

NEW CINNAMYL ESTER AND POLYALCOHOL DERIVATIVE FROM THE RHIZOMES OF *CURCUMA OLIGANTHA* VAR. *OLIGANTHA*

SHAMIM AHMAD, MOHAMMED ALI\* and SHAHID H. ANSARI

Phytochemical Research Laboratory, Department of Pharmacognosy and Phytochemistry, Faculty of Pharmacy, Jamia Hamdard (Hamdard University), New Delhi-110062, India

**Keywords:** *Curcuma oligantha* Trimen var. *oligantha*, zingiberaceae, rhizomes, oliganthylyl cinnamate, curculiganthol

*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 Sri Lanka and Karnataka (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 complexion (3). The rhizomes of this species were not investigated chemically. This paper describes isolation and structure elucidation of two new phytoconstituents from the rhizomes of *C. oligantha* var. *oligantha*.

**EXPERIMENTAL**

The melting points were determined on a Perfit apparatus and are uncorrected. The IR spectra were recorded in KBr pellets on Win IR FTS 135 instrument (Biorad, USA). <sup>1</sup>H (400 MHz) and <sup>13</sup>C (75 MHz) NMR spectra were recorded by Bruker spectropin NMR instrument in CDCl<sub>3</sub> using TMS as an internal standard. EIMS spectra 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 *Curcuma 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 was deposit-

ed in the herbarium of the Faculty of Pharmacy, Jamia Hamdard (Hamdard University), New Delhi, India.

**Extraction and isolation**

The air-dried rhizomes (3 kg) of *Curcuma oligantha* var. *oligantha* were coarsely powdered and extracted with methanol in a Soxhlet apparatus for 72 h. The methanolic extract was concentrated to give dark viscous mass (390 g). It was adsorbed on silica gel (60–120 mesh) to form slurry, which was air-dried and chromatographed over silica gel columns packed in petroleum ether. The column was eluted with petroleum ether, mixtures of petroleum ether and chloroform (90:10, 75:25, 50:50 and 25:75, v/v), pure chloroform and finally mixtures of chloroform and methanol (99.5:0.5, 99:1, 48:1, 19:1, 9:1, v/v). Various fractions were collected separately and checked by TLC for homogeneity. Similar fractions (having the same R<sub>f</sub> 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.

**Stigmasterol (1)**

Elution of the column with petroleum ether yielded colorless crystals of **1**, recrystallized from methanol, 200 mg (0.0067% yield); R<sub>f</sub>: 0.45 (benzene); m.p.: 168–169°C; [α]<sub>D</sub><sup>20</sup>: –51° (CHCl<sub>3</sub>, 0.1); IR ν<sub>max</sub> (KBr, cm<sup>-1</sup>): 3500, 2945, 2856, 1645, 1475, 1360, 1210, 1125; EIMS *m/z* (rel. int.): 412 [M]<sup>+</sup> (C<sub>29</sub>H<sub>48</sub>O) (33.1).

\* Corresponding author: e-mail: maliphyto@gmail.com; mali\_hamdard@yahoo.co.in

**Oliganthyl cinnamate (2)**

Further elution of the column with the petroleum ether yielded colorless crystals of **2**, recrystallized from methanol, 522 mg (yield 0.0174%);  $R_f$ : 0.76 (toluene); m.p.: 78–80°C;  $[\alpha]_D^{20}$ : –29.8° (CHCl<sub>3</sub>, 0.1); UV  $\lambda_{max}$  (MeOH): 222 nm (log  $\epsilon$  5.2); IR  $\nu_{max}$  (KBr, cm<sup>-1</sup>): 2926, 2860, 1725, 1648, 1540, 1470, 1160, 910, 795; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 6.47 (brm, 2H, H-5', H-9'), 6.15 (brm, 2H, H-6', H-8'), 6.09 (brm, 1H, H-7'), 5.94 (d, 1H,  $J$  = 8.5 Hz, H-3'), 5.89 (d, 1H,  $J$  = 8.5 Hz, H-2'), 4.46 (brs, 2H, H<sub>2</sub>-9), 2.40 (d, 1H,  $J$  = 5.5 Hz, H<sub>2</sub>-2a), 2.31 (d, 1H,  $J$  = 9.9 Hz, H<sub>2</sub>-2b), 2.04 (m, 1H, H-4), 1.65 (m, 1H, H<sub>2</sub>-3a), 1.41 (m, 1H, H<sub>2</sub>-3b), 1.37 (m, 1H, H<sub>2</sub>-5a), 1.32 (m, 1H, H<sub>2</sub>-5b), 1.06 (m, 1H, H<sub>2</sub>-6a), 0.96 (m, 1H, H<sub>2</sub>-6b), 0.82 (brs, 3H, Me-10), 0.77 (brs, 3H, Me-7); <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 42.32 (C-1), 21.97 (C-2), 23.40 (C-3), 40.73 (C-4), 36.78 (C-5), 33.58 (C-6), 15.02 (C-7), 54.82 (C-8), 61.48 (C-9), 19.13 (C-10), 177.72 (C-1'), 126.25 (C-2'), 125.03 (C-3'), 150.23 (C-4'), 143.26 (C-5'), 128.29 (C-6'), 124.51 (C-7'), 121.75 (C-8'), 139.61 (C-9'); EIMS  $m/z$  (rel. int.): 284 [M]<sup>+</sup> (C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>) (65.5), 147 (100), 137 (39.8), 95 (34.7), 81 (38.2), 69 (27.5), 55 (37.8).

***n*-Octacosan-7-ol (3)**

Elution of the column with chloroform furnished colorless crystals of **3**, recrystallized from methanol : acetone (1:1, v/v), 390 mg (yield 0.013%);  $R_f$ : 0.73 (chloroform: ethyl acetate 9:1, v/v); m.p.: 151–153°C;  $[\alpha]_D^{20}$ : +35° (MeOH, 0.05); IR  $\nu_{max}$  (KBr, cm<sup>-1</sup>): 3410, 2965, 2845, 1512, 1460, 1355, 1210, 725, 710; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 4.20 (dd, 1H,  $J$  = 6.5, 5.5 Hz, H-7 $\beta$ ), 1.61 (d, 2H,  $J$  = 6.3 Hz, H<sub>2</sub>-6), 1.52 (d, 2H,  $J$  = 7.1 Hz, H<sub>2</sub>-8), 1.25 (brs, 46H, 23  $\times$  CH<sub>2</sub>), 0.91 (t, 3H,  $J$  = 6.1 Hz, Me-1), 0.83 (t, 3H,  $J$  = 6.9 Hz, Me-28); EIMS  $m/z$  (rel. int.): 410 [M]<sup>+</sup> (C<sub>28</sub>H<sub>58</sub>O) (8.9), 392 (9.1), 325 (25.3), 85 (19.1).

**Curcumin (4)**

Elution of the column with chloroform-methanol (99.5:0.5, v/v) afforded yellow crystalline mass of **4**, recrystallized from methanol, 630 mg (yield 0.021%);  $R_f$ : 0.48 (toluene : chloroform 1:1, v/v); m.p.: 180–183°C; UV  $\lambda_{max}$ : 240 nm (log  $\epsilon$  3.2); IR  $\nu_{max}$  (KBr, cm<sup>-1</sup>): 3450, 3400, 2945, 2860, 2360, 1690, 1650, 1570, 1310, 980; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 7.58 (d, 1H,  $J$  = 15.72 Hz, H-8), 7.53 (d, 1H,  $J$  = 15.72 Hz, H-12), 7.06 (brs, 4H, H-2, H-5, H-15, H-18), 7.04 (brs, 1H, D<sub>2</sub>O exchangeable, OH), 6.91 (d, 2H,  $J$  = 8.50 Hz, H-6, H-19), 6.50 (d, 1H,  $J$  = 15.72 Hz, H-7), 6.45 (d, 1H,  $J$  = 15.72 Hz, H-13), 5.82 (brs, 1H, D<sub>2</sub>O exchangeable, OH), 3.90 (brs,

8H, OMe-3; OMe-17, H<sub>2</sub>-11); <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 126.44 (C-1), 120.67 (C-2), 140.18 (C-3), 148.48 (C-4), 115.11 (C-5), 109.82 (C-6), 115.11 (C-7), 122.38 (C-8), 182.75 (C-9), 55.38 (C-10), 182.75 (C-11), 122.38 (C-12), 115.11 (C-13), 122.38 (C-14), 120.67 (C-15), 140.18 (C-16), 147.26 (C-17), 120.67 (C-18), 100.62 (C-19), 55.38 (2  $\times$  OMe); EIMS  $m/z$  (rel. int.): 368 [M]<sup>+</sup> (C<sub>21</sub>H<sub>20</sub>O<sub>6</sub>) (41.6), 350 (43.5), 271 (15.8), 230 (11.3), 216 (11.5), 191 (27.4), 188 (37.4), 177 (18.2), 176 (100), 149 (26.3), 146 (7.2), 144 (32.1), 134 (12.5), 129 (11.2), 123 (17.1), 116 (10.2), 108 (9.2).

**Curroliganthol 5**

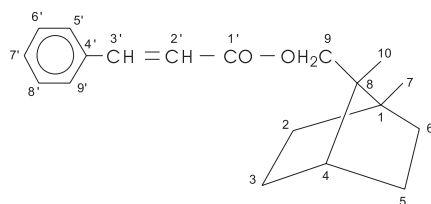
Elution of the column with chloroform-methanol (99:1, v/v) furnished pale yellow amorphous powder of **5**, recrystallized from acetone : methanol (1:1, v/v), 470 mg (yield 0.0157%);  $R_f$ : 0.87 (chloroform : methanol 4:1, v/v); m.p.: 159–161°C;  $[\alpha]_D^{20}$ : +28.7° (CHCl<sub>3</sub>, 0.1); UV  $\lambda_{max}$  (MeOH): 216 nm (log  $\epsilon$  3.2); IR  $\nu_{max}$  (KBr, cm<sup>-1</sup>): 3510, 3490, 3300, 2919, 2840, 1645, 1470, 1360, 1220, 1115, 774; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 5.16 (m, 1H, H-14), 5.11 (m, 1H, H-8), 5.06 (m, 1H, H-13), 5.01 (m, 1H, H-9), 6.24 (m, 1H, H-17), 5.81 (m, 1H, H-18), 5.28 (m, 1H, H-19), 4.21 (m, 1H,  $w^{1/2}$  = 6.1 Hz, H-7), 4.11 (d, 1H,  $J$  = 6.50 Hz, H-15 $\beta$ ), 4.07 (m, 1H,  $w^{1/2}$  = 6.5 Hz, H-6), 3.86 (m, 2H,  $w^{1/2}$  = 6.5 Hz, H-4, H-5), 2.77 (m, 2H, H<sub>2</sub>-20), 2.42 (m, 2H, H<sub>2</sub>-21), 1.54 (brm, 4H, H<sub>2</sub>-12, H<sub>2</sub>-10), 1.18 (brs, 6H, H<sub>2</sub>-11, H<sub>2</sub>-3, H<sub>2</sub>-2), 0.80 (t, 3H,  $J$  = 6.8 Hz, Me-1); <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 14.08 (C-1), 22.68 (C-2), 24.88 (C-3), 65.18 (C-4), 66.60 (C-5), 66.87 (C-6), 65.03 (C-7), 115.68 (C-8), 114.71 (C-9), 25.99 (C-10), 29.68 (C-11), 29.68 (C-12), 119.13 (C-13), 123.21 (C-14), 68.92 (C-15), 144.60 (C-16), 123.01 (C-17), 122.76 (C-18), 121.53 (C-19), 34.09 (C-20), 55.94 (C-21); EIMS  $m/z$  (rel. int.): 366 [M]<sup>+</sup> (C<sub>21</sub>H<sub>34</sub>O<sub>5</sub>) (5.6), 261 (24.7), 233 (14.0), 231 (8.8), 217 (19.1), 214 (10.6), 203 (21.2), 199 (19.8), 189 (11.3), 185 (12.3), 184 (12.1), 177 (30.6), 163 (11.1), 154 (13.0), 145 (31.5), 135 (36.9), 133 (15.9), 124 (15.2), 115 (15.3), 109 (49.1), 99 (33.6), 94 (31.3), 85 (25.1), 73 (18.3), 68 (51.6), 54 (68.2), 43 (100).

**RESULTS AND DISCUSSION**

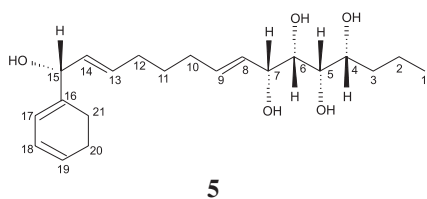
The structures of the known compounds **1**, **3** and **4** have been characterized as stigmasta-5,22-dien-3 $\beta$ -ol (stigmasterol, (**4**); *n*-octacosan-7-ol and 1,7-bis-(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione (curcumin) (**5**), respectively, on the basis of spectral data analysis.

Compound **2**, designated as oliganthyl cinnamate, was obtained as a colorless crystalline compound from petroleum ether eluants. It decolorized bromine water indicating its unsaturated nature. The IR spectrum of **2** displayed characteristic absorption bands for ester group ( $1725\text{ cm}^{-1}$ ) and unsaturation ( $1648, 1540\text{ cm}^{-1}$ ). Its molecular weight was established at  $m/z$  284 on the basis of electron impact mass and  $^{13}\text{C}$  NMR spectra consistent with the molecular formula  $\text{C}_{19}\text{H}_{24}\text{O}_2$ . The generation of the base peak at  $m/z$  147  $[\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{COO}]^+$  and another prominent peak at  $m/z$  137  $[\text{C}_{10}\text{H}_{17}]^+$  suggested that a borneol-type alcohol was esterified with cinnamic acid moiety to yield an ester. The  $^1\text{H}$  NMR spectrum of **2** exhibited two one-proton deshielded multiplets at  $\delta$  6.47 and 6.15 ppm and a one-proton multiplet at  $\delta$  6.09 ppm assigned to five aromatic protons. Two one-proton doublets at  $\delta$  5.94 ppm ( $J = 8.5\text{ Hz}$ ) and 5.89 ( $J = 8.5\text{ Hz}$ ) were ascribed to vinylic H-3' and H-2' protons. A two-proton broad signal at  $\delta$  4.46 ppm was associated with H<sub>2</sub>-9 oxygenated methylene protons. Two three-proton broad signals at  $\delta$  0.82 and 0.77 ppm were accounted to H<sub>3</sub>-10 and H<sub>3</sub>-7 tertiary methyl protons, respectively. Two one-proton doublets at  $\delta$  2.40 ppm ( $J = 5.5\text{ Hz}$ ) and 2.31 ( $J = 9.9\text{ Hz}$ ) were attributed to C-2 methylene protons. The remaining methine and methylene protons resonated in the range  $\delta$  2.04–0.96 ppm. The  $^{13}\text{C}$  NMR spectrum of **2** showed signals for oxygenated methylene carbon at  $\delta$  61.48 ppm (C-9), ester carbon at  $\delta$  177.72 ppm (C-1'), methyl carbons at  $\delta$  15.02 (C-7) and  $\delta$  19.13 (C-10) ppm and aromatic carbons in the range  $\delta$  150.23–121.75 ppm. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data were compared with the bicyclic monoterpenes (6).

The  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **2** showed correlations of H-3' with H-2' and H-5'/H-6'; H<sub>2</sub>-9 with H<sub>3</sub>-10; and H<sub>3</sub>-7 with H<sub>2</sub>-6 and H<sub>2</sub>-2. The HMBC of **2** exhibited interactions of C-1' with H<sub>2</sub>-9 and H-2'; C-4' with H-3' and H-5'/H-6'; and C-1 with H<sub>3</sub>-7 and H<sub>2</sub>-6. On the basis of these spectral data analyses and chemical reactions, the structure of **2** has been characterized as bornan-9-ol-yl cinnamate. It is a new cinnamic acid ester reported from *Curcuma* or other plant species for the first time.

**2**

Compound **5**, named, curoliganthol, was obtained as a pale yellow amorphous powder from the chloroform-methanol (99:1, v/v) eluants. It decolorized bromine water due to unstauration. Its IR spectrum showed characteristic absorption bands for hydroxyl groups ( $3510, 3490, 3300\text{ cm}^{-1}$ ) and olefinic linkage ( $1645\text{ cm}^{-1}$ ). Its mass spectrum displayed a molecular ion peak at  $m/z$  366 corresponding to cyclohexadiene containing pentadecane-pentaol chain,  $\text{C}_{21}\text{H}_{34}\text{O}_5$ . It indicated five double bond equivalents; four of them were adjusted in the four vinylic linkages and one in the cyclohexane ring. The important ion fragments at  $m/z$  109  $[\text{C}_{14}\text{-C}_{15}\text{ fission}]^+$ , 231, 135  $[\text{C}_{12}\text{-C}_{13}\text{ fission}]^+$ , 217  $[\text{231-CH}_2]^+$ , 199  $[\text{217-H}_2\text{O}]^+$ , 203  $[\text{217-CH}_2]^+$ , 185  $[\text{203-H}_2\text{O}]^+$ , 177, 189  $[\text{C}_9\text{-C}_{10}\text{ fission}]^+$ , 163  $[\text{177-CH}_2]^+$ , 149  $[\text{163-CH}_2]^+$ , 68  $[\text{177-C}_7\text{H}_9\text{O}]^+$  and 54  $[\text{163-C}_7\text{H}_9\text{O}]^+$  indicated the existence of cyclohexadiene ring and hydroxyl group at C-15 as well as olefinic linkage at  $\Delta^{13}$ . The ion peaks at  $m/z$  203, 163  $[\text{C}_7\text{-C}_8\text{ fission}]^+$ , 145  $[\text{163-H}_2\text{O}]^+$ , 94  $[\text{203-C}_7\text{H}_9\text{O}]^+$ , 233, 133  $[\text{C}_6\text{-C}_7\text{ fission}]^+$ , 115  $[\text{133-H}_2\text{O}]^+$ , 124  $[\text{233-C}_7\text{H}_9\text{O}]^+$ , 73  $[\text{C}_4\text{-C}_5\text{ fission}]^+$ , 184  $[\text{M-73-C}_7\text{H}_9\text{O}]^+$  and 43  $[\text{C}_3\text{-C}_4\text{ fission}]^+$  suggested the location of other olefinic linkage at  $\Delta^8$  and hydroxyl groups at C-4, C-5, C-6 and C-7. The  $^1\text{H}$  NMR spectrum of **5** exhibited seven one-proton multiplets at  $\delta$  6.24, 5.81, 5.28, 5.16, 5.11, 5.06 and 5.01 ppm assigned correspondingly to vinylic H-17, H-18, H-19, H-14, H-8, H-13 and H-9 protons. A one-proton doublet at  $\delta$  4.11 ppm ( $J = 6.5\text{ Hz}$ ) and three one-proton multiplets at  $\delta$  4.21, 4.07 and 3.86 ppm were accounted to hydroxymethine protons H-15 $\beta$ , H-7, H-6 and H-5, respectively. A three-proton triplet at  $\delta$  0.80 ppm ( $J = 6.8\text{ Hz}$ ) was attributed to C-1 primary methyl protons. The remaining methylene protons resonated at  $\delta$  2.77 (2H), 2.42 (2H), 1.54 (4H) and 1.18 (6H) ppm. The  $^{13}\text{C}$  NMR spectrum of **5** displayed signals for vinylic carbons at  $\delta$  115.68 (C-8), 114.71 (C-9), 119.13 (C-13), 123.21 (C-14), 144.60 (C-16), 123.01 (C-17), 122.76 (C-18) and 121.53 (C-19) ppm. The C-4, C-5, C-6, C-7 and C-15 carbinol carbons resonated at  $\delta$  65.18, 66.60, 66.87, 65.03 and 68.97 ppm, respectively. The  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **5** showed correlations of H-15 with H-14, H-13 and H-17; H-8 with H-9, H-10 and H-7; and H-4 with H<sub>2</sub>-3, H-5, H-6 and H-7. The HMBC spectrum of **5** exhibited correlations of C-16 with H-17, H-18 and H<sub>2</sub>-21; C-14 with H-13 and H-15; C-8 with H-9, and H-7; and C-5 with H-4, and H-6. On the basis of these evidences, the structure of **5** has been elucidated as 15-cyclohexa-16,18-dienyl-pentadeca-8,13-dien-4 $\alpha$ ,5 $\alpha$ ,6 $\alpha$ ,7 $\alpha$ ,15 $\alpha$ -pentaol. This is a new compound isolated from a natural or synthetic source.



## REFERENCES

1. Ansari R., Nair V.J., Nair N.C.: *Curr. Sci.* 51, 293 (1982).
2. Bhat K.G.: *Indian J. Forestry* 10, 66 (1987).
3. Kiritikar K.R., Basu B.D.: *Indian Medicinal Plants*. Sri Satguru Publications, Delhi, 11, 3335 (2000).
4. Sharma S.K., Kumar N., Singh S., Ali M.: *Asian J. Chem.* 20, 5455 (2008).
5. Chignell C.F., Bilski P., Reszka K.J., Motten A.G., Sik R.H., Dahl T.A : *Photochem. Photobiol.* 59, 295 (1994).
6. Ali M.: *Techniques in terpenoid identification*, pp. 1-51, Birla Publication, Delhi 2001.

*Received: 02. 12. 2009*