Chemical Constituents from the Fruits of *Madhuca latifolia*

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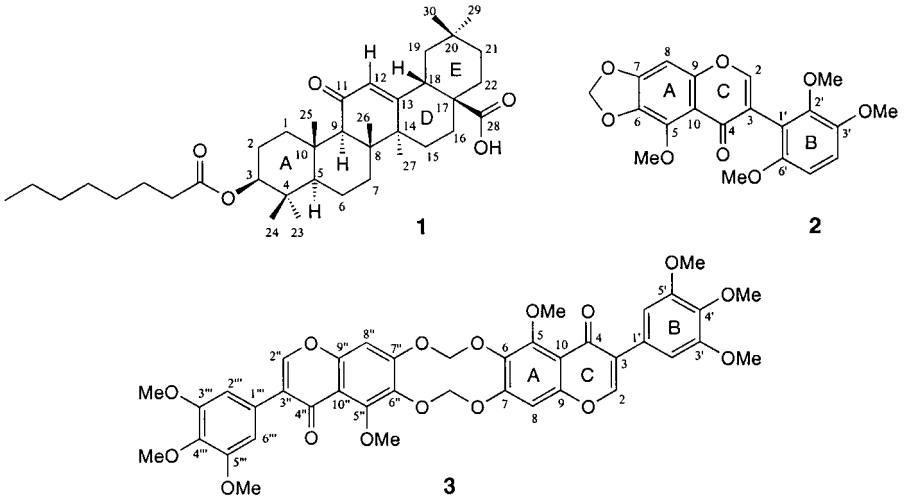
From the fruit coats of the medicinal plant *Madhuca latifolia* were isolated three new compounds, the triterpenoid madhucic acid (= 3β-(octanoyloxy)-11-oxoolean-12-en-28-oic acid; **1**), the untypical isoflavone madhushazone (= 9-methoxy-7-(2,3,6-trimethoxyphenyl)-[1,3]dioxolo[4,5-*g*][1]benzopyran-8(8*H*)-one; **2**), and a bis(isoflavone) named madhusalmone (= 5,14-dimethoxy-3,12-bis(3,4,5-trimethoxyphenyl)-1,6,8,10,15,17-hexaoxanaphtho[2′,3′:6,7]cyclodeca[1,2-*b*]naphthalene-4,13(4*H*,13*H*)-dione; **3**), as well as eight known constituents, and their structures were elucidated by spectral analysis, including 2D-NMR techniques.

Introduction. – *Madhuca latifolia* Syn. *M. indica* (Sapotaceae) is an important economic plant growing throughout the subtropical region of the Indo-Pak subcontinent [1]. The medicinal properties attributed to this plant are stimulant, demulcent, emollient, heating, and astringent [2]. The bark is a good remedy for itch, swellings, fractures, and snake-bite poisoning, internally employed in diabetes mellitus with much benefit [3]. Mahua oil is used for the treatment of skin diseases, rheumatism, headache, and as a laxative. Fruits are astringent and largely employed as a lotion in chronic ulcer, in acute and chronic tonsillitis and pharyngitis. The constituents reported from *Madhuca indica* include fatty acids [4–6], sapogenins [7], carbohydrates [6][8], triterpenoids [1][8–10], steroids [1][8–11], saponins [12][13], flavonoids [9][10][14], and glycosides [8–10][14]. In view of the attributed medicinal properties, we investigated the fruit coats of *M. indica*, which resulted in the isolation and characterization of three new constituents: madhucic acid (**1**), a pentacyclic triterpenoid, madhushazone (**2**), an untypical isoflavone, and madhusalmone (**3**), a bis(isoflavone). Moreover, eight known constituents were isolated and identified by comparison of their physical and spectral data with those reported in the literature. These included β-amyrin acetate, hitherto unreported β-amyrin caprylate, 3β-(caprylyloxy)ursolic acid, a hydrocarbon ($C_{29}H_{60}$), a triglyceride of palmito-dioleins, and three monoglycerides of stearic, oleic, and arachidic acid, respectively. These glycerides have previously been found in solid seed fats of the same species [15].

Results and Discussion. – Madhucic acid (**1**) showed the molecular-ion peak at *m/z* 596 and 596.4437 in the EI and HR-EI mass spectra, respectively, corresponding to the formula $C_{38}H_{60}O_5$, as supported by ^{13}C-NMR analysis. The UV absorption maximum at 250.2 nm indicated the presence of an enone system [16], and the IR spectrum exhibited absorptions at 1730 and 1660 cm^{-1}, corresponding to ester and α,β-unsaturated ketone C=O groups, respectively. The triterpenoidal nature of **1** was



indicated by the ^{1}H-NMR singlets at δ_H 0.84, 0.85, 0.91, 2 × 0.92, 1.11, and 1.34 ppm, corresponding to seven Me groups at quaternary C-atoms. These resonances, along with a double doublet at δ_H 2.95 ppm (J = 13.6, 3.5 Hz, H–C(18)) and a ^{13}C-NMR signal at δ_C 41.4 ppm (C(18)) indicated that the compound belongs to the oleanane series. The mass fragment at *m/z* 550 ($[M - HCOOH]^+$) suggested the presence of a COOH moiety (*Fig. 1*). The ^{1}H- and ^{13}C-NMR spectra further displayed resonances at δ_H 5.61 ppm (*s*, H–C(12)) and δ_C 128.0 ppm (C(12), assigned *via* HMQC), respectively, indicating an enone moiety in ring *B* or *C* of the triterpenoidal framework. The mass fragments at *m/z* 262 (*via retro-Diels–Alder* reaction), 234, and 217, as well as the resonances at δ_H 2.34 ppm (H–C(9)) and δ_C 61.6 ppm (C(9)), indicated that the enone moiety was in ring *C*, and the COOH group at C(17) [17], as further corroborated by strong HMBC interactions (*Table 1*).

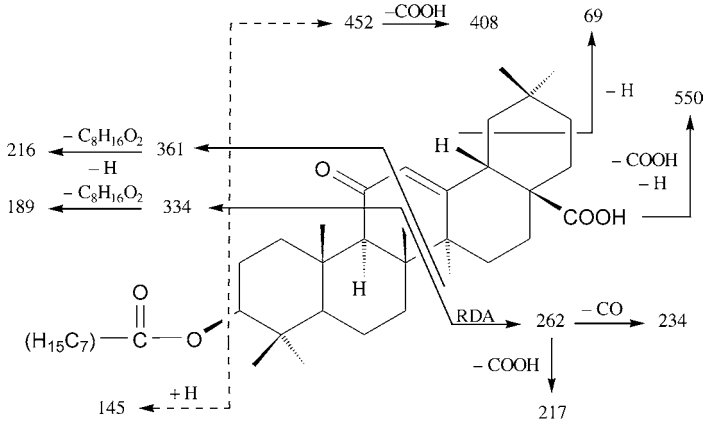


Fig. 1. *Diagnostic mass-spectral* (EI-MS) *fragmentations of* **1**. Values in *m/z*.

Table 1. *^{1}H- and ^{13}C-NMR Data of Compound* **1**. Solvent: $CDCl_3$; δ in ppm, J in Hz.

	δ_C	δ_H	HMBC
CH_2(1)	38.7	n.o.[a])	
CH_2(2)	28.9	1.35–1.43 (*m*)	
H_α–C(3)	80.2	4.47 (*dd*, *J* = 11.6, 4.6)	C(24)
C(4)	38.07		
H_α–C(5)	55.07	n.o.	
CH_2(6)	17.2	1.27 (*m*)	
CH_2(7)	32.82	1.32 (*m*)	
C(8)	43.4		
H_α–C(9)	61.6	2.34 (*s*)	C(1), C(8), C(10), C(11), C(14), C(25), C(26)
C(10)	37.1		
C(11)	200.2		
H–C(12)	128.0	5.61 (*s*)	C(8), C(9), C(14), C(18)
C(13)	168.2		
C(14)	45.1		
CH_2(15)	27.2	1.2 (*m*)	
CH_2(16)	23.5	1.69 (*m*)	
C(17)	45.91		
H_β–C(18)	41.4	2.95 (*dd, J* = 13.6, 3.5)	
CH_2(19)	44.1	1.23 (*m*)	
C(20)	30.6		
CH_2(21)	33.6	1.2 (*m*)	
CH_2(22)	31.9	1.2 (*m*)	
Me(23)	28.08	0.85 (*s*)	C(3), C(4), C(5)
Me(24)	16.72	0.85 (*s*)	C(3), C(4), C(5)
Me(25)	16.26	1.11 (*s*)	C(1), C(5), C(9), C(10)
Me(26)	19.10	0.91 (*s*)	C(8), C(9)
Me(27)	23.4	1.34 (*s*)	C(8), C(13), C(14)
C(28)	178.8		
Me(29)	32.81	0.92 (*s*)	C(19)
Me(30)	23.37	0.92 (*s*)	
C(1′)	173.6		
CH_2(2′)	34.8	2.27 (*t*, *J* = 7.5)	C(1′)
CH_2(3′)	25.1	1.6 (*m*)	C(1′)
CH_2(4′)	29.1	1.2 (*m*)	
CH_2(5′)	29.2	1.2 (*m*)	
CH_2(6′)	31.6	1.2 (*m*)	
CH_2(7′)	22.6	1.2 (*m*)	C(6′)
Me(8′)	14.1	0.87 (*t*, *J* = 7.7)	C(6′)

[a]) Not observed.

The molecular formula and ^{13}C-NMR spectral data indicated that **1** was composed of a steroidal skeleton made of 30 C-atoms and a side chain comprising eight C-atoms. The latter was identified as a capryl (= octanoyl) group (δ_H 0.87 (*t*, *J* = 7.7 Hz, Me(8′)), δ_C 14.1 (C(8′); δ_H 2.27 (*d*, *J* = 7.5 Hz, CH_2(2′)), δ_C 34.8 (C(2′)); and δ_H 1.23–1.67 (*m*, 5 CH_2)). This was further confirmed by the mass fragment observed at *m/z* 452 ([$M - C_8H_{16}O_2$]$^+$), arising from loss of caprylic acid. The latter was attached at C(3), as this position, on biogenetic grounds, usually bears an O-atom. This assumption was supported by the characteristic resonances at δ_H 4.47 ppm (*dd*, *J* = 11.6, 4.6 Hz, H_α–C(3)) and δ_C 80.2 ppm (C(3)) [16]. A NOESY interaction between H_α–C(9) and

Me(27), and between Me(25) and Me(26), indicated that Me(27) was α-oriented, whereas Me(25) and Me(26) were both β-oriented. Moreover, from the ^{1}H-NMR coupling constants, H–C(18) was assumed to be axial (β-orientation), and considering the biogenetically more reasonable *cis* junction of rings *D* and *E*, the COOH group was placed in equatorial β-position.

In the light of the above considerations, the structure of **1** was elucidated as 3β-(octanoyloxy)-11-oxoolean-12-en-28-oic acid. This is the first report of a caprylate derivative of 3β-hydroxy-11-oxoolean-12-en-28-oic acid, although the latter has been isolated from the callus-tissue cultures of *Paeonia* species [16].

Compound **2**, named madhushazone, belongs to one of the least-abundant isoflavones. The molecular formula, $C_{20}H_{18}O_8$, was inferred from the $[M+1]^+$ peak at *m/z* 387 in the FAB mass spectrum, and from the M^+ peak at *m/z* 386 in the EI mass spectrum. The structure of **2** was supported by ^{13}C-NMR and DEPT spectra, which showed a total of 20 resonances, corresponding to four Me, one CH_2, and four CH groups, as well as eleven quaternary C-atoms.

The UV spectrum of **2** showed an absorption band at 262 nm, indicating an aromatic system typical of an isoflavone skeleton [18]. In the ^{1}H-NMR spectrum (*Table 2*), a characteristic resonance for H–C(2) was observed at δ_H 7.77 ppm (*s*) and δ_C 150.4 ppm (C(2); assigned by HMQC). This assignment was confirmed by long-range connectivities between H–C(2) and C(4), C(9), and C(3) at δ_C 176.9, 154.6, and 125.7 ppm, respectively, in the corresponding HMBC spectrum. A singlet, corresponding to H–C(8) of ring *A* (δ_H 6.62; δ_C 93.2), and two *ortho*-coupled doublets at δ_H 6.89 and 6.98 ppm ($J = 8.1$ Hz each), assigned to H–C(4′) and H–C(5′) of ring *B*,

Table 2. *^{1}H- and ^{13}C-NMR Data of Compounds* **2** and **3** (trivial atom numbering). Solvent: $CDCl_3$; δ in ppm, *J* in Hz.

	2			**3**	
	δ_C	δ_H		δ_C	δ_H
H–C(2)	150.4	7.77 (*s*)	H–C(2,2″)	150.7	7.78 (*s*)
C(3)	125.2		C(3,3″)	124.5	
C(4)	176.9		C(4,4″)	175.1	
C(5)	142.5		C(5,5″)	142.2	
C(6)	135.7		C(6,6″)	135.3	
C(7)	152.2		C(7,7″)	152.7	
H–C(8)	93.2	6.62 (*s*)	H–C(8,8″)	93.2	6.63 (*s*)
C(9)	154.6		C(9,9″)	154.9	
C(10)	115.4		C(10,10″)	114.9	
C(1′)	112.8		C(1′,1‴)	127.0	
C(2′)	143.6		H–C(2′,2‴)	106.7	6.74 (*s*)
C(3′)	150.0		C(3′,3‴)	153.3	
H–C(4′)	112.2	6.89 (*d*, $J = 8.1$)	C(4′,4‴)	138.3	
H–C(5′)	124.8	6.98 (*d*, $J = 8.1$)	C(5′,5‴)	153.3	
C(6′)	150.4		H–C(6′,6‴)	106.7	6.74 (*s*)
O–CH_2–O	102.1	6.05 (*s*)	O–CH_2–O	102.2	6.06 (*s*)
*Me*O–C(5)	62.0	4.07 (*s*)	*Me*O–C(5,5″)	61.3	4.06 (*s*)
MeO	51.7	3.64 (*s*)	*Me*O–C (3′,3‴)	56.2	3.87 (*s*)
MeO	55.9	3.88 (*s*)	*Me*O–C (4′,4‴)	60.7	3.84 (*s*)
MeO	56.0	3.90 (*s*)	*Me*O–C (5′,5‴)	56.2	3.87 (*s*)

respectively, comprised the remaining aromatic ^{1}H-NMR resonances. The assignment of H–C(8) was supported by long-range HMBC connectivities to δ_C 154.6 (C(9)), 152.2 (C(7)), 135.7 (C(6)), and 115.4 ppm (C(10)) (see *Fig. 2*).

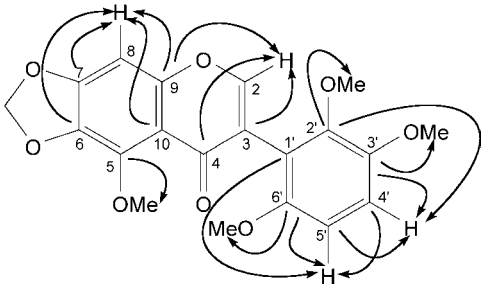


Fig. 2. *Observed HMBC interactions in compound* **2**

The ^{1}H- and ^{13}C-NMR spectra of **2** included resonances of a methylenedioxy (O–CH_2–O) group at δ_H 6.05 ppm (*s*, 2 H) and δ_C 102.1 ppm, respectively. Long-range HMBC connectivities from the O–CH_2–O H-atoms to C(7) and C(6) at δ_C 152.9 and 135.7 ppm, respectively, prompted us to attach the O–CH_2–O fragment at C(6) and C(7) of ring *A* [19]. NMR Signals attributed to four MeO groups were observed at δ_H (δ_C) 4.07 (62.0), 3.90 (56.0), 3.85 (55.9), and 3.64 (51.7) ppm. One MeO group was placed at C(5), and the remaining three had to be in ring *B* to satisfy the observed ^{1}H-NMR singlet of ring *A* and the two doublets of ring *B*.

The presence of an $[M-31]^+$ fragment in the mass spectrum of **2** indicated a MeO group at C(2′), which is usually involved in internal-ring formation [20]. The three MeO groups in ring *B* were placed at C(2′), C(3′), and C(6′) by examination of the ^{13}C-NMR spectrum. Typically, MeO-bearing C-atoms resonate at δ_C 152–158 ppm. However, aromatic 1,2-dimethoxy moieties resonate at lower field (δ_C 150–140), and doubly *ortho*-oxy-substituted ones even at δ_C 139–132 ppm [21]. An alternative structure of the 2′,3′,4′-trimethoxy type was ruled out on the basis of the chemical shifts of the three MeO-bearing C-atoms. In the alternative structure, C(3′) is expected to resonate at δ_C 139–132 ppm [22][23], but the observed value was 150 ppm.

Based on the above considerations, madhushazone (**2**) was identified as 5,2′,3′,6′-tetramethoxy-6,7-(methylenedioxy)isoflavone[1]). This novel compound is unusual because it lacks an O-atom at C(4′), an observation reported only for a few such isoflavonoids [21][22][24][25]. The absence of a 4′-oxy group is biosynthetically significant, since it renders the often proposed spiro-dienone intermediate during classical flavonoid biosynthesis improbable for these modified structures [21].

Madhusalmone (**3**) is an unusual biisoflavonoid, which has not been reported in the literature. Its spectroscopic data were similar to those of madhushazone (**2**), suggesting that it was an isoflavone, too. The ^{1}H-NMR resonances for the ring-*A* and ring-*C* H-atoms were almost similar to those of **2**. In addition, the ^{1}H- and ^{13}C-NMR spectra of **3** (see *Table 2*) showed a singlet for the ring-*B* resonance at δ_H 6.74 ppm (H–C(2′,6′)) and δ_C 106.7 ppm (C(2′,6′)), respectively, as well as two MeO signals at δ_H (δ_C) 3.87

[1]) For systematic names, see the Exper. Part.

(56.2) and 3.84 (60.7) ppm. These values indicated that ring *B* was symmetrically substituted. The assignment of rings *A*, *B*, and *C* was confirmed by an identical pattern of long-range HMBC connectivities as those observed in the case of **2** (*Fig. 2*). It was further confirmed by NOESY interactions of the resonance at δ_H 6.74 (H–C(2′,2‴)) with those at 7.78 (H–C(2,2″)) and at 3.87 ppm (MeO), as well as by ^{13}C-NMR-shift correlations for the MeO substituents, as discussed above in the case of **2**.

The molecular-ion peak of **3** was not observed in the EI mass spectrum (highest-mass signal at *m/z* 386), but the corresponding FD mass spectrum showed a peak at *m/z* 772 (= 2 × 386 Da), which revealed that **3** is a dimeric form of irisflorentin (= 5,3′,4′,5′-tetramethoxy-6,7-(methylenedioxy)isoflavone) with a symmetrical double methylenedioxy linkage. This structure was further supported by characteristic FAB-MS fragments (*Fig. 3*).

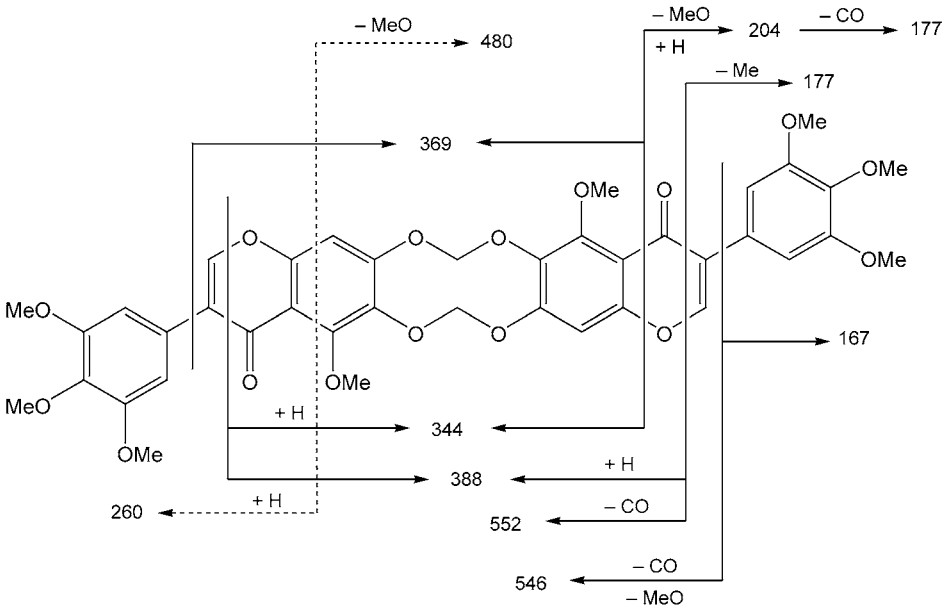
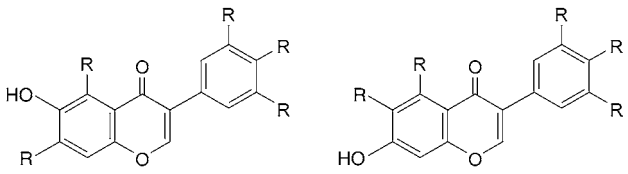


Fig. 3. *Diagnostic mass-spectral* (FAB-MS) *fragmentation of* **3**. Values in *m/z*.

The 6 → 7″ and 7 → 6″ linkages of the O–CH_2–O bridges were corroborated by long-range HMBC connectivities of the O–CH_2–O H-atoms (δ_H 6.06) with C(6,6″) at δ_C 135.3 and C(7,7″) at δ_C 152.7 ppm, respectively. Therefore, madhusalmone (**3**) was assigned the structure 5,5″,3′,3‴,4′,4‴,5′,5‴-octamethoxy-6,7″:7,6″-bis[(methylenedioxy)isoflavone][1]).

From a biogenetic point of view, madhusalmone (**3**) may arise from condensation of the isoflavones **4a** or **4b**, which are formed early in the biosynthetic sequence at the isoflavone oxidation level [26].



4a R = MeO **4b**

Experimental Part

General. Petroleum ether (PE; for chromatographic purifications): b.p. 60–80°. Vacuum liquid chromatography (VLC): silica gel *60 PF$_{254}$* (*Merck*). Column chromatography (CC): silica gel *60* (0.063–0.200 mm, 70–230 mesh; *Merck*). Prep. TLC: silica gel *60 PF$_{254}$* (*Merck*); detection at 254 and 266 nm. UV Spectra: *Hitachi U-3200* and *Secomam-Anthelei-Junior* spectrophotometers; λ_{max} in nm (log ε). IR Spectra: *Bruker Vector-22* spectrophotometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR-, COSY, NOESY, HMQC, HMBC, and *J*-Resolved spectra: *Bruker AC-300*, *AVANCE-400*, and *AVANCE*-500 (300/75, 400/100, and 500/125 MHz, resp.); chemical shifts δ in ppm rel. to $SiMe_4$ as internal standard, coupling constant *J* in Hz, temp. 25°. EI-MS: *Varian MAT-312* mass spectrometer (70 eV); source at 250°; in *m/z* (rel. %). HR-EI-MS: *Jeol JMS-600-H* mass spectrometer. FAB- and FD-MS: *Jeol JMS-HX-110* mass spectrometer.

Plant Material. The fresh fruits of *Madhuca indica* were collected in June 2000 in the region of Karachi. The plants were identified by Mr. *Sher Wali*, Department of Botany, University of Karachi, and a voucher specimen (KUH. No. 67974) was deposited in the Herbarium of the University of Karachi.

Extraction and Isolation. The fruit coatings (20 kg) and seeds (17 kg) of *M. indica* were separated manually and each extracted with MeOH at r.t. (4×). The extracts were concentrated separately under reduced pressure. Both extracts showed antimicrobial activity against *Staphylococcus aureus*, *S. saprophyticus*, *S. epidermidis*, *Streptococcus faecalis*, *Salmonella typhi para A*, *Pseudomonas aeruginosa*, and *Proteus mirabilis.* The fruit-coat extract was then partitioned between AcOEt and H_2O, and the org. phase was treated with 4% aq. Na_2CO_3 soln. The AcOEt layer (neutral fraction) was washed, dried (Na_2SO_3), and evaporated to afford a thick syrup (58 g), which was subjected to VLC (PE, PE/AcOEt, $CHCl_3$, $CHCl_3$/MeOH, then MeOH). The eluates were combined after TLC analysis to afford 20 fractions (*Fr.*). *Fr.1* (63.7 mg; 1000 ml PE) afforded a hydrocarbon of $C_{29}H_{60}$ composition (structure not further elucidated). *Fr.5* (43.5 mg; 500 ml PE/AcOEt 9:1), after purification by TLC (PE/EtOH 95:5), provided both β-amyrin acetate (20.7 mg) and β-amyrin caprylate (18.1 mg). *Fr.13* (4.4 g; 1000 ml $CHCl_3$/MeOH 9:1) was further purified by VLC (PE, PE/AcOEt, $CHCl_3$, $CHCl_3$/MeOH, then MeOH) to ultimately afford eleven subfractions. Out of these, *Fr.13.4* (58.3 mg; 500 ml PE/EtOH 7:3 → 6:4), after further purification by CC (SiO_2; $CHCl_3$, then $CHCl_3$/MeOH 95:5), afforded the triglyceride of palmito-dioleins (*Fr.13.4.1*, 5.3 mg; 48 ml $CHCl_3$), 3β-capryloxyursolic acid (*Fr.13.4.7*, 2.8 mg; 27 ml $CHCl_3$/MeOH 99:1), and the monoglyceride of oleic acid (*Fr.13.4.14–16*, 8.6 mg; 64 ml $CHCl_3$/MeOH 98:2 → 97:3). *Fr.13.5* (1.01 g; 1000 ml PE/AcOEt 6:4 → 1:1, $CHCl_3$) was further submitted to CC, affording 23 subsubfractions. Out of these, *Fr.13.5.9–12* (0.54 g; 575 ml $CHCl_3$/MeOH 99:1) were combined and subjected to CC ($CHCl_3$, then $CHCl_3$/MeOH 95:5), giving rise to 15 additional subfractions. Thereof, *Fr.13.5.9–12.11* (38.9 mg; 40 ml $CHCl_3$/MeOH 99:1), after final purification by prep. TLC ($CHCl_3$/MeOH 98:2), provided compounds **2** (9.0 mg), **3** (5.7 mg), and **1** (6.2 mg) in order of polarity. Finally, *Fr.13.7* (3.2 mg; 125 ml $CHCl_3$) and *Fr.13.8* (1.2 mg; 125 ml $CHCl_3$/MeOH 95:5) from the second VLC purification afforded the pure monoglycerides of stearic and arachidic acid, resp.

3β-(Octanoyloxy)-11-oxoolean-12-en-28-oic Acid (= *Madhucic Acid*; **1**). Yield: 6.2 mg. Amorphous powder. UV (MeOH): 250.2 (3.82), 226.2 (3.86). IR ($CHCl_3$): 2925, 2855, 1730, 1660, 1459, 1377, 1248, 1173. ^{1}H- and ^{13}C-NMR: see *Table 1.* EI-MS: see *Fig. 1.* HR-EI-MS: 596.4437 (33, M^+, $C_{38}H_{60}O_5^+$; calc. 596.4441), 550.4357 (23, $C_{37}H_{58}O_3^+$), 407.3293 (10, $C_{29}H_{43}O^+$), 217.1585 (16, $C_{15}H_{21}O^+$), 216.1544 (5, $C_{15}H_{20}O^+$).

*9-Methoxy-7-(2,3,6-trimethoxyphenyl)-[1,3]dioxolo[4,5-g][1]benzopyran-8(8*H*)-one* (= *Madhushazone*; **2**). Yield: 9.0 mg. Amorphous powder. UV (MeOH): 262 (5.75), 220 (6.04). IR ($CHCl_3$): 2924, 2854, 1732, 1592, 1442, 1405, 1256, 1165. ^{1}H- and ^{13}C-NMR: see *Table 2*. EI-MS: 386 (10, M^+), 356 (15, $[M-CH_3O]^+$), 327 (39, $[M-CO]^+$), 309 (42), 239 (37), 203 (64) 194 (28), 192 (16), 148 (54).

*5,14-Dimethoxy-3,12-bis(3,4,5-trimethoxyphenyl)-1,6,8,10,15,17-hexaoxanaphtho[2′,3′:6,7]cyclodeca[1,2-*b*]naphthalene-4,13(4*H*,13*H*)-dione* (= *Madhusalmone*; **3**). Yield: 5.7 mg. Amorphous powder. UV (MeOH):

311 (2.94), 264 (3.65), 222 (3.98). IR ($CDCl_3$): 2924, 2855, 1732, 1596, 1458, 1371, 1224, 1169. ^{1}H- and ^{13}C-NMR: see *Table 2*. FD-MS: 772 (M^+, $C_{40}H_{36}O_{16}^+$). EI-MS: 386 (10, $½M^+$), 372 (33, $[½M - CH_3]^+$), 357 (29, $[½M - CH_3O]^+$), 343 (35), 312 (20), 239 (25), 203 (48), 177 (77), 149 (100). FAB-MS: see *Fig. 3*.

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