Journal of Medicinal and Aromatic Plant Sciences 35(3-4) (2013) 142-146

Two new aliphatic compounds from the medicinal herb *Crinum defixum*

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Article History

Received: 8th July, 2012
Revised: 10th October, 2013
Accepted: 12th October, 2013

Key words

Amaryllidaceae
Crinum defixum
Hentriacontane
32-Hydroxyheptatetracontan-21, 24-Dione
Octacosan-7,19-diol

ABSTRACT

Two new aliphatic compounds namely 32-hydroxyheptatetracontan-21, 24-dione **(A$_2$)** *and octacosan-7, 19-diol* **(A$_3$)** *along with hentriacontane* **(A$_1$)** *have been isolated from the hexane soluble extract of the shoots of the medicinal plant Crinum defixum. The structures of the compounds were elucidated on the basis of spectral and chemical studies.*

INTRODUCTION

Crinum defixum (Family: Amaryllidaceae) is commonly known as 'Kar-Gawl'in hindi [4, 7]. It is a deciduous plant found in tropical, sub-tropical and warm temperate regions in Asia, Australia, Africa and America. The species is distributed from India to Borneo and is commonly found growing on river bank and swampy places in Deccan and Bengal [7]. It is a stout bulbous herb attaining the height upto 1.5m. The leaves, roots and bulbs of the plant are used medicinally. Bulbs are nausent, emollient, emetic, diaphoretic and also used in the treatment of burns, witlow and carbuncle [1, 8]. The leaves and roots are a good substitute for "ipecacuanha". The juice of the leaves is used in earache. Bulbs when crushed and roasted are used as a rubefacient and in rheumatism. In otitis a few drops of the leaf juice are instilled into the ear [4, 7]. A survey of the literature showed that 5α-hydroxyhomolycorine [6], and lycorine have been isolated from the plant. The present paper describes the isolation and structure elucidation of two new aliphatic compounds namely 32-hydroxyheptatetracontan-21, 24-dione **(A$_2$)** and octacosan-7, 19-diol **(A$_3$)** along with hentriacontane **(A$_1$)** from the shoot of *C. defixum*.

MATERIALS AND METHODS

The plants of *Crinum defixum* (voucher no. 21) were collected from "Ramgarhtal" area of Gorakhpur. The shoot tissues (stems and leaves) were air dried and extracted with hot methanol (3x10 litre) for 25 hrs in a soxhlet apparatus. The extract was filtered and concentrated by distillation of the solvent to give a viscous dark brownish semi-solid mass (350 g). The crude extract was fractionated into *n*-hexane soluble and benzene soluble fractions. The hexane soluble fraction was

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subjected to silica gel (200) column chromatography. The column was eluted with different solvents in the order of increasing polarity. The elution of the column was monitored by TLC. Chromatographically similar fractions were mixed and the solvent removed under reduced pressure. Two new compounds along with a known compound were obtained in pure form from the hexane soluble fraction (100 gm) by eluting the column with hexane and mixture of hexane and ethylacetate(9:1). All reported m.p.s are uncorrected. IR spectra were recorded on FTIR spectrophotometer ; ^{1}HNMR in $CDCl_3$ on Bruker WM-400 or Bruker DRS-300 instrument using TMS as internal standard and FAB (positive ion) mass spectra on a Jeol D-300 mass spectrometer. Silica gel (Qualigens) was used for TLC and column chromatography. Hand made TLC plates were used and spots on TLC plates were visualized under UV light, I_2 vapours as well as by heating the plates after spraying with 10% H_2SO_4.

Compounds isolated from hexane soluble fractions

Hentriacontane (A_1). $C_{31}H_{64}$ **:** It was isolated from hexane eluate and was recrystallized from hexane-ethylacetate (3:1) into colourless crystals (32mg), m.p. 66-67^{0}C : IR (KBr) V_{max} (cm^{-1}) : 2915, 2840, 1470, 1380, 730 and 720; ^{1}HNMR ($CDCl_3$ 400 MHz): d0.85(6H, t, J=7.2Hz, 2-CH_3), 1.25 (58H, brs, 29>CH_2); MS: m/z 436[M$^+$] (10.5) for $C_{31}H_{64}$, 407(22), 393(8), 379(35), 365(24), 351(16), 337(19), 323(22), 309(27), 281(7), 267(11), 253(16), 239(16), 225(8), 211(15), 183(18), 155(16), 141(28), 127(22), 113(6), 57(100). On the basis of m.p., IR, ^{1}HNMR and MS data and comparison with the available data[5] the compound was identified as hentriacontane.

$$H_3C—CH_2—(CH_2)_{27}—CH_2—CH_3$$

Fig 1: Hentriacontane (A_1)

32-Hydroxyheptatetracontan-21,24-dione (A_2). $C_{47}H_{92}O_3$: It was isolated from hexane-ethylacetate(9:1) eluate and was recrystallized from acetone into white solid mass(63 mg), m.p. 82-83^{0}C : IR(KBr) μ_{max}(cm^{-1}) : 3469, 2921, 2851, 1743, 1591, 146, 1382, 1351, 1263, 1167, 1100, 802 and 721; ^{1}HNMR($CDCl_3$ 300 MHz): d 0.86(6H, t, J=4.8Hz, 2-CH_3), 1.25(68H, brs, 34>CH_2), 1.46(4H, m, $-C\underline{H}_2-CHOH-C\underline{H}_2$), 2.02(4H, m, $2(-CO-CH_2-C\underline{H}_2)$), 2.30(8H, t, $2(-C\underline{H}_2-CO-C\underline{H}_2)$), 3.60(1H, m, $-C\underline{H}OH-$); ^{13}CNMR(DMSO-d_6): d13.8(C-1), 22.6(C-2), 31.3(C-3), 27.8(C-4), 27.7(C-5), 27.5(C-6), 27.5(C-7), 27.4(C-8), 27.3(C-9), 27.1(C-10), 27(C-11), 27(C-12), 26.9(C-13), 26.8(C-14), 28.2(C-15), 28.3(C-16), 29.2(C-17), 29.4(C-18), 24.3(C-19), 42.2(C-20), 208(C-21), 58.4(C-22), 58.7(C-23), 209(C-24), 42.5(C-25), 24.1(C-26), 29.6(C-27), 28.9(C-28), 28.1(C-29), 28.2(C-30), 39.5(C-31), 73.2(C-32), 38.8(C-33), 28.3(C-34), 28.0(C-35), 27.0(C-36), 27.2(C-37), 27.3(C-38), 27.5(C-39), 27.5(C-40), 27.6(C-41), 27.7(C-42), 27.8(C-43), 27.8(C-44), 31.7(C-45), 22.8(C-46), 14.1(C-47); MS: m/z 704[M$^+$] (15), 658(12), 651(12), 636(10), 607(27), 584(18), 556(18), 519(18), 508(18), 493(12), 474(18), 463(18), 449(21), 438(18), 437(15), 436(30), 395(15), 393(12), 381(6), 380(15), 379(12), 367(9), 339(15), 337(18), 325(15), 323(5), 311(12), 309(9), 281(15), 267(21), 255(24), 241(27), 211(9).

Octacosan-7,19-diol (A_3). $C_{28}H_{58}O_2$: It was isolated from hexane-ethylacetate(9:1) eluate and was recrystallized from chloroform into colourless shining powder(73 mg), m.p. 94-95^{0}C : IR(KBr) V_{max}(cm^{-1}) : 3427, 2964, 2925, 2853, 1596, 1383, 1352, 1262, 1096, 1024, 803, 694 : ^{1}HNMR($CDCl_3$ 300 MHz) : d 0.88(6H, t, J=7.2H_z, 2-CH_3), 1.25(40H, brs, 20>CH_2), 1.56(8H, m, $2(C\underline{H}_2-CHOH-C\underline{H}_2)$), 3.65(2H, m, $2(-C\underline{H}OH)$): ^{13}CNMR(DMSO-d_6): d14.2(C-1), 22.1(C-2), 31.6(C-3), 27.1(C-4), 27.3(C-5), 39.5(C-6), 74.1(C-7), 39.2(C-8), 28.2(C-9), 28.0(C-10), 27.9(C-11), 26.7(C-12), 26.7(C-13), 26.8(C-14), 26.9(C-15), 27.4(C-16), 27.8(C-17), 38.7(C-18), 74.8(C-19), 39.4(C-20), 27.9(C-21), 27.8(C-22), 27.6(C-23), 27.6(C-24), 27.5(C-25), 31.8(C-26), 21.9(C-27), 14.1(C-28); MS: m/z 426[M$^+$](7), 414(15), 412(12), 391(100), 390(12), 378(18), 360(15), 347(18), 341(12), 331(15), 313(10), 311(18), 299(15), 291(27), 279(39), 273(33), 269(21), 255(30), 241(24), 227(18), 213(24), 199(18), 185(12), 171(12), 129(18), 127(24), 115(54), 113(57).

Acetylation of A_3: A mixture of **A_3** (25 mg), Ac_2O and pyridine(3 ml each) was left overnight at RT. On usual work up it afforded colourless crystals of the diacetate derivative of **A_3**(10 mg); m.p. 82-83⁰C; TLC: R_f 0.87(hexane:ethylacetate; 9:1); IR(KBr) V_{max} (cm^{-1}) : 2945, 2935, 1736, 1596, 1395, 1120, 1040, 803, 720.

RESULTS AND DISCUSSION

Structure elucidation of new compounds

Compound A_2(32-Hydroxyheptatetracontan-21, 24-dione)

This compound, 63mg, m.p. 82-83⁰C was obtained from hexane-ethylacetate(9:1) eluate and was recrystallized from acetone into white solid mass. IR spectrum showed a broad absorption band at 3469cm^{-1} for hydroxyl group. A band at 1743cm^{-1} indicated the presence of carbonyl group which was confirmed by positive response towards 2,4-dinitrophenylhydrazine and a band at 721 cm^{-1} indicated the presence of a long aliphatic chain [2]. Parent ion peak (M^+) in its MS at m/z 704 led to deduce its molecular formula as $C_{47}H_{92}O_3$. The ^{13}CNMR spectrum showed the presence of two methyl, forty two methylene, one methine and two quaternary carbon atoms. A methine carbon resonating at δ73.2 was assigned to carbinolic carbon and two quaternary carbons resonating at δ208 and δ209 were assigned to carbonyl carbon. ^{1}HNMR spectrum of the compound showed a six proton triplet at δ0.86 for two terminal methyl groups and a sixty eight protons broad singlet at δ1.25 for thirty four identical methylene groups. Four protons broad multiplet at δ1.46 is attributed to two methylene units linked to carbinolic carbon. An eight protons triplet at δ2.30 is attributed to four methylene groups α to carbonyl function and a four protons multiplet at δ2.02 is due to two methylene groups β to carbonyl carbon. Above data rules out the possibility of this ketone being a methyl ketone. It was confirmed by the fact that the compound gave negative response towards haloform test. A one proton multiplet at δ3.60 is attributed to the proton attached to carbinolic carbon. It can be inferred that the compound contains two carbonyl and one carbinolic group and that the two carbonyl carbons are separated from each other by two methylene units and the carbinolic carbon is attached to two methylene units on its either side.

The mass spectrum of **A_2** showed a number of ion peaks at a regular difference of 14 amu which supported the long chain aliphatic nature of the compound. The mass spectrum led to the position of two carbonyl groups at C-21 and C-24 while the position of hydroxyl group is assigned C-32. Appearance of peaks at m/z 281, 309 and 395 is due to fission of bonds α to C-21 keto carbon while peaks appearing at m/z 437, 323, 381 and 267 is due to fission of bonds β to C-21 bearing keto group. Prominent peaks at m/z 337, 367 and 339 is due to fission of bonds α to C-24 carbonyl group while peaks at m/z 325 and 379 are due to fission of bonds β to C-24 carbonyl carbon. Peaks at m/z 438 and 380 were due to ions formed by McLafferty rearrangement. A set of quite intense peaks were recorded at m/z 211, 493, 241 and 463. These peaks were formed due to fission of bonds α to C-C on either side of carbinolic carbon while peaks at m/z 255 and 449 were formed due to β fission taking place on one side of carbinolic carbon located at C-32. Thus, on the basis of above studies, the compound **A_2** was finally identified as 32-Hydroxyheptatetracontan-21,24-dione (Fig. 2).

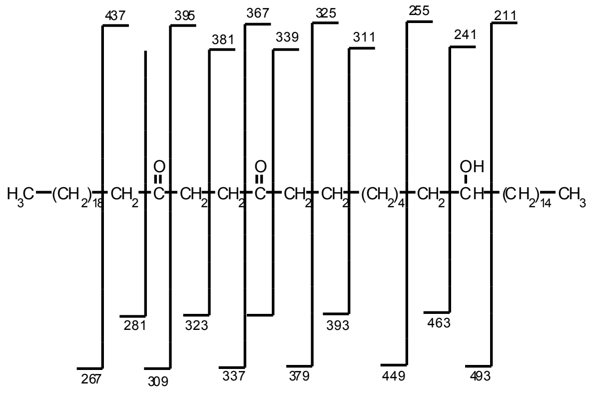

Fig 2: 32-hydroxyheptatetracontan-21, 24-dione (A_2)

Compound A_3(Octacosan-7,19-diol)

This compound, 73mg, m.p. 94-95^{0}C was obtained from hexane:ethylacetate (9:1) eluate and was recrystallized from chloroform to give colourless shining powder. IR spectrum showed a broad absorption band at 3427cm^{-1} for hydroxyl group and a band at 694cm^{-1} for the presence of a long aliphatic chain. Parent ion peak (M^+) in its MS at m/z 426 led to deduce its molecular formula as $C_{28}H_{58}O_2$. Acetylation of **A_3** afforded a diacetate derivative, m.p. 82-83^{0}C, $C_{32}H_{62}O_4$ (M^+ 510), IR 1736cm^{-1} (C=O). From molecular formula and IR spectrum, the compound was inferred as a dihydroxy derivative of Octacosane. The ^{13}CNMR spectrum showed the presence of two methyl, twenty four methylene and two methine carbon atoms. Two methine carbon atoms resonating at δ74.1 and δ74.8 were assigned to two carbinolic carbon atoms. ^{1}HNMR spectrum displayed a six proton triplet centred at δ0.88 (J=7.2Hz) for two terminal methyl groups and a forty protons broad singlet at δ1.25 for twenty identical methylene groups. An eight protons multiplet at δ1.56 is attributed to four methylene groups α to the two carbinolic carbon. It suggested that there are two hydroxyl groups and that these are not linked to each other. A two protons broad multiplet at δ3.65 is due to hydrogen attached to carbinolic carbon (-C$\underline{H}$-OH).

The mass spectrum led to the position of the two hydroxyl groups at C-7 and C-19. The mass spectrum of **A_3** showed a number of ion peaks at a regular difference of 14 amu which supported the long chain skeleton of the molecule. Further, unramified nature of the skeleton was suggested by the absence of a $[M-15]^+$ peak [3]. Appearance of peaks at m/z 115, 311 and 341 is due to fission of bonds α to C-7 carbon atom while a peak at m/z 129 is due to β fission taking place on one side of the C-7 carbinolic carbon. A set of ion peaks at m/z 127, 299 and 269 is due to α fission of C-C bond on either side of C-19 carbinolic carbon while peaks at m/z 255, 113 and 313 are produced as a result of fission of C-C bonds β to C-19 carbinolic carbon. A peak at m/z 391 is attributed to the loss of a water molecule followed by OH moiety from the molecular ion. Thus, on the basis of above studies, **A_3** was characterized as Octacosan-7,19-diol (Fig. 3).

Fig 3: Octacosan-7, 19-diol (A_3)

ACKNOWLEDGEMENTS

The authors are thankful to The Head, Department of Chemistry, DDU Gorakhpur University, Gorakhpur and SAIF, CDRI, Lucknow for providing laboratory facilities and spectral data, respectively. One of the authors (Rahul Sinha) is thankful to CSIR, New Delhi for financial assistance.

REFERENCES

1. Agarwal VS, Ghosh B. 1985. *Drug plants of India (Root Drugs)*. Kalyani publishers, New Delhi: pp. 78.
2. Bellary LJ. 1958. The Infrared Spectra of Complex Molecules, IInd edition, Methuen, London / Wiley, New York.
3. Budzikiewicz N, Djerassi C, Williams D. 1964. *Interpretation of Mass Spectra of Organic Compounds*. Holden-Day, San Francisco (USA).
4. Chopra RN, Nayar SL, Chopra IC. 1956. *Glossary of Indian Medicinal Plants*. CSIR, New Delhi, India.

5. Dargaeva TD, Brutko LI. 1976. Hentriacontane from *Scabiosa comosa*. *Chem Nat Compounds.* **12:** 471.

6. Jeffs PW, Donia AA, Campau D, Staiger D. 1985. Alkaloids of the Amaryllidaceae. 27. Structures of 9-O-demethylhomolycorine and 5.alpha.-hydroxyhomolycorine: alkaloids of *Crinum defixum, C. scabrum*, and *C. latifolium*. Assignment of aromatic substitution patterns from 1H-coupled carbon-13 spectra. *J Org Chem* **50:** 1732-1737.

7. Kirtikar KR, Basu BD. 1975. *Indian Medicinal Plants*. Vol. IV Leader press, Allahabad India: pp. 2473.

8. Mehrotra BN, Aswal BS, Bisht BS. 1987. Companion to Chopra's Glossary of Indian Medicinal Plants (BSMPS) Oscar Publications, Delhi (India).