

# STUDIES IN THE NAPHTHALENE SERIES

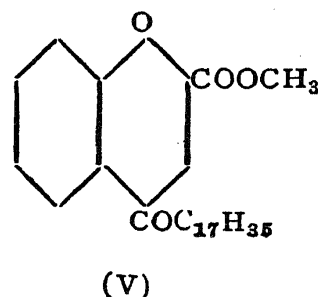
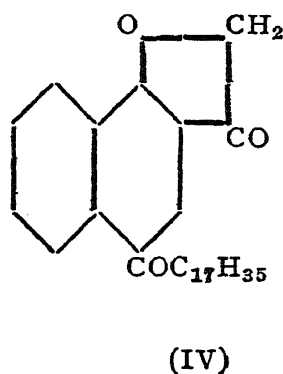
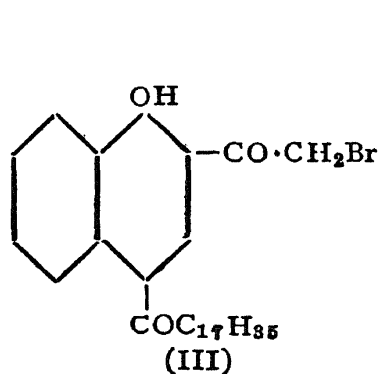
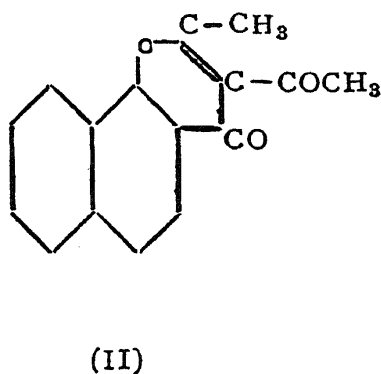
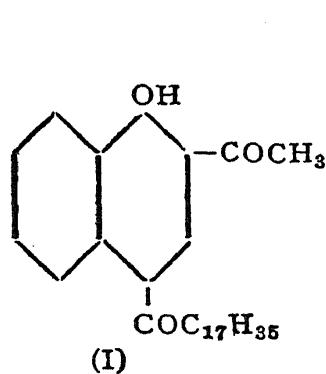
## Part XI. The Condensation of 2-Acetyl-1-naphthol and Methyl 1-hydroxy-2-naphthoate with Stearyl, Palmityl and Lauryl Chlorides

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Received March 8, 1946

IN the course of exploring the best methods of preparing 4-stearyl, -4-palmityl- and 4-lauryl-1-naphthols, we condensed 2-acetyl-1-naphthol with stearyl chloride with a view to converting 4-stearyl-2-acetyl-1-naphthol (I) into 2-methyl-3-acetyl-6-stearyl 1:4- $\alpha$ -naphthopyrone (II) which, on alkaline hydrolysis, would give 4-stearyl-1-hydroxy-2-naphthoic acid, the decarboxylation of which would furnish 4-stearyl-1-naphthol. However, as the alkaline hydrolysis of the pyrone (II) gave the original ketone (I) this synthetic route was blocked. Some interesting properties of the ketone (I) have been studied. Its bromination using one mol or excess of bromine gave 4-stearyl-2-bromacetyl 1-naphthol (III), as hot alkali converted it into 5-stearyl-3-keto- $\alpha$ -naphthacoumaranone (IV). Nitration with one mol or excess of nitric acid gave mainly 4-nitro-2-acetyl-1-naphthol with traces of 4-stearyl-2-nitro-1-naphthol. The Clemmenson reduction gave 4-stearyl-2-ethyl-1-naphthol, as the same compound was obtained by condensing stearyl chloride with



2-ethyl-1-naphthol. On heating its glacial acetic acid or propionic acid solution in presence of anhydrous zinc chloride, the ketone lost the stearyl group. Similar condensations of 2-acetyl-1-naphthol with palmityl and lauryl chlorides and the properties of the resulting products were studied.

The second route adopted for the synthesis of 4-stearyl-1-naphthol was the condensation of methyl-1-hydroxy-2-naphthoate with stearyl chloride with the hope of obtaining 1-hydroxy-2-carbomethoxy-4-stearyl-naphthalene (V), the corresponding carboxylic acid of which was expected to give 4-stearyl-1-naphthol on decarboxylation. No doubt the product (V) was formed in nearly 40% yield, but it was accompanied by an equal amount of 2-stearyl-1-naphthol, while the decarboxylation of the acid gave the final overall yield of 25% of 4-stearyl-1-naphthol. Similar condensations were carried out with palmityl and lauryl chlorides, and 4-palmityl and 4-lauryl-1-naphthols were obtained in 20% yield. Other methods are being explored.

#### EXPERIMENTAL

##### *2-Acetyl-4-stearyl-1-naphthol*

A mixture of 2-acetyl-1-naphthol (12 gm.), stearyl chloride (20 gm.) and zinc chloride (10 gm.) in nitrobenzene (60 c.c.) was kept for 48 hours, decomposed by hydrochloric acid and steam-distilled. The product crystallised from alcohol in white, flat needles, m.p. 75–76° C. (Yield 75%). Its alcoholic solution gave no colouration with ferric chloride. (Found: C, 79.6; H, 9.7.  $C_{30}H_{44}O_3$  requires C, 79.6; H, 9.6 per cent.)

*Kostanecki Reaction with the above ketone and the preparation of 2-methyl-3-acetyl-6-stearyl-1:4-a-naphthopyrone.*—The above ketone (3 gm.), sodium acetate (5 gm.) and acetic anhydride (30 c.c.) were heated in an oil-bath at 175–80° C. for 12 hours. The product was crystallised from alcohol in white, shining needles, m.p. 65–66° C. depressed to 51° C. by the original ketone. (Found: C, 78.5; H, 8.8;  $C_{34}H_{46}O_4$  requires C, 78.7; H, 8.9 per cent.)

*Hydrolysis of the above pyrone.*—The pyrone was reacted with 10 per cent. alkali and the product after hydrolysis was crystallised from alcohol in shining needles, m.p. 75–76° C. undepressed by 2-acetyl-4-stearyl-1-naphthol.

*p-Nitrophenyl-hydrazone* of the ketone was obtained from alcohol in yellowish-red, flat needles, m.p. 260–61° C. (Found: N, 7.2;  $C_{36}H_{49}O_4N_3$  requires N, 7.1 per cent.)

*Clemmensen reduction of the ketone and the preparation of 2-ethyl-4-stearyl-1-naphthol.*—The ketone (2 gm.) with amalgamated zinc (10 gm.)

and hydrochloric acid (60 c.c.) was refluxed for six hours and crystallised from alcohol in small plates, m.p. 71–72° C., depressed to 56–57° C. by the original ketone but undepressed by 2-ethyl-4-stearyl-1-naphthol prepared from stearyl chloride and 2-ethyl-1-naphthol. (Found: C, 82.0; H, 10.7;  $C_{30}H_{46}O_2$  requires C, 82.1; H, 10.6 per cent.)

*p*-Nitrophenyl-hydrazone of 2-ethyl-4-stearyl-1-naphthol gave deep-red crystals, m.p. 130–31° C. (Found: N, 7.5;  $C_{38}H_{51}O_3N_3$  requires N, 7.3 per cent.)

2-Brom-acetyl-4-stearyl-1-naphthol was prepared from the ketone (1.6 gm.) and bromine (0.2 c.c.) in acetic acid (50 c.c.) and crystallised from alcohol in white, small, flat needles, m.p. 72–73° C. The mixed m.p. with the ketone was 53–54° C. (Found: Br, 15.1;  $C_{30}H_{43}O_3$  Br, requires Br, 15.0 per cent.)

Further bromination gave the same product.

*Formation of 5-stearyl-3-keto- $\alpha$ -naphtha coumaranone.*—The solution of the bromo product (1 gm.) in caustic soda (10%; 60 c.c.) was heated for three hours. On acidifying, 5-stearyl-3-keto- $\alpha$ -naphtha-coumaranone, m.p. 66–67° C., depressed to 51–52° C. by the original compound, was obtained. (Found: C, 80.1; H, 9.3;  $C_{30}H_{42}O_3$  requires C, 79.9; H, 9.4 per cent.)

*Nitration of 2-acetyl-4-stearyl-1-naphthol.*—The ketone (1.13 gm.) was nitrated with fuming nitric acid (0.1 c.c.; d. = 1.5) in acetic acid (45 c.c.) and yellow, shining needles. m.p. 160° C. separated out. This was found to be 4-nitro-2-acetyl-1-naphthol by comparison with an authentic sample. The clear acetic acid solution, on dilution with water gave a solid which crystallised from alcohol in shining needles, m.p. 175–76° C., undepressed by the authentic sample, of 2-nitro-4-stearyl-1-naphthol. Nitration of the ketone with excess of nitric acid gave 4-nitro-2-acetyl-1-naphthol.

*Action of acetic acid and propionic acid on 2-acetyl-4-stearyl-1-naphthol in the presence of anhydrous zinc chloride.*—The ketone (1 gm.) was added to the solution of zinc chloride (2 gm.) in acetic acid (100 c.c.) and heated for three hours. The product obtained was 2-acetyl-1-naphthol as identified with an authentic specimen. Similar reaction with propionic acid gave 2-acetyl-1-naphthol.

2-Acetyl-4-palmityl-1-naphthol was prepared from 2-acetyl-1-naphthol (12 gm.), zinc chloride (9 gm.) and palmityl chloride (18 gm.) in nitrobenzene solution (60 c.c.). It was crystallised from alcohol in white flakes, m.p. 95–96° C. (yield 77%). (Found: C, 79.1; H, 9.6;  $C_{28}H_{40}O_3$  requires C, 79.2; H, 9.3 per cent.)

*p*-Nitrophenyl-hydrazone of this ketone gave red, shining flakes, m.p. 255–56° C. (Found: N, 7.6;  $C_{34}H_{45}O_4N_3$  requires N, 7.5 per cent.)

The *Kostanecki Reaction* of the ketone using acetic anhydride gave 2-methyl-3-acetyl-6-palmityl-1:4- $\alpha$ -Naphthapyrone which crystallised from alcohol in white, small plates, m.p. 75–76° C. (Found: C, 78.5; H, 8.7;  $C_{32}H_{42}O_4$  requires C, 78.3; H, 8.6 per cent.)

The pyrone regenerated the original ketone on alkaline hydrolysis.

2-Ethyl-4-palmityl-1-naphthol was obtained by the Clemmenson reduction of the ketone or by the condensation of 2-ethyl-1-naphthol with palmityl chloride. It crystallised from alcohol in small, shining flakes, m.p. 74–75° C. (Found: C, 81.7; H, 10.4;  $C_{28}H_{42}O_2$  requires C, 81.9; H, 10.3 per cent.)

The *p*-nitrophenylhydrazone crystallised from alcohol in red, lustrous flakes, m.p. 135–36° C. (Found: N, 7.6;  $C_{34}H_{47}O_3N_3$  requires N, 7.7 per cent.)

The nitration of the ketone gave mainly 4-nitro-2-acetyl-1-naphthol together with a small quantity of 2-nitro-4-palmityl-1-naphthol.

2-Bromacetyl-4-palmityl-1-naphthol obtained by brominating the ketone with one mol or excess of bromine crystallised from alcohol in small, flat needles, m.p. 67°. (Found: Br, 15.8;  $C_{28}H_{39}O_3$  Br, requires Br, 15.9 per cent.)

5-Palmityl-3-keto- $\alpha$ -naphtha-coumaranone obtained by heating with alkali solution, crystallised from alcohol in small flakes, m.p. 58–59° depressed to 44–45° by the original bromo-compound. (Found: C, 79.3; H, 9.2.  $C_{28}H_{38}O_3$  requires C, 79.5; H, 9.1 per cent.)

2-Acetyl-4-lauryl-1-naphthol prepared in the usual manner using lauryl chloride crystallised from alcohol in white, lustrous flakes, m.p. 60–61° C. (yield = 70 per cent.) (Found: C, 78.1; H, 8.6.  $C_{24}H_{32}O_3$  requires C, 78.2; H, 8.7 per cent.)

Its alcoholic solution did not give any coloration with ferric chloride.

The *p*-nitrophenylhydrazone crystallised from alcohol in yellowish red flakes, m.p. 195–96°. (Found: N, 8.1;  $C_{30}H_{37}O_4N_3$  requires N, 8.3 per cent.)

2-Methyl-3-acetyl-6-lauryl-1:4- $\alpha$ -naphthapyrone crystallised from alcohol in lustrous flakes, m.p. 56–57° depressed to 42°–43° by the original ketone. The alkaline hydrolysis gave back the original ketone. (Found: C, 80.4; H, 8.1.  $C_{28}H_{34}O_4$  requires C, 80.3; H, 8.2 per cent.)

*2-Ethyl-4-lauryl-1-naphthol* obtained by the Clemmenson reduction of the ketone or by condensing 2-ethyl-1-naphthol with lauryl chloride crystallised from alcohol in lustrous plates, m.p. 53–54° depressed to 39–40° by the original ketone. (Found: C, 81.3; H, 9.7.  $C_{24}H_{34}O_2$  requires C, 81.3; H, 9.6 per cent.)

The *p*-nitrophenyl-hydrazone of the above compound crystallised from alcohol in red, lustrous flakes, m.p. 120–21°. (Found: N, 8.7.  $C_{30}H_{49}O_3N_3$  requires N, 8.6 per cent.)

Bromination of the ketone gave only 2-brom-acetyl-4-lauryl-1-naphthol, white flakes from alcohol, m.p. 56–57° C. (Found: Br, 17.9;  $C_{24}H_{31}O_3$  Br, requires Br, 17.8 per cent.)

The bromo-product on alkali treatment gave 5-lauryl-3-keto- $\alpha$ -naphtha cumaranone, white plates from alcohol, m.p. 50–51° C. (Found: C, 78.7; H, 8.1.  $C_{24}H_{30}O_3$  requires C, 78.6; H, 8.2 per cent.)

On nitration, 2-acetyl-4-lauryl-1-naphthol gave 4-nitro-2-acetyl-1-naphthol and 2-nitro-4-lauryl-1-naphthol with one mol of nitric acid.

*Condensation of methyl-1-hydroxy-2-naphthoate with stearyl chloride—  
Preparation of 4-stearyl-1-naphthol*

A mixture of the naphthoic ester (10.5 gm.), anhydrous powdered zinc chloride (7 gm.) and stearyl chloride (15 gm.) in nitrobenzene (60 c.c.) was kept for 48 hours and then decomposed with hydrochloric acid. The nitrobenzene was steam-distilled and the product was treated with 10% alkali which gave alkali-soluble and alkali insoluble compounds. The alkali insoluble product was proved to be 2-stearyl-1-naphthol (yield 40%).

*Methyl-4-stearyl-1-hydroxy-2-naphthoate*, the alkali-soluble product was crystallised from alcohol in white shining needles, m.p. 205–06° C. (yield = 42%). (Found: C, 76.7; H, 9.3.  $C_{30}H_{44}O_4$  requires C, 76.9; H, 9.4 per cent.)

*4-Stearyl-1-hydroxy-2-naphthoic acid*.—The above ester was heated with 10% alkali for four hours. The alkali solution was neutralised, and the product after purifying crystallised from alcohol in white, shining flat needles, m.p. 230–31° C. (yield 90%). (Found: C, 76.7; H, 9.3.  $C_{30}H_{44}O_4$  requires C, 76.9; H, 9.4 per cent.)

*4-Stearyl-1-naphthol*.—The above acid was heated in an oil-bath at 240° C. for four hours. The brown product obtained was purified through alkali and crystallised from alcohol in colourless shining needles, m.p. 160–61° C. (yield 25%). (Found: C, 81.8; H, 10.2.  $C_{28}H_{42}O_2$  requires C, 81.9; H, 10.2 per cent.)

*Preparation of 4-palmityl-1-naphthol.*—A mixture of the naphthoic ester (7.5 gm.), anhydrous zinc chloride (5 gm.) and palmityl chloride (10.5 gm.) in nitrobenzene (60 c.c.) was kept for 48 hours and steam-distilled, after decomposing the product with hydrochloric acid. The product on treatment with alkali gave alkali-insoluble and alkali-soluble compounds. The former was 2-palmityl-1-naphthol (yield 45%) while the latter was methyl-4-palmityl-1-hydroxy-2-naphthoate which crystallised in small plates, m.p. 209–10° C. (yield 40%). Found: C, 76.1; H, 9.2;  $C_{28}H_{40}O_4$  requires C, 76.4; H, 9.1 per cent.)

The naphthoic ester was hydrolysed with alkali to 4-palmityl-1-hydroxy-2-naphthoic acid which crystallised from alcohol in small flakes, m.p. 240–41° C. (Found: C, 76.2; H, 9.0.  $C_{27}H_{38}O_4$  requires C, 76.0; H, 8.9 per cent.)

This on decarboxylation at 250° C. gave 4-palmityl-1-naphthol crystallising from alcohol in small flakes, m.p. 180–81° C. (yield 20%). (Found: C, 81.5; H, 9.7;  $C_{26}H_{38}O_2$  requires C, 81.7; H, 9.9 per cent.)

*Preparation of 4-lauryl-1-naphthol.*—A mixture of the naphthoic ester (7.5 gm.), zinc chloride (5 gm.) and lauryl chloride (9 gm.) in nitrobenzene (60 c.c.) was treated as before and gave alkali-insoluble 2-lauryl-1-naphthol (yield 45%) and alkali-soluble methyl-1-hydroxy-4-lauryl-2-naphthoate (yield 38%). This crystallised from alcohol in white lustrous needles, m.p. 190–91° C. (Found: C, 74.7; H, 8.5.  $C_{24}H_{32}O_4$  requires C, 75.0; H, 8.3 per cent.)

When hydrolysed with alkali, this ester gave 4-lauryl-1-hydroxy-2-naphthoic acid which crystallised from alcohol in small, white needles, m.p. 209–10° C. (Found: C, 74.3; H, 8.2;  $C_{23}H_{30}O_4$  requires C, 74.6; H, 8.1 per cent.)

4-Lauryl-1-naphthol obtained by decarboxylating the above compound at 220° C., crystallised from alcohol in white, lustrous flakes, m.p. 146–47° C. (20% yield). (Found: C, 80.8; H, 9.2.  $C_{22}H_{30}O_2$  requires C, 80.9; H, 9.2 per cent.)

We take this opportunity of thanking Rev. Father A. M. Coyne, S.J., for his kind interest and provision of facilities.

#### SUMMARY

Two methods for the preparation of 4-stearyl, 4-palmityl and 4-lauryl-1-naphthols have been worked out. One did not give the desired product but its intermediate compounds have been studied. The other method gave fairly good yields but not quite satisfactory.