Chemistry of Natural Compounds and Bioorganic Chemistry

Synthesis of heterocyclic systems with a carbohydrate fragment

1. Stereoselective synthesis of azoloanhydrosugars *via* the addition of azoles to levoglucosenone

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Levoglucosenone, the α,β-unsaturated ketone obtained by the pyrolysis of cellulose, reacts with NH-azoles in the presence of bases. In this process not only normal Michael adducts are formed, but in some cases their hydrates (*gem*-diols) are also formed. In all cases the addition proceeds stereospecifically and with good yields. 3-Nitro-*s*-triazole, 3-nitro- and 4-nitropyrazoles, 3-methyl-4-nitropyrazole, 5-nitrotetrazole, 4,5-dicarbomethoxy-*v*-triazole, 3,4-dinitropyrazole, 3(5)-methylpyrazole, pyrazole, and imidazole have been studied in this reaction. All of the adducts are characterized by NMR- and IR-spectroscopy.

Key words: levoglucosenone, azoloanhydrosugars, stereoselective Michael addition of NH-azoles, *gem*-diols.

Five-membered nitrogen-containing heterocycles with a carbohydrate substituent at nitrogen atom are of interest as potentially biologically active compounds. These compounds can be easily obtained *via* the addition of azoles to the activated C=C double bond of levoglucosenone (**1**). So far **1** has been subjected to the Michael reaction only with the C-, O- or S-nucleophiles,[1–4] the addition of N-nucleophiles has been studied by us for the first time.

Levoglucosenone has been successfully used as a chiral matrix for the synthesis of different optically active compounds and their analogs.[5–9] We have improved the method of manufacturing levoglucosenone *via* the pyrolysis of cellulose-containing materials, which makes it possible to substantially increase the yield of **1**.

The reaction of levoglucosenone with type **2** azoles proceeds in the presence of bases and can be represented by the following equation:

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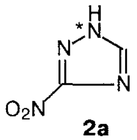
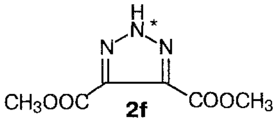
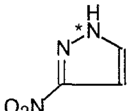
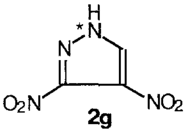
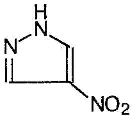
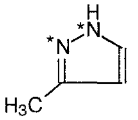
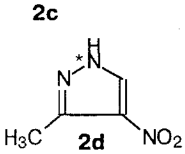
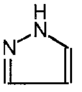
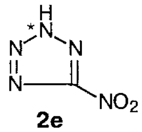
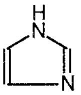
Table 1. Reaction conditions and products of the addition of azoles to levoglucosenone (**1**)

Azole	Reaction conditions**	Products (yield)	Azole	Reaction conditions**	Products (yield)
 **2a**	A	**3a** (52)	 **2f**	A	**3f** (67)
 **2b**	A	**3b** (81)	 **2g**	A	**3g** (80)
 **2c**	A	**3c** (79)	 **2h**	B	3-methyl-**3h** (59), 5-methyl-**3h** (11), **4h** (traces)
 **2d**	A	**3d** (72)	 **2i**	B	**3i** (33), **4i** (32)
 **2e**	A	**3e** (74)	 **2j**	B	**3j** (60), **4j** (20)

*The nitrogen atom to which a carbohydrate fragment adds is marked with an asterisk. **A: 20 °C, Et_3N; B: 40—50 °C, piperidine.

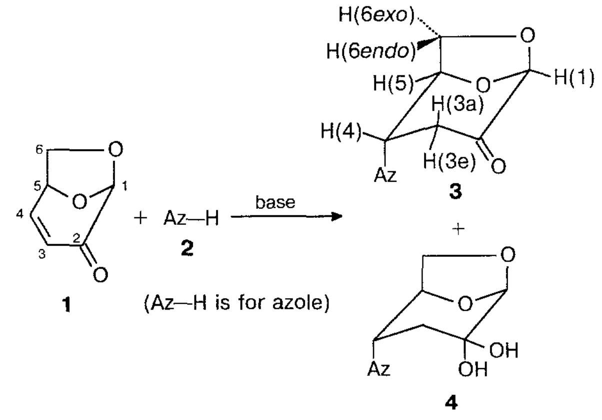


Table 2. IR pectra and melting points of compounds **3a—j** and **4i,j**

Adduct	M.p./°C	IR, ν/cm^{-1} =C—H (heterocyclic)	C=O	NO_2	OH
3a	113—114	3160	1740	1555 1325	
3b	161—162	3150 3120	1745	1535 1315	
3c	147—148	3130	1740	1530 1345	
3d	166—167	3145	1740	1550 1345	
3e	138—139		1745	1555 1315	
3f	Oil		1740*		
3g	138—140	3130	1740	1520—1560 1360—1325	
3-Me-**3h**	116—117	3100	1735		
3i+**4i**		3120—3160	1740		3370
3j+**4j**		3115, 3165	1735		3440

*The IR spectrum of compound **3f** was registered in a chloroform solution. The spectra of the other adducts were recorded using pellets pressed with KBr. **ν(COOR) 1710 cm^{-1}.

The results thus obtained are presented in Table 1.

Since it is a stronger base than Et_3N, piperidine was used in the cases of azoles of moderate NH-acidity (**2h—j**); in these cases the reaction was carried out at elevated temperatures. Nitro-substituted imidazoles, *e.g.*, 4-nitroimidazole, 2,4-dinitroimidazole, and 4-nitro-5-ethoxycarbonylimidazole, failed to enter this reaction.

In some cases not only the normal addition products of type **3** were formed, but also products corresponding to the hydration of the carbonyl group, that is *gem*-diols of type **4**. Thus, the diol **4j** precipitated together with **3j** in the course of the addition of imidazole (the NMR

Table 3. ^1H NMR spectra of compounds **3a—j** and **4c,i,j**

Adduct	δ (J/Hz)							
	H(1)	H(3e)	H(3a)	H(4)	H(5)	H(6*exo*)	H(6*endo*)	Other protons
3a	5.22 (s)	2.78 (dm[a], J = 18.0)	3.33 (dd, J = 18.0, J = 7.9)	5.23 (d[b], J = 7.9)	4.98 (br.d, J = 5.6)[c]	4.05 (dd, J = 5.6, J = 8.6)	4.27 (dd, J = 8.6, J = 1.0)	8.47 (s, 1 H, H(5'))
3b	5.19 (s)	2.91 (dm, J = 17.8)	3.45 (dd, J = 17.8, J = 7.8)	5.33 (d, J = 7.8)	5.09 (br.d, J = 5.6)	4.08 (dd, J = 5.6, J = 8.3)	4.43 (dd, J = 8.3, J = 1.0)	7.03 (d, J = 2.6, 1 H, H(4')) 7.98 (d, J = 2.6, 1 H, H(5'))
3c	5.18 (s)	2.93 (dm, J = 18.0)	3.42 (dd, J = 18.0, J = 7.9)	5.30 (d, J = 7.9)	5.12 (br.d, J = 5.7)	4.08 (dd, J = 5.7, J = 8.6)	4.42 (dd, J = 8.6, J = 1.2)	8.12 (s, 1 H, H(3')) 8.60 (s, 1 H, H(5'))
3d	5.17 (s)	2.91 (dm, J = 17.7)	3.39 (dd, J = 17.7, J = 7.8)	5.18 (d, J = 7.8)	5.10 (br.d, J = 5.6)	4.08 (dd, J = 5.6, J = 8.6)	4.41 (dd, J = 8.3, J = 1.1)	2.47 (s, 3 H, CH_3) 8.53 (s, 1 H, H(5'))
3e	5.24 (s)	3.21 (dm, J = 18.0)	3.63 (dd, J = 18.0, J = 7.5)	6.01 (d, J = 7.5)	5.28 (br.d, J = 5.6)	4.18 (dd, J = 5.6, J = 8.6)	4.18 (dd, J = 8.6, J = 1.1)	—
3f	5.16 (s)	3.19 (dm, J = 17.8)	3.42 (dd, J = 17.8, J = 7.4)	5.55 (d, J = 7.4)	5.19 (br.d, J = 5.6)	4.11 (dd, J = 5.6, J = 8.5)	4.48 (dd, J = 8.5, J = 1.2)	3.92 (s, 6 H, $2OCH_3$)
3g	5.22 (s)	2.98 (dm, J = 18.1)	3.48 (dd, J = 18.1, J = 7.8)	5.44 (dm, J = 7.8)	5.22 (br.d, J = 5.6)	4.12 (dd, J = 5.6, J = 8.5)	4.44 (dd, J = 8.5, J = 1.2)	8.90 (s, 1 H, H(5'))
3-Me-**3h**	5.16 (s)	2.78 (dm, J = 17.4)	3.28 (dd, J = 17.4, J = 7.7)	4.98 (d, J = 7.7)	4.93 (br.d, J = 5.5)	4.00 (dd, J = 5.5, J = 8.1)	4.27 (dd, J = 8.1, J = 1.0)	2.19 (s, 3 H, CH_3) 6.06 (d, J = 2.2, 1 H, H(4')) 7.50 (d, J = 2.2, 1 H, H(5'))
5-Me-**3h**	5.14 (s)	2.85 (dm, J = 17.5)	3.16 (dd, J = 17.5, J = 7.7)	5.06 (d, J = 7.7)	4.80 (br.d, J = 5.5)	Overlapped		2.34 (s, 3 H, CH_3) H(4') overlapped 7.28 (d, J = 2.3, 1 H, H(3'))
3i	5.13 (s)	2.80 (dm, J = 17.5)	3.35 (dd, J = 17.5, J = 7.9)	5.16 (d, J = 7.9)	4.96 (br.d, J = 5.5)	4.01 (dd, J = 5.5, J = 8.2)	4.37 (dd, J = 8.2, J = 1.3)	6.29 (dd, J = 2.3, J = 1.7, 1 H, H(4')) 7.45 (d, J = 1.7, 1 H, H(3')) 7.68 (d, J = 2.3, 1 H, H(5'))
3j	5.21 (s)	2.50 (dm, J = 17.6)	3.46 (dd, J = 17.6, J = 8.0)	5.12 (d, J = 8.0)	4.90 (d, J = 5.6)	4.03 (dd, J = 5.6, J = 8.2)	4.35 (dd, J = 8.2, J = 1.2)	6.94 (br.s, 1 H, H(4')) 7.15 (br.s, 1 H, H(5')) 7.60 (br.s, 1 H, H(2'))
4i	4.94 (s)	2.18 (dm, J = 15.3)	2.44 (dd, J = 15.3, J = 7.5)	4.69 (d, J = 7.5)	4.53 (br.d, J = 5.6)	3.78 (dd, J = 5.6, J = 7.8)	4.03 (dd, J = 7.8, J = 1.1)	6.29 (dd, J = 2.4, J = 1.7, 1 H, H(4')) 7.48 (d, J = 1.7, 1 H, H(3')) 7.96 (d, J = 2.4, 1 H, H(5')) 5.35 (br.s, 1 H, OH) 7.29 (br.s, 1 H, OH)
4j	5.06 (s)	1.92 (dm, J = 15.3)	2.40 (dd, J = 15.3, J = 7.7)	4.47 (dm, J = 5.6)	4.55 (d, J = 5.6, J = 7.8)	3.79 (dd, J = 5.6, J = 7.8)	3.98 (dd, J = 7.8, J = 1.1)	6.85 (br.s, 1 H, H(4')) 7.49 (br.s, 1 H, H(5')) 7.96 (br.s, 1 H, H(2')) OH overlapped
4c	5.10 (s)	2.26 (dm, J = 15.6)	2.55 (dd, J = 15.6, J = 7.4)	4.75 (d, J = 7.4)	4.79 (br.d, J = 5.5,	3.89 (dd, J = 5.5, J = 8.0)	4.11 (dd, J = 8.0, J = 1.1)	8.09 (s, 1 H, H(3')) 9.17 (s, 1 H, H(5')) 5.95 (br.s, 1 H, OH) 6.20 (br.s, 1 H, OH)

Note. The spectra of compounds **3i,j** and **4i,j** were obtained in $(CD_3)_2SO$, the others in $(CD_3)_2CO$. [a] For all of the adducts, the splitting of the signal for H(3e) into a multiplet is caused by spin coupling with H(4), H(1), and H(5); the assignment of the signals for H(3e) and H(3a) are based on their different multiplicity (see Refs. 2, 3, 21). [b] For all of the adducts, the components of the doublet are broadened due to H(4) spin interaction with H(3e) and H(5). [c] For all of the adducts, broadening of the doublet for H(5) is caused by spin interaction with H(6*endo*), H(4), and H(3e)[2,3,21].

spectra of the precipitate); these products could not be separated by chromatography or crystallization. In the reaction with pyrazole, the hydrate **4i** was detected together with **3i** (1:1) in the products of chromato-

Table 4. ^{13}C NMR spectra of compounds **3a—j** and **4c,i,j**

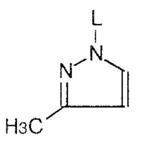
Adduct	δ (*J*/Hz)						
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Other C
3a	102.34 (d)	197.22 (s)	35.20 (dd)	61.72 (d)	76.85 (d)	66.74 (dd)	146.20 (dd, C(5'), *J* = 219.3, *J* = 2.8), 163.42 (d, C(3'), *J* = 14.2)
3b	102.40 (d)	197.45 (s)	36.47 (dd)	63.38 (d)	77.41 (d)	66.84 (dd)	103.84 (dd, C(4'), *J* = 188.5, *J* = 8.3), 132.88 (ddd, C(5')), 156.69 (dd, C(3'))
3c	102.20 (d)	197.57 (s)	36.24 (dd)	62.88 (d)	77.20 (d)	66.61 (dd)	129.41 (dt, C(5'), *J* = 197.7, *J* = 2.5), 135.88 (dd, C(3'), *J* = 197.4, *J* = 5.6), 136.89 (dd, C(4'))
3d	102.20 (d)	197.65 (s)	36.27 (dd)	62.62 (d)	77.12 (d)	66.71 (dd)	130.53 (dd, C(5'), *J* = 196.9, *J* = 2.4), 134.47 (dq, C(4'), *J* = 4.5, *J* = 2.6), 145.87 (qd, C(3'), *J* = 7.1, *J* = 5.7)
3e	102.45 (d)	196.07 (s)	35.29 (dd)	66.07 (d)	76.66 (d)	66.62 (dd)	167.24 (s, C(4'))
3f	102.41 (s)	196.71 (s)	35.30 (dd)	65.84 (d)	77.06 (d)	66.48 (dd)	53.02 (q, $2OCH_3$), 140.80 (C(5') and C(4')), 160.21 (s, 2COO)
3g	102.22 (d)	196.63 (s)	35.81 (dd)	64.06 (d)	76.86 (d)	66.62 (dd)	127.80 (d, C(4'), *J* = 4.1), 132.76 (dd, C(5')), 148.34 (d, C(3'), *J* = 6.6)
3-Me-**3h**	102.01 (d)	198.87 (s)	36.91 (dd)	61.27 (d)	77.44 (d)	66.56 (dd)	13.53 (q, CH_3), 106.06 (dd, C(4')), 129.29 (ddd, C(5')), 148.53 (dq, C(3'))
5-Me-**3h**	102.08 (d)	198.29 (s)	36.64 (dd)	57.42 (d)	77.01 (d)	66.98 (dd)	10.78 (q, CH_3), 106.32 (dd, C(4')), 138.36 (dd, C(3')), 138.17 (dq, C(5'))
3i	101.46 (d)	198.84 (s)	36.58 (dd)	60.80 (d)	77.14 (d)	66.15 (dd)	106.23 (dt, C(4')), 128.76 (ddd, C(5')), 139.11 (ddd, C(3'))
3j	100.86 (d)	199.21 (s)	37.78 (dd)	56.45 (d)	76.98 (d)	66.06 (dd)	118.37 (ddd, C(5')), 128.84 (dd, C(4')), 136.45 (d, C(2'))
4i	104.91 (d)	90.40 (s)	34.91 (dd)	58.57 (d)	78.67 (d)	66.56 (dd)	105.66 (dt, C(4')), 130.62 (dddd, C(5')), 138.32 (ddd, C(3'))
4j	103.53 (d)	90.04 (s)	36.00 (dd)	53.71 (d)	76.03 (d)	66.37 (dd)	120.31 (ddd, C(5')), 127.19 (dd, C(4')), 137.62 (d, C(3'))
4c	104.63 (d)	90.93 (s)	35.07 (dd)	60.96 (d)	75.69 (d)	66.45 (dd)	131.31 (ddd, C(5')), 135.31 (dd, C(3')), 138.02 (ddd, C(4'))

Note. The spectra of compounds **3i,j** and **4i,j** were obtained in $(CD_3)_2SO$, the others in $(CD_3)_2CO$.

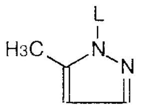
graphic purification of the reaction mixture. The hydrate **4c** was formed from **3c** when the latter was allowed to stay for a long time in acetone. The hydrates were characterized by the appearance of a carbon atom signal at ~90 ppm with the simultaneous disappearance of the carbonyl group signal at 195—200 ppm in the ^{13}C NMR spectra. In addition, in the ^{1}H NMR spectra, the upfield shift of a number of signals of the carbohydrate fragment together with the downfield shift of the signal of the heterocyclic H(5) proton, and the decrease in $J_{3a,3e}$ were observed. In the IR spectra a broad intens band at 3300—3500 cm^{-1} appeared at the same time that the intensity of the carbonyl group absorption band decreased (Tables 2,3). Judging from the presence of the signal at 90 ppm in the ^{13}C NMR spectrum of chromatographically purified adduct **3h**, it also contains an insignificant admixture of *gem*-diol. Hence, the hydrates may be formed as a result of the absorption of moisture from the air, silica gel, or solvent. Previously it has been possible to observe the hydration of the carbonyl group in type **3** derivatives only in aqueous solutions.[1,10]

The stereochemistry of the addition of azoles to **1** is of interest. As follows from the ^1H NMR spectral data (see Table 3, spin coupling constant $J_{3a,4}$ ~7.5—8 Hz), the addition of all of the reactive azoles studied proceeded face-specifically "from the bottom", that is, from the side opposite to the 1,6-anhydro bridge (see Ref. 2). These results are in full agreement with those obtained before on the stereochemistry of the addition of C-, O-, and S-nucleophiles.[1—4]

It should be noted that the position of the heterocyclic nitrogen atom to which the carbohydrate fragment becomes attached conforms with the known rules[11—13] for the reactions of electrophiles with heterocycles of this type. If a bulky electron-accepting substituent is present in the heterocyclic ring, the carbohydrate fragment adds exclusively to the nitrogen atom in the cycle that is the farthest removed from this substituent. With azoles **3a,b,g**, this was confirmed by the splitting of the signal for the unsubstituted carbon atom of the heterocycle by the H(4) atom of the carbohydrate fragment (^3J in ^{13}C NMR spectra), since for the other isomer this splitting should be observed for the substituted carbon atom. With the 5-nitrotetrazole derivative **3e**, the chemical shift of the carbon atom of the tetrazole ring (167.8 ppm) is evidence for N(2)-substitution, since its value differs substantially for 1- and 2-substituted tetrazoles.[11] In the case of **3f**, the addition to the central nitrogen atom is established by the symmetry of the NMR spectra of the heterocyclic part of the molecule. Only in the reaction of 3(5)-methylpyrazole **2h** has the formation of two isomers, 3-Me-**3h** and 5-Me-**3h**, been noted:



3-Me-**3h**



5-Me-**3h**

(L is for a carbohydrate fragment)

In the ^{13}C NMR spectrum of the reaction product the signals for the carbon atoms of the pyrazole ring are observed at 129.29 (C(5)) and 148.53 (C(3)) ppm, which is characteristic of 1,3-disubstituted pyrazoles, and also at 138.17 (C(5)) and 138.36 (C(3)) ppm, typical for 1,5-disubstituted pyrazoles. The signals at 13.53 and 10.78 ppm, related to the CH_3-group, also indicate the 1,3- and 1,5-disubstitution patterns, respectively.[14] Moreover, for one of the isomers additional coupling of the signal of an unsubstituted heterocyclic C atom can be observed (see above). Judging from the NMR spectra, the 1,3- and 1,5-isomers are in a ratio of about 6:1 (see Table 1).

Experimental

^1H NMR spectra were registered on a Bruker WM-250 instrument at 250.13 MHz. ^{13}C NMR spectra were taken using a Bruker AM-300 spectrometer operating at 75.47 MHz. IR spectra were recorded on a Specord M-80 spectrophotometer. The standard procedure for the addition reaction, IR spectra, melting points of the products (see Table 2), and their NMR characteristics (see Tables 3,4) are given below.

Levoglucosenone (**1**) was obtained *via* the pyrolysis of cotton cellulose impregnated with phosphoric acid (2 %) in a metal reactor (loading of ~300 g). Prior to impregnation, the cellulose was treated with hot 1 % HCl for 2.5 h to remove the amorphous fragments of the macromolecule, then washed with water and dried. The pyrolysis was carried out *in vacuo* (4 Torr) at 350—400 °C until the evolution of pyrolytic gases ceased (2—3 h). The pyrolysate was gathered into a collector cooled to —20 °C. The subsequent treatment was according to the procedure in the literature.[1] After the distillation, the yield of product **1** was 5—8 % (in Ref. 1 it is only 2 %).

Chromatography was always performed on silica gel using a chloroform/ethyl acetate 2:1 solvent mixture. The results of the elemental analysis of products **3a—h** were satisfactory.

3-Nitro- and 4-nitropyrazoles 2b and 2c were obtained by the nitration of pyrazole **2i** (see Refs. 15, 16). **3-Methyl-4-nitropyrazole 2d** was obtained *via* the nitration of 3-methylpyrazole **2h** (see Ref. 17). **4-Nitrotetrazole 2e** was obtained from 5-aminotetrazole by treatment with $NaNO_2$ in an acidic medium[11] followed by extraction with ether and the removal of the solvent. Compounds **2a**, **2f**, and **2g** were obtained by methods reported earlier (see Refs. 18, 19, and 20, respectively).

Standard procedure. 10 mol. % of Et_3N or piperidine (with **2a—g** or **2h—j**, respectively) were added to a solution of an azole (5 mmol) in 3 mL of CH_3CN. Then a solution of **1** (5 mmol) in 5 mL of CH_3CN was added dropwise over 40 min with stirring at 40 °C. The reaction mixture was kept for 1—2 days at room temperature (for **2a—g**) or at 40—50 °C (for **2h—i**), then the solvent was removed, and the products formed either immediately as crystals or as a gradually crystallizing oil. All of the adducts, except **3f**, were recrystallized from CH_3CN.

Compound 3f. The amounts of the starting materials were threefold less than those in the standard procedure. The product after solvent evaporation was a non-cystallizing yellow oil, that was purified chromatographically.

Compound 4c. Adduct **3c** was dissolved in acetone and the solution was allowed to stand for 3 months in a sealed NMR tube. The ^1H and ^{13}C NMR spectra taken afterwards demonstrated the formation of compound **4c**. The ratio of **3c** to **4c** in the mixture was 3:2.

Compound 4i. After the workup of the reaction mixture a dark-brown oil was obtained. The NMR indicated it to be solely adduct **3i** with only insignificant impurities. Purification afforded a yellowish oil that soon thickened into a solid consisting of a 1:1 mixture of **3i** and **4i** (the NMR data).

Compound 4j. In the course of the reaction a white precipitate was formed consisting of **3j** and **4j** (3:1) as judged from the NMR and IR spectra.

The product of the addition of **1** to **2h** was also purified chromatographically. In the process, a certain amount of pure 3-Me-**3h** isomer was isolated.

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