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NEW FATTY ACID ESTERS AND HYDROXY KETONES FROM FRUITS OF *LAURUS NOBILIS*¹

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ABSTRACT.—Three new compounds, isolated from the fruits of *Laurus nobilis*, have been characterized as 10-hydroxyoctacosanyl tetradecanoate [**1**], 1-docosanol tetradecanoate [**3**], and 11-hydroxytriacontan-9-one [**4**].

Laurus nobilis L. (Lauraceae) is a small genus of evergreen hardy trees distributed chiefly in the Mediterranean region and also widely cultivated in Europe and America as an ornamental (1). Both leaves and fruit possess aromatic, stimulant, and narcotic properties (1,2). Its oil has been used as a stimulant in sprains, and in veterinary medicine (3). Leaf oil has also been shown to have fungicidal and bactericidal activity (3).

A number of monoterpene hydrocarbons, ketones, alcohols, and sesquiterpenes have been reported from its leaf and fruit oil (4–9). From the seed, pulp, fruit, and kernal fats, several saturated fatty acids are reported, and the oil in combination with coconut oil and palm kernal oil has been used for external treatment of scaling, psoriasis, eczema, and cold sores (10).

In our present communication we have isolated and characterized two new fatty acid esters and a hydroxyketone.

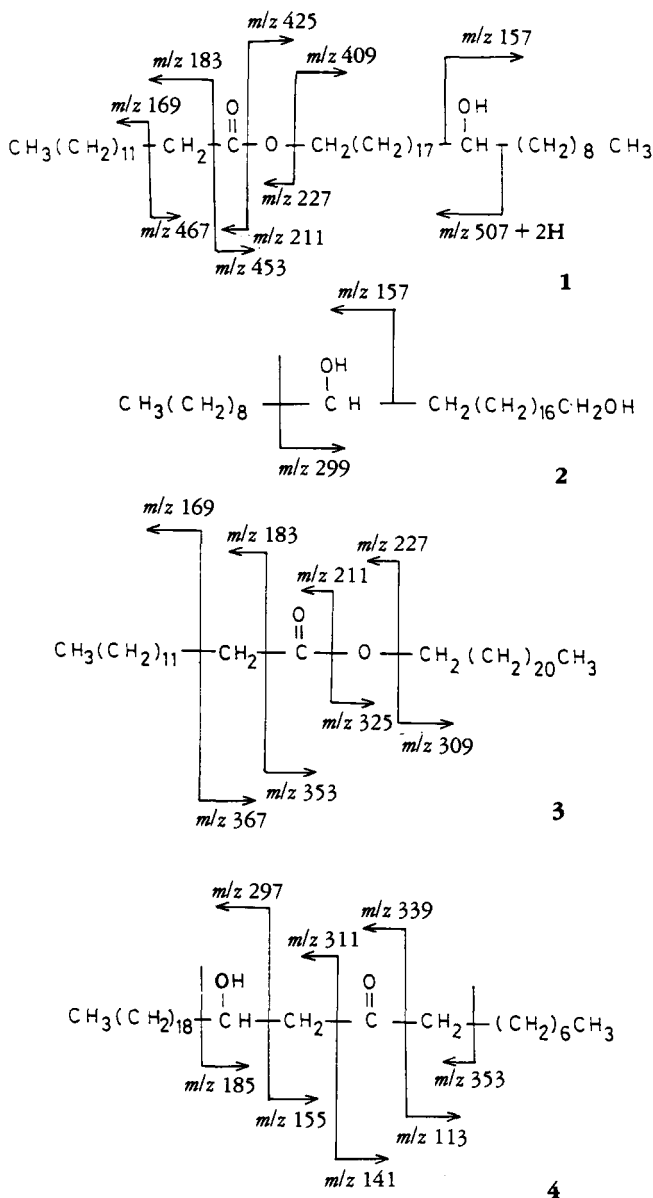
RESULTS AND DISCUSSION

Compound **1**, mp 43–45° had ir absorption bands at 3350 (OH), 1742 (ester carbonyl), and 740 and 725 cm⁻¹ (long chain). It showed an [M]⁺ at *m/z* 636 in its mass spectrum, which together with elemental analysis established the molecular formula as C₄₂H₈₄O₃. The ¹H-nmr spectrum of **1** displayed a triplet at 0.82 which integrated for two terminal methyl groups, a strong signal for methylenes as a singlet at 1.20, a triplet

for a methylene at 2.22 for (-CH₂COO-), and signals between 3.9–4.3 ppm (multiplet) for three protons assigned to an oxymethylene and an hydroxymethine. The ¹³C-nmr spectrum of **1** corroborated the presence of the ester carbonyl (173.0, s), oxymethylene (62.0, t), oxymethine (69.0, d), two methyls (13.5, 22.0 ppm, q), and methylene signals. Compound **1** formed a monoacetate, as indicated by a strong ir absorption band at 1740 cm⁻¹. Its ¹H-nmr spectrum also showed a singlet at 1.98 for acetoxy methyl, and the signal of oxymethine appeared downfield at 4.56 confirming the presence of one secondary hydroxy.

The position of ester carbonyl link in **1** was C-29 from the following facts. Alkaline hydrolysis of **1** afforded an acid, mp 55–58°, having ir bands at 1720 cm⁻¹ (COOH). Its ¹H nmr displayed signals at 0.87 (t, Me) and 1.25 [s, (CH₂)_n] and a triplet at 2.35 assigned to (-CH₂COO). The ms of this acid had an [M]⁺ at *m/z* 228 with characteristic losses of a carboxylic group and a methylene for a long chain fatty acid. It suggested the structure of the acid as tetradecanoic acid, which was finally identified by reported data in the literature (11). The neutral fraction (an alcohol) was a gummy mass that showed a strong ir absorption band at 3400 (OH) cm⁻¹, and its ¹H-nmr spectrum displayed a triplet at 0.80 (one Me), a singlet at 1.25 (CH₂'s), a triplet at 3.20 (-CH₂OH, *J* = 7 Hz), and a multiplet at 4.2 ppm (-CHOH). Its ms showed an [M]⁺ at *m/z* 426, and the fragments at 299 and 157, as indicated in structure **2**, suggested

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the structure of the alcohol at 19-hydroxy-octacosanol [2]. The ^1H -nmr spectrum was also in agreement with this structure.

Combining both acid and alcohol, the structure of this hydroxy ester was deduced as 10-hydroxyoctacosanyl tetradecanoate [1].

Compound 3, a colorless gummy mass, showed $[\text{M}]^+$ at m/z 536 in its mass spectrum, which together with elemental analysis corresponded to the molecular formula $\text{C}_{36}\text{H}_{72}\text{O}_2$. Its ir

exhibited a strong absorption band at 1740 (ester carbonyl), 1460, and 725 and 720 cm^{-1} (long chain), which suggested it to be a long chain ester. Its ^1H nmr displayed two methyls at 0.85 as triplets ($J = 7$ Hz), one oxymethylene at 4.0 as a triplet ($J = 7$ Hz), a strong signal at 1.20 for methylenes, and one triplet at 2.2 ppm for a methylene adjacent to carbonyl groups.

Alkaline hydrolysis of 3 gave an alcohol and an acid. The acid was found to

be identical to the acid obtained on alkaline hydrolysis of compound **1** in all respects.

The alcohol, colorless flakes of mp 68–69°, showed absorptions at 3425 (OH), 1430, and 720 cm^{-1} (long chain) in its ir spectrum. Its ^1H nmr displayed a methyl as a triplet at 0.88 and one oxymethylene as a triplet at 3.65 ppm. The $[\text{M}]^+$ of this alcohol was at m/z 326, corresponding to molecular formula $\text{C}_{22}\text{H}_{46}\text{O}$, and the mass fragments corresponded to a long chain primary alcohol. Finally, this alcohol was identified as 1-docosanol by comparison with literature values (12). On the basis of its hydrolysis products, compound **3** should therefore be 1-docosanol tetradecanoate. The mass spectral fragmentation data were consistent with the proposed structure.

Compound **4**, a gummy mass, gave a positive 2,4 dinitrophenylhydrazine test and showed ir bands at 3325 (broad OH), 1690 (chelated CO), 2900, 2830, 1440, 740, and 725 cm^{-1} . The ms of **4** had an $[\text{M}]^+$ at m/z 452 suggesting the molecular formula $\text{C}_{30}\text{H}_{60}\text{O}_2$. The location of CO at C-22 was deduced from the characteristic α fission ions at m/z 113, 339, 141, and 311 and the β fission ion at m/z 353. The hydroxyl group at C-20 is supported by the significant α fission ions at m/z 185, 155, and 297. As in **1**, the absence of an $[\text{M} - 15]^+$ ion further established the straight chain nature of the compound, and the presence of an $[\text{M} + 1]^+$ ion is characteristic of an asymmetrical ketone (13–15). Following the above observations, compound **4** has been characterized as 11-hydroxytriacontan-9-one [**4**].

Treatment of **4** with $\text{Ac}_2\text{O}/\text{C}_5\text{H}_5\text{N}$ afforded a keto acetate that showed ir bands at 1730 and 1700 cm^{-1} , an acetoxy methyl at 2.01 as a singlet, and an oxymethine at 3.9 as AB pattern ($J = 6.5$ Hz) in its ^1H -nmr spectrum. Its mass spectrum did not show the molecular ion but gave an ion at 434 corresponding to $[\text{M} - \text{HOAc}]^+$.

The mass fragmentation and above data are in full agreement with the assigned structure **4**.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were measured in capillaries on a Toshniwal Apparatus and are uncorrected. Ir spectra were recorded on a 399B Perkin-Elmer and ^1H -nmr spectra on a Varian FT-80A (CDCl_3 , TMS as internal standard) instrument. The mass spectra were measured with a Finnigan Mat instrument and were performed on Merck Si gel plates.

The air-dried fruits of *L. nobilis* were procured from the Kumaon local market in the month of November 1988 and were identified by taxonomists of our Institute. The voucher specimen has been deposited in the herbarium of our Institute. Fruits (2 kg) were extracted with petroleum ether (60–80°) at room temperature and concentrated to one-eighth of the original volume. To this MeOH was added in equal proportions, yielding a colorless flocculent mass. This on SiO_2 tlc showed three spots between R_f 0.30 and 0.40 (CHCl_3), which on cc on SiO_2 , eluting with petroleum ether- CHCl_3 (1:1), (1:2), and (1:3), yielded compounds designated as **3**, **1**, and **4**, respectively.

Compound 1.—Colorless crystalline solid (MeOH/ CHCl_3): mp 43–45°; $[\alpha]_D^{+20}$ ($c = 0.20$, CHCl_3); $\text{C}_{42}\text{H}_{84}\text{O}_3$; ir ν max (KBr) cm^{-1} 3410, 2920, 2850, 1742, 1460, 1375, 1230, 1155, 1110, 1070, 740, 720; ^1H nmr 0.82 (6H, t, $J = 7$ Hz, $2 \times \text{Me}$), 1.20 (CH_2 's, s), 2.22 (2H, t, $J = 7$ Hz), 3.9–4.30 ppm (3H, m, CH_2OCO , CHOH); ^{13}C nmr 13.5 (-Me), 22.0 (-Me), 24.5, 29.0, 29.10, 31.50, 34.0 ($-\text{CH}_2$), 62.0, ($-\text{CH}_2\text{OH}$), 69 (CHOH), 173.0 ppm (ester $\text{C}=\text{O}$); ms (rel. int. %) m/z $[\text{M}]^+$ 636 (3), 618 (5), 608 (2), 590 (8), 536 (10), 507 (4), 497 (3), 479 (2), 454 (3), 451 (3), 437 (2), 425 (2), 409 (2), 310 (2), 297 (2), 256 (5), 183 (3), 157 (2), 155 (10), 97 (25), 85 (30), 61 (40). Found C 78.98, H 13.3; calcd for $\text{C}_{42}\text{H}_{84}\text{O}_3$, C 79.26, H 13.26%.

HYDROLYSIS OF 1.—Compound **1** (100 mg) in EtOH (5 ml) was mixed with 10% alcoholic KOH (5 ml), and the reaction mixture was refluxed for 1 h on the H_2O bath. The reaction mixture was worked up as usual to isolate acidic and neutral fractions.

Acidic fraction.—Mp 55–58°; $\text{C}_{13}\text{H}_{27}\text{COOH}$; $[\text{M}]^+$ 228; ir ν max (neat) cm^{-1} 2960, 2920, 2840, 1720, 1610, 1460, 1330, 1260, 1010, 780, 760; ^1H nmr 0.87 (3H, t, $J = 7$ Hz, Me), 1.25 [s, $(\text{CH}_2)_n$], 2.35 ppm (2H, t, $J = 7$ Hz, CH_2CO); ms m/z 228 (85), 183 (10), 171 (5), 157 (4), 155 (3), 143 (8), 141 (10), 129 (11), 115 (13), 111 (8), 101 (10), 97 (30), 88 (35), 85 (36), 83 (25), 60 (100).

Neutral fraction 2.—Gummy mass: $[\alpha]_D +1.5^\circ$ ($c=0.15$, CHCl_3); $\text{ir } \nu \text{ max (neat) cm}^{-1}$ 3400, 2920, 1600, 1500, 1440, 1400, 1260, 1080, 1010, 900, 810; $^1\text{H nmr}$ 0.80 (3H, t, $J=7$ Hz, Me), 1.25 [s, $(\text{CH}_2)_n$], 2.05 (2H, m), 3.20 (2H, t, $J=7$ Hz, CH_2OH), 4.20 ppm (1H, m, $-\text{CHOH}$); $\text{ms } m/z$ $[\text{M}]^+$ 426 (5), 411 (7), 408 (3), 364 (6), 350 (7), 336 (7), 322 (8), 299 (8), 279 (3), 268 (2), 252 (2), 235 (1), 200 (5), 185 (5), 168 (5), 167 (4), 157 (10), 147 (6), 129 (3), 113 (3), 97 (30), 85 (35), 71 (50), 57 (100).

Monoacetate of 1.—Compound 1 (5 mg) and $\text{C}_5\text{H}_5\text{N}/\text{Ac}_2\text{O}$ were kept overnight at room temperature and worked up as usual to obtain a colorless gummy mass: $[\alpha]_D +3.0$ ($c=0.15$, CHCl_3); $\text{ir } \nu \text{ max (neat) cm}^{-1}$ 2960, 2920, 2860, 1740 (broad), 1460, 1380, 1020, 770, 715, 710; $^1\text{H nmr}$ 1.99 (3H, s, CHOAc), 2.17 (2H, t, $J=7$ Hz), 4.56 ppm (1H, m, $-\text{CHOAc}$).

Compound 3.—Colorless gummy mass: $\text{C}_{36}\text{H}_{72}\text{O}_2$; m/z $[\text{M}]^+$ 536; $\text{ir } \nu \text{ max (neat) cm}^{-1}$ 2920, 2854, 1740, 1470, 1460, 1175, 725, 720; $^1\text{H nmr}$ 0.85 (6H, t, $J=7$ Hz, $2 \times \text{Me}$), 1.20 [s, $(\text{CH}_2)_n$], 2.20 (2H, t, $J=7$ Hz, CH_2CO), 4.0 (2H, t, $J=7$ Hz, OCH_2); $\text{ms } m/z$ 536 (2), 528 (1), 484 (1), 367 (4), 353 (3), 325 (3), 309 (3), 256 (2), 255 (3), 239 (1), 241 (3), 227 (2), 213 (2), 211 (3), 197 (2), 196 (2), 183 (4), 169 (5), 157 (4), 143 (3), 129 (6), 97 (30), 85 (34), 57 (100). Found C 79.8, H 12.95; calcd for molecular formula $\text{C}_{36}\text{H}_{72}\text{O}_2$, C 80.59, H 13.43%.

HYDROLYSIS OF 3.—Compound 3 (10 mg) and alcoholic KOH 5% were mixed together, and the reaction mixture was refluxed for 1 h on the H_2O bath and worked up as usual to get the acid and alcohol.

Acidic fraction.—The acidic fraction was identical to acidic fraction of compound 1.

Alcoholic fraction.—Colorless flakes: mp 68–69; $\text{ir } \nu \text{ max (neat) cm}^{-1}$ 3425, 2915, 1590, 1500, 1430, 1400, 1250, 1080, 1010, 900, 720; $^1\text{H nmr}$ (CDCl_3) 0.88 (3H, t, $J=7$ Hz, Me), 1.25 (s, CH_2 's), 3.65 ppm (2H, t, $J=7$ Hz; CH_2OH); $\text{ms } m/z$ 326 (molecular formula $\text{C}_{22}\text{H}_{46}\text{O}$) (0.5) 308 (5), 297 (3), 255 (3), 241 (2), 199 (2), 185 (1), 143 (15), 101 (18), 99 (20), 97 (40), 83 (50), 55 (100).

Compound 4.—Colorless gummy mass: $[\alpha]_D +25^\circ$ ($c=0.30$, CHCl_3); $\text{C}_{30}\text{H}_{60}\text{O}_2$; m/z $[\text{M}]^+$ 452; $\text{ir } \nu \text{ max (neat) cm}^{-1}$ 3325, 2900, 2830, 2790, 1690, 1440, 1344, 1180, 740, 725; $^1\text{H nmr}$ 0.90 (6H, t, $J=7$ Hz, $2 \times \text{Me}$), 1.25 (s, CH_2), 2.35 (4H, t, $J=7$ Hz, COCH_2), 3.90 ppm (1H, t, $J=7$ Hz, CHOH); $\text{ms } m/z$ 452 (1), 434 (2), 409 (2), 353 (3), 325 (1), 311 (4), 297 (3), 283 (2), 218 (4), 185 (6), 354 (3.5), 169 (10), 155 (8), 156 (8), 141, 122 (5), 125 (6), 113 (10), 97 (30), 83 (50), 69 (60), 57 (100).

Monoacetate of 4.—Compound 4 with $\text{C}_5\text{H}_5\text{N}/\text{Ac}_2\text{O}$ formed monoacetate at room temperature as a gummy mass: molecular formula $\text{C}_{32}\text{H}_{62}\text{O}_3$; $\text{ir } \nu \text{ max (neat) cm}^{-1}$ 1730, 1700; $^1\text{H nmr}$ (CDCl_3) 0.88 (3H, t, $J=7$ Hz, Me), 1.23 (s, CH_2 's), 2.01 (3H, s, OAc), 3.90 ppm (1H, m, $J=6.5$ Hz, CHOAc); $\text{ms } m/z$ $[\text{M}-\text{HOAc}]^+$ 434 (1), 420 (2), 406 (2), 381 (2), 356 (3), 354 (2), 339 (5), 321 (3), 307 (11), 293 (5), 294 (5), 279 (8), 273 (4), 265 (3), 251 (4), 236 (2), 232 (2), 218 (8), 210 (5), 209 (4), 125 (6), 97 (30), 83 (80), 43 (100).

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