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ALIPHATIC COMPOUNDS FROM *CURCULIGO ORCHIOIDES* RHIZOMES

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Key Word Index—*Curculigo orchioides*, Amaryllidaceae, rhizomes, 21-hydroxytetracontan-20-one, 4-methylheptadecanoic acid

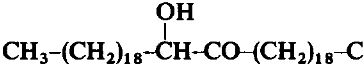
Abstract—21-Hydroxytetracontan-20-one and 4-methylheptadecanoic acid have been isolated from the rhizomes of *Curculigo orchioides* and characterized on the basis of chemical and spectroscopic evidence

INTRODUCTION

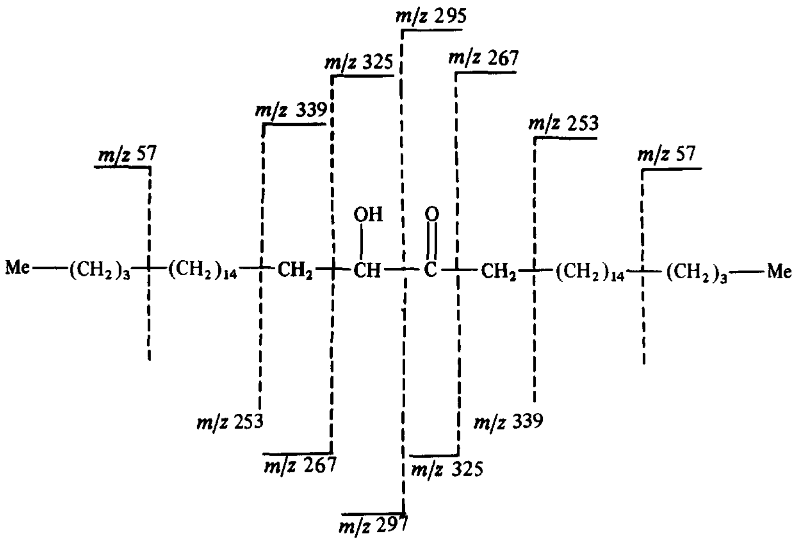
In continuation of our earlier work on the rhizomes of *Curculigo orchioides* [1] we have now isolated two more new aliphatic compounds, a hydroxy ketone and a long chain fatty acid

RESULTS AND DISCUSSION

From the acetone soluble fraction of the *n*-hexane extract of the rhizomes of *Curculigo orchioides* two crystalline compounds C and D were isolated by silica gel chromatography

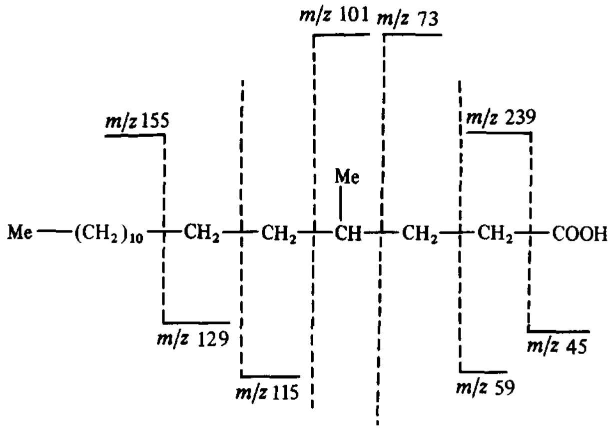
Compound C was obtained as colourless crystals after repeated crystallization from methanol, mp 77–79° The presence of carbonyl function was shown by a positive 2,4-dinitrophenylhydrazine test Elemental analyses and MW determination (592 from mass), led to the analysis of compound C as $C_{40}H_{80}O_2$ It exhibited IR absorption bands at 3450, 2920, 2460, 1725, 730 and 720 cm^{-1} showing the presence of hydroxyl, keto-carbonyl and a long aliphatic chain in the molecule A uniform loss of 14 mu was recorded in mass spectrometric studies further confirming the presence of a long aliphatic chain Furthermore, the absence of a peak corresponding to $[M-15]^+$ in the spectrum confirmed the straight chain nature of the ketone [2] The ^1H NMR spectrum of the compound displayed signals for two terminal methyl groups at δ0 82 (6H, *t*, $J = 7\ 0$ Hz) and 34 methylene groups at δ1 20 (68H, *s*) A two proton broad multiplet appearing at δ1 57 was indicative of one methylene group attached to a carbinolic carbon The appearance of a two proton triplet centred at δ2 24 ($J = 6\ 5$ Hz) suggested the presence of one methylene group α to a carbonyl function A one proton singlet appearing at δ1 94 is attributable to the alcoholic proton On the basis of IR and NMR spectra it is concluded that the compound isolated is an *n*-tetracontane derivative having hydroxyl and keto groupings at vicinal positions in the chain The assignment of the keto group to C-20 and the hydroxyl group to C-21 is deduced by the presence of α-fission ions at *m/z* 295, 297, 267, 325 and β-fission ions at *m/z* 253, 339, 325 and 267 Ion peaks at even number *m/z* 326 and 340 are also present in the mass spectrum which are formed by β-fission to the CO involving McLafferty rearrangement The above results led to the characterization of C as 21-hydroxytetracontan-20-one (**1**) The compound gave a 2,4-dinitrophenylosazone derivative, mp 90–91° Khalique [3] prepared an acyloin,  $CH_3\text{–}(CH_2)_{18}\text{–}\overset{OH}{\overset{|}{C}}H\text{–}CO\text{–}(CH_2)_{18}\text{–}CH_3$ from eicosanoic acid (arachidic acid) He also prepared its 2,4-dinitrophenylasazone derivative The melting point of **1** (77–79°) and its osazone derivative (90–91°) closely resemble those of the C_{40} α-ketol (77–78°) and its osazone derivative (90–92°), respectively Thus compound C was identified as 21-hydroxytetracontan-20-one The natural occurrence of this compound and its spectral properties are reported for the first time

Compound D was obtained as colourless crystals from methanol, mp 59–60° It analysed for $C_{18}H_{36}O_2$ from elemental analyses and MW determination (284, from mass spectrum) Its IR displayed signals between 2940–2850 (broad) and 1710 cm^{-1} which demonstrated the presence of a bonded hydroxyl and a carboxyl



$Me-(CH_2)_3-(CH_2)_{14}-CH_2-CH(OH)-C(=O)-CH_2-(CH_2)_{14}-(CH_2)_3-Me$

1



$Me-(CH_2)_{10}-CH_2-CH_2-CH(Me)-CH_2-CH_2-COOH$

2

carbonyl Usually the band for the bonded hydroxyl (str) in aliphatic acids is hidden by the strong C–H (str) Furthermore, there are seven maxima in the region between 1300–1180 cm^{-1} which are characteristics of spectra of long chain *n*-alkyl compounds in the solid state [4] A systematic difference of 14 mu in a number of ion peaks in the mass spectrum confirms the presence of a long aliphatic chain The ^{1}H NMR spectrum of the compound showed the presence of one terminal methyl group resonating as a triplet centred at δ0 90 (J = 7 5 Hz) A methyl 'distorted doublet' centred at δ0 80 suggested the presence of a methyl group as a side chain The presence of a peak at *m/z* 269 corresponding to $[M - 15]^+$ in the mass spectrum further confirms the above assignment A two proton triplet resonating at δ2 5 (J = 7 0 Hz) is attributed to one methylene unit attached to a carboxyl group A 26 proton broad singlet appearing at δ1 22 showed the presence of 13 methylene units in the molecule The methine proton resonated as a multiplet at δ1 82 From the above, it follows that the compound is heptadecanoic acid with one methyl unit as a side chain The appearance of the base peak at *m/z* 73 in its mass spectrum could be accounted for by assigning the side chain methyl to C-4 An intense peak at *m/z* 60 is explained by fission β to the carboxyl group accompanied by McLafferty rearrangement Thus compound D was identified as 4-methylheptadecanoic acid (**2**) This is the first report of the isolation of this compound from a plant source, although its biosynthesis has been reported earlier by Seyama *et al* [5] from the Harderian gland of the guinea pig and its presence in animal tissues has been characterized by Duncan *et al* [6] and Smith [7]

EXPERIMENTAL

Mps are uncorr IR spectra were recorded in KBr for compound C and in Nujol for D NMR spectra were recorded in $CDCl_3$ at 90 MHz with TMS as int standard MS were recorded on a high resolution spectrometer TLC was carried out on silica gel G and spots were located with I_2 vapour or by spraying with 10% H_2SO_4 followed by heating at 150°

Plant material Collection of rhizomes of *C orchioides* was made from the sandy side area of the Gandak river in the Deoria district (U P), India Rhizomes were washed, air dried and ground to a coarse powder

Extraction and isolation The Me_2CO soluble portion (24 g) of the hexane fraction [1] was chromatographed on a silica gel column The column was eluted with solvents of increasing polarity starting with hexane The progress of elution was monitored by TLC examination of 200 ml fractions Chromatographically similar fractions were combined and solvent removed under red pres

Compound C [*21-hydroxytetracontan-20-one* (1)] Fractions (12–20) of hexane eluate, after recrystallization from MeOH, yielded colourless crystals of compound C (80 mg), mp 77–79° IR ν_{max}^{KBr} cm^{-1} 3450, 2920, 2460, 1725, 1460, 730 and 720, ^{1}H NMR δ0 82 (6H, *t*, J = 7 0 Hz, 2Me), 1 20 (68H, *s*, 34CH$_2$), 1 57 (2H, *m*, $-\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\mathrm{C}\underline{\mathrm{H}}_2-$), 1 94 (1H, *s*, CH–O$\underline{\mathrm{H}}$), 2 24 (2H, *t*, J = 6 5 Hz, $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{C}\underline{\mathrm{H}}_2-$), MS m/z (rel int) 592 $[M]^+$ $C_{40}H_{80}O_2$ (1 5%), 564 $[M-28]^+$ (12 5), 550 $[M-42]^+$ (2 0), 536 $[M-56]^+$ (8 0), 340 $[M-252]^+$ (2 5), 339 $[M-253]^+$ (1 5), 326 $[M-266]^+$ (1 5), 325 $[M-267]^+$ (2 5), 297 $[M-295]^+$ (2 5), 295 $[M-297]^+$ (3 0), 267 $[M-325]^+$ (2 5), 253 $[M-339]^+$ (2 5), 127 $[M-465]^+$ (6 0), 57 $[M-535]^+$ (100)

Osazone derivative of C To a soln of 20 mg of compound C and 20 mg of NaOAc in 1 ml of H_2O, was added a soln of 40 mg of 2, 4-dinitrophenylhydrazine in 1 ml of HOAc acid On heating the soln for 30 min at 100° the osazone was formed The soln was cooled, diluted with H_2O and filtered to yield the solid derivative Recrystallized from MeOH, mp 90–91°

Compound D [*4-methylheptadecanoic acid* (2)] Compound D was obtained from fractions (3–10) of the hexane–C_6H_6 (3 1) eluate as colourless crystals from MeOH (70 mg), mp 59–60° IR ν_{max}^{Nujol} cm^{-1} 2940, 2850, 1710, 1312, 1295, 1279, 1285, 1235, 1203, 1188, 730 and 720, ^{1}H NMR δ0 90 (3H, *t*, J = 7 5 Hz, Me), 0 80 (3H, *d*, J = 5 5 Hz, Me), 1 22 (26H, *s*, 13CH$_2$), 1 82 (1H, *m*, $>$CH–), 2 5 (2H, *t*, J = 7 0 Hz, –C$\underline{\mathrm{H}}_2$–COOH), MS m/z (rel int) 284 $[M]^+$ $C_{18}H_{36}O_2$ (10%), 269 $[M-15]^+$ (2 5), 256 $[M-28]^+$ (82 0), 255 $[M-29]^+$ (2 5), 239 $[M-45]^+$ (2 5), 227 $[M-57]^+$ (5 0), 199 $[M-85]^+$ (15 0), 129 $[M-155]^+$ (45 0), 115 $[M-169]^+$ (15 0), 101 $[M-183]^+$ (11 0), 99 $[M-185]^+$ (10 0), 73 $[M-211]^+$ (100 0), 60 $[M-224]^+$ (83 0), 59 $[M-225]^+$ (3 5)

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