

ALIPHATIC COMPOUNDS FROM *HYOSCYAMUS MUTICUS*

ANIMESH GOSWAMI, YOGENDRA N. SHUKLA and RAGHUNATH S. THAKUR

Central Institute of Medicinal and Aromatic Plants, Lucknow 226010, India

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Key Word Index—*Hyoscyamus muticus*; Solanaceae; Egyptian henbane; 15-hydroxyheneicosanoic acid; tritriacontan-3-one; 3-hydroxytetraatriacontan-30-one; pentatriacontan-3-one; tritriacontane; sitosterol.

Abstract—Four new compounds have been isolated in trace amounts from the leaves and stems of *Hyoscyamus muticus* and are characterized as 15-hydroxyheneicosanoic acid, 3-hydroxytetraatriacontan-30-one, tritriacontan-3-one and pentatriacontan-3-one by spectral studies. Tritriacontane and sitosterol have also been isolated and identified.

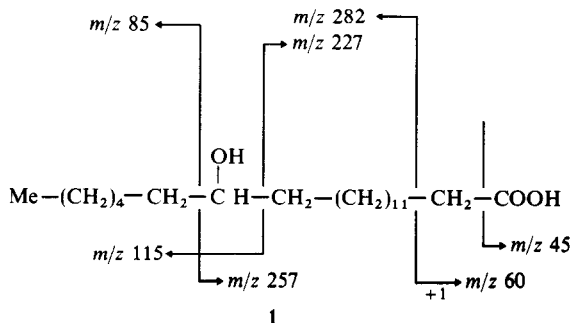
INTRODUCTION

Hyoscyamus muticus, commonly known as Egyptian henbane, is a rich source of tropane alkaloids which have mydriatic, anticholinergic and antispasmodic properties. During a large scale isolation of hyoscyamine from this plant, it was of interest to investigate the non-alkaloidal components since such compounds have not been reported from this species.

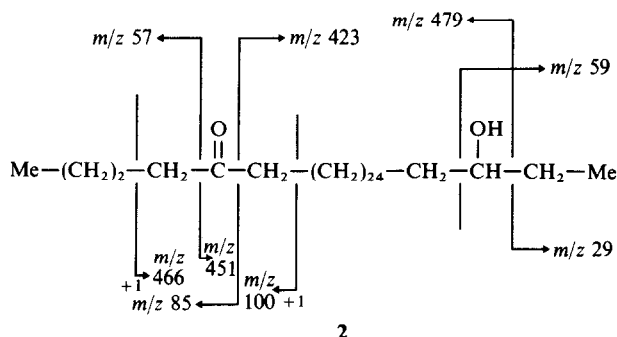
RESULTS AND DISCUSSION

Silica gel column chromatography of the *n*-hexane extract of the plant afforded six crystalline compounds—A, B, C, D, E and F.

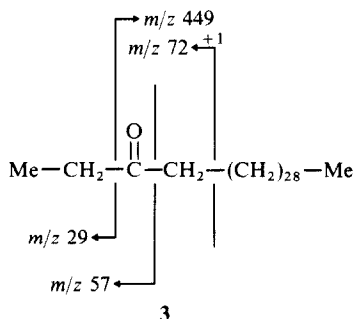
Compound B, mp 80–2°, obtained in trace quantities showed IR absorption bands for OH (3350 cm^{-1}), COOH ($1732, 2500\text{--}3000, 1460$ and 920 cm^{-1}). Its long chain nature is revealed by the presence of bands at 2950, 1460, 730 and 720 cm^{-1} . The MS of the compound displayed a M^+ at m/z 342 corresponding with $C_{21}H_{42}O_3$. The ions at m/z 45, 60 and the loss of 60 amu from the M^+ to give an ion at m/z 282 are characteristic of a terminal COOH group. The peak at m/z 60 is due to a McLafferty rearrangement [1]. The rest of the MS consists of two series of peaks resulting from cleavage of a C–C bond with retention of charge either on the O-containing fragment or on the alkyl fragment (see Experimental). The OH group has been assigned at C-15 as the significant α -fission ions are obtained at m/z 227, 115 and 257 and 85. These data led to the assignment of the structure of compound B as 15-hydroxyheneicosanoic acid (1).



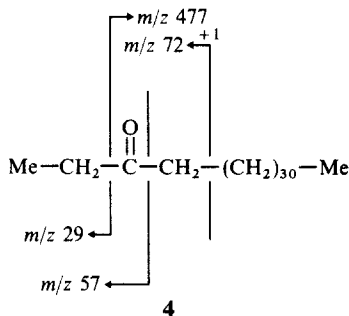
Compound C, mp 76–7° (trace amount) showed IR bands at 3460 (OH), 1715 (CO), 1385 (Me), 2930, 1470, 735 and 725 cm^{-1} (long chain) and gave a positive test with dinitrophenylhydrazine (DNPH). The MS of this compound had a M^+ at m/z 508 ($C_{34}H_{68}O_2$). The base peak at m/z 59 followed by ions at m/z 479 and 29 is assigned to α -fission of the OH group at C-3. The peaks corresponding to the fissions α and β to the CO group at C-30 are observed at m/z 57, 451, 423, 85 and at m/z 466, 100 respectively. The intense peak at m/z 58 is obtained by double rearrangement. These data strongly corroborated the structure of compound C as 3-hydroxytetraatriacontan-30-one (2).



Compound D, mp 83°, obtained in small amounts, had IR absorption bands at 1705 (CO), 2910, 2840, 1460, 725 and 715 cm^{-1} (long chain) and gave a positive DNPH test. The M^+ at m/z 478 in the MS of this compound established the molecular formula as $C_{33}H_{66}O$. The base peak in the spectrum at m/z 57 and the other peaks at m/z 449 and 29 are due to α -fission of the CO group which is located at C-3. The ion at m/z 72 is due to β -fission of the CO group which is accompanied by McLafferty rearrangement with the transfer of one ion [2]. The absence of a $M^+ - 15$ ion in the MS is indicative of a straight chain nature of this ketone [3] and the presence of a $M^+ + 1$ peak is characteristic of an unsymmetrical ketone [4]. Additional evidence for the CO at C-3 is obtained by the absence of a double rearrangement ion at m/z 58. The above data strongly suggested the structure of compound D to be tritriacontan-3-one (3).



Compound E, mp 86–7° again isolated in trace quantities, also gave a positive test with DNP. The IR spectrum bands were similar to those of 3, 1710 (CO), 2925, 2860, 1460, 740 and 730 cm⁻¹ (long chain). Its molecular formula C₃₅H₇₀O is suggested by the observation of the M⁺ ion at *m/z* 506. The position of the CO group at C-3 was indicated by the α -fission fragments at *m/z* 57 (base peak), 477, 29 and a fragment due to β -fission at *m/z* 72. The straight chain and unsymmetrical nature of the ketone was supported by the absence of a M⁺ – 15 ion and the presence of a M⁺ + 1 ion, respectively. As in 3, the absence of a double rearrangement ion at *m/z* 58 further supported the location of the CO group at C-3. The data outlined above suggested the structure of compound E to be pentatriacontan-3-one (4).



Compound F, mp 136° was identified as sitosterol by direct comparison with an authentic sample (mp, mmp, IR, NMR, MS).

Compound A, mp 68–70° had an IR spectrum typical of a straight chain hydrocarbon (2950, 2920, 2850, 1460, 1375, 728 and 720 cm⁻¹). Its molecular formula C₃₃H₆₈ was established by the M⁺ ion at *m/z* 464. The MS showed regular losses of 14 amu, which is attributed to its hydrocarbon nature. This compound has been identified as tritriacontane by comparison with the literature [5, 6].

The MS and IR data of 1, 2, 3 and 4 are in full agreement with the assigned structures. These compounds have not previously been found in nature. It is interesting to note that both C₃₃-hydrocarbon and ketone are present in the same plant.

EXPERIMENTAL

Mps are uncorr. IR spectra were recorded in KBr and 60 MHz NMR in CDCl₃ with TMS as int. ref. TLC was carried out on Si gel G and the spots were visualized with I₂ vapour and DNP-spray.

Plant material. Plant material was cultivated at the Experimental Station Kukrail of this Institute and a voucher specimen has been deposited in the Botany Department.

Extraction and isolation of compounds. Dried and powdered leaves and stems (2 kg) of *H. muticus* were extracted with cold *n*-hexane (5 × 101.). The hexane extract was freed of the solvent and the residue (27.5 g) was chromatographed over Si gel (1.2 kg, 60–120 mesh, BDH). Elution was carried out in hexane, hexane–C₆H₆ (3:1), hexane–C₆H₆ (1:1), hexane–C₆H₆ (1:3) and C₆H₆. Fractions (250 ml) were collected and monitored by TLC.

Compound A (tritriacontane). The fractions obtained from hexane elution were crystallized from Me₂CO as shiny plates, yield 2.5 g, mp 68–70° (lit. [5, 6] mp 66–7°). IR ν_{\max} cm⁻¹: 2950, 2920, 2850, 1460, 1375, 728 and 720. MS *m/z* (rel. int.): 464 (M⁺, C₃₃H₆₈, 0.9), 437 (0.3), 436 (0.6), 422 (1), 408 (0.6), 407 (0.2), 393 (3), 379 (4), 365 (5), 351 (6), 337 (6), 323 (7), 309 (8), 295 (8), 281 (8), 267 (10), 253 (10), 239 (11), 225 (12), 211 (14), 197 (16), 183 (19), 169 (21), 155 (27), 141 (33), 127 (43), 113 (56), 99 (82), 85 (99), 71 (99), 57 (99), 55 (100), 43 (99), 42 (25), 41 (59), 40 (2).

Compound B (15-hydroxyheneicosanoic acid (1)). The latter fractions eluted with hexane–C₆H₆ (3:1) were crystallized from Me₂CO–MeOH, yield 5 mg, mp 80–2°. IR ν_{\max} cm⁻¹: 3350, 3000–2500, 2950, 2920, 2850, 1732, 1170, 920, 730 and 720. MS *m/z* (rel. int.): 342 (M⁺, C₂₁H₄₂O₃, 7), 300 (6), 299 (14), 282 (6), 257 (23), 242 (10), 227 (7), 213 (6), 199 (8), 197 (9), 185 (6), 171 (6), 169 (5), 157 (6), 143 (7), 141 (7), 129 (9), 115 (9), 99 (8), 85 (13), 73 (7), 71 (22), 60 (9), 57 (37), 45 (9), 44 (72), 43 (72), 42 (17), 41 (46), 40 (100).

Compound C (3-hydroxytetritriacontan-3-one, 2). The fractions eluted with hexane–C₆H₆ (1:1) were crystallized from C₆H₆–MeOH, yield 5 mg, mp 76–7°. IR ν_{\max} cm⁻¹: 3460, 2930, 2860, 1715, 1470, 1385, 1180, 1080, 735 and 725. MS *m/z* (rel. int.): 508 (M⁺, C₃₄H₆₈O₂, 2), 479 (14), 466 (4), 461 (7), 451 (9), 433 (4), 423 (4), 419 (4), 405 (2), 281 (2), 267 (2), 253 (2), 239 (2), 225 (2), 211 (2), 197 (2), 183 (7), 169 (4), 157 (2), 155 (7), 143 (7), 141 (9), 129 (4), 127 (14), 115 (4), 113 (14), 101 (11), 100 (9), 87 (7), 85 (43), 73 (7), 71 (68), 59 (100), 58 (50), 57 (79), 55 (43), 43 (64), 29 (17).

Compound D (tritriacontan-3-one, 3). Early fractions eluted with hexane–C₆H₆ (1:3) provided a residue which was crystallized from Me₂CO–MeOH, yield 8 mg, mp 83°. IR ν_{\max} cm⁻¹: 2910, 2840, 1705, 1460, 725 and 715. MS *m/z* (rel. int.): 478 (M⁺, C₃₃H₆₆O, 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 (pentatriacontan-3-one, 4). The later fractions obtained after hexane–C₆H₆ (1:3) elution were crystallized from Me₂CO, yield 10 mg, mp 86–7°. IR ν_{\max} cm⁻¹: 2925, 2860, 1710, 1470, 740 and 730. MS *m/z* (rel. int.): 506 (M⁺, C₃₅H₇₀O, 11), 477 (33), 253 (6), 239 (6), 225 (6), 211 (6), 197 (6), 185 (11), 183 (6), 169 (6), 155 (6), 141 (6), 129 (28), 127 (8), 113 (11), 99 (11), 85 (33), 72 (6), 57 (100), 43 (83), 29 (17).

Compound F (sitosterol) was eluted with C₆H₆, yield 200 mg, mp 136° (MeOH), mmp, IR, NMR, MS and co-TLC with authentic sample.

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