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Synthesis and NMR study of pyridinocholaphanes

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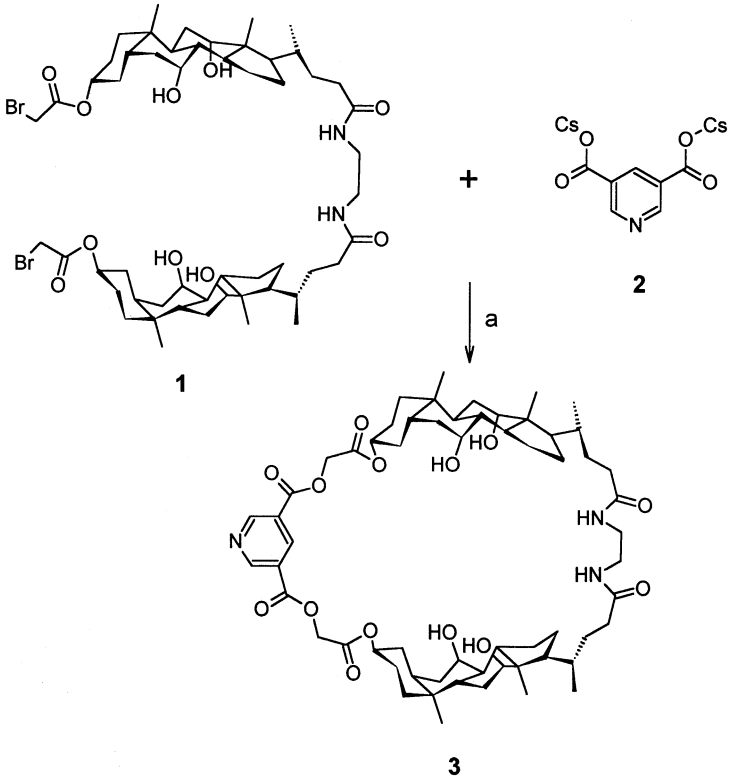
Abstract—Pyridinocholaphanes based on cholic, deoxycholic and lithocholic acids with ethylenediamine and *m*-xylylenediamine as spacers were synthesized using Cs-salt methodology. Their structures were elucidated on the basis of their IR, NMR and FAB mass spectral data. The NMR techniques, DEPT^{13}C{^{1}H}135/90 and HSQC{^{1}H–^{13}C} were used for the detailed assignment of the carbon atoms of the pyridinocholaphanes. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Remarkable progress has been made in the recent past with regard to design and synthesis of chemical models that can imitate the natural processes particularly enzymic reactions. Among these, enzymes possessing NAD^+/NADH coenzyme have received much attention due to their ability to carry out oxidation–reduction in a highly stereoselective manner.[1,2] It has been realized that the dihydronicotinamide moiety attached with macrocyclic systems are better catalysts as they can bind the substrates more effectively. Thus, various systems based on cyclophane, cyclodextrin



Scheme 1. (a) DMF, 12 h, rt, 87%.

Keywords: steroid; macrocycles; bis-cesium 3,5-pyridine dicarboxylate; DEPT-NMR; HSQC-NMR.
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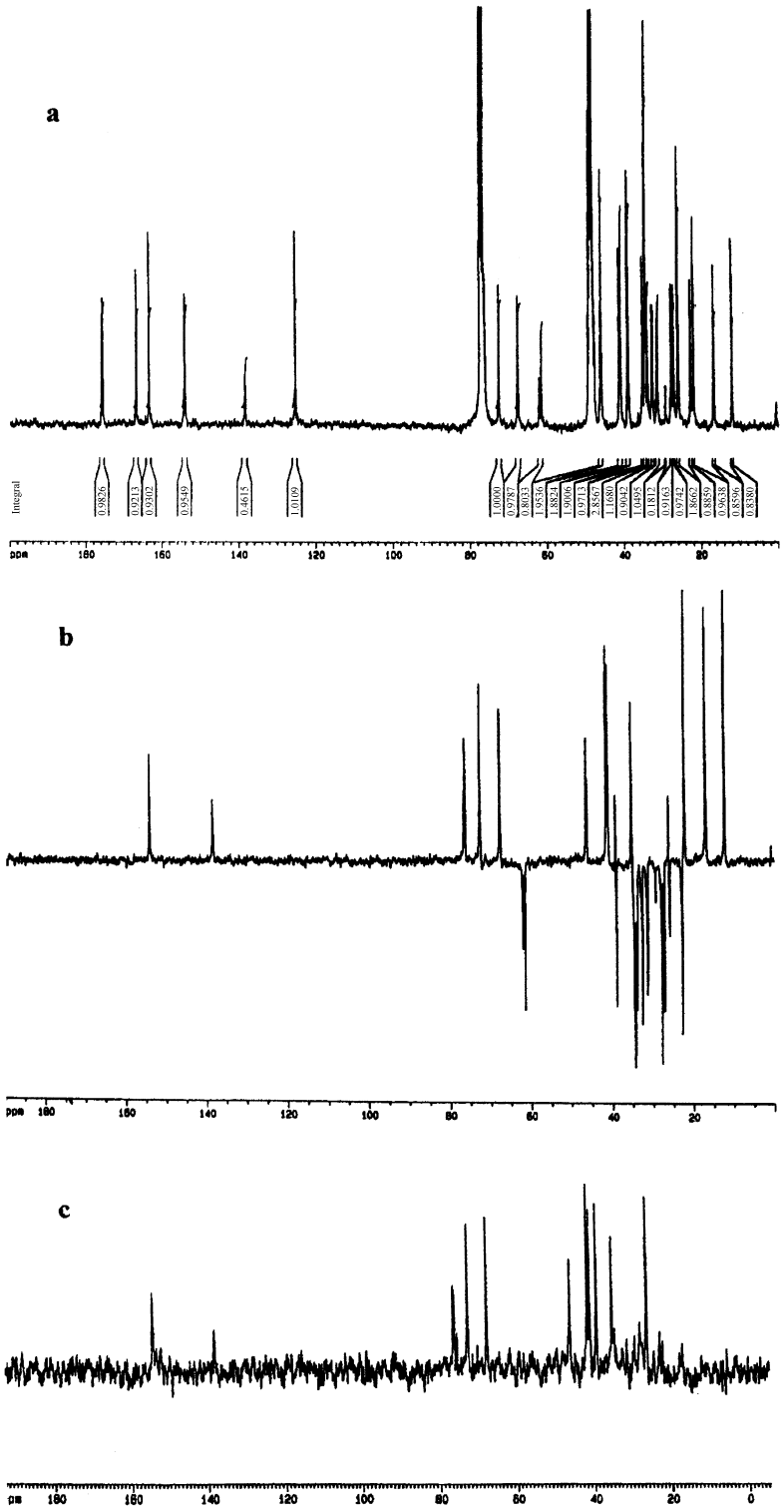
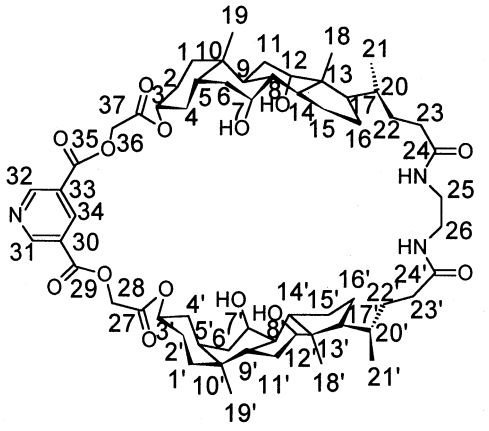


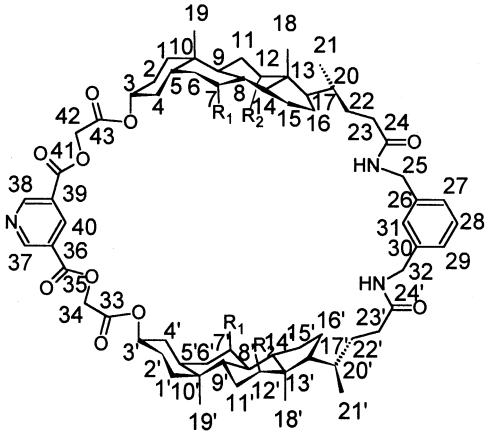
Figure 1. (a) ^{13}C spectrum (b) DEPT$^{13}C\{^{1}H\}135$- and (c) DEPT$^{13}C\{^{1}H\}90$-NMR spectrum of pyridinocholaphane **3**.

and crown-ether have been studied.[3–5] Kellogg and coworkers have designed a large number of macrocyclic dihydronicotinamide systems and have demonstrated that some of the systems give high stereoselectivity in the reduction of activated carbonyl compounds in the presence of Mg^{2+} ion.[6]

Recently, steroidal macrocyclic systems based on cholic acid have received much attention as they have been found to bind carbohydrate derivatives in enantio- and diastereoselective manner.[7–9] As a highly efficient and simple methodology for the construction of cholic acid based receptors, head to head cholaphanes, has been developed by us,[10] it is considered worthwhile to use this strategy for the design of pyridinocholaphanes as the precursors of NADH analogues. With the chiral, rigid framework and



3



R_1, R_2= OH

5a

presence of hydroxyl groups in the interior, it is likely that these macrocyclic systems may selectively bind polar substrates and prove to be potential enzyme models for dehydrogenases.

2. Results and discussion

Earlier, we have reported the synthesis of head to head cholaphanes using Cs-salt methodology. To see its general applicability, we synthesized various pyridinocholaphanes by incorporating 3,5-pyridine dicarboxylate as a spacer. Their structural identity was established on the basis of ^{1}H, ^{13}C NMR and FAB mass spectral analysis.

The precursor bis-bromoacetylcholamide **1**, was prepared by the procedure reported earlier.[10] The cyclization was carried out by treatment of **1** with bis-cesium 3,5-pyridine dicarboxylate **2** in DMF (Scheme 1) to give the pyridinocholaphane **3** in almost quantitative yield. The ^{1}H NMR spectrum of **3** showed a multiplet at δ 3.27 for amidoethylene protons and a broad singlet at δ 4.81 for $COCH_2$–O protons. The methine protons at 7- and 12-positions were observed as broad singlets at δ 3.75 and 3.88, respectively, whereas the proton at 3-position

Table 1. ^{13}C NMR spectral data δ (ppm) for compounds **3**, **5a**–**c**.

Carbon	3	5a	5b	5c
1, 1′	34.51	34.61	34.66	34.81
2, 2′	27.90	28.01	28.54	28.28
3, 3′	76.57	76.57	76.59	76.57
4, 4′	34.51	34.61	32.92	31.81
5, 5′	40.99	41.06	41.73	41.77
6, 6′	31.50	29.57	29.59	26.83
7, 7′	67.70	67.89	26.80	26.35
8, 8′	39.15	39.16	34.02	35.46
9, 9′	26.15	26.33	35.81	40.41
10, 10′	34.51	34.61	33.51	34.46
11, 11′	26.15	26.33	25.94	20.81
12, 12′	72.59	72.72	72.82	40.07
13, 13′	46.10	46.23	46.35	42.65
14, 14′	41.41	41.61	46.66	56.47
15, 15′	22.87	23.06	23.56	24.10
16, 16′	27.32	27.38	27.44	30.94
17, 17′	46.31	46.23	48.01	55.61
18, 18′	12.14	12.28	12.59	12.00
19, 19′	22.09	22.26	22.94	23.23
20, 20′	35.26	35.20	35.16	34.81
21, 21′	16.87	17.17	17.21	18.36
22, 22′	32.75	31.63	31.47	31.81
23, 23′	34.10	32.56	31.89	29.68
24, 24′	175.70	174.67	174.08	173.61
25	39.15	43.20	43.22	43.36
26	39.15	138.67	138.89	138.90
27	163.47	126.78	126.68	126.81
28	61.62	126.78	126.68	126.81
29	166.80	126.78	126.68	126.81
30	125.39	138.67	138.80	138.90
31	154.15	128.65	128.78	128.96
32	154.15	43.20	43.22	43.36
33	125.39	163.64	163.70	163.75
34	138.59	61.81	61.79	62.21
35	166.80	166.86	166.74	166.70
36	61.62	125.45	125.36	125.31
37	163.47	154.38	154.54	154.75
38		154.38	154.54	154.75
39		125.45	125.36	125.31
40		138.67	138.80	138.90
41		166.86	166.74	166.70
42		61.81	61.79	62.21
43		163.64	163.70	163.75

appeared at δ 4.61 as a multiplet. The characteristic methyl protons at 18, 19 and 21 positions appeared at 0.60 (singlet), 0.84 (singlet), and 0.92 (broad singlet), respectively. The remaining steroidal protons showed a complex pattern of signals between 0.99 and 2.50 ppm. The presence of pyridine protons at 8.85 and 9.34 ppm and protons for $COCH_2$–O– at δ 4.81 indicated the formation of **3**. The FAB mass spectrum revealed the molecular ion peak at *m/z* 1089 (MH^+). The structure of pyridinocholaphane **3** was further confirmed by its quantitative ^{13}C NMR spectrum (Fig. 1a). The detailed assignments of ^{13}C NMR signals were made on the basis of DEPT^{13}C{^{1}H}135/90- and HSQC{^{1}H–^{13}C}-NMR studies and given in Table 1.

The carbonyl carbon, C-24 of cholic acid underwent an upfield shift from 179.30 to 175.70 ppm in the pyridinocholaphane **3** due to the formation of the amide bond. The other overlapped carbonyl carbon signals at δ 166.80 and 163.47 were attributed to C-29, C-35 and C-27, C-37 carbons, respectively. The aromatic region in ^{13}C was well resolved depicting the carbon signals for C-31, C-32 at 154.15 and C-34 at 138.59 ppm. The two quaternary carbons, C-30 and C-33, appeared at 125.40 ppm, which

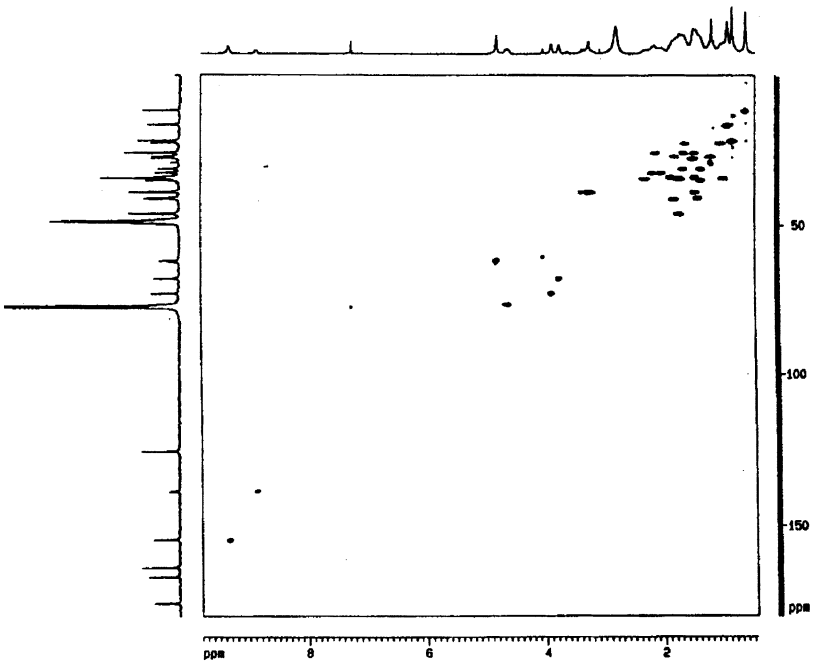
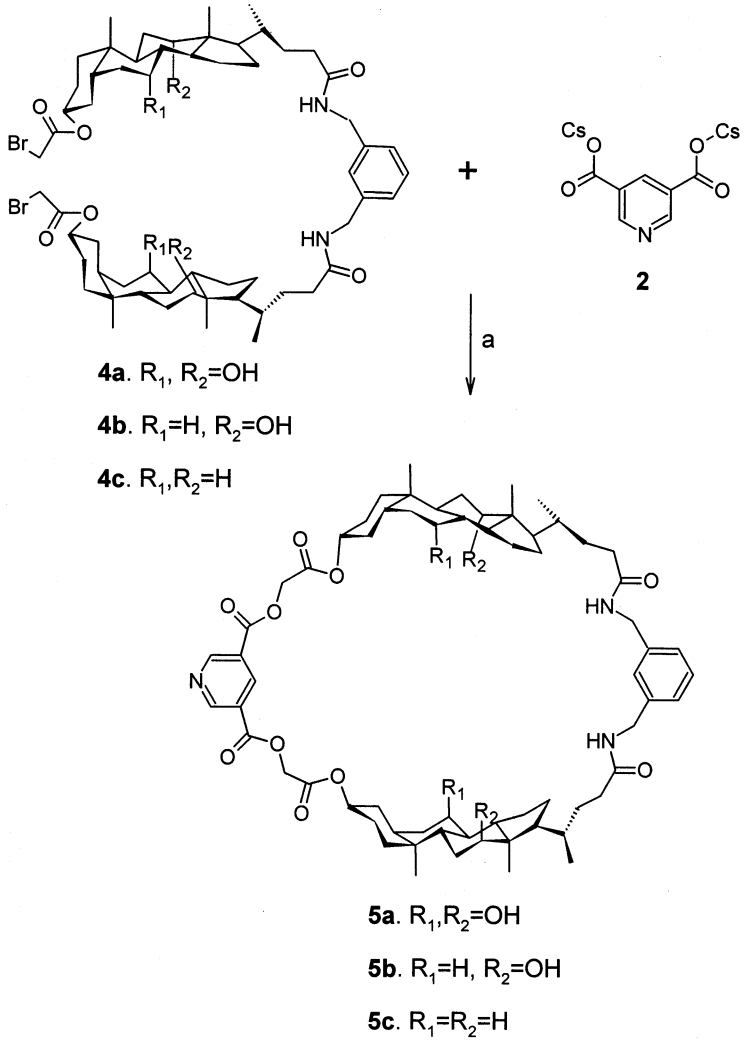


Figure 2. HSQC{^{1}H–^{13}C}-NMR spectrum of pyridinocholaphane **3**.



Scheme 2. (a) DMF, 12 h, rt, (**5a**) 85%, (**5b**) 81%, (**5c**) 78%.

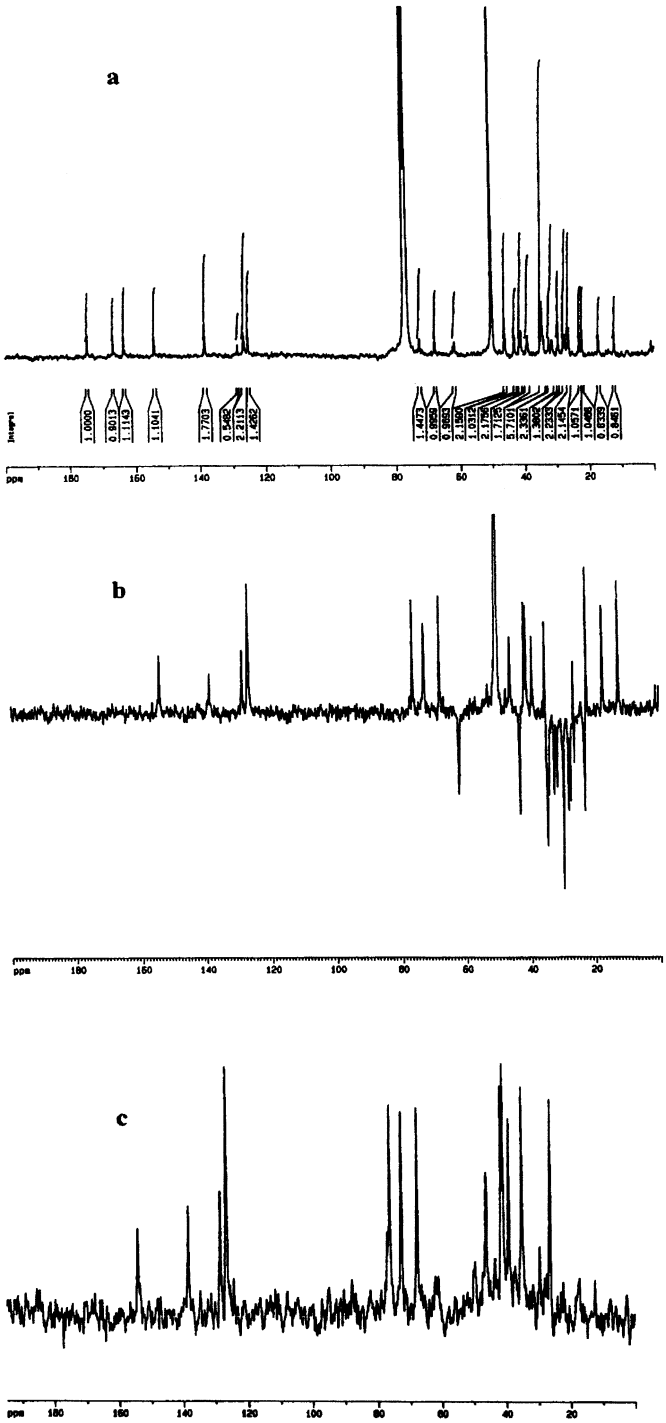


Figure 3. (a) ^{13}C spectrum, (b) DEPT$^{13}C\{^{1}H\}$135- and (c) DEPT$^{13}C\{^{1}H\}$90-NMR spectrum of pyridinocholaphane **5a**.

was confirmed by their disappearance in DEPT$^{13}C\{^{1}H\}$135-NMR spectrum (Fig. 1b). Similarly the other steroidal quaternary carbons, C-10 and C-13, were found to resonate at δ 34.51 and 46.10, respectively.

The ^{13}C NMR spectrum of pyridinocholaphane indicated two carbons less than required. This ambiguity was solved by DEPT$^{13}C\{^{1}H\}$90-NMR spectrometry (Fig. 1c), which showed a signal at δ 76.57, overlapped with $CDCl_3$ carbon signal in ^{13}C NMR spectrum. This was further supported by $\{^{1}H–^{13}C\}$HSQC-NMR spectrum of **3** (Fig. 2), revealing a cross peak at 76.57/4.61 ppm, which was assigned to overlapped methine carbons, C-3 and C-3′. It is noteworthy to observe a downfield shift in case of this methine C-3 carbon, which in case of cholic acid and cyclocholates was found to appear at 71.6 and 73.5 ppm, respectively, this probably be due to the presence of an extra ester group in case of pyridinocholaphane. The HSQC spectrum further revealed the cross peaks of methylene carbons –NH–CH_2–CH_2–NH– and –O–CH_2–CO– at 39.16/3.27 and 61.62/4.81 ppm, respectively. The cross peaks confirmed the signals for other methine carbons C-7 and C-12 at 67.71/

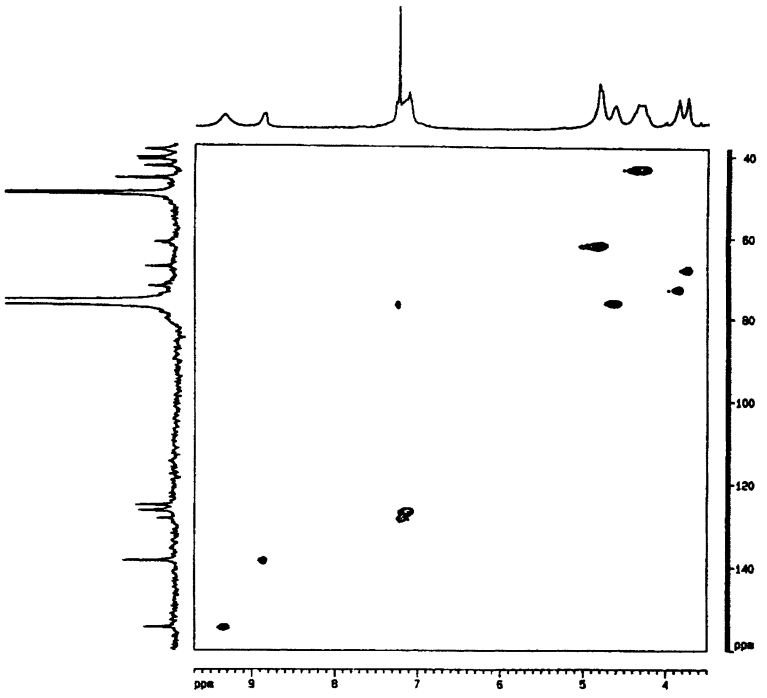


Figure 4. HSQC{^{1}H–^{13}C}-NMR spectrum of pyridinocholaphane **5a**.

3.75 and 72.59/3.88 ppm, respectively. The chemical shifts of the skeletal carbons were assigned on the basis of the literature data.[11]

For the synthesis of pyridinocholaphanes **5a**–**c**, with *m*-xylylenediamine as spacer, the bis-cholic-*m*-xylylenediamides were prepared by the method of Burrows and coworkers.[12] The selective bromoacetylation of these cholamides and cyclization of the resulting products (Scheme 2) was carried out by following the same procedure as described earlier. The ^{1}H NMR spectrum of the obtained pyridinocholaphane **5a** depicted the pyridine protons at δ 8.92 and 9.39, and phenyl protons as a multiplet at 7.20 ppm. The $-CH_2-Ph-CH_2-$ protons appeared downfield in this case as a multiplet at δ 4.37. The $-CO-CH_2-O-$ protons were observed as a broad singlet at 4.88 ppm. The rest of the steroidal protons appeared at almost the same positions as in the case of pyridinocholaphane **3**. The appearance of molecular ion peak (MH^+) at *m/z* 1165 in the FAB mass spectrum indicated the formation of pyridinocholaphane **5a**. The quantitative ^{13}C NMR spectrum (Fig. 3a) also supported the structure of pyridinocholaphane **5a**. On changing the spacer from ethylenediamine to *m*-xylylenediamine, the carbonyl carbon C-24 shifted upfield from 175.70 to 174.67 ppm. The other two sets of carbonyl carbons appeared at 166.86 and 163.64 ppm showing a minor chemical shift as compared to that of pyridinocholaphane **3**. The quantitative ^{13}C NMR spectrum of **5a** revealed an overlapped signal for two phenyl quaternary carbons (C-26, C-30) with one pyridine carbon (C-40) at 138.67 ppm. These two quaternary carbon signals were confirmed by its disappearance in DEPT^{13}C{^{1}H}135-NMR spectrum (Fig. 3b). The other phenyl carbons (C-27, C-28, C-29) and C-31 were found to resonate at 126.78 and 128.65 ppm, respectively. This was supported by the appearance of the cross peaks at δ 126.78/7.12 and 128.65/7.18 ppm in HSQC{^{1}H–^{13}C}-NMR spectrum (Fig. 4). Furthermore, the cross peaks at δ 43.20/4.37 and 61.81/4.88 revealed the methylene carbons $-CH_2-Ph-CH_2$ and $-CO-CH_2-O-CO-$, respectively. The rest of the carbon signals appeared at almost the same chemical shifts as in the pyridinocholaphane **3**. Two more pyridinocholaphanes based on deoxycholic acid **5b**, and lithocholic acid **5c**, utilizing *m*-xylylenediamine as a spacer have been synthesized. These pyridinocholaphanes were also characterized on a similar basis and their detailed assignments are given in Table 1.

3. Conclusion

Though the FAB mass spectra of pyridinocholaphanes correctly depicted the molecular ion peaks at their respective *m/z* values, the combination of NMR techniques, viz. ^{13}C quantitative, DEPT^{13}C{^{1}H}135/90 and HSQC{^{1}H–^{13}C}-NMR, proved to be an effective tool in elucidating the complex structure of pyridinocholaphanes. These pyridinocholaphanes can easily be converted into the dihydropyridine systems by standard methods, *N*-alkylation followed by reduction with sodium dithionite. The structural features of these macrocyclic steroidal dihydropyridine systems are expected to selectively bind carbohydrate based substrates and may carry out their reduction in a stereoselective manner.

4. Experimental

4.1. General

Melting points were not corrected. IR spectra were recorded on Nicolet protégé 460 spectrometer, using potassium

bromide pellet. ^{1}H, ^{13}C, DEPT$^{13}C\{^{1}H\}$135/90 and HSQC$\{^{1}H-^{13}C\}$-NMR spectra were recorded on SPECTROSPIN DPX 300 BRUKER. The chemical shifts (δ) are given relative to TMS as an internal standard. Mass spectra were obtained using a JEOL SX 102/DA-6000 Mass Spectrometer using Argon/Xenon as the FAB gas and *m*-nitrobenzyl alcohol as the matrix. Column chromatography was carried out using Qualigens silica gel 60–120 mesh.

4.1.1. Bis-cesium 3,5-pyridine dicarboxylate 2. To a solution of pyridine-3,5-dicarboxylic acid (1.67 g, 10 mmol) in DMF, cesium carbonate (3.25 g, 10 mmol) was added. After complete neutralization. the solvent was evaporated under reduced pressure, white solid of cesium salt was obtained and was dried in desiccator. Yield: 4.6 g, 92%; IR (KBr): 1600 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ: 8.64 (bs, 1H, Pyr-4-H), 9.24 (bs, 2H, Pyr-2, 6-H).

4.1.2. Cyclo-bis-(3α-acetylcholic)-ethylenediamido-3,5-pyridine dicarboxylate 3. Bis-(3α-bromoacetylcholic)-ethylenediamide **1** (206 mg, 0.19 mmol) was dissolved in dry dimethyl formamide (6 ml) and to this was added an equivalent amount of bis-cesium 3,5-pyridine dicarboxylate (86.2 mg, 0.20 mmol). The reaction mixture was stirred at room temperature for 12 h. The mixture was then filtered and the filtrate was poured on ice cold brine solution (20 ml). The solid obtained was filtered and vacuum dried. The compound was purified by column chromatography on silica gel (5% methanol/95% chloroform), to afford the product **3** as a white crystalline solid (180 mg, 87%). R_f: 0.52 (10% methanol/90% chloroform). Mp: 240°C (decom); IR (KBr): 3418, 1739, 1652 cm^{-1}; ^{1}H NMR ($CDCl_3$–CD_3OD, 300 MHz) δ: 0.60 (s, 6H, 2×18-Me), 0.84 (s, 6H, 2×19-Me), 0.93 (bs, 6H, 2×21-Me), 0.99–2.50 (48H, Steroidal H), 3.27 (m, 4H, 2×CH_2NHCO), 3.75 (bs, 2H, 2×7β-H), 3.88 (bs, 2H, 2×12β-H), 4.61 (m, 2H, 2×3β-H), 4.81 (bs, 4H, 2×$COCH_2O$), 8.85 (bs, 1H, Pyr-4-H), 9.34 (bs, 2H, Pyr-2, 6-H); ^{13}C NMR ($CDCl_3$–CD_3OD, 75 MHz), see Table 1; FAB MS Calcd for $C_{61}H_{89}O_{14}N_3$ 1089.39 (MH), Found 1089 (MH^+) (47%), 1027 (7%), 949 (8%), 917 (5%), 888 (7%), 863 (5%), 828 (4%), 705 (5%), 661 (20%), 603 (6%), 535 (6%), 461 (10%), 413 (18%), 391 (40%), 341 (12%), 327 (25%), 281 (40%), 267 (22%), 221 (20%), 207 (47%), 176 (34%), 120 (40%), 107 (58%). Anal. Calcd for $C_{61}H_{89}O_{14}N_3 \cdot 4H_2O$: C, 63.14; H, 8.42; N, 3.62. Found: C, 62.88; H, 8.35; N, 3.51.

4.1.3. Cyclo-bis-(3α-acetylcholic)-*m*-xylylenenediamido-3,5-pyridine dicarboxylate 5a. Bis-(3α-bromoacetylcholic)-*m*-xylylenediamide **4a**, (232 mg, 0.20 mmol) was dissolved in DMF (8 ml) and treated with an equivalent amount of bis-cesium 3,5-pyridine dicarboxylate (90.5 mg, 0.21 mmol) at room temperature for 12 h. The product after work up was purified by column chromatography on silica gel (5% methanol/95% chloroform), to give the product **5a** as a white crystalline solid (198 mg, 85%). R_f: 0.56 (10% methanol/90% chloroform). Mp: 170–172°C; IR (KBr): 3419, 1736, 1653 cm^{-1}; ^{1}H NMR ($CDCl_3$–CD_3OD, 300 MHz) δ: 0.66 (bs, 6H, 2×18-Me), 0.90 (s, 2H, 2×19-Me), 0.97 (bs, 6H, 2×21-Me), 1.00–2.40 (48H, Steroidal H), 3.81 (bs, 2H, 2×7β-H), 3.91 (bs, 2H, 2×12β-H), 4.37 (m, 4H, 2×$PhCH_2NH$), 4.69 (m, 2H, 2×3β-H), 4.89 (m, 4H, 2×$COCH_2O$), 7.20 (m, 4H, Ar-H), 8.92 (bs, 1H, Pyr-4-H), 9.40 (bs, 2H, Pyr-2, 6-H); ^{13}C NMR ($CDCl_3$–CH_3OD, 75 MHz), see Table 1; FAB MS Calcd for $C_{67}H_{93}O_{14}N_3$ 1187.48 (MNa), 1165.49 (MH), Found 1187 (MNa^+) (6%), 1165 (MH^+) (40%), 1147 (7%), 1089 (8%), 810 (5%), 675 (5%), 661 (28%), 460 (5%), 391 (34%), 257 (5%), 207 (13%), 176 (14%), 120 (18%). Anal. Calcd for $C_{67}H_{93}N_3O_{14} \cdot 4H_2O$: C, 65.07; H, 8.23; N, 3.39. Found: C, 64.75; H, 8.13; N, 3.29.

4.1.4. Cyclo-bis-(3α-acetyldeoxycholic)-*m*-xylylenediamido-3,5-pyridine dicarboxylate 5b. Bis-(3α-bromoacetyldeoxycholic-*m*-xylylenediamide **4b** (248 mg, 0.22 mmol) was dissolved in DMF (7 ml) and bis-cesium 3,5-pyridine dicarboxylate (100 mg, 0.23 mmol) was added. The mixture was stirred at room temperature for 12 h. The work up procedure followed was same as described earlier. The crude product was subjected to column chromatography (4% methanol/96% chloroform), to give the product **5b** as a white crystalline solid (202 mg, 81%). R_f: 0.61 (10% methanol/90% chloroform). Mp: 215°C (decom); IR (KBr): 3410, 1739, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$–CD_3OD, 300 MHz) δ: 0.66 (s, 6H, 2×18-Me), 0.91 (s, 6H, 2×19-Me), 1.02 (bs, 6H, 2×21-Me), 1.05–2.50 (52H, Steroidal H), 3.95 (bs, 2H, 2×12β-H), 4.36 (m, 4H, 2×$PhCH_2NH$), 4.88 (m, 6H, 2×$COCH_2O$ and 2×3β-H), 7.20 (m, 4H, Ar-H), 8.95 (s, 1H, Pyr-4-H), 9.46 (s, 2H, Pyr-2, 6-H). ^{13}C NMR ($CDCl_3$–CD_3OD, 75 MHz), see Table 1; FAB MS Calcd for $C_{67}H_{93}O_{12}N_3$ 1133.49 (MH), Found 1133 (MH^+) (92%), 1097 (25%), 1011 (11%), 953 (6%), 872 (20%), 759 (12%), 732 (8%), 693 (8%), 654 (10%), 622 (32%), 600 (37%), 582 (12%), 536 (12%), 512 (12%), 489 (10%), 474 (24%), 438 (42%), 377 (15%), 339 (40%), 255 (90%), 241 (45%), 225 (100%), 199 (55%), 176 (71%), 131 (100%), 107 (100%). Anal. Calcd for $C_{67}H_{93}N_3O_{12} \cdot 2H_2O$: C, 68.86; H, 8.36; N, 3.60. Found: C, 68.38; H, 8.22; N, 3.65.

4.1.5. Cyclo-bis-(3α-acetyllithocholic)-*m*-xylylenediamido-3,5-pyridine dicarboxylate 5c. Bis-(3α-bromoacetyllithocholic)-*m*-xylylenediamide **4c** (460 mg, 0.42 mmol) and bis-cesium 3,5-pyridine dicarboxylate (185.3 mg, 0.43 mmol) were dissolved in DMF (15 ml) and the solution was stirred at room temperature for 12 h. The usual work up gave the compound which was purified by column chromatography on silica gel (2% metanol/98% chloroform) to give the product **5c** as a white crystalline solid (361 mg, 78%). R_f: 0.55 (8% methanol/92% chloroform). Mp: 179–180°C; IR (KBr): 3300, 1735, 1652 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.57 (bs, 6H, 2×18-Me), 0.85 (bs, 12H, 2×19-Me and 2×21-Me), 1.07–2.50 (56H, Steroidal H), 4.32 (m, 4H, 2×$PhCH_2NH$), 4.80 (m, 6H, 2×$COCH_2O$ and 2×3β-H), 7.12 (bs, 4H, Ar-H), 8.91 (bs, 1H, Pyr-4-H), 9.38 (bs, 2H, Pyr-2, 6-H); ^{13}C NMR ($CDCl_3$, 75 MHz), see Table 1; FAB MS Calcd for $C_{67}H_{93}O_{10}N_3$ 1101.49 (MH), Found 1101 (MH^+) (23%), 1045 (6%), 820 (4%), 743 (5%), 661 (6%), 611 (5%), 477 (10%), 440 (12%), 413 (8%), 371 (24%), 341 (7%), 329 (20%), 255 (13%), 225 (15%), 201 (10%), 176 (62%), 119 (45%), 105 (85%). Anal. Calcd for $C_{67}H_{93}N_3O_{10}$: C, 73.13; H, 8.51; N, 3.81; Found: C, 73.29; H, 8.73; N, 3.98.

Acknowledgements

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