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OXO FATTY ACIDS FROM *CRYPTOCORYNE SPIRALIS* RHIZOMES

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Key Word Index—*Cryptocoryne spiralis*; Araceae; rhizomes; 22-oxononacosanoic acid; 26-oxohentriacontanoic acid.

Abstract—From the rhizomes of *Cryptocoryne spiralis* two new oxo fatty acids, 22-oxononacosanoic and 26-oxohentriacontanoic, have been isolated and their structure established by spectral data and chemical studies.

INTRODUCTION

Rhizomes of *Cryptocoryne spiralis* Fisch. (Araceae) in combination with other drugs are reported to be used [1] in infantile vomiting, cough, fever and abdominal complaints in adults. Recently we have reported two new oxo esters, ethyl 14-oxotetracosanoate and 15-oxoeicosanyl 14-oxoheptadecanoate from the hexane extract of the rhizomes of this plant [2]. In this communication we now report two new oxo acids **1** and **2** from the same source.

RESULTS AND DISCUSSION

Compound **1**, mp 77–78°, had IR absorption bands for a carboxylic acid group [3] at 3300–2500, 1700, 1270 and 920 and for a carbonyl function at 1715 cm^{-1}. The long chain nature of this keto acid was evident by the band at 715 cm^{-1}. The $[M]^+$ ion at *m/z* 452 in the mass spectrum suggested the molecular formula as $C_{29}H_{56}O_3$. The characteristic β-fission ion at *m/z* 60 indicated the presence of a terminal carboxylic acid group in the compound [4]. The position of the carbonyl group at C-22 was obtained from the prominent α and β-fission ions (involving McLafferty rearrangement) at *m/z* 353, 325, 127, 99 and at *m/z* 368, 142 and 84, respectively. A double rearrangement ion at *m/z* 58 indicated the presence of γ H atoms in both the alkyl fragments. The straight chain nature of **1** was supported by the absence of an $[M-15]^+$ ion [5] but the presence of an $[M+1]^+$ ion showed the unsymmetrical nature of the ketone [6, 7]. The ^1H NMR spectrum of **1** showed a triplet for a terminal Me group at δ0.88 (J = 6 Hz). Another triplet, integrated for six protons, was seen at δ2.22 (J = 8 Hz) which could be assigned to three CH_2 groups adjacent to carbonyl and carboxylic acid functions. The rest of the CH_2 groups were seen as a broad singlet at δ1.20.

Reduction of **1** with sodium borohydride yielded a hydroxy acid, mp 81°, which lacked a carbonyl absorption band but showed a band for a hydroxyl group at 3440 cm^{-1}. The $[M]^+$ ion was absent in its mass spectrum, the molecule losing water to give an ion at *m/z* 436 which is usually found in long chain alcohols [8]. The α-fission ions corresponding to the C-22 hydroxyl group were observed at *m/z* 355, 325, 129 and 99. Compound **1** on methylation with dimethyl sulphate and sodium hydrogen carbonate [9] yielded a methyl ester, mp 45°, having IR bands at 1735 (ester CO) and 1720 cm^{-1} (CO). On the basis of the above data this compound was characterized as 22-oxononacosanoic acid (**1**).

Compound **2**, mp 71°, showed an $[M]^+$ at *m/z* 480, which together with elemental analysis, led to the molecular formula of $C_{31}H_{60}O_3$. It had IR and NMR spectra similar to those of **1**. However, it had significant α-fission ions for a CO group at *m/z* 409, 381, 99 and 71 and the ions at *m/z* 424, 114 and 56 were due to β-fissions which established the position of the CO group at C-26. Reduction of **2** with sodium borohydride yielded a hydroxy acid, mp 86–87°. Similar to the hydroxy acid from **1** it lacked an $[M]^+$ but showed an $[M-H_2O]^+$ ion at *m/z* 464. The α-fission ions at *m/z* 411, 381, 101 and 71 were in accordance with the hydroxyl group at C-26. Compound **2** on methylation yielded a methyl ester, mp 43–44°. These data led us to characterize this compound as 26-oxohentriacontanoic acid (**2**).

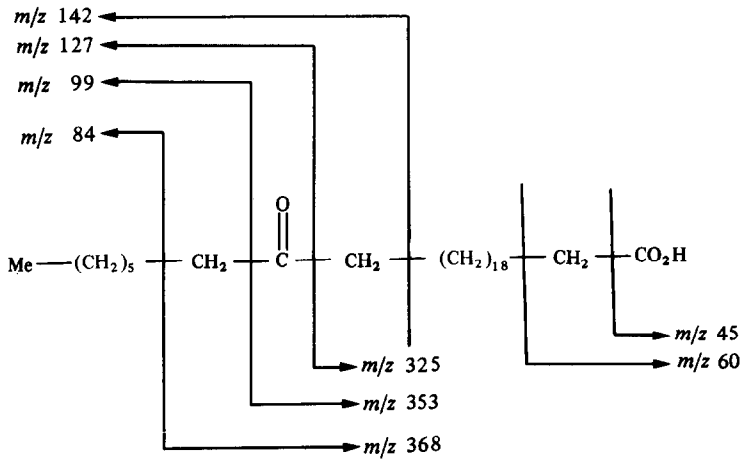
Most natural straight-chain acids, whether saturated or unsaturated, have an even number of C atoms in the molecule [10]. In the even acids oxo groups are rare but are more likely on an odd C atom. Both these observations can be explained in terms of biosynthesis. The two compounds **1** and **2**, now isolated, do not fit in with these generalisations. Odd and branched-chain acids as well as hydroxy-, oxo- and epoxy acids are also reported to exist in nature [10]. Oxo acids occur in milk fat, lipid, oil, epicuticular wax, latex and rhizome. Some examples of unusual oxo acids are:4-oxoeleostearic acid, 4-oxoparinaric acid [10], 3-oxopentadecanoic acid, 4-oxooctadecanoic acid [11], 10,13-dioxo-11-Meoctadecanoic acid [12], 14-oxotetracosanoic and 14-oxoheptadecanoic acid [2].

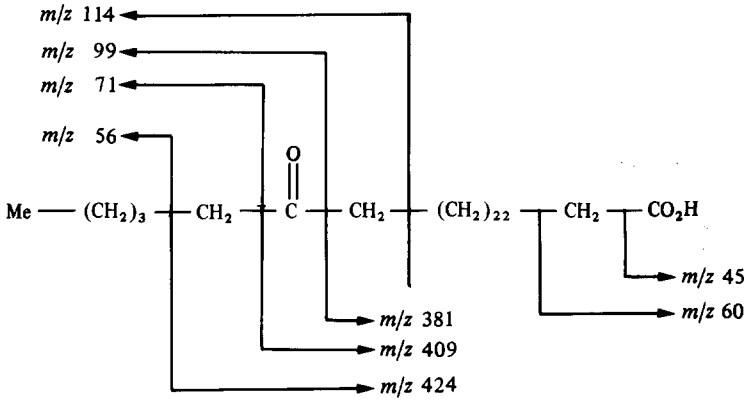
EXPERIMENTAL

Mps are uncorr. IR spectra were recorded in KBr pellets. The 90 MHz NMR spectra were measured in $CDCl_3$ with TMS as int. standard. TLC was performed on silica gel G (BDH) and the spots were visualized by exposure to I_2 vapours.

Plant material was purchased from the local market and a voucher specimen has been deposited in the Botany Department of this institute.

Extraction and isolation of compounds. Air dried and milled rhizomes of *C. spiralis* (2.5 kg) were extracted in the cold with EtOH (7 × 2.5 l.). The EtOH extract was concd to 250 ml, diluted with H_2O (500 ml) and extracted successively with *n*-hexane (6 × 500 ml, 27.85 g), $CHCl_3$ (5 × 500 ml, 2.35 g) and *n*-BuOH





(6 × 200 ml, 21.68 g). The hexane extract (27.85 g) was chromatographed over silica gel (1200 g) and the elution was carried out in hexane, hexane–C_6H_6 (3:1), hexane–C_6H_6 (1:1), hexane–C_6H_6 (1:3), C_6H_6, C_6H_6–$CHCl_3$ (3:1). Fractions collected were 250 ml and each was monitored by TLC. The homogeneity of the compounds was checked on TLC in at least three different solvent systems.

Compound **1** (*22-oxononacosanoic acid*). Earlier fractions (211–233) of C_6H_6 when freed of solvent afforded a residue, 40 mg, mp 77–78° (Me_2CO), R_f 0.58 ($CHCl_3$–MeOH, 4:1). IR ν_{max} cm^{-1}: 2910, 2840, 3300–2500, 1715, 1700, 1455, 1410, 1380, 1270, 920, 715. ^1H NMR: δ0.88 (3H, *t*, J = 6 Hz, Me) 1.20 [$(CH_2)_{23}$, *br s*], 2.22 (6H, *t*, J = 8 Hz, $-\underline{CH_2}-\overset{O}{\overset{\|}{C}}-\underline{CH_2}-$, $-\underline{CH_2}-\overset{O}{\overset{\|}{C}}-OH$). MS *m/z* (rel. int.): 452 $[M]^+$ ($C_{29}H_{56}O_3$, 5), 368(55), 353(9), 325(20), 142(3), 129(100), 127(16), 99(33), 84(33), 73(94), 71(94), 60(94), 58(16), 57(94), 45(9), 43(94).

Reduction of **1**. Compound **1** (20 mg) was dissolved in MeOH (5 ml) and $NaBH_4$ (5 mg) was added gradually. The mixture was then stirred at room temp. for 3 hr. At the end of the reaction it was diluted with H_2O (50 ml), extracted with Et_2O (4 × 50 ml), washed with H_2O (2 × 50 ml) and dried (Na_2SO_4). Removal of solvent gave a residue, mp 81° (Me_2CO). IR ν_{max} (cm^{-1}): 3440, 2920, 2860, 3300–2500, 1705, 1450, 1370, 1270, 1170, 1070, 930 and 715. MS *m/z*: 436 $[M-H_2O]^+$, 355, 325, 129, 99, 60, 57, 43.

Methylation of **1**. Compound **1** (10 mg) in Me_2CO (0.5 ml) was mixed with dry $NaHCO_3$ (4 mg) and Me_2SO_4 (0.1 ml) and the mixture heated gently under reflux for 30 hr. Solvent was then removed under red. pres. H_2O (25 ml) added, extracted with Et_2O (4 × 25 ml) and dried (Na_2SO_4). It was purified by prep. TLC (hexane–C_6H_6, 9:1) to provide a residue, 3 mg, mp 45° (MeOH–Me_2CO). IR ν_{max} (cm^{-1}): 2920, 2840, 1735, 1720, 1450, 1360, 1250, 1155, 720.

Compound **2** (*26-oxohentriacontanoic acid*). Later fractions of C_6H_6 (234–255) on removal of solvent yielded a residue, 500 mg, mp 71° (MeOH), R_f 0.57 ($CHCl_3$–MeOH, 4:1). (Found: C, 77.35; H, 12.00%, $C_{31}H_{60}O_3$ requires: C, 77.50; H, 12.50%). IR ν_{max} (cm^{-1}): 2910, 2840, 3300–2500, 1715, 1705, 1460, 1380, 1270, 1110, 925 and 715. ^1H NMR: δ0.88 (3H, *t*, J = 6 Hz, Me), 1.20 [$(CH_2)_{25}$, *br s*], 2.22 (6H, *t*, J = 8 Hz, $-\underline{CH_2}-\overset{O}{\overset{\|}{C}}-\underline{CH_2}-$, $-\underline{CH_2}-\overset{O}{\overset{\|}{C}}-OH$). MS *m/z* (rel. int.): 480 ($[M]^+$, $C_{31}H_{60}O_3$, 2), 424 (41), 409 (5), 381 (14), 114 (5), 99 (33), 73 (88), 71 (94), 60 (94), 58 (11), 56 (49), 45 (11), 43 (100).

Reduction of **2**. Compound **2** (50 mg) was dissolved in MeOH

(5 ml) and $NaBH_4$ (10 mg) added gradually. The reaction mixture was then stirred at room temp. for 3 hr. After usual work up it afforded a hydroxy acid, 20 mg, mp 86–87° (MeOH). IR ν_{max} (cm^{-1}): 3400, 2910, 2840, 3300–2500, 1700, 1440, 1355, 1260, 1170, 1050, 930 and 715. MS *m/z*: 464 $[M - H_2O]^+$, 411, 381, 101, 71, 60, 57, 43.

Methylation of **2**. To **2** (50 mg) in Me_2CO (2 ml) was added dry $NaHCO_3$ (20 mg) and Me_2SO_4 (0.2 ml) and the mixture refluxed for 30 hr. After usual work up and purification by prep. TLC (hexane–C_6H_6, 9:1), it yielded a Me ester, 10 mg, mp 43–44° (MeOH–Me_2CO). IR ν_{max} (cm^{-1}): 2910, 2840, 1735, 1715, 1460, 1380, 1260, 1165, 1110 and 715.

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