The Estimation of the Thioethoxyl Group of a Sugar Diethylmercaptal

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In the course of our investigation on the mercaptolysis[1,2] of a polysaccharide, it has become necessary to estimate the thioethoxyl group of a sugar diethylmercaptal. This group has been usually estimated by the conversion to a sulfate group by the nitric acid oxidation according to the Carius' method. But the Carius' method is somewhat time-consuming, and in addition, it can not be applied to the mercaptolysates of such polysaccharides as those of sea weeds, which contain the sulfate group in their molecules. The present paper offers a convenient method, by which the direct estimation of the thioethoxyl group of a sugar diethylmercaptal and its acetylated and methylated derivatives has been made without any possibility of the interference of the originally present sulfate group.

The method involves the acid hydrolysis[3] of the mercaptal followed by the distillation and the subsequent iodometrical titration of the liberated ethylmercaptan, as shown by the equations (1) and (2)[4].

$$R-CH(SC_2H_5)_2+H_2O=R-CHO+2C_2H_5SH \quad (1)$$

$$2C_2H_5SH+I_2=C_2H_5-S-S-C_2H_5+2HI \quad (2)$$

Experimental

Materials.—Sugar diethylmercaptals and their derivatives used in this study were prepared according to original papers. Melting point or boiling point of each compound used is included in Tables I and II.

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[1] C. Araki and S. Hirase, This Bulletin, **26**, 463 (1953).

[2] S. Hirase and C. Araki, This Bulletin, **27**, 109 (1954).

[3] E. Fischer, *Ber.*, **27**, 673 (1894).

[4] P. Klason and J. Carlson, *Ber.*, **39**, 738 (1906); J. W. Kimball, R. L. Kramer and E. E. Reid. *J. Am. Chem. Soc.*, **43**, 1199 (1921).

Apparatus and General Procedure.—The apparatus (Fig. 1) was essentially the same as that used for the estimation of the ordinary methoxyl or ethoxyl group. The trap (B) was charged with distilled water (about 20 cc.), to keep any hydrolysing agent from getting into the receiver. The receiver (C) and the sub-receiver (D), in which the reaction shown by the equation (2) occurred, were charged with an excess 0.1N-potassium iodide-iodine solution (20 cc. and 5 cc., respectively), and equal volumes of ethanol were respectively added to each receiver to increase the solubility of ethylmercaptan. An exactly weighed sample (0.1~0.2 g.) to be analysed was placed in the reaction flask (A), and hydrolysing agent, aqueous N-hydrochloric acid (10 cc.) was added.

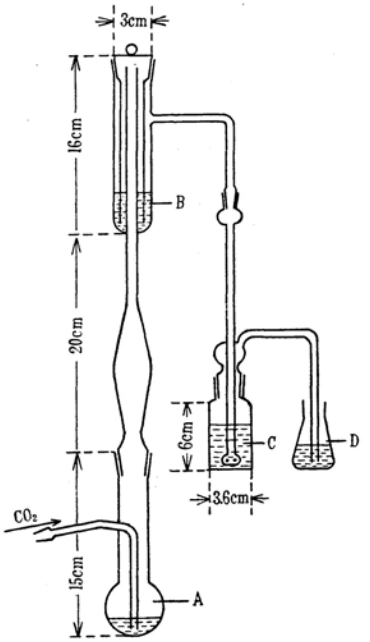

Fig. 1. The apparatus for the thioethoxyl estimation.

Then the apparatus was immediately assembled as shown in Fig. 1, all ground joints being moistened with distilled water. A slow stream of carbon dioxide free from any hydrogen sulfide was bubbled through the solution at a rate of about two bubbles a second. The reaction flask was gradually heated in a glycerol bath during thirty minutes to a gentle boiling (bath temperature 115~120°C). After keeping a gentle boiling for two hours, the excess iodine remaining in the receiver and the sub-receiver was individually titrated with a 0.1N-sodium thiosulfite solution without using a starch indicator, which is no use in the high concentration of ethanol. In most cases ethylmercaptan was perfectly absorbed in the receiver C. The quantity of the thioethoxyl group was calculated from the iodine consumed: SC_2H_5 g. = 0.06113 × 0.1N-I_2 cc. consumed.

Results

Sugar Diethylmercaptals.—The analysis of several sugar diethylmercaptals, carried out by the above method, gave satisfactory results as shown in Table I. Considerable literature[5] has recorded the difficult hydrolytic cleavage of the carbon-sulfur bonds of mercaptals. This may be due to the incomplete elimination of the liberated ethylmercaptan by distillation[6].

TABLE I

THE ESTIMATION OF THIOETHOXYL GROUPS OF SUGAR DIETHYLMERCAPTAL

Diethylmer-captal of	Sample g.	0.1N-I_2cc. consumed	SC_2H_5% found	Error
D-Galactose[3]	0.1394	9.75	42.75	+0.06
[141~143°]	0.1384	9.71	42.89	+0.20
	0.1293	9.07	42.88	+0.19
D-Glucose[3]	0.1471	10.30	42.80	+0.11
[127~128°]	0.1246	8.70	42.68	−0.01
	0.1247	8.73	42.79	+0.10
D-Mannose[3]	0.1207	8.42	42.64	−0.05
[131~133°]	0.1776	12.32	42.41	−0.28
	0.1338	9.31	42.53	−0.16
L-Arabinose[3]	0.1377	10.69	47.46	−0.18
[124~126°]	0.1165	9.10	47.75	+0.11
	0.1300	10.10	47.49	−0.15
L-Rhamnose[3]	0.1173	8.68	45.23	+0.02
[135~137°]	0.1184	8.80	45.43	+0.22
	0.1421	10.57	45.47	+0.26
3, 6-Anhydro-	0.1557	11.65	45.74	+0.19
L-galactose[1]	0.1046	7.83	45.76	+0.21
[110~111°]	0.1378	10.29	45.65	+0.10
Agarobiose[2]	0.1234	5.75	28.49	+0.09
[171~172°]	0.1517	7.01	28.25	−0.14
	0.1524	7.04	28.24	−0.15

[ ]: m.p. of the sample used for the analysis.

Acetylated and Methylated Sugar Diethylmercaptals.—Pentaacetyl and pentamethyl D-galactose diethylmercaptal were tentatively analysed by the same method as above mentioned, but analytical figures obtained were 14.7% and 30.6% (theoretical values 24.6% and 34.3%) respectively. This may be attributed to the low solubility of the sample in the hydrolysing agent, and to the resistance of

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[5] E. Stuffer. *Ber.*, **23**, 3241 (1890); E. Fisher and K. Delbrück, *Ber.*, **42**, 1476 (1909); W. Schneider, J. Sepp and O. Stiehler, *Ber.*, **51**, 220 (1918); E. Pacsu, *Ber.*, **58**. 509 (1925).

[6] D. S. Tarbell and D. P. Harnish, *Chem.*, *Rev.*, **49**, 1~90 (1951).

TABLE II
THE ESTIMATION OF THIOETHOXYL GROUPS OF FULLY ACETYLATED AND METHYLATED SUGAR DIETHYLMERCAPTALS

Diethylmercaptal of	Sample g.	0.1N-I_2 cc. consumed	SC_2H_5% found	Error
Pentaacetyl	0.1404	5.63	24.51	−0.10
D-galactose⁽⁷⁾	0.1505	6.01	24.41	−0.20
[77∼79°]	0.1446	5.80	24.53	−0.10
Pentaacetyl	0.1326	5.30	24.45	−0.16
D-glucose[8]	0.1148	4.61	24.55	−0.06
[46∼48°]	0.1774	7.07	24.36	−0.25
Tetraacetyl	0.1324	6.18	28.53	−0.26
L-arabinose[9]	0.1608	7.54	28.66	−0.13
[78∼80°]	0.1473	6.89	28.59	−0.20
Pentamethyl	0.2022	11.30	34.16	−0.11
D-galactose[10]	0.1591	8.93	34.31	+0.04
(175∼180°/4mm.)	0.1187	6.62	34.09	−0.18
Pentamethyl	0.1368	7.65	34.18	−0.09
D-glucose[10]	0.1421	7.95	34.20	−0.07
(175∼180°/4mm.)	0.1244	6.94	34.10	−0.17
Hexaacetyl	0.1258	3.71	18.03	+0.09
agarobiose[2]	0.1456	4.42	18.01	+0.07
[101∼103.5°]	0.1361	4.04	18.15	+0.21

[ ]: m.p., ( ): b.p. of the sample used for the analysis.

the sample against hydrolysis. These difficulties, however, have been overcome by putting glacial acetic acid (2 cc.) into the hydrolysing agent to increase the solubility and prolonging the heating period up to four hours. The analysis by this modified method gave good results as shown in Table II.

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[7] M. L. Wolfrom, *J. Am. Chem. Soc.*, 52, 2464 (1930).

[8] M. L. Wolfrom, *J. Am. Chem. Soc.*, 51, 2188 (1929).

[9] M. L. Wolfrom and M. R. Newlin, *J. Am. Chem. Soc.*, 52, 3619 (1930).

[10] P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, 69, 175 (1926).