Note

Ultraviolet absorption maxima of sugars containing a thiocarbonyl group

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Thiocarbonyl derivatives of sugars have received considerable attention, particularly during the past few years. Certain of these derivatives are useful as intermediates to unsaturated sugars and nucleosides[1-4], deoxy sugars[5], and deoxy thio sugars[6,7]. They also are useful in structural studies of carbohydrates as demonstrated by their n.m.r.[8,9] and o.r.d.[2,10] spectra.

We have prepared various thiocarbonyl derivatives of carbohydrates and have studied subsequent reactions which these derivatives undergo. In the course of this work, u.v. spectroscopy has been an indispensable tool.

In this report we give examples of u.v.-spectroscopic studies of thiocarbonyl derivatives and tabulate u.v. absorption maxima covering various classes of thiocarbonyl sugars. Most maxima have been reported earlier (see references in Table I). Various aspects of the ultraviolet absorption of the thiocarbonyl groups have been discussed[11].

A. Qualitative analysis. — Compounds containing different thiocarbonyl functions can be distinguished qualitatively on the basis of their u.v. absorptions (Table I). *O,S*-Dithiocarbonate esters prepared from xanthate salts often contain trithiocarbonate esters. The latter may be separated from the former by solid–liquid chromatography, and the fractions containing trithiocarbonate ester (λ_{max} 310 nm) may be distinguished from those containing *O,S*-dithiocarbonate (λ_{max} 280–285 nm).

Thiocarbonyl-containing sugars may be detected on t.l.c. plates sprayed with a fluorescent dye (Rhodamine 6G) by using a u.v. lamp. The sugars appear as dark spots or zones where the light absorption due to the thiocarbonyl function quenches the fluorescence. Sugars containing dithiobis(thioformate) groups adjacent to hydroxyl groups decompose in the presence of pyridine to the parent sugar and a thionocarbonate[13]. The dithiobis(thioformate) and thionocarbonate, but not the parent sugar, are detected under u.v. light. All three, however, are detected upon charring.

B. Course of reactions. Reactions can be monitored by following the appearance, disappearance, or shift of characteristic u.v. maxima. Xanthation of an unknown sugar may be followed by the appearance of a maximum near 303 nm[24]. This is soon accompanied by a shoulder near 340 nm due to a trithiocarbonate salt. The xanthate may be purified by gradual acidification of the mixture to the point of disappearance

TABLE I

MAJOR[a] U.V. ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS OF VARIOUS THIOCARBONYL-CONTAINING STRUCTURES

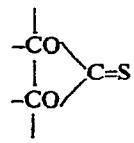
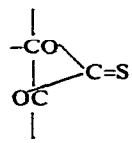
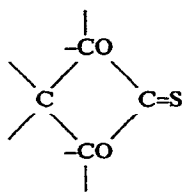
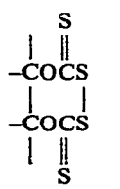
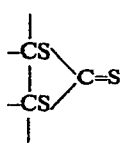
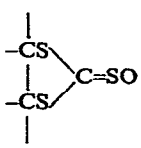
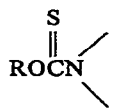
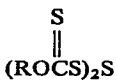
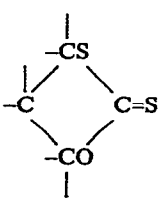
Compounds	*Structures*	λ_{max} *nm*(ε)[b]	*References*
1–6		230 (8,100–9,200)	12
7		237 (7,600)	12
8–12		234–6 (15,700–15,900)	13, 14
13, 14		235–8 (14,500–16,700)	13, 15
15		245 (13,600)	7
16–20		230–40 (15,800–18,900) 280–90 (6,600–8,900)	13-19
21		240–4 (19,900) 293–6 (8,120)	20
22–24		315–6 (11,000–15,000)	16, 17, 19
25–27		282–3 (4,400–5,100) 347–8 (10,100–10,600)	19

TABLE I *continued*

Compounds	*Structures*	λ_{max} *nm* (ε)[b]	*References*
28–31		244–53 (11,000–16,500)	21, 22
32, 33		250 (7,000)	23
34[c]		222–7 (4,000–7,000) 303–5 (6,000–10,000)	24
35		230 (9,600) 300 (6,800)	25
36, 37		228 (10,500) 298 (5,150)	25
38, 39		240 (8,300) 310 (11,500)	22, 26
40		277 (11,200)	22
41		220 (7,000) 270 (10,000)	26
42,43[d]		221–4 (7,700–7,900) 280–2 (11,700–12,400)	18,20
44,45		212–21 (11,200–13,000) 281–6 (9,350–11,900)	24
46		224–6/5,240 295–7/12,700	20

[a] $\varepsilon > 1{,}000$. [b] Recorded by Perkin–Elmer* Model 202 spectrophotometer in 1-cm quartz cells with ethanol as solvent. [c] In water. [d] In methanol.

*The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

Key to compounds in Table I:

1, Bis(methyl 4,6-*O*-benzylidene-α-D-glucopyranoside) 2,3-thionocarbonate
2, 3-*O*-Butoxythiocarbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose
3, 6-*O*-Ethoxythiocarbonyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose
4, 3-*O*-Ethoxythiocarbonyl-1,2-*O*-isopropylidene-α-D-glucofuranose
5, Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 3(or 2)-methoxythiocarbonate
6, Methyl 4,6-*O*-benzylidene-3-*O*-benzyloxythiocarbonyl-α-D-glucopyranoside
7, 1,2:5,6-Di-*O*-isopropylidene-3-*O*-phenoxythiocarbonyl-α-D-glucofuranose
8, 1,2-*O*-Isopropylidene-α-D-glucofuranose 5,6-thionocarbonate
9, 3-*O*-(3,5-Dinitrobenzoyl)-1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-thionocarbonate
10, 3,4-*O*-Isopropylidene-D-mannitol 1,2-thionocarbonate
11, Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside 2,3-thionocarbonate
12, Methyl 5-*O*-benzyl-D-ribofuranoside 2,3-thionocarbonate
13, 1,2:5,6-Di-*O*-isopropylidene-D-mannitol 3,4-thionocarbonate
14, Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate
15, Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-thionocarbonate
16, Bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-[dithiobis(thioformate)]
17, Bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) 3,3′-[dithiobis(thioformate)]
18, Bis(methyl 4,6-benzylidene-α-D-glucopyranoside) 2,2′-[dithiobis(thioformate)]
19, Bis(2,3:5,6-di-*O*-isopropylidene-D-mannofuranose) 1,1′-[dithiobis(thioformate)]
20, Bis(2,3:5,6-di-*O*-isopropylidene-D-mannitol) 1,1′-[dithiobis(thioformate)]
21, Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-[dithiobis(thioformate)]
22, 1,2-*O*-Isopropylidene-5,6-dithio-β-L-idofuranose 5,6-trithiocarbonate
23, 3-*O*-Acetyl-1,2-*O*-isopropylidene-5,6-dithio-β-L-idofuranose 5,6-trithiocarbonate
24, 1,2-*O*-Isopropylidene-5,6-dithio-3-*O*-(*p*-tolylsulfonyl)-β-L-idofuranose 5,6-trithiocarbonate
25, 1,2-*O*-Isopropylidene-5,6-dithio-β-L-idofuranose oxythiocarbonyl-5,6-trithiocarbonate
26, 3-*O*-Acetyl-1,2-*O*-isopropylidene-5,6-dithio-β-L-idofuranose oxythiocarbonyl-5,6-trithiocarbonate
27, 1,2-*O*-Isopropylidene-5,6-dithio-3-*O*-(α-tolylsulfonyl)-β-L-idofuranose oxythiocarbonyl-5,6-trithiocarbonate
28, Methyl 2-*O*-aminothiocarbonyl-4,6-*O*-benzylidene-α-D-glucopyranoside
29, Methyl 4,6-*O*-benzylidene-2-*O*-piperidinothiocarbonyl-α-D-glucopyranoside
30, Methyl 4,6-*O*-benzylidene-2-*O*-glycinothiocarbonyl-α-D-glucopyranoside
31, 3-*O*-Diethylaminothiocarbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose
32, 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose 3-chlorothioformate
33, 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose 6-chlorothioformate
34, Methyl 2-*O*-(3-*O*- and 6-*O*-) S-sodium thiolthiocarbonyl-α-D-glucopyranoside
35, 6-*O*[Hydroxythio(thiocarbonyl)]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose
36, 1,2:3,4-Di-*O*-isopropylidene-6-*O*-[methoxythio(thiocarbonyl)]-α-D-galactopyranose

37, 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[methoxythio(thiocarbonyl)]-α-D-glucofuranose
38, Bis(1,2:5,6-di-*O*-isopropylidene-3-*O*-thiocarbonyl-α-D-glucofuranose) monosulfide
39, Bis(1,2:3,4-di-*O*-isopropylidene-6-*O*-thiocarbonyl-α-D-galactopyranose) monosulfide
40, 3-*O*-Carbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 1,2:5,6-di-*O*-isopropylidene-3-*O*-thiocarbonyl-α-D-glucofuranose monosulfide
41, 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose 6-*O*-[thio(thiocarbonyl)] dimethyl phosphonate
42, Methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside methyl 2′,3′,4′-tri-*O*-methyl-6-thio-α-D-glucopyranoside 6,6′-dithiocarbonate
43, 2,3:5,6-Di-*O*-isopropylidene-1-*O*-[methylthio(thiocarbonyl)]-D-mannofuranose
44, Methyl 6-*O*-[benzylthio(thiocarbonyl)]-α-D-glucopyranoside
45, Methyl 2-*O*-[benzylthio(thiocarbonyl)]-α-D-glucopyranoside
46, Methyl 2,3-di-*O*-methyl-6-thio-α-D-glucopyranoside 4,6-dithiocarbonate

of this shoulder. When a cyclic trithiocarbonate is oxidized with chlorine, the corresponding 5,6-*S*,*S*-dithiocarbonate results[16], and the reaction can be monitored by the disappearance of the 315 nm maximum. When a xanthate salt is converted into an ester, a shift from 303 to 280–285 nm can be observed[27], and acidification with strong acid decomposes the residual xanthate to the parent alcohol.

C. Quantitative measurements. — Concentrations of thiocarbonyl derivatives separated chromatographically can be determined quantitatively when the extinction coefficient at a particular maximum is known. When methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate is treated with various nucleophiles, mixtures of 2-*O*- and 3-*O*- open chain derivatives are obtained[21]. When these isomers are separated by t.l.c. and eluted, their ratio may be determined from the u.v. spectra of the eluates.

Several thiocarbonyl components in a mixture may be determined when the extinction coefficients of each compound at several wavelengths are known. Xanthate and byproduct sulfur compounds in viscose have been determined by this method[28].

D. Chromophoric equivalent weights. — If a general value for the extinction coefficient of a particular thiocarbonyl chromophore is known, this value may be used to estimate the equivalent weight from the absorbance of a solution containing a known weight of compound. For example, xanthation of the 4- and 6-positions of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside followed by treatment with iodine and then pyridine gives a crystalline product that shows characteristic absorptions for dithiobis(thioformate)[20]. The known ε values of such derivatives make it possible to calculate the equivalent weight of the crystalline product [dithiobis(thioformate):glucoside 1:1]. When the parent glucoside is monoxanthated and treated with iodine, an amorphous product results that also shows absorptions for this group [dithiobis(thioformate):glucoside 1:2].

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