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AN OXYGENATED BRANCHED-CHAIN FATTY ACID AND ITS METHYL ESTER FROM *LAVANDULA GIBSONII**

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Key Word Index—*Lavandula gibsonii*, Labiatae, fatty acid, 3-acetoxy-16-methylheptadecanoic acid

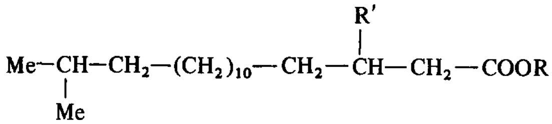
Abstract—The isolation and characterization of 3-acetoxy-16-methylheptadecanoic acid and methyl 3-acetoxy-16-methyl heptadecanoate as well as sitosterol and 5-hydroxy-6,7,4′-trimethoxyflavone from *Lavandula gibsonii* is described

INTRODUCTION

Lavandula gibsonii (*L perrottetii*) a medium sized shrub with clusters of tiny violet flowers is found on the hills of the Western Ghats of Maharashtra (India) An acetone extract of this plant has been reported to exhibit ovicidal, antifeedant, antigonadal, oviposition-deterrent and repellent properties against different insect species [1] This paper reports the isolation of a new oxygenated branched fatty acid and its methyl ester from the acetone extract of the whole plant The acid has been characterized as 3-acetoxy-16-methylheptadecanoic acid (**1**) by spectral and chemical methods

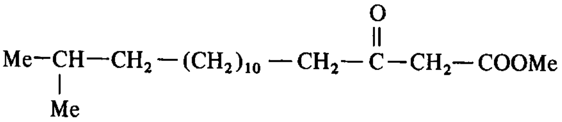
RESULTS AND DISCUSSION

Air-dried whole plant material of *L gibsonii* was powdered and extracted with acetone Chromatographic separations of the extract gave sitosterol, 5-hydroxy-6, 7, 4′-trimethoxyflavone, an ester **1a** and a new fatty acid **1** Compound **1**, a viscous liquid, analysed for $C_{20}H_{38}O_4$ (M^+,342) and contained one acetoxy group, [IR (1745, 1235 cm^{-1}), ^1H NMR δ1 98 (3H, *s*) 5 01 (1H, *br*)] and one isopropyl group [^1H NMR δ0 85 (6H, *d*), 1 56 (1H, *br*)] On alkaline hydrolysis with methanolic potassium hydroxide, **1** yielded a hydroxy acid, **2** As expected the C$\underline{H}$OAc broad signal in the original compound was shifted upfield to δ3 9 in the methyl ester (**2a**) of the hydroxy acid and the IR spectrum showed a band at 3500 cm^{-1} The mass spectrum of **2a** (M^+ 314) showed diagnostic ions at *m/z* 296 $[M-H_2O]^+$, 283$[M-OMe]^+$, 103 $[CH(OH)CH_2COOMe]^+$ and 223 $[296-CH_2COOMe]^+$ which indicate the presence of a hydroxyl group on the β carbon atom This assignment is confirmed by the spectral properties of the corresponding keto ester, **3**, obtained by Jones' oxidation of **2a** A two proton doublet at δ2 33 in **2a** is shifted to 3 30 as a sharp singlet in the ^1H NMR spectrum of **3**, which also exhibited a two proton triplet at 2 48 ($-C\underline{H}_2COCH_2COOMe$) and its IR showed bands at 1700 and 1750 cm^{-1} arising from the $COCH_2COOMe$ group The mass spectrum displayed significant peaks at *m/z* 312 $[M]^+$, 239 $[M-CH_2COOMe]^+$, 101 $[COCH_2COOMe]^+$ and 73 $[CH_2COOMe]^+$ which supports the presence of a keto group in a β-position to the ester group



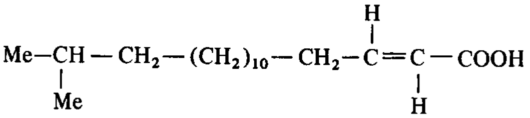
$\mathrm{Me{-}\underset{\underset{Me}{|}}{CH}{-}CH_2{-}(CH_2)_{10}{-}CH_2{-}\overset{\overset{R'}{|}}{CH}{-}CH_2{-}COOR}$

1 R = H, R′ = OAc
1a R = Me, R′ = OAc
2 R = H, R′ = OH
2a R = Me, R′ = OH
5 R = R′ = H



$\mathrm{Me{-}\underset{\underset{Me}{|}}{CH}{-}CH_2{-}(CH_2)_{10}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}COOMe}$

3



$\mathrm{Me{-}\underset{\underset{Me}{|}}{CH}{-}CH_2{-}(CH_2)_{10}{-}CH_2{-}\overset{\overset{H}{|}}{C}{=}\underset{\underset{H}{|}}{C}{-}COOH}$

4

Compound **1a** on refluxing with sodium ethoxide in ethanol produced a mixture of α, β- and β, γ-unsaturated acids from which *E*-2-16-methylheptadecenoic acid (**4**) (mp 62–63 °) could be crystallized in pure form Catalytic hydrogenation of the mixture of olefinic esters yielded on hydrolysis the known 16-methylheptadecanoic acid (16-methylmargaric acid) (**5**) [2] Thus the structure of **1** was confirmed as 3-acetoxy-16-methylheptadecanoic acid

The neutral compound obtained from the acetone extract could be distilled at 195–200 °/0 6 mm $C_{21}H_{40}O_4$, M^+,356 Its ^1H NMR and IR spectra clearly indicated it to be methyl 3-acetoxy-16-methylheptadecanoate (**1a**)

EXPERIMENTAL

General All mps are uncorr IR were run in Nujol ^1H NMR was recorded at 60 MHz in CCl_4 or $CDCl_3$ containing 1 % TMS

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*NCL communication No 3012

Chemical shifts are expressed in ppm (δ) MS were measured at 70 eV

Extraction and isolation The whole plant (roots, stem, leaves and flowers) was air dried and powdered The powdered material (1 kg) was extracted with Me_2CO (41 × 3) at room temp and the solvent removed under vacuum to afford 48 g of a highly viscous dark material The Me_2CO extract (202 g) was chromatographed on a Si gel column, which was eluted successively with C_6H_6 (fraction A), C_6H_6–Me_2CO (9 1) (fraction B), Me_2CO (fraction C) and MeOH (fraction D) Fraction B (104 g) was chromatographed (Si gel, 1 5 kg) using a C_6H_6–Me_2CO gradient solvent system The following fractions were collected B_1 (C_6H_6) (26 g), B_2 (C_6H_6 and C_6H_6–Me_2CO, 98 2) (20 g), B_3 (C_6H_6–Me_2CO gradually increasing the proportion of Me_2CO up to 15 %) (35 g), B_4 (Me_2CO) (10 g) Fraction B_2 was further chromatographed and early fractions (C_6H_6) contained sitosterol (0 46 g), mp 138–139 °, mmp Later fractions (C_6H_6) gave yellow crystalline 5-hydroxy-6,7,4′-trimethoxyflavone (1 1 g) recrystallized (petrol, C_6H_6), mp 188–190 ° (lit 189–190 ° [3] and 187–190° [4]) ^{1}H NMR ($CDCl_3$) δ 3 66 (3H, *s*, OCH_3), 3 82 (3H, *s*, OCH_3), 3 88 (3H, *s*, OCH_3), 6 35 (1H, *s*, H-3), 6 38 (1H, *s*, H-8), 6 81 (2H, *d*, $\underline{H}$-3′, $\underline{H}$-5′, $J = 11$ Hz), 7 63 (2H, H-2′, H-6′, $J = 10$ Hz) MS m/z (rel int) 328 $[M]^+$ (100 %), 313 (86), 299 (14), 285 (11 8), 282 (11), 181 (18), 153 (23), 143 (6 6), 133 (12), 89 (5 8)

Fraction B_3 was rechromatographed and early fractions (C_6H_6) gave a viscous yellow liquid, methyl 3-acetoxy-16-methylheptadecanoate (**1a**) (0 55 g), bp 195–200 °/0 6 mm, Found C, 71 16, H, 11 35, calc, for $C_{21}H_{40}O_4$ C, 70 74, H, 11 31 % IR ν_{max} cm^{-1} 2800, 1750, 1471, 1445, 1375, 1250, 1040 ^{1}H NMR (CCl_4) δ 0 88 [6H, *d*, $(C\underline{H}_3)_2CH$–, $J = 7$ Hz], 1 26 [24H, *br s*, chain–$(C\underline{H}_2)_{12}$–], 1 56 (1H, *br*, $Me_2C\underline{H}$–), 1 93 (3H, *s*, $-\underset{|}{C}HOCOC\underline{H}_3$), 2 38 (2H, *d*, $-C\underline{H}_2COOMe$, $J = 7$ Hz), 3 56 (3H, *s*, $-COOC\underline{H}_3$), 5 00 (1H, *br*, $-\underset{|}{C}\underline{H}OCOMe$) MS m/z (rel int) 356 $[M]^+$ (30 5), 341 (8 4), 325 (74), 313 (90), 297 (100), 264 (93 8), 240 (61), 222 (56), 180 (26), 128 (43) Later fractions (C_6H_6) gave a dark viscous liquid (14 5 g) which on keeping in petrol for 10 hr yielded a white solid (2 g, not investigated further) The filtrate was separated by treating with aq $NaHCO_3$ in the usual manner to form a neutral portion and the acid, 3-acetoxy-16-methylheptadecanoic acid (**1**) (7 g), pale yellow viscous liquid, which could not be distilled $C_{20}H_{38}O_4$, IR ν_{max} cm^{-1} 3300, 2900, 1745, 1712, 1450, 1235, 1025 ^{1}H NMR (CCl_4) δ 0 85 [6H, *d*, $(C\underline{H}_3)_2CH$–, $J = 7$ Hz], 1 3 [24H, *br s*, chain–$(C\underline{H}_2)_{12}$–], 1 56 (1 H, *br*, Me_2–$C\underline{H}$–), 1 98 (3H, *s*, $-\underset{|}{C}HOCOC\underline{H}_3$) 2 5 (2H, *d*, $-C\underline{H}_2COOH$, $J = 6$ Hz), 5 01 (1H, *br*, $-\underset{|}{C}\underline{H}OCOH_3$), 8 5 (1H, *br*, $-COO\underline{H}$, disappeared on addition of D_2O) MS m/z (rel int) 342 $[M]^+$ (4 8), 299 (24), 282 (100), 264 (87), 239 (28), 222 (87 3), 196 (45), 180 (26), 151 (65), 125 (52)

Deacetylation of **1** Acetoxy acid (**1**) (0 23 g) was refluxed with K_2CO_3 (0 11 g) in H_2O (1 ml) and MeOH (20 ml) for 3 hr The solvent was removed under red pres and the residue diluted with H_2O The aq soln was acidified with dilute HCl and extracted with Et_2O The Et_2O extract was washed with H_2O, dried (Na_2SO_4) and evaporated The residue (0 2 g) was crystallized from petrol 3-*Hydroxy*-16-*methylheptadecanoic acid* (**2**) was obtained as white shining plates, mp 70–71 ° Found C, 71 6, H, 12 28 Calc for $C_{18}H_{36}O_3$ C, 71 95, H, 12 08 % IR ν_{max}^{Nujol} cm^{-1} 3340, 3050, 1720, 1468, 1451, 1300, 1080, 910, 725 ^{1}H NMR (CCl_4) δ 0 85 [6H, *d*, $(C\underline{H}_3)_2CH$–, $J = 6$ Hz], 1 31 [24H, *br s*, chain–$(C\underline{H}_2)_{12}$–], 2 43 (2H, *br*, $-C\underline{H}_2$–COOH), 3 93 (1H, *br*, $-\underset{|}{C}\underline{H}OH$), 7 3 (1H, *br*, $-COO\underline{H}$) MS m/z (rel int) 282 $[M - H_2O]^+$ (85), 264 (55), 222 (42), 196 (20), 149 (38), 95 (53 5), 89 (100), 85 (35), 83 (57), 71 (80) *Methyl* 3-*hydroxy*-16-*methylheptadecanoate* (**2a**), bp 195–200 °/0 8 mm Found C, 72 86, H, 12 11 Calc for $C_{19}H_{38}O_3$ C, 72 56, H, 12 18 % IR ν_{max}^{Nujol} cm^{-1} 3500, 2950, 1725, 1453, 1449, 750 ^{1}H NMR (CCl_4) δ 0 88 [6H, *d*, $(C\underline{H}_3)_2CH$–, $J = 6$ Hz), 1 36 [24H, *br s*, chain–$(C\underline{H}_2)_{12}$–], 2 33 (2H, *d*, $-C\underline{H}_2COOMe$, $J = 6$ Hz), 2 83 (1H, *br*, $-CHO\underline{H}$), 3 75 (3H, *s*, $-COOC\underline{H}_3$), 3 90 (1H, *br* $-\underset{|}{C}\underline{H}OH$) MS m/z (rel int) 314 $[M]^+$ (3), 296 (13 5), 283 (4), 265 (11), 242 (7 5), 223 (16), 103 (100), 97 (26), 74 (46), 71 (54)

Oxidation of **2a** **2a** (0 107 g) in Me_2CO (10 ml) was treated with Jones' reagent (0 3 ml) at 15 ° with stirring After 15 min excess reagent was destroyed by adding MeOH, the reaction mixture poured in H_2O and extracted with Et_2O The Et_2O extract was washed with H_2O, dried (Na_2SO_4) and the solvent evaporated The residue (0 104 g) was distilled to yield methyl 3-keto-16-methylheptadecanoate (**3**) bp 190–195 °/0 6 mm Found C, 72 73, H, 11 5 Calc for $C_{19}H_{36}O_3$ C, 73 03, H, 11 61 % IR ν_{max} cm^{-1} 2950, 1750, 1700, 1466, 1431, 1400, 1150, 990, 714 ^{1}H NMR (CCl_4) δ 0 88 [6H, *d*, $(C\underline{H}_3)_2CH$–, $J = 6$ Hz], 1 28 [22H, *br s* chain –$(C\underline{H}_2)_{11}$–], 1 56 (1H, *br*, $Me_2C\underline{H}$–), 2 48 (2H, *t*, $-C\underline{H}_2COCH_2COOMe$, $J = 6$ Hz), 3 30 (2H, *s*, $-COC\underline{H}_2COOMe$), 3 70 (3H, *s*, $CO_2C\underline{H}_3$) MS m/z (rel int) 312 $[M]^+$ (55), 294 (39), 256 (35), 239 (45 5) 220 (23), 129 (97 5), 116 (100), 101 (60), 97 (71), 73 (17)

E-2-16-*Methylheptadecenoic acid* (**4**) **1a** (0 5 g) was refluxed with 0 1 N NaOEt in EtOH (40 ml) for 17 hr EtOH was removed under vacuum and the residue after dilution with H_2O was acidified with dilute HCl and extracted with Et_2O The Et_2O extract was washed with H_2O, dried (Na_2SO_4) and the solvent removed under red pres The residue (0 41 g) was esterified with CH_2N_2–Et_2O and the mixture of Me esters chromatographed on Si gel Petrol–C_6H_6 (3 1) eluted the mixture of olefinic esters (0 3 g) and petrol–C_6H_6 (1 1) eluted the hydroxy acid ester **2a** (0 08 g) The former mixture of esters was hydrolysed by refluxing with 0 5 N EtOH–KOH for 5 hr The mixture of acids thus obtained was crystallized from petrol to give pure **4**, mp 62–63 ° Found C, 75 91, H 11 89 Calc for $C_{18}H_{34}O_2$ C, 76 54, H, 12 13 % IR ν_{max}^{Nujol} cm^{-1} 3000, 1700, 1670, 1471, 1412, 1280, 980, 930, 720 ^{1}H NMR (CCl_4) δ 0 88 [6H, *d*, $(C\underline{H}_3)_2CH$– $J = 6$ Hz], 1 30 [22H, *br s*, chain –$(CH_2)_{11}$–], 2 15 (2H, *br*, $-C\underline{H}_2CH = CHCO_2H$), 5 36 (1H, *d*, $-CH = C\underline{H}$–CO_2H, $J = 16$ Hz), 6 7, 6 98 (1H, *t* of *d* each, $-CH_2C\underline{H} = CHCO_2H$, $J = 16$, 6 Hz) 11 3 (1H, *s*, $-COO\underline{H}$) MS m/z (rel int) 282 $[M]^+$ (35), 265 (20), 222 (17), 185 (23), 155 (14), 127 (51), 99 (70), 85 (58), 83 (92 5), 69 (100)

16-*Methylheptadecanoic acid* (**5**) The mixture of α, β- and β, γ-unsatd esters (0 062 g) was hydrogenated with PtO_2 (0 015 g) in EtOH (5 ml) The resulting ester was hydrolysed with 0 5 N EtOH–KOH to give **5**, mp 67–68 ° (petrol) (lit [2] mp 67 5–68 °) IR ν_{max}^{Nujol} cm^{-1} 2950, 1700, 1460, 1360, 915, 715 ^{1}H NMR (CCl_4) δ 0 88 [6H, *d*, $(C\underline{H}_3)_2CH$–, $J = 6$ Hz], 1 33 [26H, *br s*, chain –$(C\underline{H}_2)_{13}$–], 2 25 (2H, *br*, $-C\underline{H}_2COOH$), 10 9 (1H, *s*, $-COO\underline{H}$) MS m/z (rel int) 284 $[M]^+$ (100), 242 (44), 199 (8), 185 (31), 171 (12), 111 (18), 97 (34), 85 (48), 73 (51), 55 (59)

REFERENCES

1 Sharma, R N, Bhosale, A S, Joshi, V N, Hebbalkar, D S, Tungikar, V B, Gupta, A S and Patwardhan, S A (1981) *Phytoparasitica* **9**, 101

2 Milburn, A H and Truter, E V (1954) *J Chem Soc* 3344

3 Tatum, J H and Berry, R E (1972) *Phytochemistry* **11**, 2283

4 Patwardhan, S A and Gupta, A S (1981) *Indian J Chem* **20B**, 627