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Tetraterpenyl esters from the oleo-resin of *Commiphora myrrha* (Nees) Engl.

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ABSTRACT

*The phytochemical investigation of the oleo-resin of Commiphora myrrha (Nees) Engl. furnished with the isolation of three new tetraterpenyl esters namely 2,6,10,14,19,23,31-heptamethyl-27-methylene-dotriacos-(all Z)-12,14,16,18-tetraen-11β-ol-7β-olyl salicylate (**3**), 2,6,10,14,19,23,31-heptamethyl-27-methylene-dotriacont-(all Z)-1,12,14,16,18,27(39)-hexaen-3β,4β,5β,11β-tetraolyl-3β-salicyl-4,5,11-triacetate (**4**), and (all Z)-2,6,10,14,19,23,31-heptamethyl dotriacont-(all Z)-12,14,16,18,27(39)-pentaen-7β,11β-diolyl-7β-vanillyl-11β-acetate (**5**) and two aliphatic esters identified as n-dodecanyl myristate **1** and henetriacosanyl laurate **2**. The structures of all the compounds were elucidated on the basis of spectral data analysis.*

Keywords: *Commiphora* genus, myrrh, schizogenous cavities, tetraterpenic esters.

INTRODUCTION

Commiphora myrrha (Nees) Engl. (Burseraceae) is a small tree which grows in small sandy and rocky regions of Somalia, Sudan, Ethiopia, Kenya and Saudi Arabia. The schizogenous cavities of the stem and branches of this tree produce a scented oleo-resin which is known as myrrh. It is imported into India since long time and used in perfumery as food additive, fragrance, incense, antiseptic, astringent, stimulant, stomachic, tonic and for embalming. It is an ingredient of toothpastes, mouthwashes and dentifrices. Myrrh tincture is useful in menstrual disorders and chlorosis. In China, it is prescribed to treat wounds, inflammation and menstrual pain due to blood stagnation [1]. Cadinenes, calamenes, triacont-1-ene [2], commiphoric acids, furanosesquiterpenoids [3-10], eudesmol and triterpenoids [11] and volatile oil [12] have been reported from the oleo-resin of *C. myrrha*. This paper describes the isolation and the characterization of the tetraterpenyl and fatty esters from the oleo-resin obtained from the Khari Baoli market of Delhi.

MATERIALS AND METHODS

General experimental techniques

Melting points were determined on a Perfit melting apparatus (Haryana, India) and are uncurrected. UV spectra were measured with a Lambda Bio 20 spectrophotometer (Perkin-Elmer-Rotkreuz, Switzerland) in methanol. Infra red spectra were recorded on Bio-Rad FTIR 5000 (FTS 135, Kawloon, Hong Kong) spectrophotometer using KBr pellets; γ_{max} values are given in cm^{-1}. ^{1}H and ^{13}C NMR spectra were screened on Avance DRX 400, Bruker spectrospin 400 and 100 MHz instruments (Karlesruthe, Germany) using TMS as an internal standard. Mass spectra were scanned by effecting FAB ionization at 70 eV on a JEOL-JMS-DX 303 spectrometer (Japan) equipped with direct inlet probe system. Column chromatography was performed on silica gel (60-120 mesh; Qualigen, Mumbai, India). TLC was run on silica gel G (Qualigen). Spots were visualised by exposing to iodine vapours, UV radiation, and spraying with ceric sulphate.

Plant material

The crude drug was procured from the local market of the Khari Baoli, Delhi. The sample was authenticated by Dr. H.B. Singh, Taxonomist, NISCAIR, CSIR, New Delhi. A voucher specimen of the sample (No. N/R/C/-06-07/803/120) was deposited in the NISCAIR, RHM Division, Dr. K.S. Krishnan Marg (Near Pusa Gate), New Delhi.

Extraction and isolation

The air dried oleo-resin (2.5 kg) was coarsely powdered and extracted with methanol at room temperature for one week. The extract was filtered and concentrated under reduced pressure to get 185 g (7.4% yield) of dark brown mass. The concentrated extract of the oleo-resin was dissolved in minimum amount of methanol and adsorbed on silica gel (60-120 mesh) to form slurry. The slurry was air-dried and loaded on silica gel column (1.6 m × 16 mm × 2 mm) load in petroleum ether and then eluted successively with different solvents in increasing order of polarity in various combinations, such as petroleum ether, petroleum ether- chloroform (9:1, 3:1, 1:1, 1:3), chloroform, chloroform-methanol (19.9:0.1, 99:1, 97:3, 19:1, 93:7, 9:1, 17:3, 3:1, 3:2, 2:3) and methanol. Various fractions were collected separately and matched by TLC to check homogeneity. Similar fractions having the same R_f values were combined and crystallized. The isolated compounds were recrystallized to get pure compounds. The following compounds were isolated from the methanolic extract of *C. myrrha* oleo- resin:

***n*-Dodecanyl myristate (1)**

Further elution of the column with petroleum ether gave a colourless amorphous powder of **1**, recrystallized from acetone-methanol (1:1), 1.41 g (0.0564% yield).; R_f: 0.77 (chloroform-methanol; 97: 3); m.p.: 90- 92°C; +ve ion FAB MS *m/z (rel. int.)*: 396 $[M]^+(C_{26}H_{52}O_2)$ (15.6), 227 (33.1), 211 (26.3), 185 (26.7), 169 (73.5).

Henetriacosanyl laurate (2)

Elution of the column with petroleum ether : chloroform (1:3) produced a colourless amorphous powder of **2**, recrystallized from methanol-acetone-diethyl ether (7:2:1), 1.76 g (0.0704% yield).; R_f: 0.46 (chloroform-methanol; 17:3); m.p.: 82- 83°C; UV λ_{max} (MeOH): 213 nm (log ε 5.3); IR ν_{max} (KBr): 3020, 2927, 2857, 2359, 1726, 1605, 1522, 1432, 1215, 1044, 929, 760 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.50 (2H, brs, H_2-1′), 1.98 (2H, brs, H_2-2), 1.66 (2H, m, CH_2), 1.51 (2H, m, CH_2), 1.29 (74H, brs, 37×CH_2), 0.81 (3H, t, *J*=6.1 Hz, Me–31′), 0.79 (3H, t, *J*=6.0 Hz, Me-12); +ve ion FAB MS *m/z (rel. int.)*: 648 $[M]^+(C_{44}H_{88}O_2)$ (37.3), 633 (12.2), 183 (100), 155 (21.7), 126 (25.8).

Myrrhatetraterpenolyl salicylate (3)

Further elution of the column with chloroform furnished a brown mass of **3**, recrystallized from methanol-acetone-diethyl ether (5:3:2), 300 mg (0.012% yield); R_f: 0.55 (chloroform); m.p.: 65-66°C; UV λ_{max} (MeOH): 219, 269, 330 nm (log ε 5.6, 4.7, 2.1); IR ν_{max} (KBr): 3454, 2928, 2857, 1745, 1644, 1527, 1446, 1380, 1326, 1218, 1094, 1036, 768 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.23 (1H, m, H-3'), 7.12 (1H, m, H-6'), 7.01 (1H, m, H-4'), 6.60 (1H, m, H-5'), 5.72 (1H, dd, *J*=5.6, 7.1 Hz, H-16), 5.66 (1H, dd, *J*=7.1, 8.5 Hz, H-17) , 5.63 (1H, d, *J*=8.5 Hz, H-18), 5.50 (1H, d, *J*=5.6 Hz, H-15), 5.06 (1H, dd, *J*=6.8, 8.1 Hz, H-12), 5.01 (1H, d, *J*=6.8 Hz, H-13), 4.80 (2H, brs, H_2-39), 4.68 (1H, ddd, *J*=5.5, 5.1, 6.3 Hz, H-7α), 3.40 (1H, dd, 5.3, 8.1 Hz, H-11α), 1.81 (3H, brs, Me-36), 1.78 (3H, brs, Me-37), 1.32 (3H, d, *J*=6.1 Hz, Me-35), 1.16 (3H, d, *J*=6.3 Hz, Me-34), 1.00 (3H, d, *J*=7.2 Hz, Me-1), 1.03 (3H, d, *J*=7.0 Hz, Me-33), 0.96 (3H, d, *J*=6.6 Hz, Me-38), 0.91 (3H, *J*=6.2 Hz, Me-32), 0.89 (3H, *J*=6.3, Me-40); ^{13}C NMR ($CDCl_3$): Table 1; +ve ion FAB MS *m/z (rel. Int.)*: 704 $[M]^+$ ($C_{47}H_{76}O_4$) (1.3), 481 (10.1), 385 (14.9), 355 (39.8), 349 (22.6), 263 (25.8), 223 (31.3), 137 (41.2), 121 (33.4), 111 (15.2).

Myrrhatetraterpenolyl salicylate triacetate (4)

Elution of the column with chloroform-methanol (99:1) afforded a dark brown mass of **4**, recrystallized from methanol-acetone (1:1), 1.63 g (0.0652% yield); R_f: 0.46 (chloroform-methanol; 99:1); m.p.: 63-64°C; UV λ_{max} (MeOH): 226, 252, 265, 287, 437, 481 nm (log ε 4.5, 4.2, 4.2, 4.3, 4.1, 3.9); IR ν_{max} (KBr): 3441, 2930, 2852, 2360, 1743, 1739, 1722, 1645, 1510, 1444, 1377, 1218, 1092, 1029, 761 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.22 (1H, m, H-3'), 7.02 (1H, m, H-6'), 6.95 (1H, m, H-4'), 6.50 (1H, m, H-5'), 5.73 (1H, dd, *J*=5.5, 6.8 Hz, H-16), 5.68 (1H, dd, *J*=6.8, 8.8 Hz, H-17) , 5.61 (1H, d, *J*=8.8 Hz, H-18), 5.49 (1H, d, *J*=5.5 Hz, H-15), 5.10 (1H, dd, *J*=6.0, 8.4 Hz, H-12), 4.98 (1H, d, *J*=6.0 Hz, H-13), 4.85 (2H, brs, H2-39), 4.80 (2H, brs, H_2-1), 4.70 (1H, d, *J*=8.5 Hz, H-3α), 4.63 (1H, dd, *J*=6.2, 6.0 Hz, H-3α), 4.50 (1H, dd, *J*=8.5, 7.7 Hz, H-4α), 4.10 (1H, dd, *J*=7.7, 6.1 Hz, H-5α), 2.01 (3H, brs, $OCOCH_3$), 1.98 (3H, brs, $OCOCH_3$), 1.90 (3H, brs, $OCOCH_3$), 1.78 (3H, brs, Me-33), 1.70 (3H, brs, Me-36), 1.67 (3H, brs, Me-37), 1.30 (3H, d, *J*=6.5 Hz, Me-34), 1.20 (6H, brs, Me-32, Me-40), 0.85 (3H, d, *J*=6.3 Hz, Me-35), 0.72 (3H, d, *J*=6.0 Hz, Me-38); ^{13}C NMR ($CDCl_3$): Table 1; +ve ion FAB-MS *m/z (rel. Int.)*: 860 $[M]^+$ ($C_{53}H_{80}O_9$) (2.1), 505 (32.6), 433 (15.1), 363 (21.2), 335 (11.2), 263 (12.5), 223 (27.1), 191 (100), 111 (30.4).

Myrrhatetraterpenonolyl vanillic acetate (5)

Further elution of the column with chloroform-methanol (99:1) yielded a brown mass of **5**, recrystallized from methanol, 2.28 g (0.0912% yield); R_f: 0.65 (chloroform-methanol; 99:1); m.p. : 75-77°C ; UV λ_{max} (MeOH): 221,

268, 320, 410 nm (log ε 5.3 , 2.3, 4.2, 3.8); IR ν_{max} (KBr): 3442, 2931, 2851, 1741, 1722, 1645, 1527, 1445, 1381, 1381, 1217, 1094, 1035, 951, cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.20 (1H, d, *J*=2.5 Hz, H-2'), 7.01 (1H, m, H-6'), 6.82 (1H, d, *J*=8.5 Hz, H-5'), 6.22 (1H, m, H-5'), 5.72 (1H, dd, *J*=5.3, 7.1 Hz, H-16), 5.61 (1H, dd, *J*=7.1, 8.3 Hz, H-17) , 5.49 (1H, d, *J*=8.3 Hz, H-18), 5.41 (1H, d, *J*=5.3 Hz, H-15), 5.08 (1H, dd, *J*=5.6, 8.1 Hz, H-12), 4.90 (1H, d, *J*=5.6 Hz, H-13), 4.80 (2H, brs, H_2-39), 4.68 (1H, dd, *J*=5.5, 8.1 Hz, H-11α), 4.07 (1H, ddd, *J*=5.3, 6.2, 9.5 Hz, H-7α), 3.30 (3H, brs, OMe), 2.11 (3H, brs, $OCOCH_3$), 1.78 (3H, brs, Me-36), 1.70 (3H, brs, Me-37), 1.10 (6H, brs, Me-1, Me-33), 1.02 (3H, d, *J*=6.3 Hz, Me-34), 0.98 (3H, d, *J*=6.5 Hz, Me-35), 0.77 (3H, d, *J*=6.1 Hz, Me-38); 0.72 (3H, d, *J*=6.3 Hz, Me-32), 0.69 (3H, d, *J*=6.5 Hz, Me-40); ^{13}C NMR ($CDCl_3$): Table 1; +ve FAB-MS *m/z (rel. Int.)*: 776 $[M]^+$ ($C_{50}H_{80}O_6$) (1.3), 420 (29.8), 356 (10.1), 348 (14.2), 320 (14.7), 292 (25.8), 223 (41.6), 113 (69.8), 111 (80.6).

RESULTS AND DISCUSSION

Compounds **1**, **2** were the aliphatic esters characterized as as *n*-dodecanyl myristate and henetriacosanyl laurate, respectively (Fig. 1).

Compound **3**, named myrrhatetraterpenolyl salicylate, was obtained as brown mass from the chloroform eluants. Its IR spectrum showed characteristic absorption bands for hydroxyl group (3454 cm^{-1}), ester group (1745 cm^{-1}), unsaturation (1644 cm^{-1}) and aromatic ring (1527, 1036 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, the molecualr ion peak of **3** was determined at *m/z* 704 consistent with the molecular formula of a tetraterpenediol ester, $C_{47}H_{76}O_4$. The ion peaks generating at *m/z* 111 [C_{26}-C_{27} fission, $C_8H_{11}]^+$, 223 [C_{19}-C_{20} fission, $C_{16}H_{31}]^+$ and 481 [M-223]$^+$ suggested existence of the vinylic linkage at C-27(39). The ion fragments arising at *m/z* 355 [C_{11}-C_{12} fission, $C_{26}H_{43}]^+$, 349 [M-355]$^+$, 385 [C_{10}-C_{11} fission, $C_{27}H_{45}O]^+$, 263 [C_7- C_8 fission, $C_{16}H_{23}O_3]^+$ suggested the location of vinylic linkages from C-12 to C-19, hydroxy group at C-11 and ester function at C-7. The ^1H NMR spectrum of **3** displayed four one-proton multiplets at δ 7.23, 7.12, 7.01 and 6.60 assigned to aromatic H-3', H-6', H-4' and H-5' protons, respectively, and vinylic protons as one-proton double doublets at δ 5.72 (*J*= 5.6, 7.1 Hz), 5.66 (*J*=7.1, 8.5 Hz) and 5.06 (*J*=6.8, 8.1 Hz) and as one-proton doublets at δ 5.63 (*J*=8.5 Hz), 5.50 (*J*=5.6 Hz) and 5.01 (*J*=6.8 Hz) and as a two-proton broad singlet at δ 4.80 ascribed to *cis*-oriented H-16, H-17, H-12, H-18, H-15, H-13 and H_2-39 protons, respectively. A one-proton triplet doublet at δ 4.68 (*J*=5.5, 5.1, 6.3 Hz) and a one-proton double doublet at δ 3.40 (*J*=5.3, 8.1 Hz) were attributed correspondingly to α-oriented oxygenated methine H-7 and carbinol H-11 protons. Two three-proton broad singlets at δ 1.81 and 1.78 were accounted to C-36 and C-37 methyl protons located on the vinylic carbons C-14 and C-19, respectively. Seven three-proton doublets between δ 1.32-0.89 were due to secondary methyl protons. The ^{13}C NMR spectrum of **3** exhibited signals for ester carbon at δ 174.63 (C-7'), aromatic and vinylic carbons between 163.41-107.46, oxygenated methine carbons at δ 77.96 (C-7) and 82.78 (C-11) and methyl carbons from δ 23.63 to 8.18. On the basis of these evidences, the structure of **3** has been elucidated as 2,6,10,14,19,23,31-heptamethyl-27-methylene-dotriacos-(all Z)-12,14,16,18-tetraen-11β-ol-7β-olyl salicylate (Fig. 1). This is a new tetraterpenic ester.

Compound **4**, designated as myrrhatetraterpenolyl salicylic triacetate, was obtained as a brown mass from the chloroform-methanol (99:1) eluants. Its IR spectrum showed absorption bands for the hydroxyl group (3441 cm^{-1}), ester groups (1743, 1739, 1722 cm^{-1}), unsaturation (1645 cm^{-1}) and aromatic ring (1510, 1029 cm^{-1}). Its molecular ion peak was established at *m/z* 860 on the basis of mass and ^{13}C NMR spectra, consistent to the molecular formula of a tetraterpenic ester $C_{53}H_{80}O_9$. The ion peaks arising at *m/z* 191 [C_3-C_4 fission, $C_{11}H_{11}O_3]^+$, 263 [C_4-C_5 fission, $C_{14}H_{15}O_5]^+$, 335 [C_5-C_6 fission, $C_{17}H_{19}O_7]^+$, 363 [C_6-C_7 fission, $C_{19}H_{23}O_7]^+$, 433 [C_{10}-C_{11} fission, $C_{24}H_{33}O_7]^+$ and 505 [C_{11}-C_{12} fission, $C_{27}H_{37}O_9]^+$ indicated the existence of one of vinylic linkage at C-1, salicyloxy function at C-3 and acetoxy groups at C-4, C-5 and C-11. The ion peaks generating at *m/z* 111 [C_{26}-C_{27} fission, $C_8H_{15}]^+$ and 223 [C_{19}-C_{20} fission, $C_{11}H_{21}]^+$ suggested a vinylic linkage at C-27(39) and others between carbons C_{12} to C_{19}. The ^1H NMR spectrum of **4** exhibited four one proton multiplets at δ 7.22, 7.02, 6.95 and 6.50 assigned to aromatic protons H-3', H-6', H-4' and H-5', respectively. Vinylic protons as one-proton double doublets at δ 5.73 (*J*=5.5, 6.8 Hz), 5.68 (*J*= 6.6, 8.8 Hz) and 5.10 (*J*=6.0, 8.4 Hz) and as doublets at δ 5.61 (*J*= 8.8 Hz). 5.49 (*J*=5.5 Hz) and 4.98 (*J*=6.0 Hz) were ascribed to all cis-oriented H-16, H-17, H-12, H-18, H-15 and H-13 protons, respectively, oxygenated methine protons as a one-proton doublet at δ 4.70 (*J*=8.5 Hz) and as double doublets at δ 4.63 (*J*=6.2, 6.0 Hz), 4.50 (*J*=8.5, 7.7 Hz) and 4.10 (*J*=7.7, 6.1 Hz) attributed to α-oriented H-3, H-11, H-4 and H-5, respectively, vinylic methylene proton signals at δ 4.85 (2H, H_2-39) and 4.80 (2H, H_2-1), acetyl protons as three-proton singlets at δ 2.01, 1.98 and 1.90, and methyl protons as three-proton broad singlets at 1.78, 1.70 and 1.63, as doublets at δ 1.30 (*J*=6.5 Hz), 0.85 (*J*=6.3 Hz) and 0.72 (*J*=6.0 Hz) and as a six-proton broad singlet at δ 1.20 accounted corrrespondingly to C-33, C-36 and C-37 methyl protons attached to vinylic carbons, to C-34, C-35 and C-35 and to C-32 and C-40 secondary methyl protons. The ^{13}C NMR spectrum of **4** exhibited important signals for ester carbons between δ 175.96 – 170.11, aromatic and vinylic carbons from δ 162.18 to 107.10 and methyl carbons in the range of δ 23.03 – 08.25. These data led to formulate the structure of **4** as 2,6,10,14,19,23,31-heptamethyl-27-methylenedotriacont-(all Z)-

1,12,14,16,18,27(39)-hexaen-3β,4β,5β,11β-tetraolyl-3β-salicyl-4,5,11-triacetate (Fig. 1). This is a new tetraterpenic ester.

Table 1- ^{13}C NMR spectral data of 3, 4 and 5.

Carbon no.	**3 δ_C**	**4 δ_C**	**5 δ_C**
1.	14.01	108.14	14.88
2.	31.78	136.17	30.52
3.	23.61	82.56	23.58
4.	24.19	71.07	24.16
5.	28.24	70.94	26.60
6.	47.01	46.96	48.01
7.	77.96	29.16	77.99
8.	35.87	28.64	34.44
9.	39.78	26.42	35.12
10.	46.54	46.60	49.57
11.	82.78	82.49	83.08
12.	120.19	120.23	120.15
13.	128.36	129.41	130.06
14.	135.41	135.38	137.29
15.	124.39	124.16	125.29
16.	123.76	123.78	122.53
17.	122.21	122.32	127.86
18.	121.35	119.85	121.54
19.	136.23	135.74	136.05
20.	44.61	44.24	47.08
21.	38.64	30.98	28.83
22.	34.92	37.29	35.41
23.	44.36	45.26	45.38
24.	28.24	29.16	28.07
25.	31.52	28.82	28.83
26.	40.79	42.13	40.25
27.	137.42	138.56	136.88
28.	37.94	43.99	36.76
29.	29.55	29.16	31.51
30.	29.55	29.16	29.27
31.	29.02	22.64	37.29
32.	19.32	14.25	22.76
33.	14.82	16.82	16.21
34.	08.17	08.21	08.91
35.	22.61	23.03	19.22
36.	23.63	24.36	24.19
37.	20.96	22.16	23.67
38.	08.18	08.25	08.85
39.	107.46	107.10	107.07
40.	19.94	19.06	22.30
1'	145.08	144.53	145.04
2'	163.41	162.18	134.56
3'	133.72	133.83	160.72
4'	128.31	128.31	160.76
5'	126.18	126.43	124.67
6'	114.48	113.65	118.23
7'	174.63	174.27	173.49
O-CH_2-O	-	-	-
OMe	-	-	56.87
OAc	-	175.96, 173.06, 170.11, 20.65, 19.52, 19.49	172.09, 20.90

$CH_3\ (CH_2)_{12}CO - OCH_2\ (CH_2)_{10}\ CH_3$
1

$CH_3\ (CH_2)_{10}CO - OCH_2\ (CH_2)_{30}\ CH_3$
2

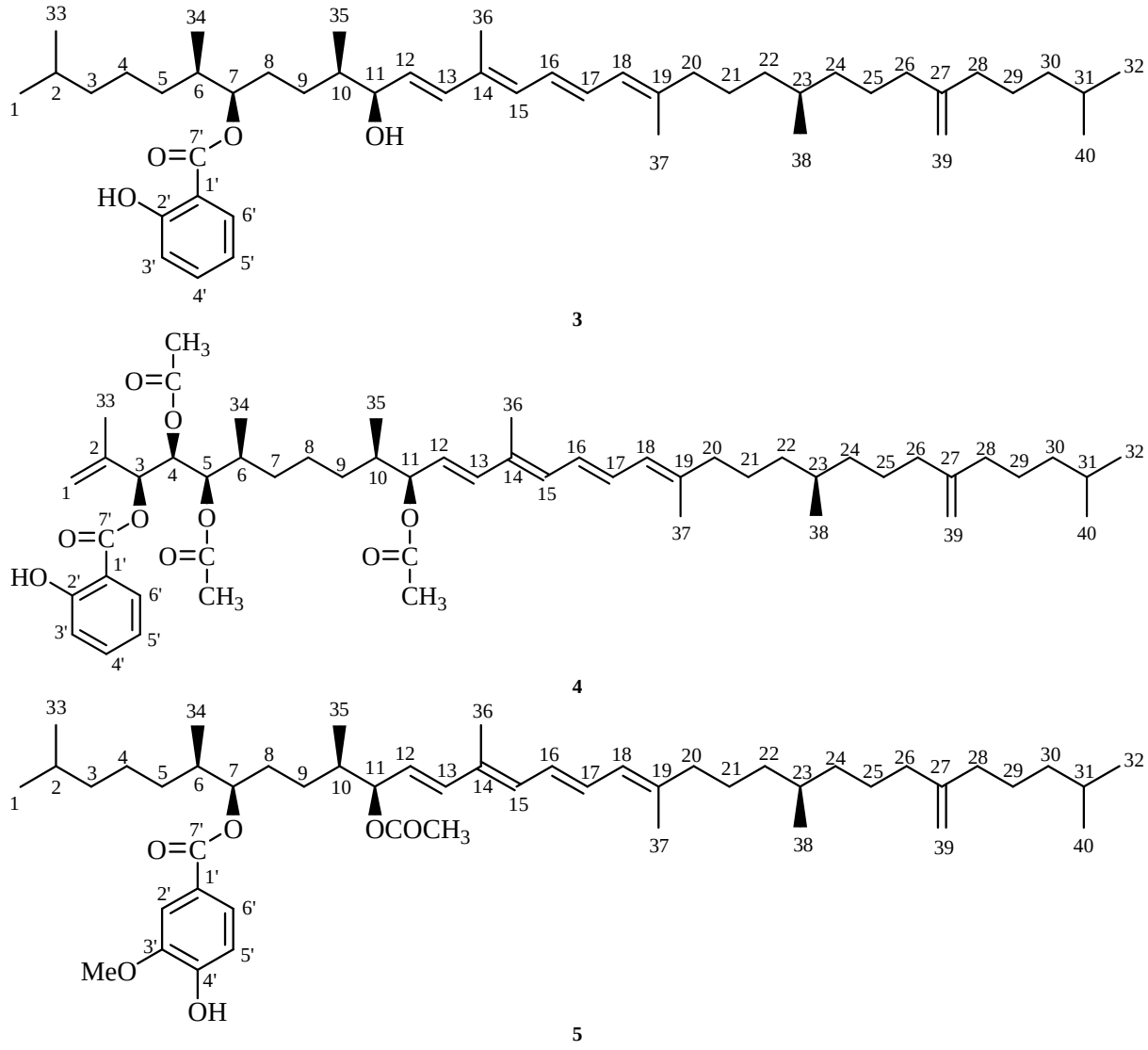

Fig. 1- The structures of compound 1-5.

Compound **5**, named myrrhatetraterpenolyl vanillic acetate, was obtained as a brown mass from the chloroform-methanol (99:1) eluants. Its IR spectrum displayed characteristic absorption bands for hydroxyl group (3442 cm^{-1}), ester groups (1741, 1722 cm^{-1}), unsaturation (1645 cm^{-1}) and aromatic ring (1527, 1035 cm^{-1}). Its molecular ion peaks was determined at *m/z* 776 on the basis of mass and ^{13}C NMR spectra consistent to the molecular formula of a tetraterpenic diester $C_{50}H_{80}O_6$. The ion fragments arising at *m/z* 113 [C_6-C_7 fission, $C_8H_{17}]^+$, 292 [C_7-C_8 fission, $C_{17}H_{24}O_4]^+$, 320 [C_9-C_{10} fission, $C_{19}H_{28}O_4]^+$, 348 [C_{10}-C_{11} fission, $C_{21}H_{32}O_4]^+$ and 420 [C_{11}-C_{12} fission, $C_{24}H_{36}O_6]^+$ suggested existence of vanillate group at C-7 and acetoxy function at C-11. The ion peaks producing at *m/z* 111[C_{27}-C_{28} fission, $C_8H_{15}]^+$ and 223 [C_{19}-C_{20} fission, $C_{16}H_{31}]^+$ supported the presence of a vinylic linkage at C-27 (39) and other vinylic linkage between C_{12}-C_{19}. The ^1H NMR spectrum of **5** exhibited two one-proton doublets at δ 7.20 (*J*=2.5 Hz) and 6.82 (*J*=8.5 Hz) and a one-proton multiplet at δ 7.01 assigned to aromatic H-2', H-5' and H-6' protons, respectively. Three one-proton double doublets at δ 5.72 (*J*=5.3, 7.1 Hz), 5.61 (*J*=7.1, 8.3 Hz) and 5.08 (*J*=5.6, 8.1 Hz), three one-proton doublets at δ 5.49 (*J*=8.3 Hz), 5.41 (*J*=5.3 Hz) and 4.90 (*J*=5.6 Hz) and a two-proton broad singlets at δ 4.80 were attributed correspondingly to all *cis*-oriented vinylic H-16, H-17, H-12, H-18, H-15, H-13 and H_2-39 protons. Two one-proton signals as a double doublet at δ 4.68 (*J*=5.5, 8.1 Hz) and as a triple doublet at δ 4.07 (*J*=5.3, 6.2, 9.5 Hz) were ascribed to α-oriented oxygenated methine H-11 and H-7, respectively. Nine three-proton signals as broad singlets at δ 3.30, 2.11, 1.78 and 1.70 and as doublets at δ 1.02 (*J*=6.3 Hz), 0.98 (*J*=6.5 Hz), 0.77 (*J*=6.1 Hz), 0.72 (*J*=6.3 Hz) and 0.69 (*J*=6.5 Hz) and a six-proton broad singlet at 1.10 were associated correspondingly to methoxy, acetyl and C-36 and C-37 methyl protons located on the vinylic carbons, to secondary C-34, C-35, C-38, C-32, C-40 and to C-1 and C-33 methyl protons. The ^{13}C NMR spectrum of **5** showed signals for ester carbons at δ 173.49 (C-7') and 172.09 (OAc), aromatic and vinylic carbons between δ 160.76-107.07, methoxy carbon at δ 56.87 and methyl carbons from δ 24.19 to 08.85. On the basis of above discussion, the

structure of **5** has been elucidated as 2,6,10,14,19,23,31-heptamethyl dotriacont-(all Z)-12,14,16,18,27(39)-pentaen-7β,11β-diolyl-7β-vanillyl-11β-acetate (Fig. 1). This is new tetraterpenic ester.

CONCLUSION

The phytochemical investigation of the oleo-resin of *Commiphora myrrha* (Nees) Engl. led to the isolation of three new tetraterpenyl esters which may be used as chromatographic markers for quality control of the drugs.

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