

# Optical rotatory dispersion studies. IX.\*

## 2,3-Unsaturated esters of aldonic acids

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Ultraviolet, ORD, and CD spectra of 2,3-unsaturated aldonic acids having *D-arabino*, *L-arabino*, *D-ribo*, *D-xylo*, *D-erythro*, and *D-threo* configuration were recorded. The signs of Cotton effects in the 250 and 210 nm region were found to be in relation with the configuration of the adjacent chiral centre. Compounds under study with a *4R* configuration reveal positive Cotton effects in the 210 nm and negative in the 250 nm region, whereas those with *4S* configuration display opposite signs.

Chiroptical technique was shown to be a useful tool when determining the configuration of chiral centres of derivatives of saccharides in acyclic form [2–17].

The absorption band of the carboxy group appears up to 200–210 nm due to a strong electron-donating hydroxy group [18]. The extension of the  $\pi$  system of the carbonyl

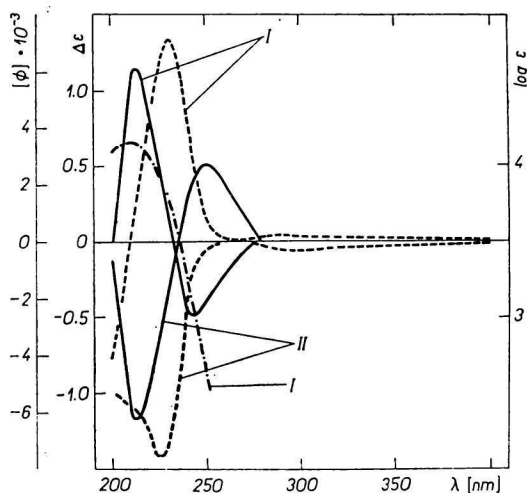


Fig. 1. Ultraviolet, ORD, and CD spectra.  
ethyl *trans*-2,3-dehydro-2,3-dideoxy-*D*-arabinoheptonate (I); ethyl *trans*-2,3-dehydro-  
-2,3-dideoxy-*L*-arabinoheptonate (II).  
- . . . . UV curve; - - - - ORD curves; ——— CD curves.

\* For Part VIII see Ref. [1].

by conjugation over the  $\alpha,\beta$ -unsaturated double bond results in a bathochromic shift of the  $n-\pi^*$  band, which is, however, smaller than that of the first  $\pi-\pi^*$  band what frequently deteriorates the reading. Crotonic acid and its anion are reported [19] to have a shoulder of little intensity ( $\log \epsilon \sim 2.10$ ) at 250 nm associated with the  $n-\pi^*$  transition of this system.

Ultraviolet, ORD, and CD data of unsaturated esters of aldonic acids are listed in Table 1. As seen, the column for UV data comprises only absorption bands of quite large intensity ( $\log \epsilon \sim 4.0$ ) associated with the  $\pi-\pi^*$  transition in the 208 to 212 nm region. The Cotton effect in the long wave (255 to 275 nm) region due to  $n-\pi^*$  transition is little pronounced. Its first extrema lie either at the positive (substances

Table 1  
Ultraviolet, ORD, and CD data

No.	UV			ORD		CD	
	C*-4	$\lambda$	( $\log \epsilon$ )		$\lambda$ ( $[\Phi]$ ) · 10 <sup>-2</sup>	$\lambda$	( $\Delta\epsilon$ )
I	R	212	(4.14)	400	(+1.0)		
				290	(+2.0)		
				265	(+0.8) min	243	(-0.51)
				230	(+71.4) max	213	(+1.29)
				200	(-40.8)		
II	S	212	(4.13)	400	(-0.7)		
				290	(-2.1)		
				260	(0.0) max	250	(+0.52)
				225	(-69.0) min	213	(-1.37)
				200	(-50.0)		
III	S	210	(3.98)	400	(-2.6)		
				280	(-10.4)		
				260	(-9.4) max		
				230	(-37.5) min		
				208	(-78.0) max		
				200	(-19.3)		
IV	S	208	(4.00)	400	(-1.8)		
				275	(-4.6) sh	243	(+0.25)
				225	(-55.4) min	215	(-2.40)
				200	(+55.4)		
V	S	209	(3.98)	400	(-0.9)		
				280	(-18.0)		
				255	(-12.1) max	247	(+0.31)
				225	(-72.1) min	215	(-4.04)
				200	(+9.0)		
VI	R	210	(4.02)	400	(+0.5)		
				300	(+1.2)		
				275	(+1.0) min		
				250	(+8.0) sh	247	(-0.31)
				225	(+68.8) max	212	(+2.02)
				200	(-53.6)		

sh — shoulder.

*I* and *VI*), or negative (substances *II–V*) rotation background. Their second extrema coalesce with the first extremum of the Cotton effect in the short-wave region (225 to 230 nm) (Fig. 1). Compounds *I* and *VI* having the 4*R* configuration in the neighbourhood of the chromophore display a negative, whilst substances *II–V* with the 4*S* configuration a positive Cotton effect at this transition. The second Cotton effect due to  $\pi-\pi^*$  transition in the 210 nm region is of opposite sign, *i.e.* compounds *I* and *VI* have a positive, *II–V* a negative Cotton effect. The second extrema of this more intense transition have not been observed with the exception of ethyl *trans*-2,3-dehydro-2,3-dideoxy-D-riboheptonate (*III*).

The CD curves, on the other hand, evidently indicate the presence of both dichroic bands of quite different intensity. The first dichroic band associated with  $n-\pi^*$  transition, which lies in the 243 to 250 nm region is little intensive ( $\Delta\epsilon < 0.5$ ), whereas that of the  $\pi-\pi^*$  transition in the 212–215 nm region is much more intensive ( $\Delta\epsilon = 1.3-4.0$ ). The ORD curves show the presence of the above-mentioned transitions either by a sole or a common extremum, the CD bands unambiguously revealing two optically active transitions.

Although no absorption bands in the  $n-\pi^*$  transition region have been observed, ORD and especially CD bands indicate this transition. It has been found that there exists a relationship between the configuration at the chiral centre nearest to the chromophore and the sign of the Cotton effect. Other chiral centres are of negligible effect on the sign.

### Experimental

The unsaturated esters of aldonic acids were synthesized according to Kochetkov, their physicochemical constants being in accord with those reported [20]. Esters *IV* to *VI* are new compounds (Table 2); their purity was checked by means of paper chromatography in the solvent system *n*-butanol–acetic acid–water 4 : 2 : 1 and by elemental analysis.

For  $C_9H_{16}O_6$  (*IV*; 220.22) calculated: 49.09% C, 7.32% H; found: 48.99% C, 7.32% H.

For  $C_8H_{14}O_5$  (*V*; 190.19) calculated: 50.51% C, 7.41% H; found: 50.48% C, 7.40% H.

Table 2

Characteristic data of the compounds studied

No.	Ethyl <i>trans</i> -2,3-dehydro- -2,3-dideoxy-	Physical constants
<i>I</i>	-D-arabinoheptonate	M.p. 132–135°C [ $\alpha$ ] <sub>D</sub> <sup>25</sup> +13.8° (c 1)
<i>II</i>	-L-arabinoheptonate	M.p. 133–135°C [ $\alpha$ ] <sub>D</sub> <sup>25</sup> –13.4° (c 1.32)
<i>III</i>	-D-riboheptonate	Sirup [ $\alpha$ ] <sub>D</sub> <sup>25</sup> –18.5° (c 2.1 CH <sub>3</sub> COOH)
<i>IV</i>	-D-xyloheptonate	Sirup [ $\alpha$ ] <sub>D</sub> <sup>25</sup> –16.4° (c 2.0)
<i>V</i>	-D-erythrohexonate	Sirup [ $\alpha$ ] <sub>D</sub> <sup>25</sup> –26.1° (c 2.15)
<i>VI</i>	-D-threohexonate	Sirup [ $\alpha$ ] <sub>D</sub> <sup>25</sup> +5.6° (c 2.0)

For  $C_8H_{14}O_5$  (VI; 190.19) calculated: 50.51% C, 7.41% H; found: 50.49% C, 7.40% H.

Ultraviolet, ORD, and CD spectra were taken with a JASCO ORD/UV-5 spectropolarimeter provided with a CD adapter in the 400–200 nm range in 10 to 0.5-mm cells at room temperature. The concentration of samples was 0.88 to 1.0 mg/ml (ethanol). Under 210 nm the samples were measured in a nitrogen atmosphere.

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