Triflate Induced Syntheses and Spectral Studies of Some Amino Sugars

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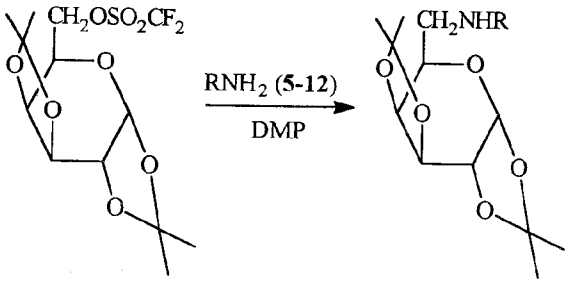
Summary: The NMR and other spectroscopic studies of some interesting amino sugars and alkaloidal-N-glycosides, synthesized by displacement of triflyl group in carbohydrates with suitably protected amines, have been discussed.

Introduction

The displacement reactions of the trifluoromethanesulfonyloxy (triflate) group from carbohydrates now has reached a sufficient magnitude that a series of research papers in the reactions of these compounds have been appeared in literature [1-5] which reveal that these can safely be used in a wide variety of situations. In a series of short communications we have reported the syntheses of new classes of 6-amino-6-deoxy sugars [6] and heterocyclic amino sugars [7] along with alkaloidal-N-glycosides [8] and quaternary amino sugars [9] through a classical S_N2 displacement of triflyl group in partially protected carbohydrates. The reactions work under extremely mild conditions and invariably provide, besides the target compounds, a small quantity of hydrolysis product which can be recovered and recycled. The isopropylidene protecting group in the sugar residues can easily be removed under mild acidic conditions. Herein we describe in detail these synthetic approaches and a detailed spectroscopic discussion of the resulting amino sugars.Of particular interest is the ^{13}C-NMR parameters of 6-amino-6-deoxy sugars because these parameters are not available in literature for this class of compounds.

Results and Discussion

1,2:3,4-Di-O-isopropyliden-α-D-galactopyranose (**3**) and 1,2:5,6-di-O-isopropyliden-α-D-glucofuranose (**4**) were prepared by previously published methods [10,11] from D-galactose and D-glucose, respectively. Reaction of these with trifluoromethanesulfonic anhydride in presence of pyridene at 0 °C provided the corresponding triflates (**1**) and (**2**) [12]. On the other hand different classes of amines were used to demonstrate the scope of reaction. These include amino acid esters namely methyl esters of L-glycine (**5**), L-alanine (**6**), L-leucine (**7**), L-phenyl alanine (**8**), L-methionine (**9**)



32: R = CH_2-COOMe
33: R = CH-CH_3 (COOMe)
34: R = CH-CH_2-$CH(CH_3)_2$ (COOMe)
35: R = CH-CH_2-Ph (COOMe)
36: R = CH-CH_2-CH_2-S-CH_3 (COOMe)
37: R = -N-$(CH_2)_3$-CH-COO-CH_2Ph
38: R = CH-CH_2-CH_2-$COOCH_2CH_3$ ($COOCH_2CH_3$)
39: R = CH-$(CH_2)_4$-NH-$COOCH_2$Ph ($COOCH_2CH_3$)

Scheme-1

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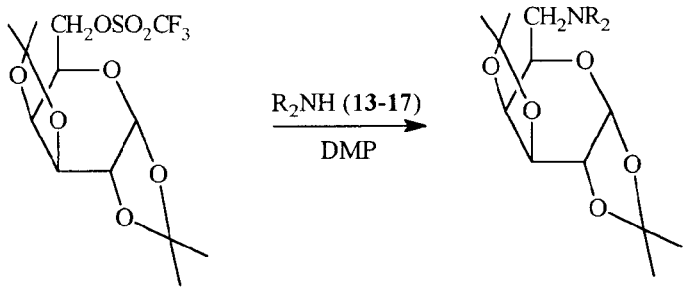
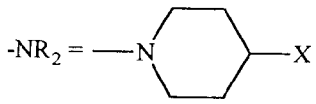
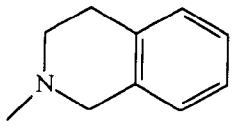
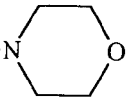
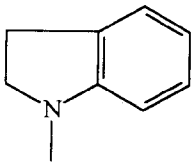


-NR_2 = 

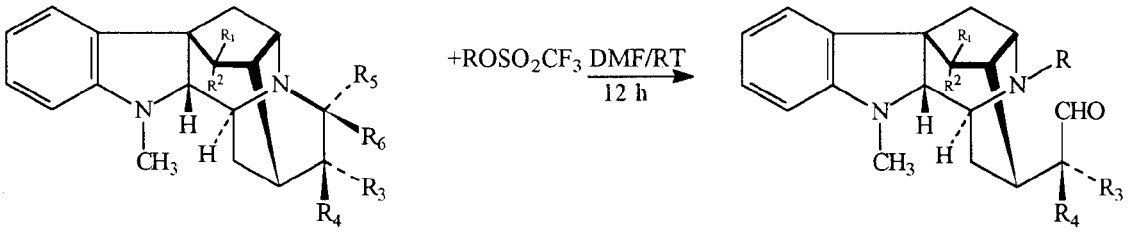
40: X = H
41: X = CH_3

43: -NR_2 = 

42: -NR_2 = 

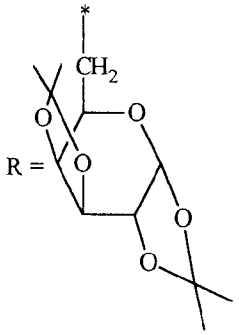
44: -NR_2 = 

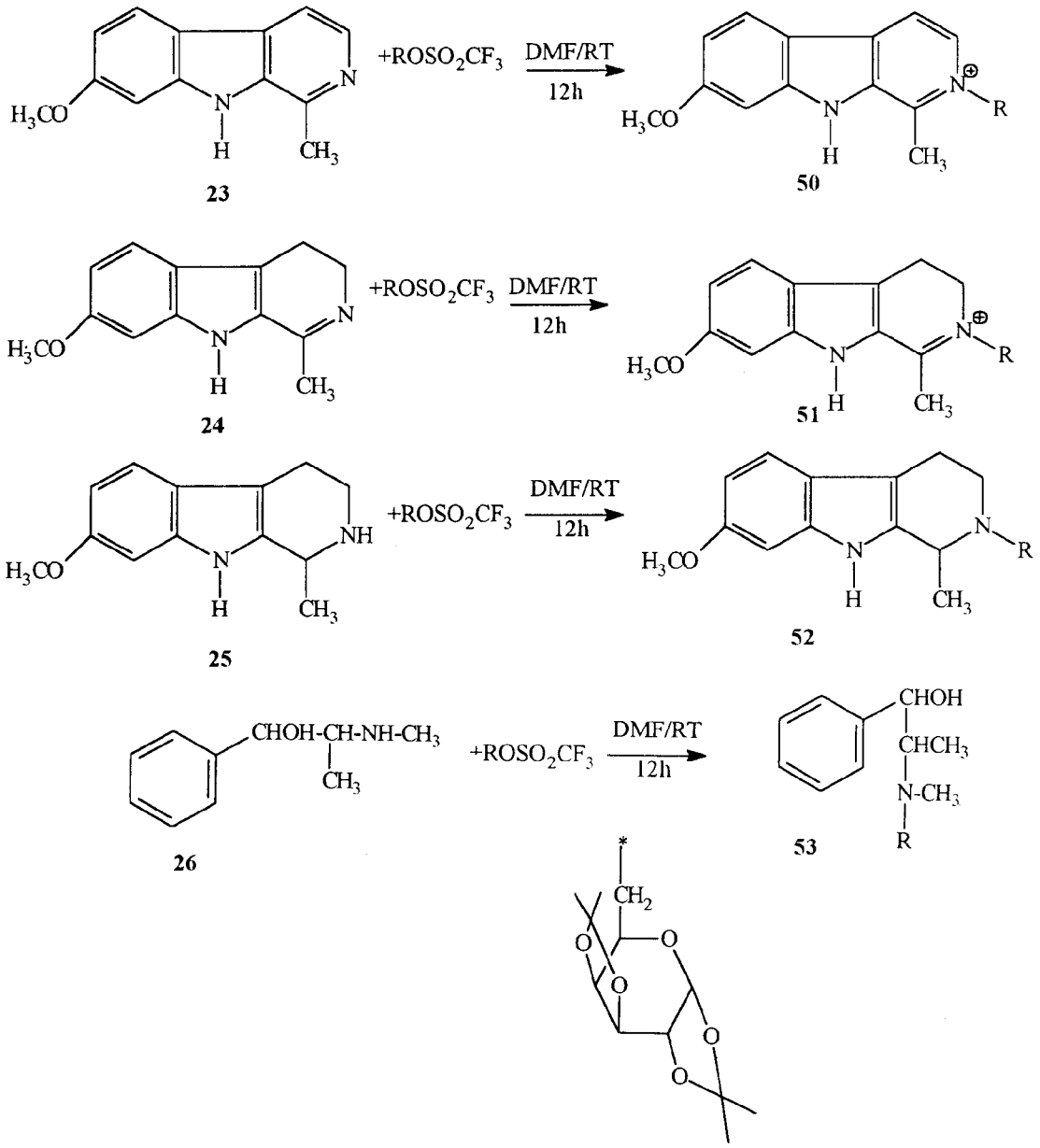
Scheme-2



18: $R_1 = R_5 = OH$, $R_2 = R_3 = R_6 = H$, $R_4 = Et$
19: $R_1 = R_6 = OH$, $R_2 = R_4 = R_5 = H$, $R_3 = Et$
20: $R_2 = R_5 = OH$, $R_1 = R_3 = R_6 = H$, $R_4 = Et$
21: $R_1 = OAc$, $R_5 = OH$, $R_2 = R_3 = R_6 = H$, $R_4 = Et$
22: $R_2 = R_5 = OAc$, $R_1 = R_3 = R_6 = H$, $R_4 = Et$

45: R_1 OH, $R_2 = R_3 = H$, $R_4 = Et$
46: $R_1 = OH$, $R_2 = R_4 = H$, $R_3 = Et$
47: $R_2 = OH$, $R_1 = R_3 = H$, $R_4 = Et$
48: $R_1 = OAc$, $R_2 = R_3 = H$, $R_4 = Et$
49: $R_2 = OAc$, $R_1 = R_3 = H$, $R_4 = Et$

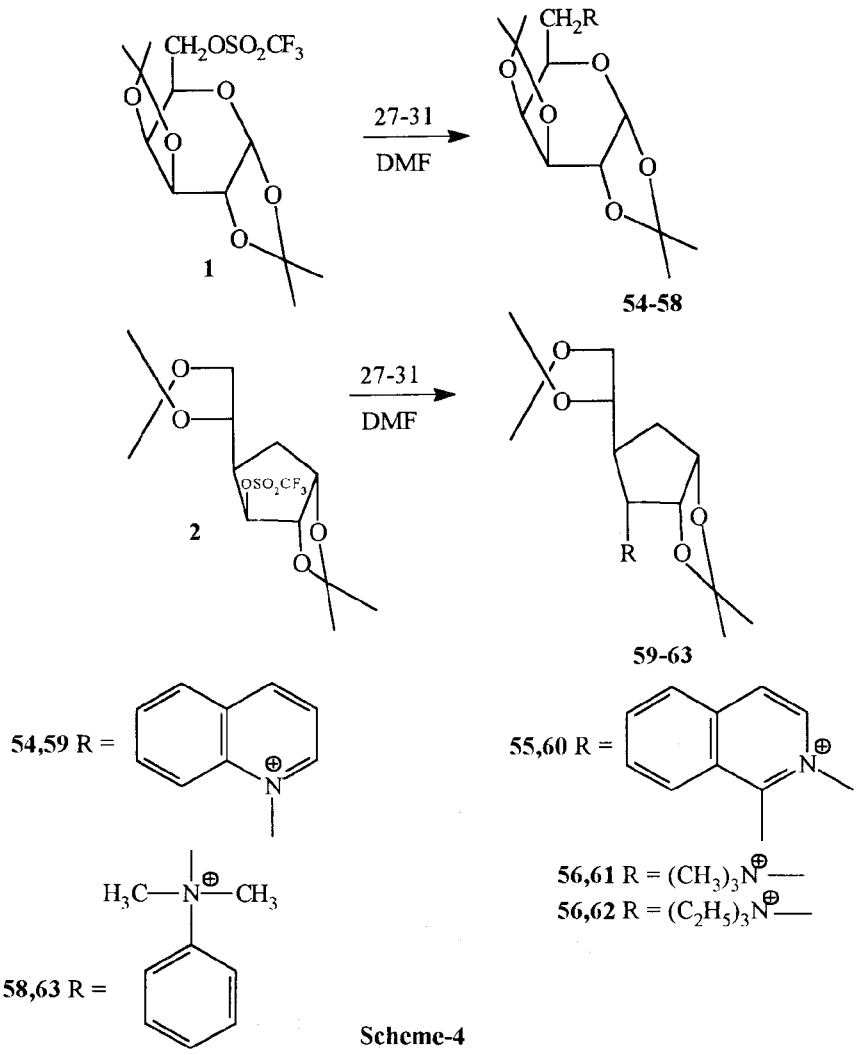
R = 



Scheme-3

along with benzyl ester of L-proline (**10**), diethyl ester of L-glutamic acid (**11**) and ethyl ester of Nε-(benzyloxy- carbonyl)-L-lysine (**12**); heterocyclic bases namely piperidine (**13**), 4-methyl piperidine (**14**), morpholine (**15**), 1,2,3,4-tetrahydroisoquinoline (**16**) and indoline (**17**); alkaloidal bases namely ajmaline (**18**), isoajmaline (**19**), sandwicine (**20**), 17-acetyl ajmaline (**21**), 17,21-diacetyl sandwicine (**22**), harmine (**23**), harmaline (**24**), tetrahydro- harmine (**25**), and ephedrine (**26**); and tertiary amines namely chinoline (**27**), isochinoline (**28**), trimethyl amine (**29**), triethyl amine (**30**) and N,N-dimethyl aniline (**31**).

The compounds (**5-26**) were, separately and respectively, used to displace the triflyl group in (**1**) while the tertiary amines (**27-31**) were used to displace the same group in (**1**) and (**2**).



Scheme-4

The reactions were carried out in dimethylformamide under the conditions described in the experimental to afford the corresponding compounds (**32-63**) (schemes 1-4) which were isolated from the reaction mixture by column chromatography over silica gel.

The structures were assigned to compounds (**32-63**) on the basis of analytical and spectral data (Tables 1-9). The reactions of (**2**) invariably led to allo-products owing to stereochemical inversion at C-3. The key evidence to this effect was provided by the coupling constants in the ^{1}H-NMR spectra, particularly $J_{2,3}$ and $J_{3,4}$. In compound **2**, H-3 shows a coupling of 3.1 Hz with H-4 but it does not couple

Table-1: FD-mass and IR spectra of 6-amino-6-deoxy sugars.

Compound	M^+peak	ν(cm^{-1})
(32)	331	3450 (NH), 1690 and 1110 (ester), 810 (isopropyl)
(33)	345	3560 (NH), 1690 and 1120 (ester), 810 (isopropyl)
(34)	387	3540 (NH), 1700 and 1130 (ester), 820 (isopropyl)
(35)	421	3550 (NH), 1710 and 1120 (ester), 820 (isopropyl), 3120 and 1600 (Ar).
(36)	405	3560 (NH), 1700 and 1120 (ester), 810 (isopropyl)
(37)	447	1150 (C-N), 1700 and 1130 (ester), 820 (isopropyl), 3060 and 1590 (Ar).
(38)	445	3560 (NH), 1710 and 1140 (ester), 810 (isopropyl).
(39)	550	3560 (NH), 1710 and 1130 (ester), 820 (isopropyl), 3080 and 1590 (Ar).

Table 2: ^{1}H-NMR spectra of 6-amino-6-deoxy sugars

Compound	H-1 $J_{1,2}$ (Hz)	H-2 $J_{2,1}$ & $J_{2,3}$ (Hz)	H-3 $J_{3,2}$ & $J_{3,4}$ (Hz)	H-4 $J_{4,3}$ & $J_{4,5}$ (Hz)	H-5 $J_{5,6}$ & $J_{5,6'}$ (Hz)	2H-6 $J_{6,5}$ & $J_{6,6'}$ (Hz)	Isopropyl	Other protons
32	5.52, d (5.07)	4.62, dd (1.84 and 8.34)	4.56, dd (2.28 and 7.14)	4.31, dd (2.37 and 5.16)	4.21, dd (1.82 and 7.89)	Ha = 3.85m; Hb = 4.10 m	1.26, 1.30, 1.39 and 1.50, s(4CH_3)	3.70 s(CH_3); 3.41, s (CH_2)
33	5.51, d (5.12)	4.61, dd (1.84 and 7.93)	4.59, dd (1.84 and 7.89)	4.32, dd (2.42 and 5.02)	4.22, dd (1.63 and 7.98)	Ha = 3.95, m; Hb= 4.21, m	1.19, 1.22, 1.30 and 1.32, s(4CH_3)	3.72 s(CH_3); 1.01, d(CH_3)
34	5.24, d (5.18)	4.60, dd (1.89 and 7.94)	4.53, dd (1.07 and 7.88)	4.35, dd (2.26 and 5.04)	4.21, dd (1.68 and 7.93)	Ha = 3.93, m; Hb = 4.23, m	1.30, 1.31, 1.23 and 1.21, s(4CH_3)	3.69, s(CH_3); 0.89, d (2CH_3)
35	5.53, d (5.11)	4.59, dd (2.10 and 7.92)	4.48, dd (1.86 and 7.98)	4.32, dd (2.28 and 4.98)	4.21, dd (1.92 and 7.88)	Ha= 3.99, m; Hb= 4.21, m	1.31, s(2CH_3); 1.43 and 1.51, s(2CH_3)	7.81-7.69, m (Ar); 3.72, s(CH_3)
36	5.49, d (5.03)	4.60, dd (2.71 and 8.02)	4.51, dd (2.66 and 7.96)	4.31, dd (2.43 and 4.93)	4.20, dd, (1.89 and 7.92)	Ha= 3.97, m; Hb = 4.21, m	1.27, 1.30, 1.38 and 1.50, s(4CH_3)	3.71, s(CH_3)
37	5.44, d (5.12)	4.61, dd (1.78 and 7.89)	4.54, dd (1.82 and 7.93)	4.32, dd (2.15 and 4.98)	4.22,dd (2.05 and 7.84	Ha = 3.89, m; Hb = 4.18, m	1.29, 1.31, 1.33 and 1,34 s(4CH_3)	3.49, t(CH_2-H); 7.38-7.21, m(Ar),
38	5.51, d (5.13)	4.59, dd (1.10 and 7.82)	4.51, dd (1.75 and 7.88)	4.33, dd (2.21 and 5.19)	4.23, dd (2.92 and 7.98)	Ha = 3.87, m; Hb= 4.16, m	1.29, s(2CH_3); 1.41, s(2CH_3)	0.89, t(2CH_3)
39	5.51, d (5.01)	4.62, dd (2.61 and 7.87)	4.53, dd (2.56 and 7.93)	4.29, dd (2.43 and 4.85)	4.18, dd (2.87 and 7.54)	Ha = 3.87, m; Hb= 4.08, m	1.25, 1.28, 1.36 and 1.48, s(4CH_3)	7.30-7.10, m(Ar), 0.87, t(CH_3)

Table-3: ^{13}C-NMR spectra of 6-amino-6-deoxy sugars

Compound	C-1	C-2	C-3	C-4	C-5	C-6	N-C	CO-	OCH_2/OCH_3	Isopropylidene	Other carbons
32	96.30	70.41	71.77	70.74	66.68	49.15	50.63	172.49	51.56	109.18, 108.44, 25.96, 25.85, 24.24, 24.23	
33	96.24	70.78	71.64	70.42	68.05	45.87	65.73	171.15	52.63	189.92, 108.42, 25.89, 25.77, 24.75, 24.24	16.03(CH_3)
34	96.41	70.44	71.42	70.65	67.18	47.45	63.14	174.15	51.63	108.92, 108.42, 25.23, 25.01, 24.38, 24.32	45.21 (CH_2); 25.31 (CH); 23.18, 22.13 (2CH_3)
35	96.30	70.44	71.44	70.64	67.20	47.49	63.04	174.64	51.51	109.04, 108.35, 25.84, 25.79, 24.80, 24.29	39.38(CH_2-Ph); 137.37-129.12(Ar)
36	96.30	70.39	71.55	70.66	67.27	47.36	60.17	175.12	51.70	109.80, 108.37, 25.93, 25.84, 24.78, 24.34	30.36(CH_2); 32.32 (CH_2-S); 15.20 (CH_3)
37	96.51	70.33	72.26	70.76	66.60	52.59	53.31 (CH_2)	173.88	65.93	108.96, 108.27, 25.92, 25.90, 24.77, 24.33	29.00, 23.14, 22.78 (3CH_3) 65.45(CH) 136.08-128.01(Ar)
38	96.30	70.82	70.97	70.67	66.51	47.24	63.63	173.71; 172.56	63.63; 66.51	108.83, 108.31, 26.27, 25.93, 24.59, 24.58	31.27(CH_2-CO); 29.65(CH_2); 14.39, 14.21(2CH_3)
39	96.51	70.39	71.54	70.64	67.18	48.23	63.45	174.84; 173.98	66.24; 64.92	109.12, 109.01, 25.83, 25.12, 24.23, 24.10	30.81, 27.12, 22.35 (3CH_2); 44.23 (CH_2-N); 136.00-107.00 (Ar); 14.21 (CH_3)

Table-4: FD-mass and IR spectra of heterocyclic amino sugars.

Com-pound	M^+peak	ν(cm^{-1})
(40)	327	1160 (C-N), 820 (isopropyl)
(41)	341	1160 (C-N), 830 (isopropyl), 1370 (CH_3)
(42)	329	1150 (C-N), 810 (isopropyl)
(43)	375	1160 (C-N), 820 (isopropyl) 3080 and 1590 (Ar).
(44)	361	1160 (C-N), 810 (isopropyl), 3100 and 1590 (Ar).

with H-2 which appears as doublet owing to coupling with H-1 ($J_{1,2}$ = 3.7 Hz). On the other hand in products **59-63**, H-2 gives a triplet due to coupling of same magnitude (3.7 Hz) with H-1 and H-3 while H-3 shows no coupling with H-4.

In all cases the reaction rates varied considerably with the nature and concentration of the

Table 5: ^{1}H-NMR spectra of heterocyclic amino sugars

Compound	H-1 $J_{1,2}$ (Hz)	H-2 $J_{2,1}$ & $J_{2,3}$ (Hz)	H-3 $J_{3,2}$ & $J_{3,4}$ (Hz)	H-4 $J_{4,3}$ & $J_{4,5}$ (Hz)	H-5 $J_{5,6}$ & $J_{5,6'}$ (Hz)	2H-6 $J_{6,5}$ & $J_{6,6'}$ (Hz)	Isopropyl	Other protons
40	5.51,d (5.08)	4.67, dd (2.43 and 8.07)	4.55, dd (2.40 and 7.92)	4.31, dd (2.52 and 4.82)	4.24, dd (2.40 and 7.18)	Ha= 3.96, m; Hb= 4.17, dd (1.38 and 7.92)	1.29, s($2CH_3$); 1.40 and 1.51, s($2CH_3$)	3.26, t(H_2-2'); 1.63, m(H_2-3'); 1.55, m(H_2-4')
41	5.51, d (4.98)	4.66, dd (2.42 and 8.12)	4.56, dd (2.42 and 8.13)	4.33, dd (4.92 and 2.52)	4.22, dd (1.98 and 5.12)	Ha= 4.07, m; Hb= 4.10, m	1.31,s($2CH_3$); 1.40 and 1.51, ($2CH_3$)	3.25, t(H_2-2'); 1.62, m(H_2-3'); 1.52, m(H2-4'); 1.01, s(CH_3)
42	5.52, d (5.12)	4.67, dd (2.34 and 8.18)	4.56, dd (2.40 and 7.92)	4.32, dd (2.52 and 5.63)	4.26, dd (2.40 and 5.12)	Ha= 3.93, m; Hb= 4.16, dd (1.88 and 7.92)	1.30, 1.31, 1.42 and 1.49, s($4CH_3$)	3.69, t(H_2C-O); 2.49, m(H_2C-N)
43	5.56, d (5.12)	4.68, dd (2.13 and 7.89)	4.60, dd (2.42 and 8.12)	4.34, dd (2.44 and 5.68)	4.27, dd (2.17 and 5.13)	Ha= 4.04, m; Hb= 4.16, dd (1.38 and 7.92)	1.24, s($2CH_3$); 1.45 and 1.54, s($2CH_3$)	7.51-7.33, m(Ar); 3.87, s(Ar-CH_2-N)
44	5.56, d (4.92)	4.62, dd (2.48 and 7.96)	4.48, dd (5.72 and 10.08)	4.33, dd (2.42 and 5.04)	4.25, dd (1.72 and 4.88)	Ha= 3.13, m; Hb= 4.22, m	1.24, 1.31, 1.45 and 1.54, s($4CH_3$)	7.08-6.82, m(Ar); 3.60, m (H_2C-N)

Table-6: FD-mass and IR spectra of alakloidal glycosides

Com-pound	M^+peak	ν(cm^{-1})
(45)	568	3620 (OH), 1170 (C-N), 3100 and 1610 (Ar), 1710 and 2750 (CHO)
(46)	568	3610 (OH), 1160 (C-N), 3080 and 1600 (Ar), 1700 and 2750 (CHO)
(47)	568	3580 (OH), 1170 (C-N), 3090 and 1600 (Ar), 1710 and 2740 (CHO)
(48)	610	3090 and 1600 (Ar), 1720 and 1140 (ester), 1160 (CN), 2750 and 1710 (CHO).
(49)	610	3120 and 1610 (Ar), 2750 and 1710 (CHO), 1720 and 1120 (ester), 1160(C-N).
(50)	455	3520 (NH), 3120 and 1610 (Ar), 810 (isopropyl)
(51)	457	3450 (NH), 3110 and 1600 (Ar), 820 (isopropyl)
(52)	458	3520 (NH), 3100 and 1590 (Ar), 1140 (C-N), 810 (isopropyl)
(53)	407	3620 (OH), 3080 and 1590 (Ar), 1140 (C-N), 810 (isopropyl).

Table 7: ^{1}H-NMR spectra of alkaloidal glycosides

Compound	H-1 $J_{1,2}$ (Hz)	H-2 $J_{2,1}$ & $J_{2,3}$ (Hz)	H-3 $J_{3,2}$ & $J_{3,4}$ (Hz)	H-4 $J_{4,3}$ & $J_{4,5}$ (Hz)	H-5 $J_{5,6}$ & $J_{5,6'}$ (Hz)	2H-6 $J_{6,5}$ & $J_{6,6'}$ (Hz)	Isopropyl	Other protons
45	5.56,d (5.01)	4.62, dd (2.40 and 7.92)	4.55, dd (2.28 and 7.83)	4.34, dd (2.16 and 5.24)	4.19, dd (1.89 and 7.82)	Ha= 3.87, m; Hb= 4.17, dd (1.08 and 7.92)	1.29, s($2CH_3$); 1.42 and 1.49, s($2CH_3$)	9.81, s(CHO); 4.32, s(H-17); 1.57, m(H-20)
46	5.52, d (5.12)	4.61, dd (2.38 and 7.90)	4.56, dd (2.18 and 7.81)	4.34, dd (2.12 and 5.13)	4.20, dd (1.89 and 7.78)	Ha= 3.86, dd (1.13 and 7.80) Hb= 4.19, dd (2.10 and 7.91)	1.31,s($2CH_3$); 1.38 and 1.42, s($2CH_3$);	9.79, s(CHO); 4.49, s(H-17) 1.28, m(H-20)
47	5.53, d (5.08)	4.62, dd (2.18 and 7.83)	4.54, dd (2.21 and 7.84)	4.35, dd (2.21 and 5.02)	4.18, dd (1.80 and 7.81)	Ha= 3.86, m; Hb= 4.20, m	1.28, 1.29, 1.38 and 1.39, s($4CH_3$)	9.83, s(CHO) 4.65,d(J=9 Hz, H-17); 2.50, m (H-16)
48	5.51, d (5.11)	4.61, dd (2.41 and 7.78)	4.55, dd (2.18 and 7.81)	4.33, dd (2.21 and 4.98)	4.19, dd (1.78 and 7.82)	Ha= 3.86, m; Hb= 4.18, dd (1.08 and 7.90)	1.28, 1.29,s 2(CH_3); 1.31, s($2CH_3$)	9.83, s (CHO); 5.07, s(H-17); 2.19,s(-$OCOCH_3$-17)

Table 7: (continued)

Compound	H-1 $J_{1,2}$ (Hz)	H-2 $J_{2,1}$ & $J_{2,3}$ (Hz)	H-3 $J_{3,2}$ & $J_{3,4}$ (Hz)	H-4 $J_{4,3}$ & $J_{4,5}$ (Hz)	H-5 $J_{5,6}$ & $J_{5,6'}$ (Hz)	2H-6 $J_{6,5}$ & $J_{6,6'}$ (Hz)	Isopropyl	Other protons
49	5.52, d (5.13)	4.62, dd (2.23 and 7.81)	4.54, dd (2.18 and 7.85)	4.34, dd (2.26 and 5.12)	4.17, dd (1.78 and 7.81)	Ha= 3.84, m; Hb= 4.21, m	1.30,s($2CH_3$); 1.37,s($2CH_3$)	9.82, s(CHO); 5.98,d(J=9Hz,H-17); 2.08, s(-$OCOCH_3$-17)
50	5.50, d (5.04)	4.60, dd (2.10 and 7.68)	4.52, dd (2.04 and 7.61)	4.32, dd (2.18 and 5.11)	4.19, dd (1.82 and 7.85)	Ha= 3.86, dd (1.23 and 7.85); Hb= 4.21, dd (1.08 and 7.90)	1.28, 1.29, 1.30 and 1.31, s($4CH_3$)	7.72-6.81,m(Ar); 3.90,s(OCH_3);2.82, s(C-CH_3)
51	5.52, d (5.12)	4.61, dd (2.01 and 7.88)	4.54, dd (2.28 and 7.85)	4.34, dd (2.16 and 5.24)	4.20, dd (1.89 and 7.82)	Ha= 3.87, m; Hb= 4.16, dd (1.09 and 7.93)	1.29 and 1.30,s ($2CH_3$); 1.38,s ($2CH_3$)	7.74-6.83,m(Ar); 3.91,s(OCH_3);3.25, t(CH_2-Ar);2.55,t (CH_2-N);2.80,s(C-CH_3)
52	5.51, d (4.98)	4.59, dd (1.89 and 7.86)	4.53, dd (2.13 and 7.68)	4.34, dd (2.01 and 5.12)	4.19, dd (1.71 and 7.78)	Ha= 3.85, m; Hb= 4.21, m	1.28 and 1.29, s($2CH_3$);1.31,s ($2CH_3$)	7.71-6.83,m(Ar);3.90, s(OCH_3);2.53,t(CH_2-N); 1.02,d(C-CH_3)
53	5.48, d (5.02)	4.62, dd (1.92 and 7.88)	4.55, dd (2.18 and 7.82)	4.33, dd (2.10 and 5.21)	4.21, dd (1.88 and 7.82)	Ha= 3.85, m; Hb= 4.20, m	1.30,s($2CH_3$); 1.31 and 1.32, s($2CH_3$)	7.71-6.67,m(Ar);3.34, t(CHOH);2.01,s(N-CH_3); 1.12,d(CH_3)

Table-8: FD-mass and IR spectra of quaternary amino sugars

Com-pound	M^+peak	$\nu(cm^{-1})$
(54)	372	3560 (N^+), 3120 and 1600 (Ar), 1180 (C-N), 820 (isopropyl)
(55)	372	3550 (N^+), 3100 and 1590 (Ar), 810 (isopropyl)
(56)	302	3560 (N^+), 1180 (C-N), 810 (isopropyl).
(57)	344	3550 (N^+), 1180 (C-N),.810 (isopropyl)
(58)	364	3560 (N^+), 3120 and 1600 (Ar), 1210 (C-N), 820 (isopropyl).
(59)	372	3540 (N^+), 1140 (C-N), 800 (isopropyl), 3110 and 1600 (Ar).
(60)	372	3120 and 1590 (Ar), 1200 (C-N), 810 (isopropyl), 3550 (N^+).
(61)	302	3550 (N^+),.1160 (C-N), 800 (isopropyl).
(62)	344	3550 (N^+), 1140 (C-N), 800 (isopropyl).
(63)	364	3550 (N^+), 3100 and 1590 (Ar), 1180 (C-N), 820 (isopropyl)

Table 9: ^{1}H-NMR spectra of quaternary amino sugars

Compound	H-1 $J_{1,2}$ (Hz)	H-2 $J_{2,1}$ & $J_{2,3}$ (Hz)	H-3 $J_{3,2}$ & $J_{3,4}$ (Hz)	H-4 $J_{4,3}$ & $J_{4,5}$ (Hz)	H-5 $J_{5,6}$ & $J_{5,6'}$ (Hz)	2H-6 $J_{6,5}$ & $J_{6,6'}$ (Hz)	Isopropyl	Other protons
54	5.46,d 4.96)	4.61, dd 1.84 and 8.24)	4.50, dd (1.88 and 7.84)	4.41, dd (2.16 and 4.13)	4.37, dd (2.56 and 8.96)	Ha= 4.18, m; Hb= 4.29, m	1.28, 1.32, 1.41 and 1.52, s($4CH_3$)	9.34-8.12,m (Ar)
55	5.43, d (4.98)	4.68, dd (2.42 and 8.12)	4.60, dd (2.428 and.8.13)	4.31, dd (2.52 and 4.92)	4.21, dd (1.98 and 5.12)	Ha= 4.15, m; Hb= 4.29, m	1.21, 1.24, 1.32 and 1.34, s($4CH_3$)	8.58-7.95,m (Ar)
56	5.53, d (5.08)	4.63, m	4.51, dd (1.88 and 7.83)	4.35, dd (2.16 and 5.04)	4.22, dd (2.13 and 7.68)	Ha= 3.91, m; Hb= 4.21, m	1.31, 1.32, 1.43 and 1.56, s($4CH_3$)	3.46, s(CH_3-N)
57	5.51, d (5.12)	4.61, dd (2.40 and 7.84)	4.47, m	4.33, dd (2.48 and 5.00)	4.26, dd (1.68 and 7.92)	Ha= 3.89, m; Hb= 4.20, m	1.33, s($2CH_3$); 1.45 and 1.53, s($2CH_3$)	2.84,q(CH_2-N); 1.31, t($3CH_3$)
58	5.61, d (5.13)	4.63, dd (2.81 and 8.12)	4.48, dd (2.76 and 7.92)	4.36, dd (2.53 and 4.92)	4.26, dd (1.82 and 7.89)	Ha= 3.87, m; Hb= 4.19, m	1.29, 1.32, 1.40 and 1.52 s($4CH_3$)	8.86-7.31,m(Ar); 3.94, s (H_3C-N)

Table 9: (continued)

Compound	H-1 $J_{1,2}$ (Hz)	H-2 $J_{2,1}$ & $J_{2,3}$ (Hz)	H-3 $J_{3,2}$ & $J_{3,4}$ (Hz)	H-4 $J_{4,3}$ & $J_{4,5}$ (Hz)	H-5 $J_{5,6}$ & $J_{5,6'}$ (Hz)	2H-6 $J_{6,5}$ & $J_{6,6'}$ (Hz)	Isopropyl	Other protons
59	6.08, d (3.60)	4.83, t (3.78)	5.20, d (3.62)	4.37, d (2.52)	3.69, m	Ha= 3.39, dd (5.36 and 8.64); Hb= 3.57, dd (3.68 and 9.16)	0.82,0.84, 0.87 and 0.89 s($4CH_3$)	9.89-8.24,m(Ar)
60	6.04, d (3.61)	4.80, t (3.96)	5.44,d (4.92)	4.37, m	3.91, m	Ha= 3.38, m; Hb= 3.62, m	0.80, 0.83, 0.86 and 0.88, ($4CH_3$)	8.59-7.98, m (Ar)
61	6.14, d (5.18)	4.75, t (4.92)	5.58,d (4.16)	4.28,d (3.18)	3.85, m	3.83-3.80, m	0.87,0.89, 0.91 and 0.93, s($4CH_3$)	3.48, s($3CH_3$.N)
62	6.10, d (5.20)	4.70, (4.81)	5.35, d (4.13)	4.35, d (2.51)	3.87, m	Ha= 3.40, m ; Hb= 3.60, m	0.83, 0.86, 0.88 and 0.91 s($4(CH_3)$	3.16, q($3CH_2$-N); 1.37, t($3CH_3$)
63	6.02, d (5.12)	4.72, t (4.78)	5.35, d (4.12)	4.28, d (2.94)	3.87, m	Ha= 3.32, m; Hb= 3.65, m	0.85, 0.87, 0.88 and 0.91 s($4CH_3$)	8.86-7.34, m(Ar); 3.94, s(H_3C-N)

amines which suggested strongly the operation of an S_N2 mechanism rather than a unimolecular process.

Experimental

Field desorption mass spectra were recorded on Finnigan MAT 112 S Mass Spectrometer. The NMR spectra were recorded on Bruker AM-400 Spectrometer in $CDCl_3$ / TMS. The IR spectra were scanned on JASCO A-302 and JASCO-IR A-1 spectrophotometers while optical rotations were recorded on Polartronic D, Schmidt and Hean.

General procedure for the syntheses of compounds (32-63)

In each case sugar triflates **1** (1 mmol) was separately dissolved in dimethylformamide (4 ml), added the corresponding amine (**5-31**) (4.0 mmol) at -20 °C, warmed slowly to room temperature and kept stirring for further 24 h. The solvent was removed in vacuo and the products (**32-58**) were isolated through column chromatography over silica gel using solvent system benzene:methanol (8:2) and identified by their elemental analyses and other spectral data.

In a similar way sugar triflate **2** was treated with amines **27-31** to get compounds **59-63.**

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