

STUDIES IN NAPHTHALENE SERIES

Part X. The Preparation and the Properties of 1-Stearyl-, 1-Palmityl- and 1-Lauryl-2-Naphthols

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IN continuation of our work in this series, we have studied the preparation and the properties of 1-stearyl-, 1-palmityl-, and 1-lauryl-2-naphthols, and many interesting results have been obtained. 1-stearyl-2-naphthol (I, $R = C_{17}H_{35}$) was readily obtained by the application of the Nencki Reaction to β -naphthol and stearic acid. This hydroxy-ketone which did not give any colouration with alcoholic ferric chloride was characterised by its *p*-nitrophenylhydrazone, and was methylated to 2-methoxy-1-stearyl-naphthalene. The Clemmenson reduction gave exclusively 1-octadecyl-2-naphthol, unaccompanied by any neutral hydroxylic product.

The Kostanecki acylation with acetic anhydride and sodium acetate gave 2-methyl-3-hexadecyl-1:4- β -naphthopyrone (II), the alkaline hydrolysis of which gave the original ketone (I). The condensation of the ketone (I) with ethylbromacetate gave ethyl 1-stearyl- β -naphthoxyacetate (III, $R = C_{17}H_{35}$), which on treatment with sodium ethoxide in absolute alcoholic solution gave 2-carbethoxy-3-heptadecyl- β -naphthacoumarone (IV, $R = C_{17}H_{35}$), the corresponding acid of which on decarboxylation yielded 3-heptadecyl- β -naphthacoumarone (V, $R = C_{17}H_{35}$).

The preparation and properties of 1-palmityl- and 1-lauryl-2-naphthols being similar to those of 1-stearyl-2-naphthol have been fully described in the experimental portion.

EXPERIMENTAL

1-Stearyl-2-naphthol.—An intimate mixture of stearic acid (19 g.), β -naphthol (7 g.) and powdered anhydrous zinc chloride (7 g.) was heated in an oil-bath at 180° C. for three hours. The warm product was poured into water containing some dilute hydrochloric acid, and the precipitated solid was filtered off and washed with water. It was then treated with 5% sodium bicarbonate solution to remove the unreacted stearic acid. The pure product crystallised from alcohol in white lustrous, small needles, m.p.

125-126° C. (depressed to 90-91° by β -naphthol). Its alcoholic solution did not give any colouration with ferric chloride. It was insoluble in dilute caustic soda solution, but soluble in most of the organic solvents (yield = 30 p.c.) (Found: C, 81.7; H, 10.1; $C_{28}H_{42}O_2$ requires C, 81.9; H, 10.2 per cent.)

The *p*-nitrophenylhydrazone was prepared by heating the ketone (0.5 g.) and 4-nitrophenylhydrazine (0.5 gm.) in alcohol (20 c.c.) under reflux for six hours. The hydrazone crystallised in reddish lustrous plates m.p. 260-61° C. (Found: N, 7.5; $C_{34}H_{47}N_3O_3$ requires N, 7.7 per cent.)

1-Stearyl-2-methoxy-naphthalene.—A mixture of 1-stearyl-2-naphthol (1 g.) anhydrous potassium carbonate (2 g.) dimethyl sulphate (5 c.c.) and dry acetone (20 c.c.) was refluxed on water-bath for 6 hours. The solution was filtered and after the removal of acetone the methylated product crystallised from petroleum ether in white, lustrous needles, m.p. 72.73° C. (Found: C, 82.2; H, 10.2; $C_{29}H_{44}O_2$ requires C, 82.1; H, 10.4 per cent.)

Clemmenson reduction of 1-stearyl-2-naphthol-preparation of 1-Octadecyl 2-naphthol.—A mixture of dilute hydrochloric acid (1:1; 35 c.c.), amalgamated zinc (5 g.), and 1-stearyl-2-naphthol (1 g.) dissolved in alcohol (20 c.c.), was heated on sand-bath under reflux for 6 hours. The cold mixture was diluted with water and extracted with ether. The ethereal layer was extracted with alkali, and the alkaline solution when acidified gave a white product which crystallised from alcohol in white plates, m.p. 75-76° C. (Found: C, 84.5; H, 11.3; $C_{28}H_{44}O$ requires C, 84.4; H, 11.1 per cent.)

Kostanecki reaction with 1-stearyl-2-naphthol and formation of 2-methyl-3-hexodecyl-1:4- β -naphthopyrone.—A mixture of 1-stearyl-2-naphthol (1 g.), powdered anhydrous sodiumacetate (1 g.) and acetic anhydride (10 c.c.) was heated in an oil-bath at 175-180° C. for 14 hours and then poured in water. The white product which separated out was crystallised from alcohol in white, lustrous, small needle, m.p. 79-80° C. It was soluble in usual organic solvents and dissolved in concentrated sulphuric acid giving a reddish brown colour. (Found: C, 82.8; H, 9.6; $C_{30}H_{42}O_2$ requires C, 82.9; H, 9.7 per cent.)

Hydrolysis of the pyrone to stearyl-2-naphthol.—The pyrone was boiled with 10 per cent. alkali under reflex for three hours. On acidifying the alkaline solution, a white product was obtained, which crystallised from alcohol in white needles, m.p. 125-126° C. and was identified as stearyl-2-naphthol by mixed m.p.

Condensation of 1-stearyl-2-naphthol with ethyl bromacetate and the preparation of ethyl-1-stearyl-p-naphthoxyacetate. A mixture of 1-stearyl-2-naphthol (4 g.), potassium carbonate (1 g.), ethyl bromacetate (4 c.c.) and dry acetone (35 c.c.) was heated on water-bath under reflux for five hours. On removing acetone, a yellowish brown liquid was obtained which was washed with water, extracted with ether, dried and recovered. It was a pale-yellow, oily liquid b.p. 279° C. (Found: C, 77.4; H, 9.8; $C_{32}H_{48}O_4$ requires C, 77.3; H, 9.7 per cent.)

Hydrolysis of ethyl-1-stearyl- β -naphthoxy acetic acid and the preparation of 1-stearyl- β -naphthoxy acetic acid.—The above ester (1 g.) was boiled with 10% alcoholic alkali (20 c.c.) under reflux for three hours. On removing alcohol and acidifying the alkali solution, a white product was obtained which was crystallised from alcohol in white flakes, m.p. 66–67° C. (Found: C, 76.8; H, 9.6; $C_{30}H_{44}O_4$ requires C, 76.9; H, 9.5 per cent.)

The p-nitrophenyl-hydrazone of the acid prepared by the usual manner crystallised from alcohol in deep-red shining plates m.p. 220–221° C. (Found: N, 6.9; $C_{38}H_{49}O_5N_3$ requires N, 7.0 per cent.)

Action of sodium ethoxide on ethyl-1-stearyl- β -naphthoxy acetate and the preparation of 2-carbethoxy-3-heptadecyl- β -naphtha coumarone.—The β -naphthoxy acetate (5 c.c.) was mixed with sodium ethoxide in absolute alcohol (Na = 2 gm.; alcohol = 40 c.c.) and the solution was heated on water-bath under reflux for three hours. On evaporating the alcohol, a colourless liquid was obtained B.P. 265° C. (Found: C, 80.5; H, 9.8; $C_{32}H_{46}O_3$ requires C, 80.3; H, 9.7 per cent.)

Hydrolysis of the above naphthacoumarone to 2-carboxy-3-heptadecyl- β -naphtha coumarone.—The above ester (3 g.) was boiled with 10 per cent. alcoholic alkali (30 c.c.) for three hours. The solid obtained on the removal of alcohol and acidification from hexane in white, flat needles m.p. 60–61° C. (Found: C, 79.8; H, 9.5; $C_{30}H_{42}O_3$ requires C, 79.9; H, 9.3 per cent.)

Decarboxylation of 2-carboxyl-3-heptadecyl- β -naphtha coumarone to 3-heptadecyl- β -naphtha coumarone.—The above acid was introduced in a flask and heated at 80° C. for four hours. The brown product obtained after washing the residue with dilute alkali crystallised from hexane in white, small needles, m.p. 49–50° C. (Found: C, 85.5; H, 10.5; $C_{29}H_{42}O$ requires C, 85.7; H, 10.4 per cent.)

1-Palmityl-2-naphthol prepared from β -naphthol (7 g.), palmitic acid (16 g.) and zinc chloride (7 g.) crystallised from alcohol in white, small plates, m.p. 115–16° C. (depressed to 85–86° C. by β -naphthol). Its

alcoholic solution gave no colouration with ferric chloride (yield 28 per cent.). (Found: C, 81.8; H, 9.7; $C_{25}H_{38}O_2$ requires C, 81.7; H, 9.9 per cent.)

The *p*-nitrophenylhydrazone of the ketone was crystallised from alcohol in red flakes, m.p. 195–96° C. (Found: N, 8.1; $C_{32}H_{43}O_3N_3$ requires N, 8.1 per cent.)

1-Palmityl-2-methoxy-naphthalene crystallised from petroleum ether in white lustrous soft needles, m.p. 68–69° C. (Found: C, 81.9; H, 10.3; $C_{27}H_{40}O_2$ requires C, 81.8; H, 10.1 per cent.)

1-Hexadecyl-2-naphthol prepared by the clemmenson reduction was crystallised from alcohol in white small plates m.p. 70–71° C. (Found: C, 84.2; H, 10.8; $C_{26}H_{40}O$ requires C, 84.4; H, 10.9 per cent.)

2-Methyl-3-tetradecyl-1:4- β -naphthopyrone was crystallised from alcohol in small, white, lustrous needles, m.p. 73–74° C. It was soluble in usual organic solvents and its solution in concentrated sulphuric acid gave brownish-yellow colouration. (Found: C, 82.9; H, 9.2; $C_{28}H_{38}O_2$ requires C, 82.8; H, 9.4 per cent.) The chromone on hydrolysis with dilute alkali gave the original ketone.

Ethyl-1-palmityl- β -naphthoxy acetate was obtained from the ketone and ethyl brom-acetate as a yellow, oily liquid, b.p. 263° C. (Found: C, 76.8; H, 9.7; $C_{30}H_{44}O_4$ requires C, 76.9; H, 9.5 per cent.)

1-Palmityl- β -naphthoxy-acetic acid prepared by the hydrolysis of ethyl-1-palmityl- β -naphthoxy acetate by alkali was crystallised from alcohol in white lustrous plates, m.p. 64–65° C. (Found: C, 76.5; H, 9.1; $C_{28}H_{40}O_4$ requires C, 76.3; H, 9.2 per cent.)

The *p*-nitrophenylhydrazone of the 1-palmityl- β -naphthoxy acetic acid was obtained from alcohol in red, lustrous, small flakes, m.p. 210–11° C. (Found: N, 7.1; $C_{34}H_{45}O_5N_3$ requires N, 7.3 per cent.)

2-carbethoxy-3-pentadecyl- β -naphtha coumarone prepared from ethyl-1-palmityl- β -naphthoxy acetate and sodium ethoxide was a colourless oily liquid b.p. 245° C. (Found: C, 80.2; H, 9.3; $C_{30}H_{42}O_3$ requires C, 80.0; H, 9.4 per cent.)

2-Carboxy-3-pentadecyl- β -naphtha coumarone obtained by the hydrolysis of 2-carbethoxy-3-pentadecyl- β -naphtha coumarone, was crystallised from petroleum ether in white plates, m.p. 56–57° C. (Found: C, 79.7; H, 9.3; $C_{29}H_{38}O_3$ requires C, 79.6; H, 9.1 per cent.)

3-Pentadecyl- β -naphtha-coumarone prepared by decarboxylating the above acid was crystallised from petroleum ether in white lustrous, small plates,

m.p. 45·46° C. (Found: C, 85·8; H, 10·3; $C_{27}H_{38}O$ requires C, 85·7; H, 10·1 per cent.)

1-Lauryl-2-naphthol prepared from β -naphthol (7 g.) lauric acid (14 g.) and zinc chloride (7 g.) crystallised from alcohol in white, lustrous flakes, m.p. 95–96° C. It was soluble in usual organic solvents (yield 25 per cent.). (Found: C, 80·7; H, 9·3. $C_{22}H_{30}O_2$ requires C, 80·9; H, 9·2 per cent.)

The *p*-nitrophenylhydrazone of the ketone crystallised from alcohol in yellowish-red, small needles m.p. 165–66° C. (Found: N, 9·0; $C_{28}H_{35}O_3N_3$ requires N, 9·1 per cent.)

1-Lauryl-2-methoxy-naphthalene crystallised from petroleum ether in white, flat needles, m.p. 54·55° C. (Found: C, 81·3; H, 9·6; $C_{23}H_{32}O_2$ requires C, 81·2; H, 9·4 per cent.)

1-Dodecyl-2-naphthol crystallised from alcohol in white lustrous, small plates, m.p. 65–66° C. (Found: C, 84·4; H, 10·2; $C_{22}H_{32}O$ requires C, 84·5; H, 10·3 per cent.)

2-Methyl-3-decyl-1 : 4- β -naphthapyrone crystallised from alcohol in white shining small flakes, m.p. 69–70° C. Its solution in concentrated sulphuric acid gave brownish-yellow colouration. (Found: C, 82·4; H, 8·5; $C_{24}H_{30}O_2$ requires C, 82·2; H, 8·6 per cent.) The pyrone on alkaline hydrolysis gave the original ketone.

Ethyl-1-lauryl- β -naphthoxy-acetate was obtained as a straw-yellow, oily liquid, b.p. 230° C., from ethyl brom-acetate and 1-lauryl-2-naphthol. (Found: C, 75·9; H, 8·7; $C_{26}H_{36}O_4$ requires C, 75·7; H, 8·8 per cent.)

1-Lauryl- β -naphthoxy-acetic acid crystallised from alcohol in white, shining plates, m.p. 47–48° C. (Found: C, 74·8; H, 8·6; $C_{24}H_{32}O_4$ requires C, 74·9; H, 8·4 per cent.)

The *p*-nitrophenyl hydrazone of the above naphthoxy acid crystallised from alcohol in red plates, m.p. 200–01° C. (Found: N, 8·3; $C_{30}H_{37}O_5N_3$ requires N, 8·1 per cent.)

2-Carbethoxy-3-undecyl- β -naphtha coumarone was obtained as a colourless oily liquid, b.p. 215° C., by the action of sodium ethoxide on ethyl-1-lauryl- β -naphthoxy acetate. (Found: C, 79·2; H, 3·5; $C_{26}H_{34}O_3$ requires C, 79·1; H, 8·7 per cent.)

2-Carboxy-3-undecyl- β -naphtha-coumarone crystallised from petroleum ether in white small plates, m.p. 42–43° C. (Found: C, 78·8; H, 8·3; $C_{24}H_{33}O_3$ requires C, 78·7; H, 8·2 per cent.)

3-Undecyl- β -naphtha coumarone was crystallised from hexane in white, lustrous plates, m.p. 36-37° C. (Found: C, 85.6; H, 9.5; $C_{23}H_{30}O$ requires C, 85.7; H, 9.4 per cent.)

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SUMMARY

1-Stearyl, 1-palmityl, and 1-lauryl-2-naphthols have been prepared by the Nencki process. These hydroxy ketones were methylated, and reduced by Clemmensen's method. They were subjected to the Kostanecki reaction, and condensed with ethyl bromacetate, to obtain the chromones and coumarones containing these long-chain alkyl groups.