

STUDY OF BARBIER-WIELAND DEGRADATION AND ARNDT-EISSERT SYNTHESIS OF LIGNOCERIC ACID*

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SUMMARY

n-Tetracosanoic and *n*-pentacosanoic acids have been prepared from lignoceric acid by Barbier-Wieland degradation and Arndt-Eistert synthesis respectively.

The controversy¹ as to whether lignoceric acid ($C_{24}H_{48}O_2$) possessed a straight chain structure or a branched one was settled when Francis *et al.*,² showed that the X-ray spacings of synthetic *n*-tetracosanoic acid and of lignoceric acid isolated from peanut oil and beechwood tar were identical. The different syntheses³⁻⁶ of lignoceric acid also lent further proof for its structure.

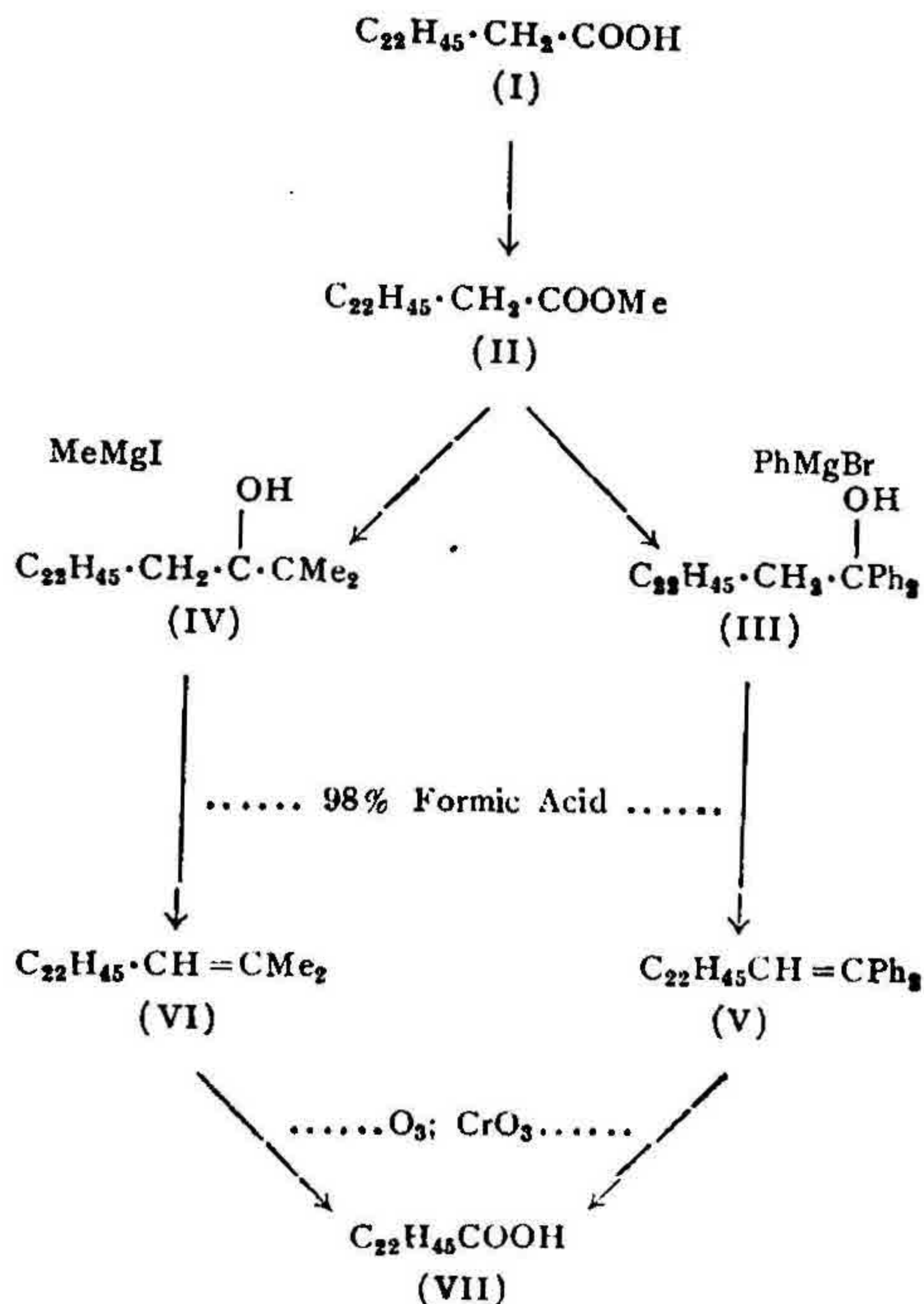
Additional support for the straight chain (normal) structure has now been furnished by preparing the *n*-tri- and penta-cosanoic acids, the lower and higher homologues of lignoceric acid, employing the Barbier-Wieland degradation⁷⁻¹⁰ and Arndt-Eistert synthesis¹¹⁻¹³ respectively on lignoceric acid isolated from *Adenantha pavonina*¹⁴ seed oil.

Grignard reaction with phenyl-magnesium bromide as well as methyl-magnesium iodide on the methyl ester (II) of lignoceric acid (I) using excess¹⁵ of the reagent yielded 1,1-diphenyl-tetracosanol-1 (III), m.p. 68-69° C., and 1,1-dimethyl-tetracosanol-1 (IV), m.p. 61-62° C., which were dehydrated with 98% formic acid to 1,1-diphenyl- Δ^1 -tetracosene (V), m.p. 48-49° C. and 1,1-dimethyl- Δ^1 -tetracosene, (VI), m.p. 51-52° C. respectively.

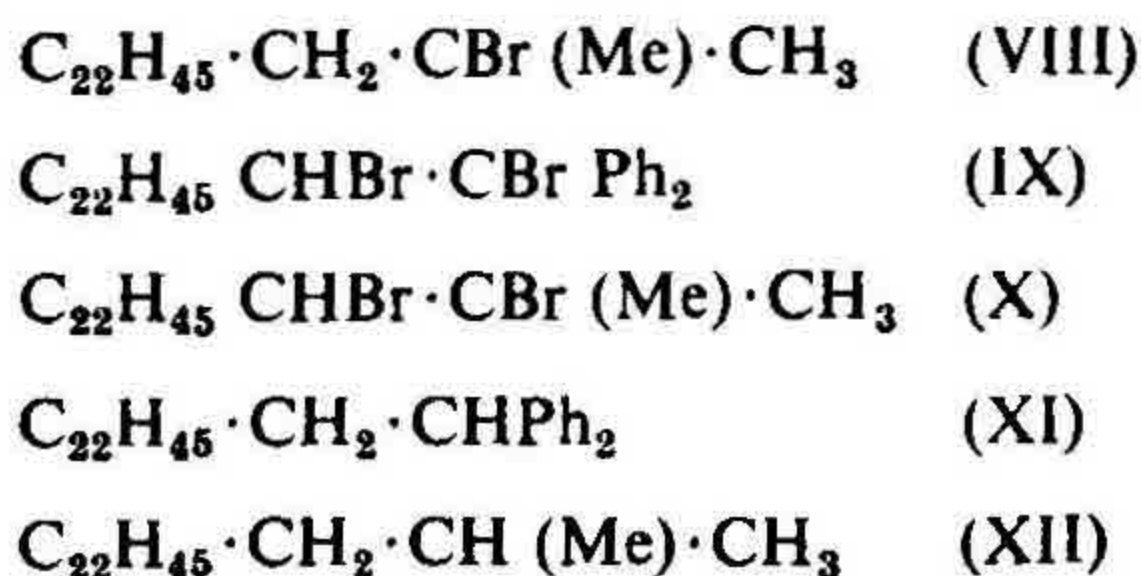
Oxidation of the ethylenic hydrocarbons V and VI with CrO_3 in glacial acetic acid⁹ yielded *n*-tricosanoic acid (VII), m.p. 76-77° C. Ozonolysis of V and VI gave better yields of the acid VII which was isolated from the reaction products through its lead salt.

On reaction with phosphorus-tribromide, carbinol-IV yielded 2-bromo-2-methyl-pentacosane (VIII), m.p. 43-44° C., while carbinol-III yielded mainly the unsaturated hydrocarbon-V. 1,2-Dibromo-1,1-diphenyl-tetracosane (IX), m.p. 72-73° C. and 2,3-dibromo-2-methylpentacosane (X), m.p. 40-42° C. were prepared by the action of bromine on V and VI respectively. Catalytic hydrogenation of

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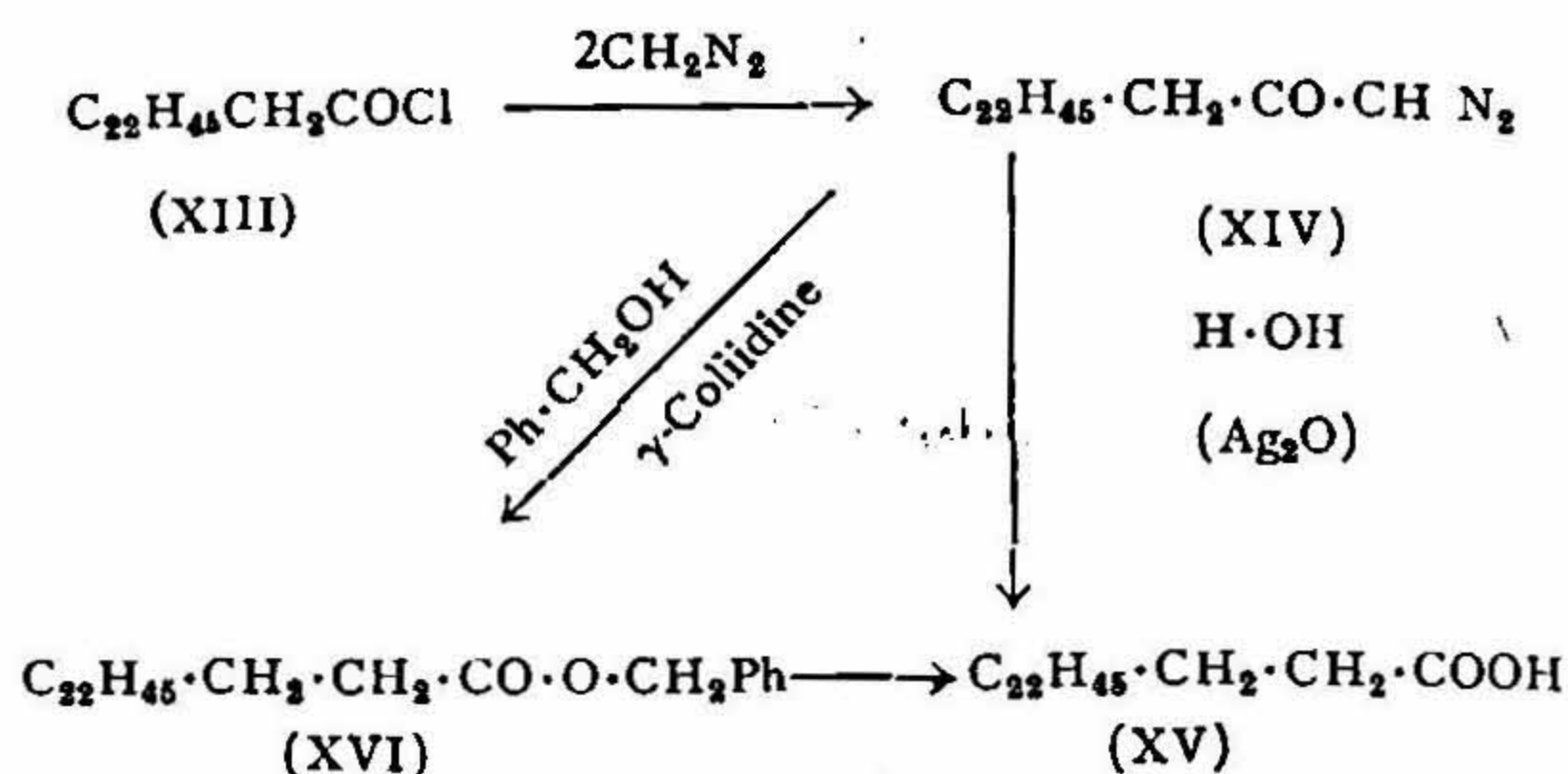


V and VI gave the corresponding saturated hydrocarbons 1,1-diphenyltetracosane (XI), m.p. 52–52.5° C. and 2-methylpentacosane (XII), m.p. 48–49° C.



Ultra-violet absorption spectra in *n*-hexane of 1,1-diphenyl- Δ^1 -tetracosene-V (λ_{max} . 249m μ ; log ϵ 4.185) and 1,1-diphenyltetracosane-XI (λ_{max} . 260 m μ ; log ϵ , 2.825 and λ_{max} . 255 m μ ; log ϵ , 2.8042) helped to distinguish them.

The crude 1-diazopentacosanone-2 (XIV) m.p. 75–77° C. prepared by the action of lignoceroyl chloride (XIII) on excess,^{16, 17} of diazomethane has been converted to *n*-pentacosanoic acid (XV), m.p. 77–79° C. through Wolff rearrangement^{14, 18} using silver oxide as also benzyl-alcohol and γ -collidine.¹⁹ The latter reagents¹⁹ gave a better yield and a purer product.



Pentacosanoic acid has been prepared from lignoceric acid by its conversion to pentacosanenitrile followed by hydrolysis.²¹

EXPERIMENTAL

*Lignoceric acid*² (I).—Powdered seeds of *Adenantha pavonina*, collected from local trees, yielded 23% of fat to carbontetrachloride extraction. The mixed acids (from 100 g. of the fat) yielded after three crystallization from alcohol (300 c.c.) an acid with m.p. 77–78° C. Purification through lead salt and subsequent two crystallizations from benzene gave a product with m.p. 80.5° C.; yield 15 g. (Equivalent: Found, 364.8; $\text{C}_{24}\text{H}_{48}\text{O}_2$ requires 368.0).

The following derivatives were prepared by reacting lignoceroyl chloride (XIII) with appropriate base.

Derivatives of Lignoceric Acid

Derivative	m.p. ° C.	Formula	Nitrogen percentage	
			Found	Requires
Amide	.. 110	$\text{C}_{24}\text{H}_{49}\text{ON}$	4.03	3.82
Anilide	.. 99–100	$\text{C}_{30}\text{H}_{53}\text{ON}$	2.92	3.16
<i>p</i> -Toluidide	.. 104	$\text{C}_{31}\text{H}_{55}\text{ON}$	3.20	3.06
<i>p</i> -Bromoanilide	.. 115–116	$\text{C}_{30}\text{H}_{52}\text{ONBr}$	2.85	2.68
<i>p</i> -Iodoanilide	.. 128–128.5	$\text{C}_{30}\text{H}_{52}\text{ONI}$	2.67	2.46

1,1-Diphenyl-tetracosanol-1 (III).—To Grignard reagent from magnesium (3.84 g.–0.16 mole), bromobenzene (25.12 g.–0.16 mole) and dry ether contained in a 500 c.c. round bottomed flask fitted with a condenser, dropping funnel and guard tube and cooled to 0° C. in an ice-bath, was added methyl lignocerate-II (15.28 g.–0.04 mole) dissolved in anhydrous benzene (100 c.c.), dropwise and

with vigorous swirling of the flask, during 30 minutes. The reaction mixture was left at this temperature for two hours and then refluxed for four hours. The reaction product was poured into ice water (300 c.c.) containing ammonium chloride with vigorous stirring. The ether-benzene layer was separated and the aqueous layer extracted twice with ether. Solvents were removed from the combined extracts and the residue was steam distilled to remove any diphenyl that might have been formed. The product left after steam distillation was crystallized repeatedly from ethanol, and benzene; m.p. 68–69° C.; yield 18.5 g. (Found: C, 86.4; H, 11.31; $C_{38}H_{58}O$ requires, C, 85.37; H, 11.47%).

1,1-Dimethyltetracosanol-1, (IV).—This was prepared in a manner similar to that of III, from methyl iodide (22.7 g.—0.16 m.), dry magnesium (3.9 g.—0.16 m.) and ester-II (15.28 g.—0.04 m.) and crystallized from ethanol and ethyl acetate; m.p. 61–62° C.; yield 14.0 g. (Found: C, 81.53; H, 14.33; $C_{26}H_{54}O$ requires, C, 81.67; H, 14.14%).

1,1-Diphenyl- Δ^1 -tetracosene (V).—The carbinol-III (16.0 g.) was heated on a water-bath for 2 hours with 40 c.c. of 98% formic acid. The reaction mixture, after cooling was poured into water (400 c.c.) and extracted thrice with benzene. The combined benzene extracts were washed with dilute alkali, then with water and dried over calcium chloride. The product from benzene extract was crystallized from alcohol and from acetone; m.p. 48–49° C.; yield 13.0 g. A portion of this product was purified also by adsorption over a column of alumina using petroleum ether (40–60° C.) as eluent; m.p. 48–49° C. (Found: C, 88.51; H, 11.42; $C_{38}H_{56}$ requires, C, 88.52; H, 11.48%).

The hydrocarbon-V decolourised bromine in carbontetrachloride readily, gave a yellow colouration with tetranitromethane and decolourized neutral potassium permanganate solution slowly. The unsaturation of the hydrocarbon expressed in iodine value units,²⁰ as estimated by hydrogenation, was 51.25; ($C_{38}H_{56}$ requires 52.05). The absorption spectrum of V in the ultra-violet region was determined in *n*-hexane using Beckmann's spectrophotometer (model-D.u. 3244 λ_{max} . 249 $m\mu$; $\log \epsilon - 4.185$).

1,1-Dimethyl- Δ^1 -tetracosene (VI).—This was prepared in a manner similar to that of V from IV (8.0 g.) and 98% formic acid (25 c.c.). It crystallised out as a waxy solid from alcohol; m.p. 51° C. It was purified by adsorption over a column of alumina using petroleum ether (40–60° C.) as eluent. The fraction, m.p. 51–52° C. obtained in the above separation was crystallized from petroleum ether, when its melting point was not altered; yield, 6.5 g. (Found: C, 85.75; H, 14.26; $C_{26}H_{52}$ requires, C, 85.72; H, 14.29%).

The hydrocarbon gave a yellow colouration with tetranitromethane, decolourized bromine in carbontetrachloride and decolourized a neutral potassium permanganate solution slowly. The unsaturation of the hydrocarbon expressed in iodine value units was 69.02; $C_{26}H_{52}$ requires, 69.8.

n-Tricosanoic acid (VII).—(A) By *Chromium trioxide* (CrO_3) oxidation⁹ of *V* and *VI*: To the hydrocarbon-*V* (3.0 g.) dissolved in glacial acetic acid (30 c.c.), chromium trioxide (2.0 g. in 5 c.c. water) was added and then warmed at 60–65° C. for four hours. Most of the acetic acid was removed *in vacuo*. The residue was treated with sulphuric acid (10 c.c., 10%) and water (100 c.c.) and extracted four times with benzene. The combined benzene extract was washed thoroughly with water and dried. On removing benzene, a residue (m.p. 60–65° C.; wt. 1.95 g.) was obtained. The acid in this mixture was separated from benzophenone, as its lead salt, which is very sparingly soluble in ethanol at room temperature. The precipitated lead salt was washed with ether to remove the last traces of benzophenone and dried. The acid obtained from the lead salt by decomposition with dilute nitric acid was crystallized from petroleum ether and from benzene; m.p. 76–77° C.; yield, 1.1 g. (Found: C, 77.8; H, 13.03; $\text{C}_{23}\text{H}_{46}\text{O}_2$ requires, C, 77.96; H, 12.99%; equivalent of the acid 351.8; $\text{C}_{23}\text{H}_{46}\text{O}_2$ requires 354.0). Anilide of the acid was prepared in the usual way; m.p. 96–97° C. (Found: N, 3.21; $\text{C}_{29}\text{H}_{51}\text{NO}$ requires, N, 3.26%).

Benzophenone was isolated from the residue left after removal of the acid, as its 2,4-dinitro-phenylhydrazone; m.p. 224–28° C.; m.p. of 2,4-dinitrophenylhydrazone of benzophenone as reported in literature is 229° C.

The oxidation of the hydrocarbon-*VI* (3.0 g.) was carried out with CrO_3 (1.8 g.) as mentioned above and the acid *VII* isolated by lead salt separation melted at 75–77° C.; its anilide; m.p. 95–97° C.

(B) *By ozonolysis of V and VI using Towers' ozonizer*.—A rapid current of ozonized oxygen was passed into a solution of the hydrocarbon-*V* (2 g.) in dry, alcohol-free ethyl acetate (80 c.c.) until (about four hours) a test portion of the solution did not give a yellow colouration with tetranitromethane. The pale yellow solid ozonide obtained after removal of the solvent under vacuum at 30–35° C. was decomposed with water (60 c.c.) by cautiously heating during five hours and standing over-night. The residue obtained from the ether extract of the reaction mixture was subjected to lead salt separation. The acid-*VII* obtained by decomposition of the lead salt was crystallized from petroleum ether and from benzene (m.p. 76–77° C.; yield, 0.75 g.). Benzophenone was identified in the alcohol filtrate.

Ozonolysis of the hydrocarbon-*VI* (1.5 g.) was carried out similarly. After the ozonolysis, acetone was detected by iodoform test in the water in the trap. The isolated acid was crystallized from petroleum ether and benzene; m.p. 76–77° C.; yield, 0.95 g.; m.p. of anilide 96–97° C.

2-Bromo-2-methyl-pentacosane (VIII).—The carbinol-*IV* (2.0 g.) dissolved in anhydrous benzene (50 c.c.) containing a few drops of pyridine, was added slowly with vigorous stirring to phosphorus tribromide (3 c.c.), cooled to 0°. The reaction mixture was left at the same temperature for two hours and then at room temperature over-night. The cooled reaction mixture was slowly added to 100 c.c.

ice-cold water. Repeated extractions with benzene and distillation of the solvent gave VIII which was purified by trituration with a small quantity of petroleum ether and crystallization from ethanol; m.p. 43–44° C. (Found: Br, 17.5; $C_{26}H_{53}Br$ requires, Br, 17.98%).

1,2-Dibromo-1,1-diphenyl-tetracosane (IX).—The bromination of the hydrocarbon-V (2.0 g.) dissolved in anhydrous ether containing a few drops of pyridine was carried out with bromine in ether at –5 to 0° C. The separated bromide-XI was filtered, washed thoroughly with water, with a dilute solution of hypo and finally with water and then dried. This was triturated thrice with small quantities of petroleum ether (40–60° C.) and crystallized from ethanol; m.p. 72–73° C. (Found: Br, 23.8; $C_{36}H_{56}Br_2$ requires, Br, 24.6%).

2,3-Dibromo-2-methylpentacosane (X).—This has been prepared in a manner similar to that of IX from hydrocarbon-VI (2.0 g.); m.p. 40–42° C.; yield, 2.5 g. (Found: Br, 29.5; $C_{26}H_{52}Br_2$ requires Br, 30.54%).

1,1-Diphenyl-tetracosane (XI).—The hydrogenation of hydrocarbon V (1.0 g.) was carried out using A.R. glacial acetic acid (20 c.c.) containing anhydrous ethyl acetate (5 c.c.) as solvent and Adam's platinum oxide as catalyst. The hydrogenation was over in one hour. The catalyst was filtered and the solvents were removed from the filtrate. The product which did not decolourize bromine in carbontetrachloride and did not give a yellow colouration with tetranitromethane, was crystallized from ethanol-ether mixture in white needles and further purified by adsorption over alumina using petroleum ether as eluent; m.p. 52–52.5° C.; yield, 0.6 g. Mixed melting point with a pure sample of V was depressed by 4° C. (Found: C, 88.39; H, 11.60; $C_{36}H_{58}$ requires, C, 88.16; H, 11.84%; λ_{max} . in *n*-hexane – 260 $m\mu$; $\log \epsilon$ – 2.825; and λ_{max} . – 255 $m\mu$; $\log \epsilon$ – 2.8042.)

2-Methyl-pentacosane (XII).—This was prepared in a manner analogous to that of XI from hydrocarbon-VI (1.0 g.); m.p. 48–49° C.; yield, 0.8 g. Mixed melting point with the hydrocarbon-VI was depressed by 3° C. (Found: C, 85.24; H, 14.72; $C_{26}H_{54}$ requires, C, 85.25; H, 14.75%).

Lignoceroyl chloride (XIII).—Lignoceric acid (8.0 g.) treated with thionyl chloride (16 c.c.) and a few drops of pyridine, yielded the acid chloride which was crystallized from dry petroleum ether; m.p. 47–49° C.; yield, 6.0 g.

*1-Diazo-*n*-pentacosanone-2* (XIV).—To an ethereal solution of diazomethane prepared from *N*-nitrosomethylurea (4.5 g.) taken in a 250 c.c. round bottomed flask and cooled below 5° C. a solution of XIII (3.86 g.; 0.01 m.) in dry benzene (30 c.c.) was added during 30 minutes. After standing for two hours at the same temperature and for 12 hours at room temperature, the solvents were removed *in vacuo* at room temperature when the diazoketone was obtained as a pale yellow amorphous solid, m.p. 75–77° C.; yield, 4.0 g. This was used as such for the preparation of *n*-pentacosanoic acid XV.

n-Pentacosanoic acid (XV).—(A) *By rearrangement*^{14, 18} *using silver oxide*.—A solution of the above diazoketone XIV (1.5 g.) in dioxane (50 c.c.) was added dropwise during 30 minutes to a stirred suspension of freshly precipitated silver oxide in water (80 c.c.) containing sodium carbonate (1.5 g.) and sodium thiosulphate (1.0 g.) in a 250 c.c. three-necked flask heated at 70° C. over a water-bath. After addition was over, the contents were heated on the boiling water-bath for three hours. Most of the dioxane was then distilled out and the aqueous portion acidified with dilute nitric acid. Ether extraction yielded the acid-XV which was crystallized from benzene; m.p. 77–79° C.; yield, 0.9 g. (Found: equivalent by silver salt method—377.5; C₂₅H₅₀O₂ has an equivalent of 382.0; C, 78.25; H, 13.01; C₂₅H₅₀O₂ requires, C, 78.53; H, 13.09%).

(B) *Rearrangement*¹⁹ *of diazoketone-XIV to benzyl ester-XVI and hydrolysis of XVI to n-pentacosanoic acid-XV*.—The diazoketone-XIV (2.5 g.), benzyl alcohol (12.5 c.c.) and γ -collidine (12.5 c.c.) were mixed in a r.b. flask (100 c.c.) fitted with a reflux condenser and heated in an oil-bath at 170° C. for 15 minutes, by which time the initial vigorous reaction had slowed down. The cooled contents of the flask were poured into ice-cold dilute hydrochloric acid and extracted with ether. On removing the ether and on drying the residue at 100° C. at 10 mm. pressure, 3.0 g. of the benzyl ester-XVI was obtained.

The above residue (3.0 g.) was refluxed with alcohol (20 c.c.) containing potassium hydroxide (2.0 g.) for four hours. The crystallized potassium salt of the acid was filtered, washed with alcohol and dried. The acid-XV obtained by decomposition of the potassium salt with dilute hydrochloric acid was crystallized from petroleum ether and benzene; acid—pale brown in colour; m.p. 79–80° C.; yield, 2.0 g. (Found: C, 78.25; H, 13.01; C₂₅H₅₀O₂ requires C, 78.53; H, 13.09%; equivalent of the acid 380.1; C₂₅H₅₀O₂ has an equivalent of 382.0).

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