# PREPARATION OF NEW OPTICALLY ACTIVE FURANOIDS CONTAINING VARIOUS AZA-HETEROCYCLIC MOIETIES

Ali Werfeli[a1], Jan Cejka[b1], Ondrej Klecan[a], Bohumil Kratochvil[b2,*] and Josef Kuthan[a2,*]

[a] *Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic; e-mail:* [1] *gebrila@vscht.cz,* [2] *kuthanj@vscht.cz*

[b] *Department of Solid State Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic; e-mail:* [1] *jan.cejka@vscht.cz,* [2] *bohumil.kratochvil@vscht.cz*

The aldehyde **2** prepared from [5-(2,3-*O*-isopropylidene-β-D-erythrofuranosyl)-2-methylfuran-3-yl]-methanol (**1**) was converted to *E,Z*-oximes **3**, **4** and imine derivative **5** by the reaction with hydroxyl-amine and pyridin-2-yl amine, respectively. The Knoevenagel reaction with malonic acid afforded exclusively the 3-substituted acrylic acid **6** while corresponding Hantzsch 1,4-dihydropyridines **7** and **8** were obtained by the reaction of aldehyde **2** with ethyl acetoacetate or acetylacetone and ammonia. 3,5-Dicyano-1,4-dihydropyridine derivative **9** was isolated only in forms of hydrates after the reaction of aldehyde **2** with 3-aminocrotonitrile. 1,4-Dihydropyridines **7** and **9** were aromatized to corresponding pyridines **10** and **11**. Isoxazoles **12**, **13** and isoxazolines **14**, **15** were prepared by 1,3-cycloaddition of appropriate dienophiles to a nitrile oxide generated from aldoximes **3**, **4**. Ferricyanide oxidation of 1-{[5-(2,3-*O*-isopropylidene-β-D-erythrofuranosyl)-2-methylfuran-3-yl]methyl}-pyridinium chloride (**17a**), -3-methylpyridinium chloride (**19a**) and the corresponding isoquinolinium chloride **21a** gave optically active pyridin-2(1*H*)-ones **22**, **23** and 2*H*-isoquinolone derivative **24** while the procedure with 2-methylpyridinium salt **18a** and 4-methylpyridinium salt **20a** led to complex mixtures of products. Reaction of 2,4,6-triphenylpyrylium perchlorate with furanoid amine **26** afforded a mixture of major 2,4,6-triphenylpyridine, minor pyridinium perchlorate **25** and primary alcohol **1**. The absolute configuration of the studied compounds has been confirmed by X-ray analysis of the Schiff base **5**.
**Key words:** Furans; 1,4-Dihydropyridines; Isoxazoles; Pyridin-2(1*H*)-ones; Ferricyanide oxidation; Gabriel synthesis; Schiff bases; X-Ray diffraction; Absolute configuration.

Achiral or racemic furan derivatives rank among compounds exhibiting a very broad exploitation in the field of biologically active substances[1–3]. On the other hand, a little is known of the application of optically active furanoids although they may interact more selectively with natural chiral receptors. In addition to the furan systems, some

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* The author to whom correspondence should be addressed.

other heterocyclic moieties like aminopyridines[4,5], 1,4-dihydropyridines[6–8] and isoxazoles[9] often cause very specific responses in various living organisms. Some specific biological activities of heterocyclic types like quaternary pyridinium salts[10,11], pyridones[12], pyrroles[13,14] and imidazo[1,2-*a*]pyridines[15,16] have been well documented and sometimes may be attributed to their structure similarities to nucleic acid bases. An idea to combine the two potentially active heterocyclic subsystems within a molecule might open a novel insight into the role of both chiral and achiral parts, namely into an interrelation between the expected selectivity associated with absolute configuration of a given furanoid and conservation of typical biological activities conditioned by an additional nitrogen heterocyclic fragment.

In this communication, an initial step towards verification of the hypothesis is realized by attempted syntheses of some model optically active furanoids containing selected nitrogen heterocyclic moieties. The presented research has been also stimulated by the findings[17] that some of recently prepared[18] optical active furanoids exhibit virostatic activities.
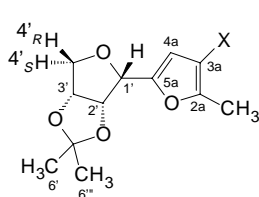
Absolute configuration of all investigated compounds should be related to that of D-glucose as the starting compound for preparation of key precursors easily obtainable using alkyl acetoacetates as the second partners[19]. The primary alcohol **1** prepared from the appropriate furanoid esters with lithium aluminium hydride[18,20] offers to be converted to more selectively reactive synthons capable of heterocyclizations. Hence, the prior $CH_2OH \rightarrow -CH=O$ activation of the starting compound **1** by its conversion to aldehyde **2** has been attempted. In addition, one of the synthesized derivatives has been investigated by X-ray measurement in order to confirm expected conservation of absolute configuration of prepared compounds with respect to that of the starting compounds[21].

Because of the decision to ketal protection of the 2′,3′-vicinal hydroxy groups in investigated compounds, all operations were performed in neutral or alkali medium. Thus, a special pyridinium chlorochromate reagent[22] adsorbed on alumina was prepared and used for the oxidation of primary alcohol **1** to corresponding aldehyde **2** without any configuration change in the parent molecular skeleton. The advantageous heterogeneous procedure makes it possible to separate a solution of **2** by simply filtration.

To test the reactivity of aldehyde **2** towards nitrogen nucleophiles the reactions with hydroxylamine and 2-aminopyridine have been attempted. The former reagent afforded a mixture of *E*- and *Z*-oximes **3** and **4** while the expected *E* Schiff base **5** was obtained in the latter case. One of the oximes forms an oil and the second isomer as well as the imine **5** were prepared as crystalline substances.

The reactivity of aldehyde **2** towards carbon nucleophiles has been tested by the Knoevenagel reaction with malonic acid giving the expected acrylic acid *E* derivative **6** in 65% yield. The successful conversion has prompted us to attempt the Hantzsch-type 1,4-dihydropyridine syntheses with aldehyde **2**. The standard cyclocondensation proce-

dure[23,24] using ethyl acetoacetate and ammonia gave the expected optically active diester **7** while the analogous treatment with acetylacetone afforded crystalline diacetyl derivative **8**. A similar 1,4-dihydropyridine heterocyclization using 3-aminocrotonitrile[25] has only led to hydrates instead of the expected free 3,5-dicyano-1,4-dihydropyridine derivative **9**.
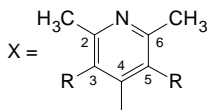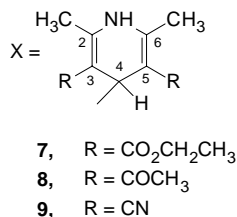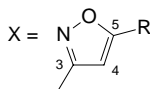


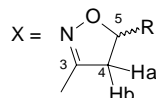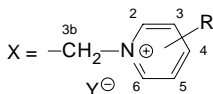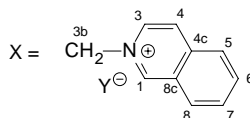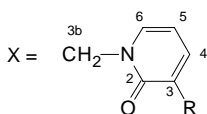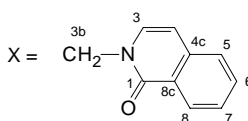The NMR spectra of the hydrates are almost identical. The lower-melting hydrate is more labile and can be transformed to the higher-melting form by heating. All attempts to obtain water-free 1,4-dihydropyridine **9** at enhanced temperatures *in vacuo* (over

$P_4O_{10}$) were unsuccessful because of a substrate decomposition. Consideration of possible molecular models suggests that both hydrates may contain a water molecule hydrogen-bonded between one of the cyano nitrogens and the heterocyclic oxygen of the tetrahydrofuran ring[17].

To support the assigned structures of amorphous diester **7** and hydrated dinitrile **9** both 1,4-dihydropyridine derivatives were heteroaromatized with the pyridinium chlorochromate reagent[26] to crystalline pyridine derivatives **10** and **11** in 80 and 85% yields.

The 1,3-dipolar cycloaddition[27] has been used to functionalize the parent furanoid skeleton with isoxazole and isoxazoline moieties. Thus, a mixture of aldoximes **3** and **4** was converted with sodium hypochlorite and triethylamine[28] to corresponding nitrile oxide which was *in situ* generated to react with appropriate dipolarophiles. In all cases optically active adducts were isolated. Phenylacetylene and propargyl alcohol gave isoxazole derivatives **12** and **13** while allyl alcohol and acrylonitrile isoxazolines **14** and **15**. As may be expected[27], the dipolarophiles having the $CH_2OH$ group afforded somewhat higher yields of products **13** and **14** (83 and 82%). Oxazolines **14** and **15** were evidently obtained as mixtures of diastereoisomers. This suggestion can be confirmed by some NMR data. Thus, a multiplet at δ 4.77 assigned to the H-5 proton consists of two overlapping quintets in the $^1H$ NMR spectrum of compound **14** and signals at δ 80.3 and 108.3 assigned to the C-3′ and C-4′ carbons are near doublets in the $^{13}C$ NMR spectrum of compound **15**. A similar formation of diastereoisomeric adducts has been described with chiral oximes[29] or chiral dipolarophiles[30,31].

Preparation of optically active quaternary aza-heterocyclic salts was the next step of the experiments. Because nicotinamide was found to be successfully quaternized with 3-chloromethyl furanoid **16** to corresponding NADH model[18], the same procedure could be applied to other pyridine-like nucleophiles. Thus, the Menshutkin reaction of chloromethyl derivative **16** with pyridine and its methyl derivatives in nitromethane at room temperature yielded 71–85% of corresponding optically active quaternary chlorides **17a**–**20a** as hygroscopic substances which were characterized by conversion to crystalline tetraphenylborates **17b**–**20b**. Analogously, isoquinoline with reagent **16** gave chloride **21a** and tetraphenylborate **21b**, while quinoline and acridine afforded only traces of quaternary salts under the same conditions.

All quaternary chlorides **17a**–**21a** are easily but not too selectively oxidizable by the standard procedure[32,33] (Decker oxidation) with potassium ferricyanide and potassium hydroxide but individual products were isolated from the reaction mixtures only in the case of the starting salts **17a**, **19a** and **21a**. Thus, optically active pyridin-2(1*H*)-one derivatives **22** and **23** were obtained in 30 and 38% yields as pure oily substances and similar isoquinolin-1(2*H*)-one **24** was isolated even in 50% yield. The limited success may be associated with the known sensitivity of furan derivatives to oxidizing agents[34].

In connection with an idea of trying the extended Decker oxidation[35], it has been attempted to prepare quaternary perchlorate **25** by a general procedure[36] from 2,4,6-tri-phenylpyrylium perchlorate and optically active primary amine **26**. Compound **26** was prepared by the Gabriel synthesis starting from chloromethyl derivative **16** and potassium phthalimide *via* crystalline *N*-phthalimido intermediate **27** and by final hydrazinolysis. However, it has been found out that the reaction of the mentioned perchlorate with amine **26** resulted in a complex reaction mixture of major 2,4,6-triphenylpyridine, minor perchlorates **25**, **28** and hydroxymethyl derivative **1** from which only the major product was easily isolable. This unexpected behaviour of pyrylium salts to a primary amine has not yet been reported in the current literature[36,37] but optically active furanoids do not seem to be suitable compounds for the study of the new transformation. Hence, the problem is being under study using simpler achiral amines[38].

Physico-chemical properties of the prepared optically active furanoids are given in Table I. Exhaustive assignments of proton and carbon signals in the $^1$H and $^{13}$C NMR spectra of the prepared compounds are shown in Tables II and III for the parent skeleton and in Experimental part for different functionalities in the position 3a. The *Z* configuration of the crystalline aldoxime **4** has been suggested on the basis of the unusually down-field shifted H-4a signal (Table II) probably due to an anisotropic interaction between the furan ring and the CH=NOH functionality. A restricted rotation around the C3a–C4 bond in the molecules of 1,4-dihydropyridines **7**, **8** and pyridine derivative **10** follows from observation of magnetic nonequivalence of the pairs of symmetrical ring carbons and hydrogen protons in the NMR spectra (see Experimental).

Although NMR arguments in favour of the *trans* configuration at the C1′–C2′ bond in all furanoids obtained from D-glucose have been reported[21] the absolute configuration has been additionally proved by X-ray analysis of the Schiff base **5**. The results are given in Fig. 1, Tables IV and V. The key conclusion is that the relative configuration at the C1′-C2′ bond (in Fig. 1, the C15–C22 bond) is really *trans* and is important considering the easily epimerizable asymmetric centre C1′. In addition, the usual *E*
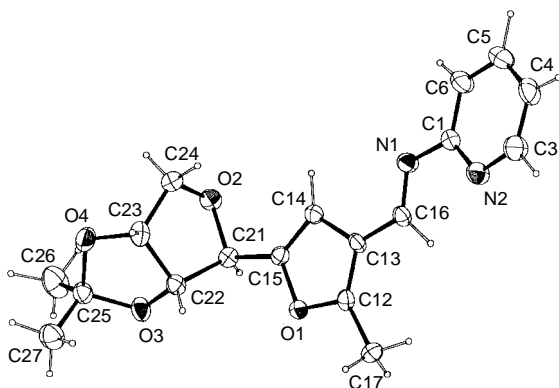


Fig. 1

The ORTEP drawing of compound **5** with the atom numbering used in Table V

configuration at the imine bond (in Fig. 1, the N1–C16 bond) is clearly demonstrated. All calculated bond lengths and valence angles show no remarkable deviations with respect to expectation.

## EXPERIMENTAL

All temperature data are not corrected. Melting temperatures are determined on a Boetius block. NMR spectra ($\delta$, ppm; $J$, Hz) were measured on a GEMINI 300 HC instrument (deuteriochloroform solutions, TMS as internal standard) at 297 K. IR spectra ($\tilde{\nu}$, cm$^{-1}$; CHCl$_3$) were taken on a FTIR spectrometer NICOLET 704. Optical rotations $[\alpha]_D$ were obtained using a Jasco DIP-370 polarimeter at 20 °C. Composition of reaction mixtures and purity of the investigated compounds were followed by TLC (Silufol UV$_{254}$ plates).

### Pyridinium Chlorochromate Adsorbed on Alumina

Pyridine (4.75 g, 60 mmol) was added to chromium trioxide (6 g, 60 mmol) in 6 M HCl (11 ml) within 10 min at 40 °C. The mixture was kept at 10 °C untill a yellow-orange solid was formed. Reheating to 40 °C resulted in formation of a solution. Alumina (50 g) was then added under stirring at 40 °C and the solvents were evaporated. The orange solid was finally dried *in vacuo* for 2 h at room temperature.

### 5-(2,3-*O*-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furaldehyde (**2**)

The above mentioned reagent (7.5 g, 6.1 mmol) was added to a solution of alcohol **1** (ref.[18]; 0.96 g, 3.8 mmol) in benzene (10 ml). The reaction suspension was stirred for 2 h, the solid filtered off and washed with 3 × 15 ml portions of ether. The filtrates were evaporated and chromatographed on silica gel (40/100, 110 g, ether–petroleum ether 3 : 1). Fractions containing aldehyde 2 were collected and evaporated and the product was recrystallized from ether. For characteristics, see Table I. $^1$H NMR spectrum: 9.89 s, 1 H (CH=O). $^{13}$C NMR spectrum: 185.19 CH (CH=O). Other NMR characteristics are given in Tables II and III.

### (*E*)- and (*Z*)-5-(2,3-*O*-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furaldoximes **3** and **4**

A solution of hydroxylamine hydrochloride (0.17 g, 2.4 mmol) and sodium acetate (0.24 g, 3 mmol) in water (5 ml) was added to a stirred solution of aldehyde **2** (0.5 g, 1.98 mmol) in methanol (10 ml). The reaction mixture was refluxed for 2 h, cooled and poured into water (10 ml). Methanol was evaporated, the aqueous mixture was extracted with dichloromethane (3 × 20 ml) and the collected organic layers were dried over sodium sulfate and evaporated. The residue containing *E*- and *Z*-oximes **3**, **4** (0.39 g, 74%) was subjected to a column chromatography on silica gel (40 g, ether–petroleum ether 1 : 3) which gave isomer **3** as an oil of $R_F$ = 0.46 (Silufol, ether–petroleum ether 1 : 3), $[\alpha]_D$ –111.9 ° (*c* 1.5, EtOH). $^1$H NMR spectrum: 8.00 s, 1 H (CH=N). $^{13}$C NMR spectrum: 139.73 C (C=N), and crystalline isomer **4** of $R_F$ = 0.26, $[\alpha]_D$ –72.1°, the corresponding chemical shifts $\delta_H$ 7.24 s and $\delta_C$ 43.55. The physical characteristics of the crystalline isomer **4** are given in Table I, other NMR characteristics of isomers **3** and **4** are given in Tables II and III. On heating a quantitative transformation of isomer **3** to isomer **4** has been observed under various conditions (in substance, in solvents).

Table I

Characteristic data of the prepared furanoids

| Compound | M.p., °C | Yield, % [α]$_D$ (c, CHCl$_3$) | Formula M.w. | Calculated/Found | | |
|---|---|---|---|---|---|---|
| | | | | % C | % H | % N |
| **2** | 57–59 | 40 | $C_{13}H_{16}O_5$ | 61.90 | 6.39 | – |
| | | –87.7 (1) | 252.3 | 61.56 | 6.66 | – |
| **4** | 115–116 | 23[a] | $C_{13}H_{17}NO_5$ | 58.42 | 6.41 | 5.24 |
| | | –72.2 (0.65) | 267.3 | 58.11 | 6.44 | 5.07 |
| **5** | 149–150 | 67 | $C_{15}H_{18}O_6$ | 61.20 | 6.17 | – |
| | | –103.2 (1) | 194.3 | 61.61 | 6.29 | – |
| **6** | 151–152 | 65 | $C_{18}H_{20}N_2O_4$ | 65.84 | 6.14 | 8.53 |
| | | –90.8 (0.5) | 328.4 | 65.70 | 6.25 | 8.36 |
| **7** | 42–46 | 50 | $C_{25}H_{33}NO_8$ | 63.14 | 6.99 | 2.95 |
| | | –57.6 (0.5) | 475.5 | 63.27 | 7.41 | 2.65 |
| **8** | 194–196[b] | 65 | $C_{23}H_{29}NO_6$ | 66.49 | 7.04 | 3.37 |
| | | –60.7 (1) | 415.5 | 66.35 | 7.08 | 3.46 |
| **9**[c] | 81–83 | 73[d] | $C_{21}H_{25}N_3O_5$ | 63.15 | 6.31 | 10.52 |
| | | –52.8 (0.5) | 399.4 | 63.50 | 6.11 | 10.28 |
| **9**[e] | 209–211 | 73[d] | $C_{21}H_{25}N_3O_5$ | 63.15 | 6.31 | 10.52 |
| | | –111.7 (0.4) | 399.4 | 63.04 | 6.29 | 10.40 |
| **10** | 80–82 | 80 | $C_{25}H_{31}NO_8$ | 63.41 | 6.60 | 2.96 |
| | | –56.3 (1) | 473.5 | 63.16 | 6.72 | 2.81 |
| **11** | 127–128 | 85 | $C_{21}H_{21}N_3O_4$ | 66.48 | 5.58 | 11.07 |
| | | –65.4 (1) | 397.4 | 66.45 | 5.59 | 11.05 |
| **12** | 126–127 | 72 | $C_{21}H_{21}NO_5$ | 68.65 | 5.76 | 3.81 |
| | | –83.2 (0.5) | 367.4 | 68.69 | 5.74 | 3.74 |
| **13** | 139–141 | 83 | $C_{16}H_{19}NO_6$ | 59.81 | 5.96 | 4.36 |
| | | –82.3 (0.4) | 321.3 | 59.72 | 6.16 | 4.18 |
| **14** | 85–93[f] | 82 | $C_{16}H_{21}NO_6$ | 59.43 | 6.55 | 4.33 |
| | | –53.6 (1) | 323.3 | 59.19 | 6.85 | 4.24 |
| **15** | 64–85[b,f] | 53 | $C_{16}H_{18}N_2O_5$ | 60.37 | 5.70 | 8.80 |
| | | –102.6 (1) | 318.3 | 60.50 | 5.88 | 8.65 |
| **17b** | 171–172 | 87 | $C_{42}H_{42}BNO_4$ | 79.37 | 6.66 | 2.20 |
| | | –37.6 (1) | 635.6 | 79.38 | 6.64 | 2.27 |

TABLE I
(*Continued*)

| Compound | M.p., °C | Yield, % $[\alpha]_D$ (c, CHCl$_3$) | Formula M.w. | Calculated/Found | | |
|---|---|---|---|---|---|---|
| | | | | % C | % H | % N |
| **18b** | 147–148 | 71 −33.5 (1) | C$_{43}$H$_{44}$BNO$_4$ 649.6 | 79.14 78.90 | 6.86 6.89 | 2.15 2.09 |
| **19b** | 161–162 | 80 −31.8 (1) | C$_{43}$H$_{44}$BNO$_4$ 649.6 | 79.14 79.07 | 6.86 6.88 | 2.15 2.12 |
| **20b** | 176–177 | 85 −19.8 (1) | C$_{43}$H$_{44}$BNO$_4$ 649.6 | 79.14 79.07 | 6.86 6.95 | 2.15 2.05 |
| **21b** | 137–139 | 90$^g$ −34.6 (0.9) | C$_{46}$H$_{44}$BNO$_4$ 687.7 | 80.58 80.43 | 6.47 6.38 | 2.04 1.97 |
| **22** | oil | 30$^g$ −55.4 (2.5) | C$_{18}$H$_{21}$NO$_5$ 331.4 | 65.24 65.28 | 6.39 6.21 | 4.23 4.30 |
| **23** | oil | 38$^g$ −46.7 (2.5) | C$_{19}$H$_{23}$NO$_5$ 345.4 | 66.07 66.15 | 6.71 6.84 | 4.06 3.98 |
| **24** | oil | 50 −45.8 (0.9) | C$_{22}$H$_{23}$NO$_5$ 381.4 | 69.28 69.31 | 6.08 6.10 | 3.67 3.59 |
| **26** | oil | 89$^g$ −86.1 (0.7) | C$_{13}$H$_{19}$NO$_4$ 253.3 | 61.64 61.30 | 7.56 7.64 | 5.53 5.35 |
| **27** | 130–131 | 81$^g$ −66.0 (0.5) | C$_{21}$H$_{21}$NO$_6$ 383.4 | 65.79 65.84 | 5.52 5.58 | 3.65 3.63 |

$^a$ See Experimental; $^b$ decomposition; $^c$ lower-melting hydrate; $^d$ crude mixture of isomers; $^e$ higher-melting hydrate; $^f$ a mixture of diastereoisomers; $^g$ yield of crude products.

(*E*)-5-(2,3-*O*-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-(2-pyridyliminomethyl)furan (**5**)

A solution of aldehyde **2** (0.5 g, 1.98 mmol) and 2-aminopyridine (0.186 g, 1.98 mmol) in dry benzene (25 ml) was azeotropically dehydrated by refluxing under a Dean–Stark water trap. The solvent was evaporated and the resulted syrupy product was crystallized from ether. Recrystallization from ether gave white crystals of m.p. 151–152 °C. $^1$H NMR spectrum: 9.05 s, 1 H (CH=N); 7.13 dd, 1 H, $J$ = 7.1 and 5.0 (H-5); 7.26 d, 1 H, $J$ = 7.8 (H-3); 7.71 ddd, 1 H, $J$ = 7.9, 7.5 and 1.9 (H-4); 8.45 d, 1 H, $J$ = 3.8 (H-6). $^{13}$C NMR spectrum: 120.38 CH (C-5), 122.21 CH (C-3), 138.73 CH (C-4), 149.39 CH (C-6), 155.10 (CH=N), 161.87 C (C-2).

TABLE II
^{1}H NMR data of the parent skeleton in the prepared furanoids

| Compound | H-1' (s) | H-2' (d) $J(2',3')$ | H-3' (dd) $J(3',2')$, $J(3',4'_S)$ | H-4$'_R$ (d) $J(4'_R,4'_S)$ | H-4$'_S$ (dd) $J(4'_S,4'_R)$ $J(4'_S,3')$ | Me-6' (s) | Me-6'' (s) | H-4a (s) | Me-2a (s) |
|---|---|---|---|---|---|---|---|---|---|
| **2** | 5.03 | 4.93 6.7 | 4.89 6.1, 3.7 | 4.06 10.8 | 3.88 10.6, 3.7 | 1.55 | 1.36 | 6.54 | 2.58 |
| **3** | 5.03 | 4.95 6.1 | 4.89 6.0, 3.4 | 4.04 10.8 | 3.90 10.7, 3.8 | 1.55 | 1.36 | 6.45 | 2.34 |
| **4** | 5.05 | 4.97 6.0 | 4.91 m | 4.05 10.7 | 3.90 10.7, 3.8 | 1.56 | 1.37 | 7.00 | 2.41 |
| **5** | 5.02 | 4.95 6.57 | 4.91 6.2, 3.4 | 4.07 10.6 | 3.94 10.6, 3.8 | 1.38 | 1.56 | 6.39 | 2.40 |
| **6** | 5.07 | 4.98 6.17 | 4.90 5.9, 3.7 | 4.05 10.9 | 3.89 10.7, 3.8 | 1.55 | 1.36 | 6.75 | 2.53 |
| **7** | | 4.89 s[a] | | 3.92–4.00 m[b] | | 1.51 | 1.33 | 5.96 | 2.29 |
| **8** | | 4.86–4.92 m[a] | | 3.98 10.7 | 3.93 10.6, 3.1 | 1.51 | 1.33 | 5.93 | 2.23 |
| **9**[d] | 4.98 | 4.97–4.91 m[c] | | 4.03 10.4 | 3.99 10.6, 3.4 | 1.52 | 1.36 | 6.06 | 2.30 |
| **9**[e] | 4.97 | 4.96–4.91 m[c] | | 4.03 10.4 | 3.96 10.6, 3.4 | 1.53 | 1.36 | 6.06 | 2.30 |
| **10** | 5.01 | 4.87–4.92 m[c] | | 4.02 10.6 | 3.83 10.5, 3.2 | 1.54 | 1.36 | 6.15 | 2.09 |
| **11** | 5.09 | 4.99 6.05 | 4.91 5.9, 3.8 | 4.07 10.4 | 3.93 10.4, 3.8 | 1.55 | 1.36 | 6.44 | 2.34 |
| **12** | 5.09 | 5.01 6.1 | 4.94 6.0, 3.8 | 4.08 10.4 | 3.96 10.6, 3.9 | 1.58 | 1.39 | 6.54 | 2.58 |
| **13** | 5.06 | 4.98 6.3 | 4.93 6.0, 3.8 | 4.07 10.4 | 3.94 10.5, 3.8 | 1.57 | 1.38 | 6.36 | 2.53 |
| **14** | 5.01 | 4.03 6.6 | 4.88 6.0, 3.8 | 4.03 10.4 | 3.63 10.4, 4.3 | 1.53 | 1.35 | 6.36 | 2.46 |
| **15** | 5.00 | 4.92 6.05 | 4.89 6.0, 3.3 | 4.04 10.4 | 3.89 10.4, 3.4 | 1.53 | 1.35 | 6.34 | 2.48 |
| **17a** | 4.88 | 4.87 m | | 3.96 10.5 | 3.87 10.5, 3.4 | 1.31 | 1.50 | 6.43 | 2.50 |
| **18a** | 4.90 | 4.88 m | | 4.00 10.6 | 3.87 10.6, 3.9 | 1.33 | 1.51 | 6.20 | 2.44 |
| **19a** | 4.90 | 4.88 m | | 3.98 10.7 | 3.83 10.7, 3.2 | 1.33 | 1.51 | 6.44 | 2.49 |
| **20a** | 4.83 | 4.83 m | | 3.90 10.4 | 3.85 10.4, 3.7 | 1.26 | 1.44 | 6.43 | 2.42 |
| **21b** | 4.92 | 4.87 7.1 | 4.84 6.6, 3.4 | 4.01 10.4 | 3.80 10.4, 3.3 | 1.34 | 1.53 | 5.73 | 2.20 |

TABLE II
(*Continued*)

| Compound | H-1′ (s) | H-2′ (d) $J(2',3')$ | H-3′ (dd) $J(3',2')$, $J(3',4'_S)$ | H-4$_R'$ (d) $J(4'_R,4'_S)$ | H-4$_S'$ (dd) $J(4'_S,4'_R)$ $J(4'_S,3')$ | Me-6′ (s) | Me-6″ (s) | H-4a (s) | Me-2a (s) |
|---|---|---|---|---|---|---|---|---|---|
| **22** | 4.94 | 4.90 6.9 | 4.87 6.0, 3.4 | 3.98 10.4 | 3.88 10.4, 3.4 | 1.33 | 1.52 | 6.16 | 2.32 |
| **23** | 4.92 | 4.87 7.4 | 4.85 6.0, 3.4 | 3.96 10.4 | 3.85 10.4, 3.3 | 1.31 | 1.50 | 6.14 | 2.10 |
| **24** | 4.94 | 5.89 6.6 | 4.85 6.0, 3.8 | 3.98 10.4 | 3.86 10.4, 3.8 | 1.25 | 1.52 | 6.18 | 2.37 |
| **26** | 5.00 | 4.93 6.4 | 4.90 6.1, 3.8 | 4.00 10.6 | 3.91 10.4, 3.8 | 1.35 | 1.54 | 6.20 | 2.22 |
| **27** | 4.93 | 4.87 m | 4.87 m | 3.97 10.4 | 3.87 10.4, 3.2 | 1.33 | 1.52 | 6.25 | 2.40 |

[a] One signal, 3 H, for H-1′, H-2′ and H-3′; [b] absorption, 2 H, for H-4$_S'$ and H-4$_R'$; [c] absorption, 2 H, for H-2′ and H-3′; [d] higher-melting hydrate; [e] lower-melting hydrate.

### 3-[5-(2,3-*O*-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furyl]acrylic Acid (**6**)

A mixture of aldehyde **2** (0.5 g, 1.9 mmol), pyridine (15 ml), piperidine (0.01 ml) and malonic acid (0.4 g, 3.8 mmol) was refluxed for 5 h and then poured into water (100 ml). After treatment with concentrated hydrochloric acid to pH 5–6, the brownish crystalline product was purified by column chromatography on silica gel and crystallized from cyclohexane–ether, see Table I. $^1$H NMR spectrum: 6.04 d, 1 H, $J = 15.6$ (H-2); 7.6 d, 1 H, $J = 15.6$ (H-1). $^{13}$C NMR spectrum: 116.19 CH (C-1), 137.77 CH (C-2), 172.82 C (CO). Other NMR data are given in Tables II and III.

### 3,5-Bis(ethoxycarbonyl)-2,6-dimethyl-4-[5-(2,3-*O*-isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furyl]-1,4-dihydropyridine (**7**)

A mixture of aldehyde **2** (0.504 g, 2 mmol) and ethyl acetoacetate (0.52 g, 4 mmol) in ethanol (10 ml) was added at 0 °C to a saturated solution of ammonia in ethanol (1.2 ml). The reaction was refluxed for 4 h and allowed to stand overnight at room temperature. Evaporation of the solvent to dryness gave a hygroscopic uncrystallizable foam. The material was purified by column chromatography (silica gel, 50 g, petroleum ether–ether 1 : 5). 1,4-Dihydropyridine **7** was obtained as a hygroscopic amorphous powder. $^1$H NMR spectrum: 1.25 t, 6 H, $J = 7.1$ (CH$_3$-R); 2.26 s and 2.27 s, 6 H (CH$_3$-2,6); 4.10 q, 4 H, $J = 7.1$ (CH$_2$-R); 4.77 s, 1 H (H-4); 5.96 s, 1 H (NH). $^{13}$C NMR spectrum: 15.10 CH$_3$ (R); 20.19 CH$_3$ and 20.22 CH$_3$ (CH$_3$-2,6), 30.76 CH (C-4); 60.41 CH$_2$ (R), 103.76 C (C-3,5), 144.79 C (C-2,6), 168.12 and 168.15 (CO-3,5). Other NMR data, see Tables II and III.

### 3,5-Diacetyl-2,6-dimethyl-4-[5-(2,3-*O*-isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furyl]-1,4-dihydropyridine (**8**)

The reaction of aldehyde **2** (0.756 g, 3 mmol) and acetylacetone (0.6 g, 3 mmol) in ethanol (10 ml) with ethanolic ammonia (1.8 ml) was carried out by the same procedure as previously described.

1,4-Dihydropyridine **8** was obtained as a yellow crystalline compound. [1] H NMR spectrum: 2.24 s and 2.25 s, 6 H ($CH_3$-2,6); 2.29 s and 2.33 s, 6 H ($CH_3$-R); 4.82 s, 1 H (H-4); 6.34 s, 1 H (NH). ^{13}C NMR spectrum: 20.69 $CH_3$ ($CH_3$-2,6), 30.59 $CH_3$ and 30.69 $CH_3$ ($CH_3$-R), 31.58 CH (C-4), 113.43 C and 113.46 C (C-3,5), 144.12 C (C-2,6), 197.85 C and 197.98 C (CO-R). Other NMR characteristics, see Tables II and III.

TABLE III
^{13}C NMR chemical shifts of the parent skeleton in the prepared furanoids

| Com-pound | C-1′ | C-2′ | C-3′ | C-4′ | C-5′ | C-6′ | C-6″ | C-2a | C-3a |
|---|---|---|---|---|---|---|---|---|---|
| **2** | 84.34 | 81.87 | 80.30 | 73.57 | 113.78 | 27.22 | 25.70 | 152.15 | 123.86 |
| **3** | 84.27 | 81.89 | 80.36 | 73.38 | 113.72 | 27.15 | 25.63 | 150.51 | 115.29 |
| **4** | 84.34 | 81.90 | 80.38 | 73.49 | 113.57 | 27.23 | 25.65 | 151.45 | 115.24 |
| **5** | 84.34 | 81.89 | 80.44 | 73.63 | 113.57 | 27.21 | 25.67 | 151.99 | 118.68 |
| **6** | 84.26 | 81.86 | 80.29 | 73.32 | 113.46 | 27.12 | 25.59 | 151.50 | 121.47 |
| **7** | 84.35 | 81.97 | 80.63 | 73.48 | 113.31 | 27.23 | 25.65 | 147.66 | 125.86 |
| **8** | 84.12 | 81.79 | 80.41 | 73.45 | 113.23 | 27.07 | 25.43 | 147.17 | 125.48 |
| **9**[a] | 84.27 | 81.87 | 80.60 | 73.62 | 113.43 | 27.17 | 25.54 | 149.32 | 119.25 |
| **9**[b] | 84.25 | 81.85 | 80.57 | 73.61 | 113.45 | 27.16 | 25.52 | 149.31 | 119.30 |
| **10** | 84.22 | 81.86 | 80.22 | 73.21 | 113.39 | 27.06 | 25.57 | 150.81 | 116.48 |
| **11** | 84.04 | 81.85 | 80.41 | 73.62 | 113.53 | 27.12 | 25.61 | 150.01 | 115.81 |
| **12** | 84.56 | 82.05 | 80.58 | 73.67 | 113.64 | 27.39 | 25.89 | 151.17 | 111.55 |
| **13** | 84.39 | 81.95 | 80.43 | 73.56 | 113.61 | 27.22 | 25.68 | 151.10 | 111.30 |
| **14** | 84.30 | 81.88 | 80.05 | 73.50 | 113.60 | 27.18 | 25.65 | 150.98 | 112.14 |
| **15** | 84.29 | 81.83 | 80.33 | 73.59 | 113.69 | 27.19 | 25.63 | 151.67 | 110.43 |
| **17a** | 84.20 | 81.76 | 80.24 | 73.50 | 113.53 | 27.13 | 25.54 | 153.84 | 115.65 |
| **18a** | 84.35 | 81.83 | 80.45 | 73.68 | 112.36 | 27.22 | 25.67 | 152.73 | 113.69 |
| **19a** | 84.23 | 81.78 | 80.28 | 73.52 | 113.58 | 27.16 | 25.58 | 153.81 | 113.77 |
| **20a** | 84.08 | 81.65 | 80.13 | 73.33 | 113.35 | 27.00 | 25.44 | 153.46 | 113.87 |
| **21b** | 84.33 | 81.81 | 80.34 | 73.70 | 112.62 | 27.21 | 26.64 | 152.98 | 113.70 |
| **22** | 84.62 | 81.98 | 80.73 | 73.30 | 113.74 | 27.60 | 26.05 | 151.64 | 116.00 |
| **23** | 84.21 | 81.80 | 80.32 | 73.33 | 113.35 | 27.10 | 25.52 | 151.26 | 115.91 |
| **24** | 84.26 | 81.84 | 80.40 | 73.35 | 113.40 | 27.14 | 25.55 | 151.07 | 116.32 |
| **26** | 84.40 | 81.97 | 80.50 | 73.40 | 113.38 | 27.20 | 25.64 | 150.11 | 121.66 |
| **27** | 84.30 | 81.90 | 80.35 | 73.36 | 113.40 | 27.20 | 25.61 | 151.46 | 116.04 |

[a] Higher-melting hydrate; [b] lower-melting hydrate.

3,5-Dicyano-2,6-dimethyl-4-[5-(2,3-*O*-isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furyl]-1,4-dihydropyridine (**9**)

A solution of aldehyde **2** (1 g, 4 mmol) and 3-aminocrotonitrile (0.658 g, 8 mmol) in ethanol (15 ml) was refluxed for 4.5 h. Then 10% AcOH (1 ml) was added, and the mixture was kept at room temperature overnight. Evaporation of the solvent to dryness gave a hygroscopic foam. The product was chromatographed (silica gel, 80 g, chloroform–acetone 2 : 1). First fractions were collected and evaporated. Crystallization of the residue from water gave the higher-melting hydrate of 1,4-dihydropyridine **9**. $^1$H NMR spectrum: 2.07 s and 2.10 s, 6 H (CH$_3$-2,6); 4.27 s, 1 H (H-4); 6.19 s, 1 H (NH). $^{13}$C NMR spectrum: 9.09 CH$_3$ (CH$_3$-2,6), 33.54 CH (C-4), 84.96 C and 85.05 C (C-3,5), 122.64 C (CN-R), 146.06 C and 146.00 C (C-2,6). The following fractions afforded the lower-melting hydrate of product **9** by repeated chromatography (silica gel, 50 g, chloroform–acetone 9 : 1), see Table I. $^1$H NMR spectrum: 2.04 s and 2.08 s, 6 H (CH$_3$-2,6); 4.26 s, 1 H (H-4); 6.53 s, 1 H (NH).

TABLE IV
Data collection and refinement parameters of the compound **5**

| | |
|---|---|
| Crystal dimensions | $0.28 \times 0.33 \times 0.68$ mm |
| Diffractometer and radiation used | Enraf–Nonius CAD4, $\lambda$(CuK$\alpha_1$) = 1.54056 Å |
| Scan technique | $\omega/2\theta$ |
| Temperature | 293 K |
| No. and $\theta$ range of reflections for lattice parameter refinement | 20; 35–40° |
| Range of *h*, *k* and *l* | 0→6, 0→10, –27→27 |
| Standard reflections monitored in interval; intensity fluctuation | 60 min; 0.7% |
| Total number of reflections measured; $2\theta$ range | 2 196; 0–104° |
| No. of unique reflections | 1 111 |
| No. of observed relections | 1 094 |
| Criterion for observed reflections | $I > 1.96\sigma(I)$ |
| Function minimized | $\sum w \, (\mid F_o\mid - \mid F_c \mid)^2$ |
| Weighting scheme | Chebychev polynomial[42] |
| Parameter refined | 297 |
| Value of *R*, *wR* and *S* | 0.0437; 0.0465; 1.3234 |
| Ratio of max. least-squares shift to e.s.d. in the last cycle | 0.04 |
| Max. and min. heights in final map | 0.197, –0.226 e Å$^{-3}$ |
| Source of atomic scattering factors | International Tables for X-Ray Crystallography[43] |
| Programs used | CRYSTALS (ref.[44]), PARST (ref.[45]), SIR92 (ref.[46]) |

^{13}C NMR spectrum: 9.12 $CH_3$ ($CH_3$-2,6), 33.57 CH (C-4), 85.15 C and 85.10 C (C-3,5), 122.61 C (CN-R), 145.95 C and 145.91 C (C-2,6). Other NMR data are given in Tables II and III.

3,5-Bis(ethoxycarbonyl)-2,6-dimethyl-4-[5-(2,3-O-isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furyl]pyridine (**10**)

A solution of dihydropyridine **7** (0.475 g, 1 mmol) in dichloromethane (5 ml) was dropwise added under stirring to a suspension of pyridinium chlorochromate on alumina (4.8 g, 4 mmol) in dichloromethane (10 ml). After 6 h, the solid was filtered off and washed with acetone (3 × 5 ml). The combined filtrates were evaporated and the crude pyridine derivative **10** was purified by column

TABLE V
Final atomic parameters of the compound **5** with e.s.d.'s in parentheses. $U_{eq} = 1/3 \ \Sigma i \Sigma j \ U_{ij} \ a_i^* a_j^* \ \mathbf{a}_i \mathbf{a}_j$

| Atom | $x$ | $y$ | $z$ | $U_{iso}$, Å$^2$ |
|------|------|------|------|------|
| O2  | 0.6686(4) | −0.2222(2) | 0.46417(8) | 0.0417(16) |
| O3  | 0.3678(4) | −0.1056(3) | 0.38663(8) | 0.0462(18) |
| O4  | 0.6841(5) | −0.1727(3) | 0.34886(9) | 0.0546(19) |
| O11 | 0.5265(4) | 0.1033(2) | 0.50831(8) | 0.0369(14) |
| N1  | 1.1126(5) | 0.0702(3) | 0.6169(1) | 0.0420(21) |
| N2  | 1.2618(6) | 0.2469(3) | 0.6642(1) | 0.0495(11) |
| C1  | 1.2623(6) | 0.1196(3) | 0.6525(1) | 0.0398(21) |
| C3  | 1.4151(9) | 0.2862(4) | 0.6961(2) | 0.0584(33) |
| C4  | 1.5724(8) | 0.2100(5) | 0.7181(1) | 0.0581(29) |
| C5  | 1.5700(9) | 0.0801(4) | 0.7059(2) | 0.0613(30) |
| C6  | 1.4160(7) | 0.0350(4) | 0.6730(1) | 0.0529(28) |
| C12 | 0.6316(6) | 0.1700(3) | 0.5452(1) | 0.0347(20) |
| C13 | 0.7978(6) | 0.0984(3) | 0.5650(1) | 0.0323(19) |
| C14 | 0.7959(6) | −0.0235(3) | 0.5385(1) | 0.0353(20) |
| C15 | 0.6333(5) | −0.0169(3) | 0.5052(1) | 0.0324(20) |
| C16 | 0.9498(7) | 0.1397(3) | 0.6029(1) | 0.0352(20) |
| C17 | 0.5456(9) | 0.3053(4) | 0.5542(2) | 0.0458(29) |
| C21 | 0.5398(6) | −0.1059(3) | 0.4667(1) | 0.0348(23) |
| C22 | 0.5454(7) | −0.0510(4) | 0.4151(1) | 0.0374(22) |
| C23 | 0.7579(6) | −0.1062(4) | 0.3917(1) | 0.0404(24) |
| C24 | 0.8475(8) | −0.1976(4) | 0.4305(1) | 0.0487(27) |
| C25 | 0.4535(7) | −0.1461(4) | 0.3403(1) | 0.0425(24) |
| C26 | 0.338(1) | −0.2718(6) | 0.3267(2) | 0.0696(42) |
| C27 | 0.427(1) | −0.0414(5) | 0.3026(2) | 0.0629(35) |

chromatography (chloroform–acetone 9 : 1) and crystallization (heptane), see Table I. $^1$H NMR spectrum: 1.11 dt, 6 H (CH$_3$-R); 2.56 s, 6 H (CH$_3$-2,6); 4.15 dq, 4 H (CH$_2$-R). $^{13}$C NMR spectrum: 14.32 CH$_3$ and 14.40 CH$_3$ (CH$_3$-R), 23.34 CH$_3$ (CH$_3$-2,6), 61.95 CH$_2$ (CH$_2$-R), 128.54 C (C-3,5), 138.7 C (C-4), 155.82 C (C-2,6), 168.21 C (CO).

### 3,5-Dicyano-2,6-dimethyl-4-[5-(2,3-O-isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furyl]-pyridine (**11**)

White crystals of pyridine derivative **11** (see Table I) were obtained employing the above-mentioned procedure from the more stable hydrate of 1,4-dihydropyridine **9** (10 mg, 0.025 mmol) and pyridinium chlorochromate (86 mg) in dichloromethane (5 ml). $^1$H NMR spectrum: 2.83 s, 6 H (CH$_3$-2,6). $^{13}$C NMR spectrum: 25.26 CH$_3$ (CH$_3$-2,6), 65.82 C (C-3,5), 108.23 C (C-4), 115.81 (CN), 153.4 C (C-2,6).

### 3-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methylfuran-3-yl]-5-phenyl-1,2-oxazole (**12**)

A solution of E- and Z-oxime **3** and **4** (0.5 g, 1.87 mmol) in dichloromethane (10 ml) was dropwise added at 0 °C to a good stirred mixture of phenylacetylene (0.95 g, 9.35 mmol), triethylamine (0.04 ml), dichloromethane (8 ml) and 10% solution of sodium hypochlorite in water (3.3 ml). The reaction mixture was stirred for 7 h at room temperature and then 10% NaOCl solution (3.0 ml) in water was portionwise added at reflux during 8 h. After cooling the aqueous layer was extracted with dichloromethane (2 × 5 ml). Organic extracts were collected, dried with sodium sulfate and evaporated *in vacuo*. Crystallization of the residue from ethanol and ether afforded white crystals of pyridine derivative **11**. $^1$H NMR spectrum: 6.6 s, 1 H (H-4); 7.43–7.52 m, 3 H (*m-, p*-Ph); 7.82 dd, 2 H, J = 7.7 and 1.9 (*o*-Ph). $^{13}$C NMR spectrum: 98.78 CH (CH-4), 128.13 C (*i*-Ph), 126.51 CH (*o*-Ph), 129.63 CH (*m*-Ph), 130.84 CH (*p*-Ph), 157.74 C (C-3), 170.54 C (C-5).

### 3-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methylfuran-3-yl]-5-hydroxymethyl-1,2-oxazole (**13**)

The reaction of E- and Z-oxime **3** and **4** (0.5 g, 1.87 mmol), propargyl alcohol (0.52 g, 9.35 mmol), and triethylamine (0.04 m) in dichloromethane (6 ml) with 10% NaOCl in water (3.3 ml) was carried out in the same way but it was completed within 3 h. Product **13** was isolated by crystallization from ether. $^1$H NMR spectrum: 2.07 t, 1 H, J = 6.3 (OH); 4.81 d, 2 H, J = 5.9 (CH$_2$); 6.49 s, 1 H (H-4). $^{13}$C NMR spectrum: 57.35 CH$_2$ (CH$_2$), 101.28 CH (C-4), 157.28 C (C-3), 171.94 C (C-5). Other NMR data are given in Tables II and III.

### 3-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methylfuran-3-yl]-5-hydroxymethyl-4,5-dihydro-1,2-oxazole (**14**)

The reaction of E- and Z-oxime **3** and **4** (0.5 g, 1.87 mmol), allyl alcohol (0.54 g, 9.35 mmol), triethylamine (0.04 ml) in dichloromethane (8 ml) with 10% aqueous sodium hypochlorite (8.5 ml) carried out as described above was completed within 5.5 h. The product **14** was purified by column chromatography (chloroform–acetone 2 : 1) and crystallized from ether, see Table I. $^1$H NMR spectrum exhibits an ABX system, 3.21 qu ($\delta_{AB}$ 3.19 and 3.22), 2 H, J = 16.5, 11.0 and 7.7 (H-4); 3.81 ddd, 2 H, J = 12.1, 3.3 and 3.8 (CH$_2$O); 3.83 dd, 1 H, J = 3.3 (H$_C$); 3.90 dd, 1 H, J = 3.8 (H$_D$); 4.77 m, 1 H (H-5); 1.96 br (OH). $^{13}$C NMR spectrum: 84.30 CH (C-5), 38.57 CH$_2$ (C-4), 64.25 CH$_2$ (CH$_2$OH), 150.98 C (C-3). Other NMR data are given in Tables II and III.

5-Cyano-3-[5-(2,3-*O*-isopropylidene-β-D-erythrofuranosyl)-2-methylfuran-3-yl]-4,5-dihydro-1,2-oxazole (**15**)

The reaction of *E*- and *Z*-oxime **3** and **4** (0.5 g, 1.87 mmol), acrylonitrile (0.496 g, 9.35 mmol), triethylamine (0.04 ml) in dichloromethane (12 ml) with 10% aqueous sodium hypochlorite (11.6 ml) was completed within 2 h at room temperature and crude **15** was crystallized from methanol. ^{1}H NMR spectrum: 3.57 d, 1 H, *J* = 7.7 (Hb-4); 3.61 dd, 1 H, *J* = 16.5 and 11.0 (Ha-4); 5.28 d, 1 H, *J* = 10.9 (H-5). ^{13}C NMR spectrum: 43.20 $CH_2$ (C-4), 66.50 CH (C-5), 80.29 and 80.33 (C-3′), 117.74 C (CN), 108.27 and 108.32 (C-4′), 151.54 C (C-3).

### Preparation of Pyridinium Chlorides 17a–20a

A solution of the chloromethyl derivative **16** (ref.[18]; 0.5 g, 1.8 mmol) in freshly distilled nitromethane (5 ml) was added to a solution of a pyridine (1.26 mmol) in nitromethane (10 ml) and the reaction mixture was kept at room temperature for 3–6 days. The solvent was evaporated under diminished pressure and the pale brown, hygroscopic residue was taken up in a water–toluene mixture 1 : 1 (50 ml). The mixture was stirred for 2 h, the water phase was removed, evaporated to dryness and the residue was dried under pressure to give crude chlorides **17a–20a** as hygroscopic solid foams. For purification, the products were dissolved in water, charcoal added, set aside for several hours, and then filtered. The filtrates were evaporated and a small amount of dry ether was added. Flocculent white precipitates were formed in all cases in 71–85% yields (Table I) and after the ^{1}H and ^{13}C NMR assignments (see Tables II and III) the salts were used in further transformations.

*1-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furylmethyl]pyridinium chloride* (**17a**). ^{1}H NMR spectrum: 6.08 s, 2 H (H-3b); 9.23 brs, 2 H (H-2,6); 8.05 t, 2 H, *J* = 7.0 (H-3,5); 8.46 t, 1 H, *J* = 7.0 (H-4). ^{13}C NMR spectrum: 146.84 CH (C-4), 145.24 CH (C-2,6), 129.13 CH (C-3,5), 56.87 $CH_2$ (C-3b). $[\alpha]_D$ –73.1° (*c* 1, $CHCl_3$).

*1-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furylmethyl]-2-methylpyridinium chloride* (**18a**). ^{1}H NMR spectrum: 9.57 d, 1 H, *J* = 5.5 (H-6); 7.90 m, 2 H (H-4,5); 7.69 m, 1 H (H-3); 6.03 s, 2 H (H-3b); 3.0 s, 3 H (Me-2). ^{13}C NMR spectrum: 158.80 C (C-2), 142.36 CH (C-6), 142.22 CH (C-4), 129.0 CH (C-3), 125.68 CH (C-5), 55.27 $CH_2$ (C-3b), 22.50 $CH_3$ (Me-2). $[\alpha]_D$ –78.4° (*c* 1, $CHCl_3$).

*1-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furylmethyl]-3-methylpyridinium chloride* (**19a**). ^{1}H NMR spectrum: 9.37 s, 1 H (H-2); 9.34 d, 1 H, *J* = 5.9 (H-6); 8.17 d, 1 H, *J* = 8.1 (H-4); 7.9 t, 1 H, *J* = 6.1 and 7.9 (H-5); 6.08 s, 2 H (H-3b); 2.59 s, 3 H (Me-3). ^{13}C NMR spectrum: 146.30 CH (C-2), 145.1 CH (C-6), 142.80 CH (C-4), 140.24 C (C-3), 128.28 CH (C-5), 56.61 $CH_2$ (C-3b), 19.50 $CH_3$ (Me-3). $[\alpha]_D$ –53.0° (*c* 1, $CHCl_3$).

*1-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furylmethyl]-4-methylpyridinium chloride* (**20a**). ^{1}H NMR spectrum: 9.30 d, 2 H, *J* = 6.1 (H-2,6); 7.77 d, 2 H, *J* = 5.6 (H-3,5); 6.02 s, 2 H (H-3b); 2.56 s, 3 H (Me-4). ^{13}C NMR spectrum: 159.66 C (C-4), 144.60 CH (C-2,6), 129.50 CH (C-3,5), 55.70 $CH_2$ (C-3b), 22.66 $CH_3$ (Me-4). $[\alpha]_D$ –67.0° (*c* 1, $CHCl_3$).

### Preparation of Pyridinium Tetraphenylborates 17b–20b

Crude chlorides **17a–20a** (1 mmol) in minimum quantities of water were treated with saturated aqueous solution of sodium tetraphenylborate (1 mmol). The precipitates obtained in almost quantitative yields were crystallized from ethanol affording brownish prisms of tetraphenylborates **17b–20b**, see Table I.

2-[5-(2,3-*O*-isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furylmethyl]isoquinolinium
Tetraphenylborate (**21b**)

The reaction of 3-chloromethyl derivative **16** (ref.[18]; 1.8 mmol) with isoquinoline was carried out in the same way as in the case of the pyridine but the aqueous solution of crude chloride **21a** was treated with a saturated aqueous solution of sodium tetraphenylborate (1.8 mmol) and the precipitated salt **21b** (yield 90%) was crystallized from ethanol, see Table I. ^{1}H NMR spectrum: 7.9 m, 1 H; 7.37–7.8 m, 5 H; 7.23 d, 1 H, $J = 6.6$ (isoquinoline moiety); 7.53 m, 8 H; 6.87 t, 8 H, $J = 7.1$ and 7.7; 7.60 t, 4 H, $J = 7.1$ and 7.7 (BPh$_4$). ^{13}C NMR spectrum: 148.75 CH (C-1); 135.39 CH, 132.95 CH, 131.81 CH, 131.54 CH, 129.42 CH, 128.58 CH and 126.96 CH (C-3, C-4, C-5, C-6, C-7 and C-8); 137.67 C and 127.93 C (C-4c and C-8c); 56.30 CH$_2$ (C-3b); 165.90 C, 165.24 C, 164.60 C and 164.00 C (BPh$_4$); 136.76 CH, 126.67 CH and 122.70 CH (BPh$_4$). Other NMR data for the parent skeleton are given in Tables II and III.

### Ferricyanide Oxidation of Chlorides **17a**, **19a** and **21a**

An aqueous sodium hydroxide (0.3 g in 1 ml H$_2$O) was added dropwise to a stirred solution of a chloride **17a**, **19a** or **21a** (1.42 mmol) and potassium ferricyanide (0.5 g) in water (5 ml) at the temperature not exceeding 5 °C. After 1 h, another portion of potassium ferricyanide (0.5 g) was added and the reaction mixture was stirred for 3 h at room temperature. The water phase was extracted with chloroform, the collected extracts were dried over anhydrous sodium sulfate and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (chloroform–acetone 2 : 1) to give syrupy pyridone derivatives **22–24**, see Table I. ^{1}H and ^{13}C NMR assignments for the parent skeleton are given in Tables II and III.

*1-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furylmethyl]pyridin-2(1H)-one* (**22**). ^{1}H NMR spectrum: 7.21–7.31 m, 2 H (H-4 and H-6); 6.55 d, 1 H, $J = 9.3$ (H-3); 6.12 t, 1 H, $J = 6.6$ and 8.1 (H-5); 4.83 s, 2 H (H-3b). ^{13}C NMR spectrum: 163.42 C (C-2), 140.22 CH (C-4), 137.43 CH (C-6), 121.90 CH (C-3), 107.13 CH (C-5), 44.21 CH$_2$ (C-3b). IR spectrum: 1 660 (C=O), 1 568 (furan ring).

*1-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furylmethyl]-2-methylpyridin-2(1H)-one* (**23**). ^{1}H NMR spectrum: 7.12 m, 2 H (H-4 and H-6); 6.95 t, 1 H, $J = 6.1$ and 9.6 (H-5); 4.81 s, 2 H (H-3b). ^{13}C NMR spectrum: 163.49 C (C-2), 137.25 CH (C-6), 134.61 CH (C-4), 130.58 C (C-3), 106.47 CH (C-5), 44.12 CH$_2$ (C-3b).

*1-[5-(2,3-O-Isopropylidene-β-D-erythrofuranosyl)-2-methyl-3-furylmethyl]isoquinolin-1(2H)-one* (**24**). ^{1}H NMR spectrum: 8.43 d, 1 H, $J = 7.7$ (H-8); 7.46–7.65 m, 3 H (H-5, H-6 and H-7); 7.04 d, 1 H, $J = 7.1$ (H-3); 6.48 d, 1 H, $J = 7.1$ (H-4); 4.92 s, 2 H (H-3b). ^{13}C NMR spectrum: 162.77 C (C-1); 137.60 C (C-4c); 122.40 (C-8c); 133.86 CH (C-3); 131.33 CH, 128.53 CH, 127.57 CH and 126.57 CH (C-5, C-6, C-7 and C-8); 107.13 CH (C-4); 43.60 CH$_2$ (C-3b).

### *N*-{[5-(2,3-*O*-Isopropylidene-β-D-erythrofuranosyl)-2-methylfuran-3-yl]methyl}phthalimide (**27**)

A solution of 3-chloromethyl derivative **16** (ref.[18]; 1.7 g, 6.2 mmol) in freshly distilled dimethylformamide (5 ml) was added dropwise to a stirred suspension of potassium phthalimide (1.4 g, 7.5 mmol) in the same solvent (5 ml) and the reaction mixture was heated at 110 °C for 2 h. The solvent was evaporated under diminished pressure and the residue was codistilled with toluene. The crude material was purified by column chromatography on silica gel (heptane–acetone 2 : 1) and crystallized from ethanol–water (10 : 1) giving compound **27** as white crystals, see Table I. ^{1}H NMR spectrum: 7.68–7.73 m and 7.80–7.85 m, 4 H (H-4, H-5, H-6 and H-7); 4.56 s, 2 H (H-3b). ^{13}C NMR spec-

trum: 168.63 C (C-2,9), 132.85 C (C-3,8), 134.63 CH (C-5,6), 123.85 CH (C-4,7), 33.01 $CH_2$ (C-3b). IR spectrum: 1 715 (C=O).

### 3-Aminomethyl-5-(2,3-O-isopropylidene-β-D-erythrofuranosyl)-2-methylfuran (**26**)

A mixture of compound **27** (0.5 g, 1.3 mmol), aqueous 80% hydrazine hydrate (300 ml) and 95% ethanol (100 ml) was refluxed for 4 h and then a second portion of hydrazine hydrate solution (300 ml) was added. After an additional 2 h reflux no starting material was detected according to TLC (heptane–acetone 1 : 1). Ethanol was evaporated and the residue was extracted with chloroform (3 × 30 ml); the collected organic extracts were dried over anhydrous sodium sulfate. Evaporation of the solvent gave amine **26** as an oily, optically active substance, see Table I. $^1$H and $^{13}$C NMR spectra: 4.56 s, 2 H and 37.42 $CH_2$ (C-3b), other assignments are given in Tables II and III.

### Attempt at Preparation of Perchlorate **25**

The aminomethyl derivative **26** (250 mg, 1 mmol) and 2,4,6-triphenylpyrylium perchlorate[39] (310 mg, 0.76 mmol) in acetonitrile (10 ml) were stirred at room temperature for 2 h. The reaction mixture was then refluxed for 6 h and evaporated. The brown oily residue was investigated by $^1$H NMR measurement according to which it contained a 4.4 : 2 : 1 : 1.2 mixture of 2,4,6-triphenylpyridine [7.95 s, 2 H (H-3,5 of the pyridine ring); 7.76 d, 2 H, J = 7.1 (o-Ph4); 8.21 d, 4 H, J = 7.1 (o-Ph2,6); 7.52 m, 9 H (m-,p-Ph2,4,6)], perchlorate **25** [5.70 s, 1 H (H-4a); 5.51 s, 2 H (H-3b); 2.25 s, 3 H (Me-2a); 1.50 s, 3 H (H-6″); 1.30 s, 3 H (H-6′)], perchlorate **28** [6.20 s, 1 H (H-4a); 4.21 s, 2 H (H-3b); 2.32 s, 3 H (Me-2a); 1.55 s, 3 H (H-6″); 1.39 s, 3 H (H-6′)] and primary alcohol[18] **1** [6.24 s, 1 H (H-4a); 4.40 s, 2 H (H-3b); 2.20 s, 3 H (Me-2a); 1.53 s, 3 H (H-6″); 1.33 s, 3 H (H-6′)]. Then the evaporated residue was extracted with 20 × 3 ml of hot petroleum ether, the combined eluents were cooled and the precipitated white crystals of 2,4,6-triphenylpyridine (80 mg) were filtered off; m.p. 135–136 °C (ether), reported[40] m.p. 134–135 °C (ethanol). Evaporation of the mother liquors gave the mixture of compounds **1**, **25** and **28** which was not separated.

### Crystal Structure Determination of the Compound **5**

$C_{18}H_{20}N_2O_4$ ($M_r$ = 328.37), orthorhombic system, space group $P2_12_12_1$ (No. 19), a = 5.9642(7) Å, b = 10.273(1) Å, c = 27.03(1) Å, V = 1 655.8(7) Å$^3$, Z = 4, $D_{calc}$ = 1.317 g cm$^{-3}$, μ(CuKα) = 0.073 mm$^{-1}$, F(000) = 696.

The structure was solved by direct methods and subsequent Fourier techniques. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares based on F values. Empirical absorption correction was applied[41]. The hydrogen atoms were placed in positions found from ideal geometry with $U_{iso}$ = $U_{eq}$ of the attached atoms. The positional and isotropic thermal parameters of hydrogen atoms were refined in the final stage of refinement. Data collection and structure parameters are listed in Table IV. Final coordinates and thermal parameters of non-hydrogen atoms are given in Table V.

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