C-Nucleoside Studies. Part 8.[1] Synthesis of 3-β-D-Arabinofuranosylpyrazole from D-Mannose

By **J. Grant Buchanan,* M. Encarnación Chacón-Fuertes,** and **Richard H. Wightman,** Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS

Treatment of 3(5)-(1,2:4,5-di-*O*-isopropylidene-D-*manno*-pentahydroxypentyl)pyrazole (6) with acetone and concentrated sulphuric acid caused isomerisation to 3(5)-(2,3:4,5-di-*O*-isopropylidene-D-*manno*-pentahydroxypentyl)pyrazole (10). Reaction with 1-fluoro-2,4-dinitrobenzene and triethylamine, and subsequent treatment with methanesulphonyl chloride afforded 1-(2,4-dinitrophenyl)-3-(1-*O*-methylsulphonyl-2,3:4,5-di-*O*-isopropylidene-D-*manno*-pentahydroxypentyl)pyrazole (14) in 71% overall yield. On treatment with dilute hydrochloric acid in dioxan, or, preferably, with boron trichloride in dichloromethane followed by methanolysis, (14) afforded 1-(2,4-dinitrophenyl)-3-(β-D-arabinofuranosyl)pyrazole (16) in up to 58% yield. Treatment of dinitrophenyl derivative (16) with methanolic ammonia gave an 86% yield of 3(5)-β-D-arabinofuranosylpyrazole (2).

THE discovery of the *C*-nucleoside antibiotics [2] has led to considerable interest in the synthesis [3] of the naturally occurring antibiotics, and of a wide range of analogues.

Previous papers in this series [4,5] have described syntheses of 3-(2,3,5-tri-*O*-benzyl-β-D-ribofuranosyl)pyrazole (1), related to the pyrazole-containing *C*-nucleosides formycin, formycin B, and pyrazofurin (pyrazomycin).[2] These syntheses used as starting materials suitably protected derivatives of D-ribose. We have also been interested in the development of complementary routes to *C*-nucleoside analogues in which all six carbon atoms of a hexose sugar are used in the formation of a *C*-pentofuranosyl heterocycle. In this paper we describe the application of this principle to the synthesis of 3(5)-β-D-arabinofuranosylpyrazole (2).

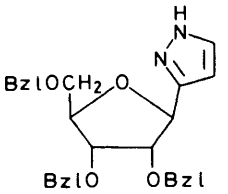
Reaction of 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (3) with ethynylmagnesium bromide, as described previously,[6] yielded 1,2-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-oct-1-ynitol (4) (65%) together with *ca.* 5% of the D-*glycero*-D-*galacto*-isomer. Oxidation of acetylenic diol (4), either pure or in admixture with its epimer, using activated manganese dioxide, produced the ketose (5),[6] which on treatment with hydrazine hydrate in ethanol gave the pyrazole (6) in 93% yield.[5]

When pyrazole (6) was treated with 0.5M-hydrochloric acid at reflux, the pentitol (7) could be isolated in 87% yield. We had hoped that by prolonged acid treatment it might be possible to obtain the arabinofuranosylpyrazole (2) directly, by ring closure from O-4′ to C-1′, relying on the ability of C-1′ to sustain a partial positive charge.[7,8] Such a reaction has been used in the synthesis of pseudouridine [9,10] by ring closure of a D-*altro*-pentitol intermediate. In the case of pseudouridine,[9,10] pyrazofurin,[11,12] and certain ribofuranosylbenzenes [13] the ring-closed products are themselves labile and undergo anomerisation under acidic conditions. No cyclised product could be detected after treatment of (7) with boiling 0.5M-hydrochloric acid for several hours. It seems that the basicity of the pyrazole ring, causing it to be protonated under these conditions, precludes the development of cationic character at C-1′. Similar resistance to 1′,4′-anhydride formation has been described [14] in derivatives (8) of 6-azauracil. When the configuration of the polyol side-chain was D-*gluco* or D-*galacto*, no ring closure took place. The D-*allo*- and D-*altro*-isomers gave only 2′,5′-anhydrides, a result in keeping with the known ease of cyclisation of polyols containing a D-*ribo*-configuration.[7,8,15] It may be noted in addition that (7) has the D-*manno*-configuration, one of those most unfavourable for cyclisation.[8,15] Sprinzl and Farkaš have obtained, as intermediates, some pyrazole derivatives of structure (9), but do not report any attempts at ring closure.[16]

In order to obtain arabinofuranose derivatives of type (2) it now appeared necessary to establish a good leaving group at C-1′. Our experiments in this direction are now described.

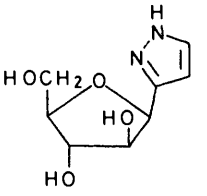
It is known [17,18] that isopropylidene acetals containing a *trans*-fused dioxolan ring (αT in the nomenclature of Barker and Bourne [17]) are thermodynamically more stable than *cis*-isomers (αC). In particular, L-rhamnitol (6-deoxy-L-mannitol) forms the 1,2:3,4-di-*O*-isopropylidene derivative [19] when treated with acetone, concentrated sulphuric acid, and anhydrous copper sulphate, *i.e.* under equilibrating conditions. When the pentitol (7) was treated with anhydrous acetone containing sulphuric acid, a di-*O*-isopropylidene derivative was formed in 81% yield which was isomeric with compound (6). The same isomer could be formed directly in 93% yield, by treatment of pyrazole (6) with acetone and sulphuric acid. Spectroscopic data support the formulation of this isomer as 3(5)-(2,3:4,5-di-*O*-isopropylidene-D-*manno*-pentahydroxypentyl)pyrazole (10), containing the more favourable *trans*-disubstituted dioxolan ring. We expected that conversion of alcohol (10) into a sulphonic ester, followed by removal of the isopropylidene groups by acid hydrolysis, should lead to cyclisation with formation of the arabinofuranosylpyrazole (2).[20,21] Treatment of pyrazole (10) with an equimolar amount of toluene-*p*-sulphonyl chloride led to the isolation of the *N*-*p*-tolylsulphonyl derivative (11) as a chromatographically and spectroscopically pure syrup in 60% yield. Subsequent acetylation afforded the syrupy acetate (12), whose ^{1}H n.m.r. spectrum showed another low field signal corresponding to H-1′. Equally, treatment of pyrazole (10) with an equivalent of methanesulphonyl chloride gave a mixture of sulphonic ester and

sulphonamide. We therefore decided to protect the pyrazole ring before sulphonylation.

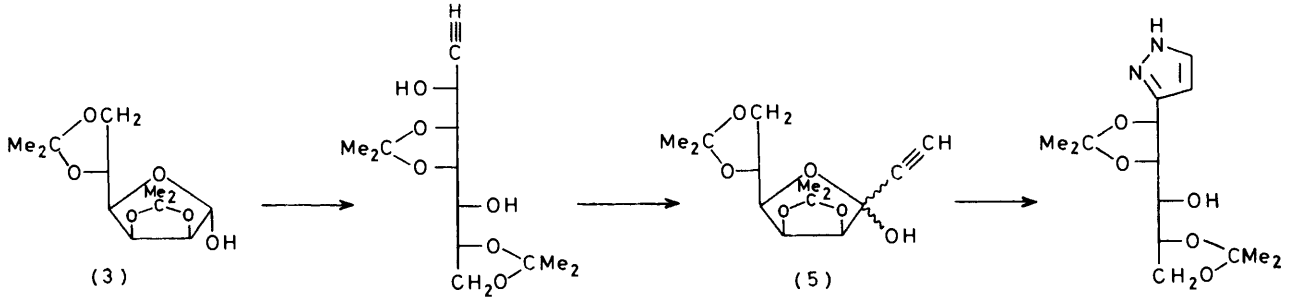


Bzl = $PhCH_2$

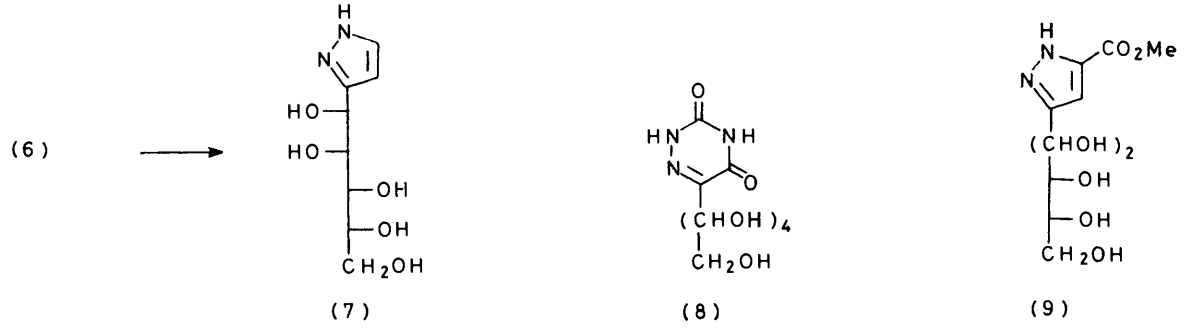
(1)



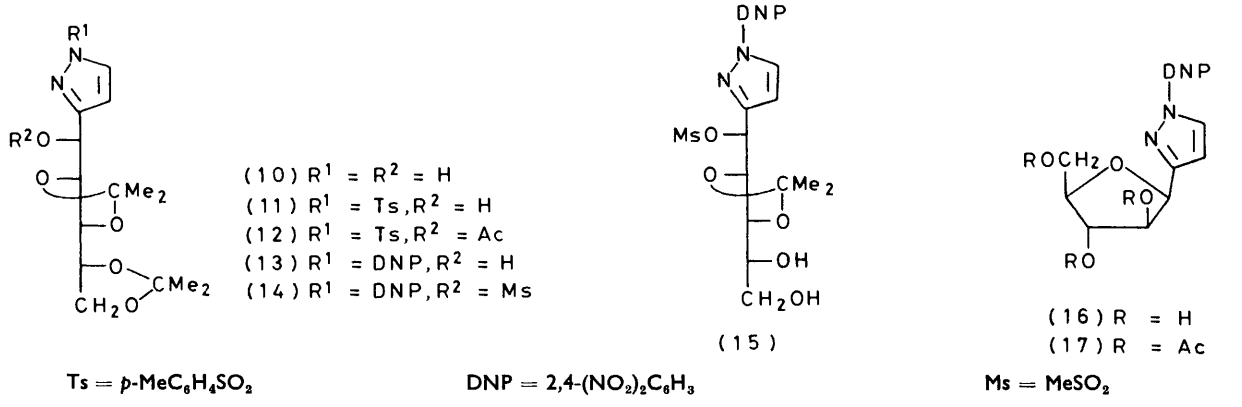
(2)



(3) (4) (5) (6)



(6) (7) (8) (9)



(10) $R^1 = R^2 = H$
(11) $R^1 = Ts, R^2 = H$
(12) $R^1 = Ts, R^2 = Ac$
(13) $R^1 = DNP, R^2 = H$
(14) $R^1 = DNP, R^2 = Ms$

(15)

(16) R = H
(17) R = Ac

Ts = p-$MeC_6H_4SO_2$ DNP = $2,4\text{-}(NO_2)_2C_6H_3$ Ms = $MeSO_2$

Crocker and Hall [22] found that 1-(2,4-dinitrophenyl)-pyrazole was converted into pyrazole and 2,4-dinitrophenol by chromatography on alumina and that it was also sensitive to sodium hydroxide or methoxide. Finar and Hurlock [23] used this method of degradation to identify a nitration product of 1-phenylpyrazole. Wilshire [24] later showed that pyrazole reacts with 1-fluoro-2,4-dinitrobenzene (FDNB) in the presence of triethylamine to form the 1-(2,4-dinitrophenyl)pyrazole (1-DNPpyrazole) in good yield, opening the way to the use of the DNP group as an acid-stable, alkali-labile protecting group for pyrazoles. A benzene solution of

pyrazole (10) was therefore treated with a slight excess of FDNB in the presence of triethylamine to yield the DNP derivative (13) in 89% yield. This was converted smoothly into the crystalline methanesulphonate (14) (81%) on treatment with methanesulphonyl chloride in pyridine. Wilshire [24] reports that 1-DNPimidazole is light sensitive. We have found it necessary to protect all our DNP compounds from light, particularly during chromatography.

The behaviour of sulphonate (14) with mineral acid was then studied. Treatment of the sulphonate with dioxan containing dilute hydrochloric acid gave, at room temperature, the mono-*O*-isopropylidene derivative (15). The preferential removal of the 4′,5′-*O*-isopropylidene group is likely, by comparison with the behaviour of other compounds in the mannitol series.[19,25,26] At reflux temperature removal of the second isopropylidene group was slow. A new triol was formed, which was isolated in 53% yield after chromatography. It was subsequently found that the same triol could be formed more conveniently, and in somewhat higher yield (58%), by treatment of methanesulphonate (14) with a large excess of boron trichloride in dichloromethane at low temperature,[27,28] followed by methanolysis of the resultant borate complexes. The product was readily purified by column chromatography.

Spectroscopic data for the triol support the structure 1-(2,4-dinitrophenyl)-3-(β-D-arabinofuranosyl)pyrazole (16), which is the expected structure if displacement of the mesyloxy group to form a furanoid ring [20,21] occurs with inversion of configuration. In particular, the ^{1}H n.m.r. spectrum ([$^2H_5$]pyridine; 100 MHz) showed a doublet for H-1′ at δ 4.77, with a coupling constant of 3.0 Hz. This value is nearer to that for a β-D-*arabino*-configuration,[29] rather than an α-D-*arabino*-orientation but the structure rests mainly on the mode of formation. Triol (16) readily formed a triacetate (17), the n.m.r. spectrum of which could be analysed in favour of a β-D-arabinofuranosyl structure (see Experimental section).

Although the hydrolysis of the 2′,3′-*O*-isopropylidene group in (14), having a *threo* (αT) configuration, would be expected to be slow, it is likely that extra stability in this case is due to the sulphonyloxy group on C-1′. It is well known, for example, that glycosides of sugar 2-sulphonates are only slowly hydrolysed under acidic conditions.[30]

When DNP derivative (16) was treated with a saturated solution of ammonia in methanol, 3-(β-D-arabinofuranosyl)pyrazole (2) could be isolated in 86% yield after ion-exchange chromatography.[31] This substance was non-crystalline, and a crystalline salt could not be prepared, but analytical and spectroscopic data are fully in accord with the assigned structure.

EXPERIMENTAL

The general methods used were as stated in Part 2.[32] Adsorption chromatography was carried out using Kieselgel H type 60 (Merck); an external pressure was applied to the top of columns. For t.l.c. precoated aluminium-backed plates [Kieselgel HF_{254} type 60 (Merck)] were used.

3(5)-(D-*manno-Pentahydroxypentyl*)*pyrazole* (7).— The pyrazole (6) [5] (1.5 g) in 0.5M aqueous hydrochloric acid (75 ml) was heated under reflux for 0.5 h. After neutralisation with lead carbonate, the solution was filtered and evaporated to yield a solid residue, which was recrystallised from ethanol to give the *pentitol* (7) (0.9 g, 87%), m.p. 173—175°, $[\alpha]_D$ −23.3° (*c* 0.43 in H_2O); $\nu_{max.}$ (KBr) 3 290 (OH, NH), and 1 530 cm^{-1} (C=N), δ(100 MHz; D_2O) 3.45—4.15 (5 H, m), 4.78 (1 H, d, *J* 6 Hz, H-1′), 6.36 (1 H, d, *J* 2 Hz, H-4), 7.60 [1 H, d, *J* 2 Hz, H-5(3)] (Found: C, 44.0; H, 6.4; N, 12.8. $C_8H_{14}N_2O_5$ requires C, 44.0; H, 6.5; N, 12.8%).

3(5)-(2,3:4,5-*Di*-O-*isopropylidene*-D-manno-*pentahydroxypentyl*)*pyrazole* (10).—(*a*) The pyrazole (6) [5] (8.0 g) was dissolved in anhydrous acetone (400 ml) containing sulphuric acid (5 ml) and the solution was left to stand at 20° for 5 h, when t.l.c. of a neutralised sample indicated only a trace of the starting material. The solution was neutralised with anhydrous sodium carbonate, filtered, and evaporated. The residue was crystallised from benzene–light petroleum to yield the *pyrazole* (10) (7.4 g, 93%), m.p. 127—129°, $[\alpha]_D$ +31.48° (*c* 0.8 in chloroform); $\nu_{max.}$ (KBr) 3 260 (OH, NH), 1 385, and 1 375 cm^{-1} (CMe_2); δ(100 MHz; $CDCl_3$) 1.33 (3 H, s), 1.36 (6 H, s), and 1.44 (3 H, s) (all CMe_2), 3.7—4.2 (6 H, m, becoming 5 H on D_2O exchange), 4.90 (1 H, d, *J* 6 Hz, H-1′), 6.25 (1 H, s, H-4), and 7.44 [1 H, s, H-5(3)] (Found: C, 56.2; H, 7.6; N, 9.3. $C_{14}H_{22}N_2O_5$ requires C, 56.4; H, 7.4; N, 9.4%).

(*b*) The pentitol (7) (0.20 g) was stirred with anhydrous acetone (10 ml) containing sulphuric acid (0.1 ml). A homogeneous solution was formed after 10 min, and after 4 h the solution was neutralised with anhydrous sodium carbonate, filtered, and evaporated. The solid residue was recrystallised from benzene–light petroleum to yield the pyrazole (10) (0.22 g, 81%), identical with the material described in (*a*).

Treatment of Pyrazole (10) *with Toluene*-p-*sulphonyl Chloride, and Acetylation of the Product.*—A solution of the pyrazole (10) (0.60 g) and toluene-*p*-sulphonyl chloride (0.38 g) in dry pyridine (3 ml) was allowed to stand at room temperature for 20 h. The product was isolated with chloroform and purified by chromatography on silica gel. Elution with ether afforded the *N*-tosyl derivative (11) as a chromatographically pure syrup (0.55 g, 60%); $\nu_{max.}$ (film) 3 440br (OH), 1 535 (C=N), 1 375—1 385 (CMe_2), 1 185 ($-SO_2-$), 3 065, 1 600, 1 500, and 815 cm^{-1} (aromatic); δ (100 MHz; $CDCl_3$) 1.16 (3 H, s), 1.28 (6 H, s), 1.40 (3 H, s) (all CMe_2), 2.36 (3 H, s, CH_3Ar), 3.42 (1 H, d, *J* 4 Hz, OH), 3.60—4.15 (5 H, m), 4.80 (1 H, dd, *J* 5 and 4 Hz, H-1′), 6.42 (1 H, d, *J* 2 Hz, H-4), 7.23 (2 H, d, *J* 9 Hz, Ar), 7.78 (2 H, d, *J* 9 Hz, Ar), 7.96 (1 H, d, *J* 2 Hz, H-5).

This material (0.1 g) was treated with acetic anhydride (0.2 ml) in dry pyridine (1 ml) at room temperature. The solution was evaporated *in vacuo*, and pyridine was removed by evaporation of ethanol from the residue, yielding the acetate (12) as a syrup: δ (100 MHz; $CDCl_3$) 0.88, 1.30, 1.34, 1.48 (each 3 H, s, CMe_2), 2.08 (3 H, s, AcO), 2.40 (3 H, s, $ArCH_3$), 3.55—4.05 (4 H, m), 4.24 (1 H, dd, *J* 8 and 3 Hz, H-2′), 6.04 (1 H, d, *J* 3 Hz, H-1′), 6.40 (1 H, d, *J* 2 Hz, H-4), 7.24 (2 H, d, *J* 8 Hz, Ar), 7.80 (2 H, d, *J* 8 Hz, Ar), 7.96 (1 H, d, *J* 2 Hz, H-5).

1-(2,4-*Dinitrophenyl*)-3-(2,3:4,5-*di*-O-*isopropylidene*-D-manno-*pentahydroxypentyl*)*pyrazole* (13).—A solution of the

pyrazole (10) (5.0 g) and 2,4-dinitrofluorobenzene (3.4 g) in benzene (250 ml) containing triethylamine (3.5 ml) was heated under reflux for 2 h. Evaporation left a dark yellow syrup; chromatography on silica gel, and elution with benzene–ethyl acetate (2 : 1) have the *DNP derivative* (13) (6.9 g, 89%), as a yellow syrup, $[\alpha]_D$ +21.6° (*c* 0.88 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 440br (OH), 1 540 (C=N), 1 555 and 1 350 ($-NO_2$), 1 385 and 1 375 (CMe_2), 3 040, 3 060, 1 600, and 1 505 cm^{-1} (aromatic); δ (100 MHz; $CDCl_3$) 1.35, 1.37, 1.39, 1.45 (each 3 H, s, CMe_2), 3.50 (1 H, d, *J* 4 Hz, exchangeable with D_2O, OH), 3.7—4.2 (5 H, m), 4.80 (1 H, dd, *J* 6 and 4 Hz, becoming d, *J* 6 Hz on D_2O exchange, H-1′), 6.60 (1 H, d, *J* 2 Hz, H-4), 7.52 (1 H, d, *J* 9 Hz, H-6″), 7.63 (1 H, d, *J* 2 Hz, H-5), 8.35 (1 H, dd, *J* 9 and 2 Hz, H-5″), and 8.52 (1 H, d, *J* 2 Hz, H-3″) (Found: C, 51.6; H, 5.2; N, 12.1. $C_{20}H_{24}N_4O_9$ requires C, 51.7; H, 5.2; N, 12.1%).

1-(2,4-*Dinitrophenyl*)-3-(1-O-*methylsulphonyl*-2,3:4,5-*di*-O-*isopropylidene*-D-manno-*pentahydroxypentyl*)*pyrazole* (14).—To a stirred solution of the DNPpyrazole (10) (5.86 g) in dry pyridine (60 ml) was added dropwise at room temperature methanesulphonyl chloride (3.25 ml, 3 mol. equiv.), and the mixture was kept overnight. After addition of water, the product was isolated with chloroform. Chromatography on silica gel, elution with benzene–ethyl acetate, and recrystallisation of the resultant yellow solid from ethanol gave the *methylsulphonyl derivative* (14) (5.5 g, 81%), m.p. 136—138°, $[\alpha]_D$ +21.2° (*c* 1.4 in $CHCl_3$); $\nu_{max.}$ (KBr) 1 555 ($-NO_2$), 1 540 (C=N), 1 390, 1 380 and 1 375 (all CMe_2), 1 350 ($-SO_2-$), 3 060, 3 050, 3 035, 1 600, and 1 510 cm^{-1} (aromatic); δ (100 MHz; $CDCl_3$) 1.20, 1.32, 1.37, 1.43 (each 3 H, s, CMe_2), 2.88 (3 H, s, $MeSO_2$), 3.63 (1 H, t, *J* 7 Hz, H-3′), 3.8—4.2 (3 H, m), 4.43 (1 H, dd, *J* 7 and 3.5 Hz, H-2′), 5.83 (1 H, d, *J* 3.5 Hz, H-1′), 6.75 (1 H, d, *J* 2 Hz, H-4), 7.68 (1 H, d, *J* 8 Hz, H-6″), 7.74 (1 H, d, H-5), 8.42 (1 H, dd, *J* 8 and 2 Hz, H-5″), and 8.56 (1 H, d, *J* 2 Hz, H-3″) (Found: C, 46.3; H, 4.9; N, 10.4; S, 5.9. $C_{21}H_{26}N_4SO_{11}$ requires C, 46.5; H, 4.8; N, 10.3; S, 5.9%).

Treatment of Pyrazole (14) *with Mild Acid*.—A solution of pyrazole (14) (0.25 g) in dioxan (10 ml) containing 0.5M aqueous hydrochloric acid (0.25 ml) was maintained at room temperature for 48 h. After neutralisation with lead carbonate, the filtered solution was extracted with chloroform. Evaporation of the dried chloroform extracts yielded a syrup which was chromatographed on silica gel, eluting with ethyl acetate to yield the monoisopropylidene compound (15) (0.22 g, 95%) as a pale yellow foam, δ (100 MHz; $CDCl_3$) 1.20, 1.27 (each 3 H, s, CMe_2), 2.85 (3 H, s, SO_2Me), 3.50—3.80 (m), 4.45 (1 H, m), 5.80 (1 H, s, *J* 4 Hz, H-1′), 6.70 (1 H, d, *J* 2 Hz, H-4), 7.68 (1 H, d, *J* 8 Hz, H-6″), 7.75 (1 H, d, *J* 2 Hz, H-5), 8.40 (1 H, dd, *J* 8 and 2 Hz, H-5″), and 8.52 (1 H, d, *J* 2 Hz, H-3″).

1-(2,4-*Dinitrophenyl*-3-(β-D-*arabinofuranosyl*)*pyrazole* (16). —(*a*) A solution of pyrazole (14) (125 mg) in dioxan (5 ml) containing 0.5M-hydrochloric acid (0.12 ml) was heated at 100° for 5 h. The cooled solution was neutralised with lead carbonate, filtered, and evaporated to give a yellow syrup. This was purified by preparative layer chromatography eluting with ethyl acetate–isopropanol (7 : 1) to yield the arabinofuranosylpyrazole (16) (45 mg, 53%) as a syrup identical (t.l.c., i.r.) with the material prepared in (*b*) below.

(*b*) A cooled solution of pyrazole (14) (2.5 g) in dichloromethane (10 ml) was slowly added by syringe through a septum to a stirred solution of boron trichloride (25 g) in methylene chloride (200 ml) at −78°. The mixture was maintained at −78° for 2 h, the cooling bath was removed, and methanol–dichloromethane (1 : 1, 200 ml) was added dropwise whilst the mixture was allowed to warm to room temperature. The solvents were evaporated, and the residue co-evaporated several times with methanol. The resultant syrup was chromatographed on silica gel, eluting with ethyl acetate–propan-2-ol (7 : 1) to yield the *arabinofuranosylpyrazole* (16) (0.98 g, 58%) as a yellow syrup, $[\alpha]_D$ +84.3° (*c* 0.98 in EtOH); $\nu_{max.}$ (KBr) 3 400br (OH), 1 600 and 1 505 (aromatic), 1 540, and 1 347 cm^{-1} ($-NO_2$); δ (100 MHz; [$^2H_5$]pyridine) 4.1—4.3 (2 H, m), 4.4—4.7 (2 H, m), 4.77 (1 H, d, *J* 3 Hz, H-1′), 4.90 (1 H, s), 6.58 (3 H, s, exchangeable with D_2O, OH), 7.08 (1 H, d, *J* 2.5 Hz, H-4), 7.80 (1 H, d, *J* 9 Hz, H-6″), 8.18 [1 H, d, *J* 2.5 Hz, H-5(3)], 8.38 (1 H, dd, *J* 9 and 2 Hz, H-5″), and 8.81 (1 H, d, *J* 2 Hz, H-3″) (Found: C, 45.7; H, 4.1; N, 15.1. $C_{14}H_{11}N_4O_8$ requires C, 45.9; H, 3.9; N, 15.3%).

1-(2,4-*Dinitrophenyl*)-3-(2,3,5-*tri*-O-*acetyl*-β-D-*arabinofuranosyl*)*pyrazole* (17).—The arabinofuranosylpyrazole (16) (250 mg) was allowed to stand in pyridine (2 ml) and acetic anhydride (1.5 ml) overnight, and the product was then isolated with chloroform. Chromatography of the resultant syrup (330 mg) on silica gel, eluting with benzene–ethyl acetate (2 : 1) yielded the *triacetate* (270 mg, 82%) as a yellow syrup. Attempted crystallisation of this material from methanol–water gave a yellow amorphous powder, m.p. 60°, $[\alpha]_D$ +52.4° (*c* 1.14 in $CHCl_3$), $\nu_{max.}$ (KBr) 1 750 (C=O), 1 540 and 1 350 (NO_2), 3 060, 3 040, 1 600, and 1 505 cm^{-1} (aromatic); δ (100 MHz; $CDCl_3$) 1.98, 2.10, 2.13 (each 3 H, s, AcO), 4.1—4.5 (3 H, m, H-4′, -5′), 5.15 (1 H, dd, $J_{3',4'}$ 2.7, $J_{2'3'}$, 1.2 Hz, H-3′), 5.32 (1 H, d, *J* 4 Hz, H-1′), 5.45 (1 H, dd, $J_{1'2'}$, 1.2 Hz, H-2′), 6.64 (1 H, d, *J* 2.2 Hz, H-4), 7.76 (1 H, d, *J* 2.2 Hz, H-5), 7.84 (1 H, d, *J* 9 Hz, H-6″), 8.50 (1 H, dd, *J* 9 and 2.5 Hz, H-5″), and 8.68 (1 H, d, *J* 2.5 Hz, H-3″) (Found: C, 49.0; H, 4.1; N, 11.7. $C_{20}H_{20}N_4O_{11}$ requires C, 48.8; H, 4.1; N, 11.4%).

3(5)-β-D-*Arabinofuranosylpyrazole* (2).—A solution of DNPpyrazole (16) (0.98 g) in saturated methanolic ammonia (20 ml) was stirred at room temperature for 35 h and then evaporated to dryness. The residue was partitioned between water and ethyl acetate. The syrup (0.51 g) obtained on evaporation of the aqueous phase was applied to a column (20 ml) of freshly regenerated Amberlite IR-400 (HO^-) resin. The column was eluted with a gradient of 10—50% methanol in water to yield 3(5)-β-D-*arabinofuranosylpyrazole* (2) (0.46 g, 86%) as a syrup, homogenous by t.l.c. [ethyl acetate–propan-2-ol–water (2 : 2 : 1)], $[\alpha]_D$ +61.7° (*c* 0.87 in water); $\nu_{max.}$ (film) 3 340 cm^{-1} (OH, NH); δ (100 MHz; D_2O) 3.8—4.1 (3 H, m), 4.2—4.4 (2 H, m), 5.34 (1 H, d, *J* 4.2 Hz, H-1′), 6.56 (1 H, d, *J* 2.2 Hz, H-4), and 7.83 [1 H, d, *J* 2.2 Hz, H-5(3)]; *m/e* 200 (*M*), 169 (*M* − CH_2OH), and 97 (heterocycle + 30) (Found: C, 47.8; H, 6.3; N, 14.0. $C_8H_{12}N_2O_4$ requires C, 48.0; H, 6.0; N, 14.0%).

We thank the Spanish Science Research Council and Ministry of Education and Science for a Fellowship (to M. E. C.-F.).

[8/259 *Received*, 14*th February*, 1978]

REFERENCES

[1] Part 7, J. G. Buchanan, A. R. Edgar, M. J. Power, and C. T. Shanks, *J.C.S. Perkin I*, 1979, 225.

[2] R. J. Suhadolnik, 'Nucleoside Antibiotics,' Wiley–Interscience, New York, 1970.

[3] S. Hanessian and A. G. Pernet, *Adv. Carbohydrate Chem. Biochem.*, 1976, **33**, 111.
[4] J. G. Buchanan, A. R. Edgar, M. J. Power, and G. C. Williams, *Carbohydrate Res.*, 1977, **55**, 225.
[5] J. G. Buchanan, A. D. Dunn, A. R. Edgar, R. J. Hutchison, M. J. Power, and G. C. Williams, *J.C.S. Perkin I*, 1977, 1786.
[6] J. G. Buchanan, A. D. Dunn, and A. R. Edgar, *J.C.S. Perkin I*, 1976, 68.
[7] B. G. Hudson and R. Barker, *J. Org. Chem.*, 1967, **32**, 3650.
[8] R. Barker, *J. Org. Chem.*, 1970, **35**, 461.
[9] D. M. Brown, M. G. Burdon, and R. F. Slatcher, *J. Chem. Soc.* (*C*), 1968, 1051.
[10] U. Lerch, M. G. Burdon, and J. G. Moffatt, *J. Org. Chem.*, 1971, **36**, 1507.
[11] R. L. Hamill, personal communication.
[12] S. De Bernardo and M. Weigele, *J. Org. Chem.*, 1976, **41**, 287.
[13] L. Kalvoda, *Coll. Czech. Chem. Comm.*, 1973, **38**, 1679.
[14] M. Bobek, J. Farkaš, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1969, **34**, 1673.
[15] J. Baddiley, J. G. Buchanan, and B. Carss, *J. Chem. Soc.*, 1957, 4138
[16] M. Sprinzl and J. Farkaš, *Coll. Czech. Chem. Comm.*, 1967, **32**, 3787.
[17] S. A. Barker and E. J. Bourne, *J. Chem. Soc.*, 1952, 905; *Adv. Carbohydrate Chem.*, 1952, **7**, 137.
[18] J. A. Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 1.
[19] M. A. Bukhari, A. B. Foster, J. Lehmann, and J. M. Webber, *J. Chem. Soc.*, 1963, 2287.
[20] J. Defaye and V. Ratovelomanana, *Carbohydrate Res.*, 1971, **17**, 57.
[21] T. Ogawa, M. Matsui, H. Ohrui, H. Kuzuhara, and S. Emoto, *Agric. and Biol. Chem.* (*Japan*), 1972, **36**, 1449.
[22] H. P. Crocker and R. H. Hall, *J. Chem. Soc.*, 1955, 4489.
[23] I. L. Finar and R. J. Hurlock, *J. Chem. Soc.*, 1957, 3024.
[24] J. F. K. Wilshire, *Austral. J. Chem.*, 1966, **19**, 1935; 1967, **20**, 1663.
[25] L. F. Wiggins, *J. Chem. Soc.*, 1946, 13.
[26] N. Baggett, K. W. Buck, A. B. Foster, R. Jefferis, B. H. Rees, and J. M. Webber, *J. Chem. Soc.*, 1965, 3382.
[27] T. G. Bonner and N. M. Saville, *J. Chem. Soc.*, 1960, 2851.
[28] G. Trummlitz, D. B. Repke, and J. G. Moffatt, *J. Org. Chem.*, 1975, **40**, 3352.
[29] E. M. Acton, A. N. Fujiwara, L. Goodman, and D. W. Henry, *Carbohydrate Res.*, 1974, **33**, 135.
[30] H. B. Wood, jun., and H. G. Fletcher, jun., *J. Amer. Chem. Soc.*, 1958, **80**, 5242.
[31] C. A. Dekker, *J. Amer. Chem. Soc.*, 1965, **87**, 4027.
[32] J. G. Buchanan, A. D. Dunn, and A. R. Edgar, *J.C.S. Perkin I*, 1975, 1191.