the residue which crystallized. Crystallization was completed on standing for several days at 0°; yield 6.7 g. (73%).

In addition to reduction of benzyl glycosides this method was successfully applied to the reduction of the benzyl group from 3-benzyl 2,4,6-trimethyl-D-glucose without reduction of the aldehydic group. The 2,4,6-trimethyl-D-glucose was crystallized from carbon tetrachloride, m. p. 126°. When mixed with an authentic sample of 2,4,6-trimethyl-D-glucose, the melting point was not depressed.

Summary

1. A new method of separation of the cleavage products of methylated disaccharides has been developed. This involves conversion of the methylated disaccharide to two benzyl glycosides, treatment with benzyl alcohol in the presence of an acid, separation of the glycosides by fractionation under high vacuum, and reduction of the benzyl glycosides to give the methylated monosaccharides.

2. This method gives good yields (85%) of the tetramethyl monosaccharides and fair yields (50%) of the trimethyl monosaccharides.

3. Two new crystalline benzyl glycosides, (presumably α-forms) have been prepared; benzyl 2,3,4-trimethyl-D-glucoside, and benzyl 2,4,6-trimethyl-D-glucoside. Three new sirupy benzyl glycosides (presumably mixtures of the α- and β-forms) have been prepared: benzyl 2,3,4,6-tetramethyl-D-galactoside, benzyl 2,3,4,6-tetramethyl-D-glucoside, and benzyl 2,3,6-trimethyl-D-glucoside.

IOWA CITY, IOWA

RECEIVED JUNE 28, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, CALIFORNIA]

Aluminum Monolaurate and Proposed Structures for Aluminum Soaps[1]

BY CHARLES G. MCGEE[2]

The chemistry of aluminum soaps has long been in confusion. It has been stated: that only mono soaps exist,[3,4] that only a basic compound intermediate between mono- and di-soaps exists together with various sorption products,[5] and that the mono- as well as the di- and tri-soaps all exist.[6] Di-soaps have been prepared by several authors,[7,8,9] while efforts to prepare tri-soaps[10,11] failed.

It is the purpose of this paper to present evidence concerning the existence of aluminum mono-soaps. In the course of this work, no compounds were prepared having a ratio of exactly one molecule of fatty acid per atom of aluminum, but the preparations obtained had approximately one to one ratios and were stable under a wide variety of conditions. It is believed that these are true compounds, of the nature of copolymers, and that as a result exact stoichiometric composition is not necessarily to be expected. Products containing from 1.2–0.8 molecules of fatty acid per aluminum atom will be referred to as aluminum mono-soaps.

The materials used in this study are those used in the previously reported work.[8] Analysis was carried out by ashing or by a split analysis in which the aluminum was determined by a standard procedure using 8-hydroxyquinoline and the fatty acid determined by precipitation and weighing.

Aluminum Mono-Soaps

Preparation from Aluminum Di-soaps, Accompanied by Alcoholysis.—In the course of an investigation on the free acid content of commercial aluminum soaps, it was noted that the use of hot methanol for extraction gave much higher results than when acetone was employed. Analysis of these residues indicated that they approximated the composition then expected for a compound of the formula $Al(OH)_2$-fatty acid.

However, this reaction was repeated on samples of aluminum dilaurate prepared by Smith, *et al.*[9] Exhaustive treatment with hot methanol gave products containing 1.2–1.0 molecules of fatty acid per aluminum atom. The initial reaction is always accompanied by a marked physical change in the soap from a powder to a plastic mass. The reaction required several minutes at the boiling point of the methanol, and many days at room temperature. The plastic product contained large amounts of methanol and much free fatty acid. It gradually hardened over a period of several days, after which it was ground up and retreated with the methanol. During later treatments, it frequently reconsolidated.

To examine this assumed reaction, a weighed sample of aluminum dilaurate was treated with methanol, and the weight of fatty acid liberated and the loss in weight of the soap were determined. It was found that after drying *in vacuo*

---

[1] Study conducted under Contract OEMsr-1057 between Stanford University and the Office of Emergency Management, recommended by Division 11.3 of the National Defense Research Council, and supervised by Prof. J. W. McBain.

[2] Present address: Stanford Research Institute, Stanford, California.

[3] Alexander, reports to Div. 11.3, NDRC.

[4] Galley and Puddington, *Can. J. Research*, **B26**, 155–160 (1948).

[5] Eigenberger and Eigenberger-Bittner, *Kolloid Z.*, **91**, 287 (1940).

[6] Lawrence, *J. Inst. Petroleum*, **31**, 312 (1945). British Petroleum Warfare Board Memo No. 368.

[7] Ostwald and Rideal, *Kolloid Z.*, **69**, 185 (1934).

[8] Markowicz, *Färber Ztg.*, **34**, 326 (1928).

[9] Smith, Pomeroy, McGee and Mysels, THIS JOURNAL, **70**, 1053 (1948).

[10] McBain and McClatchie, *ibid.*, **54**, 3226 (1932).

[11] Licata, *Drugs, Oils & Paints*, **51**, 148 (1936).

over phosphorus pentoxide, the aluminum soap retained one molecule of methanol per molecule of soap initially present and lost one molecule of fatty acid. This indicates that methanolysis, analogous to hydrolysis, takes place. Similar reactions were observed with ethanol and higher alcohols, and with a solution of 10% water in acetone.

Direct Preparation of Aluminum Mono-soaps.—Aluminum mono-soaps were prepared directly in methanol by adding aqueous ammonium hydroxide to a solution of aluminum nitrate and lauric acid in hot methanol. If an excess of ammonia was added quickly, a finely divided product, which often consolidated on further treatment with hot methanol, was obtained. Most of these products contained distinctly more than one molecule of lauric acid per aluminum atom, even after they had been washed free of salts with methanol. Continued treatment with hot methanol, or methanol plus water, was necessary to bring the acid content down. Extraction with acetone did not alter the acid content. The material began to decompose at 250° without melting; at 270° it softened to a brown transparent mass.

Aluminum mono-soaps were prepared from aluminum hydroxide by precipitating the hydroxide in aqueous solution, washing it with water and then methanol, and finally adding a solution of lauric acid in methanol and heating. A slow reaction took place, leading to the formation of a gummy mass similar to that obtained in the other reactions.

An attempted direct precipitation in water yielded a mixture of at least two products, one containing 1.5 molecules of lauric acid per aluminum atom and soluble in a benzene–acetone mixture, the other containing about 0.6 molecule of lauric acid per aluminum atom, insoluble in benzene–acetone and unaffected chemically by it.

Direct Conversion of Monolaurate to Dilaurate by Reaction with Lauric Acid.—Shreve, Pomeroy and Mysels[12] had found that no water was formed in the benzene distillation of a mixture of aluminum monolaurate and lauric acid. They concluded that no reaction forming dilaurate had taken place. Later evidence showed that the monolaurate may have contained methoxyl groups. Reaction with lauric acid would have produced methanol, which would not have been detected in the benzene distillation. Hence, the reaction was reinvestigated, using acetone as a solvent. A large excess of lauric acid was employed, the mixture was refluxed, the acetone evaporated and the mixture dried over phosphorus pentoxide. It was then extracted repeatedly with cold acetone until the acetone was substantially free of fatty acid. Analysis of the residue showed that it contained 1.9 molecules of lauric acid per aluminum atom, indicating that substantial conversion to dilaurate had taken place.

Behavior of Aluminum Monolaurate toward Organic Solvents.—Aluminum laurates containing less than 1.2 molecule of lauric acid per aluminum atom are not noticeably soluble in the common organic solvents at room temperature. At its boiling point (171°), butyl cellosolve dissolved a fair amount, the solution gelling upon cooling. The residue from this treatment retained the composition of the original material.

Certain mixed solvents were effective in dissolving certain aluminum mono-soaps, methanol–benzene in particular. The solubility varied greatly with the composition of the soap. No solvents were found for products containing less than one molecule of lauric acid per aluminum atom. Treatment with solvents for fatty acids did not reduce the acid content of these materials.

The Nature of Aluminum Mono-soaps.—The question immediately arises as to whether these materials are true compounds or merely sorption products of lauric acid on hydrous alumina. The evidence seems strongly in favor of true compounds. Treatment of di-soaps with methanol always yields products having about one molecule of lauric acid per aluminum atom. Extended treatment with organic solvents does not significantly lower the acid content further. Treatment of aluminum hydroxide with lauric acid gives a product similar in every way to that from the degradation of dilaurate. With some products, solution can be effected in methanol–benzene mixtures from which the dissolved material can be precipitated by the addition of excess of methanol or acetone. The precipitated material is similar to the original material. Mono-soap was converted by reaction with lauric acid into di-soap which is a well-defined compound.[9]

The Structure of Aluminum Mono-soaps.—A rational structure for the aluminum mono-soaps can be built up on the basis of the known preference of aluminum for octahedral coördination. Each fatty acid ion will occupy two adjacent corners of the octahedron with hydroxyl (or methoxyl) groups in the other four. In order to maintain electrical neutrality, each of the hydroxyl groups must be shared. If neighboring aluminum ions share edges of the octahedra, long chains of the type shown in Fig. 1 will be formed. Structures based on corner and face sharing seem much less probable. The suggested structure would be expected to produce a non-crystalline material, as is observed. Powder X-ray diffraction photographs yield only diffuse halos, even after prolonged heating of the solid in methanol.

Low solubility is conferred by the high molecular weight and by a mechanism analogous to vulcanization. An aluminum hydroxide octa-

---

[12] Shreve, Pomeroy and Mysels, *J. Phys. and Coll. Chem.*, **51**, 963 (1947).

Fig. 1.

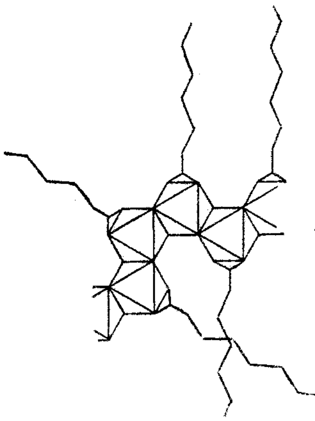
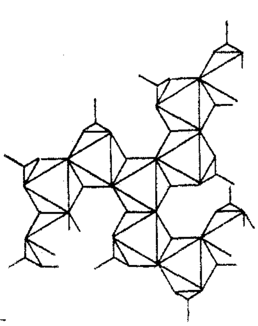


Fig. 2



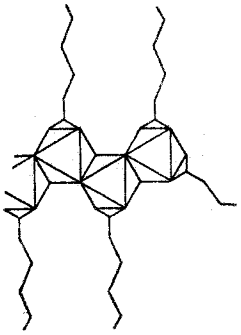


Fig. 3.

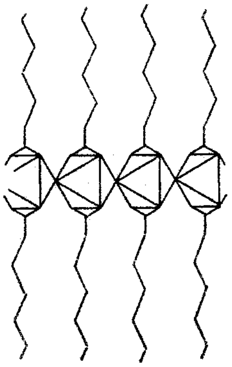


Fig. 4.

hedron can join three chains by sharing its edges with three molecules of mono-soaps as in Fig. 2.

If the chains terminate in di-soap molecules as in Fig. 3, it will be seen that the composition of the material may vary from that of a di-soap to aluminum hydroxide, depending upon the chain length and degree of cross linking. Since products containing close to one molecule of fatty acid per aluminum atom were obtained under a fairly wide variety of conditions, it seems probable that chains of mono-soap molecules predominate and that the term mono-soap is justified when referring to these materials. The high ratio of fatty acid to aluminum found in many cases may be due to incomplete conversion and/or failure to extract completely the free acid.

The physical behavior of these substances is similar in many respects to certain high polymers. They are much more soluble in mixed than in single solvents (although this is true of ordinary sodium soaps also), they are soluble in butyl cellosolve, they lack a definite melting point, they are frequently elastic and sometimes sticky when not free from solvent. They give gels in solvents and their solutions show very high viscosity.

Structure of Aluminum Di-soaps

Some of the physical properties of aluminum di-soaps are also polymer-like, but they have not been reported with a fibrous X-ray structure. Ross and McBain[13] found by X-ray diffraction that they are crystalline and suggested a structure in analogy with that of sodium soaps.

An alternative suggestion is shown in Fig. 4. Here the two carboxyl groups occupy four of the coördinating positions while the two remaining positions contain hydroxyl ions which are shared to form a chain. This structure has been proposed by Grey[14] who, however, did not note that these chains would have to end in charged groups. It will be seen from Fig. 5a that a chain ending as shown will possess a net charge of minus one-half on the terminal group, while a chain ending as in Fig. 5b or 5c will possess a charge of plus one-half. This is an important feature of this structure, for it provides a reasonable mechanism for the observed association of aluminum di-soaps in dilute solutions.[14,15]

Fig. 5a.

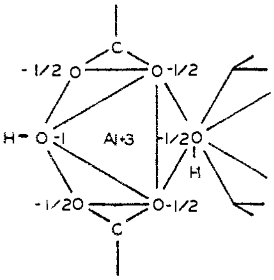
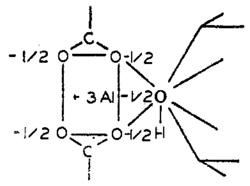


Fig. 5b.



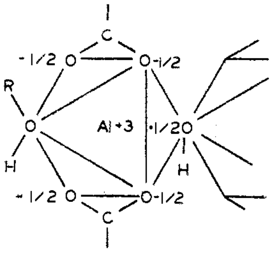


Fig. 5c.

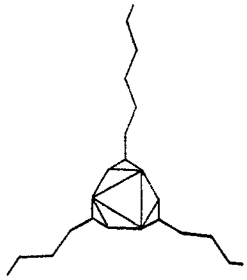


Fig. 6.

The suggested structure for aluminum di-soaps permits a much more regular arrangement of the molecules than did the structure for mono-soaps. Adjacent di-soap chains would be held together by both van der Waals forces between the hydrocarbon chains and hydrogen bonds between the hydrogen of the shared hydroxyl ions and the oxygen atoms of the carboxyl groups. The observed melting points may correspond to the breaking of these two forces, leaving the individual aluminum soap chains intact, since the molten soap possesses extremely high viscosity. In aluminum di-soap–hydrocarbon systems, the forces holding the hydrocarbon chains together

---

(13) Ross and McBain, *Oil and Soap*, **23**, 214 (1946).

(14) Grey, *Trans. Faraday Soc.*, **42B**, 197 (1946).

(15) McBain and Working, *J. Phys. and Colloid Chem.*, **51**, 947 (1947).

would be largely eliminated, leaving only the hydrogen bonds holding the aluminum soap chains to one another. Hence, the gel–jelly transition, which was found[16] to be largely independent of temperature for different aluminum di-soaps in a given solvent, may be a melting process taking place with only the hydrogen bonds left.

The effects of various substances upon aluminum di-soap in hydrocarbon systems can be interpreted on the assumption of the above model. Compounds which can coördinate with the aluminum ion will reduce the chain length and hence the viscosity, and usually increase the rate of solution or gelation of soap. Alcohols, water, amines and higher fatty acids all show this behavior.[17] Lower fatty acids increase the time required for gelation. This might be due to metathesis and resultant precipitation of less-soluble aluminum di-soaps on the surface of the particles, or simply to the possibility that although the rate of solution was increased, the dissolving chains were broken down by the acid so that some time had to elapse before the concentration of long chains was sufficient to gel the system.

McBain and Working[15] found that in benzene, the viscosity of aluminum di-soap solutions often increases with increasing temperature. This might be due to unfolding of chains, thus increasing the asymmetry of the particles. There were long time aging effects present, however, and what the situation would be at equilibrium is not clear. Mysels[18] reported no increase in viscosity with increase in temperature in cyclohexane, but observed very long time effects in the aging of the systems which sometimes led to anomalous results. His observations fit in well with the picture of reorganizing long chains.

McBain and Working[15] also found by osmometry that aluminum dilaurate was associated in benzene solutions as dilute as 0.001% by weight. The degree of association was found to increase very rapidly with increased concentration, but the effect of moisture was not examined. The jellies of aluminum dilaurate are very sensitive to moisture,[19] and it is possible that residual moisture in the soap and benzene gave rise to the apparent decreased association in the dilute solutions.

The dilaurate is characterized by a modest degree of crystallinity, solubility in hydrocarbons, reversible association, formation of jellies from gels at well-defined temperatures, and instability in the presence of water and alcohols. On the other hand, the monolaurates had low crystallinity, very low solubility in hydrocarbons, formation only of gels, no jellies, and stability in the presence of alcohols. These properties are reasonably in accord with the proposed structures based upon identical principles for both compounds.

Aluminum Tri-soaps

Attempts to prepare tri-soaps by treating an aluminum alcoholate with a fatty acid have failed.[10,11] A structure analogous to those suggested for mono- and di-soaps, Fig. 6, in which the oxygen atoms of three carboxyl groups occupy the six coördination positions, would appear stable. It gives a reasonable explanation of the failure of attempts to prepare tri-soaps, since the molecule would be expected to possess a solubility very similar to that of the fatty acid; in fact, because of the shape of the molecule and the resultant difficulty of fitting into a compact crystal lattice, the tri-soap might be a liquid, miscible with the solvents used to extract the free acid. Hence, if produced, it would be found with the free acid and not in the residue, as assumed by previous workers.

Detailed Preparation of Aluminum Monolaurates

From Aluminum Dilaurate and Methanol.—Four grams of aluminum dilaurate was boiled with 100 ml. of methanol for ten minutes. The methanol was removed by filtration and the solid was then washed with a 20-ml. portion of methanol and three 15-ml. portions of acetone. Evaporation of the methanol yielded a considerable quantity of lauric acid. The solid was dried in a vacuum desiccator. On ashing it was found to contain 8.4% aluminum; theoretical of $Al(OH)_2L$ is 10.4%; theoretical for $Al(OH)L_2$ is 6.1%. On repeating the treatment with methanol the aluminum content rose to 9.2%.

From Aluminum Dilaurate in Benzene Solution and Methanol.—A 2-g. portion of a monolaurate prepared from dilaurate and methanol was dissolved in 30 ml. of benzene by wetting it with methanol, adding the benzene and heating. An excess of methanol was added to the solution, reprecipitating the aluminum soap as an elastic material containing a large amount of solvent. This material was dried and analyzed. It contained 8.8% aluminum and had a ratio of 1.1 laurate to 1 aluminum.

From Aluminum Dilaurate and Methanol with a Material Balance.—1.677 g. of aluminum dilaurate (6.28% aluminum; theory 6.10%) was placed in a weighed 50-ml. centrifuge tube; 20 ml. of dried methanol was added and the tube was stoppered. It was allowed to stand overnight at room temperature; 10 ml. more of methanol was added, the solid was separated by centrifuging and 20 ml. of the supernatant liquid was pipetted out, transferred to another weighed tube and evaporated. An additional 20 ml. of dried methanol was added to the solid and the process repeated. After the third treatment the alcohol was raised to its boiling point to hasten the removal of the acid.

It was found that 0.669 g. (3.34 mmoles.) of lauric acid had been removed from the dilaurate. The dilaurate had lost only 0.538 g. The differ-

---

[16] McBain, Mysels and Smith, *Trans. Faraday Soc.*, **42B**, 173 (1946).

[17] Smith, Rogers and Mysels, communication.

[18] Mysels, *J. Colloid Sci.*, **2**, 375 (1947).

[19] McRoberts and Schulman, *Nature*, **162**, 101 (1948).

ence, 0.131 g. (3.8 mmoles.) represents the amount of methanol retained by the aluminum soap after drying in a vacuum over phosphorus pentoxide. It is slightly above the 3.34 mmoles. of acid extracted, but in good agreement with the 3.79 mmoles. of dilaurate originally present. It is probable that the extracted acid is low, due to the clumping of the particles during the experiment, and subsequent failure to extract completely the freed acid.

By Precipitation in Methanol.—37.5 g. (0.1 mole) of $Al(NO_3)_5 \cdot 9H_2O$ and 20 g. (0.1 mole) of lauric acid was dissolved in 200 ml. of boiling methanol; 20 ml. of concentrated ammonium hydroxide was added as quickly as possible. A very voluminous precipitate formed and 600 ml. of methanol were added to disperse the product. It was washed repeatedly with hot methanol and finally with acetone. After drying it contained 10.0% aluminum. It was treated with two portions of boiling methanol, after which it contained 10.6% aluminum. A small portion of this material was sealed in an evacuated capillary and heated. It began to decompose at 250° without melting. At 270° it softened to a brown transparent mass.

From Aluminum Hydroxide and Lauric Acid.—2.41 g. (0.01 mole) of $AlCl_3 \cdot 6H_2O$ was dissolved in 30 ml. of distilled water and a slight excess of ammonia was added. The aluminum hydroxide was centrifuged off and washed four times with methanol; 6.0 g. (0.03 mole) of lauric acid was then added and the mixture was heated to 70°. A gelatinous white precipitate formed which began to clump together after a few minutes. Within fifteen minutes it had formed a soft plastic mass, similar to that formed by treating dilaurate with methanol. This was dried, ground under methanol, and washed twice with hot methanol. During the second wash it again clumped together. It was washed with acetone and dried. It contained 7.8% aluminum and had almost 1.4 molecules of laurate per atom of aluminum.

Acknowledgment.—The author wishes to acknowledge the stimulating direction of Professor J. W. McBain, the many thought-provoking discussions with Drs. K. J. Mysels and G. H. Smith, and the financial assistance of the Colgate–Palmolive–Peet Company during the latter portion of this work.

Summary

The preparation and properties of aluminum mono-soaps have been described. It has been suggested that aluminum mono-soaps are polymers in which the repeating units are alumina octahedra joined by sharing edges, with the carboxyl groups occupying the remaining positions.

The structure of aluminum di-soaps has also been discussed. A polymer structure has been suggested in which alumina octahedra are joined by sharing two opposite corners, which carboxyl groups occupying the remaining four. An attempt has been made to correlate such a structure with the known properties of the di-soaps.

Aluminum tri-soaps have likewise been discussed. Possible structures have been suggested and reasons for failure hitherto to prepare them have been considered.

STANFORD UNIVERSITY, CALIF. RECEIVED JUNE 9, 1948

[CONTRIBUTION FROM COLGATE–PALMOLIVE–PEET CO.]

The Autoxidation of Methyl Oleate

BY JOHN ROSS, ARTHUR I. GEBHART AND J. FRED GERECHT

It has been shown that autoxidation of olefinic compounds involves, in effect, addition of a molecule of oxygen with formation of a hydroperoxide group on a carbon atom adjacent to an olefinic group. Farmer, *et al.*, further developed this view and suggested a free radical chain reaction mechanism.[1]

Autoxidation, of the various resonance forms of methyl oleate, *via* such mechanism, should give rise to the structures:

$CH_3(CH_2)_6CH_2CH{=}CHCH(OOH)(CH_2)_6COOCH_3$,
$CH_3(CH_2)_6CH{=}CHCH(OOH)CH_2(CH_2)_6COOCH_3$
$CH_3(CH_2)_6CH_2CH(OOH)CH{=}CH(CH_2)_6COOCH_3$,
$CH_3(CH_2)_6CH(OOH)CH{=}CHCH_2(CH_2)_6COOCH_3$

We have examined autoxidation of methyl oleate with oxygen in the presence of ultraviolet light at 35° and found evidence that such is the case.[2]

The position of the hydroperoxide group was determined as follows: The mixture of hydroperoxides of methyl oleate was reduced to methyl hydroxyoleates, hydrogenated to methyl hydroxystearates, and oxidized to methyl ketostearates. After saponification, 9- and 10-ketostearic acids were isolated pure by fractional crystallization. The 8- and 11-ketostearic acids were not isolated pure, but their presence was demonstrated by conversion to suberic and nonane dicarboxylic acids, respectively, by hydrolysis of the amides obtained by Beckmann transformation of the oxime.

Evidence for the position of the ethylenic

---

[1] W. A. Waters, *Ann. Repts. on Progress Chem. (Chem. Soc. London)*, 130, **42**, 1945 (1946).

[2] Farmer, *et al.*, *J. Chem. Soc.*, 545 (1943), in a study of autoxidation of methyl oleate did not identify structurally any of the products of oxidation but later felt that all four hydroperoxides were probably present. In his examination of substituted cyclohexenes the structural evidence presented for the existence of four position isomers appears doubtful.