SOME XANTHATE METHYL ESTERS OF GLUCOSE[1]

By Amiya K. Sanyal[2] and C. B. Purves

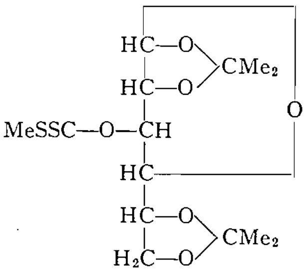
ABSTRACT

The following compounds were thought to be new: 1,2-mono-*O*-isopropylidene-D-glucofuranose-3-*S*-methyl xanthate, m.p. 102°, $[\alpha]_D^{24}$ −27.8°; methyl-4,6-*O*-benzylidene-α-D-glucopyranoside-2,3-di-*S*-methyl xanthate, m.p. 100°, $[\alpha]_D^{22}$ −18.1°; and 1,2;3,5-di-*O*-methylene-α-D-glucofuranose-6-*S*-methyl xanthate, m.p. 99°, $[\alpha]_D^{21}$ +27.3° in chloroform. Partial hydrolysis of the isopropylidene and methylene derivatives yielded some glucose-3-*S*-methyl xanthate and glucose-6-*S*-methyl xanthate as crude sirups. The 6-xanthate greatly excelled the 3-xanthate in stability toward acid. The chromatographic behavior of both was determined.

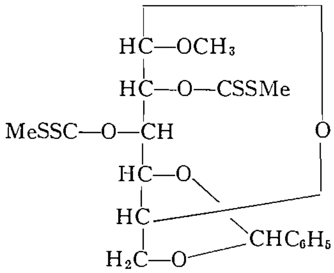
INTRODUCTION

Although xanthate salts are very readily decomposed by acid, a recent research (20) confirmed the claim that the *S*-methyl xanthate esters of simple alcohols are often remarkably stable in acidic conditions. The location of the substituents in cellulose sodium xanthates (viscose) might therefore be determined by conversion to the *S*-methyl esters, hydrolysis to the corresponding glucose derivatives, and identification of the latter. In order to explore this possibility, attempts have now been made to prepare some of the relevant glucose-*S*-methyl xanthates, to determine their stability toward acids and their behavior in chromatography.

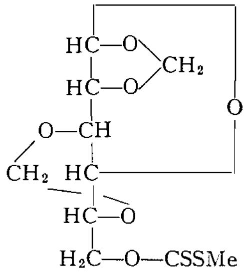
In 1927 Freudenberg and Wolf (4) shook 3-sodio-1,2;4,5-di-*O*-isopropylidene glucofuranose first with carbon disulphide to form the 3-xanthate salt, and then with methyl iodide to obtain the crystalline 3-*S*-methyl ester (I). They apparently did not succeed in selectively hydrolyzing the isopropylidene groups and therefore recovered neither glucose-3-*S*-methyl xanthate nor its monoisopropylidene derivative. A repetition of this work showed that the yield of I could be increased from 52% to nearly 90% of theory, based on the



I



II



III

---

[1] *Manuscript received December 9, 1955.*
Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and from the Wood Chemistry Division, Pulp and Paper Research Institute of Canada, Montreal, Que. Abstracted from a Ph.D. thesis submitted to the University by A.K.S. in August, 1953.

[2] *Present address: 12/1/4 Monoharpukar Road, Calcutta-26, India.*

diisopropylidene glucose that reacted. The substance (I) was then submitted to acetolysis in an attempt to replace the isopropylidene by acetyl groups, as Hann, Hudson, and their numerous collaborators succeeded in doing with similar cyclic acetals (6, 13, 22). Although analyses suggested that some of the isopropylidene had indeed been replaced by acetyl groups, the impure product failed to crystallize, and eventually the method was abandoned. The diisopropylidene methyl xanthate was then hydrolyzed with concentrated nitric acid in ethyl acetate as described by Coles, Goodhue, and Hixon (2) for the removal of the 5,6-isopropylidene group from 1,2;5,6-di-*O*-isopropylidene glucofuranose, but some xanthate groups were lost and the product was an impure sirup. The realization that this xanthate ester was not nearly so resistant toward acidic reagents as those studied by Vincent (20) led to an attempt to prepare a more stable derivative by oxidizing I with 30% aqueous hydrogen peroxide in glacial acetic acid. Unlike Vincent's experience with octadecyl-*S*-methyl xanthate, this oxidation failed to yield a stable crystalline derivative retaining all of the original sulphur, but produced extensive decomposition. Details of these and other negative experiments have been omitted from this account.

Freudenberg, Dürr, and Hochstetter (3) found that boiling methanolic hydrogen chloride removed the isopropylidene group in the 5,6-position of diisopropylidene glucose 40 times more rapidly than the one in the 1,2-position. By restricting the action of a 0.15% hydrogen chloride solution to eight minutes, it was found possible to prepare a pure, crystalline mono-*O*-isopropylidene glucose-3-*S*-methyl xanthate from the diisopropylidene derivative in about 35% yield, 30% of the starting material being recovered unchanged. When chromatographed on paper, using *n*-butanol saturated with water as the solvent and ammoniacal silver nitrate as the spray, the mono- and diisopropylidene methyl xanthates had R_f values of 0.92 and 0.97, respectively. The former compound produced a yellow spot with the spray immediately, but the latter developed a dark gray spot only after the paper had been heated at 100° for a few minutes. The two compounds could therefore be distinguished readily.

In order to study the hydrolysis of the monoisopropylidene methyl xanthate, a 2% solution in 0.05 *N* aqueous hydrochloric acid was boiled under reflux and the change in optical rotation was observed at intervals. After 105 min. the xanthate group was obviously decomposing but the specific rotation of 22.5° was not far from the value of 13° roughly estimated for glucose-3-*S*-methyl xanthate from the molecular rotations of its monoisopropylidene derivative, of 1,2-*O*-isopropylidene glucose, and of glucose, in water or alcohol. The crude product when chromatographed yielded faint spots corresponding to glucose (R_f 0.20), to the isopropylidene methyl xanthate (R_f 0.92), and to an unknown substance. The major spot, with R_f 0.65, was attributed to the desired glucose-3-*S*-methyl xanthate. This compound partly decomposed when an attempt was made to free it from the associated glucose by a fermentation with yeast (16). A product whose purity was estimated from its sulphur content to be about 90% resulted when monoisopropylidene glucose methyl xanthate was boiled for two hours in 50% methanol containing 1% of sulphuric acid, which was then neutralized with barium carbonate. Some of the starting material, 54%, was recovered unchanged, and the crude glucose-3-*S*-methyl xanthate was isolated by evaporating the frozen aqueous liquor. The most satisfactory method of preparing glucose-3-*S*-methyl xanthate proved to be the partial hydrolysis of the more accessible diisopropylidene compound (I) in hot 80% acetic acid, which was used by Ness, Hann, and Hudson (12) in a similar case. Although 55% of the monoisopropylidene derivative was recovered, it was easy to eliminate the acetic acid and to purify the glucose-3-*S*-methyl xanthate by chromatography on a cellulose column. The product gave only a single spot of R_f 0.65 when chromatographed on paper, but nevertheless persisted as an uncrystallized, light yellow oil containing somewhat less than the calculated amount of sulphur.

The xanthation of methyl-4,6-*O*-benzylidene-α-D-glucoside was next undertaken. Although attempts to prepare the intermediate 2,3-di-sodio derivative with sodium in liquid ammonia according to Muskat (11) were not successful, the derivative apparently formed in high yield when a solution of the benzylidene compound in dioxane was mixed with a colloidal suspension of sodium in toluene. The subsequent addition of carbon disulphide to the suspension, followed still later by the addition of methyl iodide, produced crude, crystalline methyl 4,6-*O*-benzylidene-α-D-glucopyranoside-2,3-di-*S*-methyl xanthate (II) in about 70% yield. All attempts to remove the benzylidene group, or the benzylidene and methyl glucosidic groups, selectively led to yellow, evil-smelling oils containing less sulphur than the amounts expected for glucose-2,3-di-*S*-methyl xanthate or for the corresponding methyl glucoside. No single substance could be detected in these oils by the chromatographic methods used, and the attempt to prepare glucose-2,3-di-*S*-methyl xanthate was abandoned owing to the instability of the xanthate ester groups.

The most suitable compound from which to attempt a synthesis of glucose-6-*S*-methyl xanthate appeared to be the di-*O*-methylene glucose-6-acetate synthesized by Hough, Jones, and Magson (7), which was characterized as the 1,2;3,5-di-*O*-acetal by Schmidt, Distelmaier, and Reinhard (17) and later by Shyluk, Honeyman, and Timell (18). The replacement of the *O*-acetyl group by a sodium atom proceeded smoothly in alcoholic sodium hydroxide, and subsequent treatments with carbon disulphide and with methyl iodide produced the new, crystalline 1,2;3,5-di-*O*-methylene glucofuranose-6-*S*-methyl xanthate (III) in 84% yield. This compound was difficult to hydrolyze and the methylene and xanthate ester groups appeared to be removed at roughly the same rate. The most economic procedure found for the preparation of glucose-6-*S*-methyl xanthate was to boil a solution of the dimethylene derivative in 6% aqueous-alcoholic sulphuric acid for about three hours; about 80% of the starting material was recovered and recycled, and the hydrolyzates were accumulated. When these hydrolyzates were chromatographed on a cellulose column, a substance was isolated which had a single R_f value of 0.84 in the system used, and a sulphur content close to that required by glucose-6-*S*-methyl xanthate (S, 23.7%). All attempts to crystallize the product, or its tetraacetate, failed. In addition to glucose (R_f 0.13) the hydrolyzate contained a minor amount of a sirup containing 9.2% of sulphur and with an R_f value of 0.70. This sirup was presumably a decomposition product of the methyl xanthate, because the product from a similar hydrolysis prolonged for 68 hr., when chromatographed on paper, yielded the spot expected for glucose, and others with R_f values of 0.30, 0.56, and 0.70, the one at R_f 0.84 being absent.

Ness, Hann, and Hudson (13) showed that acetolysis replaced the methylene acetal rings in a trimethylene mannitol with acetyl and acetoxymethyl groups, while Lieser and Leckzyck (10) found that acetolysis at 0° did not affect a xanthate group. By combining the techniques used in these researches, it proved possible to cleave di-*O*-methylene-glucose-6-acetate to a presumed tri-*O*-acetyl-di-*O*-acetoxymethyl derivative and to deacetylate the latter to glucose. A repetition of the work with the xanthate ester (III) produced a sirup with the composition of a diacetyl diacetoxymethyl glucose methyl xanthate, but attempts to deacylate this substance, even with very mild conditions, resulted in some dexanthation. According to a paper chromatogram, the product contained a little glucose, much of the 6-*S*-methyl xanthate of R_f 0.84, and a little of the related substance of R_f 0.70.

The *S*-methyl xanthates (I), (II), and (III) were also hydrolyzed with cold concentrated hydrochloric acid in conditions suitable for the complete hydrolysis of a cellulose-*S*-methyl xanthate to the corresponding glucose derivatives. As expected, the 3-*S*-methyl xanthate group in (I) was completely removed and nothing but glucose was detected in the product; no substance was recognized in the hydrolyzate of the 2,3-di-*S*-methyl xanthate (II), but the 6-*S*-methyl xanthate (III) yielded 70% of a sirup containing glucose, glucose-6-*S*-methyl xanthate (R_f 0.84), and the derived substance of R_f 0.70. These experiments confirmed the observation that an *S*-methyl xanthate group located in the sixth position of glucose was much more stable toward acid than were those in the second and third positions.

EXPERIMENTAL

Analytical

Sulphur was determined according to Waters (21) by oxidizing 0.05 to 0.1 gm. samples with bromine – nitric acid and estimating the resulting sulphuric acid as the barium salt. Microdeterminations on 1–5 mgm. samples containing 10–20% sulphur were fairly accurate when the Grote combustion to sulphur dioxide was used, as described by Sundberg and Royer (19). The dioxide was oxidized by 3% aqueous hydrogen peroxide to sulphuric acid, which was increased in amount by the addition of exactly 10 ml. of 0.01 *N* acid before being titrated to exactly pH 5.5 with 0.004 *N* sodium hydroxide. The determination of acetyl groups by saponification (9) was inaccurate in presence of *S*-methyl xanthates, but Clark's saponification followed by steam-distillation (1) gave good results. The almost complete failure of the *S*-methyl xanthate group to yield methyl iodide (20) in a customary determination of alkoxyl groups (15) was confirmed.

Techniques used in paper chromatography were based on the description given by Partridge (14), butanol saturated with water being the solvent and ammoniacal silver nitrate usually being the spray.

*1,2;5,6-Di-O-isopropylidene-*D*-glucofuranose-3-S-methyl Xanthate (I)*

The 1,2;5,6-di-*O*-isopropylidene glucofuranose was prepared from glucose, acetone, anhydrous zinc chloride, and phosphoric acid as described by Glen, Myers, and Grant (5). After several recrystallizations, the melting point and specific rotation in water attained the correct values of 112–113° and $[\alpha]_D^{20}$ $-18.8°$ (*c*, 2.04), respectively.

An excess of sodium in the form of thin plates was added in nine installments during 24 hr. to a solution of 50 gm. of diisopropylidene glucose in 200 ml. of dry ether kept under reflux on a steam bath. The ether solution was decanted and the residual sodium was washed three times with ether. The solution and washings containing the sodio-derivative were combined, cooled, mixed with 50 ml. of carbon disulphide, and kept at room temperature for 12 hr. The ether layer containing any unchanged diacetone glucose was then decanted, and the residual semisolid, cream-colored mass of crude xanthate salt was mixed with 15 ml. of pure methyl iodide. After being vigorously shaken at intervals during an hour to disintegrate the mass, the suspension was kept near 20° for six hours and was then filtered. The combined filtrate and washings were evaporated under nitrogen, and the solid residue was distilled at 150–160° and 0.6–0.7 mm. pressure. When a solution of the yellow distillate in ether was allowed to evaporate slowly, 61 gm. of crystals melting at 57–60° separated. This yield of the *S*-methyl xanthate amounted to 90% of theory, instead of 52% as reported by Freudenberg and Wolf (4). After recrystallization from petroleum ether the substance had the correct sulphur content, melted at 58–60°, and had a specific levo rotation of $[\alpha]_D^{22} -15.5°$ in chloroform (*c*, 2.00). The recorded values (4) were m.p. 61° and $[\alpha]_{5460}^{16}$ $-14.6°$ in acetylene tetrachloride.

One gram of the crystalline methyl xanthate dissolved within five minutes when shaken at room temperature with 50 ml. of 37% hydrochloric acid. After six hours, when the solution had become dark red and developed an unpleasant odor, an equal volume of water was added. Six days later, and after further dilution with water, the acid was neutralized with basic lead carbonate and evaporated to dryness under diminished pressure. Extraction of the residue with five 25 ml. volumes of ethanol removed 0.5 gm. of a red sirup, which when chromatographed on paper gave a single spot corresponding to glucose.

*Mono-O-isopropylidene-*D*-glucofuranose-3-S-methyl Xanthate*

(*a*) A solution of 135 gm. of the diisopropylidene derivative in 140 ml. of absolute methanol containing 0.15% of anhydrous hydrogen chloride was heated under reflux for eight minutes. The solution was cooled, neutralized with basic lead carbonate, and filtered, lead being later removed as the sulphide from the filtrate. After being evaporated near 20° and under reduced pressure, the clear liquor left a residue which partly crystallized within two days. This residue was dissolved in hot ligroin (b.p. 80–110°) and the solution on cooling deposited 46 gm. (38.5%) of the product, m.p. 94–98°. Approximately 45 gm. (30%) of the unchanged diisopropylidene methyl xanthate was recovered from the mother liquor. A 3.3 gm. sample of the mono derivative when thrice recrystallized from 200 to 300 ml. of hot ligroin yielded 2 gm. of pure material melting at 101–102.5°. The specific levorotation was $[\alpha]_D^{24}$ $-27.8°$ in chloroform (*c*, 2.00). Found: C, 42.5, 42.5; H, 5.9, 6.0; S, 20.7, 21.0%. Calc. for $C_{11}H_{18}O_6S_2$: C, 42.6; H, 5.8; S, 20.6%.

When a similar methanolysis of the diisopropylidene derivative was continued for about one hour, a 60–70% yield by weight was obtained of a white, evil-smelling, amorphous material which became liquid and discolored when exposed to the air. The substance was insoluble in ether but soluble in methanol. Found: S, 20.1; OCH_3, 2.8, 2.2%. The low value for apparent methoxyl made the formation of any methyl glycoside very doubtful.

Some of the crystalline monoisopropylidene glucose-*S*-methyl xanthate, 0.5 gm., was dissolved in 25 ml. of 0.05 *N* hydrochloric acid in aqueous ethanol (1 vol.: 1 vol.). Since the optical rotation as observed in a 2 dm. tube did not change within 12 hr. at room temperature, the solution was heated under reflux on a steam bath. After 0, 15, 30, 60, 75, and 105 min. the observed rotations corresponded to specific rotations of −27.5°, −12.5°, −3.8°, +5.0°, +7.5°, and +22.5°. The xanthate ester group was then decomposing, to judge from the odor and turbidity of the solution. The removal of hydrochloric acid from this solution by silver carbonate caused immediate blackening even at room temperature, and the use of Amberlite IR-4B anion exchange resin also removed half of the sulphur. The odor of mercaptan was strong when this resin was regenerated, first with alkali and then with acid. Basic lead carbonate was finally adopted as the neutralizing agent because no blackening occurred unless the solution was warmed. The lead was later removed as the sulphide, the clear filtrate was extracted with chloroform to recover most of the residual monoisopropylidene-glucose-*S*-methyl xanthate, and the aqueous phase was chromatographed on paper with the results already discussed.

(*b*) Following the method described by Ness, Hann, and Hudson (12), 2 gm. of diisopropylidene glucose-3-*S*-methyl xanthate was dissolved in 50 ml. of 80% acetic acid. The solution was heated under reflux for 30 min. in an oil bath kept at 120°, and was then evaporated to a sirup under reduced pressure. This sirup was extracted with 30 ml. of chloroform, and the dried extract on evaporation yielded 1.1 gm. (55%) of material which solidified on being stirred with ligroin. The solid, m.p. 75–88°, was shown by chromatographic methods to be the monoisopropylidene methyl xanthate contaminated with a small amount of the diisopropylidene derivative. The portion, 0.4 gm., of the above sirup which was insoluble in chloroform was saved (see below).

Glucose-3-S-methyl Xanthate

A solution of the above 0.4 gm. of sirup in 25 ml. of acetone was filtered, and a portion of the clear filtrate was chromatographed on paper. A small amount of glucose appeared to be present, together with a large amount of the compound supposed to be glucose-3-*S*-methyl xanthate and a trace of a third substance of intermediate R_f value. An accumulation of 4.5 gm. of the sirup from several hydrolyses, and which had an average sulphur content of 20.45%, was then purified by passage through a cellulose column. The column was eluted with 1200 ml. of *n*-butanol saturated with water, and the eluate was collected in 21 fractions. Fractions Nos. 11 to 17 inclusive gave only one spot with an R_f value of 0.65 on a paper chromatogram. These fractions when combined and evaporated yielded 3 gm. of glucose-3-*S*-methyl xanthate as a light yellow sirup. Found: S, 20.1, 20.2%. Calc. for $C_8H_{14}O_6S_2$: S, 23.7%. The compound was not quite pure, and repeated attempts to crystallize it failed.

Methyl-4,6-O-benzylidene-α-D-glucopyranoside-2,3-di-S-methyl Xanthate

α-Methyl-D-glucoside and benzaldehyde were heated together as described by Irvine and Scott (8), and the resulting benzylidene derivative melted correctly at 163–164°. Eight grams of sodium, colloidally dispersed in 50% concentration in toluene, was added to a solution containing 8 gm. of methyl-4,6-benzylidene-α-D-glucoside in 50 ml. of dry, pure dioxane. The replacement of the dioxane by 800 ml. of dry benzene, or of the sodium by alcoholic sodium methylate followed by evaporation, was not successful. After being cooled in order to moderate the initial evolution of hydrogen, the suspension was kept warm on a steam bath for three hours, when a further 2 gm. of the dispersed sodium was added and heating was continued for eight hours. The suspension was then cooled, well mixed with 25 ml. of carbon disulphide, and kept overnight at room temperature to form the sodium xanthate. Methyl iodide, 9 ml., was added and after being kept for seven hours at room temperature the suspension was filtered free of sodium salts. The latter were washed three times with dry benzene, after which the filtrate and washings were evaporated under diminished pressure, finally in a desiccator. The red, viscous residue soon crystallized, yielding 9.2 gm. (72%) of crude methyl-4,6-*O*-benzylidene-α-D-glucoside-2,3-di-*S*-methyl xanthate melting at 65–84°. Two recrystallizations from 75% ethanol, followed by an extraction with ligroin and a recrystallization from 80% ethanol, left 4 gm. of the product as pure white crystals melting at 99–100.5°. The substance had a specific rotation of $[\alpha]_D^{22}$ $-18.1°$ in chloroform (*c*, 1.66). Found: C, 46.9, 47.3; H, 4.7, 5.0; S, 27.3, 27.4%. Calc. for $C_{18}H_{22}O_6S_4$: C, 46.8; H, 4.8; S, 27.7%.

When chromatographed on paper, the dixanthate ester formed an intense spot near the solvent front. The parent substance, methyl benzylidene glucoside, left no record on this chromatogram. A 0.5 gm. sample of the dixanthate ester was then hydrolyzed with concentrated hydrochloric acid as described for the diisopropylidene glucose 3-*S*-methyl xanthate, and 0.23 gm. of an amorphous solid was recovered. Found: S, 10.3, 9.9%. When aniline phthalate was the spray, this solid produced no spot on a paper chromatogram, and presumably contained no glucose. Another hydrolysis involved heating a solution of 1 gm. of the dixanthate ester in a mixture of ethanol, 160 ml., water, 30 ml., and concentrated sulphuric acid, 6 ml., under reflux on the steam bath for two hours. After neutralization to pH 6 and complete evaporation, the liquor yielded salts and 0.3 gm. of a yellow sirup soluble in chloroform. Found: S, 16.0, 16.1%. This sirup when chromatographed on paper gave one spot of R_f 0.87, ammoniacal silver nitrate being the spray. No spot was developed with an aniline phthalate spray, as was the case when substituted glucose-3 and 6-*S*-methyl xanthates were hydrolyzed.

1,2;3,5-Di-O-methylene-α-D-glucofuranose-6-S-methyl Xanthate

The procedure of Hough, Jones, and Magson (7) was used to prepare the corresponding 6-acetate from glucose, 162 gm., paraformaldehyde, 165 gm., glacial acetic acid, 500 ml., and concentrated sulphuric acid, 75 ml. The crude, partly crystallized product, 83 gm. (37%), on recrystallization from methanol yielded 32 gm. of pure material melting correctly at 103–105°.

Five grams of sodium hydroxide, 25 gm. of the bismethylene-6-*O*-acetylglucose, and 50 ml. of absolute ethanol were shaken together until the bismethylene derivative went completely into solution owing to deacetylation. Water, 10–15 ml., was then added to dissolve the residual sodium hydroxide and two hours later the yellow solution was evaporated to dryness *in vacuo*, finally by the addition and evaporation of 25 ml. of benzene. The bismethylene glucose was extracted from this residue by dry benzene, 100 ml., boiling under reflux, and after the extract had cooled it was mixed with an excess of sodium colloidally dispersed in 25 ml. of dry benzene. After the initial reaction had subsided, 2 gm. of sodium dispersed in toluene was added, together with 25 ml. of benzene. The mixture was kept next day near 75° for four hours, cooled, and shaken with 25 ml. of carbon disulphide. The following day, when the formation of the sodium xanthate was judged to be complete, 30 ml. of methyl iodide was added to the suspension. After being shaken occasionally during a few hours, the suspension was filtered and the residual salts were washed three times with 25 ml. volumes of benzene. Evaporation of the filtrate and washings yielded 32 gm. (108%) of crude product melting at 77–88°, increased to 97–99° by recrystallization from 500 ml. of 70% ethanol followed by extraction with low-boiling ligroin. The yield of pure white needles was 25.1 gm., or 84%, and the specific rotation, $[\alpha]_D^{21}$ +27.3° in chloroform (*c*, 2.15). Found: C, 40.8, 41.1; H, 5.0, 5.1; S, 21.3, 21.7%. Calc. for $C_{10}H_{14}O_6S_2$: C, 40.8; H, 4.8; S, 21.8%.

A 1-gm. sample was hydrolyzed in concentrated hydrochloric acid as described for the diisopropylidene-3-*S*-methyl xanthate. A residue, 0.1 gm., (m.p. 81–92°) failed to dissolve within six hours and was removed. The cream-colored solution was then diluted with an equal volume of water and kept for six days, when the color had deepened only to light yellow. After being neutralized, this solution was evaporated to dryness, and an alcoholic extract of the residue yielded 0.7 gm. of a yellow sirup when evaporated in a desiccator. A portion of this sirup when chromatographed on paper, using an aniline phthalate spray, yielded a faint spot corresponding to glucose, and two major spots (R_f 0.84 and 0.70, see below) corresponding to glucose-6-*S*-methyl xanthate.

Glucose-6-S-methyl Xanthate

One gram of the pure bismethylene derivative was boiled under reflux after solution in 150 ml. of a mixture made up from absolute ethanol, 160 ml., water, 30 ml., and concentrated sulphuric acid, 6 ml. Although some of the xanthate survived when the solution was boiled for 68 hr., more was hydrolyzed to glucose or was decomposed, and the time was restricted to 165 min. The solution was evaporated near 35° to 10 ml., and was diluted with 100 ml. of water to precipitate 0.8 gm. of unchanged bismethylene derivative (m.p. 91–96°). After neutralization with barium carbonate and filtration, the filtrate on evaporation yielded 0.15 gm. (17%) of a sirup. An accumulation of such sirups from several hydrolyses was extracted with acetone, and 2 gm. of an oil was recovered from the extract. This oil was eluted from a cellulose column with a total of 1400 ml. of *n*-butanol saturated with water. Of the 34 fractions of eluate collected, Nos. 2 to 8 inclusive yielded a single spot of R_f 0.84 when chromatographed on paper, with ammoniacal silver nitrate as the spray. When these fractions were combined and evaporated, 1.1 gm. of crude glucose-6-*S*-methyl xanthate remained as a yellow sirup which could not be crystallized. Found: S, 20.7, 21.4%. Calc. for $C_8H_{14}O_6S_2$: S, 23.7%. Fractions Nos. 22 to 26 inclusive when chromatographed on paper each yielded a single spot of R_f 0.71; these fractions together gave 70 mgm. of a sirup whose nature was not determined. Found: S, 9.1, 9.3%.

The supposed glucose-6-*S*-methyl xanthate, 0.65 gm. (R_f 0.84), was acetylated with 20 ml. of acetic anhydride containing 0.4 gm. of anhydrous zinc chloride for 24 hr. at room temperature. The solution was poured into ice and water, the mixture was neutralized and extracted with ether. Evaporation of the extract left a yellow sirup which was dried in a vacuum desiccator over phosphorus pentoxide. Yield 0.9 gm. or 85%. Found: S, 12.2, 12.5; acetyl, 38.0, 38.1%. Calc. for 1,2,3,4-tetra-*O*-acetyl glucopyranose-6-*S*-methyl xanthate: $C_{16}H_{22}O_{10}S_2$: S, 14.6; acetyl, 39.3%.

Acetolysis of Bismethylene-glucose-6-S-methyl Xanthate

Anhydrous zinc chloride, 0.1 gm., was added to a solution of 1 gm. of the pure xanthate ester in 5 ml. of acetic anhydride. The mixture was warmed on a steam bath and shaken occasionally until the zinc chloride completely dissolved. After being left at room temperature for 16 hr., the product was precipitated by pouring the solution into ice and water. A yellow sirup, presumably a diacetyl diacetoxymethyl glucose-6-*S*-methyl xanthate, was obtained. Yield 1.6 gm. or 90%. Found: C, 42.9, 42.9; H, 5.0, 5.2; S, 12.7, 12.0%. Calc. for $C_{18}H_{26}O_{12}S_2$: C, 43.4; H, 5.2; S, 12.8%.

In order to deacetylate the above product, an accumulation of 5.2 gm. was dissolved in 100 ml. of absolute methanol, and a total of 2 ml. of 1.5 *N* barium methylate in methanol was added at intervals to maintain the pH between 7.0 and 7.5 for four days (23). The pH was then adjusted to 5.5 with dilute sulphuric acid, and the filtrate from the precipitated barium sulphate was cautiously evaporated to a sirup weighing 2.2 gm. (70%). The pungent smell of formaldehyde was evident during this evaporation. A paper chromatogram of this sirup showed that it contained a little glucose, while an intense spot at R_f 0.84 and a light one at R_f 0.70 suggested the presence of much glucose-

6-S-methyl xanthate. Aniline phthalate was the spray. No recognizable product was obtained when the deacetylation was carried out by Kunz and Hudson's method (9) employing 0.1 *N* sodium hydroxide in aqueous acetone at −10°.

ACKNOWLEDGMENTS

One of us (A.K.S.) wishes to thank the Visking Corporation, Chicago, for the Fellowship, and the Pulp and Paper Research Institute of Canada for the summer stipend, which enabled him to take part in the research. Both authors thank the National Distillers Chemical Company, Cincinnati, Ohio, for the gift of the sodium dispersed in toluene.

REFERENCES

1. Clark, E. P. Ind. Eng. Chem. Anal. Ed. 8: 487. 1936.
2. Coles, H. W., Goodhue, L. D., and Hixon, R. M. J. Am. Chem. Soc. 51: 519. 1929.
3. Freudenberg, K., Dürr, W., and Hochstetter, H. v. Ber. 61: 1735. 1928.
4. Freudenberg, K. and Wolf, A. Ber. 60: 232. 1927.
5. Glen, W. L., Myers, G. S., and Grant, G. A. J. Chem. Soc. 2568. 1951.
6. Hann, R. M., Haskins, W. T., and Hudson, C. S. J. Am. Chem. Soc. 64: 1614. 1942.
7. Hough, L., Jones, J. K. N., and Magson, M. S. J. Chem. Soc. 1525. 1952.
8. Irvine, J. C. and Scott, J. P. J. Chem. Soc. 103: 575. 1913.
9. Kunz, A. and Hudson, C. S. J. Am. Chem. Soc. 48: 1978. 1926.
10. Lieser, T. and Leckzyck, E. Ann. 519: 279. 1935.
11. Muskat, I. E. J. Am. Chem. Soc. 56: 2449. 1934.
12. Ness, A. T., Hann, R. M., and Hudson, C. S. J. Am. Chem. Soc. 64: 982. 1942.
13. Ness, A. T., Hann, R. M., and Hudson, C. S. J. Am. Chem. Soc. 65: 2215. 1943.
14. Partridge, S. M. Nature, 158: 270. 1946.
15. Peniston, Q. P. and Hibbert, H. Paper Trade J. 109 (No. 17): 46. Oct. 26, 1939.
16. Purves, C. B. and Hudson, C. S. J. Am. Chem. Soc. 56: 708. 1934.
17. Schmidt, O. T., Distelmaier, A., and Reinhard, H. Ber. 86: 741. 1953.
18. Shyluk, W. P., Honeyman, J., and Timell, T. E. Can. J. Chem. 33: 1202. 1955.
19. Sundberg, O. E. and Royer, G. L. Anal. Chem. 24: 907. 1952.
20. Vincent, D. L. and Purves, C. B. Unpublished.
21. Waters, C. E. Ind. Eng. Chem. 12: 482. 1920.
22. Wolfe, J. K., Hann, R. M., and Hudson, C. S. J. Am. Chem. Soc. 64: 1493. 1942.
23. Zemplén, G. and Pacsu, E. Ber. 62: 1613. 1929.