

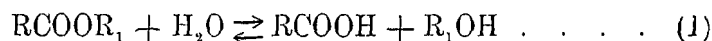
*Citation:*

Eldik Thieme, B.W. van, The action of concentrated sulphuric acid on glycerol esters of saturated monobasic fatty acids, in:

KNAW, Proceedings, 10 II, 1907-1908, Amsterdam, 1908, pp. 855-860

**Chemistry.** — "*The action of concentrated sulphuric acid on glycerol esters of saturated monobasic fatty acids.*" Preliminary communication. By B. W. VAN ELDIK THIEME. (Communicated by Prof. S. A. HOOGWERFF).

As is well known, the saponifications may generally be represented by the equation :

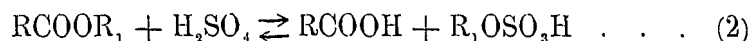


that is we shall always obtain an equilibrium between the reacting molecules which is dependent on the temperature, on the medium and on the nature of the ester.

The velocity of the saponification is moreover very low and is vigorously accelerated by hydrogen ions ; so long, however, as the quantity of the acid added does not considerably modify the nature of the medium the equilibrium will not be changed thereby.

In the technics of fat-saponification dilute sulphuric acid is used as catalyst, for instance in the Twitchell process ; from the above it follows that we must not expect the process to complete its course, it is considered satisfactory when the fat is resolved to 94 à 96% of free fatty acids.

If we use a stronger acid the process becomes modified. Firstly, we are dealing with another medium (in practice where the quantity of acid is small the medium itself is changeable during the process), secondly we have besides the first process also the following :



which means the expulsion of one of the acid residues by the other one.

Here also, however, we may expect the reaction to be reversible so that it will be completely to the right only when :

- a. The sulphuric acid added, is anhydrous (100%).
- b. An excess of acid is added to dry fat,
- c. The temperature at which the action takes place, is kept within definite limits. From this it follows, that the statement of BÜTTE<sup>1)</sup> that butterfat is completely saponified by sulphuric acid of sp. gr. 1.8355 (corresponding with 93.5% of H<sub>2</sub>SO<sub>4</sub>) cannot possibly be correct. 5 grams of butterfat are heated in an Erlenmeijer flask of one litre capacity to 100°, 10 c.c. of 93.5% sulphuric acid are added and the whole heated for 10 minutes in a waterbath at 30—32°. 150 c.c. of water are added next.

<sup>1)</sup> Chem. Zeit. N°. 12 1894 pg. 204, also KREIS Chem. Zeit. N°. 76 1892 pg. 1394.

Moreover, the high temperature at which the action of the acid takes place is unsuitable for the purpose of a complete saponification, because, as will be seen, it is just the increase in temperature which causes the shifting of the equilibrium in equation (2) towards the left. On repeating BÜNTZ's method I obtained the following figures: With 93.5% acid the butter fat was resolved to 81.0% of free fatty acid

„	98.5%	„	„	„	„	„	„	„	89.7%	„	„	„	„
„	100.0%	„	„	„	„	„	„	„	92.2%	„	„	„	„

From these figures, the influence of the concentration of the sulphuric acid is very obvious; also the imperfection of the method so that it cannot be a matter of surprise that it has been entirely abandoned.

In order to get a better insight into the action of concentrated sulphuric acid on fats I chose as starting material pure trilaurin prepared from Tangkallak fat obtained from the fruits of *Cylicodaphne Litsaea*, a tree growing in West Java. The fat consists of trilaurin and triolein so that it is easy to prepare trilaurin from the same by recrystallisation from ether.

The sulphuric acid employed was 100.0% as determined by titration. Experiment *a* took place at a temperature of 18°, experiment *b* and *c* at 1—2°. Time of action 30 minutes.

*a* 1 mol. of trilaurin to 6.5 mol. of  $H_2SO_4$  gave 86.6% free fatty acid

*b* 1 „ „ „ „ 26.0 „ „  $H_2SO_4$  „ 95.5% „ „ „

*c* 1 „ „ „ „ 52.0 „ „  $H_2SO_4$  „ 100.0% „ „ „

the reaction:

trilaurin + sulphuric acid = glyceroltrisulphuric acid + lauric acid seems, therefore, only practically complete with a very large excess of sulphuric acid and at a low temperature, for if experiment *c* is repeated and then again heated at 60° for 1½ hour, a shifting towards the left takes place and trilaurin is regenerated. The course of the investigation is briefly as follows:

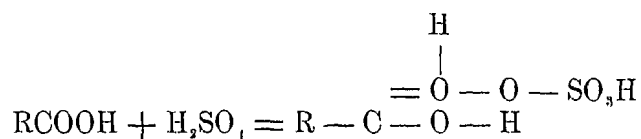
The 100.0% sulphuric acid is weighed in a flask which is then corked and placed in ice water. The weighed trilaurin is now added in small quantities. As by the action of the acid on trilaurin heat is generated no fresh portion of trilaurin must be added until the previous lot has dissolved<sup>1)</sup>. When all the trilaurin has dissolved and the time of action has expired the contents of the flask are

<sup>1)</sup> From this evolution of heat with saturated compounds it follows that no undue importance should be attached to MAUMENÉ's experiment (Compt. rend. 1882. 35 pg 572) where this evolution of heat is made use of to detect unsaturated compounds.

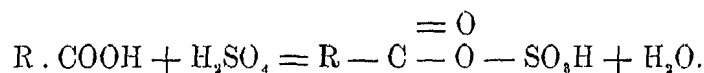
poured on to pounded ice in order to prevent as much as possible a rise in temperature and consequent saponification. Sufficient alcohol is now added so as to obtain a 60% alcohol mixture and this is then shaken with a mixture of ether and petroleum ether. After washing with water the ether is evaporated. In experiment *c* a substance was left with ester number 0 and acid number 280.5, which points to pure lauric acid. This proves that all the trilaurin was decomposed.

On repeating experiment *c* with subsequent heating at 60° for 1½ hour and removing the sulphuric acid in the manner described a substance was obtained with acid number 246.8 and saponification number 280.9; ester number 34.1. As trilaurin possesses an ester number 263.8, 12.9 % of trilaurin has been regenerated.

As regards the lauric acid which in the previous equation occurs together with glyceroltrisulphuric acid it must be remarked that this unites with  $H_2SO_4$  to molecular compounds which are more or less soluble in benzene. Now if trilaurin is dissolved in 100 % acid (experiment *c*) and if this is shaken with dry benzene both lauric acid and sulphuric acid may be detected in that solvent. Compounds of a similar character have been described by HOOGWERFF and VAN DORP <sup>1)</sup>. In these additive compounds the oxygen is sometimes taken as quadrivalent such as:



Others, H. MEIJER <sup>2)</sup>, believe in the existence of a kind of mixed acid anhydrides:



The latter is improbable as then we should want in all these compounds exactly 1 mol. of water of crystallisation for 1 mol. of the two acids. We already noticed in the saponification of butter fat that the concentration of the acid plays an important part; this is also the case with trilaurin. If now at a temperature of 1—2° we allow 52 mols. of 94.6% sulphuric acid to act on 1 mol. of trilaurin for 30 minutes a substance was obtained, after removal of the sulphuric acid, consisting of 80% of lauric acid and 20% of undecomposed glyceride. This glyceride was separated from the

<sup>1)</sup> Recueil XVIII 1899 bl. 211.

<sup>2)</sup> Monatshefte für Chemie 24 p. 840.

lauric acid and its ester number found to be 244.0. The ester numbers of trilaurin, dilaurin and monolaurin are respectively 263.8, — 246.1 and 204.7 so that the separated glyceride is a mixture.

The mono- and dilaurin are probably formed here from compounds like  $C_{11}H_{23}(OR)(O \cdot SO_3H)_2$  and  $C_{11}H_{23}(OR)_2(O \cdot SO_3H)$  by decomposition with water  $R = C_{11}H_{23}CO$ .

Similar compounds are still under investigation. In the action of concentrated  $H_2SO_4$  on nitroglycerol analogous reactions occur. NATIAN and RINTOUL<sup>1)</sup> in an article on: Nitro-glycerine und seine Darstellung write:

“Die Absorption des Nitroglycerins durch die Abfallsäure ist nicht nur ein Lösungsvorgang. Es findet noch eine zweite Reaktion statt, zwischen der Schwefelsäure und dem Nitroglycerine, unter Bildung von Sulfoglycerin und Salpetersäure. Diese umkehrbare Reaktion gelangt schnell in den Gleichgewichtszustand, so dass bei einer normalen Abfallsäure eine Hälfte des gesamten absorbierten Nitroglycerin als Sulfoglycerin vorhanden ist; während der Rest tatsächlich als Nitroglycerin in Lösung geht.”

The reverse reaction (2) which still takes place at 60° even in the presence of a large excess of acid: glyceroltrisulphuric acid + lauric acid = trilaurin + sulphuric acid is to a certain extent comparable to the synthesis of glycerides according to GRÜN and SCHACHT<sup>2)</sup>. They, however, write:

“Die Esterificirung des Glycerins durch Schwefelsäure bleibt — auch bei Anwendung von grossen Überschüssen an Säure — bei der quantitativen Bildung von Glycerindischwefelsäure  $(C_3H_5(OH)(O \cdot SO_3H)_2)$  stehen, dementsprechend treten auch bei der Einwirkung der organischen Säuren auf diese Verbindungen nur zwei Acyle in das Glycerinmolekül; man gelangt zur Diglyceriden.”

“Die Bildung von Mono- und Triglyceriden konnte beim Einhalten der unten angegebenen Bedingungen nicht constatirt werden; ebenso wenig die Bildung anderer Nebenproducte.”

It seems to me that this conclusion cannot conform to theory: it is also in conflict with my own observations. First of all, glycerol-disulphuric acid is never formed quantitatively in the esterification of glycerol by sulphuric acid, secondly byproducts are formed in their synthesis from diglycerides.

If one part of glycerol is dissolved in four parts of 98.3% sulphuric acid there is formed chiefly a mixture of glyceroldi- and trisulphuric

<sup>1)</sup> Chemiker Zeitung No. 20. 1908. p. 246.

<sup>2)</sup> Berichte 38 p. 2284 (1905) see also Berichte 40 p. 1778 (1907).

acid, also a small proportion of the mono-acid. If to this mixture is added palmitic acid dissolved in  $H_2SO_4$ , a substance is obtained with an ester number of 205.1; the ester numbers of tripalmitin and dipalmitin are respectively 208.8 and 197.6. By one single recrystallisation from absolute alcohol, nearly chemically pure tripalmitin with an ester number of 208.1 and m.p.  $64-65^\circ$  could be isolated. Therefore, a mixture of dipalmitin and tripalmitin has been the main product. The barium salt prepared by me according to their method possesses another composition as stated by them; it should, however, be observed that  $C_3H_6O_5S_2Ba + 2H_2O$  does *not* require 7.63% of  $H_2O$  but 8.50%.

One part of chemically pure glycerol D 1.261 was dissolved in 4 parts of 98.5% sulphuric acid. After 15 minutes an equal volume of water was added, the liquid was neutralised with barium carbonate and after removal of the barium sulphate by filtration the liquid was evaporated in vacuum. After adding a little alcohol it is again evaporated so as to get rid as much as possible of the water.

If now, an excess of absolute alcohol is added, a thick white precipitate of syrupy consistence is formed, which is shaken several times vigorously with alcohol to remove any free glycerol. The precipitate solidifies after a while and is then dried in vacuum over  $P_2O_5$  to constant weight.

3.132 grams of the dried salt gave on evaporation with sulphuric acid 1.7380 grams of  $BaSO_4 = 55.49\%$  of sulphate or 32.65% of barium 0.7740 grams gave 0.4295 grams of sulphate = 55.49% or 32.65% of barium.

Calculated for the Ba salt of the anhydrous di-acid 60.24%  $BaSO_4$ .  
 " " " " " " " " " mono-acid 48.67%

On heating the dried compound for  $1\frac{1}{2}$  hour at  $105^\circ$  in an air-bath it turns brown and evolves acrolein. In this operation 1.059 grams lost 0.011 grams or 1.03%.

Therefore, a mixture of barium salts has formed which may be readily explained by the fact that on diluting the mixture of glycerol and sulphuric acid, the tri-acid already formed passes into lower acids.

CLAESSON<sup>1)</sup>, who was the first to prepare glycerolsulphuric acid also observed this conversion of the tri-acid into the lower acids.

He prepared the tri-acid from anhydrous glycerol and chlorosulphonic acid; his statement that this tri-acid, on boiling with water or dilute acids, is readily and completely resolved into glycerol and sulphuric acid is, however, incorrect; at least after boiling for one

<sup>1)</sup> Journal für praktische Chemie [2] Bd. 20. p. 1. 1879.

hour there still remains a portion of the acid combined with glycerol in the form of a mono-acid.

Glyceroltrisulphuric acid was prepared by me according to CLAESSON from anhydrous glycerol and chlorosulphuric acid. 1.619 grams of the acid was dissolved in water and boiled for an hour, the solution was neutralised with barium hydroxide and the resulting barium sulphate weighed. If the sulphuric acid had been eliminated completely 3.411 grams of barium sulphate ought to have been formed but only 2.121 grams were found; therefore 0.542 grams of sulphuric acid was left in combination with glycerol.

The above experiments, therefore, throw a little more light on the sulphuric acid saponification of fats. Further communications will follow shortly.

Gouda, 5 April 1908.

Laboratory Candle Works.

**Palaeontology.** — “*On Dulichium vespiforme* sp. nov. from the brick-earth of Tegelen.” By Mr. CLEMEND REID F. R. S. and Mrs ELEANOR M. REID B.Sc. (Communicated by Prof. G. A. F. MOLENGRAAFF).

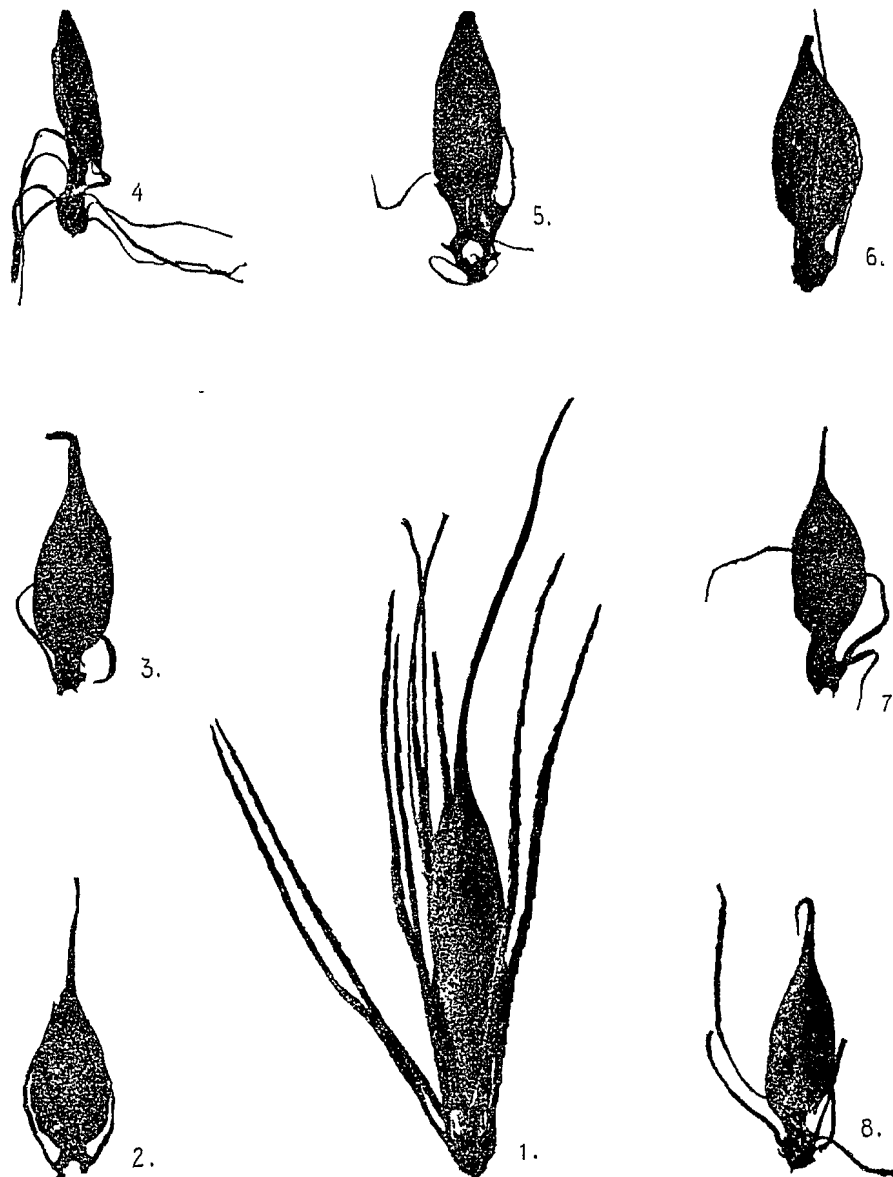
In our paper on the Fossil Flora of Tegelen published in 1907 <sup>1)</sup> we figured a fruit provisionally referred to *Rhynchospora*, though it did not possess the articulate beak of that genus. All the specimens then available were so much distorted and injured by germination that it was difficult to determine what the character of the perfect fruit would be. In addition to this, the most perfect specimen appeared to possess a quadrate base and 8 setae, characters unknown in *Dulichium*, to which genus the fruit was in other respects comparable.

Since the publication of our paper we have obtained more material, thanks to the kindness of Dr. LORIÉ and Baron L. GREINDL. This new material and a closer examination of the specimens before collected, enables us now to describe the fruit as a new species belonging to *Dulichium*, a genus now confined to America, though already recorded by Dr. N. HARTZ as occurring in an interglacial peat-moss in Denmark <sup>2)</sup>. Dr. HARTZ's specimens are referred, we think correctly, to the only living species, *Dulichium spathaceum*; our fruits are very different.

<sup>1)</sup> Verhand. Kon. Akad. Wetensch. (Tweede Sectie). Deel XIII, No. 6, fig. 105.

<sup>2)</sup> Dansk. geol. Forening 10, 1904, p. 13.

CLEMEND REID and Mrs ELEANOR M. REID. "On *Dulichium vespiforme*  
sp. nov. from the brick earth of Tegelen."



1. *Dulichium spathaceum* L. C. RICH. Recent, America. 2—8. *Dulichium vespiforme* sp. nov. Fossil, Tegelen. All the figures are magnified to the same scale — 12 diameters.

Proceedings Royal Acad. Amsterdam. Vol. X.