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# LIPID CONSTITUENTS FROM *STELLARIA MEDIA**

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**Key Word Index**—*Stellaria media*; Caryophyllaceae; lipids; 6,7-dimethylheptacosane; 3-methyl-6-hydroxyheneicos-3-enyl acetate; 5-acetoxydotetracont-3-en-1-ol; triacontanol; antifeedant.

**Abstract**—In addition to hentriacontane, hexacosanyl palmitate, methyl stearate, pentacosanol, triacontanol, triacontanoic acid, sitosterol and its *β*-D-glucoside, three new compounds isolated from *Stellaria media* have been characterized as 6,7-dimethylheptacosane, 3-methyl-6-hydroxyheneicos-3-enyl acetate and 5-acetoxydotetracont-3-en-1-ol by spectral data and chemical studies. Triacontanol showed significant inhibition of feeding activity against the insects, *Spilosoma obliqua* and *Spodoptera litura*.

## INTRODUCTION

*Stellaria media*, commonly known as chickweed, is found throughout the Himalayas up to an altitude of 4300 m [1]. It is reported to be very useful in the treatment of inflammations of the digestive, renal, respiratory and reproductive tracts. The plant is employed in plasters used for broken bones and swellings. It also possesses diuretic, expectorant and antiasthmatic properties [2]. Some phenolic acids, flavones [3], fatty esters [4] and gypsogenin [5] were reported earlier from this species. The present paper describes the characterization of three novel compounds as well as the antifeedant, triacontanol, and the antiinflammatory, *β*-sitosterol-*β*-D-glucoside and hentriacontane.

## RESULTS AND DISCUSSION

Silica gel CC of the *n*-hexane and chloroform fraction of the methanol extractives of the plant afforded 11 compounds (**1–11**). Compound **2** showed IR bands at 2950, 2910, 2840, 1450, 720 (long chain), 1380 cm$^{-1}$ (Me). The mass spectrum of the compound had an $[M]^+$ ion at *m/z* 408 suggesting the molecular formula $C_{29}H_{60}$. The presence of an ion at *m/z* 393 $[M - Me]^+$ and the ratio of abundances of $[M - Me]^+/[M]^+$ indicated the compound to be branched having methyl groups as substituents [6]. The mass spectrum of **2** also indicated that the intensity of $C_nH_{2n+1}$ peaks, after a maximum at $n = 4$, steadily declined up to $n = 21$, followed by a strong ion at $n = 22$ (*m/z* 309). This ion at $n = 22$ $[M - 99]^+$ suggested the attachment of one methyl group at C-7 [7]. Other strong ions at *m/z* 337 and 71 suggested the location of a second methyl group at C-6. The $^1$H NMR spectrum of the compound was consistent with the proposed structure as 6,7-dimethylheptacosane (**2**).

Compound **7** exhibited IR absorption bands at 3400 (OH), 1740, 1260 (OAc). 1616 (double bond), 1380 (Me), 1450 and 722 cm$^{-1}$ (straight chain). The mass spectrum of **7** indicated an $[M]^+$ at *m/z* 382 suggesting the molecular formula $C_{24}H_{46}O_3$. The loss of a water molecule was seen at *m/z* 364, while the location of the OH group was assigned at C-6, since significant α-fission ions were observed at *m/z* 299, 113 and 83. Characteristic ions at *m/z* 42 ($CH_2=CO$), 43 (MeCO), 59 and 323 suggested the presence of an aceotxyl group at one end of the molecule, whereas the strong ions at *m/z* 313 and 69 showed $[CH=CMe–CH_2–Me]^+$ to be at the other end of the molecule. The loss of 15 mu from the $[M]^+$ suggested that a methyl group was as a substituent and this was assigned at C-3 due to the presence of the ion at *m/z* 353. Significant ions at *m/z* 353, 313 and 69 indicated the location of the double bond at C-3. The $^1$H NMR spectrum of this compound displayed two singlets at $\delta$1.60 and 2.0 for olefinic Me and OAc groups, respectively, three triplets at $\delta$5.30, 0.85 and 4.20 for an olefinic proton, a terminal Me group and $CH_2$–OAc protons, respectively, and a multiplet at $\delta$3.65 for a CHOH proton. These data suggested the structure of this compound to be 3-methyl-6-hydroxyheneicos-3-enyl acetate (**7**).

Compound **8** had IR absorption bands similar to **7** and its mass spectrum showed an $[M]^+$ at *m/z* 662 suggesting the molecular formula $C_{44}H_{86}O_3$. The presence of a terminal OH group ($[M - H_2O]^+$, *m/z* 644) was suggested by the ion at *m/z* 631. The loss of 60 mu (AcOH) from the $[M]^+$ generated an ion at *m/z* 602 indicating the presence of an acetyl group which was assigned at C-5 due to the presence of significant α-fission ions at *m/z* 591, 519, 143 and 71. The location of the double bond was established at C-3 since significant ions

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were seen at *m/z* 617, 591 and 71. These assignments were substantiated by the $^1$H NMR spectrum wherein the acetyl group was seen at $\delta$2.10, the double bond at $\delta$5.10 and the $CH_2OH$ and CHOAc protons at $\delta$3.40 and 4.20, respectively. Thus, the results obtained established the structure of this ester as 5-acetoxydotetracont-3-en-1-ol (**8**).

Compound **1**, **3–6** and **9–11** were identified as hentriacontane, hexacosanyl palmitate, methyl stearate, pentacosanol, triacontanol, triacontanoic acid, $\beta$-sitosterol and $\beta$-sitosterol-$\beta$-D-glucoside, respectively, by chromatographic and spectral comparison with authentic samples. Recently triacontanol has been reported for the first time to possess antifeedant activity against the boll weevil [8]. In our studies, triacontanol has shown 91, 79, 56 and 54% feeding deterrence for *Spodoptera litura*, and 62, 34, 25 and 4% for *Spilosoma obliqua* at 2000, 1500, 1000 and 500 ppm, respectively. Antiinflammatory activity of this species was attributed to the known antiinflammatory agents, hentriacontane [9] and $\beta$-sitosterol-$\beta$-D-glucoside [10].

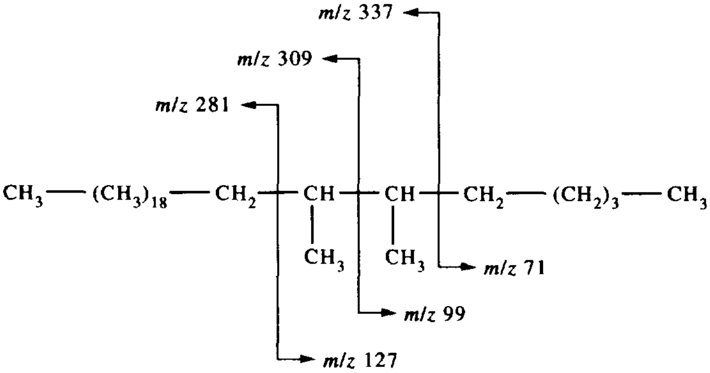
## EXPERIMENTAL

Mps: uncorr. IR spectra: recorded in KBr and $CHCl_3$ and 80 MHz $^1$H NMR spectra in $CDCl_3$ with TMS as int. standard. TLC was carried out on silica gel G and spots visualized by exposure to $I_2$ vapours. Plant material was collected from a local area and identified in our Botany Department where a voucher specimen has been deposited.

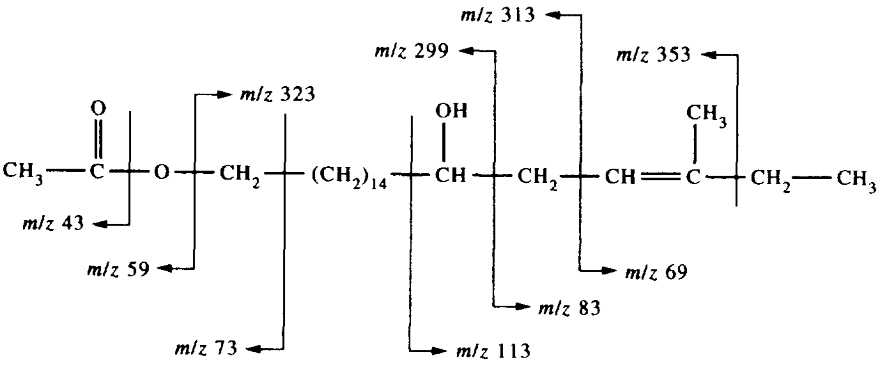
*Extraction and isolation of compounds.* Dried and powdered aerial parts (1 kg) of *S. media* (L.) Vill, were extracted with MeOH (5 × 5 l) and the combined extracts concd *in vacuo* to 200 ml. $H_2O$ (200 ml) was added and the extract then fractionated into *n*-hexane (6 × 500 ml, 17 g), $CHCl_3$ (5 × 100 ml, 2 g) and *n*-BuOH (7 × 100 ml, 3.6 g). The hexane and $CHCl_3$ frs being identical in TLC composition were combined and a portion (16 g) chromatographed over silica gel (600 g, 60–120 mesh). Elution was carried out using varying proportions of hexane, $CHCl_3$ and MeOH, collecting frs of 200 ml and monitoring composition by TLC.

*6,7-Dimethylheptacosane* (**2**). Removal of solvent from hexane frs 4–8 yielded a residue, 20 mg, mp 60°. IR $\nu_{max}$ cm$^{-1}$: 2950, 2910, 2840, 1450, 1380, 720, $^1$H NMR: $\delta$0.85 (6H, *t*, $J = 6$ Hz, 2 × terminal Me), 0.75 (6H, *d*, $J = 6$ Hz, 2 × CH–Me), 1.50 (2H, *m*, 2 × –CH), 1.20 (46 H, *br s*, $(CH_2)_{23}$). MS *m/z* (rel. int.): 408 $[M]^+$ ($C_{29}H_{60}$, 1) 393 [M − Me]$^+$ (6), 378 [M − 2 × Me]$^+$ (4), 337 (10), 309 (15), 281 (5), 127 (12), 99 (30), 71 (90), 57 (100), 43 (60).

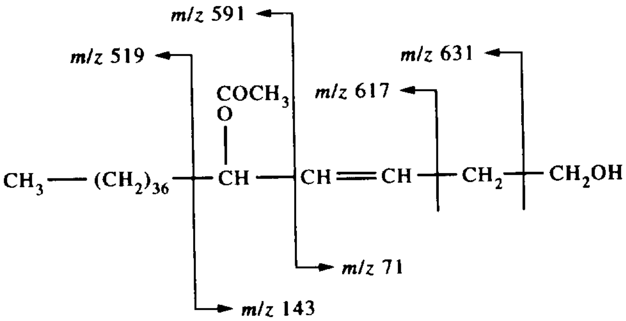
*3-Methyl-6-hydroxyheneicos-3-enyl acetate* (**7**). Removal of solvent from $CHCl_3$–hexane (1:9) frs 107–140 provided a viscous residue, 38 mg. IR $\nu_{max}$ cm$^{-1}$: 3400, 2950, 1740, 1616, 1450, 1380, 1260, 1025, 722, $^1$H NMR:



**2**



**7**



**8**

δ0.85 (3H, *t*, $J$ = 6 Hz, terminal Me), 1.60 (3H, *s*, olefinic Me), 2.0 (3H, *s*, -OAc), 3.65 (1H, *m*, -CHOH), 5.30 (1H, *t*, $J$ = 5 Hz, olefinic proton), 4.20 (2H, *t*, $J$ = 6 Hz, -O-CH$_2$-), 1.25 (28H, *br s*, (CH$_2$)$_{14}$), 1.40 (4H, *m*, (CH$_2$)$_2$). MS *m/z* (rel. int.): 382 $[M]^+$ ($C_{24}H_{46}O_3$, 1), 367 $[M - Me]^+$ (1), 364 $[M - H_2O]^+$ (1), 353 (6), 323 (5), 313 (16), 299 (6), 113 (12), 83 (20), 73 (25), 69 (44), 59 (5), 43 (88), 42 (100).

5-*Acetoxydotetracont*-3-*en*-1-*ol* (**8**). Removal of solvent from CHCl$_3$-hexane (1:9) frs 141–146 furnished a residue, 14 mg. IR $\nu_{max}$ cm$^{-1}$: 3385, 2950, 1739, 1620, 1450, 1390, 1250, 1170, 720. $^1$H NMR: δ0.85 (3H, *t*, $J$ = 6 Hz, terminal Me), 2.10 (3H, *s*, -OAc), 5.10 (2H, *m*, C = C), 3.40 (2H, *t*, $J$ = 5 Hz, -CH$_2$OH), 4.20 (1H, *m*, -CHOAc), 1.25 (72H, *br s*, (CH$_2$)$_{36}$), 1.40 (2H, *m*, 2-H$_2$). MS *m/z* (rel. int.): 662 $[M]^+$ ($C_{44}H_{86}O_3$, 6), 644 $[M - H_2O]^+$ (3), 631 (5), 617 (4), 602 (1), 591 (3), 519 (2), 143 (10), 85 (60), 71 (65), 57 (85), 43 (100).

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