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A new strategy for the synthesis of hydroxylated pyrrolizidinic alkaloids by highly stereoselective indium-mediated allylation of pyrrolidinic aldehydes

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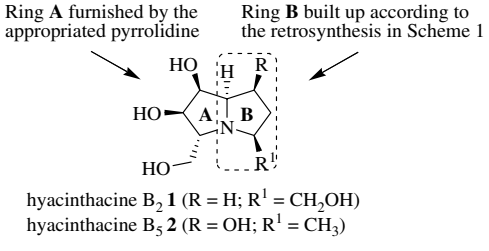
Abstract—Indium-mediated allylation of *N*-Cbz-L-prolinal **3**, under Grignard conditions, was carried out with high yield and stereoselectivity (de = 90%) to afford intermediate (2*S*,1′*R*)-*N*-benzyloxycarbonyl-2-(1′-hydroxybut-3′-en-1′-yl)pyrrolidine **4**, which was transformed in two steps into (1*R*,3*R*,7a*S*)-1-hydroxy-3-hydroxymethylpyrrolizidine **9**. Commercial Cbz-L-proline was a source of functionalization and chirality.

1. Introduction

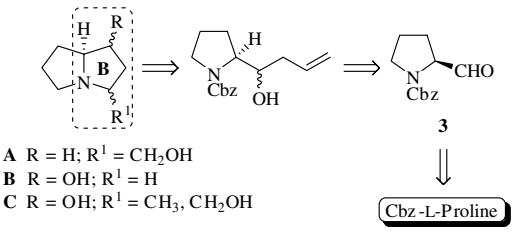
Continuing with our most recent efforts[1] on the synthesis of polyhydroxylated pyrrolizidinic alkaloids (PHPAs), we were interested in exploring the possibility of preparing those with higher and a more diverse degree of functionalization in the **B**-ring, such as the hyacinthacines[2] shown in Figure 1, and other analogues of interest for SAR studies as glycosidase inhibitors.

According to Figure 1, the preparation of the target PHPAs can be accomplished as follows: ring **A** comes from a suitable and orthogonally protected polyhydroxypyrrolidine,[3] which will transfer its chirality and functional groups to the final compound, whereas the **B** ring, with the appropriate stereochemistry and functionalization, can be built up following a synthetic strategy similar to that outlined in Scheme 1, where the retrosynthesis for less elaborated 3-hydroxymethyl **A**, 1-hydroxy-**B** and 1-hydroxy-3-methyl- or 1-hydroxy-3-hydroxymethylpyrrolizidine (**C**), with chiralities matching those in the target molecules is displayed, and consists of a stereocontrolled carbon-chain lengthening and subsequent cyclization. Accordingly, *N*-Cbz-L-prolinal **3**, easily prepared[4] from commercially available *N*-benzyloxycarbonyl-L-proline, would be an excellent starting material for these purposes in order to investigate not only the suitability of the synthetic proposal, but also controlling its stereochemical outcomes, and consequently application of those results to the preparation of more complex targets **1** and **2**.



hyacinthacine B_2 **1** (R = H; $R^1 = CH_2OH$)
hyacinthacine B_5 **2** (R = OH; $R^1 = CH_3$)

Figure 1. Hyacinthacine B_2 **1** and B_5 **2**.



A R = H; $R^1 = CH_2OH$
B R = OH; $R^1 = H$
C R = OH; $R^1 = CH_3, CH_2OH$

Scheme 1. Retrosynthesis of pyrrolizidines A, B and C from Cbz-L-proline.

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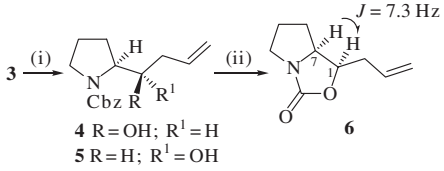
C-Allylation of **3** with $TiCl_4$-mediated allylsilane,[5] or instead that of its *N*-trityl-derivative with the same organometallic reagent and BF_3:Et_2O-mediated or allylmagnesium bromide[6] has previously been reported. Even though moderate to good yields, as well as high stereoselectivities resulted in some cases, we were interested in exploring the same C-alkylation but using indium[7] as a metal promoter.

2. Results and discussion

Indium-mediated reaction of **3** under Grignard conditions[7d] (Scheme 2), gave, after column chromatography, (2*S*,1′*R*)-*N*-benzyloxycarbonyl-2-(1′-hydroxybut-3′-en-1′-yl)pyrrolidine **4** (t_R 7.65 min) in 78% yield, although GLC analysis of the reaction mixture, before work-up and column chromatography, seemed to indicate the presence of a small amount (≈5%) of the corresponding (2*S*,1′*S*)-epimer **5** (t_R 7.80 min), which could not be isolated. Although a synthesis of **4** and **5** has been previously published,[5] data on their optical spectroscopic properties that would allow the determination of the configuration of our compounds, were not included in that report. Thus, upon treatment of **4** with aq KOH, bicyclic carbamate **6** was isolated showing identical spectroscopic data to that previously reported[5,6] for (1*R*,7*S*)-tetrahydro-1-(2-propenyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one, indicating a *cis*-configuration for H(1,7) and hence an (*R*)-configuration at C(1′) in **4**.



Scheme 2. Reagents and conditions: (i) $H_2C{=}CHCH_2InBr$/THF/−78 °C; (ii) aq KOH/THF/rt.

The transition states displayed in Figure 2, account for the the high stereoselectivity found in the above process. Thus, the $J_{1',2} \approx 0$ Hz value in **3** is compatible with conformations **3a** and **3b**, where an orthogonal disposition for the formyl and H(2) protons is present. Of both conformations, only **3a** could account for the chelated model proposed by Singh et al.,[8] where in the transition state, the metal promoter interacts with both formyl oxygen and the heterocyclic nitrogen atoms **TS1**‡ and **TS2**‡. It is easy to conclude that in **TS1**‡, which leads to diastereomer **4**, attack of the nucleophile on the top face would be favoured due to a less crowding than that showed by **TS2**‡.

Surprisingly, when compound **4** was epoxidized with MCPBA (see Fig. 3 and Scheme 3) only one compound, which was identified as (2*S*,1′*R*,3′*S*)-*N*-benzyloxycarbonyl-2-(3′,4′-epoxi-1′-hydroxybut-1′-yl)pyrrolidine **7**, was isolated. Due to the presence of typical carbamate rotamers in **7**, scarce structural and stereochemical information could be obtained from its spectroscopic data, nevertheless its HRMS-spectrum was consistent with the proposed structure. The high stereoselectivity found in this reaction, is noteworthy and can be justified on the basis of the transition state (**A**‡) displayed in Figure 3, where according to an extension of Henbest's statement,[9] the peroxyacid is tethered by the hydroxyl group at C(1′) through a hydrogen bond in such a way that epoxidation took place on the *si*-face affording **7**.

Catalytic hydrogenation of **7** (see Scheme 3) caused a tandem process consisting on its N-deprotection to the intermediate pyrrolidine **8**, followed by a spontaneous and highly favoured 5-*exo*-tet[10] intramolecular cyclization to afford (1*R*,3*R*,7a*S*)-1-hydroxy-3-hydroxymethylpyrrolizidine **9** isolated as its di-*O*-acetate **10** after conventional acetylation of the reaction mixture. A procedure similar to this, but with a different open-chain γ,δ-epoxiamine leading to polyhydroxylated pyrrolidine derivatives, have previously been reported by others.[11]

The structure of **10** was determined on the basis of its ^1H and ^{13}C NMR spectroscopic data. In addition, ^1H–^1H and ^1H–^{13}C COSY and extensive NOE-difference experi-

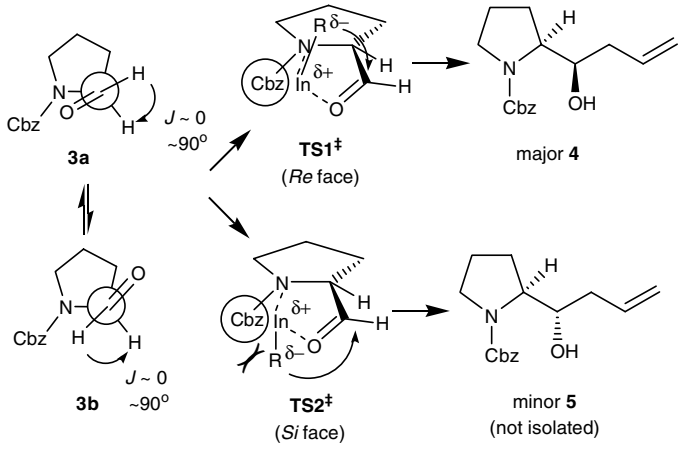


Figure 2. Conformations **3a** and **3b** accounting for the $J_{1',2}$ value and transition states TS1‡ and TS2‡ leading to homoallylic alcohols **4** and **5**, respectively.

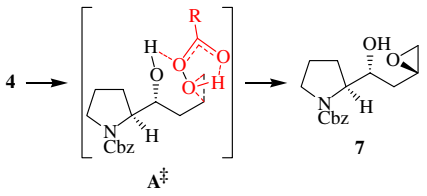
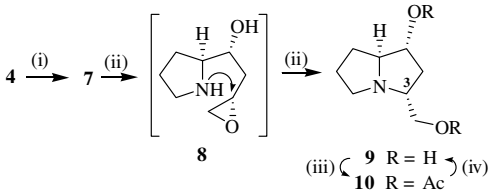


Figure 3. Epoxidation of **4** according to the Henbest model.



Scheme 3. Reagents and conditions: (i) MCPBA/Cl_2CH_2, rt; (ii) 10% Pd–C/H_2; (iii) Ac_2O/py, rt; (iv) MeONa (cat.)/MeOH, rt.

ments (see Fig. 4) allowed the assignment of its ^1H and ^{13}C NMR signals as well as the configuration of the stereogenic centre at C(3). In this context, the definitive NOE interaction between H(1)–H(3) was crucial in order to achieve such an assignment not only in **10**, but also that at C(3′) in **7**. Finally, conventional Zemplen de-O-acetylation of **10** afforded the required target molecule **9**.

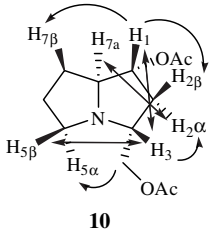


Figure 4. Main NOE interactions in **10**.

3. Conclusions

We have developed a new strategy for the preparation of the **B** ring in natural, densely polyhydroxylated, pyrrolizidinic alkaloids with a high degree of stereocontrol via C-allylation and tandem allylic epoxidation–intramolecular cyclization reactions. These results will be extended to the synthesis of more complex molecules in due course.

4. Experimental

Solutions were dried over $MgSO_4$ before concentration under reduced pressure. The ^1H and ^{13}C NMR spectra were recorded with Bruker AMX-300, AM-300 and ARX-400 spectrometers for solutions in $CDCl_3$ (internal Me_4Si). IR spectra were recorded with a Perkin–Elmer FT-IR Spectrum One instrument and mass spectra with a Hewlett–Packard HP-5988-A and Fisons mod. Platform II and VG Autospec-Q mass spectrometers. Optical rotations were measured in solutions of $CHCl_3$ (1-dm tube) with a Jasco DIP-370 polarimeter. GLC was performed on a Hewlett–Packard 6890 gas chromatograph equipped with split/splitless injector, a flame-ionization detector and a capillary HP-5 column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) at 10 min at 230 °C program to 250 °C, 20 °C/min; the He flow rate was 0.7 ml/min and the injection port and the zone-detector temperatures were 250 °C. TLC was performed on precoated silica gel 60 F_{254} aluminium sheets and detection by employing a mixture of 10% ammonium molybdate (w/v) in 10% aqueous sulfuric acid containing 0.8% cerium sulfate and heating. Column chromatography was performed on silica gel (Merck, 7734). The non-crystalline compounds, whose elemental analyses are not include, were shown to be homogeneous by chromatographic methods and characterized by NMR, MS and HRMS.

4.1. Indium-mediated allylation reaction of *N*-Cbz-L-prolinal 3

To a vigorously stirred suspension of indium metal (1 g, 8.7 mmol) in anhydrous THF (10 ml), allyl bromide (1.1 ml, 12.6 mmol) was added and the mixture refluxed until most of the metal had disappeared (1 h). The mixture was then cooled to −78 °C, and a solution of **3**[4b] (1 g, 4.2 mmol) in the same solvent (5 ml) added dropwise. After 15 min, GLC revealed the absence of **3** and the presence of two new products (t_R 7.65 and 7.80 min) in a 95:5 ratio, respectively. The reaction mixture was concentrated and the residue subjected to column chromatography (Et_2O–hexane 1:2 → Et_2O → Et_2O–MeOH, 15:1) to yield (2*S*,1′*R*)-*N*-benzyloxycarbonyl-2-(1′-hydroxybut-3′-en-1′-yl)pyrrolidine **4** (900 mg, 78%) as a colourless syrup; $[\alpha]_D^{26} = -56$ (*c* 1, $CHCl_3$). IR (neat): 3450 (OH) and 1681 cm^{-1} (C=O). NMR data (300 MHz): ^1H, δ 7.35 (m, 5H, Ph), 5.88 (m, 1H, H-3′), 5.17–4.98 (m, 4H, CH_2Ph, H-4′*cis*,4′*trans*), 3.98–3.29 (m, 5H, H-1′,2,5a,5b,OH) and 2.17–1.71 (m, 4H, H-3a,3b,4a,4b); ^{13}C (75 MHz, inter alia): δ 136.70, 128.58, 128.12 and 127.98 (Ph), 135.39 (C-3′), 117.22 (C-4′), 72.09 (C-1′), 67.20 (CH_2Ph), 63.12 (C-2), 47.84 (C-5), 37.46 (C-2′), 26.89 and 24.40 (C-3,4). Mass spectrum (LSIMS): *m*/*z*: 298.1418 [M^++Na] for $C_{16}H_{21}NO_3Na$ 298.1419 (deviation +0.5 ppm).

4.2. (1*R*,7*S*)-Tetrahydro-1-(2-propenyl)-1*H*,3*H*-pyrrolo-[1,2-*c*]oxazol-3-one 6

To a solution of **4** (168 mg, 0.61 mmol) in THF (3 ml) an aqueous solution of KOH (100 mg) in water (5 ml) was added and the mixture left at rt for two weeks. GLC analysis then revealed the absence of **4** and the appearance of a new product (t_R = 2.98 min). The reaction mixture was concentrated and the residue dissolved in Cl_2CH_2, washed with brine, supported on silica gel and then chromatographed (Et_2O–hexane 2:1) to yield **6** (20 mg, 20%) with spectroscopic data in accordance with those previously reported[6] $[\alpha]_D^{26} = -20$ (*c* 0.6, $CHCl_3$). IR (neat) 3079 (C=CH), 1755 (C=O) and 1643 cm^{-1} (C=C). NMR data (300 MHz): ^1H, δ 5.79

(dddd, 1H, $J_{1'a,2'}$ 6.1, $J_{1'b,2'}$ 7.3, $J_{2',3'cis}$ 10.2, $J_{2',3'trans}$ 17.3 Hz, H-2′), 5.18 (dq, 1H, $J_{3'cis,3'trans} = J_{1'a,3'trans} = J_{1'b,3'trans} = 1.6$ Hz, H-3′*trans*), 5.15 (dq, 1H, $J_{1'a,3'cis} = J_{1'b,3'cis} = 1.3$ Hz, H-3′*cis*), 4.69 (q, 1H, $J_{1,1'a} = J_{1,1'b} = J_{1,7} = 7.3$ Hz, H-1), 3.79 (ddd, 1H, $J_{6a,7}$ 5.2, $J_{6b,7}$ 10.9 Hz, H-7), 3.63 (dt, 1H, $J_{4a,5a} = J_{4a,5b} = 8$, $J_{4a,4b} = 11.3$ Hz, H-4a), 3.16 (ddd, 1H, $J_{4b,5a}$ 9.4, $J_{4b,5b}$ 3.3 Hz, H-4b), 2.58 (m, 1H, H-1′a), 2.36 (m, 1H, H-1′b), 2.06 (m, 1H, H-5a), 1.86 (m, 1H, H-5b), 1.76 (m, 1H, H-6a) and 1.49 (dq, 1H, $J_{5a,6b} = J_{5b,6b} = J_{6b,7} = 7.7$, $J_{6a,6b}$ 10.4 Hz, H-6b); ^{13}C (75 MHz): δ 161.59 (C-3), 132.33 (C-2′), 118.70 (C-3′), 75.39 (C-1), 63.24 (C-7), 45.78 (C-4), 34.91 (C-1′), 25.18 (C-5) and 25.01 (C-6).

4.3. (2*S*,1′*R*,3′*S*)-*N*-Benzyloxycarbonyl-2-(3′,4′-epoxi-1′-hydroxybut-1′-yl)pyrrolidine 7

To a stirred solution of **4** (1.13 g, 4.1 mmol) in anhydrous CH_2Cl_2 (5 ml) was added a solution of MCPBA (2.12 g, 6.15 mmol) in the same solvent (25 ml). After 24 h TLC (Et_2O) revealed the absence of **4** and the presence of a slower-running product. The reaction mixture was filtered and the filtrate subsequently washed with 10% aq Na_2SO_3, 5% aq K_2CO_3 and brine. The organic phase was concentrated to a residue that was subjected to column chromatography (Et_2O) to afford **7** (900 mg, 75%) as a colourless syrup; $[\alpha]_D^{26} = -47$ (*c* 0.8, $CHCl_3$). IR (neat) 3432 (OH), 1699 (CO), 753 and 699 cm^{-1} (aromatic) NMR data (300 MHz): ^{1}H, δ 7.40–7.30 (m, 5H, Ph), 5.19–5.08 (m, 2H, CH_2Ph), 4.10–2.45 (6 m, 8H, H-2,5a,5b,1′,3′,4′a,4′b,OH) and 2.10–1.90 (m, 6H, H-3a,3b,4a,4b,2′a,2′b); ^{13}C, (75 MHz, inter alia) δ 136.60, 128.61, 128.19 and 128.00 (Ph), 67.30 (CH_2Ph), 63.63 (C-2), 50.75 (C-3′), 47.87 and 47.77 (C-4′,5), 35.34 (C-2′), 27.22 and 24.26 (C-3,4). Mass spectrum (LSIMS): *m*/*z*: 314.1362 [M$^+$+Na] for $C_{16}H_{21}NO_4Na$ 314.1368 (deviation +2.0 ppm).

4.4. (1*R*,3*R*,7a*S*)-1-Acetyloxy-3-acetyloxymethyl-pyrrolizidine 10

Compound **7** (900 mg, 3.1 mmol) in anhydrous MeOH (20 ml) was hydrogenated under the presence of 10% Pd–C (80 mg) at 65 psi for 15 h. TLC (MeOH) revealed no **7** but compounds with very low mobility. The catalyst was filtered off washed with MeOH and the filtrate and washings concentrated to a residue that was conventionally acetylated in pyridine (1 ml) with Ac_2O (1 ml) and DMAP (50 mg) for 3 h. TLC (MeOH) then showed a faster-running product. The acetylation reaction was concentrated to a residue that was dissolved in CH_2Cl_2 and washed with water. The aqueous phase was basified with Na_2CO_3 and extracted with EtAcO. The combined organic extracts were concentrated and the residue purified by chromatography (EtAcO) to afford pure **10** (200 mg, 27%) as a colourless syrup; $[\alpha]_D^{26} = -18$ (*c* 0.4, $CHCl_3$). NMR data (300 MHz): ^{1}H, δ 4.83 (dt, 1H, $J_{1,2\alpha} = J_{1,2\beta} = 6.4$, $J_{1,7a}$ 4.5 Hz, H-1), 4.00 (d, 2H, $J_{3,8}$ 6.3 Hz, H-8,8), 3.42 (dt, 1H, $J_{7\alpha,7a} = J_{7\beta,7a} = 7.1$ Hz, H-7a), 2.96 (m, 2H, H-3,5α), 2.65 (dt, 1H, $J_{5\alpha,5\beta}$ 10.9, $J_{5\beta,6\alpha} = J_{5\beta,6\beta} = 6.4$ Hz, H-5β), 2.32 (dt, 1H, $J_{1,2\beta} = J_{2\beta,3} = 6.7$, $J_{2\alpha,2\beta}$ 13.4 Hz, H-2β), 2.02 and 1.99 (2 s, 6H, 2CH_3CO), 1.91 (ddt, 1H, *J* 5.7, *J* 7.5, $J_{7\alpha,7\beta}$ 14.4 Hz, H-7α), 1.78–1.63 (m, 3H, H-2α,6α,6β) and 1.50 (ddt, 1H, H-7β); ^{13}C (75 MHz): δ 170.90 and 170.80 (CH_3CO), 78.38 (C-1), 70.15 (C-7a), 68.09 (C-8), 63.26 (C-3), 55.19 (C-5), 34.86 (C-2), 30.07 (C-7), 25.31 (C-6), 21.14 and 20.94 (2CH_3CO).

4.5. (1*R*,3*R*,7a*S*)-1-Hydroxy-3-hydroxymethyl-pyrrolizidine (9)

To a solution of **10** (190 mg, 0.78 mmol) in anhydrous MeOH (10 ml) was added MeONa/MeOH (2 M, 0.2 ml) and the mixture left at rt for 24 h. TLC (AcOEt) then revealed the absence of **10** and the presence of a slower-running compound. The reaction mixture was concentrated and the residue chromatographed (CH_2Cl_2–MeOH–NH_4OH 6:2:0.5) to yield **9** as a syrup (100 mg, 82%); $[\alpha]_D^{26} = +1$, $[\alpha]_{405}^{26} = +1.4$ (*c* 0.8, MeOH). IR (neat) 3351 cm^{-1} (OH). NMR data (300 MHz, MeOH-D_4): ^{1}H, δ 3.87 (dt, 1H, $J_{1,7a}$ 6.2, $J_{1,2} = J_{1,2'} = 8.6$ Hz, H-1), 3.57 (dd, 1H, $J_{3,8}$ 5.8, $J_{8,8'}$ 10.7 Hz, H-8), 3.51 (dd, 1H, $J_{3,8'}$ 5.8 Hz, H-8′), 3.24 (dt, 1H, $J_{7,7a}$ 7, $J_{7',7a}$ 4.6 Hz, H-7a), 2.91–2.77 (m, 2H, H-5,5′), 2.73 (quin, 1H, $J_{2,3} = J_{2',3} = 6$ Hz, H-3), 2.23 (br dt, 1H, $J_{2,2'}$ 12.2 Hz, H-2), 1.88 (dq, 1H, $J_{6,7} = J_{6',7} = 7$, $J_{7,7'}$ 12.1 Hz, H-7), 1.82–1.63 (m, 3H, H-6,6′,7′) and 1.58 (br dt, 1H, H-2′); ^{13}C (75 MHz): δ 77.41 (C-1), 73.17 (C-7a), 67.82 (C-3), 66.70 (C-8), 56.04 (C-5), 39.22 (C-2), 31.04 (C-7) and 25.74 (C-6). Mass spectrum (LSIMS): *m*/*z*: 157.1099 [M$^+$] for $C_8H_{15}NO_2$ 157.1103 (deviation +2.2 ppm).

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