

Note

New aliphatic compounds from the seeds with pods of *Derris robusta*

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Received 17 December 1997; accepted (revised) 8 March 1999

From the seeds with pods of *Derris robusta* two new aliphatic compounds have been isolated and characterised as octa cos-3-one **1** and 23-hydroxy-octa cos-5-ene-3-one **2** on the basis of spectral and chemical evidences.

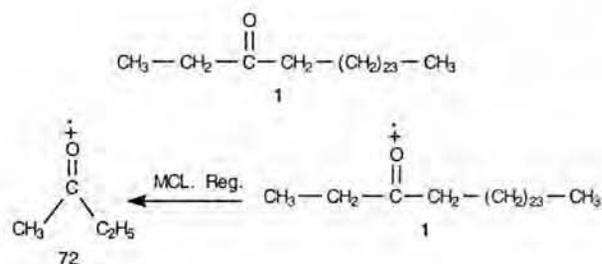
*Derris robusta* Benth (Leguminosae)<sup>1-3</sup> is highly distributed in the Himalayas from Kumaon eastward and western parts of the Indian peninsula. *Derris* is employed for pest control<sup>4</sup> in horticulture, agriculture and in poultry. It has also been employed in the moth proofing compounds. Earlier robustic acid<sup>5</sup>, rotenone<sup>6</sup>, robustigenin<sup>7</sup> and derrone<sup>8</sup> have been isolated from the different parts of *D. robusta* plant. We have now isolated two new compounds long chain aliphatic ketone and hydroxy ketone from the seeds of *D. robusta* with pods.

The dried and crushed seeds with pods of *D. robusta* were extracted with pet. ether and then extracted with EtOH. The concentrated ethanolic extract was subjected to flash column chromatography over silica gel with increasing order of their polarity. The pure hexane fraction gave the creamish white compound **1** (m.p. 65°) and ethyl acetate:methanol (8:2, v/v) fraction yielded the white compound **2** (m.p. 76°). Homogeneity and purity of these compounds were established by TLC.

Compound **1**, m.p. 65°, responded positively to 2,4-dinitrophenyl hydrazine test showing the presence of carbonyl function in the compound. Elemental analysis and molecular weight determination from mass spectrum, established the molecular formula as C<sub>28</sub>H<sub>56</sub>O (M<sup>+</sup> 408). The appearance of the absorption bands at 1710, 735 and 725 cm<sup>-1</sup> indicated the presence of carbonyl group and long aliphatic chain in the compound<sup>9</sup>. The <sup>1</sup>HNMR spectrum of the compound **1** showed the presence of terminal methyl groups as triplet at δ 0.90 (t, 6H, 2×CH<sub>3</sub>)<sup>10,11</sup>. Singlet at δ 1.28 integrating for 46 protons showed the presence of 23 methylene units. A four proton triplet appearing at δ 2.22 was attributed to two methylene

units attached to the carbonyl carbon. The mass spectrum of the compound gave C<sub>n</sub>H<sub>2n+1</sub>, C<sub>n</sub>H<sub>2n</sub> and C<sub>n</sub>H<sub>2n-1</sub> with high abundances (80-100%) for lower fragments. The mass spectrum of the compound also showed the separation of most of the fragments by 14 mass units and decrease in abundance with increasing molecular weight of long straight chain hydrocarbon. The above mention data showed that the compound may be aliphatic ketone. The presence of the carbonyl group at position-3 was deduced from base peak at m/z 57 formed by α-fission<sup>12</sup>.

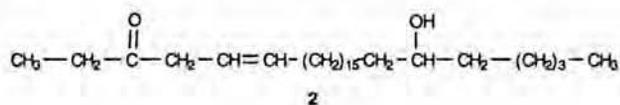
The formation of the fragment at m/z 72 by McLafferty rearrangement (Scheme I) confirmed the position of carbonyl group. The fragments at m/z 211, 253, 295, 337 confirmed the presence of straight chain skeleton and was further confirmed by the absence of an (M-15)<sup>+</sup> ion<sup>13</sup>. These results led to the characterisation of compound **1** as octa cos-3-one.



Scheme I

Compound **2**, m.p. 76°, C<sub>28</sub>H<sub>54</sub>O<sub>2</sub> (M<sup>+</sup> 422) showed the IR absorption bands at 3420 (OH), 1720 (C=O group), 1630 (double bond), 730 and 720 cm<sup>-1</sup> (long ali. chain). Absorption bands at 2970 and 1630 cm<sup>-1</sup> showed the presence of a double bond. Presence of bands at 2920, 2850 and 720 cm<sup>-1</sup> and absence of absorptions in the aromatic region suggested it to be a long chain aliphatic compound. It decolourised KMnO<sub>4</sub> solution and Br<sub>2</sub> solution confirming the presence of unsaturation in the compound. It formed hydrazone with 2,4-DNP confirming the presence of carbonyl group. The <sup>1</sup>HNMR spectrum exhibited absorption peaks at δ 5.2 (t, 2H, -CH=CH, J=15 Hz) for methine protons and at 1.90 (d, 2H, -CO-CH<sub>2</sub>) for two methylene protons at C-4 position. Further study of <sup>1</sup>HNMR spectrum showed the triplet at δ 0.94 (t, 6H, 2×CH<sub>3</sub>) for the presence of two methyl groups. A

broad singlet at  $\delta$  1.4 (brs, 36 H,  $18 \times \text{CH}_2$ ) indicated the presence of 18 methylene groups. Signal at  $\delta$  2.26 (q, 2H,  $-\text{CH}_2-\text{CO}$ ) showed the presence of one methylene group at C-2 position. The  $J$  values of vinylic protons clearly indicated the presence of trans configuration of the double bond in the compound. A four proton multiplet appearing at  $\delta$  2.04 (m, 4H,  $\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2$ ) was attributed to the two methylene units attached to the carbinolic carbon. Multiplet at 2.6 (brm, 1H, CHOH, unresolved) was due to the proton of a methine group bearing the hydroxyl group. Hydroxyl proton resonated as a singlet at  $\delta$  1.67. From the studies of IR and  $^1\text{H}$ NMR it was concluded that the compound was a long chain unsaturated aliphatic hydroxy ketone. The precise nature of the structure of the compound was largely identified from its mass spectrum. It exhibited the molecular ion peak at  $m/z$  422 and many other prominent peaks ( $\alpha$ -fission ions at  $m/z$  365 and 57) which showed the presence of keto group at C-3 position and  $\beta$ -fission ions at  $m/z$  322 and 72. The fragments at  $m/z$  321, 101, 351 confirmed the position of hydroxyl group to be C-23. The straight chain nature<sup>13</sup> was confirmed by the absence of  $(M^+-15)$  ion and the presence of  $(M+1)^+$  ion peak suggested the unsymmetrical nature of the compound<sup>14,15</sup>. Thus, the compound **2** was characterised as 23-hydroxy-octa cos-5-ene-3-one.



### Experimental Section

All m.ps are uncorrected. IR spectra were recorded in KBr on a Perkin Elmer spectrometer,  $^1\text{H}$ NMR spectra on a 90 MHz Varian spectrometer respectively in deuterated benzene using TMS as internal standard and mass spectra were recorded on a Jeol JMS-300-D instrument. Silica gel G was used for TLC; spots were visualised by exposure to  $\text{I}_2$  vapours.

**Extraction and isolation.** The air dried and crushed seeds with pods of *Derris robusta* (5 kg) were extracted with pet. ether and then extracted with ethanol. The concentrated ethanolic extract was subjected to column chromatography over a silica gel

and eluted with different organic solvents of increasing polarity starting with hexane. Each fractions were collected and checked by TLC. Those fractions having same composition were mixed and stripped off solvent. The pure hexane fraction yielded the compound **1** (98 mg) and ethyl acetate-methanol (8:2 v/v) fraction yielded the compound **2** (165 mg).

Compound **1**, m.p. 65°; IR(KBr): 1710 (C=O group), 735 and 725 (aliphatic chain)  $\text{cm}^{-1}$ ; PMR (Benzene- $d_6$ ) (90 MHz):  $\delta$  0.90 (6H, t,  $2 \times \text{CH}_3$ ), 1.28 (46H, br s,  $23 \times \text{CH}_2$ ), 2.22 (4H, t,  $\text{H}_2\text{C}-\text{CO}-\text{CH}_2$ ); MS (ref. int):  $m/z$  408  $M^+$ , 337, 295, 253, 211, 72 and 57 ( $\text{C}_2\text{H}_5\text{CO}$ , base peak).

Compound **2**, m.p. 76°; IR(KBr): 3420, 2970, 2920, 1720, 1630, 2850, 730 and 720  $\text{cm}^{-1}$ ; PMR (Benzene- $d_6$ ) (90 MHz):  $\delta$  0.94 (6H, t,  $2 \times \text{CH}_3$ ), 1.4 (36H, brs,  $18 \times \text{CH}_2$ ), 1.67 (1H, s,  $-\text{OH}$ ), 1.90 (2H, d,  $-\text{CO}-\text{CH}_2$ ), 2.04 (m, 4H,  $\text{H}_2\text{C}-\text{CH}(\text{OH})-\text{CH}_2$ ), 2.26 (2H, q,  $-\text{CH}_2-\text{CO}$ ), 2.6 (1H, brm, CHOH, unresolved), 5.2 (2H, t,  $J=15$  Hz,  $-\text{CH}=\text{CH}-$ ); MS: (ref. int.);  $m/z$  422  $M^+$  365, 351, 337, 322, 321, 101, 72, 57, 29.

### References

- 1 Kirtikaran K R & Basu B D, *Indian medicinal plants* (L M Basu, India), 1933.
- 2 Chopra R N, Nayar S L & Chopra I C, *Glossary of Indian medicinal plants* (CSIR, New Delhi), 1956.
- 3 Rastogi & Mehrotra, in *Compendium of Indian medicinal plants*, Vol. 1, (PID, New Delhi), 1990, 83.
- 4 Molyneux F, *Aust Chem Process*, 25, 1972, 9.
- 5 Mercier & Christiane C R, *Acad Sci Ser*, 270, 1970, 1422.
- 6 Delfel & Norman E, *J Ass Off Anal Chem*, 56, 1973, 1343.
- 7 Chibber S S & Sharma R P, *Phytochemistry*, 18, 1979, 1082.
- 8 Chibber S S & Sharma R P, *Phytochemistry*, 19, 1980, 1857.
- 9 Belamy L J, *The infrared spectra of complex molecules* (Chapman & Hall, London), 1976, 152.
- 10 Dyer J R, *Applications of absorption spectroscopy of organic compounds* (Prentice Hall of India, New Delhi), 1984, 43.
- 11 Silverstein R M, Bassler G C & Morrill T C, *Spectroscopic identification of organic compounds* (John Wiley & Sons Inc, New York), 1974, 142.
- 12 Budzikiewicz H, Djerassi C & Williams D H, *Interpretation of mass spectra of organic compounds* (Holder-Day, San Francisco), 1965, 6.
- 13 Stoianoya-Ivanova B & Hadjieva P, *Phytochemistry*, 8, 1969, 1549.
- 14 Baynon J N, Leater G R, Saunders R A & Williams A E, *Trans Faraday Soc*, 57, 1961, 1259.
- 15 Chakravarti D & Debanath N B, *J Indian Chem Soc*, 51, 1974, 260.