Monatshefte für Chemie 138, 1297–1302 (2007)
DOI 10.1007/s00706-007-0729-8
Printed in The Netherlands

Monatshefte für Chemie
Chemical Monthly

One-pot Amberlite IR-120 Catalysed Synthesis of Glycosyl Dihydropyridones[#]

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Received May 16, 2007; accepted May 23, 2007; published online September 24, 2007

Summary. The one-pot reaction of β-glycosyl amino acids with β-ketoesters in the presence of Amberlite IR-120 resin and 4 Å molecular sieve in refluxing toluene resulted in the respective dihydropyridones in fair to good yields.

Keywords. β-Glycosyl β-amino acid; Dihydropyridones; C-Nucleosides; Amberlite IR 120 resin; β-Ketoesters.

Introduction

Dihydropyridones are useful and interesting building blocks for the synthesis of a large number of heterocyclic compounds of great biological significance [1, 2]. Because of their aminoenone moiety, these can be used in nucleophilic addition (both 1,2- and 1,4-addition), electrophilic substitution, and enolate alkylation reactions [3]. The utility of substituted dihydropyridones as organic building blocks is well documented [3, 4] and can be summarized in Fig. 1. Very recently, (2*R*)-hydroxymethyldihydropyridinone has been successfully used as a versatile chiral building block for the synthesis of several piperidine alkaloids [5].

Due to the growing interest in synthesis and medicinal applications of dihydropyridones, their practical preparative protocol is of paramount importance for medicinal and synthesis chemists. Earlier reported methods for their synthesis include (i) the use of organometallics and 1-acyl salts of 4-methoxy pyridine [6a, b], (ii) conversion of β-aryl-β-amino acids to dihydropyridones [6c–e], (iii) hetero *Diels-Alder* reaction of aromatic imines in presence of a chiral catalyst [6f–i], (iv) palladium catalyzed carbonylation of vinyl oxazolidinones followed by enolisation and then stereoselective quench with a diverse range of electrophiles [7a], (v) multi-step conversion of aryl amino acids into 2,3-dihydropyridones [7b], (vi) *via* β,γ-unsaturated-α-bromoketene/imine cycloaddition to 3-bromo-5,6-dihydropyridin-2-ones [7c], (vii) reacting methoxyallene with isothiocyanates, iodomethane followed by electrocyclization [7d], (viii) four-component reaction of phosphonate, nitriles, aldehydes, and isocyanoacetates to afford functionalized 3-isocyano-3,4-dihydro-2-pyridones [7e], (ix) a very recent report using sulfinimine derived *N*-sulfinyl-δ-amino-β-ketophosphonates, where the phosphoryldihydropyridone thus obtained was efficiently used for the synthesis of (−)-myrtine [7f], and (x) treating 2-(2-acetyl-1-methyl-3-oxobutyl)-*N*-aryl-3,3-bis(ethylthio)acrylamides (obtained by BF_3OEt_2 catalysed reaction of hydroxyketene-*S*,*S*-acetals and active methylene compounds) with NaOH and then with $TiCl_4$ in presence of NEt_3 [7g].

However, most of these synthesis methods are associated with one or the other limitations, such as low availability of starting material, or employment of harsh reaction conditions, involvement of toxic chemicals, long reaction times, and moreover two or more steps and thus, the synthesis of dihydropyridones has become a field of increasing interest in synthesis organic chemistry during the past few years.

[#] CDRI communication No. 6470

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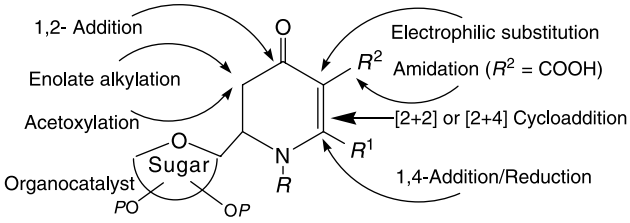
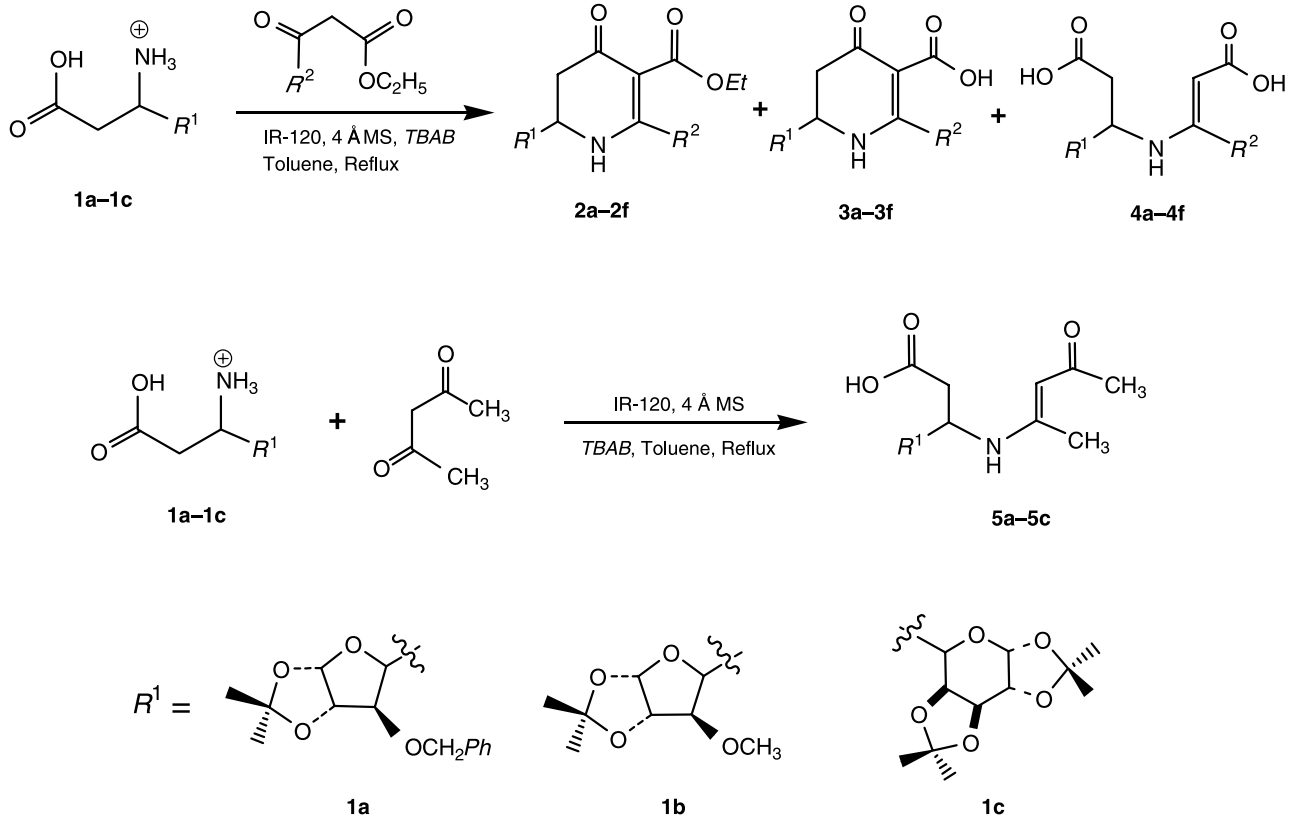


Fig. 1. Synthesis utility of 2,3-dihydro-4-pyridones

Results and Discussion

In continuation of our work on the development of biologically active compounds from sugars [8, 9], we have also reported a two-step process for the synthesis of glycosyl dihydropyridones (C-nucleoside), which involves Amberlite IR-120 catalysed synthesis of glycosyl enamines followed by NaH mediated cyclization [10]. In this NaH mediated cyclization method it is sometimes difficult to isolate the products and the yields of dihydropyridones are also not encouraging. This has led to search for an alternative method for their synthesis. We thought if glycosyl amino acids instead of esters are used the resulting enamine having a carboxyl substituent would lead *via* an acid catalysis to a carbocation, which would be attacked by the electron rich β-carbon of the enamine to give the dihydropyridone. Thus, condensation of 5-(amino-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-gluco- and -β-L-ido-1,4-furanos-5-yl)heptuuronoic acid (**1a**) [8e] with ethyl acetoacetate in presence of IR-120 resin and 4 Å MS in refluxing toluene resulted in the formation of a mixture of three products over a long reaction period. The products were isolated by column chromatography and were characterized as glycosyl 2,3-dihydropyridones **2a** and **3a** with 5-carbethoxy and 5-carboxy substituents and a dibasic acid **4a**.

Since application of a phase transfer catalyst (PTC) is known to enhance the rate of such reactions and hence it prompted us to see its effect on the progress of reaction. Thus, addition of tetrabutylammonium bromide (*TBAB*) to the above reaction led to reduce the time period to 2 hours and better yields of cyclized dihydropyridones were observed. The same reaction of the above glycosyl amino acid **1a**



Scheme 1

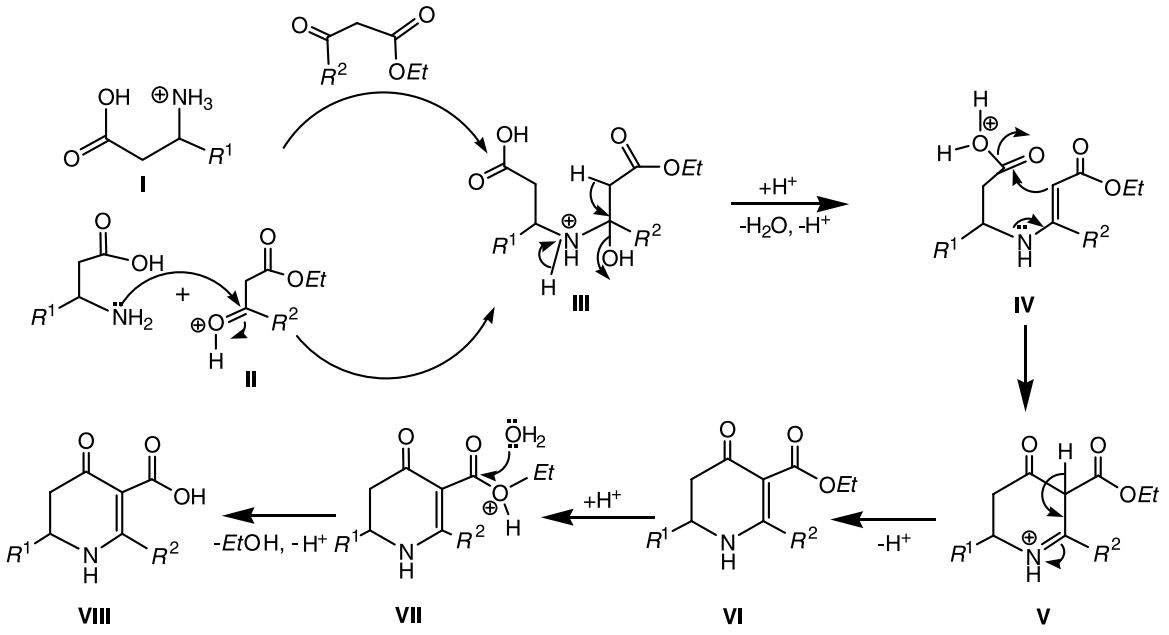


Fig. 2. Proposed mechanism

with ethyl butyrylacetate resulted in the formation of three products, the cyclized dihydropyridones with 5-carbethoxy **2b**, 5-carboxy substitutent **3b** and dibasic acid **4b** in the ratio 60:20:20. However, the reaction of glycosyl amino acid **1a** and acetylacetone after several hours of refluxing in toluene with or without *TBAB* resulted only in the uncyclized enamino monobasic acid **5a** in 85% isolated yield, similar to our earlier observation [10]. Similarly, the reaction of glycosyl amino acids **1b** [8e] and **1c** [9a,b] with ethyl acetoacetate and ethyl butyrylacetate in refluxing toluene in presence of molecular sieve resulted in the formation of cyclized dihydropyridones **2** and **3** with carbethoxy and carboxy substituents and dibasic acid **4**. Compounds **1b** and **1c** on similar reaction with acetylacetone here too gave only uncyclised monobasic acids **5b** and **5c** in 80 and 85% yield.

To the best of our knowledge this is the first report of an IR-120 resin catalysed synthesis of glycosyl dihydropyridones. The method is very simple as it requires only filtration and evaporation of solvent followed by purification by column chromatography.

The mechanism proposed for the above condensation reaction involves protonation of the β-keto oxygen and then nucleophilic attack by the amino functionality of β-glycosyl β-amino acids to the same β-keto carbonyl carbon resulting in a tetrahedral intermediate **III**. The latter may undergo dehydration, yield to formation of β-glycosyl enamine that on further protonation at acid functionality **IV** followed by simultaneous intramolecular nucleophilic attack by the carbanion to the electrophilic carbonyl carbon species, and subsequent removal of proton would result in formation of the glycosyl dihydropyridones **VI**. The corresponding acids **VIII** may be results of IR-120 resin catalysed subsequent hydrolysis of **VII**, *i.e.*, the removal of C_2H_5OH from that of the glycosyl dihydropyridones **VII** as shown in Fig. 2.

In conclusion, we developed a new, simple, and economical method for the synthesis of glycosyl dihydropyridones, which may serve as scaffolds for the stereoselective synthesis of diverse classes of compounds of biological significance. The method may be extended to other β-amino acids too.

Experimental

Glassware was dried over an open flame before use in connection with an inert atmosphere (N_2) and solvents were evaporated under reduced pressure at temperature <55°C. Thin layer chromatography (TLC) was performed using silica gel 60 F-254 plates with I_2 vapors as detecting agents followed by spraying with 5% H_2SO_4 in ethanol. Silica gel (230–400 mesh) was used for column chromatography. *TMS* (0.0 ppm) was used as an internal standard in ^{1}H NMR and $CDCl_3$ (77.0 ppm) in ^{13}C NMR. Infrared spectra were recorded from KBr pelletes by a Perkin Elemer RX-1 spectrometer. Elemen-

tal analyses were performed on a Perkin-Elmer 2400 C, H, N analyzer and values were found to be within ±0.4% of the calculated values. Unless otherwise stated, all materials were obtained from commercial suppliers Sigma Aldrich Company and Spectrochem Pvt. Ltd. and were used without further purification.

General Procedure for the Synthesis of Compounds

A mixture of 1.0 g β-glycosyl-β-amino acid (**1a**; 2.74 mmol), 0.45 cm^3 ethyl acetoacetate (2.89 mmol) and 0.5 g Amberlite IR-120 resin in presence of 0.5 g molecular sieve (4 Å) and 0.2 g *TBAB* in 20 cm^3 anhydr. toluene fitted with a *Dean-Stark* apparatus to remove water formed during reaction, was refluxed under magnetic stirring for 3 h. The resin and molecular sieve were filtered off and the solvent was evaporated under reduced pressure. The residue obtained was chromatographed over SiO_2 column using a gradient starting from $CHCl_3$:*Me*OH (98:2) to give 0.71 g **2a** (60%) as colorless oil. Further elution of column with $CHCl_3$:*Me*OH (94:6) afforded 0.19 g **3a** (16%) along with dibasic acid **4a**.

6-(3′-O-Benzyl-1′,2′-O-isopropylidene-α-D-xylotetrafuranos-4′-yl)-3-carbethoxy-2-methyl-1,4,5,6-tetrahydropyridine-4-one (**2a**, $C_{23}H_{29}NO_7$)

Yield 60%; colorless oil, FAB MS: $m/z = 432$ $[M+H]^+$; IR (KBr): $\bar{\nu} = 3414$, 1720, 1640, 1540 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.32$ (m, 5H, *Ar-H*), 5.95 (d, $J =$ 3.6 Hz, 1H, *H*-1′), 5.89 (bs, 1H, NH), 4.68 (d, $J = 11.7$ Hz, 1H, OCH_A*Ph*), 4.66 (d, $J = 3.6$ Hz, 1H, *H*-2′), 4.48 (d, $J =$ 11.7 Hz, 1H, OCH_B*Ph*), 4.26 (q, $J = 7.4$ Hz, 2H, OCH_2CH$_3$), 4.12 (m, 2H, H-4′, H-6), 3.97 (d, $J = 3.1$ Hz, 1H, H-3′), 2.38 (m, 2H, H-5), 2.22 (s, 3H, C=CCH_3), 1.50, 1.33 [2s, each 3H, C(CH_3)$_2$], 1.28 (t, $J = 7.1$ Hz, 3H, OCH$_2$CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 187.1$ (*C*OCH$_2$), 167.0 (*C*OOC$_2$H$_5$), 165.7 (N*C*=C), 136.6 (*Ar*-C), 129.1, 128.9, 128.3 (*Ar-C*H), 112.6 [>*C*(CH$_3$)$_2$], 105.3 (NC=*C*), 104.2 (C-1′), 82.2 (C-2′), 81.7 (C-4′), 81.0 (C-3′), 72.6 (O*C*H$_2$*Ph*), 60.5 (O*C*H$_2$CH$_3$), 51.6 (C-6), 38.3 (C-5), 27.1, 26.5 [2×>C(*C*H$_3$)$_2$], 14.7 (OCH$_2$*C*H$_3$) ppm.

6-(3′-O-Benzyl-1′,2′-O-isopropylidene-α-D-xylotetrafuranos-4′-yl)-3-carbethoxy-2-propyl-1,4,5,6-tetrahydropyridine-4-one (**2b**, $C_{25}H_{33}NO_7$)

According to the procedure described for **2a** [10]. Yield 55%; colorless oil, FAB MS: $m/z = 460$ $[M+H]^+$; IR (KBr): $\bar{\nu} = 3268$ (NH), 1705 (OC=O), 1547 (N–C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.31$ (m, 5H, *Ar-H*), 5.96 (d, $J = 3.6$ Hz, 1H, *H*-1′), 5.90 (bs, 1H, NH), 4.69 (d, 1H, $J = 11.7$ Hz, OCH_A*Ph*), 4.68 (d, $J = 3.6$ Hz, 1H, H-2′), 4.48 (d, 1H, $J = 11.7$ Hz, OCH_B*Ph*), 4.25 (q, $J = 7.2$ Hz, 2H, OCH_2CH$_3$), 4.19 (dd, $J = 6.0$ Hz, 9.6 Hz, 1H, H-4′), 3.99 (m, 1H, H-6), 3.93 (d, $J = 3.3$ Hz, 1H, H-3′), 2.40 (m, 4H, H-5, CH_2CH_2CH$_3$), 1.60 (m, 2H, CH$_2$CH_2CH$_3$), 1.57, 1.31 [2s, each 3H, C(CH_3)$_2$], 1.28 (t, $J = 7.8$ Hz, 3H, OCH$_2$CH_3), 0.88 (t, $J = 7.5$ Hz, 3H, CH$_2$CH$_2$CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 186.6$ (*C*OCH$_2$), 173.0 (*C*OO*Et*), 168.1 (N*C* = C), 136.8, 135.7 (*Ar*-C), 128.1, 127.8, 127.3 (*Ar-C*H), 111.6, 110.6 [*C*(CH$_3$)$_2$], 104.7, 104.3 (C-1), 81.5 (NC=*C*H), 81.2, 80.2, 77.2 (C-2, C-3, C-4), 71.5 (O*C*H$_2$*Ph*), 59.4 (O*C*H$_2$CH$_3$), 53.3 (C=*C*H$_2$CH$_2$), 50.8 (C-5), 38.9, 37.3 (C=CCH$_2$*C*H$_2$CH$_3$), 32.3 (C-6), 26.5, 25.9 [2×>C(*C*H$_3$)$_2$], 14.1, 13.7 (2×CH$_3$) ppm.

6-(1′,2′:3′4′-Di-O-isopropylidene-α-D-galactopentapyranos-5′-yl)-3-carbethoxy-2-methyl-1,4,5,6-tetrahydropyridine-4-one (**2e**, $C_{20}H_{29}NO_8$)

According to the procedure described for **2a** [10]. Chromatographed over silica gel using *n*-hexane:ethyl acetate (65:35). Yield 62% as colorless oil; MS FAB: $m/z = 412$ $[M+H]^+$; IR (neat): $\bar{\nu} = 3381$ (NH), 1702 (OC=O), 1632 (N–C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 5.55$ (d, $J = 4.9$ Hz, 1H, diastereomeric H-1′), 4.64 (dd, $J = 7.9$, 2.4 Hz, 1H, H-3′), 4.37, 4.35 (dd, $J = 4.9$, 2.4 Hz, 1H, H-2′), 4.20 (m, 3H, H-4′, OCH_2CH$_3$), 3.89 (m, 1H, H-6), 3.75 (d, $J = 7.6$ Hz, 1H, H-5′), 2.69, 2.52 (2m, each 1H, H-5$_A$, H-5$_B$), 2.29 (s, 3H, C=CCH_3), 1.50, 1.43 (2s, each 3H, C(CH_3)$_2$), 1.32 (s, 6H, C(CH_3)$_2$), 1.23 (t, $J = 7.0$ Hz, 3H, diastereomeric OCH$_2$CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 187.63$ (C=O), 167.03 (*C*OOC$_2$H$_5$), 166.03 (N*C*=C), 110.21, 109.56 [2×>*C*(CH$_3$)$_2$], 104.32 (NC=*C*), 96.66 (C-1′), 71.21 (C-3′), 70.90 (C-2′), 68.72 (C-4′), 65.87 (C-5′), 60.47 (OCH$_2$CH$_3$), 52.67, 51.70 (C-6), 37.99, 37.44 (C-5), 26.38, 26.19, 25.26, 24.49 [2×>C(*C*H$_3$)$_2$], 22.19, 22.10 (C=C*C*H$_3$), 14.75 (OCH$_2$*C*H$_3$) ppm.

6-(1′,2′:3′4′-Di-O-isopropylidene-α-D-galactopentapyranos-5′-yl)-3-carbethoxy-2-propyl-1,4,5,6-tetrahydropyridine-4-one (**2f**, $C_{22}H_{33}NO_8$)

According to the procedure described for **2a**. Chromatographed over silica gel using *n*-hexane:ethyl acetate (70:30). Yield 63% as colorless oil; MS FAB: $m/z = 440$ $[M+H]^+$; IR $\bar{\nu} = 3380$ (NH), 1710 (OC=O), 1550 (N–C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 5.53$ (d, $J = 4.9$ Hz, 1H, diastereomeric H-1′), 4.64 (dd, $J = 7.4$, 2.4 Hz, 1H, H-3′), 4.35 (dd, $J = 4.9$, 2.2 Hz, 1H, H-2′), 4.25 (m, 3H, H-4′, OCH_2CH$_3$), 3.90 (m, 1H, H-6), 3.78 (d, $J = 7.6$ Hz, 1H, H-5′), 2.53 (m, 4H, H-5, *C*H$_2$CH$_2$CH$_3$), 1.61 (2m, 2H, CH$_2$*C*H$_2$CH$_3$), 1.48, 1.44 [2s, each 3H, C(CH_3)$_2$], 1.33 [s, 6H, C(CH_3)$_2$], 1.27 (t, $J = 7.7$ Hz, 3H, diastereomeric OCH$_2$CH_3), 0.96 (t, $J = 7.4$ Hz, 3H, diastereomeric CH$_2$CH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) $\delta = 206.5$ (C=O), 166.5 (*C*OO*Et*), 165.03 (N*C*=C), 109.9, 109.2 [2×>*C*(CH$_3$)$_2$], 103.3 (NC=*C*), 96.9 (C-1′), 71.9 (C-3′), 71.4 (C-2′), 71.0 (C-4′), 67.2, 66.9 (C-5′), 62.9 (O*C*H$_2$CH$_3$), 47.9, 47.5 (C-6), 50.8, 50.1 (–*C*H$_2$CH$_2$CH$_3$), 49.8, 45.6 (C-5), 26.2, 25.3 [2×C(*C*H$_3$)$_2$], 17.2 (–CH$_2$*C*H$_2$CH$_3$), 13.8 (OCH$_2$*C*H$_3$, CH$_2$CH$_2$*C*H$_3$) ppm.

6-(3′-O-Benzyl-1′,2′-O-isopropylidene-α-D-xylotetrafuranos-4′-yl)-3-carboxyl-2-methyl-1,4,5,6-tetrahydropyridine-4-one (**3a**, $C_{21}H_{25}NO_7$)

Yield 16%; colorless oil, FAB MS: $m/z = 404$ $[M+H]^+$; IR (KBr): $\bar{\nu} = 3400$, 1715, 1650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.30$ (m, 5H, *Ar-H*), 5.92 (d, $J = 3.6$ Hz, 1H, *H*-1′), 5.80 (bs, 1H, NH), 4.67 (d, $J = 12.0$ Hz, 1H, OCH_A*Ph*), 4.66 (d, $J = 3.6$ Hz, 1H, *H*-2′), 4.47 (d, $J = 12.0$ Hz, 1H, OCH_B*Ph*), 4.10 (m, 2H, H-4′, H-6), 3.95 (d, $J = 3.0$ Hz, 1H,

H-3′), 2.36 (m, 2H, H-5), 2.20 (s, 3H, C=CCH_3), 1.48, 1.30 [2s, each 3H, C(CH_3)$_2$] ppm.

6-(3′-O-Benzyl-1′,2′-O-isopropylidene-α-D-xylotetrafuranos-4′-yl)-3-carboxylic-2-propyl-1,4,5,6-tetrahydropyridine-4-one (**3b**, $C_{23}H_{29}NO_7$)
Yield 20%; colorless oil; FAB MS: $m/z = 432$ $[M+H]^+$, IR (KBr): $\bar{\nu} = 3405$, 1724, 1660 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.31$ (m, 5H, *Ar-H*), 5.96 (d, $J = 3.6$ Hz, 1H, *H*-1′), 4.67 (m, 2H, H-2′, OCH_A*Ph*), 4.47 (d, $J = 11.4$ Hz, 1H, OCH_B*Ph*), 4.07 (m, 1H, H-4′), 3.95 (d, $J = 3.0$ Hz, 1H, H-3′), 3.20 (m, 1H, H-6), 2.39 (m, 4H, H-5, CH_2CH$_2$CH$_3$), 1.56 (m, 2H, CH$_2$CH_2CH$_3$), 1.47, 1.31 [2s, each 3H, >C(CH_3)$_2$], 0.87 (t, $J = 7.3$ Hz, 3H, CH$_2$CH$_2$CH_3) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 206.3$ (*C*OCH$_2$), 174.4 (*C*OOH), 166.1 (N*C*=C), 136.8 (*Ar*-C), 128.5, 128.0 (*Ar*-*C*H), 112.3 [>*C*(CH$_3$)$_2$], 109.9 (NC=*C*), 104.8 (C-1′), 81.9 (C-2′), 79.4 (C-4′), 77.4 (C-3′), 71.7 (OCH_2*Ph*), 48.7 (*C*H$_2$CH$_2$CH$_3$), 45.61 (C-6), 45.2 (C-5), 26.7, 26.2 [2 × >C(*C*H$_3$)$_2$], 16.6 (CH$_2$*C*H$_2$CH$_3$), 13.4 (CH$_2$CH$_2$*C*H$_3$) ppm.

6-(1′,2′:3′4′-Di-O-isopropylidene-α-D-galactopentapyranos-5′-yl)-3-carboxylic-2-propyl-1,4,5,6-tetrahydropyridine-4-one (**3f**, $C_{20}H_{29}NO_8$)
Yield 20%; colorless oil, FAB MS: $m/z = 394$ [M-17]$^+$; IR (KBr): $\bar{\nu} = 3345$, 1719, 1637 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.54$, 5.50 (2d, $J = 3.0$ Hz, 1H, diastereomeric H-1′), 4.59 (dd, $J = 7.6$, 1.7 Hz, 1H, H-3′), 4.38 (m, 3H, H-2′, H-4′, H-5′), 4.09 (m, 1H, H-6), 2.80 (m, 2H, H-5), 2.52 (t, $J = 7.4$ Hz, CH_2CH$_2$CH$_3$), 1.60 (m, 2H, CH$_2$CH_2CH$_3$), 1.50, 1.43 [2s, 6H, >*C*(CH$_3$)$_2$], 1.31 [s, 6H, [>*C*(CH$_3$)$_2$], 0.91 (t, $J = 7.4$ Hz, 3H, CH$_2$CH$_2$CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 206.1$, 205.8 (diastereomeric *C*OCH$_2$), 175.1, 174.6 (N*C*=C), 166.1, 165.9 (*C*OOH), 109.3, 108.7 [*C*(CH$_3$)$_2$], 96.3 (C-1′, NC=*C*), 71.6 (C-3′), 71.0 (C-2′), 70.8 (C-4′), 66.9 (C-5′), 49.8 (*C*H$_2$CH$_2$CH$_3$), 47.5 (C-6), 35.2 (C-5), 25.9, 25.0, 24.2 [2 × >C(*C*H$_3$)$_2$], 16.8 (CH$_2$*C*H$_2$CH$_3$), 13.5 (CH$_2$CH$_2$*C*H$_3$) ppm.

4(R/S)-(3′-O-Benzyl-5′-carboxyl-5′-deoxy-1′,2′-O-isopropylidene-α-D-xylofuranos-5′-yl)aminopent-3-ene-2-one (**5a**, $C_{22}H_{29}NO_7$)
According to the procedure described for **2a**, where **1a** was reacted with acetylacetone in presence of IR-120 resin and *TBAB* for 2 h as above gave a crude mass from which resin was filtered off and the residue obtained after evaporation of solvent was purified by column over SiO_2 using $CHCl_3$:*Me*OH (94:6) as eluent to give **5a** in diastereoisomeric ratio (75:25) as colorless oil. Yield 85%; MS FAB: $m/z = 420$ $(M+H)^+$; IR (neat): $\bar{\nu} = 3400$ (NH), 1720 (OC=O), 1614 (N–C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta =$ 10.86 (br, s, 1H, NH), 7.34 (m, 5H, *Ar*H); 5.92 (d, $J = 3.8$ Hz, 1H, H-1′), 4.93 (s, 1H, C=CH), 4.68 (d, $J = 11.7$ Hz, 1H, OCH_A*Ph*), 4.62 (d, $J = 3.8$ Hz, 1H, H-2′), 4.49 (d, $J = 11.7$ Hz, 1H, OCH$_B$*Ph*), 4.20 (m, 1H, H-4′), 4.05 (m, 1H, H-5′), 3.91 (d, $J = 3.3$ Hz, 1H, H-3′), 3.41 (s, 3H, OCH$_3$), 2.36 (m, 2H, H-6′), 2.00, 1.95 (2s, each 3H, C=CCH$_3$, COCH$_3$); 1.48, 1.31 [2s, each 3H, 12H, C=CCH$_3$, COCH$_3$, 2 × >C(CH_3)$_2$] ppm.

Acknowledgements

The authors thank Dr. *C.M. Gupta*, Director, CDRI for his encouragement and ICMR, New Delhi for financial support. We thank RSIC and CDRI staff for spectral data and microanalysis.

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