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A NEW FATTY ACID FROM *USNEA MERIDENSIS*

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Key Word Index—*Usnea meridensis*; lichen; methyl 3,4-dicarboxy-3-hydroxy-19-oxoeicosanoate; structural determination.

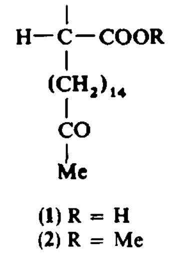
Abstract—The structure of a new fatty acid from *Usnea meridensis* was established by chemical and spectroscopic methods as methyl 3,4-dicarboxy-3-hydroxy-19oxoeicosanoate.

Recently we reported [1] the isolation and structural elucidation of α-(15-hydroxyhexadecyl)itaconic acid from *Usnea aliphatica* Hale. In this paper we report the isolation of a closely related compound from *Usnea meridensis* Hale and assign it structure (**1**) on the following evidence.

Elemental analysis and MS were in agreement with a molecular formula of $C_{23}H_{40}O_8$. The presence of a Me ester was shown by PMR (δ 3.65) and the facile hydrolysis of (**1**) with KOH. The solubility of the compound in $NaHCO_3$ and the formation of a tri Me ester on reaction with CH_2N_2 showed the compound to be a dicarboxylic acid. A positive iodoform reaction and signals at δ 2.1 (*s*, 3H) and δ 2.43 (*t*, 2H, J = 7 Hz) were characteristic of the Me—CO—CH_2— function. IR absorptions at 3520 and 3500 cm^{-1} in the acid and its ester, respectively, were typical of an OH group whose tertiary nature was shown by the absence of an oxy methine proton in the PMR spectrum. The most informative feature of the PMR in Me_2CO-d_6 was an AB quartet centered at δ 2.95 (J = 15 Hz), typical of nonequivalent geminal protons, and a distorted triplet *ca* δ 2.67 (J = 7 Hz). The large pyridine induced solvent shift (*ca* 1 ppm) of these signals showed the methine and methylene protons to be vicinal to the OH group and indicated the presence of a citric acid type function in the molecule. Comparison of this spectrum with that of caperatic acid (**3**), which also contains the citric group, showed the two spectra to be almost identical except that the signal of the terminal Me of (**3**) are replaced by those due to the Me—CO—CH_2— group of (**1**). The spectra of the corresponding diMe esters and hydrolysis products show the same similarity.

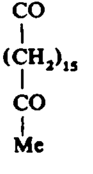
The position of the carbomethoxy group in (**1**) was deduced from oxidation with $NaBiO_3$, a compound which cleaves *vic*-glycols and α-hydroxy acids to aldehydes or ketones [2]. The PMR of the major reaction product (**4**), formed by decarboxylation of the initially produced β-keto acid, showed singlets at δ 3.65 (3H) and δ 3.33 (2H), and a triplet at δ 2.45 (2H, J = 7 Hz) characteristic of the —CH_2—CO—CH_2—CO_2Me group. The crude reaction mixture showed no peaks attributable to the isomeric β-keto ester and, consequently, the position of the carbomethoxy group is as shown in (**1**). Caperatic acid, whose absolute configuration is unknown and whose optical rotation is similar to that of (**1**), has been shown [3] to have the Me ester at the same position. The MS of (**1**) is very similar to that of (**3**) and both compounds show the parent ion at M^+-$2H_2O$ (P^+), typical of a citric acid derivative; diagnostically significant ions occur at *m/e* 377 (P^+-OMe) and *m/e* 350 (P^+-C_3H_6O). An intense ion at *m/e* 184 ($C_8H_8O_5$, 12%) can be accounted for by a McLafferty rearrangement of P^+ to afford (**5**).

The biosynthesis of the lichen fatty acids and lactones is believed [4] to involve the initial formation of either palmitoyl—or myristoyl—SCoA, the α-methylene of which then undergoes aldol type condensation with a C_4-keto acid to form norcaperatic and α-dodecylcitric acid, respectively. These acids in turn serve as precursors for the two series, differing by a C_2H_4 unit, into which the majority of these compounds can be divided. Compound (**1**) is a probable precursor for a third series of which α-(15-hydroxyhexadecyl)itaconic acid is a member.



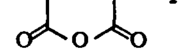
$$\begin{array}{l} CH_2\text{—}COOMe \\ \quad | \\ HO\text{—}C\text{—}COOR \\ \qquad | \\ H\text{—}C\text{—}COOR \\ \qquad | \\ (CH_2)_{14} \\ \quad | \\ CO \\ \quad | \\ Me \end{array}$$

(**1**) R = H
(**2**) R = Me



$$\begin{array}{l} CH_2\text{—}COOMe \\ \quad | \\ CO \\ \quad | \\ (CH_2)_{15} \\ \quad | \\ CO \\ \quad | \\ Me \end{array}$$

(**4**)



(**5**)

EXPERIMENTAL

The lichen was collected on tree trunks in El Valle Grande (alt 3000 m) near the town of Merida (MKF 314 on deposit in the herbarium of this faculty). TLC on Si gel HF_{254} using C_6H_6–dioxane–HOAc (90:25:4) showed usnic (R_f 0.6), norstictic (R_f 0.42) and the fatty acid (R_f 0.1). The fatty acid was detected by spraying with a soln of bromocresol green in EtOH (20 mg in 100 ml; 0.1 N NaOH added sufficient to give a blue colour). Subsequent spraying of the same plate with H_2SO_4 (10%) showed the aromatics with the same colours as previously reported [5]. Ground air-dried thallus (30 g) was successively extracted with petrol, C_6H_6, and Me_2CO in a Soxhlet apparatus. The petrol and Me_2CO extracts afforded usnic and norsticitic acids respectively. Concn of the C_6H_6 soln gave (**1**) as a white solid, mp 125° ($MeOH$–H_2O). $[\alpha]^{25}_{578}$ -15.4 (*c* 0.06, dioxane), $\nu^{KBr}_{max}(cm^{-1})$; 3500, 1730, 1705, 1680, 1250, 1215, 725, 715, PMR 60 Hz (Me_2CO, δ): *ca* 1.4 ($13 \times CH_2$), 2.1 (*s*, 3H), 2.43 (*t*, CH_2, $J = 7$ Hz), 2.63, 2.9, 3.07, 3.33 (AB *q*, 2H, $J = 16$ Hz), 2.65 (*t*, 1H), 3.65 (*s*, 3H), MS (*m/e*): 408 (M^+-$2H_2O$, 3%), 337 (15), 350 (11), 333 (7), 323 (11), 235 (5), 221 (9), 184 (12), 153 (4), 126 (6), 125 (15). (Found: C, 62.31; H, 9.11. $C_{23}H_{40}O_8$ requires: C, 62.12; H, 9%).

DiMe ester of (**1**). A soln of the acid (50 mg) in Me_2CO (20 ml) was treated with excess CH_2N_2 to afford the tri Me ester (**2**) as a white solid, mp 41–44°. $\nu^{KBr}_{max}(cm^{-1})$: 3520, 1750–1715, 1230, 1160; δ ($CDCl_3$): *ca* 1.4 ($13 \times CH_2$), *ca* 2.68 (*m*, 1H), 2.1 (*s*, 3H), 2.4 (*t*, CH_2, $J = 7$ Hz), 2.53, 2.8, 3, 3.33 (AB *q*, 2H, $J = 16$ Hz), 3.66, 3.71, 3.81 (*s*, 3H each). MS (*m/e*): 473 ($M^+ + 1$), 472 (M^+), 414, 413, 381 (413–32, m^* 351.1), 355, 349 (381–32, m^* 319.7), 323 (355–32, m^* 293.9), 101.

Oxidation. The acid **1** (100 mg) in Me_2CO (20 ml) was treated with an $NaBiO_3$ (120 mg) and stirred at room temp. for 4 hr. The resulting clear soln was diluted with H_2O and extracted with Et_2O. The soln was washed with $NaHCO_3$, H_2O, dried and evapd to yield a white solid (72 mg) which contained one major and two minor components. Chromatography on Si gel and elution with $CHCl_3$ gave the major component as white crystals, mp 85° (hexane). $\nu^{KBr}_{max}(cm^{-1})$: 1742, 1705, 1260, 1165; δ ($CDCl_3$): *ca* 1.4 ($13 \times CH_2$), 2.13 (*s*, 3H), 2.45 (*t*, $2 \times CH_2$, $J = 7$ Hz), 3.33 (*s*, 2H), 2.65 (3H).

Hydrolysis. The acid **1** (50 mg) was dissolved in 5% KOH (10 ml) and stirred at room temp. for 4 hr. The soln was acidified and the ppt. recrystallized from $EtOH$–H_2O, mp 132–133°. $\nu^{KBr}_{max}(cm^{-1})$: 3480, 1760 *br*, 1270, 1254, 1238, 728, 715; δ (C_5D_5N): ($13 \times CH_2$), 2.1 (*s*, 3H), 2.39 (*t*, 2H, $J = 7$ Hz), 3.33, 3.6, 3.8, 4.06 (AB *q*, 2H, $J = 16$ Hz), *ca* 3.5 (1H, partly obscured by quartet)

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A NEW TRITERPENOID ALCOHOL FROM *TREMA ORIENTALIS*

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Key Word Index—*Trema orientalis*; Ulmaceae; new pentacyclic triterpenoid alcohol.

Abstract—Substances isolated from the stem-bark of *Trema orientalis* include a new pentacyclic triterpenoid alcohol, for which the name trematol is proposed. From its physical and chemical properties a partial structure is assigned, consisting of an arborane or a migrated hopane skeleton, with a 3β-hydroxyl group and minor modifications in rings D and E.

RESULTS AND DISCUSSION

From the stem-bark of *Trema orientalis*, a reportedly [1] hypotensive plant, the triterpenes simiarenol [2], simiarenone [3], sitosterol and two other triterpenoid alcohols have been isolated. These two alcohols are very similar in polarity and were therefore quite difficult to isolate pure and free of contamination by each other. However, after very careful column chromatography over activated alumina, monitored by TLC and IR, followed by repeated recrystallizations, monitored by mp determinations and TLC, we were able to obtain the less polar alcohol, for which we propose the name trematol, as a pure crystalline solid, in very small quantity. The other, more polar, alcohol was also isolated in a very small