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

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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. 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_{44}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. The \(^{1}H\) NMR spectrum of 1 showed a triplet at \(\delta 0.87\) for 3 protons of one terminal methyl and a 36 protons broad singlet at \(\delta 1.25\) for 18 methylene units present in identical environment. A singlet at \(\delta 3.66\) for the COOCH\(_3\) group, a triplet at \(\delta 5.29\) (J=4 Hz) for two olefinic protons, a multiplet at \(\delta 1.62\) 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 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. 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\(_{50}\)O\(_{2}\) 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\(_{54}\)O\(_{2}\) (M^+ 438) which confirmed the presence of only one acetylable hydroxyl group in the molecule.

\(^{1}H\) NMR spectrum of 2 depicted a triplet at \(\delta 0.88\) for two methyl groups, broad singlet at \(\delta 1.26\) for 44 protons of the CH\(_2\) group present in identical environment. A singlet at \(\delta 0.88\) for broad singlet at \(\delta 1.25\) for 18 methylene units present in identical environment. A singlet at \(\delta 3.66\) for the COOCH\(_3\) group, a triplet at \(\delta 5.29\) (J=4 Hz) for two olefinic protons, a multiplet at \(\delta 1.62\) 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 at 760 cm\(^{-1}\). All these data indicated 2 to be a long chain unsaturated ester.

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 \(\alpha\)-cleavage at C-8\(^9\). This was finally confirmed by the presence of \(\alpha\)-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
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 CDCl₃ 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 I₂ vapours and/or by spraying with 5% vanillin-H₂SO₄ 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 x 4.5 L) and MeOH (3 x 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-CHCl₃ (1:1), CHCl₃, CHCl₃-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-CHCl₃, yielding compound 1 (54 mg).
Fraction no. 3 (2.05 g) eluted with CHCl₃ was rechromatographed on a silica gel column using CHCl₃ and increasing proportions of CHCl₃-MeOH yielding compound 2 (32 mg).

**Methyl (19Z)-pentacosenoate 1.** White solid, mp 45-47°, yield 54 mg; IR (KBr) : 3080 (CH, unsat.), 2854 (CH₃), 1736 (C=O), 1450, 1380, 1144 (C-O), 760, 730 cm⁻¹; ¹H NMR : δ 0.87 (3H, t, J=6 Hz, CH₃), 1.25 (3H, brs, 18 × CH₂), 1.62 (4H, m, 2 × CH₂-CH=CH₂), 2.30 (2H, t, J=7 Hz, CH₂COO), 3.66 (3H, s, COOCH₃), 5.29 (4H, s, COOH), 5.32 (2H, t, J=6 Hz, CH₃), 5.4 mg); IR (KBr) : 3070, 2925, 1695, 1555, 1460, 1380, 1250 cm⁻¹; IH NMR : 3.94 (2H, t, J=6 Hz, CH₂), 1.26 (44H, brs, 22 × CH₂), 0.88 (6H, t, J=6 Hz, CH₃), 1.26 (36H, brs, 18 × CH₂), 1.64 (4H, m, 2 × CH₂-CH=CH₂), 2.28 (2H, t, J=7 Hz, CH₂COO), 5.32 (2H, d, J=4Hz, CH=CH); EIMS m/z (rel. int.) : 380 [M⁺] (2.8), 324 (1.8), 297 (5.4), 268 (3.2), 265 (2.7), 237 (2.9), 209 (2.4), 181 (3.4), 167 (4.7), 153 (5.4), 125 (18.6), 112 (22.7), 87 (21.2), 59 (21.4), 56 (60.0), 43 (80.0). (Found : C, 78.82; H, 14.10). C₃₇H₇₈O₂ requires C, 81.84; H, 14.00 %.

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 work up it afforded (19Z)-pentacosenoic acid 3 (8 mg) as amorphous solid; IR (KBr) : 3085, 2850, 1700 cm⁻¹ (C=O); ¹H NMR : δ 0.88 (3H, t, J=6Hz, CH₃), 1.2 (6H, brs, 18 × CH₂), 1.64 (4H, m, 2 × CH₂-CH=CH₂), 2.28 (2H, t, J=7 Hz, CH₂COO), 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 (5.4), 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 × CH₃), 1.26 (44H, brs, 22 × CH₂), 1.59 (4H, m, 2 × CH₃-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). C₃₇H₇₈O requires C, 81.81; H, 14.14 %.

**Acetylation of 2.** Compound 2 (5 mg), Ac₂O and C₅H₅N (0.5 mL each) was allowed to stand overnight at room temperature. On usual work up, 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).

**CrO₃-Oxidation of 2.** Compound 2 (10 mg) dissolved in C₅H₅N (0.5 mL) and CrO₃-C₅H₅N (10 mg, dried in vacuo, P₂O₅ 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, 1695, 1540, 1470, 1100, 1029, 800, 730 and 720 cm⁻¹; ¹H NMR : δ 0.90 (6H, t, J=8.0 Hz, 2 × CH₃), 1.25 (40H, brs, 20 × CH₂), 1.75 (4H, m, 2 × CH₂-CH₂-CO-), 2.20 (4H, t, J=6.0 Hz, 2 × CH₂-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