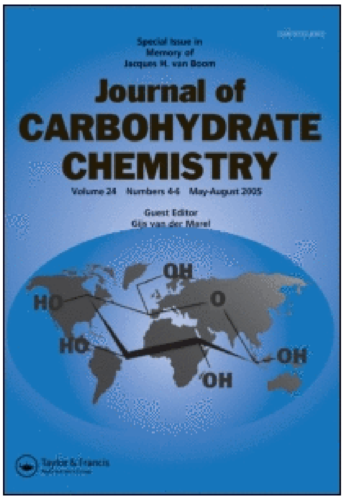

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NEW COMPOUNDS ISOLATED FROM THE PYROLYSIS OF CELLULOSE

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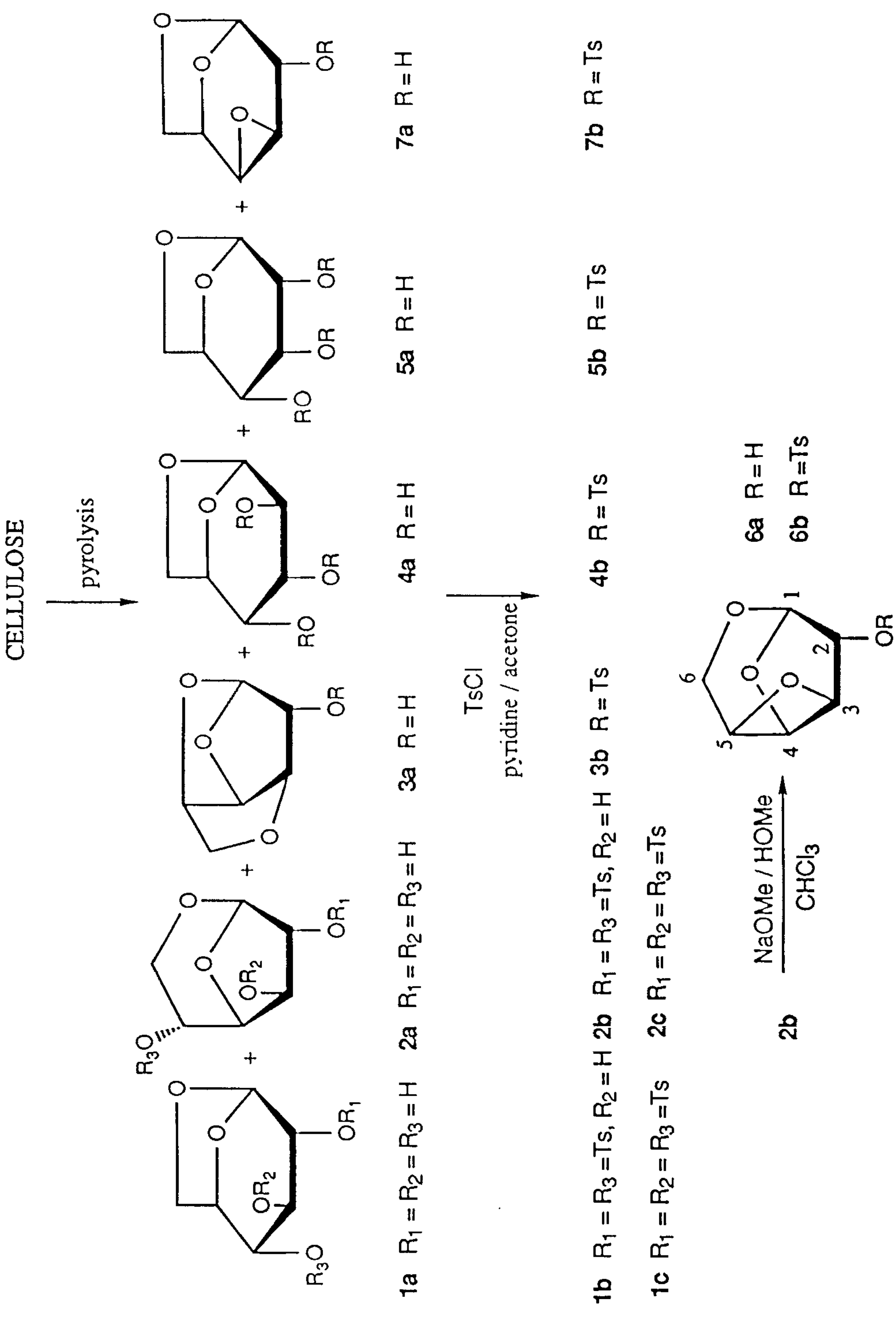
ABSTRACT

Two so far unknown minor compounds 1,6-anhydro-ß-D-altropyranose and 1,6-anhydro-ß-D-allopyranose were isolated during the classic pyrolysis of cellulose in the presence of copper powder. Although for one of them a new intermediate must be proposed, their occurence can be explained from already proven or postulated intermediates.

INTRODUCTION

Several methods are described for the preparation of 1,6-anhydro-ß-D-glucopyranose (ß-glucosan)(**1a**),[1,2] the pyrolysis of starch[3] or cellulose[4,5] being the most attractive. Tosylation of ß-levoglucosan affords several partially tosylated derivatives which can be used for further transformations.[6] Some side products occurring in trace quantities formed during the pyrolysis of cellulose (and isolated as tosylated or acetylated derivatives) were thoroughly studied by Köll and co-workers[7,8] and provided insight into the pyrolysis proces. Thus they identified 1,6-anhydro-ß-D-glucofuranose (**2a**) with NMR. Köll and Schulz also identi-



1a $R_1 = R_2 = R_3 = H$ **2a** $R_1 = R_2 = R_3 = H$ **3a** $R = H$ **4a** $R = H$ **5a** $R = H$ **7a** $R = H$

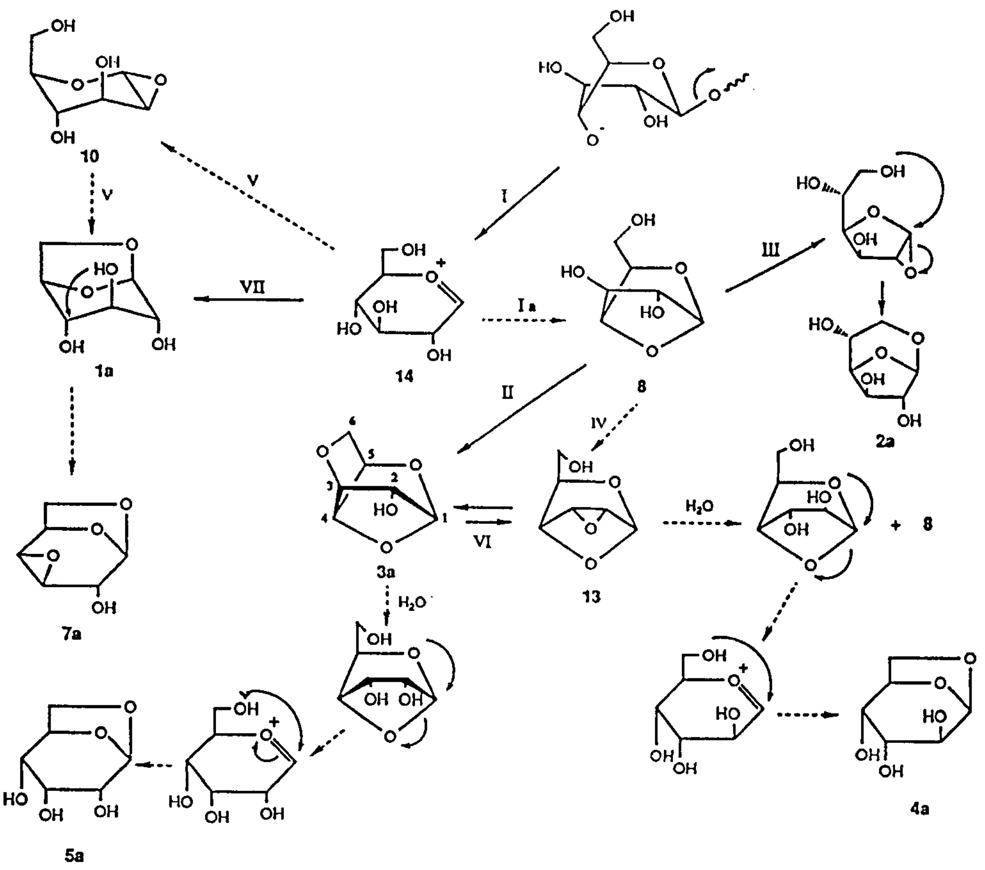
1b $R_1 = R_3 = Ts, R_2 = H$ **2b** $R_1 = R_3 = Ts, R_2 = H$ **3b** $R = Ts$ **4b** $R = Ts$ **5b** $R = Ts$ **7b** $R = Ts$

1c $R_1 = R_2 = R_3 = Ts$ **2c** $R_1 = R_2 = R_3 = Ts$

6a $R = H$

6b $R = Ts$

Scheme 1



tified 1,6:3,5-dianhydro-α-**L**-idofuranose (**6a**)[7,8] as a further anhydro derivative that they obtained from 1,6-anhydro-5-*O*-tosyl-ß-**D**-glucofuranose.

Earlier Bedford and Gardiner[9] had isolated the dianhydro derivative (**3a**) among the pyrolysis compounds of cellulose. It was derivatized and identified as 1,4:3,6-dianhydro-2-*O*-tosyl-α-**D**-glucopyranose (**3b**).

Among the side compounds that we isolated in the present study from the pyrolysis of cellulose we identified for the first time, after tosylation, the tri-*O*-tosyl derivatives of 1,6-anhydro-ß-**D**-altropyranose (**4a**) and 1,6-anhy-

TABLE 1. ^{13}C NMR Data of 1,6-Anhydro-2,3,4-tri-*O*-Tosyl-ß-**D**-Altropyranose (**4b**) in $CDCl_3$ Solution.

Chemical Shifts:

C-1	C-2	C-3	C-4	C-5	C-6	CH_3	aromatic carbons
99.4	71.8	67.0	69.2	74.7	65.5	21.7	129.8-130.0 127.9-128.2

dro-ß-**D**-allopyranose (**5a**) present in less than 1 % (Scheme 1), which may be a further link to understanding the pyrolysis process of cellulose.

RESULTS AND DISCUSSION

When we compare the ^{13}C NMR spectrum of **4b** (see Table 1) with those reported for tri-O-acetylated 1,6-anhydro-ß-**D**-hexopyranoses, a close similarity with the *altro*-modification[10,11] is obvious. The interproton coupling constants we found for **4b** (see Table 2) are furthermore very similar to those found in 1,6-anhydro-ß-**D**-altropyranose.[12] Likewise, the vicinal and geminal coupling constants as extracted from the ^{1}H NMR spectrum of **5b** (see Table 2) can only be corroborated with a 1,6-anhydro-*allo* configuration.[12]

This work describes for the first time compounds isolated from the pyrolysis of cellulose that do not have the *gluco*-configuration, or a configuration immediately derived from a structure with the *gluco*-configuration. Recently the pyrolysis of cellulose in the presence of inorganic salts has been thoroughly studied[13] and it has been surmised that during the unknown thermal history of the sample secondary reactions may occur. In our reactions copper powder was indeed used. We propose a formation process of **4a** and **5a** using partially proven cation intermediates or an already postulated neutral intermediate (**3a**). The role of secondary reactions in this case is not straightforward.

TABLE 2. ^{1}H NMR Data of the Ring Protons in **4b** and **5b** in $CDCl_3$.

Chemical Shifts :

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-6'
4b	5.32	4.50	4.55	5.01	4.88	3.83	3.82
5b	5.50	4.47	4.52	4.67	4.82	3.72	3.66

Coupling Constants :

Compound	$^{3}J_{1,2}$	$^{3}J_{2,3}$	$^{3}J_{3,4}$	$^{3}J_{4,5}$	$^{3}J_{5,6}$	$^{3}J_{5,6'}$
4b	1.2	9.1	4.3	2.6	1.3	4.8
5b	2.4	4.4	4.4	2.4	1.0	5.2

	$^{2}J_{6,6'}$	$^{4}J_{1,5}$	$^{5}J_{2,5}$
4b	8.9	1.5	-
5b	8.8	~1.0	1.0

Recently arguments were advanced[13] which doubted the heterolytic mechanism for the formation of levoglucosan from cellulose pyrolysis.[15] Essig and coworkers[13] proposed a heterolytic scission of the glucosyl oxygen bond in cellulose so that the one new cellulose chain ends with a resonance-stabilized glucosyl cation and the other adds a proton to form a normal cellulose non-reducing end group. The latter is the starting compound in Scheme 1, to give (via pathway I) glycosyl cation **14**, itself the precursor of **1a** (via pathway VII), **8** (via pathway Ia) and **10** (via pathway V). Compound **8** is the starting compound for three other pathways, where II and IV lead to **4a** and **5a**. The glucosyl cation (**14**) can be postulated as the crucial intermediate leading to **1a**, **8** and **10**. Paths II and III, starting from 1,4-anhydro-α-D-glucopyranose (**8**) have been suggested by Halpern and Patai.[18]

The *allo*-derivative **5a**, the C-3 epimer of levoglucosan, can be explained if we accept an attack of water on C-3 of a 3,6-anhydro structural fragment as e.g. in the tricyclic intermediate **3a** (Scheme 1, path II and following). In order to explain the formation of **4a** where both centers C(2) and C(3) are epimerized we propose the intermediate 1,4:2,3-dianhydro-α-**D**-allopyranose **13** (Scheme 1, path IV or VI), which was not isolated. Since water is the main substance in the volatile fraction,[15] an SN2 like hydrolytic cleavage of the oxirane ring in **13** may lead on one hand to 1,4-anhydro-α-**D**-altropyranose which reacts further to **4a**, while on the other hand to the initial 1,4-anhydro compound **8**. The hydrolytic opening of the rather stabile 3,6-anhydro bridge in **3a**, with formation of the *allo*-configuration, may need catalysis by acids, which are known to be formed during pyrolysis of cellulose.[16,17] Compound **7a** can now be postulated to be formed from **1a**. This 3,4-anhydride formation is facilitated by the 3,4-*trans*-diaxial disposition obtained after 1,6-anhydro bridge formation.

Studies on the opportunity for secondary reactions in the presence of copper powder and on the involvement of water molecules are the subject of forthcoming considerations.

SUMMARY

We propose in this scheme step Ia leading from the glucosyl cation to **8**, step V leading from the glucosyl cation via **10** to **1a** and an additional step leading from **1a** to **7a**. We further propose two reactions implementing water: a) a reaction on **3a** leading to **5a** and b) reaction path IV leading to **4a**, where intermediate **13** is necessary. Our proposals are indicated by a dashed arrow in the Scheme 1.

EXPERIMENTAL

Cellulose was pyrolyzed as described by Cottrell and co-workers.[5] Impure ß-glucosan was isolated from the dark brown syrup by crystallization (acetone). After tosylation with 2.2 mole equivalents of tosyl chloride and crystallization of 1,6-anhydro-2,4-di-*O*-tosyl-ß-**D**-glucopyranose, a second crop of crystals could be obtained by adding more water to the filtrate. Thin layer chromatography (silica gel; chloroform : ethyl acetate (9:1)) showed a mixture of five tosylated sugars (R_f = 0.74, 0.66, 0.57, 0.44 and 0.27). Chromatography on silica with 20:1 chloroform-ethyl acetate gave: 1,6-anhydro-2,3,5-tri-*O*-tosyl-ß-**D**-glucofuranose (**2c**), R_f = 0.74, mp 125-126 °C, $[\alpha]_D$ -14.5° (c 1.33 in chloroform); 1,6-anhydro-2,3,4-tri-*O*-tosyl-ß-**D**-glucopyranose (**1c**); R_f = 0.66, mp 104-105 °C, $[\alpha]_D$ -18.7° (c 1.15 in chloroform); 1,6-anhydro-2,5-di-*O*-tosyl-ß-**D**-glucofuranose (**2b**); R_f = 0.44, mp 172-173 °C (lit. 137-138 °C[7], 158-159 °C[8]), $[\alpha]_D$ -43.9° (c 1.08 in chloroform) and 1,6-anhydro-2,4-di-*O*-tosyl-ß-**D**-glucopyranose (**1b**); R_f = 0.27, mp 116-119 °C, $[\alpha]_D$ -43.3° (c 1.02 in chloroform).

The fraction that gave the fifth spot (R_f = 0.57) was actually a mixture. When eluated in benzene:ethyl acetate 15:1, four spots appeared: R_f = 0.29, 0.24 (major compound), 0.21 and 0.18. Separation by HPLC, performed on a Waters M6000A (column: 500 mm x 6.8 mm, silica gel 10 μ), (hexane:ethyl acetate 27:73) gave the pure compounds. They were identified by ^{1}H NMR spectroscopy and by physical data as: 1,6:3,4-dianhydro-2-*O*-tosyl-ß-**D**-galactopyranose (**7b**), R_f = 0.29, mp 148-149 °C, $[\alpha]_D$ -40.2° (c 1.4 in chloroform);[19] 1,4:3,6-dianhydro-2-*O*-tosyl-α-**D**-glucopyranose (**3b**), R_f = 0.24, mp 86-87 °C, $[\alpha]_D$ +56.9° (c 1.1 in chloroform); 1,6-anhydro-2,3,4-tri-*O*-tosyl-α-**D**-altropyranose (**4b**), R_f = 0.21, mp 173-174 °C, $[\alpha]_D$ -68° (c 0.38 in chloroform) and 1,6-anhydro-2,3,4-tri-*O*-tosyl-ß-**D**-allopyranose (**5b**), R_f = 0.18, mp 154-155°, $[\alpha]_D$ not measured.

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