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ORIGINAL ARTICLE

Phytoconstituents from the rhizomes of *Curcuma aromatica* Salisb.

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Abstract Phytochemical investigation of the chloroform extract of the rhizomes of *Curcuma aromatica* Salisb. (Zingiberaceae) yielded three new phytoconstituents characterized as *n*-heneitriacontan-14-one; *n*-pentatriacontan-5-one; 11α-cyclopentyl-*n*-decan-1-ol (curcumapentadecanol) along with the known compounds stigmasterol and *n*-nonacosan-1-ol. The structures of these phytoconstituents have been elucidated on the basis of structural data analysis and chemical reactions.

1. Introduction

Curcuma aromatica Salisb. (Zingiberaceae), commonly known as jangli haldi or yellow zedoary, is an erect perennial herb scattered throughout India and cultivated in West Bengal and Kerala. The rhizomes are tuberous, large, orange-red and aromatic; substituted for turmeric and applied externally to cure bruises, sprains, skin eruptions, infections and to improve complexion (Anonymous, 2001). The rhizomes contained zederone (Neerja et al., 2001), curdione, neocurdione, curcumol, tetramethyl pyrazine, 1,2-hexadecanediol (Huang et al., 2000), 9-oxo-neoprocurcumenol (Etoh et al., 2003; Madhu et al., 2010), neoprocurcumenol (Madhu et al., 2010), curcumin (Minami et al., 2009; Itokawa et al., 2008; Jiang et al., 2005) and volatile oil mainly composed of β-curcumene, *ar*-curcumene, xanthorrhizol, germacrone, camphor, curzerenone, 7-methanoazulene, 1,8-cineole, β-elemene and linalool (Kojima et al., 1998; Choochote et al., 2005; Al-Reza et al., 2010). The present paper describes the isolation and structural elucidation of the phytoconstituents of the rhizomes of *C. aromatica* procured from Delhi.

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2. Experimental

2.1. General

The melting points were determined on a Perfit apparatus and are uncorrected. The IR spectra were recorded in KBr pellet on

Win IR FTS 135 instrument (Biorad, USA). ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra were recorded by Bruker spectrospin NMR instrument in $CDCl_3$ using TMS as internal standard. EIMS were scanned at 70 eV on a Jeol D-300 instrument (Jeol, USA). Column chromatography was performed on silica gel (Merck, 60–120 mesh) and thin layer chromatography on silica gel G-coated TLC plates (Merck). The percentage yields of the isolated phytoconstituents were calculated on the basis of the dried plant material.

2.2. Plant material

The rhizomes of *C. aromatica* (3 kg) were obtained from Khari Baoli market, Delhi and identified by Prof. M.P. Sharma, Taxonomist, Department of Botany, Faculty of Science, Jamia Hamdard (Hamdard University). A voucher specimen was deposited in the herbarium of the Faculty of Pharmacy, Jamia Hamdard (Hamdard University), New Delhi, India.

2.3. Extraction and isolation

The air-dried rhizomes (3 kg) of *C. aromatica* were coarsely powdered and extracted with chloroform in a Soxhlet apparatus for 72 h. The chloroform extract was concentrated under reduced pressure to obtain a dark viscous mass (375 g). It was adsorbed on silica gel (60–120 mesh) to form slurry, air-dried and chromatographed over silica gel (1.5 kg) column (i.d. 6.0 cm) packed in *n*-hexane. The column was eluted successively with *n*-hexane, mixtures of *n*-hexane and petroleum ether (9:1, 3:1, 1:1, and 1:3), pure petroleum ether, petroleum ether–chloroform (9:1, 3:1, 1:1, and 1:3) and finally with chloroform. Various fractions were collected separately and matched by TLC to check homogeneity. Similar fractions (having same R_f values) were combined and crystallized. The isolated compounds were recrystallized to get the pure compound(s). The physicochemical and spectral data of the isolated compounds are reported below:

2.4. n-Heneitriacontan-14-one (**1**)

Elution of the column with *n*-hexane-petroleum ether (1:1) furnished colourless amorphous powder of **1**, recrystallized from acetone: methanol (1: 1), 860 mg (0.0287% yield); R_f: 0.47 (petroleum ether–chloroform, 9:1); m.p. 60–61 °C; IR U_{max} (KBr): 2917, 2850, 2360, 1703, 1461, 937, 794, 720 cm^{-1}; ^{1}H NMR: δ 2.36 (1H, d, J = 7.5 Hz, H_2-13a), 2.31 (1H, d, J = 7.5 Hz, H_2-13b), 2.02 (1H, d, J = 7.5 Hz, H_2-15a), 1.98 (1H, d, J = 7.5 Hz, H_2-15b), 1.65 (2H, m, CH_2), 1.60 (2H, m, CH_2), 1.25 (48H, brs, $24 \times CH_2$), 0.90 (3H, t, J = 8.5 Hz, Me-1), 0.84 (3H, t, J = 6.0 Hz, Me –31); ^{13}C NMR: δ 203.11 (C-14), 42.22 (CH_2-13), 39.77(CH_2-15), 34.01 (CH_2), 31.92 (CH_2), 31.58 (CH_2), 29.69 ($15 \times CH_2$), 29.43 (CH_2), 29.24 (CH_2), 29.07 (CH_2), 28.24 (CH_2), 24.69 (CH_2), 23.07 (CH_2), 22.69 (CH_2), 21.08 (CH_2), 14.11 (CH_3-31), 11.98 (Me-1); EIMS m/z (rel. int.): 450 $[M]^+$ ($C_{31}H_{62}O$) (20.4), 412 (15.2), 411 (15.3), 395 (34.6), 267 (41.8), 239 (50.1), 211 (35.1), 197 (11.2), 183 (31.9), 141 (21.2), 127 (35.2), 113 (15.2), 97 (79.2), 85 (71.5), 71 (92.3), 57 (100), 43 (95.7).

2.5. Stigmasterol (**2**)

Elution of the column with petroleum ether yielded colourless crystals of **2**, recrystallized from methanol, 240 mg (0.008% yield); m.p. 168–169 °C; $[\alpha]^{30}_D$: −51° ($CHCl_3$, 0.1); UV λ_{max} (MeOH): 233 nm (log ε 2.5); IR t_{max} (KBr): 3500 cm^{-1}; EIMS m/z (rel. int.): 412 $[M]^+$ ($C_{29}H_{48}O$) (33.1), 397 (30.6), 394 (52.4), 273 (22.6), 255 (49.0), 240 (9.2), 230 (22.9), 213 (20.6), 198 (16.1).

2.6. n-Nonacosan-1-ol (**3**)

Elution of the column with petroleum ether–chloroform (3:1) afforded colourless amorphous powder of **3**, recrystallized from methanol: diethyl ether (1:1), 620 mg (0.0207% yield); R_f: 0.41 (toluene); m.p. 88–89 °C; IR t_{max}: 3500, 795, 715 cm^{-1}; EIMS m/z (rel. int.): 424 $[M]^+$ $C_{29}H_{60}O$ (9.3).

2.7. n-Pentatriacontan-5-one (**4**)

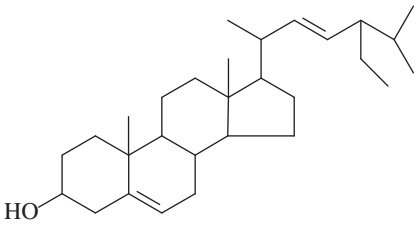
Elution of the column with petroleum ether–chloroform (1:3) gave colourless amorphous powder of **4**, recrystallized from chloroform: methanol (1:1), 220 mg (0.0073% yield); R_f: 0.51 (chloroform: ethyl acetate: 9:1); m.p. 135–137 °C; UV λ_{max}: 208 nm (log ε 3.3); IR t_{max} (KBr): 2950, 2845, 2360, 1705, 1470, 1360, 1205, 1165, 795 cm^{-1}; ^{1}H NMR: δ 2.30 (2H, d, J = 9.0 Hz, H_2-4), 2.25 (2H, d, J = 7.29 Hz, H_2-6), 1.52 (2H, m, CH_2), 1.38 (2H, m, CH_2), 1.18 (56H, brs, $28 \times CH_2$), 0.83 (3H, t, J = 6.3 Hz, Me-1), 0.78 (3H, t, J = 6.6 Hz, Me-35); ^{13}C NMR: δ 202.11 (C-5), 33.88 (C-4), 31.92 (C-6), 29.69 ($27 \times CH_2$), 25.94 (CH_2), 24.69 (CH_2), 22.69 (CH_2), 14.11 (Me-35), 14.09 (Me-1); EIMS m/z (rel. int.): 506 $[M]^+$ ($C_{35}H_{70}O$) (6.3), 477 (10.0), 449 (27.5), 421 (21.2), 407 (9.2), 393 (26.6), 379 (8.4), 337 (7.3), 309 (8.9), 225 (6.8), 183 (14.8), 169 (10.0), 127 (37.1), 113 (14.3), 110 (29.2), 97 (61.5), 85 (69.8), 71 (90.3), 57 (100), 43 (70.6).

2.8. Curcumapentadecanol (**5**)

Elution of the column with chloroform furnished colourless lustrous crystals of **5**, recrystallized from chloroform: methanol (1:1), 140 mg (0.0047% yield); R_f: 0.84 (chloroform: ethyl acetate: 9:1); m.p. 100–101 °C; IR t_{max} (KBr): 3450, 2955, 2845, 1460, 1310, 795 cm^{-1}; ^{1}H NMR: δ 3.70 (1H, d, J = 6.3 Hz, H_2-1a), 3.46 (1H, d, J = 6.3 Hz, H_2-1b), 2.17 (1H, m, $w½$ = 5.1 Hz, H-11β), 1.98 (2H, brs, H_2-12), 1.85 (2H, brs, H_2-15), 1.57 (4H, brs, H_2-13, H_2-14), 1.44 (4H, brs, H_2-2, H_2-9), 1.25 (12H, brs, $6 \times CH_2$), 0.88 (2H, m, CH_2-3); ^{13}C NMR: δ 62.38 (C-1), 32.76 (C-11), 29.17 ($11 \times CH_2$), 25.05 (CH_2), 22.20 (CH_2); EIMS m/z (rel. int.): 226 $[M]^+$ ($C_{15}H_{30}O$) (18.7), 211 (6.1), 139 (5.3), 125 (14.1), 111 (16.8), 97 (61.3), 83 (73.8), 69 (100), 55 (71.0), 43 (75.1).

3. Results and discussion

The structures of the known compounds **2** and **3** have been characterized as stigmasta-5, 22-dien-3β-ol (stigmasterol) (Sharma et al., 2008) and *n*-nonacosan-1-ol (Zhang and Guo, 2001), respectively, on the basis of spectral data analysis.



2

$$HO-\overset{2}{C}H_2-(CH_2)_{27}-\overset{29}{C}H_3$$

3

Compound **1** was obtained as a colourless amorphous powder from chloroform extract column with *n*-hexane-petroleum ether (1:1) eluants. It responded positively to 2, 4-DNP test indicating the presence of a carbonyl function in the molecule (Siddiqui and Ali, 1997). Its IR absorption exhibited characteristic band at 1703 cm^{-1} for the carbonyl group and the bands at 794 and 720 cm^{-1} were typical for long aliphatic chain. The mass spectrum of **1** displayed a molecular ion peak at *m/z* 450 consistent to the molecular formula of an acyclic aliphatic ketone, $C_{31}H_{62}O$. It indicated one double bond equivalent, which was adjusted in the carbonyl group. The absence of $[M-Me]^+$ ion indicated its straight chain nature (Stoianova-Ivanova and Hadijieva, 1969) whereas the presence of $[M+1]^+$ ion arose due to the unsymmetrical nature (Chakravarti and Debnath, 1974; Dubrowski et al., 1980). More intense clusters of the ion peaks corresponding to C_nH_{2n+1} (*e.g.*, *m/z* 57, 71, 85, 99, 113, 127, etc.) in comparison to that relating to C_nH_{2n-1} (*e.g.*, 55, 69, 83, 97, 111, 125, etc.) also supported the acyclic saturated nature of the compound (Misra et al., 1989). From the above facts it was clear that the compound might be a carbonyl derivative of C_{31} hydrocarbon. The appearance of intensified ions at *m/z* 239 $[CH_3(CH_2)_{16}]^+$, 211 $[OC(CH_2)_{12}CH_3]^+$ due to C_{14}–C_{15} fission and at *m/z* 267 $[CH_3(CH_2)_{16}CO]^+$ and 183 $[(CH_2)_{12}CH_3]^+$ due to C_{13}–C_{14} fission supported the location of carbonyl group at C-14. The ^{1}H NMR spectrum of **1** displayed four one-proton doublets at δ 2.36, 2.31 and at 2.02 and 1.98, all having coupling constant of 7.5 Hz, assigned to methylene H_2-13 and H_2-15 protons, respectively, adjacent to the C-14 carbonyl group. Two three-proton triplets at δ 0.90 (J = 8.5 Hz) and 0.84 (J = 6.0 Hz) were ascribed to the correspondingly terminals C-1 and C-31 primary methyl protons. Two multiplets at δ 1.65 (2H) and 1.60 (2H) and a broad signal at δ 1.25 (48H) were associated with the remaining 26 methylene protons. The ^{13}C NMR spectrum of **1** exhibited a deshielded signal at δ 203.11 assigned to C-14 carbonyl carbon. The carbon signals at δ 14.11 and 11.98 were attributed to the terminal C-31 and C-1 methyl carbons, respectively. The remaining methylene carbons appeared between δ 42.22 and 21.08. On the basis of these evidences, the structure of **1** has been elucidated as *n*-heneitriacontan-14-one. This is a new aliphatic ketone isolated from a natural source for the first time.

$$\overset{31}{C}H_3(CH_2)_{15}\overset{15}{C}H_2-\overset{14}{\overset{O}{\overset{||}{C}}}-\overset{13}{C}H_2(CH_2)_{10}-\overset{2}{C}H_2-\overset{1}{C}H_3$$

1

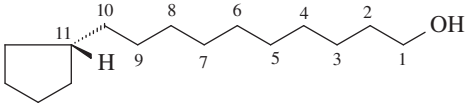
Compound **4**, an aliphatic ketone, was obtained from the petroleum ether–chloroform (3:1) eluants as a colourless amorphous powder. It responded positively to 2, 4-DNP test for carbonyl group and displayed IR characteristic absorption band for carbonyl group (1705 cm^{-1}). It had a molecular ion peak at *m/z* 506 in the mass spectrum corresponding to the molecular formula of an aliphatic ketone $C_{35}H_{70}O$. The intensified ion fragments appearing all of sudden at *m/z* 57 $[CH_3(CH_2)_3]^+$, 449 $[OC(CH_2)_{29}\ CH_3]^+$ due to C_4–C_5 fission and at *m/z* 85 $[CH_3(CH_2)_3\ CO]^+$ and 421 $[(CH_2)_{29}\ CH_3]^+$ due to C_5–C_6 fission indicated the location of the carbonyl group at C-5. The ^{1}H NMR spectrum of **4** exhibited two two-proton doublets at δ 2.30 (J = 9.0 Hz) and 2.25 (J = 7.29 Hz) assigned to methylene H_2-4 and H_2-6 protons adjacent to the carbonyl group. Two three-proton triplets at δ 0.83 (J = 6.3 Hz) and 0.78 (J = 6.6 Hz) were accounted to terminal C-1 and C-35 methyl protons. The remaining methylene protons resonated at δ 1.52 (2H), 1.38 (2H) and 1.18 (56H). The ^{13}C NMR spectrum of **4** depicted important carbon signals for keto carbon at δ 202.11 (C-5) and methyl carbons at 14.09 (C-1) and 14.11 (C-35). On the basis of these evidences, the structure of **4** has been established as *n*-pentatriacontan-5-one. This is an unknown aliphatic ketone reported from a natural or synthetic source for the first time.

$$\overset{1}{C}H_3-\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2-\overset{5}{\overset{O}{\overset{||}{C}}}-\overset{6}{C}H_2(CH_2)_{28}-\overset{35}{C}H_3$$

4

Compound **5**, named curcumapentadecanol, was obtained as a colourless lustrous crystalline mass from chloroform eluants. Its IR spectrum exhibited characteristic absorption bands for the hydroxyl group at 3450 cm^{-1}. Its mass spectrum displayed a molecular ion peak at *m/z* 226 corresponding to a cyclic ring containing aliphatic alcohol, $C_{15}H_{30}O$. It indicated one double bond equivalent that was adjusted to a cyclic ring. Higher intensities of ion peaks relating to C_nH_{2n-1} (*e.g.*, 69, 83, 97, 111, 125, etc.) in comparison to C_nH_{2n+1} (*e.g.*, 71, 85, 99, 113, 127, etc.) supported the existence of the cyclic ring in the molecule. The generation of the base peak at *m/z* 69 $[C_5H_9]^+$ indicated the location of the cyclopentane ring at one of the terminal of the aliphatic chain. The ^{1}H NMR spectrum of **5** showed two one-proton doublets at δ 3.70 (J = 6.3 Hz) and 3.46 (J = 6.3 Hz) assigned to oxygenated methylene H_2-1 protons. A one-proton

multiplet at δ 2.17 ($w½$ = 5.1 Hz) was ascribed to 11β-methine proton. The remaining methylene protons appeared between δ 1.98 and 0.88. The ^{13}C NMR spectrum of **5** depicted C-1 oxygenated methylene carbon at δ 62.38, C-11 methine carbon at δ 32.76 and methylene carbons at δ 29.17 ($11 \times CH_2$), 25.05 (CH_2) and 22.20 (CH_2). The absence of any signal beyond δ 3.70 in the ^1H NMR spectrum and δ 62.38 in the ^{13}C NMR spectrum supported the saturated nature of the molecule. The DEPT spectrum of **5** showed the presence of one each of hydroxymethylene (C-1) and methine (C-11) carbons and other methylene carbons. On the basis of these evidences the structure of **5** has been established as 11α-cyclopentyl-*n*-decan-1-ol. This is a new aliphatic alcohol containing a cyclopentyl ring in the molecule. Terminal cyclic ring substituted aliphatic compounds have been isolated from *Mangifera indica* root bark (Gupta and Ali, 1999), *Desmotrichum fimbriatum* pseudobulb (Ali et al., 2003), *Nardostachys jatamansi* rhizomes (Singh and Ali, 2003), *Oryza sativa* (Chung et al., 2005) and *Curcuma oligantha* var. *lutea* (Ahmad et al., 2010).



5

4. Conclusion

The present work characterized several chemical compounds from the rhizomes of *C. aromatica*. The existing knowledge regarding its phytoconstituents may be increased by the present phytochemical investigation which is useful as this drug is used in the traditional Indian system of medicine.

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