was evaporated and the residue was crystallised from light petroleum–acetone to give the *sarcosine derivative* **17** (0.4 g, 82%), as pale yellow crystals, m.p. 94 °C; ν_{max}/cm^{-1} 1750 (C=O) and 1510 and 1350 (NO_2); δ_H(60 MHz) 1.3 (3 H, t, CH_2CH_3), 2.1 (3 H, s, C–Me), 3.1 (3 H, s, N–Me) and 4.0–4.45 (4 H, m, 2 × CH_2). (Found: C, 44.4; H, 5.8; N, 23.65. $C_9H_{14}N_4O_4$ requires C, 44.62; H, 5.78; N, 23.24%).

3,7-*Dimethyl*-6,7-*dihydro*-1H-*pyrazolo*[3,4-b]*pyrazin*-5(4H)-*one* **18**.—The nitro compound **17** (0.13 g) in ethanol (20 cm^3) was hydrogenated overnight, using palladium-on-charcoal (5%; 30 mg) as catalyst. Filtration, evaporation and chromatography of the residue on silica, eluting with ethyl acetate, gave *pyrazolopyrazine* **18**, (0.07 g, 78%), m.p. 210 °C (decomp.); ν_{max}/cm^{-1} 1650 (C=O); δ_H[100 MHz, $(CD_3)_2SO$] 2.05 (3 H, s, C–Me), 2.62 (3 H, s, N–Me) and 3.48 (2 H, s, CH_2) (Found: M^+, 166.083. $C_7H_{10}N_4O$ requires *M*, 166.085).

3(5)-(2-*Hydroxyethylidene*)-2-*oxopropyl*-5(3)-*methyl*-4-*nitropyrazole* **19**.—To a solution of sodium (23 mg) in methanol (3 cm^3) at 0 °C was added acetylacetone (0.3 cm^3), followed by 3-methyl-1,4-dinitropyrazole **6** (0.172 g) in ether (2 cm^3). The mixture was maintained for 30 min at 0 °C, neutralised with acetic acid and evaporated. The residue was partitioned between water and ethyl acetate. The dried organic layer was evaporated, and the solid residue was crystallised from ethyl acetate-light petroleum to give the *enol* **19** (0.16 g, 70%), m.p. 125–126 °C; ν_{max}(KBr)/cm^{-1} 1600 (enolised β-diketone); δ_H(60 MHz) 1.9 (6 H, s, 2Me) and 2.6 (3 H, s, Me) (Found: C 47.75; H, 4.9, N; 18.9. $C_9H_{11}N_3O_4$ requires C, 48.00; H, 4.88; N, 18.66%).

3(5)-*Methyl*-4-*nitro*-5(3)-(2-*oxopropyl*)*pyrazole* **20**.—To a solution of sodium (35 mg) in methanol (3 cm^3) was added acetylacetone (0.5 cm^3), followed by 3-methyl-1,4-dinitropyrazole **6** (0.172 g) in ether (2 cm^3). The mixture was heated under reflux for 15 min, neutralised with acetic acid and evaporated to dryness. The residue was partitioned between ethyl acetate and water, and the dried organic layer was evaporated to give a solid which on recrystallisation from ethyl acetate–light petroleum gave the *ketone* **20** (0.1 g, 54%), m.p. 162–163 °C; ν_{max}(KBr)/cm^{-1} 1710 (C=O) and 1500 and 1360 (NO_2); δ_H[60 MHz, $(CD_3)_2CO$] 2.24 (3 H, s, Me), 2.6 (3 H, s, Me) and 4.2 (2 H, s, CH_2); *m/z* 183 (M^+) (Found: C, 45.8; H, 4.85; N, 23.25. $C_7H_9N_3O_3$ requires C, 45.90; H, 4.92; N, 22.95%).

Ethyl 5(3)-*Methyl*-4-*nitropyrazol*-3(5)-*ylacetate* **21**.—To a stirred solution of sodium (23 mg) in ethanol (3 cm^3) was added ethyl acetoacetate (0.25 cm^3), followed by 3-methyl-1,4-dinitropyrazole **6** (0.172 g) in ether (2 cm^3). The mixture was kept at 40 °C for 3 h, neutralised with acetic acid and evaporated. Chromatography of the residue on silica, eluting with ether–light petroleum (7:3) gave the *nitro ester* **21** (0.105 g, 50%), m.p. 133–134 °C; ν_{max}(KBr)/cm^{-1} 1700 (C=O), 1485 and 1360 (NO_2); δ_H(60 MHz) 1.2 (3 H, t, CH_2CH_3), 2.5 (3 H, s, Me), 4.1 (2 H, s, CH_2) and 4.3 (2 H, q, CH_2CH_3); *m/z* 213 (M^+) (Found: C, 44.6; H, 4.95; N, 19.55. $C_8H_{11}N_3O_4$ requires C, 45.07; H, 5.16; N, 19.71%).

Dimethyl [3(5)-*Methyl*-4-*nitropyrazol*-5(3)-*yl*]*malonate* **22**.—To a stirred solution of sodium (35 mg) in methanol at 10 °C was added dimethyl malonate (0.34 cm^3), followed by 3-methyl-1,4-dinitropyrazole **6** (0.172 mg) in ether (2 cm^3). After 30 min at 10 °C, the solvent was evaporated, and the residue was chromatographed on silica, eluting with ethyl acetate–light petroleum (1:3) to yield the *malonate* **22** (0.14 g, 55%), m.p. 198 °C; ν_{max}(KBr)/cm^{-1} 1750 (C=O) 1500 and 1360 (NO_2); δ_H[60 MHz, $(CD_3)_2CO$] 2.7 (3 H, s, C–Me) and 3.8 (6 H, s, OMe); *m/z* 257 (M^+) (Found: C, 41.65; H, 4.15; N, 16.3. $C_9H_{11}N_3O_6$ requires C, 42.02; H, 4.28; N, 16.34%).

1-*Acetyl*-3-(2,3,5-*tri*-O-*acetyl*-β-D-*ribofuranosyl*)*pyrazole* **23**.—The tribenzyl ether **1** (9.08 g) in ethanol (170 cm^3) and cyclohexene (85 cm^3) was heated under reflux with palladium hydroxide-on-carbon (20%, 2.5 g) for 26 h. The cooled mixture was filtered through Celite, which was washed well with ethyl acetate. The organic layers were evaporated, and the resultant syrup was dissolved in acetic anhydride (100 cm^3) and pyridine (200 cm^3). The mixture was left for 18 h and then evaporated. The residue was partitioned between ethyl acetate and water. The dried organic layer was evaporated to give a residue which

was chromatographed on silica, with ether–light petroleum (1:1) as eluent, to give the *tetraacetyl compound* **23** (6.73 g, 95%) as a colourless syrup, $[\alpha]_D$ −9.9° (*c* 3.4 in chloroform); δ_H(200 MHz) 2.09, 2.11, 2.12 (each 3 H, s, OAc), 2.69 (3 H, s, NAc), 4.16–4.44 (3 H, m, 4′-H, 5′-H_2), 5.11 (1 H, d, $J_{1',2'}$ 5.46, 1′-H), 5.35 (1 H, app. t, *J ca.* 5.4, 3′-H), 5.51 (1 H, app. t, *J ca.* 5.4, 2′-H), 6.50 (1 H, d, $J_{4,5}$ 2.86, 4-H) and 8.23 (1 H, dd, $J_{5,6}$ 2.83, $J_{5,1'}$ 0.38, 5-H); δ_C(50 MHz) 20.41 (×2), 20.58, 21.45 (COMe), 63.49 (5′-C), 71.62, 74.41. 77.17, 79.59 (1′-4′-C), 108.01 (C-4), 129.13 (C-5), 154.29 (C-3) and 169.18, 169.44, 169.54 and 170.28 (4 × CO); *m/z* 369 (MH^+) and 326 ($M^+ - CH_2CO$) (Found: C, 52.3; H, 5.6; N, 7.9. $C_{16}H_{20}N_2O_8$ requires C, 52.17; H, 5.43; N, 7.61%).

1,4-*Dinitro*-3-(2,3,5-*tri*-O-*acetyl*-β-D-*ribofuranosyl*)*pyrazole* **2**.—Trifluoroacetic anhydride (2.94 g) was added dropwise with stirring, over 10 min to a stirred solution of the tetraacetyl compound **23** (1.472 g) and ammonium nitrate (1.12 g) in TFA (trifluoroacetic acid) (15 cm^3), maintained at 0 °C. The mixture was allowed to warm to room temperature, and, after 3 h, when TLC indicated complete reaction, the mixture was diluted with dichloromethane (50 cm^3) and washed rapidly with ice-cold water (2 × 50 cm^3). The residue after evaporation of the organic layers was chromatographed on silica, eluting with light petroleum–ether (1:1) to yield the dinitro compound **2** (1.585 g, 95%) with properties as previously reported.[3] Additional data: δ_H(200 MHz) 2.09, 2.11, 2.12 (each 3 H, s, OAc), 4.20 (1 H, dd, J_{gem} 11.7, $J_{5'a,4'}$ 4.50, 5′$_a$-H), 4.38 (1 H, m, 4′-H), 4.47 (1 H, dd, $J_{5'b,4'}$ 3.06, 5′$_b$-H), 5.41 (1 H, app. t, *J* 5.6, 3′-H), 5.61 (1 H, d, $J_{1',2'}$ 5.36, 1′-H), 5.69 (1 H, app. t, *J* 5.4, 2′-H) and 9.03 (1 H, s, 5-H); δ_C(50 MHz) 20.31, 20.38, 20.56 (COMe), 62.88 (C-5′), 71.38, 73.43, 75.59, 80.09 (C-1′,4′), 124.81 (C-5), 134.04, 144.47 (C-3 and -4) 169.49, 169.59 and 170.53 (COMe).

3(5)-*Methylthio*-4-*nitro*-5(3)-(2,3,5-*tri*-O-*acetyl*-β-D-*ribofuranosyl*)*pyrazole* **26**.—To a solution of sodium methanethiolate (0.210 g) in dry methanol (15 cm^3) was added dropwise with stirring over 10 min a solution of the dinitro compound **2** (0.832 g) in methanol (10 cm^3). After a further 0.5 h, the mixture was neutralised with acetic acid and evaporated. The residue was partitioned between ethyl acetate and water, and the dried organic layer evaporated to give a syrup that was chromatographed on silica, with light petroleum–ether (3:1) as eluent to give the *thioether* **26** (0.63 g, 76%) as a pale yellow foam; ν_{max}(KBr)/cm^{-1} 3400 (NH), 1750 (C=O), 1490 and 1365 (C–NO_2); δ_H(200 MHz) 2.07, 2.15, 2.20 (each 3 H, s, OAc), 2.55 (3 H, s, SMe), 4.23 (1 H, dd, *J* 12.2, 2.44, 5′$_a$-H), 4.41 (1 H, m, 4′-H), 4.58 (1 H, dd, *J* 12.2, 6.1, 5′$_b$-H), 5.17 (1 H, dd, $J_{3',4'}$ 7.20, $J_{3',4'}$ 7.20, $J_{3',2'}$ 4.97, 3′-H), 5.52 (1 H, dd, $J_{2',3'}$ 4.94, $J_{2',1'}$ 3.28, 2′-H) and 5.65 (1 H, d, *J* 3.27, 1′-H); *m/z* 417 (M^+), 357 (M^+ − AcOH) and 297 (M^+ − 2AcOH) (Found: M^+, 417.0860. $C_{15}H_{19}N_3O_9S$ requires *M*, 417.0841).

3(5)-*Methylsulphonyl*-4-*nitro*-5(3)-(2,3,5-*tri*-O-*acetyl*-β-D-*ribofuranosyl*)*pyrazole* **27**.—(*a*) A solution of sulphide **26** (0.41 g) and *m*-chloroperbenzoic acid (474 mg) in dichloromethane (25 cm^3) was stirred at room temperature for 16 h. The solution was washed with aqueous sodium hydrogen carbonate, dried and evaporated. Chromatography on silica, with light petroleum–ethyl acetate (5:1) as eluent, and crystallisation from ethyl acetate–light petroleum, gave the *sulphone* **27** (0.413 g, 92%), m.p. 104–108 °C; ν_{max}(KBr)/cm^{-1} 3500 (NH), 1745 (C=O), 1520 and 1370 (C–NO_2), 1325 and 1230 (SO_2); δ_H(200 MHz) 2.10, 2.13, 2.17 (each 3 H, s, OAc), 3.42 (3 H, s, SO_2Me), 4.25 (1 H, dd, J_{gem} 11.8, $J_{5'a,4}$ 2.35, 5′$_a$-H), 4.41 (1 H, dt, *J ca.* 6.5, 2.3, 4′-H), 4.53 (1 H, dd, $J_{5'b,4}$ 6.9, 5′$_b$-H), 5.19 (1 H, dd, $J_{3',4'}$ 6.37, $J_{3',2'}$ 5.35, 3′-H), 5.51 (1 H, app. t, *J ca.* 4.7, 2′-H) and 5.63 (1 H, d, *J* 4.27, 1′-H) (Found: C, 39.7; H, 4.3; N, 8.9. $C_{15}H_{19}N_3O_{11}S$ requires C, 40.08; H, 4.23; N, 9.35%) [Found: MH^+(FAB) 450.0812. $C_{15}H_{20}N_3O_{11}S$ requires *M*H, 450.0818].

(*b*) Methanesulphonyl chloride (1.146 g) was added dropwise to a stirred solution of $Na_2SO_3 \cdot 7H_2O$ (2.52 g) and $NaHCO_3$ (1.68 g) in water (15 cm^3) maintained at 0 °C. After 3 h, a solution of the dinitro compound **2** (0.932 g) in methanol was added dropwise. After 1 h, the mixture was extracted with ethyl acetate (3 × 25 cm^3), and the organic layer was processed as in (*a*) to give the *sulphone* **27** (0.584 g, 65%), with properties identical with those of material prepared in (*a*).

3(5)-*Methylsulphonyl*-4-*nitro*-5(3)-(β-D-*ribofuranosyl*)*pyrazole* **28**.—A solution of the sulphone **27** (0.36 g) in methanol (20 cm^3) saturated with ammonia was stirred at room temperature for 24 h. The residue after evaporation was dissolved in water (5 cm^3) and chromatographed on IRA-400 resin (acetate ion form), with aqueous acetic acid (0.1 mol dm^{-3}; 100 cm^3) as eluent. The product, after lyophilisation, was crystallised from ethanol–ether to give the *triol* **28** (0.21 g, 80%), m.p. 225–235 °C (decomp.), $[\alpha]_D$ +62.9° (*c* 0.35 in water); ν_{max}(KBr)/cm^{-1} 3570, 3480 (OH,NH), 1585 and 1345 (C–NO_2) and 1320 and 1145 (SO_2); δ_H[200 MHz, $(CD_3)_2SO$] 3.44 (3 H, s, SO_2Me), 3.62 (1 H, dd, *J* 12, 3, 5′$_a$-H), 3.75 (1 H, dd, *J* 12, 2, 5′$_b$-H), 3.8–4.2 (3 H, m, 2′,3′,4′-H), 5.1 (1 H, d, *J* 6, exchangeable with D_2O, OH), 5.29 (1 H, d, *J* 3.5, 1′-H) and 5.5 (1 H, d, *J* 6, exchangeable OH) [Found: MH^+ (FAB) 324.0527. $C_9H_{14}N_3O_8S$ requires *M*H, 324.0502].

4-*Amino*-3(5)-*methylsulphonyl*-5(3)-(β-D-*ribofuranosyl*)*pyrazole Hydrochloride* **29**·HCl.—The nitro compound **28** (0.20 g) and palladium-on-charcoal (10%, 0.1 g) in methanol (30 cm^3) were stirred under a hydrogen atmosphere for 3 h. After filtration and evaporation to dryness, the residue was dissolved in methanol (20 cm^3) into which was passed dry HCl gas. The solvent was evaporated, the residue was dissolved in water, and the mixture was lyophilised to give a solid. This solid was dissolved in a few drops of methanol, and ether was added to give a precipitate which, on filtration and drying, gave the *amine hydrochloride* **29**·HCl (0.19 g, 96%), m.p. 140–150 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3400br (OH, NH) and 1315 and 1130 (SO_2); δ_H(200 MHz, D_2O) 3.30 (3 H, s, SO_2Me), 3.66 (1 H, dd, *J* 12.5, 3.5, 5′$_a$-H), 3.71 (1 H, dd, *J* 12.5, 3.0, 5′$_b$-H), 4.1–4.25 (3 H, m, 2′-, 3′-, 4′-H) and 5.03 (1 H, d, *J* 6.84, 1′-H) [Found: MH^+ (FAB) 294.0748. $C_9H_{16}N_3O_6S$ requires *M*H, 294.0760].

Methyl [4-*Nitro*-3(5)-(2,3,5-*tri*-O-*acetyl*-β-D-*ribofuranosyl*)-*pyrazol*-5(3)-*ylthio*]*acetate* **30**.—To a solution of sodium methoxide (0.243 g) in methanol was added methyl mercaptoacetate (0.5 cm^3), and, after 1 h, the dinitro compound **2** (1.25 g) in methanol (10 cm^3) was added dropwise. After a further 1 h, the mixture was neutralised with acetic acid and evaporated. The residue was partitioned between ethyl acetate and water, and the material on evaporation of the dried organic layer was crystallised from ether to give the *thioether* **30** (1.0 g, 70%), m.p. 128–130 °C; ν_{max}(KBr)/cm^{-1} 3350 (NH), 1765 and 1735 (C=O) and 1565 and 1350 (C–NO_2); δ_H(200 MHz) 2.09, 2.13, 2.16 (each 3 H, s, OAc), 3.79 (3 H, s, OMe), 3.90 (2 H, AB system, *J* 15, –CH_2–), 4.28 (1 H, dd, J_{gem} 11.98, $J_{5'a,4'}$ 2.42, 5′$_a$-H), 4.37 (1 H, m, 4′-H), 4.52 (1 H, dd, $J_{5b',4}$ 5.49, 5′$_b$-H), 5.19 (1 H, dd, $J_{3',4'}$ 6.57, $J_{3',2'}$ 5.11, 3′-H), 5.46 (1 H, dd, $J_{2',1'}$ 3.93, 2′-H) and 5.61 (1 H, d, $J_{1',2'}$ 3.90, 1′-H); *m/z* 475 (M^+), 415 (M − HOAc)$^+$, 401 (M − CH_3CO_2Me)$^+$ (Found: C, 43.0; H, 4.5; N, 8.5. $C_{17}H_{21}N_3O_{11}S$ requires C, 42.94; H, 4.42; N, 8.84%).

Methyl 4-*Nitro*-3(5)-(2,3,5-*tri*-O-*acetyl*-β-D-*ribofuranosyl*)-*pyrazol*-5(3)-*ylsulphonylacetate* **31**.—A solution of sulphide **30** (0.90 g) and *m*-chloroperbenzoic acid (0.90 g) in dichloromethane (25 cm^3) was stirred at room temperature for 24 h. The

mixture was washed with aqueous sodium sulphite, dried and evaporated to give a residue which was chromatographed on silica gel, with ether as eluent to yield the *sulphone* **31** (0.91 g, 95%), m.p. 126–128 °C, $[\alpha]_D$ +78.2° (*c* 0.9 in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3330 (NH), 1770 and 1745 (C=O), 1520 and 1340 (C–NO_2), 1340 and 1115 (SO_2); δ_H(200 MHz) 2.12, 2.17, 2.20 (each 3 H, s, OAc), 3.78 (OMe), 4.23 (1 H, dd, J_{gem} 12.2, $J_{5'a,4'}$ 2.46, 5'$_a$-H), 4.44 (1 H, m, 4'-H), 4.61 (2 H, AB system, *J* 14.9, $-CH_2-$), 4.65 (1 H, dd, $J_{5'b,4'}$ 7.26, 5'$_b$-H), 5.21 (1 H, dd, $J_{3',4'}$ 6.06, $J_{3',2'}$ 5.21, 3'-H), 5.50 (1 H, app. t, *J ca.* 4.7, 2'-H), 5.67 (1 H, d, $J_{1',2'}$ 4.41, 1'-H) and 12.3 (1 H, br, s, NH) (Found: C, 40.0; H, 4.0; N, 7.9. $C_{17}H_{21}N_3O_{13}S$ requires C, 40.23; H, 4.14; N, 8.28%) [Found: MH^+ (FAB) 508.0856. $C_{17}H_{22}N_3O_{13}S$ requires *M*H, 508.0873].

3(5)-[(*Carbamoyl*)*methyl*]*sulphonyl*-4-*nitro*-5(3)-(β-D-*ribofuranosyl*)*pyrazole* **32**.—A solution of nitroester **31** (0.488 g) in dry methanol (20 cm^3) was saturated at 0 °C with ammonia, and the mixture was left at room temperature overnight. The residue after evaporation was dissolved in water (10 cm^3) and applied to a column of IRA-400 resin (acetate form) which was washed with water (100 cm^3) and eluted with aqueous acetic acid (2 mol dm^{-3}; 100 cm^3). The residue, after lyophilisation, was crystallised from ethanol–ethyl acetate to give the *amido triol* **32** (0.258 g, 73%), m.p. 206–212 °C (decomp.), $[\alpha]_D$ +67.0° (*c* 0.97 in water); ν_{max}(KBr)/cm^{-1} 3480, 3300br (NH, OH), 1660 and 1620 (amide), 1560 and 1340 (C–NO_2) and 1340 and 1130 (SO_2); δ_H(200 MHz, D_2O) 3.82 (1 H, dd, J_{gem} 12.7, $J_{5'a,4'}$ 3.3, 5'$_a$-H), 3.95–4.18 (3 H, m, 3'-, 4'-, 5'$_b$-H), 4.33 (1 H, dd, $J_{2',3'}$ 4.27, $J_{2',1'}$ 2.83, 2'-H) and 5.51 (1 H, d, $J_{1',2'}$ 2.80, 1'-H) [Found: MH^+ (FAB) 367.0544. $C_{10}H_{15}N_4O_9S$ requires *M*H 367.0560].

4-*Amino*-3(5)-[(*carbamoyl*)*sulphonyl*-5(3)-(β-D-*ribofuranosyl*)*pyrazole* **33**.—The nitro amide **32** (0.21 g) was hydrogenated in methanol (20 cm^3), using palladium-on-charcoal (5%; 0.2 g) as catalyst, for 3 h. Filtration, evaporation and crystallisation of the residue from ethanol–ethyl acetate yielded *amino amide* **33** (0.152 g, 79%), m.p. 170–176 °C; ν_{max}(KBr)/cm^{-1} 3450–3360 (OH, NH), 1670 and 1620 (amide), 1320 and 1120 (SO_2); δ_H(200 MHz, D_2O) 3.73 (1 H, dd, J_{gem} 12.5, $J_{5'a,4'}$ 4.04, 5'$_a$-H), 3.78 (1 H, dd, $J_{5'b,4'}$ 3.28, 5'$_b$-H), 4.07 (1 H, app. q, *J ca.* 3.5, 4'-H), 4.17 (1 H, dd, $J_{3',2'}$ 5.46, $J_{3',4'}$ 3.40, 3'-H), 4.24 (1 H, dd, $J_{2',1'}$ 7.31, 2'-H), 4.89 (1 H, d, *J* 7.31, 1'-H) [Found: MH^+ (FAB) 337.0812. $C_{10}H_{17}N_4O_7S$ requires *M*H, 337.0818].

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