Two new lipid constituents of *Nigella sativa* (Seeds)

Neelima Singh, Manjul Verma, Darshana Mehta & B K Mehta*

School of Studies in Chemistry, Vikram University, Ujjain 456 010, India

Received 25 November 2002; accepted (revised) 1 July 2005

The hexane extract of *Nigella sativa* seeds yields two new aliphatic compounds. The compounds have been characterized as 16-triecosen-7-ol 1 and 6-nonadecanone 2 using IR, $^1$H NMR, $^{13}$C NMR, EIMS and chemical evidences.

**Keywords:** *Nigella sativa* 16-triecosen-7-ol 6-nonadecanone

**IPC:** Int.Cl.$^7$ C 07 A 61 K 31/12, 31/045

*Nigella sativa* belongs to the family Ranunculaceae, commonly known as “Kalaungi”. It is a spicy plant, that has bronchodilatory, hypertensive, antibacterial and immune protecting activities. The seeds are commonly believed to have carminative, stimulatory and diaphoretic properties. The seeds contain an alkaloid nigellidine, sterols like cholestrol, campestrol, stigmasterol, $\beta$-sitosterol, $\alpha$-spinasterol, saponin, nigellone, nigellimine and nigellicine. Herein we describe the isolation and structure elucidation of two new compounds from unsaponifiable matter of hexane extract.

**Results and Discussion**

The shade dried seeds were extracted with hexane and the extract was saponified to yield unsaponifiable matter which was separated by column chromatography on alumina grade III. Repeated column chromatography yielded two compounds in pure form. Their structures were established by spectroscopic and chemical means.

**16-Trieocosen-7-ol (Compound 1)** The mass spectrum showed $M^+$ at 338, C$_{23}$H$_{46}$O (52 mg, chloroform: methanol). Its IR spectrum in KBr showed the presence of hydroxyl group and unsaturation (3427, 1637 cm$^{-1}$) in the molecule. The long chain aliphatic nature of the molecule was established by the presence of bands at 2922, 2849, 1460 and 735-725 cm$^{-1}$. $^1$H NMR spectrum (300 MHz, CDCl$_3$, TMS) showed a triplet for six protons at $\delta$ 0.99 ($J$=7.5 Hz) due to terminal methyl groups. The OH proton resonated at $\delta$ 1.5 as a singlet (D$_2$O exchangeable). Two multiplets for one and two protons at $\delta$ 3.6 and 5.1 were due to carbinolic group and double bond respectively. The methylene protons adjacent to carbinolic group and double bonds resonated as triplets at $\delta$ 1.6 and 1.7 respectively. The remaining methylene protons merged into a singlet at $\delta$ 1.27.

The position of hydroxyl group and unsaturation was determined from its mass fragmentation pattern. Abundant fragments at m/z 115 and 85, and 253, formed by $\alpha$ cleavage indicated the position of hydroxyl group at C-7 (ref. 13,14). The position of unsaturation at C-7 was confirmed by abundant fragments at m/z 253, 85 and 227, 111. The $^{13}$C NMR (BB, DEPT I, II) showed peaks at 121.6, 63.2, 38.5, 34.6, 32.32, 29.3, 27.5, 18.9 and 16.4 ppm. All these data leads in the identification of compound 1 as 16-triecosen-7-ol and being reported for the first time by us.

**6-Nonadecanone (Compound 2)** The mass spectrum showed $M^+$ at 282, C$_{19}$H$_{38}$O (40 mg, methanol); Its IR spectrum in KBr has shown it to be an aliphatic ketone (1705 cm$^{-1}$). $^1$H NMR spectrum (400 MHz, CDCl$_3$, TMS) showed a triplet for six protons at $\delta$ 0.99 ($J$=7.5 Hz) due to terminal methyl groups. A triplet at $\delta$ 2.35 for four protons was assigned to $\alpha$ methyl to carbonyl group and protons $\beta$ to carbonyl group resonated at $\delta$ 1.6 as a triplet. The remaining methylene protons merged into a singlet at $\delta$ 1.3.

The mass spectrum showed characteristic pattern for aliphatic compound. It showed abundant fragments at m/z 99, 211 by $\alpha$- cleavage, which indicated the position of carbonyl group at C-6. It was further confirmed by McLafferty rearrangement (m/z...
114\textsuperscript{16,17}. The \textsuperscript{13}C NMR (BB, DEPT I, II, III) showed peaks at 14.1 ppm for C-1 and C-19, at 22.67 ppm for C-2 and C-18, at 29.66 ppm for C-3, at 24.73 ppm for C-4 and C-8, at 31.93 ppm for C-5, at 179.0 ppm for C-6 (-C=O), at 33.97 ppm for C-7, at 29.22 ppm for C-9, at 29.42 ppm for C-17 and at 29.09 ppm for C-10 and C-16. Thus on the basis of the above evidences, the compound \textit{2} was characterized as 6-nonadecanone. It is a new compound and being reported for the first time by us.

**Experimental Section**

General Procedure: Melting points were uncorrected, \textsuperscript{1}H NMR spectra were recorded on 300 MHz Varian XL spectrometer and 400 MHz Bruker WM spectrometer; \textsuperscript{13}C NMR spectra on a Varian XL 75 MHz spectrometer; IR spectra in KBr on a Perkin Elmer-377 spectrometer; and EIMS on a Jeol-JMS D 300 mass spectrometer. The column chromatography was carried out on alumina Gr.III and TLC on silica gel G. Spots were visualized by iodine vapour or charring with H\textsubscript{2}SO\textsubscript{4}-vanillin spray. The seeds of \textit{N. sativa} were collected from the nearby area of Ujjain city, identified from School of Studies in Botany, Vikram University, Ujjain.

**Extraction and Isolation of the compounds**

The seeds (16 kg) shade dried, cleaned, powdered and extracted with hexane in soxhlet extractor for 72 hr. The extract was concentrated by rotary evaporator to afford oil (265 mL). The oil was saponified by alcoholic potash method. Usual work-up yielded (32 g) unsaponifiable matter, which was separated by repeated column chromatography on alumina. The column was eluted by solvents of increasing polarity. The fractions were collected in bulk and monitored by TLC. The hexane and benzene eluate on repeated column chromatography yielded two compounds in pure form.

\textbf{16-Triecosen-7-ol (Compound 1)}: M\textsuperscript{+} 338, C\textsubscript{23}H\textsubscript{46}O (52 mg, CHCl\textsubscript{3}: methanol), m.p. 153-54°C, isolated from benzene: ether (95:05, v/v). IR (KBr): 3427, 2922, 2849, 1637, 1460, 1210, 1030 and 735-725 cm\textsuperscript{-1}; \textit{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 0.99 (6H, t, 2 x-CH\textsubscript{3}, \(J=7.5\) Hz), 1.27 (22H, bs, 11 x-CH\textsubscript{2}), 1.5 (1H, s, -OH, D\textsubscript{2}O exchangeable), 1.6 (4H, t, 2 x-CH\textsubscript{2}-CH-OH), 1.7 (4H, t, 2 x-CH\textsubscript{2}-CH=CH-), 3.6 [(1H, m, -CH-(OH)-] and 5.1 (2H, m, -CH=CH-, \(J=7\) Hz); EIMS m/z (rel.int., %): M\textsuperscript{+} 338(0.5), 310(1.0), 283(1.2), 266(1.2), 253(5.7), 236(1.1), 222(3.7), 208(1.2), 195(1.0), 167(1.0), 136(3.4), 125(5.85), 115(21.5), 111(8.0), 98(30.2), 85(57.1), 84(34.4), 71(100) and 57(43.0); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}, BB, DEPT I, II): 121.6, 63.2, 38.5, 34.6, 32.32, 29.3, 27.5, 18.9 and 16.4 ppm.

\textbf{16-Triecos dibromo-7-ol (Compound 1a)}: M\textsuperscript{+} 496, C\textsubscript{23}H\textsubscript{46}OBr\textsubscript{2} (methanol). Compound \textit{1} (20 mg) in acetone (15 mL) was added to a solution of 2 ml bromine in 20 ml of glacial acetic acid with stirring in 1 hr. After usual work-up, crystalline solid was obtained, which was recrystallised from methanol, m.p. 234°C; EIMS m/z (rel. int., %): M\textsuperscript{+} 496(2.3), 500(2.3), 498(4.5), 481(2.5), 453(2.7), 425(2.9), 415(4.2), 413(7.8), 411(4.3), 381(6.0), 353(3.9), 325(3.0), 321(4.9), 319(4.9), 297(5.0), 269(5.1), 271(9.4), 273(5.0), 227(4.7), 179(9.1), 177(9.0), 115(7.6), 85(49.5), 71(63.0), 56(100), 43(48.7), etc.

\textbf{6-Nonadecanone (Compound 2)}: M\textsuperscript{+} 282, C\textsubscript{19}H\textsubscript{38}O (40 mg, methanol), mp. 59-60°C, isolated from benzene fraction of the column. It showed single spot on TLC using solvent system hexane:ether:acetic acid (9:1:0.5, v/v). It is a new compound and being reported for the first time by us.

**Acknowledgement**

Authors are grateful to RSIC, CDRI, Lucknow and RSIC, IIT-Bombay, Mumbai for spectral analysis and UGC, New Delhi for financial assistance.

**References**