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Preliminary communication

Specific structural assignments for *O*-acetyl group resonances in the ^{1}H-n.m.r. spectrum of 1,2,3-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose

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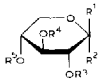
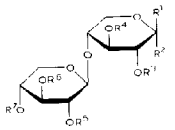
Wood of angiosperms contains usually 3–5% *O*-acyl (*O*-acetyl and *O*-formyl) groups[1,2]. Extraction of holocellulose from these sources under mild conditions (*e.g.*, dimethyl sulfoxide and water) provides, in some cases, D-xylans having a high acetyl content. On extraction with dimethyl sulfoxide, a chlorite holocellulose from white-birch wood gave a D-xylan containing 5.3 *O*-acetyl groups per 10 D-xylose residues[3]. Consequently the presence of these substituents may lead to the isolation, by enzymic degradation, of partially acetylated oligoxylose derivatives. Recently, in our laboratory, samples of xylobiose containing acetyl groups were isolated[4] from "exploded wood". In order to determine the location of these groups in disaccharides, one of the methods consists in acetylating with ($^2H_3$)-acetic anhydride the compound to completion, under mild conditions, and to investigate the resonances of the acetyl groups by ^{1}H-n.m.r. spectroscopy. With this aim, we have determined unambiguously all of the six acetyl group resonances of 1,2,3-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose (**14**) from its ^{1}H-n.m.r. spectrum recorded for a solution in ($^2H_6$)benzene (see Table I).



1 R^1 = OAc, R^2 = H, R^3 = R^4 = Ac, R^5 = H
2 R^1 = H, R^2 = Br, R^3 = R^4 = R^5 = Ac
3 R^1 = H, R^2 = Br, R^3 = R^4 = R^5 = CD_3CO
4 R^1 = OAc, R^2 = H, R^3 = Ac, R^4 = R^5 = H
5 R^1 = OAc, R^2 = H, R^3 = Ac, R^4 = CD_3CO, R^5 = H
6 R^1 = OAc, R^2 = H, R^3 = Ac, R^4 = H, R^5 = CD_3CO
7 R^1 = H, R^2 = Br, R^3 = R^4 = R^5 = Ac



8 R^1 = OAc, R^2 = H, R^3 = R^4 = Ac, R^5 = R^6 = R^7 = CD_3CO
9 R^1 = OAc, R^2 = H, R^3 = R^4 = R^5 = R^6 = Ac, R^7 = H
10 R^1 = OAc, R^2 = H, R^3 = R^4 = R^5 = R^6 = Ac, R^7 = CD_3CO
11 R^1 = OAc, R^2 = H, R^3 = R^4 = R^5 = R^7 = Ac, R^6 = CH_2ClCO
12 R^1 = OAc, R^2 = H, R^3 = R^4 = R^5 = R^7 = Ac, R^6 = H
13 R^1 = OAc, R^2 = H, R^3 = R^4 = R^5 = R^7 = Ac, R^6 = CD_3CO
14 R^1 = OAc, R^2 = H, R^3 = R^4 = R^5 = R^6 = R^7 = Ac
15 R^1, R^2 = H, OH, R^3 = R^4 = R^5 = R^6 = R^7 = Ac
16 R^1 = CD_3CO_2, R^2 = H, R^3 = R^4 = R^5 = R^6 = R^7 = Ac
17 R^1 = OAc, R^2 = H, R^3 = R^6 = R^7 = OAc, R^4 = CD_3CO

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Treatment of 1,2,3-tri-*O*-acetyl-β-D-xylopyranose[5] (**1**) with 2,3,4-tri-*O*-($^2H_3$)-acetyl-α-D-xylopyranosyl bromide (**3**), in the presence of $Hg(CN)_2$ and $HgBr_2$ in acetonitrile solution at room temperature for 24 h gave 1,2,3-tri-*O*-acetyl-4-*O*-[2,3,4-tri-*O*-($^2H_3$)-acetyl-β-D-xylopyranosyl]-β-D-xylopyranose (**8**) in 60% yield, and the α-linked disaccharide isomer, 1,2,3-Tri-*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose (**9**), prepared[6] as the peracetylated disaccharide described previously[7], was acetylated to completion with ($^2H_3$)acetic anhydride under conditions that prevented migration (benzene as solvent and pyridine adjusted to stoichiometry) to afford, in quantitative yield, the 4′-labeled xylobiose **10**. 1,2,3-Tri-*O*-acetyl-4-*O*-(2,4-di-*O*-acetyl-3-*O*-chloroacetyl-β-D-xylopyranosyl)-β-D-xylopyranose[8] (**11**)* {$[\alpha]_D^{20}$ −46° (*c* 1, chloroform)} was deprotected by heating with 20:10:3 (v/v) 1,2-dichloroethane–methanol–pyridine for 2 days at 50° to give **12*** purified by chromatography. Upon acetylation with ($^2H_3$)acetic anhydride, **12** gave the 3′-labelled xylobiose **13**. Treatment of a solution of 1,2,3-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose (**14**) in 1,2-dichloroethane with a solution of hydrogen bromide in acetic acid, followed by hydrolysis of the bromide formed with Ag_2O and water gave in nearly quantitative yield the disaccharide **15** having free OH-1. In the presence of an adjusted proportion of the ($^2H_3$)acetylating reagent, **15** gave a mixture of the anomers of **14**. The pure β anomer **16**, labeled at C-1, was isolated by crystallization from ethyl ether. Partial acetylation of 1,2-di-*O*-acetyl-β-D-xylopyranose[9] (**4**) with ($^2H_3$)-acetic anhydride afforded 1,2-di-*O*-acetyl-3-*O*-($^2H_3$)acetyl-(**5**) and -4-*O*-($^2H_3$)acetyl-β-D-xylopyranose (**6**) having the same physical properties as the nondeuterated compounds[9], both in crystalline form. Condensation of **5** with 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (**2**), under the same conditions as those used for the preparation of **8**, gave the 3-*O*-($^2H_3$)acetylxylobiose **17** in 60% yield.

TABLE I

SPECIFIC STRUCTURAL ASSIGNMENTS[a] FOR ACETYL GROUP RESONANCES IN THE ^{1}H-N.M.R. SPECTRUM[b] OF COMPOUND **14**

OAc-1	*OAc-2*	*OAc-3*	*OAc-2′*	*OAc-3′*	*OAc-4′*
1.585	1.727	1.779	1.671	1.712	1.611

[a] Chemical shifts (δ) relative to the signal of Me_4Si.
[b] Spectrum recorded at 200 MHz for a solution in ($^2H_6$)benzene.

The ^{1}H-n.m.r. spectrum of **14** for a solution in ($^2H_6$)benzene showed six signals in the range δ 1.5–1.8 (Fig. 1) corresponding to the resonances of the six acetyl groups. The ^{1}H-n.m.r. spectrum of **8** for a solution in ($^2H_6$)benzene showed, in the same region, three

*Satisfactory elemental analyses and n.m.r. data were obtained for **11** and **12**.

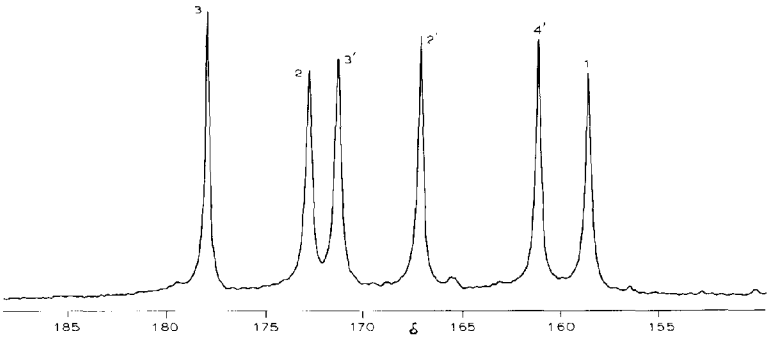

Fig. 1. The acetyl group signals in the ^{1}H-n.m.r. spectrum of compound **14** at 200 MHz for a solution in ($^2H_6$)benzene.

signals corresponding to the resonances of OAc-1, -2, and -3. Thus, comparison between the signals of **8** and **14** allowed to allocate the signals between reducing and nonreducing units. The chemical shifts of OAc-3′ and -4′ were attributed by labeling the acetyl group at O-4′ (**9** → **10**) and O-3′ (**12** → **13**); and the resonance of OAc-2′ was obtained by difference. The same approach identified the resonances of the acetyl groups of the reducing unit. Acetylation of **15** with ($^2H_3$)acetic anhydride gave **16**, the ^{1}H-n.m.r. spectrum of which allocated the resonance of OAc-1, comparison between the signals of **17** and **14** allocated the resonance of OAc-3.

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