Discussions

The chromatographic evidence shows that the natural presence of varying proportion of minor quantities of higher saturated fatty acids can be easily detected by the concentration of saturated fatty acids by lead salt separation procedure followed by thin-layer chromatography. Any other procedure for concentration of saturated fatty acids would of course lead to similar improvement such as low temperature crystallisation, urea adduct separation[5] or *Bertram*'s oxidation [6–8] subject of course to limitation of particular procedures. Similarly the *Renard*'s procedure[9] which estimates the presence of arachidic and lignoceric acids can be adapted to chromatographic technique such as described. The lead salt separation which also separates trans acids e. g. isooleic acid from hydrogenated fats and high molecular weight monoethenoid acids e. g. erucic acids can be followed by thin-layer chromatography on silver nitrate impregnated plates as described by *B. DeVries*[10] for the detection of such acids.

Acknowledgements

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Hydration of Acetylenic Fatty Acids

By *R. Kannan, M. Sc., Dr. M. W. Roomi, Dr. M. R. Subbaram* and *Dr. K. T. Achaya*

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Hydration of 9,10-stearolic and 13,14-behenolic acids with concentrated sulphuric acid produces almost equal amounts of the corresponding oxo acids. On the other hand 6,7-stearolic acid yields a mixture of 74.5 % of C_7 and 25.5 % of C_6 oxostearic acids, perhaps because of the proximity of the acetylenic bond to the carboxyl group. Undec-10-ynoic acid yields 10-ketoundecanoic acid as the sole product thus exhibiting Markownikoff addition during hydration of a terminal triple bond.

Über die Anlagerung von Wasser an dreifach ungesättigte Fettsäuren

Die Wasser-Anlagerung an 9,10-Stearol- und 13,14-Behenolsäure mit konzentrierter Schwefelsäure liefert nahezu gleiche Mengen der entsprechenden Oxosäuren. Andererseits ergibt 6,7-Stearolsäure ein Gemisch aus 74.5 % C_7- und 25.5 % C_6-Oxostearinsäure, wahrscheinlich weil hier die Dreifachbindung näher an der Carboxylgruppe liegt. Aus 10-Undecinsäure erhält man 10-Ketoundecansäure als einziges Additionsprodukt gemäß der Markownikoff'schen Regel.

La fixation d'eau sur des acides gras à triple liaison

La fixation d'eau sur les acides 9,10-stéarolique et 13,14-béhénolique avec de l'acide sulfurique concentré fournit des quantités presqu'égales des oxoacides (cétoacides) correspondants. Par ailleurs, l'acide 6,7-stéarolique fournit un mélange de 74.5 % d'acide C_7- et 25.5 % d'acide C_6-oxostéarique, vraisemblablement parce qu'ici, la triple liaison se situe plus près du groupe carboxyle. L'acide 10-undécolique fournit exclusivement de l'acide 10-cétoundécanoïque, suivant la règle de Markownikoff.

О присоединении воды к жирным кислотам тройной ненасыщенности.

При присоединении воды к 9,10-стеароловой и 13,14-бегеноловой кислотам с помощью концентрированной серной кислоты образуются почти равные количества соответствующих оксокислот. С другой стороны из 6,7-стеароловой кислоты образуется смесь из 74.5 % C_7- и 25.5 % C_6-оксостеариновой кислоты, вероятно вследствие расположения тройной связи ближе к карбоксильной группе, Из 10-ундециновой кислоты образуется 10-кетоундекановая кислота как единственный продукт присоединения согласно правилу Марковникова.

Freezing-point curves[1, 2], phase diagram[3] and thermal data[4] have so far been used to investigate the hydration of acetylenic fatty acids, more especially 9,10-stearolic acid. *G. M. Robinson* and *R. Robinson*[1] were the first to show that the hydration of 9,10-stearolic acid produces 42.4 % of 9-oxostearic acid, the 10-isomer making up the rest. Later, phase diagram[3] and thermal[4] studies were employed to show that the hydration proceeded in a random attack resulting in an equal mixture of the oxo isomers. *T. F. Grey* et al.[2] extended this investigation to the hydration of behenolic and tariric acids. Making use of freezing-point data they concluded that the hydration product of behenolic acid comprised 72.5 % of 13-oxodocosanoic acid and 27.5 % of the 14-isomer. Their study on the hydration of tariric acid proved to be inconclusive.

Thus all studies on the hydration of acetylenic acids have been based on physical or thermal methods. We report in this communication the use of a chemical degradative approach to the problem such as has been recently used in examination of the course of catalytic hydrogenation of epoxy fatty acids[5, 6]. The acetylenic fatty acids chosen for hydration are 9,10-stearolic, 13,14-behenolic, 6,7-stearolic and undec-10-ynoic acids, providing variety of chain length and double bond position.

The hydration of acids was carried out at room temperature using concentrated sulphuric acid. The resulting keto acids were converted by *J. Baruch*'s procedure[7] of

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oximation, rearrangement of the oxime and subsequent hydrolysis of the amide, to a mixture of mono- and dicarboxylic acids. The dicarboxylic acids were separated from the mono- by steam distillation and quantitated either directly by column chromatography[8] or as their methyl esters by GLC analysis.

The hydration product of 9,10-stearolic acid, m. p. 70°—72° C, was found by column chromatography to yield 47 % mole of sebacic and 53 % mole of azelaic acids. Thus hydration of stearolic acid is an essentially random attack on the triple bond resulting in an almost equal mixture of the oxo acids. Since the centre of unsaturation is as far as 9 carbon atoms away from the carboxyl group, any inductive effect of the latter is not pronounced. This is again evident in the analysis of the hydration product (m. p. 78°—80° C) of behenolic acid. Quantitation by GLC analysis of the mixed dicarboxylic esters showed that the original mixture of the oxo acids was made up of 53.2 % mole of 13-oxodocosanoic and 46.8 % mole of 14-oxodocosanoic acids. This observation is in contradiction to that of *T. F. Grey* et al.[2] who deduced from freezing point data that the hydration product of behenolic acid consisted of 72.5 % of 13- and 27.5 % of 14-oxodocosanoic acids. Our findings for behenolic acid accord with those for stearolic acid, and we believe that the hydration of both acids proceeds in a random fashion.

In the hydration of 6,7-stearolic acid, the resulting product, m. p. 68.5°—70.5° C, was found by similar means to be a mixture of 74.5 % mole of the 7-oxostearic acid and 25.5 % of the 6-isomer. The predominance of the 7-isomer over the 6- could perhaps be due to the inductive effect of the carboxyl group, which is here nearer to the acetylenic linkage than in the earlier examples.

Undecynoic acid, an acetylenic acid with a terminal triple bond, on hydration with sulphuric acid yields a product of m. p. 56°—58° C which was identified as 10-ketoundecanoic acid both by the usual degradation procedure and also by its reduction with sodium borohydride to 10-hydroxyundecanoic acid. This hydroxy acid gave a single spot by a thin-layer chromatographic method which separates even adjacent positional isomers[9]. Thus hydration of a terminal triple bond yields solely the penultimate isomer arising from *Markownikoff* addition[10]. To check the possible role of the carboxyl group, the methyl ester of undecynoic acid, the corresponding alcohol undecynol and undecynyl acetate were all subjected to hydration. The methyl ester gave the same product as undecynoic acid showing hydrolysis of the methyl group during the conditions of hydration. Undecynol gave 10-ketoundecanol, while undecynyl acetate was hydrolysed to the alcohol during hydration to yield 10-ketoundecanol.

Experimental

Full experimental details are given of the studies with 9,10-stearolic acid; these also apply to the other acetylenic acids.

The Acetylenic Acids[11]

To a cooled solution of oleic acid (60 g, I. V. 90.2) in chloroform (150 ml), bromine (30 g) was added dropwise. When the addition was over the mixture was stirred for 3 hrs and left overnight. Distillation of the chloroform, and working up with ether furnished dibromostearic acid (90 g) as a thick viscous liquid.

Dibromostearic acid (90 g), potassium hydroxide (180 g), water (50 ml) and ethanol (750 ml) were taken in a 3-litre round bottomed flask and refluxed on a water bath for 8 hrs. Most of the alcohol was removed under reduced pressure, and the product dissolved in water and acidified with cold dil. sulphuric acid. The brown solid that separated was filtered, washed, air-dried and crystallised from ethanol to give a crystalline white solid, m. p. 44°—45° C.

Analysis	Found	C 76.7 %	H 11.1 %
$C_{18}H_{32}O_2$	Calcd.	C 77.1 %	H 11.5 %

Petroselinic[12] and erucic[13] acids similarly gave 6,7-stearolic (m. p. 50° C) and behenolic (m. p. 56° C) acids as crystalline (ethanol) white solids. Undecenoic acid (b. p. 154°—156° C/ 6.5 mm) on bromination-dehydrobromination afforded undecynoic acid (b. p. 177°—182° C/15 mm) which on recrystallisation from petroleum ether gave the pure acid (m. p. 41° to 42° C).

The purity of the above products was judged by thin-layer chromatography[14].

Hydration Studies

9,10-stearolic acid (14 g) was taken in a conical flask cooled in ice-salt mixture and ice-cold sulphuric acid (100 ml) added dropwise with frequent shaking. When the addition was over, the flask was kept at room temperature overnight. The contents were poured into ice-cold water, washed free of acid and dried to give 13.5 g of a light brown solid (m. p. 70°—72° C), 9(10)-ketostearic acid.

Analysis	Found	C 72.8 %	H 11.1 %
$C_{18}H_{34}O_3$	Calcd.	C 72.4 %	H 11.5 %

The presence of both oxo-isomers was confirmed by the reduction of the hydration product (0.5 g) in methanol (40 ml) with sodium borohydride (0.3 g) at room temperature. The product (0.4 g), m. p. 80°—82° C yielded two spots when examined by TLC[9].

Similarly 6(7)-oxooctadecanoic acid, m. p. 68.5°—70.5° C and 13(14)-oxodocosanoic acid, m. p. 78°—80° C, were prepared from 6,7-stearolic and behenolic acids. Undecynoic acid (9 g) yielded 7.5 g of oxoundecanoic acid (m. p. 54° to 56° C).

6(7)-Oxooctadecanoic acid			
Analysis	Found	C 72.8 %	H 11.2 %
$C_{18}H_{34}O_3$	Calcd.	C 72.4 %	H 11.5 %
13(14)-Oxodocosanoic acid			
Analysis	Found	C 74.1 %	H 12.2 %
$C_{22}H_{42}O_3$	Calcd.	C 74.6 %	H 11.9 %
Oxoundecanoic acid			
Analysis	Found	C 65.7 %	H 10.6 %
$C_{11}H_{20}O_3$	Calcd.	C 66.0 %	H 10.1 %

Oximation

A mixture of 9(10)-oxooctadecanoic acid (9.6 g), hydroxylamine hydrochloride (3.5 g), potassium hydroxide (6.5 g) in water (20 ml) and ethanol (120 ml) was refluxed for 6 hrs on

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a water bath. Ethanol was removed under reduced pressure and the residue poured into a beaker and acidified with dil. sulphuric acid. The mixture on extraction with ether gave a yellow viscous oily liquid.

The oximes of the other acids similarly prepared were yellow viscous oils.

Beckmann Rearrangement

A mixture of oxime from 9,10-stearolic acid (9 g) and sulphuric acid (72 ml) was heated for 1 hr in a 3-necked flask on a water bath with stirring. On pouring the mixture into ice, a brown solid (substituted amide), 7 g, separated.

Hydrolysis of the Amides

The substituted amides (6 g) were dissolved in 30 % potassium hydroxide solution (50 ml) and heated in an autoclave at 180°—200° C for 6 hrs. After cooling, the mixture was acidified with 1 : 1 hydrochloric acid, steam distilled to remove monocarboxylic acids and the residue extracted three times with petroleum ether. The combined petroleum ether extract was washed twice with water to remove any dibasic acids, and the aqueous layer combined with the main aqueous portion and exhaustively extracted with ether to furnish the dicarboxylic acids.

Analysis of Dicarboxylic Acids

a) By Column Chromatography[8]

1) Dicarboxylic acids from 9,10-stearolic acid hydration

The dibasic acid residue (4 mg) in tertiary butanol (1 ml) was transferred to a buffered (18 ml of citrate buffer, 1 M, pH 5.4) silicic acid (100 mesh *Mallinckrodt*, 25 g) column (20 mm diam.). The dicarboxylic acids were eluted with various concentrations of n-butanol in chloroform (100 ml each of 0, 1.5, 3, 5 and 10 % n-butanol in chloroform). Eluates of 5 ml were collected and titrated with 0.01 N alcoholic sodium hydroxide using m-cresol purple indicator solution (0.04 %). The two peaks obtained were identified as those due to sebacic and azelaic acids after co-chromatography with authentic samples. The molar proportion of azelaic and sebacic acids was found to be 53 and 47 % respectively.

2) Dicarboxylic acid from hydration of undecynoic acid

The dicarboxylic acid residue was identified as sebacic acid by column chromatography. Co-chromatography with a pure specimen of sebacic acid showed only one peak.

Methyl undecynoate (100°—102° C/4 mm) gave the same oxoundecanoic acid (m. p. 54°—56° C) as that obtained by hydration of undecynoic acid.

b) By GLC Analysis of the Methyl Esters of Dicarboxylic Acids

GLC analysis of the esters was carried out in an *F & M* Model 720 Unit, provided with thermal conductivity detectors. The stainless steel column (1/16 inch × 2 ft) was packed with 10 % SE 30 on Chromosorb W (40—60 mesh). Temperatures at the injection port and detector block were respectively 250° and 230° C. Programming was done from 120° to 200° C at the rate of 5° C/min. Attenuation was kept at 4; bridge current 120 milliamperes; carrier gas hydrogen; flow rate 60 ml/min.; sample size 2 μl.

1) Dicarboxylic acids from hydration of behenolic acid

The dicarboxylic acid residue was esterified with diazomethane and analysed by GLC. Two peaks for C_{13} and C_{14} dicarboxylic esters were found, corresponding to molar percentages of 46.8 and 53.2 respectively.

2) Dicarboxylic acids from hydration of 6,7-stearolic acid

The esters obtained by diazomethane treatment of the dicarboxylic acid residue were analysed by GLC. Two peaks corresponding to adipate and pimelate emerged, the respective molar percentages being 25.5 and 74.5.

Eine Apparatur zur automatischen Bestimmung des Fließ-/Tropfpunktes von Wachsen nach Ubbelohde*

Von Dr. D. Roemer und Ing. A. Hochreiter, Farbwerke Hoechst AG, Werk Gersthofen

Es wird über eine Apparatur berichtet, welche die Fließ- und Tropfpunkte von je 12 Wachsproben automatisch zu bestimmen gestattet. Ein Thermostat wird programmiert hochgeheizt. Ein Zwölfpunktdrucker zeichnet die Temperaturen der Wachsproben auf. Beim Fließbeginn wird durch die halbkugelförmige Kuppe eine Lichtschranke unterbrochen, deren Kontakte umlegen. Der Schreibereingang wird kurzgeschlossen und damit der Fließpunkt angezeigt. Fällt nun der Wachstropfen, wird der Lichtweg wieder freigegeben, die Kontakte nehmen ihre Ausgangslage ein, und die Tropftemperatur wird registriert.

An Apparatus for the Automatic Determination of Ubbelohde's Flow-/Drop-Point of Waxes

An apparatus for automatically determining the flow and droppoints of twelve wax samples at a time is described. A thermostat is heated by programming to high temperature. A twelvepoint recorder records the temperatures of the wax samples. As soon as the flow begins, a semispherical head breaks the path of the light whose contacts shift. The recorder current is short circuited and with it the flow point is indicated. As the wax drop falls, the light path becomes free again, the contacts acquire their original positions and the droping temperature is registered.

Un appareillage pour la détermination automatique du point d'écoulement/point de goutte des cires suivant Ubbelohde

On décrit un appareillage qui permet la détermination automatique et simultanée du point d'écoulement/point de goutte de 12 échantillons de cire. Un thermostat est programmé à température élevée. Un dispositif à 12 pistes enregistre les températures des échantillons. Le début de l'écoulement provoque, par le dome semi-sphérique, l'interruption d'un relais photoélectrique dont les contacts se rabattent. L'entrée de l'enregistreur est mise en court-circuit, ce qui indique le point d'écoulement. Lorsque la goutte tombe, le trajet lumieux redevient libre, les contacts reprennent leur position initiale et le point de goutte est enregistré.

Аппаратура для автоматического определения точек течения/каплепадения восков по методу Уббелоде.

Описывается аппаратура, с помощью которой возможно автоматическое определение точек течения и каплепадения для 12 соединений соответственно. Нагревание термостата производится программированием. Температура восковых проб записывается двенадцатиточечным печатным аппаратом. При начинающимся течении прерывается световой барьер, контакты которого поворачиваются. Вход самописца замыкается накоротко. Этим регистрируется точка течения. Когда падает капля воска, открывается путь для света, возвращаются контакты в исходное положение, регистрируется температура каплепадения.

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