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# NON-ALKALOIDAL CONSTITUENTS FROM *SOLANUM TORVUM* LEAVES

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**Key Word Index**—*Solanum torvum*, Solanaceae, leaves, 2,3,4-trimethyltriacontane, octacosanyl triacontanoate, 5-hexatriacontanone, triacontanol, 3-tritriacontanone, tetratriacontanoic acid, sitosterol, stigmasterol, campesterol

**Abstract**—Three new compounds A, B and C, isolated from the leaves of *Solanum torvum* have been characterized as 2,3,4-trimethyltriacontane, octacosanyl triacontanoate and 5-hexatriacontanone by spectral data and chemical studies Triacontanol, 3-tritriacontanone, tetratriacontanoic acid, sitosterol, stigmasterol and campesterol have also been isolated and identified

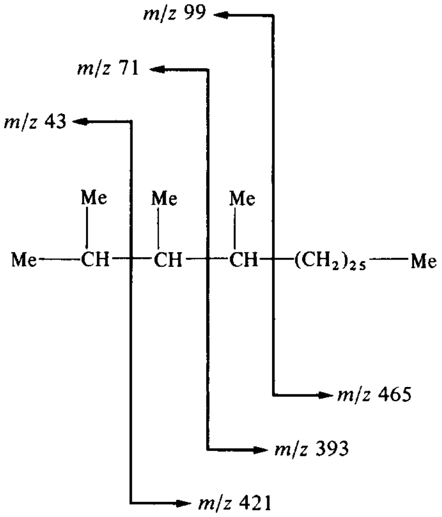
## INTRODUCTION

*Solanum torvum* is distributed throughout India, except the western desert area, Malaya, China, Philippines and tropical America [1, 2] A decoction of fruits is given for cough ailments and is considered useful in cases of liver and spleen enlargement The plant is sedative, diuretic and digestive and the leaves are used as a haemostatic in the Cameroons [3] Several alkaloid and steroid sapogenins have already been isolated from this plant [4–7] Since no work has been reported on the hexane extractives of the leaves of *S torvum*, a detailed investigation was undertaken

## RESULTS AND DISCUSSION

Silica gel CC of the *n*-hexane extract of the plant afforded seven crystalline compounds, A, B, C, D, E, F and G

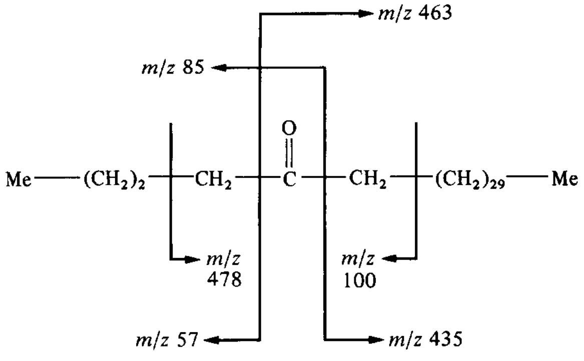
Compound A, mp 58°, obtained in trace quantities showed IR absorption bands at 2940, 2910, 2840, 1460, 755, 725, 715 (long chain), 1372, 1358, 1140 $cm^{-1}$ (isopropyl group) [8] The mass spectrum of the compound displayed a $M^+$ ion at $m/z$ 464 corresponding with $C_{33}H_{68}$ The formation of an ion at $m/z$ 449 $[M - Me]^+$ indicated the compound to be of branched chain nature carrying the methyl group as a substituent A close examination of the mass spectrum of the compound showed that the intensity of $C_nH_{2n} + 1$ peaks, after a maximum at $n = 6$, steadily declined up to $n = 27$, followed by a strong peak at $n = 28$ ($m/z$ 393) From the intense peak at $n = 28$ $[M - 71]^+$, it follows that one methyl group is attached at C-4 [9] The significant ions at $m/z$ 421 and 43 indicated the presence of a methyl of the isopropyl group at C-2 while the third methyl group could be placed at C-3 because of the intense ion at $m/z$ 71 These fragmentations are depicted in structure **1** The $^1H$ NMR spectrum of the compound indicated the presence of five methyl groups One of the terminal methyls appeared as a triplet at $\delta$ 0 84 ($J = 4$ Hz) and the two methyls of the isopropyl function as a doublet at $\delta$ 0 80 ($J = 5$ Hz) The two methyl groups at C-3 and C-4 also appeared as doublets at $\delta$ 0 78 ($J = 4$ Hz) These data are in full agreement with the structure of compound A as 2,3,4-trimethyltriacontane (**1**)



**1**

Compound B, mp 70° had IR absorption bands at 2910, 2840, 1460, 1380, 725, 715 (long chain), 1730 and 1260 $cm^{-1}$ (ester group) The mass spectrum of this compound indicated a $M^+$ ion at $m/z$ 844 suggesting a molecular formula of $C_{58}H_{116}O_2$ The $^1H$ NMR spectrum of the compound showed two triplets, $J = 6$ Hz at $\delta$ 3 90 and 2 14, for methylene protons of $-CH_2-O-CO-$ and $-COCH_2-$, respectively Alkaline hydrolysis of this ester gave an acid, mp 94°, $M^+$ 452, $C_{30}H_{60}O_2$, identified as triacontanoic acid by comparison of literature data [10] and an alcohol, mp 82°, identified as octacosanol [11] Compound B, therefore, is identified as octacosanyl triacontanoate

Compound C, mp 78°, obtained in traces, showed IR absorption bands at 1708 (CO), 2907, 2840, 1460, 1370, 725 and 720 $cm^{-1}$ (long chain) and gave a positive DNPH test The $M^+$ at $m/z$ 520 in the mass spectrum of the compound established the molecular formula as $C_{36}H_{72}O$ The location of the carbonyl group at C-5 is obtained from the α-fission ions at $m/z$ 57, 463, 85, 435 and the β-fission ions, involving McLafferty rearrangement, at $m/z$ 478 and 100 [12] The ion at $m/z$ 58 is obtained by double rearrangement and is characteristic for a ketone having a $\gamma$-H in both alkyl fragments The absence of a $[M-15]^+$ ion in the mass spectrum is indicative of the straight chain nature of this ketone [13] The $^1H$ NMR spectrum of the compound displayed a triplet, $J = 6$ Hz at $\delta$ 2 28, for four protons of the two methylene groups adjacent to the carbonyl function The above data strongly suggested the structure of compound C to be 5-hexatriacontanone (**2**)



2

Compound D, mp 83° showed IR absorption bands at 3280 (OH), 2900, 2830, 1460, 1380, 1060, 725 and 715 cm$^{-1}$ (long chain) This compound was identified as triacontanol by mass spectrometry, NMR, acetate, mp 72° and comparison of literature data [14]

Compound E, mp 83° had IR absorption bands at 1700 (CO), 2900, 2830, 1460, 1380, 725 and 715 cm$^{-1}$ (long chain) Treatment of this compound with 2,4-dinitrophenylhydrazine provided 2,4-dinitrophenylhydrazone, mp 115–117° while reduction with sodium borohydride gave a new alcohol, mp 92° (3-hydroxytritriacontane) This compound has been identified as 3-tritriacontanone by direct comparison with an authentic sample (mp, mmp, MS, NMR) [15] This report constitutes the second isolation of this compound in nature

Compound F, mp 95° showed IR absorption bands for carboxyl groups (1700, 3500–3000, 920) and long chain (2900, 2830, 1452, 1372, 720, 710 cm$^{-1}$) Its molecular formula $C_{34}H_{68}O_2$ was established by the $M^+$ ion at $m/z$ 508 This compound has been identified as tetratriacontanoic acid by comparison with the literature data [16]

Compound G, mp 140° (positive Liebermann–Burchard test) was resolved into sitosterol, stigmasterol and campesterol by GC and mass spectrometry The ions at $m/z$ 414, 412 and 400 corresponding to the MWs of these compounds and the subsequent fragmentations from these ions were observed in the mass spectra

The structure of compounds A, B and C as 2,3,4-trimethyltriacontane, octacosanyl triacontanoate and 5-hexatriacontanone, respectively, are in full agreement with data now available These compounds have not been found previously in nature

## EXPERIMENTAL

Mps are uncorr IR spectra were recorded in KBr and 90 MHz NMR spectra in $CDCl_3$ with TMS as int ref TLC was carried out on Si gel G and the spots were visualized by exposure to $I_2$ vapour or spraying with 2,4-dinitrophenylhydrazine

Plant material was obtained from Dehradun (U P ) and a voucher specimen has been deposited in the Botany Department

*Extraction and isolation of compounds* Dried and powdered leaves (5 5 kg) of *S torvum* were extracted with *n*-hexane (5 × 10 l ) The hexane extract was concd to dryness (62 9 g) and part of this (60 g) was chromatographed over Si gel (1 5 kg, 60–120 mesh, BDH) Elution was carried out in hexane, hexane–$C_6H_6$ (3 1), hexane–$C_6H_6$ (1 1) and $C_6H_6$ Fractions (250 ml) were collected and monitored by TLC The homogeneity of the compounds was checked on TLC in at least four different solvent systems

*Compound A* (2,3,4-*trimethyltriacontane* (**1**)) Removal of solvent from the hexane fractions (1–4) afforded a residue, 10 mg, mp 58° (hexane), $R_f$ 0 99 (hexane) IR $\nu_{max}$ cm$^{-1}$ 2940, 2910, 2840, 1460, 1372, 1358, 1140, 755, 725 and 715 $^1H$ NMR $\delta$ 0 84 (3H, *t*, $J = 4$ Hz, $H_3$-30), 0 80 (6H, *d*, $J = 5$ Hz, isopropyl), 0 78 (6H, *d*, $J = 4$ Hz, $H_3$-3, $H_3$-4), 1 52 (1H, *m*, H-2), 1 88 (2H, *m*, H-3, H-4), 1 20 [50 H, *s*, $(CH_2)_{25}$] MS $m/z$ (rel int ) 464 $[M]^+$ ($C_{33}H_{68}$, 1 5), 449 $[M-Me]^+$ (1 3), 436 $[449-CH]^+$ (5), 421 $[436-Me]^+$ (5 2), 408 $[421-CH]^+$ (5 7), 393 $[408-Me]^+$ (9), 380 $[393-CH]^+$ (7), 365 (5 6), 99 (90), 85 (99 9), 71 (99 9), 57 (99 9), 55 (100), 43 (99 9)

*Compound B* (*octacosanyl triacontanoate*) Removal of solvent from the hexane–$C_6H_6$ (3 1) eluates (30–48) gave a residue, 35 mg, mp 70° (hexane), $R_f$ 0 86 (hexane–$C_6H_6$, 1 1) IR $\nu_{max}$ cm$^{-1}$ 2910, 2840, 1730, 1460, 1380, 1260, 725 and 715 $^1H$ NMR $\delta$ 0 78 (6H, *br s*, terminal Me), 1 19 [106 H, *s*, $(CH_2)_{53}$], 3 90 (2H, *t*, $J = 6$ Hz, $-CH_2-O-CO$), 2 14 (2H, *t*, $J = 6$ Hz, $-OC-CH_2-$) MS $m/z$ (rel int ) 844 $[M]^+$ ($C_{58}H_{116}O_2$, 2) The compound (20 mg) was refluxed with 5% alcoholic KOH (10 ml) for 5 hr At the end of the reaction it was diluted with $H_2O$ (50 ml) and extracted with $Et_2O$ (4 × 25 ml) The extract was washed with $H_2O$ (2 × 50 ml) and dried ($Na_2SO_4$) Removal of solvent gave a residue, mp 82° ($Me_2CO$) identified as octacosanol MS $m/z$ (rel int ) 410 $[M]^+$ ($C_{28}H_{58}O$, absent), 392 $[M-H_2O]^+$ (1), 378 (1), 364 (1), 336 (1), 322 (1), 308 (2), 284 (1), 279 (16), 167 (43), 150 (13), 149 (100), 113 (20), 99 (2), 97 (39), 85 (19), 71 (54), 57 (91), 55 (48), 43 (59), 41 (35) The aq layer left after the above extraction was acidified with dil HCl and extracted with $Et_2O$ (4 × 25 ml) The extract was washed with $H_2O$ (2 × 50 ml) and dried ($Na_2SO_4$) Removal of solvent provided a residue, mp 94° (MeOH) identified as triacontanoic acid MS $m/z$ (rel int ) 452 ($M^+$, $C_{30}H_{60}O_2$, 1), 407 (1), 392 (5), 378 (2), 364 (4), 350 (1), 141 (1), 127 (6), 113 (9), 99 (13), 85 (37), 71 (61), 60 (1), 57 (100), 55 (69), 45 (1), 43 (82), 41 (33), 40 (27)

*Compound C* (5-*hexatriacontanone* (**2**)) Removal of solvent from hexane–$C_6H_6$ (3 1) eluates (89–107) furnished a residue, 20 mg, mp 78° ($Me_2CO$), $R_f$ 0 43 (hexane–$C_6H_6$, 1 1) IR $\nu_{max}$ cm$^{-1}$ 2907, 2840, 1708, 1460, 1370, 725 and 720 $^1H$ NMR $\delta$ 0 83 (6H, *br s*, $H_3$-1, $H_3$-36), 1 20 [62 H, *s*, $(CH_2)_{31}$], 2 28 (4H, *t*, $J = 6$ Hz, $H_2$-4, $H_2$-6) MS $m/z$ (rel int ) 520 $[M]^+$ ($C_{36}H_{72}O$, 0 26), 478 (9), 463 (3), 435 (1), 100 (6), 85 (29), 71 (50), 59 (100), 58 (52), 57 (39), 43 (53), 41 (13)

*Compound D* (*triacontanol*) Removal of solvent from the hexane–$C_6H_6$ (1 1) eluates (114–173) provided a residue, 350 mg, mp 83° ($Me_2CO$) IR $\nu_{max}$ cm$^{-1}$ 3280, 2900, 2830, 1460, 1380, 1060, 725 and 715 $^1H$ NMR $\delta$ 0 85 (3H, *br s*, $H_3$-30), 1 20 [56H, *s*, $(CH_2)_{28}$], 3 55 (2H, *t*, $J = 6$ Hz, $H_2$-1) MS $m/z$ (rel int ) 438 $[M]^+$ ($C_{30}H_{62}O$, absent), 420 $[M-H_2O]^+$ (3), 406 (5), 141 (5), 127 (8), 113 (10), 99 (15), 85 (40), 71 (56), 57 (100), 55 (75), 43 (80) Compound D (50 mg) was added to pyridine (2 ml), $Ac_2O$ (2 ml) and the mixture left overnight at room temp When worked-up it afforded a residue, mp 72° ($Me_2CO$) IR $\nu_{max}$ cm$^{-1}$ 2904, 2820, 1735, 1460, 1380, 1235 and 720

*Compound E* (3-*tritriacontanone*) Removal of solvent from hexane–$C_6H_6$ (1 1) eluates (174–210) afforded a residue, 500 mg, mp 83° ($Me_2CO$) IR $\nu_{max}$ cm$^{-1}$ 2900, 2830, 1700, 1460, 1380, 725 and 715 $^1$H NMR $\delta$ 0 80 (6H, *br s*, $H_3$-1, $H_3$-33), 1 18 [56H, *s*, $(CH_2)_{28}$], 2 22 (4H, *t*, *J* = 6 Hz, $H_2$-2, $H_2$-4) MS *m/z* (rel int) 478 $[M]^+$ ($C_{33}H_{66}O$, 14), 449 (7), 337 (3), 323 (3), 309(3), 295 (3), 281 (3), 267 (3), 253 (3), 225 (3), 211 (3), 197 (3), 183 (3), 169 (3), 155 (3), 141 (7), 127 (7), 113 (14), 99 (17), 85 (21), 72 (7), 57 (100), 43 (61), 29 (20) Compound E (100 mg) was dissolved in MeOH (50 ml) and $NaBH_4$ (40 mg) added gradually The mixture was stirred at room temp for 4 hr then diluted with $H_2O$ (150 ml) and extracted with $Et_2O$ (4 × 100 ml) The extract was washed with $H_2O$ (2 × 100 ml) and dried ($Na_2SO_4$) Removal of solvent left a residue, mp 92° ($Me_2CO$) identified as 3-hydroxytritriacontane IR $\nu_{max}$ cm$^{-1}$ 3320, 2906, 2840, 1440, 1380, 1040 and 720

*Compound F* (*tetratriacontanoic acid*) Removal of solvent from the fractions (216–234) of $C_6H_6$ furnished a residue, 100 mg, mp 95° ($Me_2CO$), $R_f$ 0 14 ($C_6H_6$–$Me_2CO$, 9 1) IR $\nu_{max}$ cm$^{-1}$ 3500–3000, 2900, 2830, 1700, 1452, 1372, 920, 720 and 710 MS *m/z* (rel int) 508 $[M]^+$ ($C_{34}H_{68}O_2$, 2), 494 (2), 480 (2), 452 (3), 424 (2), 396 (29), 382 (16), 340 (10), 297 (3), 269 (3), 241 (3), 199 (3), 171 (7), 157 (3), 143 (3), 129 (39), 115 (10), 101 (6), 97 (23), 85 (29), 83 (29), 73 (55), 71 (42), 69 (39), 60 (55), 57 (81), 55 (60), 45 (6), 43 (100), 41 (58)

*Compound G* (*sitosterol, stigmasterol and campesterol*) Removal of solvent from $C_6H_6$ fractions (240–257) yielded a residue, 900 mg, mp 140° (MeOH) This was a mixture of sitosterol, stigmasterol and campesterol by GC and MS

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