Ammonia Laboratory, Oppau.
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IDENTIFICATION AND CONSTITUTION OF THE BRANCHED CHAIN
ACIDS FROM THE FISCHER-GATSCH FATTY ACIDS

Synopsis

In earlier work there has been reported the contents, proportional amount and distribution of the normal and branched chain paraffin acids from Fischer-Gatsch, Riebeck paraffin and T.T.H. oxidation products.

Among the paraffin acids the branched chain acids are singular because they lead to undesirable products in the biological decomposition of fatty acids and also, especially the lower ones, impart an undesirable odor to soap.

In spite of their importance there is little known concerning the constitution of these fatty acids.

In the following work Fischer-Gatsch fatty acid fractions containing acids of 10-11 carbon atoms and rich in branched chain acids have been taken, a decomposition and separation effected, and the constitution of the branched chain acids contained therein determined.

Through the extensive work which will be described a suitable analytical method of decomposition was evolved and employed.

It has been found that:

(1) In the acid fraction of 10 carbon atoms associated with decanoic there were only small amounts of 2-methyl and 3-methyl nonanoic acids.

(2) In the acid fraction of 11 carbon atoms there was associated with hendecanoic (undecylic acid) 2 methyl-, 3 methyl-, and 4 methyl decanoic acids. Besides these there were more complicated branched chain acids present but the amounts of these latter substances were too small to afford work to clarify their constitution.

In the literature there are a series of decomposition reactions given which permits the determination of the acid chain length by yielding the acid next lower in the series.
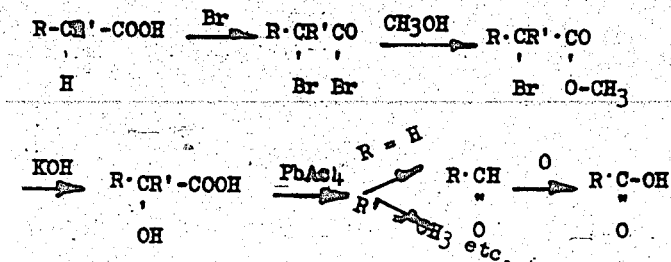
It served our purpose to check this method and finally through the objective employment of the data of Mendel[1] to evolve a method which would afford information permitting the identification and structure to be

(1) Mendel and J. Coops, Rec. Trav. chim. Pays-Bas 53, 1939, p. 1133

ascertained of branched chain fatty acids of the Fischer-Gatsch oxidation product.

In the analytic work the checking of the other methods will be reported in a following paper. This work concerns itself only with the final practical analytic decomposition and its products while that in Report 1666 deals with their recognition.(2)

According to Mendel's method the acids are brominated and converted to their respective brom acids and then these are esterified to their methyl esters. By treating the methyl esters with aqueous KOH the hydroxy acids are produced. These are then reacted according to Criegee with lead tetra-acetate while blowing air through the mixture. A splitting occurs and a carbon atom about one part oxidizes to aldehyde and then to a shorter acid.

$$R\text{-}CR'\text{-}COOH \xrightarrow{Br} R\cdot CR'CO \xrightarrow{CH_3OH} R\cdot CR'\cdot CO$$

$$\quad\quad H \quad\quad\quad\quad\quad Br\ Br \quad\quad\quad\quad Br\ O\text{-}CH_3$$

$$\xrightarrow{KOH} R\cdot CR'\text{-}COOH \xrightarrow{PbAc_4} \begin{array}{c} R = H \\ R\cdot CH \xrightarrow{O} R\cdot C\text{-}OH \\ CH_3\ etc. \quad O \quad\quad O \end{array}$$

$$\quad\quad\quad\quad OH$$

Mendel had only degraded straight chain acids to the next lower one in series.

From the above equations it is evident that in this case when two hydrogens are attached to the secondary carbon atom that only one acid can be produced. If there is an alkyl group on the secondary carbon atom then by blowing with air not only is an acid produced but also a ketone, so far as the last Criegee has not been followed and this has been the case in the experiments following.

This is the prescribed method for the determination of the branched chain in a certain acid.

A ketone also appears everytime in the recovered products of the decomposition where only one carbon has been split off. We can infer the position of the branching from the number of times the decomposition has been repeated and yields a ketone.
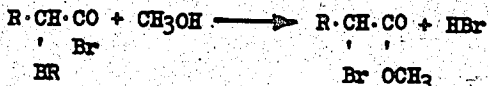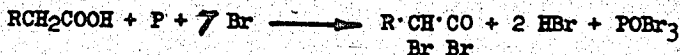
When mixtures of branch chain acids are taken various ketones appear in the decomposition products.

Let us take two acids, for example one of which has the branching in the 3 position and the other in the 5 position. In the first case a ketone is produced through two decompositions successively; this indicates the 3 position. In the second case a ketone is produced repeatedly through 4 decompositions.

(2) Report 1666, Dr. G. Melan, B. Weiss. "The Identification and Separation of Aldehydes and Ketones".

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The exact description of this degradation process is given in the following below:
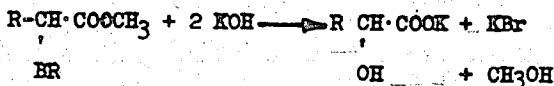
1. Preparation of the Bromester

$$RCH_2COOH + P + 7 Br \longrightarrow R \cdot CH \cdot CO + 2 HBr + POBr_3$$
$$\qquad\qquad\qquad\qquad\qquad Br \; Br$$

$$R \cdot CH \cdot CO + CH_3OH \longrightarrow R \cdot CH \cdot CO + HBr$$
$$\quad Br \qquad\qquad\qquad\qquad\qquad Br \; OCH_3$$
$$BR$$

In an apparatus with all ground glass joints one mol of the particular acid and one mol of phosphorus is heated to 58° under reflux and stirring, and four mols of bromine (slight excess) are gradually added dropwise. The temperature is gradually raised until HBr is evolved at a good rate. The temperature is then raised to 70°. 40 g. of acid take about 6-7 hours to react.
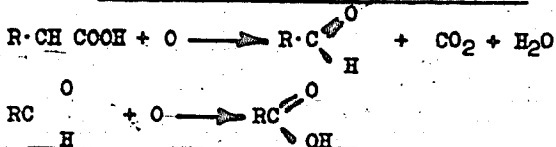
At the end of the reaction the brominated product is separated from phosphorus oxybromide and allowed to slowly run into methanol. After standing overnight the excess methanol is distilled off, the residue taken up in ether and washed with bisulphite solution, and finally with water until neutral. The pure bromester is obtained by distillation. The yield is about 82% of theoretical.

2. Preparation of the α Hydroxy Acid

$$R-CH \cdot COOCH_3 + 2 KOH \longrightarrow R \; CH \cdot COOK + KBr$$
$$\quad BR \qquad\qquad\qquad\qquad\qquad\quad OH \qquad + CH_3OH$$

$$R \cdot CH \cdot COOK + HCl \longrightarrow R \cdot CH \; COOH + KCl$$
$$\quad OH \qquad\qquad\qquad\qquad\qquad\quad OH$$

One mol of the bromester is saponified with somewhat more than two mols of KOH in a 10% solution at boiling temperature under reflux for two hours. This solution is then diluted with water, any unsaponifiable matter removed by shaking with petroleum ether and the hydroxy acids are liberated by acidifying the separated alkaline solution. The liberated acids are taken up in petroleum ether, the ether washed free of mineral acid, then dried and the ether distilled off. The yield is 100% calculated from the bromester.

3. Splitting with Lead Tetra-Acetate

$$R \cdot CH \; COOH + 0 \longrightarrow R \cdot C \overset{O}{\underset{H}{\diagup}} + CO_2 + H_2O$$
$$\quad O$$

$$RC \underset{H}{\diagup} + 0 \longrightarrow RC \overset{O}{\underset{OH}{\diagup}}$$
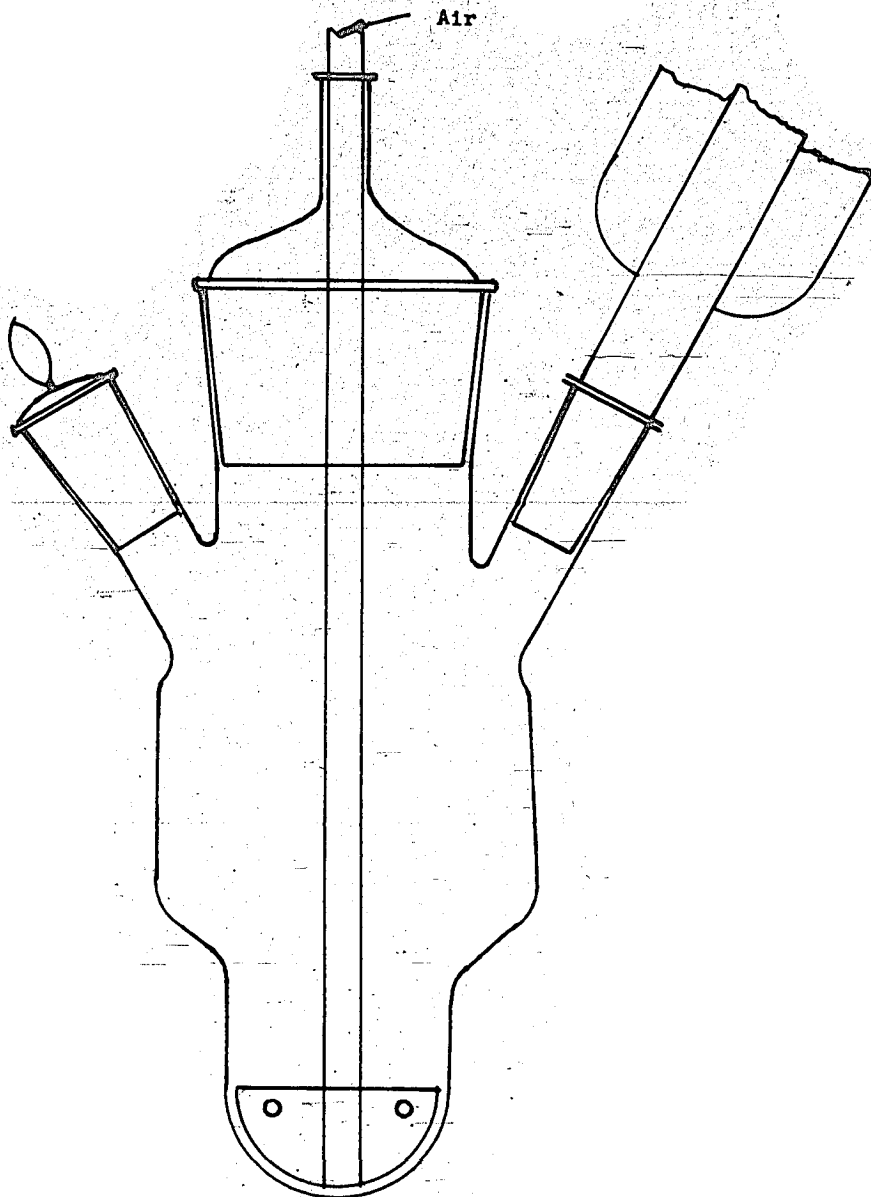
Air

Fig. 1

Apparatus for the
oxidation and splitting of acids with
lead tetra-acetate.

a. The Apparatus

For the success of the reaction it is important that the mixture be well stirred while at the same time a rapid stream of air is bubbled through. The reaction is carried out in the specified apparatus as shown in the diagram. (Figure 1).

It consists of a cylindrical vessel with a neck from the sides of which are supported two other necks. All are fitted with ground glass joints. One small neck serves as a means of filling with lead tetra-acetate while the other small neck connects to a reflux condenser.

Through the top neck a stirrer enters and a stream of air is passed through the hollow axle into the reaction mixture. At the top of the condenser there is a calcium chloride tube. The whole apparatus is placed in a water bath that is heated to 50-60°.

b. Procedure for the Splitting

To the dry flask there is added one mol of the hydroxy acid and about an equal volume of benzine (B.P. 60-70°) and the solution is warmed to 50-60°. A mixture of 1/8 mol of the hydroxy acid and somewhat more than 1/4 mol of lead tetra-acetate is gradually added over a period of about one hour. At the start a gentle stream of dried air is led into the reaction mixture. Small amounts of benzine are lost through the air stream and therefore the benzine must be replenished from time to time. After the addition of all reagent the mixture is heated with constant stirring for four more hours. At the end the excess lead tetra-acetate is removed by the addition of glycol which dissolves it and forms a viscous layer under the benzine.

The benzine solution is decanted from the viscous lower layer and the latter is diluted with water and extracted with more benzine. The benzine solutions are combined. They contain all the acids which have been degraded one carbon atom, and resp. small amounts of their lead salts, some lead tetra-acetate, some remaining aldehydes, ketones, and some of the desired branched chain acids from the original material.

The removal of the water soluble lead salts (lead tetra-acetate) is next effected by washing with water several times. To remove the water insoluble lead salts the benzine solution is extracted with 60 cc of 70% acetic acid for every mol of hydroxy acid present.

The benzine is carefully distilled off and the remaining acetic acid which contains the decomposition product is refluxed for one hour. This is next extracted with ether, the separated ether extractions washed with water, then dried and the ether distilled off.

In the residue remaining there are those acids which have been degraded one carbon atom, some remaining aldehyde and also some ketone.

The separation of aldehyde and ketone is effected by shaking vigorously with cold barium hydroxide solution until red to phenolphthalein (spot test) and then the solution is heated to the boiling point and just enough

barium hydroxide solution added so that the pink color remains, (Barium Salt I). The solution is made faintly acid with one drop of acetic acid and in a suitable vessel the carbonyl compounds are steam distilled out under reduced pressure In order to prevent loss through volatility of the acids it is necessary to use care and good cooling. From the aqueous distillate the carbonyl compounds are extracted with ether, the ether dried and then carefully distilled off Aldehydes and in this case also ketones remain behind.

To separate these two from one another, the aldehyde is oxidized to the corresponding acid by blowing with oxygen at 70° for eight hours, the ketone-acid mixture neutralized with $Ba(OH)_2$ and steam distillation repeated in the same manner as described above. (Barium Salt II).

Then the recovered ketone is separated from non-ketone impurities by the method of Girard and identified by suitable means.

The identification of the α methyl ketone which appears when a methyl group is a chain branch is tested for by the salicylaldehyde method which has previously been found reliable.(3)

The recovery of the acids obtained from the decomposition process is effected through the phosphoric acid decomposition of Barium Salts I & II The liberated acids are extracted by ether, and after isolation of the acids on evaporating the ether, the acid residue is esterified with methyl alcohol (5% H_2SO_4 as a catalyst) and the pure ester obtained by fractional distillation. With the ester fraction the process is repeated.

The yield of the acid which has been degraded one carbon atom from a sample, that for example, contains C_{10}-C_{11} acids is about 60-70% of the theoretical. With acids of lower chains the yield is somewhat better

The yield of ketone from a branched chain acid, for example α-methyl lauric acid is about 80% of the theoretical.

Through degradation decompositions this analysis can now be carried out on suitable acid mixtures from Fischer-Gatsch fatty acids. Through careful fractional distillation there can be obtained one acid fraction with C_{10} and another with C_{11}. Upon each of the acid mixtures the degradation decomposition can be worked and from the constitution of the branched chain acids obtained from each, information of the original acids can be obtained.

1. Decomposition of the Acid Mixture of the C_{11} Fraction from Fischer-Gatsch Fatty Acids

From treatment of two portions of 52.3 grams each of the mixture of C_{11} acids with bromine and phosphorus followed by adding methanol to the reaction mixture, the α bromester was prepared. The yield of the raw ester was about 148 grams. (97% of theoretical). By vacuum distillation 120 g. of the pure ester (80% of theoretical) was obtained with the proper bromine content of 28.6% (Theo: is 28.65%).

(3) Report 1666, Dr. Melan, Dr. Weiss.

From the last, 92 g. of the α hydroxy acid was prepared by treatment with 10% KOH, and 84.5 g. of this was oxidized and split by lead tetra-acetate. The crude oxidation product from the above was 76 g.

To separate the carbonyl compounds from the crude acids it is neutralized with $Ba(OH)_2$ and the carbonyl compounds steam distilled over. From the distillate 5.8 g. of carbonyl compounds were obtained.

By oxidizing the aldehydes to acids with a stream of oxygen the acids produced thereby were separated as barium salts leaving 3.7 g. of pure ketone.

In purifying with the aid of Girard's Reagent several ketone reactions all strongly positive were shown. The salicylaldehyde test was particularly good. By the separation of the α methyl ketone from the decomposition degradation of the original acid mixture the presence of 2-methyl decanoic acid is ascertained.

From the combined barium salts (from the acids of decomposition) the C_{10} acid was isolated, and this was freed from impurities by conversion to the methyl ester and distillation. The ester gives the proper Sap. No. of 301.3; however the M.P. is far under that of the normal C_{10} acid ester. This indicates the presence of esters of other branched chain acids in the mixture. Further separation is necessary.

The Decomposition Repeated

Forty (40) grams of the mixture of C_{10} acids are as usual converted to the α brom methyl ester and purified by distillation. The yield of pure ester was 56.4 g. (82% of theoretical). By treatment of KOH solution 39.5 g. of the hydroxy acid was recovered and this gave 32.5 g. of crude oxidation product after treatment with lead tetra-acetate.

From the oxidation product 8 g. of carbonyl compounds were separated. This when blown with oxygen and the resulting acids further separated as barium salts gave 5.4 g. of pure ketone. This ketone, purified by Girard's method, exhibited all the ketone reactions and tested very well with the salicylaldehyde reagent.

Through the separation of α methyl ketone from the decomposition products of the C_{10} acids, the presence of α methyl nonanoic acid in the acid mixture is inferred.

Therefore from only one acid in the original mixture of C_{11} acids can α methyl nonanoic acid originate and its appearance proves the presence of 3-methyl decanoic acid in the original mixture.

From the combined barium salts (which originated from the decomp.) the C_9 acid was isolated, converted to its methyl ester and purified by distillation. The ester showed the proper Sap. No. but the M.P. of the ester was lower in this case also than that of the ester of the normal C_9 acid. This indicated the presence of other branched chain acids and made it necessary to repeat the degradation once more.

16.6 g. of the mixture of the C_9 acids were converted to their brom methyl esters in the usual way and purified by vacuum distillation. The yield of pure ester with the proper bromine content was 22 g. Through treatment with KOH, 16.6 g. of the α hydroxy acid was recovered and this through oxidation with lead tetra-acetate yielded 12.5 g. of the crude oxidation product.

From this oxidation product 1.92 g. of carbonyl compounds were separated and these after blowing with oxygen gave 1.46 g. of crude ketone. The ketone reactions are good; the salicylaldehyde reaction particularly strong.

Through the separation of α methyl ketone from the decomposition products of the C_9 acids, the presence of 2-methyl octanoic acid in the mixture is inferred.

Therefore from only one acid in the original mixture, of C_{11} acids can 2-methyl octanoic acid originate and this is 4-methyl decanoic acid. This proves the presence of 4-methyl decanoic acid in the original mixture.

From the combined barium salts the C_8 acids were separated and through distillation their methyl esters were purified. The ester showed the correct Sap. No. but again the M.P. was lower than that of the ester of the normal acid. This indicated the presence of esters of still other branched chain acids. Here, because of lack of material, the substance was not subjected to further degradation.

In the mixture of C_{11} acids, besides the normal acid there has been identified 2-, 3-, and 4-methyl decanoic acids.

2. Decomposition of the Acid Mixture of the C_{10} Fraction from the Fischer-Gatsch Fatty Acids

200 g. of the mixture of crude C_{10} acids was brominated and through treatment of the brominated products with methanol, the α brom methyl ester was prepared. By vacuum distillation 258 g. of the pure ester was obtained. (80% of Theo).

Through treatment with KOH solution 256 g. of the α brom methyl ester produced 182 g. of crude α hydroxy acid, which when subjected to the oxidation splitting in two portions with lead tetra-acetate, yielded 150 g. of the crude oxidation product.

The separation of the carbonyl compounds was effected by the steam distillation of the solution after fixing the acids produced from the above as their barium salts. 11 g. of carbonyl compounds were separated from the distillate.

In the carbonyl mixture from above by oxidizing the aldehydes to acids and separating them by distillation - 3 g. of crude ketone was recovered.

The ketone was purified by use of the Girard reagent and as usual strong ketone reactions were observed. The salicylaldehyde test was strongly positive.

Through the separation of the α methyl ketone by decomposition of the mixture of C_{10} acids the presence of 2-methyl nonanoic acid is inferred.

From the combined barium salts the acid is isolated and after conversion to the methyl ester this is purified by distillation.

While the Sap. No. agreed with the accepted value, the M.P. was 44° as compared with -36° of the normal C_9 methyl ester. This indicated that there were other branched chains present.

The Decomposition Repeated Once More

In two portions 75 g. of the C_9 acids was converted to the α brom ester in the usual manner. The yield of crude ester was 118 g. (97% of theoretical).

Through vacuum distillation 91 g. of the pure ester was obtained. This was as usual converted to the hydroxy acid and 60 g. of this was split and oxidized with lead tetra-acetate. This yielded 59 g. of the crude oxidation product.

In a similar manner as before 6.5 g. of carbonyl compounds were separated from the above. These carbonyl compounds after oxidation and separation of the acids yielded a crude ketone. This ketone after purification by distillation gave a carbon-hydrogen analysis as determined by combustion as follows: C,-74.5%; H,-12.32%. The theoretical values for $C_8H_{16}O$ are C- 74.9% and H- 12.5%. The salicylaldehyde test is strongly positive.

In the course of decomposition of C_9 acid, an α methyl ketone has been separated and its source inferred as 2-methyl octanoic acid. This acid could have had its source only in 2-methyl nonanoic acid in the degradation of the original mixture of C_{10} acids.

Therefore 2-methyl nonanoic acid has been identified in the mixture of C_{10} acids.

From the combined barium salts originating from the decomposition, the C_8 acids were isolated. These acids were converted to the methyl ester and purified by distillation. A small fraction first came over of lower B.P. but the main fraction distilled at a constant temperature of 92° at 19 mm.

It had the measured values of:

Sap. No. 354   F.P.   -42° to -41°   C -67.84%   H   -11.61%

This is compared with the values for the methyl ester of octanoic acid:

Sap. No. 354   F.P.   -42° to -41°   C - 67.84%   H - 11.4%

and therefore there is close agreement.

From the above it is seen that the methyl ester of octanoic acid is present.

It is concluded that:

In the mixture of acids recovered from the oxidation of the C_{10} fraction of Fischer-Gatsch fatty acids there is found decanoic acid and besides small amounts of 2-methyl nonanoic and 3-methyl nonanoic acids as impurities.

Summary

In the present work a method is shown which is suitable for the determination of the constitution of paraffinic acids and especially those with branched chains.

The acid is converted to the α brom methyl ester, the α hydroxy acid produced from this, and the latter undergoes a splitting and oxidation by lead tetra-acetate while blowing with air.

From straight chain acids the acid next lower in series is produced in this manner.

When an α branched acid is treated in this manner a ketone is produced among the decomposition products.

When the recovered decomposition products are again subjected to an oxidation and splitting and a ketone again appears in the decomposition products then the position of the branching can be determined.

This decomposition analysis was used on Fischer-Gatsch fatty acids in fractions with resp. 10 and 11 carbon atoms and which were rich in branched chains.

Thereby it has been found:

In the C_{10} acid fraction besides decanoic acid there has been identified and found only small amounts of 2-methyl-, and 3-methyl nonanoic acids.

In the C_{11} acid fraction besides hendecanoic acid there has been identified and found 2-methyl-, 3-methyl- and 4-methyl decanoic acids. Besides these acids there was evidence of still other branched chain acids but because of lack of material their constitution could not be determined.

This work was done between mid-February and mid-August (1942) with other work in the Ammonia Laboratory in Dr. Jahrstorfer's group.

Signed:

Melan

Weiss