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New long chain alcohol and ester from *Papaver somniferum* (Poppy) seeds

S K Agarwal*, Sushma Verma, Sudhir S Singh & Sushil Kumar

Aromatic Plant Chemistry Division, Central Institute of Medicinal and Aromatic Plants, P O CIMAP, Lucknow 226 015, India

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Two new compounds, methyl-(19Z)-pentacosenoate **1** and 8-heptacosanol **2** have been isolated from the seeds of *Papaver somniferum* and characterised by spectral analysis.

Papaver somniferum (Papaveraceae) is an important rabi crop of northern India and is known for its narcotic properties. Seeds are important due to their nutritive value. Fatty acids, especially, the linoleic acid besides having nutritional value, has the desirable character of lowering of cholesterol level in human system. Anti-carcinogenic and some other significant pharmaceutical properties are reported in it. The capsule or fruits of the plant is a rich source of opium resin. The alkaloids are of considerable medicinal importance throughout the world[1,2]. This paper describes the isolation and characterization of two minor long chain compounds, an unsaturated ester **1** and a saturated secondary alcohol **2**.

The hexane extract of poppy seeds on repeated silica gel column chromatography yielded two compounds **1** and **2** identified as methyl-(19Z)-pentacosenoate and 8-heptacosanol, respectively and their structures were elucidated by physico chemical data.

Compound **1**, mp 45-47°, $C_{26}H_{50}O_2$ (M^+, 394) confirmed by EIMS. Its IR spectrum demonstrated bands at 3080 (CH for unsaturation), 1736 (C=O), 1144 (-C-O-), 760, 730 cm^{-1} (long aliphatic chain) [3,4].

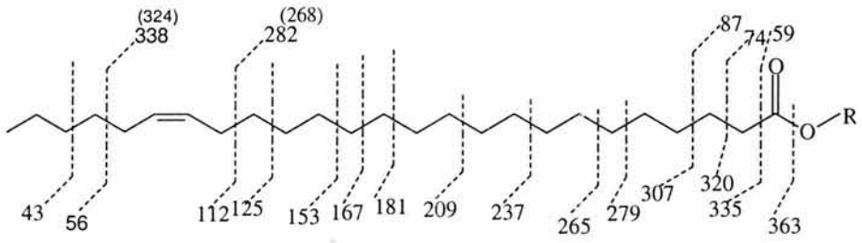
^1H NMR spectrum of **1** showed a triplet at δ 0.87 for 3 protons of one terminal methyl and a 36 protons broad singlet at δ 1.25 for 18 methylene units present in identical environment. A singlet at δ 3.66 for the $COOCH_3$ group, a triplet at δ 5.29 (J=4 Hz) for two olefinic protons, a multiplet at δ 1.62 for the four protons of CH_2 group adjacent to two olefinic protons[5,6]. The *cis* nature of the double bond was evident from the NMR coupling constant and IR band[7] at 760 cm^{-1}. All these data indicated **2** to be a long chain unsaturated ester.

Appearance of a number of ion fragments with systematic difference of 14 mass units and absence of a peak corresponding to $[M-15]^+$ in the mass spectrum of **1** confirmed the straight chain nature of the compound. Its mass fragmentation pattern and its alkaline hydrolysis[8], which afforded (19Z)-pentacosenoic acid **3**, determined the position of the ester group. Abundant fragments at m/z 74 and 320 formed by Mc-Lafferty rearrangement in compound **1** indicated the position of the ester group[9,10]. The other significant ions at m/z 56, 338 and 112, 282 located the double bond at C-19 by the Mc-Lafferty rearrangement. Thus, on the basis of above evidences, compound **1** was assigned the structure as methyl-(19Z)-pentacosenoate.

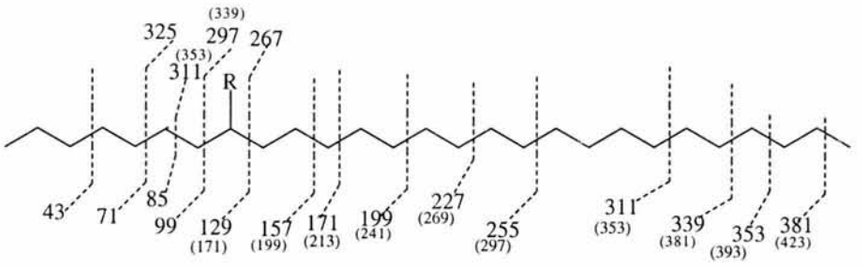
Compound **2** had a molecular formula $C_{27}H_{56}O$ as indicated by its molecular ion at m/z 396 in its EIMS and elemental analysis. The presence of the hydroxyl and aliphatic nature of molecule were revealed by absorption bands at 3376 and 3024, 1426, 1374, 732 cm^{-1}, respectively in its IR spectra. Acetylation of **2** afforded a monoacetate derivative **2a**, $C_{29}H_{58}O_2$ (M^+ 438) which confirmed the presence of only one acetylable hydroxyl group in the molecule.

^1H NMR spectrum of **2** depicted a triplet at δ 0.88 for two methyl groups, broad singlet at δ 1.26 for 44 methylene protons, multiplet at δ 1.59 for four CH_2 protons adjacent to CHOH group, and multiplet at δ 3.7 corresponded to hydroxy methine proton[5,6].

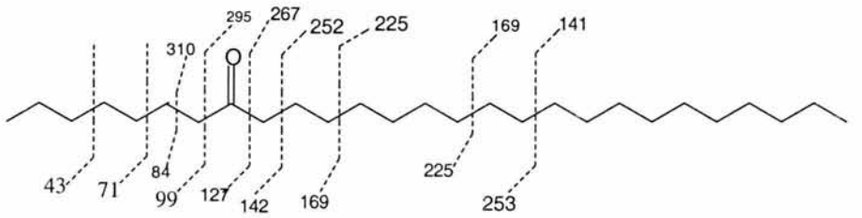
The occurrence of a number of ion peaks at a uniform difference of 14 mass units and the absence of $[M-15]^+$ in its mass spectrum suggested the straight chain nature of the molecule. The position of the OH group was determined by appearance of mass fragments at m/z 99, 297, 129 and 267 due to α-cleavage at C-8[9]. This was finally confirmed by the presence of α-fission peaks at m/z 99, 279 (339-AcOH), 171, 267 in the MS of its acetate **2a**. The oxidation of **2** with CrO_3-pyridine complex gave the



1 R=CH_3
3 R=H (MS peaks are given in paranthesis)



2 R=OH
2a R=OAc (MS peaks are given in paranthesis)



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known compound heptacosanone-8 **4**. Thus, the structure of compound **2** was established as 8-heptacosanol.

Experimental Section

Mps were determined on a Toshniwal apparatus and are uncorrected. The IR spectra were recorded on Perkin Elmer 399B in KBr. The 200 MHz ^1H NMR spectra of **1, 2** and **3** were obtained on a Bruker spectrometer in $CDCl_3$ with TMS as internal standard. EIMS were obtained on a JEOL D-300 mass spectrometer at 70 eV. CC and TLC were carried out on silica gel (Ranbaxy). The spots were visualized by exposure to I_2 vapours and/or by spraying with 5 % vanillin-H_2SO_4 followed by heating at 105° for 5 min. The seeds of *Papaver somniferum* were collected from CIMAP farm and were identified by Botany Department, CIMAP where a voucher specimen has been maintained.

Extraction and isolation of compounds. The air dried and grounded seeds (2.0 kg) of *Papaver somniferum* were extracted with hexane (3 × 4.5 L) and MeOH (3 × 4.0 L) successively at room temperature. The methanol extract was concentrated to get brown coloured mass (99.38 g). This MeOH extract was chromatographed on a silica gel column and eluted successively with hexane, hexane-$CHCl_3$ (1:1), $CHCl_3$, $CHCl_3$-MeOH (1, 3, 5, 10, 20, 50 %). The eluates were monitored by TLC and grouped into 10 fractions.

Fraction no. 1 (1.43 g) eluted with hexane was rechromatographed on a silica gel column using hexane and increasing proportions of hexane-$CHCl_3$ yielding compound **1** (54 mg).

Fraction no. 3 (2.05 g) eluted with $CHCl_3$ was rechromatographed on a silica gel column using $CHCl_3$ and increasing proportions of $CHCl_3$-MeOH yielding compound **2** (32 mg).

Methyl (19Z)-pentacosenoate 1. White solid, mp 45-47°,yield 54 mg; IR (KBr) : 3080 (CH, unsat.), 2854 (CH), 1736 (C=O), 1450, 1380, 1144 (C-O), 760, 730 cm^{-1}; ^1H NMR : δ 0.87 (3H, t, *J*=6 Hz, CH_3), 1.25 (36H, brs, 18 × CH_2), 1 .62 (4H, m, 2 × CH_2-CH=CH), 2.30 (2H, t, *J*=7 Hz, CH_2COO), 3.66 (3H, s, $COOCH_3$), 5.29 (2H, t, *J*=4 Hz, CH=CH); EIMS m/z (rel. int.) : 394 $[M]^+$ (2.1), 363 (5.9), 338 (1.8), 335 (2.3), 320 (3.4), 307 (2.1), 282 (5.5), 279 (4.5), 265 (2.4), 237 (2.1), 209 (5.3), 181 (3.4), 167 (4.7), 153 (5.4), 125 (18.6), 112 (22.7), 87 (16.4), 74 (21.2), 59 (21.4), 56 (60.0), 43 (80.0). (Found : C, 78.82; H, 12.48. $C_{26}H_{50}O_2$ requires : C, 79.18; H, 12.69 %).

Alkaline hydrolysis of 1. Compound **1** (15 mg) was refluxed with alcoholic KOH (5 %, 2.5 mL, 1 hr), diluted with water (3.0 mL) and after usual workup it afforded (19Z)-pentacosenoic acid **3** (8 mg) as amorphous solid; IR (KBr) : 3086, 2850, 1700 cm^{-1} (C=O); ^1H NMR : δ 0.88 (3H, t, *J*=6Hz, CH_3), 1.26 (36H, brs, 18 × CH_2), 1.64 (4H, m, 2 × CH_2–CH=CH), 2.28 (2H, t, *J*=7 Hz, CH_2COO), 5.32 (2H, d, *J*=4Hz, CH=CH); EIMS m/z (rel. int.) : 380 $[M]^+$ (2.8), 324 (1.8), 307 (3.6), 279 (5.4) 268 (3.2), 265 (2.7), 237 (2.9), 209 (2.4), 181 (3.4), 167 (4.7), 153 (4.9), 125 (17.6), 112 (20.4), 97 (14.2), 71 (21.2), 43 (88.0).

8-Heptacosanol 2. Colourless liquid, 32 mg; IR (KBr) : 3376 (OH), 3024 (CH), 1426, 1374, 1028 (C-O), 732 cm^{-1} (long chain); ^1H NMR : δ 0.88 (6H, t, *J*=6.0 Hz, 2 × CH_3), 1.26 (44H, brs, 22 × CH_2), 1.59 (4H, m, 2 × CH_2-CHOH), 3.7 (1H, m, CHOH,); EIMS m/z (rel. int.) : 396 $[M]^+$ (11.2), 381 (6.6), 353 (7.2), 339 (7.3), 325 (3.6), 311 (4.7), 297 (8.3), 267 (8.1), 255 (23.7), 227 (4.6), 199 (5.3), 171 (4.1), 157 (4.3), 129 (18.1), 99 (10.6), 85 (27.0), 71 (21.8), 57 (100.0), 43 (68.2) (Found : C, 81.76; H, 14.10. $C_{27}H_{56}O$ requires C, 81.81; H, 14.14 %).

Acetylation of 2. Compound **2** (5 mg), Ac_2O and C_5H_5N (0.5 mL each) was allowed to stand overnight at room temperature. On usual workup, the mixture afforded colourless amorphous solid of **2a** (4 mg); MS m/z (rel. int.) : 438 $[M]^+$(2.1), 423 (2.8), 393 (2.8), 381 (3.3), 353 (3.4), 339 (3.6), 297 (3.1), 279 (2.4), 269 (3.4), 267 (3.0), 241 (4.3), 213 (4.7), 199 (3.4), 171 (8.2), 99 (8.1), 85 (20.0), 71 (21.0), 57 (100.0), 43 (80.2).

CrO_3-Oxidation of 2. Compound **2** (10 mg) dissolved in C_5H_5N (0.5 mL) and CrO_3-C_5H_5N (10 mg, dried *in vacuo*, P_2O_5) slurry was mixed together with stirring at 0-5° for 6 hr. The reaction mixture was worked up as usual. The amorphous solid product was obtained, which was identified as heptacosanone-8 (**4**, 5.4 mg); IR (KBr) : 2910, 2845, 1715, 1575, 1470, 1100, 1020, 800, 730 and 720 cm^{-1}; ^1H NMR : δ 0.90 (6H, t, *J*=8.0 Hz, 2 × CH_3), 1.25 (40H, brs, 20 × CH_2), 1.75 (4H, m, 2× –CH_2-CH_2-CO-), 2.20 (4H, t, *J*=6.0 Hz, 2× CH_2-CO-); MS m/z (rel. int.) : 394 $[M]^+$(1.9), 310 (3.0), 295 (6.8), 267 (1.9), 253 (2.2), 252 (12.4), 225 (12.7), 169 (3.0), 142 (23.8), 141 (36.3), 127 (41.8), 99 (12.8), 84 (43.6), 71 (100), 43 (33.0).

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References

1 *Wealth of India : Raw materials*,Vol. VII, (PID. CSIR, New Delhi), **1966**, 234 & 246.

2 Verma S, Agarwal S K, Singh S S, Siddiqui M S & Kumar S, *J Med Arom Plant Sci* 21(2), **1999**, 442.

3 Dyer J R, *Application of absorption spectroscopy of organic molecules*, **1984**, 33.

4 Bellamy L J, *The Infrared spectra of complex molecules*, (John Wiley & Sons), **1975**.

5 Silverstein R M, Bassler G C & Morril T C, *Spectrometric Identification of Organic Compounds*, **1981**.

6 Gwanikar R & Mehta B K, *Indian J Chem*, 33B, **1994**, 897.

7 Nakanishi K & Soloman P H, *Infrared Absorption Spectroscopy*, Holden-Day, San Francisco, **1977**, 17.

8 Gupta M M, Shukla Y N & Lal R M, *Phytochemistry*, 22(9), **1983**, 1969.

9 Das K G & James E P, *Organic mass spectroscopy*, 79, **1976**, 161.

10 Mc-Lafferty F W, *Interpretation of mass spectra*, **1971**, 99.