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Note

Isomerisation, with allylic rearrangement, of hex-2-enopyranoside 4-xanthate esters*

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In previous reports, we have described thermal allylic-rearrangement reactions undergone by 2,3-dideoxy-hex-2-enopyranosides possessing azidodeoxy-[2], deoxythiocyanato-[2], and vinyl ether[3] functions at C-4 Suprafacial [3,3]-sigmatropic rearrangements led stereospecifically to 3,4-dideoxy-hex-3-enopyranosides with azidodeoxy-, deoxyisothiocyanato-, and deoxy-*C*-formylmethyl groups at C-2, respectively The 2,3-unsaturated starting materials with the *threo* configuration, *i e*, those possessing *quasi*-axial migrating groups, reacted uniformly faster than the *erythro* analogues By this means, *N*-bonded functional groups, which were convertible into biochemically important *N*-acetylamino-groups, and 2-carbon branch-chains could be introduced at C-2 We now report an analogous introduction of a sulphur-bonded group at this position

Allylic thionoacyl esters[4], thionocarbonates[7], and (alkylthio)thionocarbonyl esters (xanthates)[6] would be expected to permit transmission of oxygen-bonded functionality from C-4 of hex-2-enopyranoside derivatives to sulphur-bonded functionality at C-2 of hex-3-enopyranosyl analogues, and the last type of derivative has been taken to exemplify this principle

The dixanthates **1** and **2** were prepared from ethyl 2,3-dideoxy-α-D-*erythro*- and -*threo*-hex-2-enopyranoside, respectively, and on heating in solution they gave *erythro*- and *threo*-3,4-unsaturated-2-(methylthio)carbonylthio compounds **3** and **4**, respectively, as main products The allylic, secondary ester protons (H-2) in compounds **3** and **4** resonated at substantially higher fields than did the corresponding allylic protons (H-4) of the starting materials (Table I), which indicates that (methylthio)thiocarbonyl to (methylthio)carbonylthio group rearrangement had occurred[7] The occurrence of allylic rearrangements is established by the finding in the mass

*Unsaturated Carbohydrates Part XIX[1]

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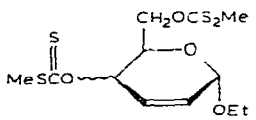
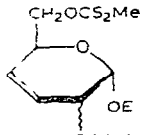
spectrum of compound **1** of an ion with *m/e* 204 derived by retrodienic loss of the C-5,C-6 fragment OHC CH_2OCS_2Me, and in the spectrum of the rearranged product **3** an ion with *m/e* 280 derived by analogous loss of ethyl formate[8] Important confirmatory evidence was obtained from the $J_{1,2}$ values[2] (Table I), and the finding that the signs of the optical rotations of the products were opposite to those of the corresponding starting esters[2 3]



1 2



3 4

1 3 D-*erythro*-isomers 2,4 D-*threo*- somers

TABLE I

N M R DATA FOR COMPOUNDS **1–4**

Compound	*Chemical shifts (δ, $CHCl_3$)*						*Coupling constant $J_{1,2}$ (Hz)*
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6,6′*	
1	5 08	5 99	5 99	6 25	4 5	4 7	1 5
2	5 20	6 25	6 25	6 02	4 82	4 7	2 5
3	5 00	4 6	5 75	5 75	4 6	4 7	3 5
4	5 05	4 22	6 00	6 00	4 73	4 7	<1

Whereas the *threo*-product **4** appeared to be formed specifically, a second compound accompanied **3** in the products of thermolysis of the *erythro*-dixanthate (**1**) By elemental analysis, it was concluded to have lost carbon oxysulphide, as xanthates are known to do[9], because an S_Ni loss of this kind would be expected to occur with retention of configuration, and because the product had the opposite sign of rotation from compound **1**, it is believed to have a 3,4-dideoxy-2-thio-D-*erythro*-hex-3-enopyranoside structure. As the H-6,6′ resonances were 0 88 p p m upfield relative to those of the starting material, it was concluded that the primary ester had also undergone change The compound was not further investigated

EXPERIMENTAL

Ethyl 2,3-dideoxy-4,6-di-O-[(methylthio)thiocarbonyl]-α-D-erythro-hex-2-enopyranoside (**1**). — Ethyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside[10] (2 0 g) was heated in toluene (15 ml) at 40° for 6 h in the presence of sodium powder (1 5 g) Diethyl ether (100 ml) was then added and the mixture was heated under reflux for a

further 1 h After cooling, the ether suspension was decanted, carbon disulphide (20 ml) was added, and heating under reflux was continued for 6 h and then for a further 2 h after methyl iodide (20 ml) had been added Removal of the precipitated sodium iodide and the solvent gave a yellow syrup which, after chromatography on a column of silica gel, afforded the syrupy diester **1** (2 0 g, 50%), $[\alpha]_D$ +146° (*c* 1, chloroform) The n m r spectrum was consistent with the assigned structure

Anal Calc for $C_{12}H_{18}O_4S_4$ C, 40 7, H, 5 1, S, 36 2 Found C, 41 7, H, 5 1, S, 36 3

*Ethyl 3,4-dideoxy-2-*S-[*(methylthio)carbonyl*]-*6-*O-[*(methylthio)thiocarbonyl*]-*2-thio-α-*D-erythro-*hex-3-enopyranoside* (**3**) — The dixanthate **1** (0 2 g) was heated at 140° for 2 h in *N,N*-dimethylformamide to give two products (t l c analysis) which were separated on a column of silica gel The more mobile component, crystallised from ethanol, was **3** (75 mg, 37%), m p 65°, $[\alpha]_D$ −100° (*c* 1, chloroform)

Anal Found C, 40 6, H, 5 1, S 35 7

The less mobile fraction (50 mg, 25%) did not crystallise and had $[\alpha]_D$ −130° (*c* 1, chloroform)

Anal Calc for $C_{11}H_{18}O_3S_3$ C, 45 0, H, 6 1 S, 32 7% Found C, 45 6, H, 6 3, S, 30 0

*Ethyl 2,3-dideoxy-*4,6-*di-*O-[*(methylthio)thiocarbonyl*]-α-D-threo-*hex-2-enopyranoside* (**2**) — The *threo*-diol[11] (0 2 g, prepared from the 6-benzoate[3]) was converted, as described above for **1**, into the dixanthate **2** (0 32 g, 80%), which was isolated directly It had m p 57–58°, $[\alpha]_D$ −202° (*c* 1, chloroform)

Anal Calc for $C_{12}H_{18}O_4S_4$ C, 40 7 H, 5 1, S, 36 2 Found C, 40 6, H, 4 9, S, 35 9

*Ethyl 3,4-dideoxy-2-*S-[*(methylthio)carbonyl*]-6-O-[*(methylthio)thiocarbonyl*]-*2-thio-α-*D-threo-*hex-3-enopyranoside* (**4**) — The *threo*-dixanthate (0 1 g) was heated in toluene (5 ml) at 100° for 1 h, after which no change could be detected by t l c However, on removal of the solvent, a syrup was obtained which was shown by n m r spectroscopy to be the pure, rearranged ester **4**, $[\alpha]_D$ +50° (*c* 1, chloroform)

Anal Found C, 40 8, H, 5 0, S 35 9

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