form 85% of the 2,3-dimethylmethylglucoside was obtained in the chloroform extract. The solubility of the glucoside in chloroform is so marked that we have found extraction by chloroform of an aqueous solution (8–10% concentration) of the crude material a useful method of purification. (These experiments were carried out by Dr. A. C. Waine.)

Summary

The oxidation of 2,3,6-trimethylglucose under various conditions has been studied, with results contrary to the conclusions of Irvine and McGlynn. 2,3,6-Trimethyl-γ-gluconolactone is a crystalline substance the properties of which diverge widely from those ascribed to this lactone by the above authors. It is shown that dimethylmethylglucoside is readily extracted from aqueous solution by chloroform. The bearing of these results on the critical views of Irvine concerning the chemistry of sucrose and other disaccharides is discussed.

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The Preparation of Some Higher Aliphatic Sulfonic Acids

BY C. R. NOLLER AND J. J. GORDON

The work of Reychler[1a] and of McBain and his associates[1b] has shown that cetyl sulfonic acid has unique properties for the investigation of soap solutions, but it has the disadvantage that it is not very soluble in water at temperatures below 50°. Sulfonic acids giving colloidal aqueous solutions but having a lower molecular weight should be more satisfactory but none appear to have been described between C_8 and C_{16}. Accordingly the straight chain aliphatic sulfonic acids containing from nine to fourteen carbon atoms have been prepared in quantity and in a pure state and we wish to report on their preparation at the present time. The work on the physical properties of their solutions will be reported by others at a future date.

The general methods available for preparing aliphatic sulfonic acids in quantity are few in number and in general unsatisfactory. Attempts to prepare esters of sulfonic acids from ethyl chlorosulfonate and alkylmagnesium halides by Mr. Poe Liang in this Laboratory were not successful, nor did the direct oxidation of the disulfides lead to satisfactory results. The method used in the present work has been the nitric acid oxidation of the lead mercaptide, a procedure first described by Williams.[2] In all cases the starting material was the corresponding alcohol.

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(1) (a) Reychler, *Bull. soc. chim. Belg.*, **27**, 110, 217, 300 (1913); (b) Norris, *J. Chem. Soc.*, **121**, 2161 (1922); McBain and Williams, *Colloid Symposium Annual*, **7**, 105 (1929).

(2) Williams, Ph.D. Thesis, Stanford University, 1929. See forthcoming article by McBain and Williams, THIS JOURNAL (1933).

Alcohols.—Nonyl alcohol was prepared by the action of ethylene oxide on heptylmagnesium bromide; decyl, lauryl, and undecylenyl alcohols by the reduction of the methyl esters of the corresponding acids[3] by means of sodium and absolute alcohol;[4] undecyl alcohol by the catalytic reduction of undecylenyl alcohol; tridecyl alcohol by the action of formaldehyde on laurylmagnesium bromide. The alcohols all boiled over less than 3° ranges.

Bromides.—The alcohols were converted into the bromides by the method of Kamm and Marvel[5] in 65 to 80% yields and boiled over a 3° range or less. It appears that two of the bromides have not been previously described. Their physical properties and analyses were as follows: myristyl bromide, b. p. 175–178° at 20 mm.; d_{20}^{20} 0.9322; n_D^{20} 1.4582; Br found, 28.5, calcd. 28.8. Tridecyl bromide, b. p. 164–167° at 23 mm.; d_{20}^{20} 0.9644; n_D^{20} 1.4574; Br found, 29.9, calcd. 30.4.

Mercaptans.—The method used for the preparation of the mercaptans was an adaptation of a procedure for heptyl mercaptan which had been kindly supplied to us by Mr. W. W. Hartman of the Eastman Kodak Company. The general method of preparing mercaptans by the reduction of disulfides with zinc in acid solution was first reported by Friedländer.[6]

In a 3-liter flask was placed 187 g. of sodium sulfide ($Na_2S\cdot 9H_2O$), 700 cc. of water and 32 g. of powdered sulfur and the mixture shaken, with warming on a steam-bath, until a clear solution was obtained. This was diluted with 850 cc. of methyl alcohol, and the flask fitted with a mechanical stirrer, reflux condenser and 500-cc. dropping funnel. The solution was heated to boiling and 1 mole of the alkyl bromide run in rapidly. The reaction does not begin at once but lags from one to four minutes. Heating was stopped during the addition and cautiously resumed a few minutes later. Refluxing and stirring was continued for one hour, after which time the mixture was poured into a beaker containing two or three times its volume of cold water.

After standing overnight the crude dialkyl disulfide was separated and placed with 335 cc. of approximately 50% (1 vol. concn.—2 vol. water) sulfuric acid solution in a 2-liter round-bottomed flask, fitted with a mechanical stirrer and reflux condenser. The mixture was heated to boiling, and 87 g. of zinc dust added in small portions, with the temperature near the boiling point. Then 50 cc. of concentrated sulfuric acid was added in small portions through the condenser, and gentle heating continued for ten minutes. If the heating was continued for a longer period, the reaction became very violent and foamed over. Stirring was continued for one hour, the mixture diluted with an equal volume of cold water and filtered with suction. The mercaptan layer was separated from the filtrate and the zinc residue extracted with two 200-cc. portions of methyl alcohol. The alcohol was distilled, the main portion of mercaptan added to the extracted portion and the whole washed with 150 cc. of hot water, separated and distilled at reduced pressure, from a modified Claisen flask having a 40-cm. fractionating side arm.

The sulfur content is low, indicating the probable presence of the corresponding alcohol since the latter might arise by hydrolysis of the bromide and would be difficult

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(3) Methyl caprate was obtained by the fractionation of the mixed methyl esters from the seed fat of the California bay tree, which unpublished work at this Laboratory has shown to consist of approximately one-third methyl caprate and two-thirds methyl laurate.

(4) One change in the procedure of Ford and Marvel, "Organic Syntheses," 1930, Vol. X, p. 62, for the reduction of esters was made which largely eliminated the formation of emulsions during washing, and foaming during distillation. The crude product was washed once or twice with hot water, which can be done without the formation of emulsions, the water layer separated and the oil placed in a large open beaker. If an emulsion formed during the washing, it was broken by the addition of salt. The oil was then heated in the beaker with stirring to 150–175° until foaming stopped and then transferred while hot to a distilling flask and the distillation carried out without difficulty.

(5) Kamm and Marvel, "Organic Syntheses," Vol. I, 1932, p. 23.

(6) Friedländer, *Ber.*, **39**, 1066 (1906).

TABLE I

MERCAPTANS

	Yield, %	Boiling point, °C.	Pressure, mm.	d^{20}_{20}	n^{20}_{D}	% S Calcd.	Found
Nonyl[a]	80.0	100–104	20	0.8386	1.45197	20.0	19.7
Decyl[b]	81.5	125–127	19	.8410	1.45367	18.4	18.0
Undecyl	76.0	138–141	21	.8432	1.45816	17.0	16.7
Lauryl	81.0	153–155	24	.8450	1.45886	15.8	15.1
Tridecyl	87.5	162–166	22	.8468	1.45906	14.8	14.0
Myristyl	83.5	176–180	22	.8484	1.46005	13.9	12.9

[a] Ellis and Reid, THIS JOURNAL, **54,** 1684 (1932). [b] V. Braun, Teuffert and Weissbach, *Ann.*, **472,** 139 (1929).

to remove by distillation.[7] The mercaptans were free of halogen and sufficiently pure for our purpose since the impurities were removed in the subsequent purification of the lead mercaptide and sulfonate.

Lead Mercaptides and Sulfonates.—A solution of 0.8 mole of the mercaptan in 750 cc. of 95% alcohol was added slowly, with rapid stirring, to a solution of 150 g. of lead acetate in 750 cc. of 50% alcohol. In preparing the solutions of the higher mercaptans, lauryl, tridecyl and myristyl, it was necessary to add a small amount of ether to get the mercaptan entirely into solution. The mercaptide precipitated as a bright orange salt which immediately turned to a light canary yellow color. This was filtered with suction and washed twice with water and once with one liter of acetone and dried. The dry salt was powdered and added, in small portions, to one liter of 50% nitric acid in a 5-liter round-bottomed flask. The mixture was kept well mixed by shaking the flask after adding each portion of salt. It was necessary in some cases to heat the acid slightly after adding the first two or three portions to start the reaction and to prevent a too vigorous reaction due to an accumulation of unreacted mercaptide. A white salt settling to the bottom of the flask and the evolution of copious brown fumes indicate the progress of the reaction. After all the mercaptide had been added the mixture was allowed to stand for one hour with occasional shaking, diluted with 3 liters of cold water and filtered with suction. The salt was washed twice with water, filtered as dry as possible and then extracted with two or more 1500-cc. portions of hot acetone, until no further precipitate could be obtained upon chilling the filtrate in a freezing solution.

TABLE II

LEAD SULFONATES

Mercaptan used	Yield, %	Pb, % Calcd.	Found[b]
Nonyl	16.7[a]	33.3	33.0
Decyl	75.5	31.9	31.5
Undecyl	83.0	30.5	30.4
Lauryl	76.0	29.3	29.4
Tridecyl	58.8	28.2	28.3
Myristyl	68.5	27.2	27.5

[a] The low yield of lead nonylsulfonate appears to be due to its greater solubility in dilute nitric acid. [b] Analyses for lead were by titration with ammonium molybdate solution according to Treadwell-Hall, "Analytical Chemistry," 6th ed., Vol. II, p. 618.

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[7] The method for the analysis of mercaptans of Kimball, Kramer and Reid [THIS JOURNAL, **43,** 1199 (1921)] did not give a satisfactory end-point, probably because the disulfides formed are for the most part insoluble solids which enclose unreacted mercaptan. Since this work was completed Sampey and Reid [*ibid.*, **54,** 3404 (1932)] have applied the iodimetric method to benzene solutions but we have not tried this modification for the higher mercaptans.

On cooling the acetone extracts of the lead sulfonates, a white crystalline product usually separated, which in the case of the lead lauryl sulfonate melted at 45–46°. No attempt was made to identify these impurities.

Sulfonic Acids.—A 6-mm. glass tube drawn out to 1.5 mm. at one end was sealed into the wall of a 500-cc. round-bottomed flask in such a way that the narrow end extended to the bottom of the flask. The flask was connected to a reflux condenser by means of a ground-glass joint. Fifty grams of lead salt and 250 cc. of dry isopropyl alcohol were placed in this flask and well mixed. The suspension was heated to refluxing for twenty to thirty minutes while dry hydrogen chloride was introduced through the small tube. The progress of the reaction was easily followed by the appearance of the salt. The lead sulfonate remained in suspension in the alcohol and was of a lustrous white appearance, whereas the lead chloride was a flat white and settled to the bottom of the flask, leaving a clear solution above it. After complete decomposition the suspension was cooled and the lead chloride filtered onto a sintered glass filter.

The filtrate was transferred to a 750-cc. flask fitted to a distilling bend 22 mm. in diameter with a ground-glass connection. The solvent was evaporated at 3–4 mm. pressure keeping an external bath at 80–90°. It was not possible to remove all of the solvent in this way, but the solutions were evaporated until they became very viscous, or, in some cases, began to crystallize. Then 150 cc. of freshly distilled ether was added and the whole was transferred to a 500-cc. separatory funnel. One hundred and fifty cubic centimeters of water was added and the mixture thoroughly shaken. The ether layer was removed and the water solution was extracted with three 100-cc. portions of ether. The aqueous solution was then drawn from the funnel into an open beaker and evaporated at reduced pressure over calcium chloride. It was necessary to control carefully the pressure, to keep the solution from foaming over the beaker. As the solution became more concentrated it gradually became more viscous until it finally set to a pasty mass of liquid crystal form. It was impossible to dry it further over calcium chloride, so it was transferred to another desiccator over phosphorus pentoxide and the drying was continued at the same pressure. It was necessary to break up lumps of solid matter occasionally during this further drying. The final product was a white crystalline solid, analysis by titration showing it to be a monohydrate of the sulfonic acid. Anhydrous samples for analysis were dried at 3 mm. and 80°.

TABLE III

SULFONIC ACIDS

Lead sulfonate used	Yield, %	Melting point, °C. Hydrate	Melting point, °C. Anhyd.[b]	Neutral equivalent Hyd. Found	Neutral equivalent Anhyd. Calcd.	Neutral equivalent Anhyd. Found	S, % Calcd.	S, % Found
Nonyl[a]	84.7	...	46	...	208.2	210.0	15.38	15.30
Decyl[a]	60.0	...	46.5	...	222.2	223.5	14.40	15.00
Undecyl	84.0	40–41	49	253.0	236.2	235.9	13.55	13.46
Lauryl	92.0	43–45	52	267.5	250.2	249.5	12.79	12.82
Tridecyl	80.2	48–49	58	281.3	264.2	266.4	12.11	12.01
Myristyl	81.0	55–56	65.5	295.5	278.2	277.0	11.50	11.42

[a] Nonyl and decyl sulfonic acids were obtained directly in the anhydrous state. [b] The melting points for the anhydrous products are not capillary melting points but are approximate values taken in the tubes in which the sample was dehydrated.

The benzylaniline salts of the sulfonic acids were found to be non-hygroscopic, were readily purified by crystallization from ether containing a small amount of alcohol, and possessed sharp melting points.[8] While the melting points do not vary as much as

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(8) Unpublished work with M. L. Farrow has shown that benzylaniline salts are satisfactory derivatives for sulfonic acids in general.

might be desired, the compounds are readily distinguished by titrating their hot solutions with standard alkali.

TABLE IV

BENZYLANILINE ALKYLSULFONATES

	Melting point, °C.	N, % Calcd.	N, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
Nonyl	90.5–91.0	3.58	3.70	391	396
Decyl	84.0–84.5	3.45	3.49	405	406
Undecyl	84.6–84.7	3.28	3.34	419	421
Lauryl	91.0–91.2	3.23	3.18	433	435
Tridecyl	87.5–88	3.13	3.09	447	445
Myristyl	82.5–82.7	3.04	2.95	461	462

Summary

The normal aliphatic mercaptans and sulfonic acids containing from nine to fourteen carbon atoms have been prepared in quantity and in a pure state. The benzylaniline salts of the sulfonic acids are described as derivatives.

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Acetylene Polymers and their Derivatives. VI. Vinylethinylmagnesium Bromide and Some of its Reactions

BY WALLACE H. CAROTHERS AND GERARD J. BERCHET

As might be expected from its structure, vinylacetylene (I) reacts rapidly with ethylmagnesium bromide. The reaction proceeds smoothly and apparently involves only the acetylenic hydrogen; the behavior of the product indicates that it is vinylethinylmagnesium bromide (II). It reacts in the typical manner with a variety of reagents.

Acetone yields vinylethinyldimethylcarbinol (III), a colorless liquid whose structure is established by its hydrogenation to *n*-butyldimethylcarbinol. On standing, it polymerizes to a colorless, transparent resin.

The action of carbon dioxide on vinylethinylmagnesium bromide apparently gives vinylpropiolic acid (IV), but it was not found possible to isolate this substance in a state of high purity. Above 110° it polymerizes explosively, and even at lower temperatures it is rapidly converted into a tough, insoluble, rather elastic mass.

The products (V and VI) obtained from α-naphthyl isocyanate and from triphenylchloromethane are stable crystalline solids.

$CH_2{=}CH{-}C{\equiv}CH$ I

$CH_2{=}CH{-}C{\equiv}C{-}MgBr$ II

$CH_2{=}CH{-}C{\equiv}C{-}COH(CH_3)_2$ III