A new lupane-type triterpenoid fatty acid ester and other isolates from *Ophiorrhiza shendurunii*

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Abstract

A new pentacyclic triterpenoid fatty acid ester, lupan-20-ol-3(β)-yl hexadecanoate (1), together with lupan-20-ol-3(β)-yl acetate (2), olean-18-en-3(β)-yl hexadecanoate (3), dotriacontanoic acid (4), stigmasterol (5), rubiadin (6), nonadecanoic acid (7), palmitic acid (8) and camptothecin (9) were isolated from the hexane and chloroform extracts of *Ophiorrhiza shendurunii* from south India. Structures of the isolates were determined by \textsuperscript{1}H-, \textsuperscript{13}C-, \textsuperscript{13}C-DEPT, \textsuperscript{1}H-\textsuperscript{1}H COSY, HMBC, HSQC, NOESY NMR, FT-IR, DART-MS, ESI-MS, alkaline hydrolysis, derivatization, GC-MS and HPTLC analyses. *O. shendurunii* hexane and chloroform extracts showed significant activities against *Candida albicans* and *Fusarium oxysporum*. Compounds 1 to 3 showed only moderate antiyeast/antifungal activities.

**Keywords:** *Ophiorrhiza shendurunii*, pentacyclic triterpenoid fatty acid ester, lupan-20-ol-3(β)-yl hexadecanoate, antifungal activity.
Fig. S1 Spectral data of Lupan-20-ol-3(β)-yl hexadecanoate (1)

Key NOESY correlations of lupan-20-ol-3(β)-yl hexadecanoate (1).
$^1$H NMR
$^1$H NMR EXPANSION 01
$^{13}$C NMR
$^{13}$C NMR EXPANSION 01
$^{13}$C NMR EXPANSION 02
$^{13}$C NMR EXPANSION 03
HMBC EXPANSION 01
SAIFNM130925A-01(OsHe3) NOSEY

SAIF Cochin
SAIFNM130925A-01(OsHe3) NOSEY

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ppm

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SAIF Cochin

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SAIFNM130925A-01(OsHe3) NOSEY

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ppm
MASS SPECTRUM

Relative Intensity

m/z

191.13  229.13  302.12  355.98  428.28  429.28  664.43  683.46

409.27  410.27  427.28  655.44

Spec. Record Interval: 0.4[s]
Ring Lens Volt: 9[V]
Time of Maximum: 0.401[min]
Operator Name: admin
GC-MS TIC

File: C:\msdchem2\EOIL2013\july\ranjith\26071305.D
Operator: 
Acquired: 26 Jul 2013 15:47 using AcqMethod ESSENTIALOIL_MANUAL700 M.M
Instrument: Instrument #2
Sample Name: OSHe 3H
Misc Info: 
Vial Number: 1
GC-MS MASS SPECTRUM (Methyl ester of hexadecanoic acid)
Spectral data of other isolated compounds (2 to 9)

Lupan-20-ol-3(β)-yl acetate (2): White amorphous solid; m. p. 245°C; IR \( \lambda_{\text{max}} \) cm\(^{-1}\): 3494, 2941, 1714, 1455, 1370, 1263, 1190, 1160, 979; HRESI-MS \( m/z \): 509.1899 (M+Na)+, calculated mass for C\(_{32}\)H\(_{54}\)O\(_3\)Na 509.3970; spectral data (\(^1\)H, \(^{13}\)C NMR, correlation data) of (2) were comparable with literature data (Yuruker et al. 1998). Compound (2), lupan-20-ol-3(β)-yl acetate, has an acetate group at C3 instead of the long chain fatty acid ester side chain in (1) (Fig. 1). Spectral data of (2) were matching with literature (Yuruker et al. 1998) and also with the terpenoid skeleton of (1).

Olean-18-en-3(β)-yl hexadecanoate (3): White waxy solid; m. p. 75°C; IR \( \lambda_{\text{max}} \) cm\(^{-1}\): 2917, 2850, 1726, 1465, 1454, 1378, 1265, 1247, 1221, 1173, 981, 718; ESI-MS \( m/z \): 663.47 (M+Na)+; spectral data (\(^1\)H, \(^{13}\)C NMR, correlation data) of (3) were comparable with Ragasa et al. 2012. Compound (3), olean-18-en-3(β)-yl hexadecanoate (Fig. 1), has a double bond (C18, C19) and a long chain fatty acid side chain at C3 (Ragasa et al. 2012).

Dotriacontanoic acid (4): White amorphous solid; m. p. 95°C; IR \( \lambda_{\text{max}} \) cm\(^{-1}\): 2915, 2848, 1737, 1704, 1472, 1462, 1217, 729, 719; DART-MS \( m/z \): 481.36 (M+H)+; spectral data (\(^1\)H, \(^{13}\)C NMR, correlation data) of (4) were comparable with Parmar et al., 1998.

Stigmasterol (5): Compound (5) (Fig. 1) was identified by comparison of its IR spectrum, m. p. and NMR data with literature (De-Eknamkul and Potduang 2003).

Rubiadin (6): Yellow solid; m. p. 291°C; DART MS: 255.14 (M+H\(^+\)); IR \( \lambda_{\text{max}} \) cm\(^{-1}\): 3390, 2921, 2515, 1659, 1619, 1579, 1548, 1503, 1479, 1394, 1335, 1300, 1133, 967, 710; \(^{13}\)C NMR: 161.93 (C1), 119.93 (C2), 163.48 (C3), 108.07 (C4), 126.14 (C5), 134.04 (C6), 134.23 (C7), 127.02 (C8), 187.08 (C9), 183.22 (C10), 130.88 (4a), 132.42 (C8a), 110.03 (C9a), 133.08 (C10a), 8.14 (CH\(_3\)), 2.095 (CH\(_3\)), 7.154 (C4), 7.810 (C5), 7.931 (C8), 8.189 (C6), 8.206 (C7) (Fig. 1).

Nonadecanoic acid (7): White solid; m. p. 68°C; DART MS: 299.06 (M+H\(^+\)); IR \( \lambda_{\text{max}} \) cm\(^{-1}\): 2956, 2915, 2848, 1695, 1471, 1429, 1411, 1347, 1330, 1295, 1187, 1099, 934, 720; \(^{13}\)C NMR: 180.76,
Hexadecanoic acid (Palmitic acid) \textbf{(8)}: White solid; m. p. 63$^\circ$C; DART-MS: 257.19 (M+H$^+$); IR $\nu_{\text{max}}$ cm$^{-1}$: 2955, 2915, 2848, 1695, 1463, 1429, 1411, 1347, 1330, 1295, 1187, 1099, 934, 720; $^{13}$C NMR: 180.41, 34.12, 31.96, 29.72, 29.70, 29.67, 29.39, 29.27, 29.09, 14.70, 22.72, 14.13; $^1$H NMR: 2.346 (t), 1.63 (m), 1.25-1.30 (brs), 0.88 (t).

Camptothecin \textbf{(9)}: Pale yellowish solid; m. p. 275$^\circ$C; LC-EI-MS, m/z: 349.52 (M+H$^+$); IR $\nu_{\text{max}}$ cm$^{-1}$: 3430, 2938, 1737, 1650, 1600, 1579, 1499, 1437, 1349, 1323, 1233, 1197, 1156, 1164, 1040, 1005, 916, 829, 724; $^1$H NMR ($\delta$): 5.28 (H-5), 8.66 (H-7), 8.10 (d, H-9, J = 8.0), 7.70 (t, H-10, J = 7.2), 7.85 (t, H-11, J = 7.6), 8.16 (d, H-12, J = 8.4), 7.37 (s, H-14), 5.41 (dd, H-17 J = 16.4, 23.4), 0.90 (t, H-18, J = 7.2), 1.89 (H-19), 6.30 (H-OH); $^{13}$C NMR ($\delta$): 152.6 (C2), 145.5 (C3), 50.1 (C5), 129.7 (C6), 131.5 (C7), 128.0 (C8), 128.4 (C9), 127.5 (C10), 130.26 (C11), 129.0 (C12), 148.1 (C13), 96.7 (C14), 150.0 (C15), 119.1 (C16), 156.8 (C16a), 65.3 (C17), 7.7 (C18), 30.7 (C19), 72.4 (C20), 172.2 (C21) (Fig. 1).

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