CIRCULAR DICHROISM OF ACETYLATED METHYL GLYCOSIDES

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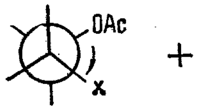
The circular dichroism (CD) spectra of a number of acetylated methyl glycosides, from mono- to tetra-O-acetates, have been obtained. The signs of the CD maxima of the n-π^* transitions (210-215 nm) of the O-acetate groups have been predicted, and these predictions coincide with the figures obtained experimentally.

Lipid A from the cell walls of Gram-negative bacteria contains ester groupings $-O-CO-R$ together with amide groupings NHCO [1]. These ester groupings are weak chromophores with n$-\pi^*$-electronic transitions in the 210-215 nm region [2], overlapping with the n$-\pi^*$ transition of the amide chromophore [3]. Consequently, it appeared of interest, before passing to a study of the circular dichroism (CD) spectrum of lipid A, to investigate the CD spectra of model compounds including such ester groupings. In the present work we consider the CD and UV-absorption spectra of methyl L-arabinopyranoside, methyl D-lyxopyranoside, L-rhamnopyranoside, D-xylopyranoside, D-glucopyranoside, D-galactopyranoside, and D-mannopyranoside with different numbers of O-acetate groups.

The positions and amplitudes of the CD maxima for the O-acetates of methyl glycosides investigated are given in Table 1. The majority of compounds each has a CD maximum in the 210-215 nm region. No Cotton effect (CE) was found for methyl 3-O-acetyl-2,4-di-O-methyl-β-D-xylopyranoside. As an example, Figure 1 shows the CD spectra (curves 1) and UV absorption spectra (curves 2) of methyl 2,3,4-tri-O-acetyl-β-D-xylopyranoside (a) and methyl 2,3,4-tri-O-acetyl-β-L-rhamnopyranoside (b) in methanol. The maxima in the CD and UV-absorption spectra in the 210-215 nm region are due to the n$-\pi^*$transition of the O-acetate group [2]. In the UV spectra the band of the n$-\pi^*$ transition appears in the form of a shoulder on the band of the $\pi-\pi^*$ transition, the maximum of which is beyond the limit of accessibility of nonvacuum spectrophotometers (below 180 nm). The CD spectra of all the compounds investigated have a point of intersection with the axis of abscissas at about 190 nm, which shows a difference in the signs of the bands of the n$-\pi^*$ and $\pi-\pi^*$ transitions in methanol. The same relationship of the signs of the CD bands of n$-\pi^*$ and $\pi-\pi^*$ transitions has been observed previously for the amide chromophore [3].

On the basis of an analysis of the CD spectra of the mono- and di-O-acetates of methyl glycosides, Borén et al. [4] obtained an empirical dependence of the signs of a CE of a chromophore on the dihedral angle between the O-acetate and a neighboring oxygen atom [4]. It was found that fragment (1) of a Newman projection gave a CE with a positive sign and fragment (2) one with a negative sign:



(1)

(2)

where X = $-O-$, $-OH$, $-OMe$, $-OAc$, $-CH_2OH$, $-CH_2OAc$.

Furthermore, it was suggested that the magnitude of the influence of the X grouping on the observed CE decreases in the sequence $CH_2OH \geq CH_2OAc \gg -O- > OH > OMe > OAc$.

We have used this relationship to analyze the CD spectra of methyl glycosides differing from those investigated by Borén et al. both in structure and in the number of O-acetate groups. Table 1 gives, together with the measured signs of the CD bands of the n$-\pi^*$ transitions of the acetylated methyl glycosides, those predicted

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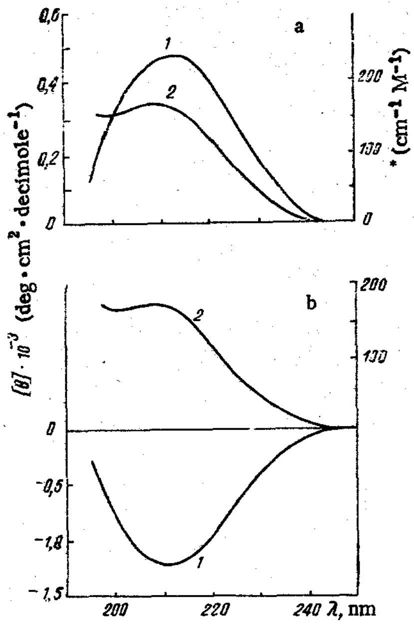

Fig. 1. CD spectra (1) and UV absorption spectra (2) of methyl 2,3,4-tri-O-acetyl-β-D-xylopyranoside (a) and methyl 2,3,4-tri-O-acetyl-β-L-rhamnopyranoside (b) in methanol.

TABLE 1. Positions and Amplitudes of the CD Maxima of a Number of Acetylated Methyl Glycosides

Compound	λ_{max}, nm	$[\Theta]^0$	Predicted sign
Methyl 3-O-acetyl-2,4-di-O-methyl-β-D-xylopyranoside	None		None
Methyl 4-O-acetyl-2,3-di-O-methyl-β-D-xylopyranoside	212	+2080	+
Methyl 2,3-di-O-acetyl-4-O-methyl-β-D-xylopyranoside	206	+180	+
Methyl 2,4-di-O-acetyl-3-O-methyl-β-D-xylopyranoside	214	+580	+
Methyl 3,4-di-O-acetyl-2-O-methyl-α-L-rhamnopyranoside	220	-340	-
Methyl 2,3,4-tri-O-acetyl-α-D-xylopyranoside	213	-330	-
Methyl 2,3,4-tri-O-acetyl-β-D-xylopyranoside	212	+480	+
Methyl-2,3,4-tri-O-acetyl-α-D-lyxopyranoside	212	+2310	+
Methyl 2,3,4-tri-O-acetyl-α-L-rhamnopyranoside	212	-1200	-
Methyl 2,3,4-tri-O-acetyl-β-L-rhamnopyranoside	212	-1220	-
Methyl 2,3,4-tri-O-acetyl-β-L-arabinopyranoside	213	-2600	-
Methyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside	210	-3600	-
Methyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside	212	-2560	-
Methyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside	215	-440	+
Methyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranoside	212	-4050	-

in accordance with the rules of Borén et al. As can be seen, for the majority of compounds investigated the predicted sign coincides with that found experimentally. Thus, for methyl 3-O-acetyl-2,4-di-O-methyl-β-D-xylopyranoside the absence of a CE was predicted, which agrees with our findings.

For the tetra-O-acetates, the sign of the CE due to the influence of the CH_2OAc group on the 4-O-acetate group must correspond to the observed sign of the CD maximum, since according to Borén's rules the influence of a CH_2OAc group on a O-acetate chromophore is much greater than the influence of the other groups. But for the 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside the CH_2OAc group would give a positive sign; however, we have recorded a negative CD maximum for this compound. This discrepancy between the predicted and observed signs of the CE requires further investigation. It must be mentioned that a similar discrepancy was found by Borén et al. for methyl 2,6-di-O-acetyl-β-D-galactopyranoside [4].

EXPERIMENTAL

Samples of acetylated methyl glycosides were synthesized methods described previously [5]. UV absorption spectra were recorded on a Beckman Acta MVI spectrophotometer in the 200-250 nm interval. CD spectra were recorded on a Jobin Yvon Dichrographe III instrument in the same spectral interval. Spectrally pure

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*As in Russian original — Publisher.

methanol was used as the solvent, the concentration of the solutions being 1-2 mg/ml. The amplitudes of the CD maxima given in Table 1 are expressed in units of molecular ellipticity, deg $\cdot$cm$^2\cdot$decimole^{-1}.

SUMMARY

The methyl glycoside O-acetates investigated have in the CD spectra the band of an $n-\pi^*$ transition at about 210-215 nm, the sign of which is determined in accordance with the rules of Borén et al., and the band of a $\pi-\pi^*$ transition below 190 nm opposite in sign to the former.

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BIOSYNTHESIS OF THE ALKALOIDS OF *Anabasis aphylla*

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The dynamics of the accumulation of free amino acids and the main alkaloids have been determined, and 15 free amino acids have been detected and identified, 11 having been determined quantitatively. The amounts of the main alkaloids have also been determined. An interrelationship of the amino acid lysine with the alkaloids has been shown. The interconversion of pachycarpine into aphylline and aphyllidine with the formation of a lactam group has been demonstrated experimentally.

We have previously published a series of papers on the study of the biosynthesis of the alkaloids of *Anabasis aphylla* L. [1-3]. In the present paper we considered the interrelationship between the amino acid metabolism and the biosynthesis of the alkaloids, and also the last stage in the biosynthesis of the alkaloids of *A. aphylla* aphylline and aphyllidine, i.e., the possibility of the formation of these alkaloids by the oxidation of pachycarpine with the production of a lactam group.

We studied the dynamics of the accumulation of amino acids and alkaloids in plants of the third year of vegetation over a space of six months (from May to October). The plants were obtained from the Zonal Experimental Station of VILR [All-Union Scientific Institute of Medicinal Plants], Bugun' region, Chimkent province. The free amino acids and alkaloids were extracted by a known method [4, 5] from the freshly collected material.

The results obtained (Tables 1 and 2) show that the total amount of alkaloids in the epigeal parts of the plant gradually increase, reaching a maximum in August, and then fall (Table 2). In the hypogeal organs, beginning with the period of fruit bearing (August) the total amount of alkaloids increases, reaching 2.0% in October.

The increase in the total amount of alkaloids in the epigeal parts of the plant may be considered as the accumulation of nitrogen necessary for the following vegetation period.

The interconnection between the amounts of free amino acids and of alkaloids can be judged from the following fact: in the period of the vigorous synthesis of alkaloids in August, the total amount of free amino acids in the epigeal parts falls sharply. This is possibly connected with the synthesis of alkaloids and the accumulation of proteins in the seeds.

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