

**NEW ALIPHATIC CONSTITUENTS FROM THE RHIZOMES OF
CURCUMA OLIGANTHA TRIMEN VAR. *OLIGANTHA***

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ABSTRACT

Silica gel column chromatography of the petroleum ether and methanolic extracts of the rhizomes of *Curcuma oligantha* Trimen var. *oligantha* (Zingiberaceae) yielded three new phytoconstituents characterized as *n*-heptacosan-9-ol; *n*-pentatriacont-9-en-5-one; *n*-nonacos-11-ene along with the known compounds stigmaterol; *n*-octacosan-7-ol and curcumin. The structures of these phytoconstituents have been elucidated on the basis of structural data analysis and chemical reactions.

KEYWORDS: *Curcuma oligantha* var. *oligantha*; Zingiberaceae, Rhizomes, Phytoconstituents.

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INTRODUCTION

Curcuma oligantha Trimen var. *oligantha* (Zingiberaceae) is an erect perennial herb with white flowers spotted yellow at the throat of the labellum. It is distributed in Karnataka and Sri Lanka^{1,2}. The *Curcuma* rhizomes are large, tuberous, orange-red and aromatic and substituted for turmeric. The rhizomes are prescribed to treat bruises, sprains, skin eruptions, infections and to improve complexion³. A cinnamyl ester is reported from *C. oligantha* rhizomes⁴. This paper describes isolation and structure elucidation of three new aliphatic constituents from the rhizomes of *C. oligantha* var. *oligantha*.

MATERIALS AND METHODS

General experimental procedure

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). ¹H (300 MHz) and ¹³C (75 MHz) spectra were recorded by Bruker spectrospro NMR instrument in CDCl₃ 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).

Plant Material

The rhizomes of *C. oligantha* var. *oligantha* (3 kg) were collected from Udupi, Karnataka and identified by Prof. K. G. Bhat, Taxonomist, Department of Botany, Poornaprajna College, Udupi, Karnataka. A voucher specimen No. PRL/JH/08/43 is deposited in the herbarium of Department of Pharmacognosy and Phytochemistry, Faculty of Pharmacy, Jamia Hamdard, New Delhi, India.

Extraction and isolation

The air-dried rhizomes (3 kg) of *Curcuma oligantha* var. *oligantha* were coarsely powdered and successively extracted with petroleum ether and then with methanol in a Soxhlet apparatus for 48 hours each. The petroleum ether and methanolic extracts were dried separately to obtain dark viscous brown masses (320, 390 g, respectively). The dried extracts petroleum ether and methanol extracts were adsorbed on silica gel (60-120 mesh) to form slurries. The slurries were air-dried and chromatographed over silica gel columns packed in *n*-hexane and petroleum ether, respectively. The petroleum ether extract column was eluted successively with *n*-hexane, mixtures of *n*-hexane and petroleum ether (9:1,

3:1, 1:1, and 1:3) and finally with petroleum ether. The methanolic extract column was eluted with petroleum ether, mixture of petroleum ether and chloroform (9:1, 3:1, 1:1 and 1:3), pure chloroform and finally mixture of chloroform and methanol (99.5:0.5, 99:1, 98:2, 95:5, 90:10). 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).

Column chromatography of Petroleum ether extract *n*-Heptacosan-9-ol (1)

Elution of the column of petroleum ether extract with *n*-hexane yielded colourless amorphous powder of **1**, recrystallized from chloroform : methanol (1: 1), 195 mg (0.0065 %yield); R_f : 0.33 (*n*-hexane); m.p.: 60-62^o C; $[\alpha]_D^{30}$: -12.5^o (CHCl₃, 0.1); UV_{max} (MeOH): 209 nm (log_{max} (KBr): 3450, 2955, 2845, 1470, 1360, 1120, 725 cm⁻¹; ¹H NMR (CDCl₃): δ 3.98 (1H, dd, $J=6.6, 6.6$ Hz, H-9 β), 2.21 (4H, m, H₂-8, H₂-10), 1.54 (6H, m, 3 \times CH₂), 1.18 (38H, brs, 19 \times CH₂), 0.81 (3H, t, $J=6.1$ Hz, Me-1), 0.79 (3H, t, $J=6.0$ Hz, Me-27); ¹³C NMR (CDCl₃): δ 68.38 (C-9), 42.10 (C-8), 39.27 (C-10), 34.41 (CH₂), 33.57 (CH₂), 31.92 (CH₂), 29.68 (10 \times CH₂), 29.27 (3 \times CH₂), 28.68 (CH₂), 25.94 (CH₂), 25.03 (CH₂), 24.39 (CH₂), 22.67 (CH₂), 21.72 (CH₂), 19.31 (Me-1), 14.10 (Me-27); EIMS m/z (rel. int.): 396 [M]⁺ (C₂₇H₅₆O) (7.1), 367 (8.9), 353 (6.2), 339 (6.5), 295 (12.2), 283 (56.6), 262 (45.9), 256 (17.8), 221(18.2), 191 (19.8), 177 (20.8), 141(23.9), 113 (19.2), 95 (43.2), 83 (43.2), 81 (81.2), 71 (45.0), 69 (100), 57 (51.7), 55 (63.3), 43 (86.5).

n-Pentatriacont-9-en-5-one (2)

Elution of the column of the petroleum ether extract with *n*-hexane-petroleum ether (1:1) furnished colourless amorphous powder of **2**, recrystallized from acetone : methanol (1: 1), 320 mg (0.0107 %yield); R_f : 0.45 (petroleum ether); m.p.: 70-72^o C; UV_{max} (MeOH): 242 nm (log_{max} (KBr): 2950, 2842, 1710, 1650, 1470, 1320, 1110, 725 cm⁻¹; ¹H NMR (CDCl₃): δ 5.27 (1H, m, H-9), δ 5.06 (1H, m, H-10), 2.37 (2H, dd, $J=7.41, 7.59$ Hz, H₂-4), 2.30 (2H, dd, $J=7.02, 7.32$ Hz, H₂-6), 2.09 (2H, m, H₂-8), 2.01 (2H, m, H₂-11), 1.25 (52H, brs, 26 \times CH₂), 0.90 (3H, t, $J=6.3$ Hz, Me-1), 0.85 (3H, t, $J=6.9$ Hz, Me-35); ¹³C NMR (CDCl₃): δ 202.11 (C-5), 127.37 (C-9), 125.16 (C-10), 33.97 (CH₂), 31.92 (CH₂), 29.69 (CH₂), 29.44 (CH₂), 29.24 (22 \times CH₂), 29.06 (2 \times CH₂), 24.68 (CH₂), 22.69 (CH₂), 14.16 (CH₃-1), 14.11 (CH₃-35); EIMS m/z (rel. int.): 504 [M]⁺ (C₃₅H₆₈O) (21.6), 447 (19.2), 419 (63.2), 377 (40.0), 351

(24.6), 195 (45.6), 181 (23.6), 167 (59.6), 153 (43.8), 137 (13.8), 127 (23.9), 125 (38.6), 111 (74.2), 97 (86.9), 85 (42.6), 83 (83.2), 57 (91.3).

n-Nonacos-11-ene (3)

Elution of the column of methanolic extract with petroleum ether-chloroform (1:3), gave buff-coloured amorphous powder of **3**, recrystallized from ethanol, 220 mg (0.0073 % yield); R_f : 0.81 (toluene); m.p.: 87-89^o C; IR_{max} (KBr): 2960, 2855, 1635, 1530, 1465, 1310, 1105, 735, 710 cm⁻¹; ¹H NMR (CDCl₃): δ 5.34 (2H, m, H-11, H-12), 2.81 (1H, d, $J=5.12$ Hz, H-13a), 2.71 (1H, d, $J=5.64$ Hz, H-13b), 2.04 (2H, m, H₂-10), 1.61 (2H, m, CH₂), 1.31 (6H, brs, 3 \times CH₂), 1.27 (38H, brs, 19 \times CH₂), 0.95 (3H, t, $J=6.7$ Hz, Me-1), 0.85 (3H, t, $J=6.3$ Hz, Me-29); ¹³C NMR (CDCl₃): δ 129.29 (C-11), 127.31 (C-12), 33.28 (C-13), 30.86 (C-15), 28.56 (16 \times CH₂), 28.19 (3 \times CH₂), 26.21 (CH₂), 24.24 (CH₂), 24.11(CH₂), 21.53 (CH₂), 18.42 (C-1), 13.30 (C-29); EIMS m/z (rel. int.): 406 [M]⁺(C₂₉H₅₈)(9.8), 265 (68.9), 239 (21.6), 167 (38.3), 153 (14.8), 141 (39.6), 139 (34.2), 125 (48.6), 111 (68.2), 97 (69.3), 83 (71.2).

Column chromatography of methanol extract

Stigmasterol (4)

Further elution of the column of the methanolic extract with petroleum ether (1:3) yielded colourless crystals of **4**, recrystallized from methanol, 200 mg (0.0067 % yield); R_f : 0.45 (benzene); m.p.: 167-168^o C; $[\alpha]_D^{30}$: -51^o (CHCl₃, 0.1); UV_{max} (MeOH): 233 nm (log_{max} (KBr): 3500, 2945, 2856, 1645, 1475, 1360, 1210, 1125 cm⁻¹; EIMS m/z (rel. int.): 412 [M]⁺ (C₂₉H₄₈O) (33.1).

n-Octacosan-7-ol (5)

Elution of the column of methanolic extract with chloroform, furnished colourless crystals of **5**, recrystallized from methanol : acetone (1:1), 390 mg (0.013 % yield); R_f : 0.73 (chloroform: ethyl acetate :: 9:1); m.p.: 151-153^o C; $[\alpha]_D^{30}$: +35^o (MeOH, 0.05); IR_{max} (KBr): 3410, 2965, 2845, 1512, 1460, 1355, 1210, 725, 710 cm⁻¹; ¹H NMR (CDCl₃): δ 4.20 (1H, dd, $J=6.5, 5.5$ Hz, H-7 β), 1.61 (2H, d, $J=6.3$ Hz, H₂-6), 1.52 (2H, d, $J=7.1$ Hz, H₂-8), 1.25 (46H, brs, 23 \times CH₂), 0.91 (3H, t, $J=6.1$ Hz, Me-1), 0.83 (3H, t, $J=6.9$ Hz, Me-28); EIMS m/z (rel. int.): 410 [M]⁺(C₂₈H₅₈O) (8.9), 392 (9.1), 325 (25.3), 85 (19.1).

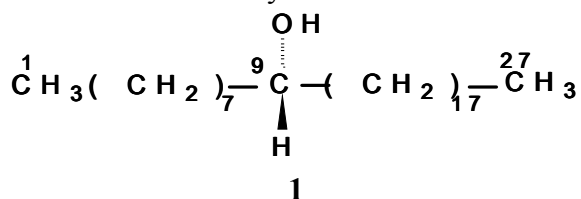
Curcumin (6)

Elution of the column of methanolic extract with chloroform-methanol (99.5:0.5) afforded yellow crystalline mass of **6**, recrystallized from methanol, 630 mg (0.021 %yield); R_f : 0.48 (toluene : chloroform :: 1:1); m.p.: 180-183^o C; UV_{max}: 240 nm (log

ν_{\max} (KBr): 3450, 3400, 2945, 2860, 2360, 1690, 1650, 1570, 1310, 980 cm^{-1} ; EIMS m/z (rel. int.): 368 $[\text{M}]^+$ ($\text{C}_{21}\text{H}_{20}\text{O}_6$) (41.6).

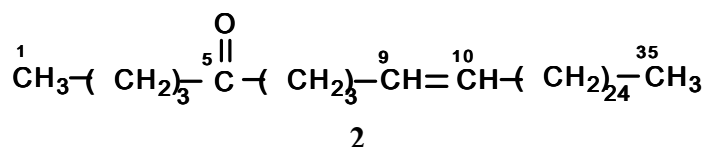
RESULTS AND DISCUSSION

Compound **1** was obtained as a colourless amorphous powder from the petroleum ether extract column from *n*-hexane eluants. Its IR spectrum displayed characteristic absorption bands for hydroxyl group (3450 cm^{-1}) and long aliphatic chain (725 cm^{-1}). It has a molecular ion peak at m/z 396 in its mass spectrum consistent with the molecular formula of a saturated alcohol $\text{C}_{27}\text{H}_{56}\text{O}$. The mass spectrum yielded $\text{C}_n\text{H}_{2n+1}$, C_nH_{2n} and $\text{C}_n\text{H}_{2n-1}$ ions in higher abundances for lower fragments. The most of the fragments were separated by 14 mass units. The absence of $[\text{M}^+-\text{Me}]$ ion suggested its straight chain nature. The presence of $[\text{M}^++1]$ ion arose due to its unsymmetrical nature^[5-7]. The generation of important ion peaks at m/z 283 $[\text{HOCH}(\text{CH}_2)_{17}\text{CH}_3]^+$ and 113 $[\text{CH}_3(\text{CH}_2)_7]^+$ suggested the location of the hydroxyl group at C-9. The ^1H NMR spectrum of **1** showed a one-proton double doublet at δ 3.98 ($J=6.6, 6.6 \text{ Hz}$) assigned to carbinol H-9 β . Two three-proton triplets at δ 0.81 ($J=6.1 \text{ Hz}$) and 0.79 ($J=6.0 \text{ Hz}$) were attributed to C-1 and C-27 primary methyl protons. The remaining methylene protons appeared at δ 2.21 ($2 \times \text{CH}_2$), 1.54 ($3 \times \text{CH}_2$) and 1.18 ($19 \times \text{CH}_2$). The ^{13}C NMR spectrum of **1** exhibited signals for carbinol carbon (δ 68.38), methyl carbons (δ 19.31, Me-1; 14.10, Me-27) and methylene carbons between δ 42.10-21.72. On the basis of these evidences, the structure of **1** has been established as *n*-heptacosan-9- α -ol. This is an unreported aliphatic alcohol from a natural or synthetic source.



Compound **2** was obtained as a colourless amorphous powder from petroleum ether extract column with *n*-hexane-petroleum ether (1:1) eluants. It responded positively to olefinic linkage and carbonyl group. Its IR spectrum displayed characteristic absorption bands for carbonyl group (1710 cm^{-1}), unsaturation (1650 cm^{-1}) and long aliphatic chain (725 cm^{-1}). It had a molecular ion peak at m/z 504 in the mass spectrum consistent with the molecular formula $\text{C}_{35}\text{H}_{68}\text{O}$. It indicated two double bonds equivalent adjustable one each to the olefinic linkage and carbonyl group. The prominent ion peaks at m/z 57 $[\text{CH}_3(\text{CH}_2)_3]^+$, 447 $[\text{M}-57, \text{OC}(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_{24}\text{CH}_3]^+$, 85 $[\text{CH}_3(\text{CH}_2)_3\text{CO}]^+$

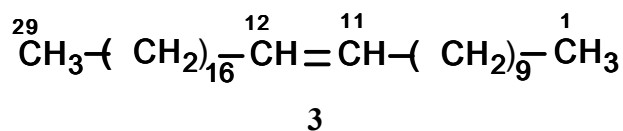
and 419 $[\text{M}-85, (\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_{24}\text{CH}_3]^+$ suggested the location of the carbonyl functional group at C-5. The appearance of the ion peaks at m/z 127 $[\text{CH}_3(\text{CH}_2)_3\text{CO}(\text{CH}_2)_3]^+$, 377 $[\text{M}-127, \text{CH}=\text{CH}(\text{CH}_2)_{24}\text{CH}_3]^+$, 153 $[\text{CH}_3(\text{CH}_2)_3\text{CO}(\text{CH}_2)_3\text{CH}=\text{CH}]^+$ and 351 $[\text{M}-153, (\text{CH}_2)_{24}\text{CH}_3]^+$ indicated the existence of the vinylic linkage at C-9^[8,9]. The ^1H NMR spectrum of **2** showed two one-proton multiplets at δ 5.27 and 5.06 assigned to unsaturated C-9 and C-10 protons. Two multiplets at δ 2.09 and 2.01, integrated for two protons each, were attributed to C-8 and C-11 methylene protons attached to olefinic carbon. Two two-proton double doublets at δ 2.37 ($J=7.41, 7.59 \text{ Hz}$) and δ 2.30 ($J=7.02, 7.32 \text{ Hz}$) were assigned to methylene H₂₋₄ and H₂₋₆, respectively, adjacent to the carbonyl group. Two three-proton triplets at δ 0.90 ($J=6.3 \text{ Hz}$) and 0.85 ($J=6.9 \text{ Hz}$) were attributed to terminal C-1 and C-35 primary methyl protons, respectively. The remaining methylene protons resonated at δ 1.25. The ^{13}C NMR spectrum of **2** showed signals for carbonyl carbon (δ 202.11), vinylic carbons at δ 127.35 (C-9) and 125.16 (C-10), methyl carbons (δ 114.16, Me-1; 14.11, Me-35) and methylene carbons between 33.97-22.69. On the basis of the foregoing account, the structure of **2** has been formulated as *n*-pentatriacont-9-en-5-one. This is an unreported aliphatic ketone isolated from a natural or synthetic source for the first time.



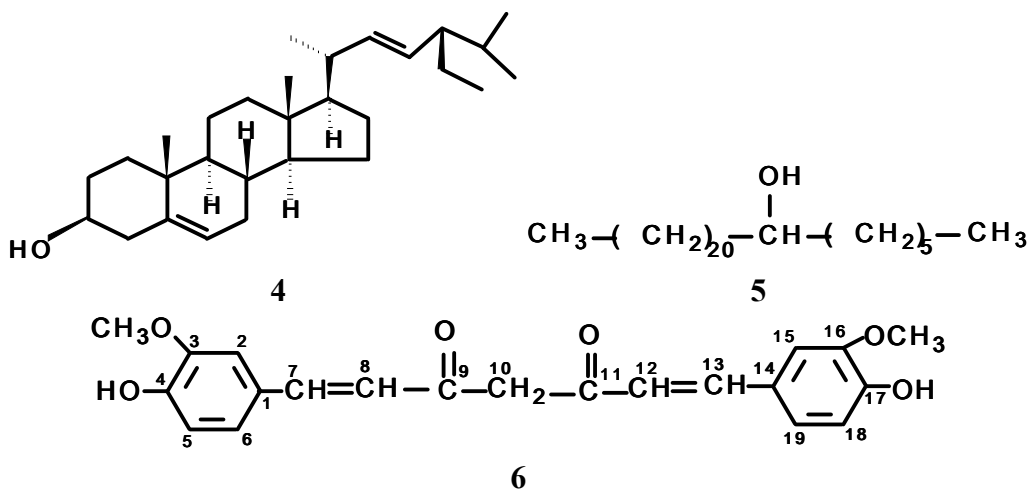
Compound **3**, obtained as an amorphous powder from the methanolic extract column with petroleum ether-chloroform (1:3) eluants, responded positively to vinylic linkage. Its IR spectrum showed absorption bands for unsaturation (1635 cm^{-1}) and long aliphatic chain ($735, 710 \text{ cm}^{-1}$). The mass spectrum of **3** displayed a molecular ion peak at m/z 406 ($\text{C}_{29}\text{H}_{58}$) and ions corresponding to $\text{C}_n\text{H}_{2n+1}$, C_nH_{2n} and $\text{C}_n\text{H}_{2n-1}$ separated by 14 mass units. The generation of the prominent ion peaks at m/z 141 $[(\text{CH}_2)_9\text{CH}_3]^+$, 265 $[\text{M}-141, \text{CH}_3(\text{CH}_2)_{16}\text{CH}=\text{CH}]^+$, 239 $[\text{CH}_3(\text{CH}_2)_{16}]^+$ and 167 $[\text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CH}]^+$ suggested the existence of the vinylic linkage at C-9. The ^1H NMR spectrum of **3** exhibited a two-proton multiplet at δ 5.34 assigned to unsaturated C-11 and H-12 protons. Two one-proton doublets at δ 2.81 ($J=5.12 \text{ Hz}$) and 2.71 ($J=5.64 \text{ Hz}$) were ascribed to C-13 methylene protons attached to C-12 unsaturated carbon. One multiplet at δ 2.01, integrated for two protons, was associated with C-

10 methylene protons attached to C-11 vinylic carbon. Two three-proton triplets at δ 0.95 ($J=6.7$ Hz) and 0.85 ($J=6.3$ Hz) were associated with terminal C-1 and C-29 primary methyl protons. The remaining methylene protons appeared at δ 1.61 ($1 \times \text{CH}_2$), 1.31 ($3 \times \text{CH}_2$) and 1.27 ($19 \times \text{CH}_2$). The absence of any signal between δ 5.34 and 2.81 ruled out the location of any carbinol proton in the molecule. The ^{13}C NMR spectrum of **3** displayed important signals at δ 129.29 and 127.31 for C-11 and C-12 vinylic carbons, respectively, 18.42 and 13.30 for primary C-1 and C-29 methyl carbons, respectively and between δ 33.28-21.53 for remaining methylene carbons. The absence of any signals between δ 127.31 and 33.28 ruled out the location of any carbinol carbon in the molecule. On the basis of these spectral

data analyses and chemical reactions, the structure of **3** has been characterized as *n*-nonacos-11-ene. This is a new compound isolated from a natural or synthetic source for the first time.



The structures of the known compounds **4**, **5** and **6** have been characterized as stigmasta-5, 22-dien-3 β -ol (stigmasterol)^[10]; *n*-octacosan-7-ol and 1,7-bis-(4-hydroxy-3-methoxyphenyl)-1, 6-heptadiene-3, 5-dione (curcumin)^[11], respectively, on the basis of spectral data analysis.



CONCLUSION

The present work characterized several chemical constituents from the rhizomes of *C. oligantha* var. *oligantha*. The existing knowledge about the phytoconstituents of *Curcuma* species is increased by phytochemical investigation of this unexplored species. The present phytoconstituents may be used as fingerprinting markers for quality control of *C. oligantha*.

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