nol was added, and a solution of 0.5 mole (70.1 g.) of methyl butylpropiolate in 1 mole (32 g.) of absolute methanol added dropwise. The temperature was maintained at 50°. After two hours the mixture was allowed to cool to room temperature, then 10 g. of moderately powdered anhydrous potassium carbonate was added. The sludge was permitted to settle overnight, the supernatant liquid decanted and the excess methanol removed by distillation. The residue was fractionated under vacuum. If, on repeated fractionation, the product did not distill at constant index of refraction, a few crystals of *p*-toluenesulfonic acid were added to the combined fractions which were distilled once again.[12]

Addition of Bromine to Butylpropiolic Acid.—To 0.1 mole (12.6 g.) of butylpropiolic acid dissolved in an equal volume of anhydrous carbon tetrachloride was added, dropwise and with constant shaking, 0.1 mole (16 g.) of bromine dissolved in an equal volume of anhydrous carbon tetrachloride. The flask was kept cool and a drop of bromine in excess served to indicate the endpoint of the reaction. All volatile matter was drawn off and the residue distilled under vacuum.

Action of Hydrogen Chloride on Butylpropiolic Acid.—No reaction occurred when dry hydrogen chloride was bubbled for four hours through a warm solution of 0.048 mole (6 g.) of butylpropiolic acid in twice its volume of anhydrous benzene. Bismuth trichloride (1 g.) was ineffective as a catalyst.

Preparation of Butylpropiolamide.—To a solution of 10 ml. of liquid ammonia in 10 ml. of absolute methanol was added 0.035 mole (5 g.) of methyl butylpropiolate. After standing overnight the volatile matter was evaporated from the residue which solidified on cooling. The amide was purified by repeated crystallization from 95% ethanol.

Preparation of 1-Phenyl-3-butyl-5-pyrazolone.—To 0.035 mole (5 g.) of methyl butylpropiolate was added 0.026 mole (2.8 g.) of phenylhydrazine. The mixture was heated at 130° for four hours. The product was washed with ether and repeatedly crystallized from aqueous alcohol.

Summary

1. *n*-Alkylpropiolic acids may be obtained in satisfactory yield by the consecutive reaction of sodium acetylide with alkyl bromide, sodamide and solid carbon dioxide.

2. Four acids were made in this manner and five derivatives of each prepared and characterized.

NOTRE DAME, INDIANA RECEIVED JANUARY 25, 1941

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Synthesis of 2-Pentadecenoic and 2-Heptadecenoic Acids

BY WALTER M. LAUER, WALTER J. GENSLER AND ELMER MILLER[1]

The synthesis and characterization of the higher unsaturated acids is of importance in connection with the chemistry of fats and oils. A number of unsaturated acids, which have been obtained from natural sources, have not been well characterized and relatively few have been synthesized. The present work describes the preparation of 2-pentadecenoic and 2-heptadecenoic acids by the adaptation of methods previously used. The following series of steps will make clear the method of synthesis which was employed.

$$\mathrm{RCH_2COOH} \xrightarrow{\mathrm{Br_2}} \mathrm{RCHBrCOOH} \xrightarrow{\mathrm{KOH}} \mathrm{RCHOHCOOH} \xrightarrow{\mathrm{Pb(OAc)_4}} \mathrm{RCHO} \xrightarrow[\text{pyridine}]{\mathrm{CH_2(COOH)_2}} \mathrm{RCH{=}CHCOOH}$$

It will be noted that this series of reactions increases the length of the carbon chain by one, and since acids containing an even number of carbon atoms are readily available, the higher α,β-unsaturated acids containing an uneven number of carbon atoms become more accessible.

Measurements of the absorption spectra of 2-pentadecenoic and 2-heptadecenoic acids are indicated in Fig. 1, together with the corresponding data of van der Hulst[2] for 2-octadecenoic acid. The absorption coefficients were determined according to Henri's method described by

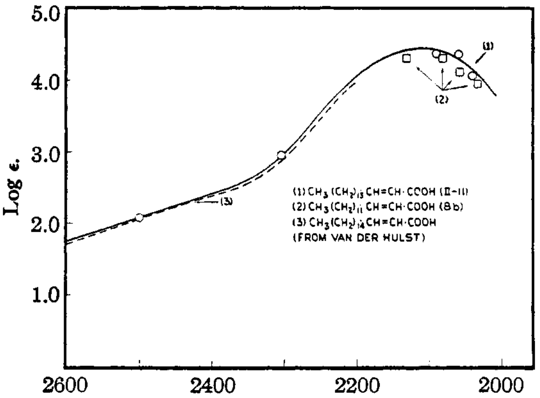

Fig. 1.—Absorption spectra of α,β-unsaturated acids.

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(1) Department of Botany, The University of Minnesota.

(2) Van der Hulst, *Rec. trav. chim.*, **54**, 639–643 (1935).

Belkengren, *et al.*[3] The spectrographic equipment permitted measurements down to 2000 Å. The absorption curves for 2-pentadecenoic and 2-heptadecenoic acids are in good agreement with the values obtained by van der Hulst for 2-octadecenoic acid. The maximum observed at 2100 Å. is the first member of a series which extends below 2000 Å. The scattering of points at 2000 Å. is in part due to spectrographic limitations of the equipment.

Evidence for the structures assigned to the two acids which were synthesized in the present work is supplied by ozonolysis.

Experimental

α-Hydroxymyristic acid was prepared by the action of aqueous potassium hydroxide on α-bromomyristic acid, essentially according to the procedure of LeSueur.[4]

Tridecanal was obtained from α-hydroxymyristic acid by pyrolysis and also by oxidative means.

(a) **Pyrolysis of α-hydroxymyristic acid** (m. p. 80–80.5°) was carried out at 11 mm. using a 10-g. sample in a Claisen flask. Distillation occurred at 153° with a bath temperature of 280°. The distillate was taken up in ether and a small amount of the lactide of α-hydroxymyristic acid (m. p. 81.5–83.5° after recrystallization) was separated by filtration. The ether soluble portion was distilled through a packed column. Tridecanal (2.54 g., b. p. 132–136° at 8 mm.; m. p. approx. 15°) was obtained in 30% yield. On standing for twenty-four hours in a tightly stoppered flask which was kept cold, the aldehyde polymerized.

(b) **Oxidation with Lead Tetraacetate.**—Oxidations were carried out with both α-hydroxymyristic and α-hydroxypalmitic acids. Various experiments were performed using glacial acetic acid or benzene as solvents. The time of action of the oxidizing agent as well as the temperature were changed. The reaction was also carried out with lead tetraacetate that had not been isolated from the acetic acid in which it had been formed. The most satisfactory procedure, which is similar to that of Oeda,[5] follows.

α-Hydroxymyristic acid (10 g.) and pure lead tetraacetate (19 g.) were placed in a flask together with glacial acetic acid (150 ml.). The temperature of the mixture was raised to 65°, at which point reaction occurred with gas evolution. The temperature rose to 70° and the reaction mixture became homogeneous. After three minutes, the action subsided and a small sample on mixing with water gave no precipitate of lead dioxide.

Water (300 ml.) was then added, the solution was cooled, and the top layer of aldehyde was separated. The crude aldehyde, dissolved in ether, was washed with water and dried over sodium sulfate. Distillation under reduced pressure yielded the aldehyde.

Tridecanal (b. p. 150–155° at 28 mm.) was obtained in 55% yield. The tridecanal semicarbazone (m. p. 105.5–106.5°; previously reported 106°) was prepared in the usual way. The 2,4-dinitrophenylhydrazone (m. p. 107–108°) was also prepared.

Pentadecanal (b. p. 155–160° at 12–14 mm.) was prepared in 58% yield by oxidation of α-hydroxypalmitic acid. The pentadecanal semicarbazone melted at 108–109° and the 2,4-dinitrophenylhydrazone of pentadecanal, after crystallization from alcohol, showed a melting point of 107.5–108°.

Both tridecanal and pentadecanal polymerize rapidly. On crystallization from ether, the polymer of tridecanal melted at 61.5–62° and the corresponding polymer of pentadecanal melted at 69–70°. These values agree with those reported by LeSueur.[4]

2-Pentadecenoic acid and 2-heptadecenoic acid were prepared by following the directions which Zaar[6] used for the synthesis of lower homologs. Since the procedure was practically identical in the two cases, only the synthesis of 2-heptadecenoic acid is described.

Pentadecanal (14.5 g.) was mixed with malonic acid (6.66 g.) dissolved in dry pyridine (18.2 ml.) and allowed to stand at room temperature for four days. The flask was closed with a mercury seal. The reaction mixture became homogeneous on the third day. After standing at room temperature for four days, the reaction mixture was heated on the steam-bath for seven hours in order to complete the decarboxylation. Acidification with dilute hydrochloric acid precipitated the unsaturated acid. An ether solution of the acid was then washed with water and dried. The ether solution yielded the acid which was crystallized from acetone.

(a) A yield of 8.6 g. (50%) of the **2-heptadecenoic acid** (m. p. 57.5°) was obtained.

Anal. Calcd. for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02 Found: C, 75.96; H, 12.00.

The **amide** (m. p. 110–110.5°) was prepared from the acid chloride and ammonia.

Anal. Calcd. for $C_{17}H_{33}ON$: C, 76.34; H, 12.44. Found: C, 76.39; H, 12.60.

The **p-bromoanilide** (m. p. 115–116°) also was prepared.

Anal. Calcd. for $C_{23}H_{36}ONBr$: C, 65.39; H, 8.59. Found: C, 65.02; H, 8.44.

(b) **2-Pentadecenoic acid** (m. p. 47.5–48°), prepared in the manner described for the seventeen carbon compound, was crystallized from acetone.

Anal. Calcd. for $C_{15}H_{28}O_2$: C, 74.99; H, 11.76. Found: C, 74.70; H, 11.64.

2-Pentadecenoic Acid Amide (m. p. 111.5–112.5°).

Anal. Calcd. for $C_{15}H_{29}ON$: C, 75.24; H, 12.22. Found: C, 75.15; H, 11.94.

2-Pentadecenoic Acid p-bromoanilide (m. p. 114–114.5°).

Anal. Calcd. for $C_{21}H_{32}ONBr$: C, 63.95; H, 8.18. Found: C, 63.84; H, 8.11.

Ozonolysis of 2-Pentadecenoic Acid and 2-Heptadecenoic Acid.—Ozonolysis was carried out using chloroform as the solvent at the temperature of an ice–salt-bath.

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[3] R. Belkengren, *et al.*, paper presented at the Detroit meeting of the American Chemical Society, Sept. 1940.

[4] LeSueur, *J. Chem. Soc.*, **87**, 1902 (1905).

[5] J. Oeda, *J. Chem. Soc. Japan*, **9**, 8 (1934).

[6] Zaar, *Ber., Schimmel and Co.*, 299 (1929). See also Boxer and Linstead, *J. Chem. Soc.*, 740 (1931).

Decomposition of the ozonide was accomplished in accordance with the method of Whitmore and his coworkers.[7]

The resulting aldehyde was divided into two parts, one of which was converted to the semicarbazone and the other to the 2,4-dinitrophenylhydrazone. The results follow.

(a) The semicarbazone prepared from the aldehyde produced by ozonolysis of 2-pentadecenoic acid melted at 103.5–104.5°. An authentic specimen of tridecanal semicarbazone (m. p. 105.5–106.5°), mixed with the semicarbazone produced by ozonolysis, showed a m. p. of 104.5–105.5°.

(b) The 2,4-dinitrophenylhydrazone derived from the aldehyde produced by the ozonolysis of 2-pentadecenoic acid melted at 107–108°, and showed no melting point depression when mixed with an authentic specimen of the 2,4-dinitrophenylhydrazone of tridecanal.

Anal. Calcd. for $C_{19}H_{30}O_4N_4$: C, 60.28; H, 8.00. Found: C, 60.05; H, 8.07.

(c) Likewise the semicarbazone derived from 2-heptadecenoic acid by ozonolysis was identical with an authentic specimen of the semicarbazone of pentadecanal.

(d) The 2,4-dinitrophenylhydrazone (m. p. 107.5–108°) obtained from the aldehyde produced by the ozonolysis of 2-heptadecenoic acid was analyzed.

Anal. Calcd. for $C_{21}H_{34}O_4N_4$: C, 62.04; H, 8.43. Found: C, 61.81; H, 8.54.

A mixed melting point with an authentic specimen showed no depression.

Summary

A series of reactions has been outlined by which it is possible to convert the higher saturated fatty acids into α,β-unsaturated acids with one more carbon atom. 2-Pentadecenoic and 2-heptadecenoic acids have been prepared in this way starting with myristic and palmitic acids, respectively.

MINNEAPOLIS, MINN. RECEIVED JANUARY 10, 1941

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[7] Whitmore, *et al.*, THIS JOURNAL, **54**, 3710 (1932); **56**, 176 (1934).

[CONTRIBUTION FROM THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH, DIVISION OF ORGANIC CHEMISTRY]

Isolation of a New Phytosterol: Campesterol

BY ERHARD FERNHOLZ AND H. B. MACPHILLAMY[1]

In a previous communication from this Laboratory[2] the possibility that 22,23-dihydrobrassicasterol is present in natural phytosterol mixtures was considered. With this in mind an attempt was made to isolate this sterol from several natural oils. While we have not been able to find any 22,23-dihydrobrassicasterol, we have obtained an isomeric sterol whose properties indicate that it has not before been isolated. Since the isolation was first accomplished from rapeseed oil (*Brassica campestris* L.) we have called it campesterol. Further experiments have shown that it can also be isolated from soya bean oil and wheat germ oil, but it was not found in either cottonseed oil or tall oil.

The sterol was obtained from the acetate residues after the removal of any sterols which gave insoluble acetate tetrabromides. After debromination and hydrolysis of the soluble portion, the free sterol mixture was subjected to repeated recrystallizations from acetone, some fifteen to eighteen being necessary to obtain a substance with a constant melting point. Recrystallizations from ethanol were quite unsatisfactory. Several other methods of purification such as chromatographic adsorption, bromine–digitonin precipitation[3] and attempts at selective hydrolysis of the *p*-toluenesulfonic esters[4] effected no appreciable separation. The pure campesterol as finally obtained had a melting point of 157–158° and $[\alpha]^{23}\text{D}$ −33°.

Titration with perbenzoic acid showed the presence of only one double bond and this fact together with the analytical data of the *m*-dinitrobenzoate indicate an empirical formula of $C_{28}H_{48}O$. It is therefore an isomer of 22,23-dihydrobrassicasterol but a comparison of their constants in Table I shows the difference.

TABLE I

Compound	M. p., °C.	$[\alpha]^{23}\text{D}$
Campesterol	157–158	−33°
Acetate	137–138	−37
Benzoate	158–159	− 8.6
m-Dinitrobenzoate	202–203	− 6.0
22,23-Dihydrobrassicasterol[1]	158	−46
Acetate	145	−46
Benzoate	162	−19
m-Dinitrobenzoate	197.5	−17

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[1] The preparation of this study for publication was carried out by H. B. M. after the untimely death of Dr. Fernholz.

[2] Fernholz and Ruigh, THIS JOURNAL, **62**, 3346 (1940).

[3] Schöenheimer, *Z. physiol. Chem.*, **192**, 80 (1930).

[4] Stoll, *ibid.*, **207**, 147 (1932); **246**, 1 (1937).