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Spectroscopic Properties of Methyl Triacetyl-α- and β-L-Rhamnosides

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The spectroscopic properties (IR-, mass- and PMR-spectra) of methyl triacetyl-α- and β-L-rhamnosides (*1* and *2*) have been investigated.

The present investigation was carried out primarily to facilitate the interpretation of spectral data for acetylated derivatives of natural carotenoid rhamnosides.[1,2]

EXPERIMENTAL

Methyl triacetyl-α-L-rhamnoside (*1*) and its β-anomer (*2*) were prepared by standard acetylation with acetic anhydride in pyridine of methyl α-L-rhamnoside and methyl β-L-rhamnoside, respectively, obtained from the collection of Professor N. A. Sørensen, this Institute.

The α-anomer (*1*), chromatographically homogeneous on thin-layer (kieselgel G, benzene, developer conc. H_2SO_4/ethanol 1:1), crystallized as plates from chloroform-petroleum ether, m.p. 88°C (reported 88–89°C [3]), $[\alpha]_{589}^{25} = -60.2 \pm 4$ % (reported $[\alpha]_D^{20} = -60.1$ [3]), yield 33 mg.

The β-anomer (*2*), chromatographically homogeneous in the above system, crystallized as needles from ethanol, m.p. 153°C (reported 152–153°C [3]), yield 10 mg.

Acetylation of L-rhamnose with acetic anhydride in pyridine gave tetraacetyl-L-rhamnose (*4*) as a viscous oil.

RESULTS AND DISCUSSION

The IR spectra (KBr, Fig. 1) exhibited gross features corresponding to reported spectra [3] but exhibited considerably better fine-structure. Vibrations characteristic of the α-anomer (*1*) were at 1290, 1180, 900, 840 (see Ref. 4 for a discussion of this band) and 800 cm^{-1}, and of the β-anomer (*2*) at 1408, 1210, 1170, 1105, 1040, 750 and 725 cm^{-1}. Absorption at 975 cm^{-1} present in spectra of *1* and *2* has been ascribed to terminal methyl.[5]

The mass spectra of *1* and *2* differed only in peak intensities and exhibited characteristic peaks at *m/e* 303 (M−1), 273 (M−31), 244 (M−60), 200, 184 (244−60, metastable peak at 139), 157, 144, 142 (184−42, metastable peak at

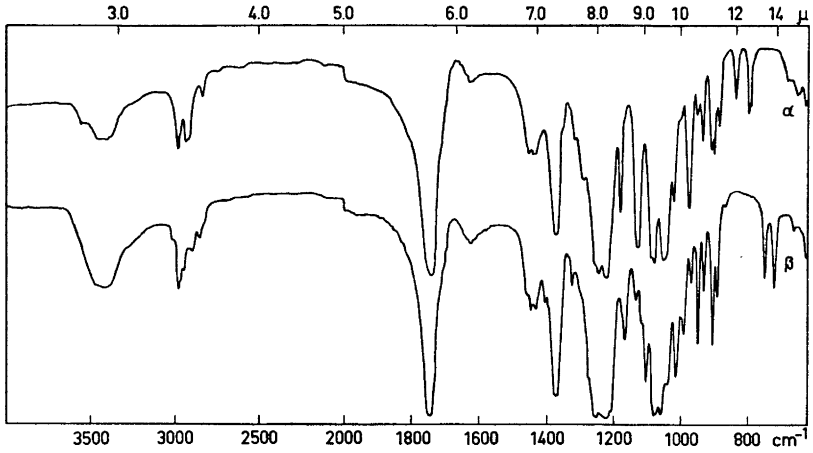


Fig. 1. Infrared spectra (KBr) of methyl triacetyl-α-L-rhamnoside (*1*) and methyl triacetyl-β-L-rhamnoside (*2*).

139), 140, 129, 126, 115, 113, 103, 102, 100, 99, 87, 83, 82, 74, 73, 71, 60, 58 and 43 (base peak). Prominent peaks due to elimination of acetic acid and ketene from the molecular ion and fragment ions were observed, and their origin supported by metastable ions. A prominent peak at *m/e* 157, previously found by Biemann *et al.*[6] in spectra of hexose acetates and interpreted as *a* was observed. Loss of ketene from *a* was supported by a metastable ion, in agreement with Biemann's scheme. Peaks due to elimination of acetic acid and ketene from the non-abundant triacetyl oxonium ion (*m/e* 273) were not observed. For

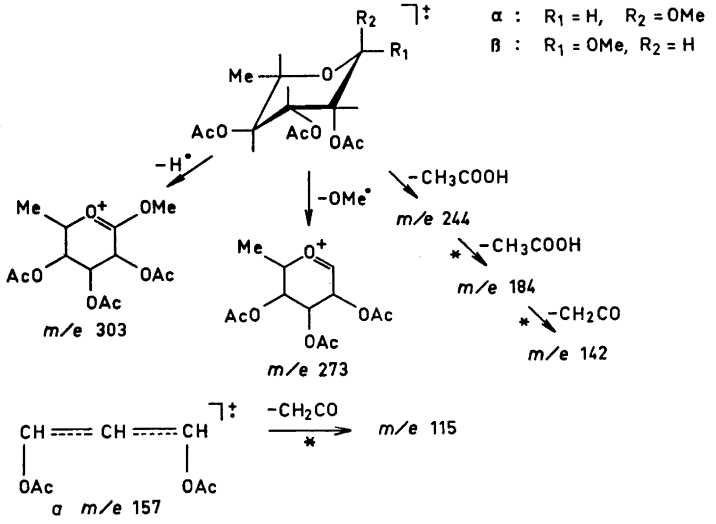


Table 1. PMR ($CDCl_3$, 60 MHz) signal assignments for methyl triacetyl-α-L-rhamnoside (*1*) and methyl triacetyl-β-L-rhamnoside (*2*).

Protons	α-Anomer (*1*)	β-Anomer (*2*)
H-1	5.35 τ,eq,broad s, W_H=3cps	5.46 τ,ax,d,J_{1-2}=1cps(ax,eq)
H-2	4.77 τ,eq,dd,J_{1-2}=*ca.* 2cps (eq,eq),J_{2-3}=3cps(eq,ax)	4.54 τ,eq,dd,J_{1-2}=1cps (ax,eq),J_{2-3}=2.8cps(eq,ax)
H-3	4.68 τ,ax,dd,J_{2-3}=3cps (eq,ax),J_{3-4}=10cps(ax,ax)	*ca.* 4.9 τ } not first order
H-4	4.95 τ,ax,dd,J_{3-4}=10cps- (ax,ax),J_{4-5}=9cps(ax,ax)	*ca.* 5.9 τ } not first order
H-5	6.14 τ,ax,dq,J_{4-5}=9cps- (ax,ax),J_{4-Me}=6.5cps	6.43 τ,ax,dq,J_{4-5}=9cps,J_{5-Me}=6.5cps
OMe	6.60 τ,ax,s	6.49 τ,eq,s
OAc-2	7.87 τ,ax,s	7.83 τ,ax,s
OAc-3 OAc-4	7.97,8,01 τ,eq,eq,s	7.97,8,01 τ,eq,eq,s
Me	8.79 τ,eq,d,J=6.5cps	8.70 τ,eq,d,J=6.5cps

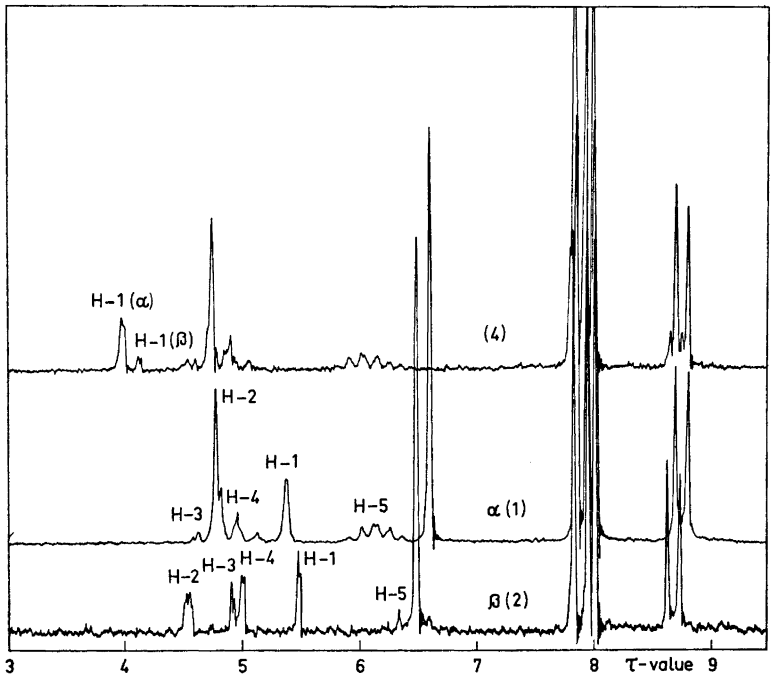
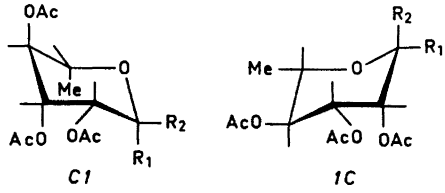


Fig. 2. Proton magnetic resonance spectra ($CDCl_3$, 60 MHz, 40°C) of methyl triacetyl-α-L-rhamnoside (*1*), methyl triacetyl-β-L-rhamnoside (*2*) and tetraacetyl-α- and β-L-rhamnoside (*4*).

the α-anomer (*1*) the *m/e* 273 peak was considerably stronger than for *2*, (3.5 % contra 0.06 % of base peak) indicating that the methoxy group at C-1 may occupy the sterically unfavourable axial position in the α-anomer, facilitating its elimination,[7] that is corresponding to $^1C_4 = 1C$ conformation.[8,9]

PMR spectra ($CDCl_3$, 60 MHz, 40°C) of *1* and *2* are presented in Fig. 2. Plausible signal assignments based on expanded spectra, suggesting that both *1* and *2* occur in *1C* conformation, are given in Table 1.

For the α-anomer (*1*) our assignments are in gross agreement with those of Bohlmann *et al.*[10] for ethyl triacetyl-α-L-rhamnoside (*3*). In particular the H-1,H-2 coupling constant for *1* rules out an axial-axial relationship and *C1* conformation, and the H-4,H-5 coupling constants for *1* and *2* clearly demonstrate an axial-axial coupling as required by the *1C* conformation.



1 (α): R_1 = H, R_2 = OMe

2 (β): R_1 = OMe, R_2 = H

The results agree with the general principle that equatorial ring protons and methoxy substituents give rise to resonances downfield to their axial counterparts and equatorial acetoxy groups upfield to equatorial ones.[11] The various coupling constants are further within the predicted range,[12,13] and the half-height width of the H-1 signal of *1* (W_H = 3 cps) corresponds to an equatorial proton.[13]

In free or fully acetylated pyranoses the anomeric proton is known to resonate at lowest field.[9,14] The apparent anomalous high field signal of the anomeric proton in *1* and *2* relative to the H-2,H-3 and H-4 protons is ascribed to the substituent effect. The PMR spectrum of tetra-acetyl-L-rhamnose (*4*) examined for comparison, supported this assignment. *4*, prepared by acetylation of rhamnose, was estimated from its PMR spectrum (Fig. 2) to contain *ca.* 72 % of the α-anomer (*4a*) and *ca.* 28 % of the β-anomer (*4b*). Relevant to the present discussion is the paramagnetic shift of the anomeric proton of *4a* to τ 3.98 and of *4b* to τ 4.15 (*cf.* Table 1).

The PMR results for *1* and *2* demonstrate that in acetylated rhamnosides the anomeric proton is not necessarily the ring proton occurring at lowest field, its chemical shift depending on the nature of the aglycone.

In conclusion, direct comparison of spectral data for *1* and *2* and acetylated L-rhamnosides with more complicated aglycones, may possibly allow conclusions concerning the identification and conformation of rhamnose and the stereochemistry of the glycosidic linkage.

For the carotenoid rhamnosides examined[1,2] the mass-spectrometric fragmentation of the carbohydrate moiety proceeded mainly by a different route.

The preference for β-configuration in oscillaxanthin [2] from PMR evidence must be considered tentative in view of spectral quality and unknown influence of the aglycone. In light of the present interpretation (Table 1) the following assignments of the carbohydrate ring protons in oscillaxanthin (= oscillol-2,2'-dirhamnoside) hexaacetate (100 MHz) [2] are plausible: H-5 τ 6.01,ax,dq, $J_{4-5}=10$ cps (ax, ax), $J_{5-Me}=6$ cps; H-4 τ 5.20, ax, t, $J_{4-5}=10$ cps (ax,ax), $J_{4-3}=10$ cps (ax, ax); H-3 τ 5.07, ax, dd, $J_{3-4}=10$ cps (ax, ax), $J_{3-2}=3.5$ cps (ax, eq); H-2 τ 4.86, eq. d, $J_{2-3}=3.5$ cps (ax, eq), $J_{1-2}=ca.$ 0 cps; H-1 τ 4.57 ?, $W_H=2.5$ cps (eq. ?). These data are taken to support the *1C*(L) conformation of the rhamnose moiety. However, further evidence is needed to establish the stereochemistry of the anomeric proton.

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