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Oligomeric secoiridoid glucosides from *Jasminum abyssinicum* ☆

Francesca Romana Gallo [a,*], Giovanna Palazzino [a], Elena Federici [a], Raffaella Iurilli [a], Franco Delle Monache [b], Kusamba Chifundera [c], Corrado Galeffi [a]

[a] *Dipartimento del Farmaco, Istituto Superiore di Sanità, V. le Regina Elena 299, 00161 Rome, Italy*
[b] *CNR, Centro Chimica dei Recettori, Università Cattolica S. Cuore, L.F. Vito 1, 00168 Rome, Italy*
[c] *Institut Supérieur d'Ecologie pour la Conservation de la Nature, Lwiro, P.O. Box 293 Cyangugu, Rwanda*

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Abstract

From the root bark of *Jasminum abyssinicum* (Oleaceae) collected in Congo was isolated tree oligomeric secoiridoid glucosides named craigosides A–C. The three compounds are esters of a cyclopentanoid monoterpene with an iridane skeleton, esterified with three, two and two, respectively, units of oleoside 11-methyl ester. The structures were elucidated by spectroscopic methods and chemical correlations.

Keywords: *Jasminum abyssinicum*; Oleaceae; Root bark; Oligomeric secoiridoid glucosides; Craigoside A; Craigoside B; Craigoside C

1. Introduction

Genus *Jasminum* (Oleaceae) includes beyond 200 species, some of which are used in folk medicine or cultivated to obtain essential oil from the fragrant flowers. The term *Jasminum* (Oleaceae) was first mentioned in the ''Materia Medica'' of Dioscoride (I A.D.). The phytochemical studies of the aerial parts of some species, *J. sambac* [Soland.] (Tanahashi et al., 1988), *J. mesnyi* Hance (Tanahashi et al., 1989), *J. urophyllum* Hemsl. (Shen and Hsieh, 1997) and *J. nudiflorum* Lindl. (Tanahashi et al., 2000), resulted in the isolation of some secoiridoid glucosides, in particular of oligomeric consisting of oleoside units linked to a cyclopentanoid monoterpene named iridane.

This study deals with the structure elucidation of three oligomeric secoiridoid glucosides, two trimer and one tetramer, isolated from the root bark of *Jasminum abyssinicum* R. Br. (= Hochst. ex DC.) and named craigosides A, **1**, B, **2**, and C, **3**, as a tribute to L.C. Craig (Craig and Post, 1949) and his apparatus of counter-current distribution (CCD) utilised for our separations. The aerial parts of this plant are used in Traditional Medicine in the South Kivu Province, Congo against endoparasitic worms and for treatment of mumps (Chifundera, 2001).

2. Results and discussion

Craigoside A, **1**, is an amorphous powder, $C_{61}H_{86}O_{34}$ (ICR-FTMS, m/z 1385.48602 $[M+Na]^+$), $[\alpha]_D^{20} = -185$ (MeOH), λ_{max} 233 nm (log ε 4.54). Its ^1H and ^{13}C NMR spectra (Tables 1 and 2) showed *inter alia* a pattern of signals corresponding to oleoside methyl ester, *viz*., an acetalic methine and an anomeric methine, a vinylic oxymethine, an ethylidene and a carbomethoxy. In agreement with the molecular formula of **1**, the signals of some carbons (6, 8, 9, 1′, 4′ and 6′) of this iridoid moiety appeared in triplicate and in particular the methoxy group, δ 52.05, 52.03 and 52.00. This accounted for the presence of three oleoside methyl ester units and thus the presence of cyclic esters engaging two carboxylic groups of the same oleoside could

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* Corresponding author. Tel.: +39 06 49903055; fax: +39 06 49903060.
E-mail address: gallo@iss.it (F.R. Gallo).

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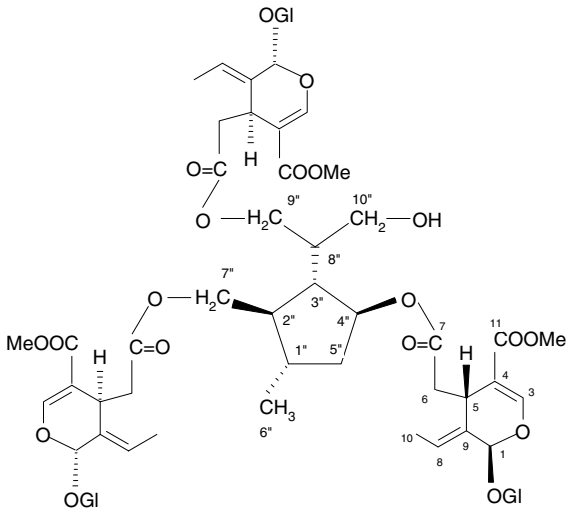
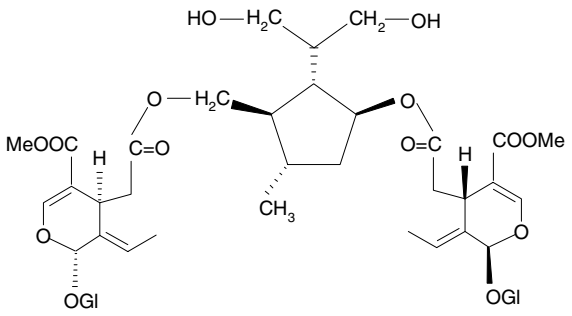
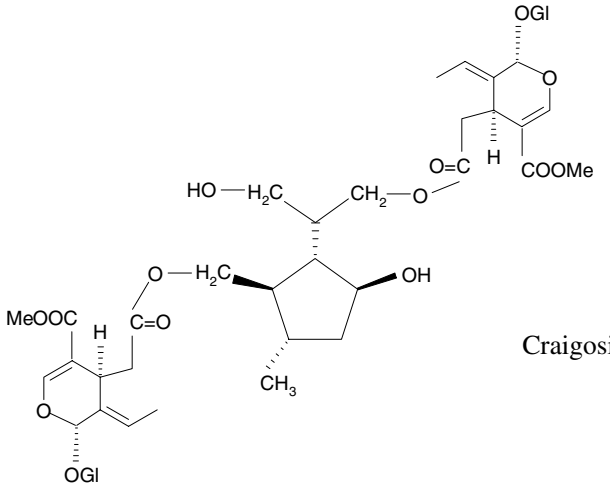


Craigoside A **(1)**



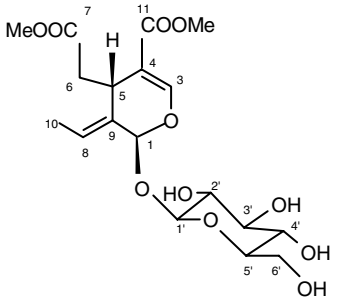
Craigoside B **(2)**



Craigoside C **(3)**

be ruled out. The LR HETCOR observed in **1** between the α-β unsaturated carboxyl group, δ 168.6, and the methoxy group, δ 3.72, accounted for the methyl ester in position 11 of the iridoid and therefore the other carboxyl group, (C-7, δ 173.1), was engaged in the linkage with the non-iridoidic moiety. The 10 minor ^{13}C signals of craigoside A due to this last part of the molecule corresponded to a cyclopentanoid monoterpene, endowed with three oxymethylene groups, δ 68.4, 65.1 and 61.2, an oxymethine, δ 80.0, and a methyl group, δ 19.7.

By alkaline hydrolysis of **1** and subsequent methylation with diazomethane, dimethyl oleoside, **4**, and tetraol iridane **5**, $C_{10}H_{20}O_4$ (ICR-FTMS, *m/z* 227.12552 $[M + Na]^+$), $[\alpha]_D^{26} = +2.4$ (MeOH), were obtained. This last substance appeared different from the two known tetraols **6** and **7** obtained by saponification of sambacosides A, E and F of *J. sambac* (Tanahashi et al., 1988) and of jasurosides C and D of *J. urophyllum* (Shen and Hsieh, 1997), respectively. In particular, the cyclic methylene of **5**, instead of at δ 37.7 and 37.0, as in **6** and **7**, respectively, resonated at higher chemical shift (δ 43.2), as in the known triol **8** (δ 43.7) obtained from nudiflosides A–C of *J. nudiflorum* (Tanahashi et al., 2000) and having an hydroxy group in position 4″ instead of 5″.



Dimethyl oleoside **(4)**

The HETCOR and selective ^1H-^1H decoupling of the tetra-acetyl derivative of **5**, **9**, gave full account of its structure and relative stereochemistry. Thus the irradiation of H-4″ of the acetoxymethine (δ 5.12, quintet, $J = 6.0$, 3.0 and 3.0) made the two signals of the adjacent methylene, δ 1.52, *dq*, $J = 13.5$, 10.5 and 6.0, H_a-5″, and δ 1.83, *m*, $J = 13.5$, 6.8 and 3.0, H_b-5″, into two *dd* with the loss of the couplings of $J = 6.0$ and 3.0, respectively. Moreover,

Table 1
^{1}H NMR spectroscopic data of compounds **1**, **2**, **3** and **5** in CD_3OD

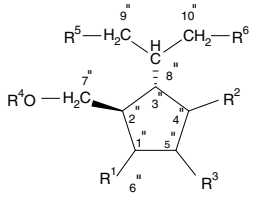
Position	**1**	**2**	**3**	**5**
1	5.97, *bs* 5.94, *bs*	5.96, *s* 5.94, *s*	5.95, *s*	
3	7.54, *s* 7.53, *s*	7.54, *s* 7.55, *s*	7.55, *s*	
5	4.10, *dd* (11.0; 4.8)	4.16, *dd* (11.0; 4.8)	4.29, *dd* (11.0; 4.8) 4.19, *dd* (11.0; 4.8)	
6 a	2.72, *dd* (13.0; 4.8)	2.76, *dd* (13.0; 4.8) 2.70, *dd* (13.0; 4.8)	2.76, *dd* (13.0; 4.8)	
6 b	2.49, *dd* (13.0; 11.0)	2.51, *dd* (13.0; 11.0) 2.47, *dd* (13.0; 11.0)	2.52, *dd* (13.0; 11.0) 2.48, *dd* (13.0;11.0)	
8	6.10, *bq* (6.8)	6.12, *bq* (6.8) 6.11, *bq* (6.8)	6.11, *bq* (6.8) 6.10, *bq* (6.8)	
10	1.77, *d* (6.8) 1.75, *d* (6.8) 1.73, *d* (6.8)	1.76, *d* (6.9)	1.77, *d* (6.8) 1.75, *d* (6.8)	
MeO	3.72, *s*	3.74, *s*	3.73, *s*	
1′	4.82, *d* (7.6)	4.83, *d* (7.6)	4.83, *d* (7.6)	
2′-5′	[A]	[A]	[A]	
6′ a	3.66, *m*	3.66, *m*	3.66 *m*	
6′ b	3.94, *m*	3.99, *m*	3.99 *m*	
1″	1.93, *m*	1.94, *m*	1.93, *m*	1.97, *m* (6.9; 6.9)
2″	1.69, *m*	1.68, *m*	1.69, *m*	1.51, *m*
3″	1.91, *m*	1.90, *m*	1.90, *m*	1.75, *m* (5.1)
4″	5.11, *m*	5.11, *m*	4.10, *m*	4.08, *q* (5.1; 5.1; 5.1)
5″ a	1.52, *ddd* (12.6; 6.7; 3.6)	1.53, *ddd* (13.0; 6.7; 2.5)	1.52, *ddd* (12.5; 6.7; 3.5)	1.48, *m* (11.9; 6.9; 5.1)
5″ b	1.95, *m*	1.86, *m*	1.88, *m*	1.70, *m* (11.9; 5.1)
6″	1.09, *d* (6.5)	1.10, *d* (6.6)	1.07, *d* (6.6)	1.03, *d* (6.9)
7″	4.05 *m*	4.06, *m*	4.05, *m*	3.70, *m*
8″	1.89 *m*	1.83, *m*	1.86, *m*	1.70, *m*
9″	4.12 *m*	3.66 *m*	3.63 *m*	3.63, *m* 3.61, *m*
10″	3.59 *m*	3.68 *m*	4.11 *m*	3.59, *m*

[A] In the range 3.3–3.5.

the irradiation in the range of δ 4.0–4.2 corresponding to the three acetoxymethylenic groups made the signal of H-8″ (δ 2.11, *m*) into a doublet with $J = 6.3$ and the signal of H-2″ (δ 1.63, *m*) into a perfect triplet, $J = 9.0$. The dihedral angle of H-2″ both with H-1″ and H-3″ consistent with this last coupling was about 140° (*trans* relationship with both) and it corresponded to a position of C-2″ out of the plane of the other four carbons of the cyclopentanoid ring, thus allowing a quasi equatorial allocation of the substituents in 2″ and 3″. This ring conformation in **9** was in agreement with the coupling constants $J = 3.0$ Hz between H-3″ and H-4″ and between H-4″ and H_b-5″ corresponding to the dihedral angle of about 115° (*trans* relationship for both).

In tetraol **5**, the signal δ 4.08 of H-4″ was a quartet, due to the identical coupling constant, $J = 5.1$, with H-3″, H_a-5″ and H_b-5″. The *cis* relationship between HO-4″ and H_b-5″ was further confirmed by the downfield shift of the latter, δ 1.70, respect to H_a-5″, δ 1.48, owing to the anisotropic effect of the former.

In order to establish the absolute configuration of tetraol **5**, according the Mosher's method through esterification of the secondary alcoholic function with (*S*)-MTPA and (*R*)-MTPA (Ohtani et al., 1991), tetraacyl derivatives **10** and **11** were prepared, respectively. The results of $\Delta\delta$ (^{1}H NMR) ($\delta_S - \delta_R$) showed, in line with the models of Fig. 1, the β configuration of the hydroxyl group in 4″. The structure **5** was thus unambiguously established for the tetraol iridane of craigoside A.



B= *(S)*-MTPA radical
C= *(R)*-MTPA radical

	R^1	R^2	R^3	R^4	R^5	R^6
5	-- Me	–OH	H	H	OH	OH
6	-- Me	H	–OH	H	OH	OH
7	–Me	H	-- OH	H	OH	OH
8	--Me	–OH	H	H	H	OH
9	--Me	–OAc	H	Ac	OAc	OAc
10	--Me	–OB	H	B	OB	OB
11	--Me	–OC	H	C	OC	OC

The three 11-methyl oleoside units on tetraol **5** in craigoside A, **1**, were assigned in positions 4″, 7″ and 9″ on the

Table 2
^{13}C NMR spectroscopic data of compounds **1**, **2**,**3** and **5** in CD_3OD

Position	1	2	3	5
1	95.2	95.3; 95.2	95.2; 95.1	
3	155.1	155.5	155.3	
4	109.4; 109.3	109.8; 109.7	109.5	
5	31.8; 31.7	31.9; 31.8	32.0	
6	41.4; 41.3; 41.2	41.6; 41.4	41.4; 41.3	
7	173.1	173.0; 172.9	173.4; 173.3	
8	125.0; 124.9; 124.8	125.1; 125.0	125.0	
9	130.9; 130.7;130.6	130.6; 130.5	130.8; 130.7	
10	13.8	13.9;13.8	13.9	
11	168.6	168.8; 168.7	168.8; 168.7	
MeO	52.05; 52.03; 52.00	52.1; 52.0	52.2; 52.1	
1′	100.9; 100.8; 100.7	100.9; 100.8	100.9; 100.8	
2′	74.7	74.9; 74.8	74.9; 74.8	
3′	78.4; 78.3	78.6; 78.5	78.5	
4′	71.5; 71.4; 71.3	71.6	71.6; 71.5	
5′	77.9	78.0	78.0	
6′	62.9; 62.8; 62.7	62.8; 62.7	62.6	
1″	37.0	37.3	35.7	35.1
2″	49.5	49.8	49.6	51.9
3″	49.9	49.7	52.6	52.6
4″	80.0	80.3	74.4	75.5
5″	41.3	41.8	43.6	43.2
6″	19.7	20.0	20.7	20.9
7″	68.4	68.7	67.7	65.8
8″	43.5	46.8	42.8	46.3
9″	65.1	62.7	61.6	62.7
10″	61.2	62.0	64.2	61.9

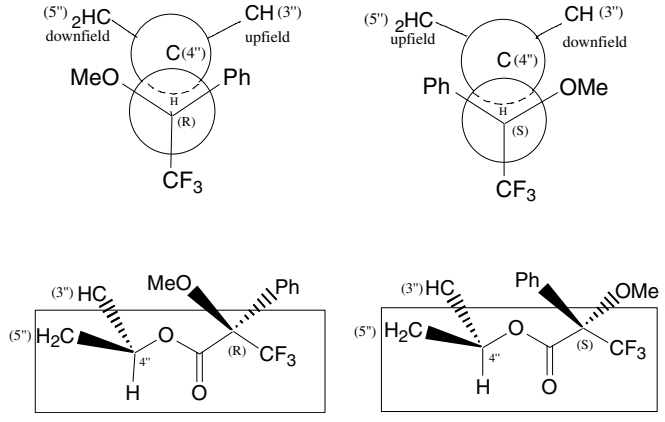


Fig. 1. Configurational correlation models for the (*R*)-MTPA derivatives and the (*S*)-MTPA derivatives proposed by Mosher.

basis of the α downfield effects (and the β upfield effects) on the ^{13}C resonances respect to the corresponding ones of the tetraol. Thus the chemical shifts of C-4″, C-7″ and C-9″ in **5**, δ 75.5, 65.8 and 62.7, respectively, moved to δ 80.0, 68.4 and 65.1 in craigoside A.

Craigoside B, **2**, is an amorphous powder, $C_{44}H_{64}O_{24}$ (ICR-FTMS, *m/z* 999.36655 $[M + Na]^+$), $[\alpha]_D^{20} = -170$ (MeOH), λ_{max} 236 nm (log ε 4.29). Its ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) showed the signals typical of 11-methyl oleoside, the most of them in duplicate. By alkaline hydrolysis and subsequent methylation, the aforementioned tetraol **5**, and dimethyl oleoside, **4**, were obtained. The downfield shifts observed in **2** only for C-4″, δ 80.3, and C-7″, δ 68.7, respect to the corresponding values of the tetraol, δ 75.5 and 65.8, respectively, showed unambiguously the positions of the two iridoid moieties in the molecule of craigoside B. Respect to craigoside A, **1**, the absence of an iridoid unit at C-9″ in craigoside B, **2**, resulted in the upfield shift of C-9″ itself from δ 65.1 to 62.7 and the downfield shift of C-8″ from δ 43.5 to 46.8.

Craigoside C, **3**, is an amorphous powder, $C_{44}H_{64}O_{24}$ (ICR-FTMS, *m/z* 999.37081 $[M + Na]^+$), $[\alpha]_D^{20} = -160$ (MeOH), λ_{max} 236 nm (log ε 4.26). Its ^{1}H and ^{13}C NMR data are reported in Tables 1 and 2, respectively. The alkaline hydrolysis of this trimer, isomer of **2**, and the subsequent methylation with diazomethane likewise gave tetraol **5** and dimethyl oleoside, **4**. The downfield shifts observed in **3** only for C-7″, δ 67.7, and C-10″, δ 64.2, respect to the corresponding values of **5**, δ 65.8 and 61.9, besides the β upfield shifts for C-2″ and C-8″ in the former, gave account of the positions 7″ and 10″ for the two oleoside 11-methyl ester units.

The CD curve of craigoside A, having the same configuration at C-8″ as molihuaside E from *J. sambac* (Zhang et al., 1995), showed an additional band at 247 nm besides the band at 228 nm.

In summary, the oligomeric secoiridoid glucosides, new respect to the previously described ones occurring in the aerial parts of *Jasminum* genus plants, have been isolated from the root bark of *J. abyssinicum* from Congo. The three oligomeric, craigoside A, tetramer, and craigosides B and C, trimer, have the same cyclopentanoid monoterpene, which is a tetraol iridane, **5**, esterified by oleoside 11-methyl ester units.

3. Experimental

3.1. General

A Craig-Post apparatus, 200 stages, 10:10 ml, upper and lower phase, for the CCD. ^{1}H NMR, 300 MHz, ^{13}C NMR, 75 MHz, TMS as internal standard, chemical shifts (δ) in ppm, coupling constants (*J*) in Hz, Varian Gemini 300. ICR-FTMS, high resolution, APEX II Bruker; ESI-MS, Thermo Finnigan, and FAB-MS, VG 7070 EQ-HF. CD, Jasco 710.

3.2. Plant material

Root barks of *J. abyssinicum* R. Br. were collected in March 1999 near Bukavu (South Kivu Province, Congo). The plant material was identified in the Institut Supérieur d'Ecologie pour la Conservation de la Nature, Lwiro (Cyangugu, Rwanda), where a voucher specimen (Mubeza, B 346) is deposited.

3.3. Extraction and isolation

Air-dried root barks (310 g) were extracted three times with MeOH. The residue from the evaporation of the sol-

vent (32.6 g) was dissolved in water (350 ml) and extracted with EtOAc (2 × 300 ml). The aqueous phase evaporated to dryness under vacuum gave as residue 26.5 g.

Six grams of this was submitted to CCD with the biphase system H_2O:EtOAc:*n*-PrOH discontinuously changing the ratio from 10:9:1 to 10:7:3. The separations were monitored by TLC, silica gel F_{254}, solvent *n*-BuOH:-H_2O:HOAc = 4:5:1 (upper phase); detection by fluorescence quenching and/or by spray reagent anisaldehyde: H_2SO_4:HOAc:EtOH = 0.5:0.5:0.1:9. Three of the nine collected fractions, J6, 514 mg, J7, 441 mg, and J6/7, 138 mg, were submitted to CCD on recycling with the solvent system H_2O:EtOAc:*n*-PrOH = 10:7:3 and three pure compounds, craigoside C, **3**, 203 mg, craigoside B, **2**, 170 mg, and craigoside A, **1**, 366 mg, were obtained.

3.4. Craigoside A (*1*)

Amorphous powder, $[\alpha]_D^{20} = -185$ (MeOH, *c* 0.5), UV (MeOH), λ_{max} nm (log ε): 233 (4.54); CD (MeOH), λ nm ([Θ]): 211 (-8.1×10^7), 228 (-12.7×10^7), 247 (-8.8×10^7). Molecular formula $C_{61}H_{86}O_{34}$, ICR-FTMS *m/z*: 1385.48602 $[M + Na]^+$, calcd 1385.48927; ESI-MS *m/z*: 1386.6, 16 $[M + Na]^+$, 1224.3, 100 $[M + Na - 162]^+$, 1062.4, 7 $[M + Na - 162 \times 2]^+$, 982.4, 67 [M + Na − an iridoid − H_2O]$^+$, 819.3, 32 [M + Na − an iridoid − H_2O − 162]$^+$. ^{1}H and ^{13}C NMR data in Tables 1 and 2, respectively.

3.5. Craigoside B (*2*)

Amorphous powder, $[\alpha]_D^{20} = -170$ (MeOH, *c* 0.4), UV (MeOH), λ_{max} nm (log ε): 236 (4.29); CD (MeOH), λ nm ([Θ]): 233 (-7.0×10^7). Molecular formula $C_{44}H_{64}O_{24}$, ICR-FTMS *m/z*: 999.36655 $[M + Na]^+$, calcd 999.36797; ESI-MS *m/z*: 1000.3, 41 $[M + Na]^+$, 837.3, 55 [M + Na − 162]$^+$, 595.3, 100 [M + Na − an iridoid − H_2O]$^+$. ^{1}H and ^{13}C NMR data in Tables 1 and 2, respectively.

3.6. Craigoside C (*3*)

Amorphous powder, $[\alpha]_D^{20} = -160$ (MeOH, *c* 0.4), UV (MeOH), λ_{max} nm (log ε): 236 (4.26); CD (MeOH), λ nm ([Θ]): 232 (-5.7×10^7). Molecular formula $C_{44}H_{64}O_{24}$, ICR-FTMS *m/z*: 999.37081 $[M + Na]^+$, calcd 999.36797; ESI-MS *m/z*: 999.5, 34 $[M + Na]^+$, 837.3, 100 [M + Na − 162]$^+$, 595.3, 15 [M + Na − an iridoid − H_2O]$^+$. ^{1}H and ^{13}C NMR data in Tables 1 and 2, respectively.

3.7. Acetylation of craigosides A–C

Each substance (50 mg) was acetylated with pyridine and Ac_2O (each, 0.5 ml). After evaporation of the reagents under vacuum, the compound was purified by CC (silica gel, solvents cyclohexane:EtOAc = 2:8) to give the corresponding pure peracetate.

3.7.1. Craigoside A tredeca-acetate

Crystals from cyclohexane, mp 87–89 °C, $[\alpha]_D^{24} = -153$ ($CHCl_3$, *c* 0.4). ^{1}H NMR ($CDCl_3$) δ: 7.46 (3H, *s*, H-3 × 3); 6.01, 5.99 (3H, *bq*, *J* = 6.7, H-8 × 3); 5.72 (3H, *bs*, H-1 × 3); 5.28 (3H, *t*, *J* = 9.3, H-3′ × 3); 5.13 (3H, *t*, *J* = 9.3, H-4′ × 3); 5.12 (3H, *dd*, 9.3, 7.8, H-2′ × 3); 5.11 (1H, *m*, H-4″); 5.06 (3H, *d*, *J* = 7.8, H-1′ × 3); 4.33 (3H, *dd*, *J* = 12.3, 3.2, H_a-6′ × 3); 4.10 (3H, *dd*, *J* = 12.3, 1.5, H_b-6′ × 3); 3.96 (3H, *dd*, *J* = 11.0, 4.8, H-5 × 3); 3.78 (3H, *m*, *J* = 9.3, 3.2, 1.5, H-5′ × 3); 3.71 (9H, *s*, MeO × 3); 2.66 (3H, *dd*, *J* = 13.0, 4.8, H_a-6 × 3); 2.42 (3H, *dd*, *J* = 13.0, 11.0, H_b-6 × 3); 2.11 (1H, *m*, H-8″); 2.08, 2.04 (39H, *s*, CH_3CO × 13); 1.94 (1H, *m*, H_b-5″); 1.86 (1H, *m*, H-3″); 1.75 (9H, *d*, *J* = 6.9, H_3-10 × 3); 1.65 (1H, *m*, H-2″); 1.51 (1H, *m*, H_a-5″); 1.05 (3H, *d*, *J* = 6.3, H_3-6″). ^{13}C NMR δ: 170.9, 170.4, 170.0 (C-7 × 3); 169.3, 169.2 (CH_3CO × 13); 166.6 (C-11 × 3); 152.9 (C-3 × 3); 128.5, 128.2 (C-9 × 3); 124.7, 124.5 (C-8 × 3); 108.5, 108.4 (C-4 × 3); 97.0 (C-1″ × 3); 93.7 (C-1 × 3); 77.9 (C-4″); 72.4 (C-5′ × 3); 72.1 (C-3′ × 3); 70.6 (C-2′ × 3); 68.0 (C-4′ × 3); 67.0 (C-7″); 63.2 (C-9″); 62.4 (C-10″); 61.5 (C-6′ × 3); 51.4 (MeO × 3); 48.5 (C-3″); 47.7 (C-2″); 40.2 (C-5″); 39.8 (C-6 × 3); 38.9 (C-8″); 35.8 (C-1″); 29.9 (C-5 × 3); 21.0, 20.6 (CH_3CO × 13); 19.4 (C-6″); 13.5 (C-10 × 3).

3.7.2. Craigoside B deca-acetate

Crystals from cyclohexane, mp 73–75 °C, $[\alpha]_D^{24} = -133$ ($CHCl_3$, *c* 0.4). ^{1}H NMR ($CDCl_3$) δ: 7.46, 7.45 (2H, *s*, H-3 × 2); 6.01 (2H, *bq*, *J* = 6.6, H-8 × 2); 5.73, 5.72 (2H, *s*, H-1 × 2); 5.28 (2H, *t*, *J* = 9.4, H-3′ × 2); 5.15 (2H, *t*, *J* = 9.4, H-4′ × 2); 5.13 (1H, *m*, H-4″); 5.12 (2H, *dd*, *J* = 9.4, 8.1, H-2′ × 2); 5.06, 5.04 (2H, *d*, *J* = 8.1, H-1′ × 2); 4.33 (2H, *dd*, *J* = 12.3, 4.5, H_a-6′ × 2); 4.11 (2H, *dd*, *J* = 12.3, 2.1, H_b-6′ × 2); 4.00, 3.96 (2H, *dd*, *J* = 11.0, 4.8, H-5 × 2); 3.80 (2H, *m*, *J* = 9.4, 4.6, 2.1, H-5′ × 2); 3.71 (6H, *s*, MeO × 2); 2.71, 2.62 (2H, *dd*, *J* = 13.0, 4.8, H_a-6 × 2); 2.45, 2.40 (2H, *dd*, *J* = 13.0, 11.0, H_b-6 × 2); 2.11 (1H, *m*, H-8″); 2.09, 2.04, 2.03 (30H, *s*, CH_3CO × 10); 1.96 (1H, *m*, H_b-5″); 1.84 (1H, *m*, H-3″);1.76 (6H, *d*, *J* = 6.9, H_3-10 × 2); 1.65 (1H, *m*, H- 2″); 1.52 (1H, *m*, H_a-5″); 1.05 (3H, *d*, *J* = 6.3, H_3-6″). ^{13}C NMR δ: 171.3, 170.9 (C-7 × 2); 170.8, 170.7, 170.3, 169.5, 169.0 (CH_3CO × 10); 166.9 (C-11 × 2); 153.2 (C-3 × 2); 128.8, 128.7 (C-9 × 2); 125.0, 124.8 (C-8 × 2); 108.8 (C-4 × 2); 97.4, 97.3 (C-1′ × 2); 94.2, 94.0 (C-1 × 2); 77.8 (C-4″); 72.8 (C-5′ × 2); 72.4 (C-3′ × 2); 71.0 (C-2′ × 2); 68.5 (C-4′ × 2); 67.3 (C-7″); 63.6 (C-9″); 62.8 (C-10″); 61.9 (C-6′ × 2); 51.6 (MeO × 2); 49.1 (C-3″); 48.1 (C-2″); 40.7 (C-5″); 40.2, 40.1 (C-6 × 2); 39.2 (C-8″); 36.0 (C-1″); 30.4, 30.3 (C-5 × 2); 21.0, 20.8 (CH_3CO × 10); 19.6 (C-6″); 13.8, 13.7 (C-10 × 2).

3.7.3. Craigoside C deca-acetate

Crystals from cyclohexane, mp 69–71 °C, $[\alpha]_D^{24} = -114$ ($CHCl_3$, *c* 0.4). ^{1}H NMR ($CDCl_3$) δ: 7.47 (2H, *s*, H-3 × 2); 6.01 (2H, *bq*, *J* = 7.2, H-8 × 2); 5.71 (2H, *bs*, H-1 × 2); 5.28 (2H, *t*, *J* = 9.6, H-3′ × 2); 5.14 (2H, *t*, *J* = 9.6, H-4′ × 2); 5.13 (1H, *m*, H-4″); 5.12 (2H, *dd*, *J* = 9.6, 8.1, H-2′ × 2); 5.04 (2H, *d*, *J* = 8.1, H-1′ × 2); 4.33 (2H, *dd*, *J* = 12.3, 4.2,

H_a-6′ × 2); 4.07 (2H, *dd*, *J* = 12.3, 1.8, H_b-6′ × 2); 4.02 (2H, *dd*, *J* = 11.0, 4.8, H-5 × 2); 3.78 (2H, *m*, *J* = 9.6, 4.2, 1.8, H-5′ × 2); 3.72 (6H, *s*, MeO × 2); 2.70, 2.69 (2H, *dd*, *J* = 13.0, 4.8, H_a-6 × 2); 2.44 (2H, *dd*, *J* = 13.0, 11.0, H_b-6 × 2); 2.11 (1H, *m*, H-8″); 2.08, 2.03, 2.02, 2.00 (30H, *s*, C*H*$_3$CO × 10); 1.96 (1H, *m*, H_b-5″); 1.84 (1H, *m*, H-3″); 1.76 (6H, *d*, *J* = 6.9, H_3-10 × 2); 1.63 (1H, *m*, H-2″); 1.54 (1H, *m*, H_a-5″); 1.05 (3H, *d*, *J* = 6.6, H_3-6″). ^{13}C NMR *δ*: 171.0, 170.8 (C-7 × 2); 170.5, 170.4, 170.2, 170.0, 169.2, 169.1 (CH$_3$*C*O × 10); 166.5 (C-11 × 2); 152.9 (C-3 × 2); 128.4 (C-9 × 2); 124.7 (C-8 × 2); 108.5 (C-4 × 2); 97.0, 96.9 (C-1′ × 2); 93.7, 93.6 (C-1 × 2); 76.9 (C-4″); 72.4 (C-5′ × 2); 72.1 (C-3′ × 2); 70.7 (C-2′ × 2); 68.1 (C-4′ × 2); 66.1 (C-7″); 63.2 (C-9″); 62.5 (C-10″); 61.6 (C-6′ × 2); 51.3 (MeO × 2); 48.4 (C-3″); 48.0 (C-2″); 40.5 (C-5″); 39.8, 39.7 (C-6 × 2); 38.9 (C-8″); 35.2 (C-1″); 30.0, 29.9 (C-5 × 2); 21.0, 20.4 (*C*H$_3$CO × 10); 19.1 (C-6″); 13.4 (C-10 × 2).

3.8. Alkaline hydrolysis of craigosides A–C. Methylation with diazomethane

Each compound (300 mg) was treated with 0.5 M NaOH (5 ml). After 20 h the solution was neutralized with weakly acid cation-exchanger (H^+ form) and concentrated in vacuum to dryness. The residue was dissolved in MeOH and methylated with an ethereal solution of diazomethane. After 2 days the residue obtained by evaporation of the solvents was submitted to CCD with solvent system H_2O:*n*-BuOH:EtOAc = 10:7.5:2.5 and dimethyl oleoside, **4**, and tetraol iridane, **5**, were separated. The former was identified by NMR and rotatory power (Tanahashi et al., 1988).

3.8.1. Tetraol iridane (5)

Syrop, $[\alpha]_D^{26} = +2.4$ (MeOH, *c* 0.4). Molecular formula $C_{10}H_{20}O_4$, ICR-FTMS *m*/*z*: 227.12552 $[M + Na]^+$, calcd 227.12538; FAB-MS *m*/*z*: 205, 100 $[M + 1]^+$, 187, 66 $[M - 17]^+$. ^{1}H and ^{13}C NMR data in Tables 1 and 2, respectively.

3.9. Acetylation of 5: iridane tetra-acetate (9)

Tetraol iridane **5** (28 mg) was acetylated with pyridine and Ac_2O (each, 1 ml). After evaporation of the reagents under vacuum, the product was purified by CC (silica gel, solvents cyclohexane:EtOAc = 3:7) to give the corresponding tetra-acetate. Oily, $[\alpha]_D^{23} = +14.2$ ($CHCl_3$, *c* 0.3). Molecular formula $C_{18}H_{28}O_8$, FAB-MS *m*/*z*: 372 (1, M), 329 (3, M-Ac), 313 (3, M-AcO), 269 (45, M-Ac-AcOH), 150 (100). ^{1}H NMR ($CDCl_3$) *δ*: 5.12 (1H, *quintet*, *J* = 6.0, 3.0, 3.0, H-4″); 4.17, 4.05 (2H, *m*, H_2-9″); 4.13, 3.99 (2H, *m*, H_2-10″); 4.11, 4.00 (2H, *m*, H_2-7″); 2.11 (1H, *m*, *J* = 6.3, H-8″); 2.08, 2.06, 2.05, 2.02 (12H, *s*, C*H*$_3$CO × 4); 1.96 (1H, *m*, *J* = 9.0, 6.3, 3.0, H-3″); 1.94 (1H, *m*, *J* = 10.5, 9.0, 6.8, 6.6, H-1″); 1.83 (1H, *m*, *J* = 13.5, 6.8, 3.0, H_b-5″); 1.63 (1H, *m*, *J* = 9.0, 9.0, H-2″); 1.52 (1H, *dq*, *J* = 13.5, 10.5, 6.0, H_a -5″); 1.07 (3H, *d*, *J* = 6.6, H_3-6″). ^{13}C NMR *δ*: 169.9 (CH$_3$*C*O × 4); 77.1 (C-4″); 66.1 (C-7″); 63.4 (C-9″); 62.4 (C-10″); 48.6 (C-3″); 48.1 (C-2″); 40.5 (C-5″); 39.0 (C-8″); 35.2 (C-1″); 21.1, 20.7 (*C*H$_3$CO × 4); 19.1 (C-6″).

3.10. (S)-MTPA tetra-ester of 5 (10)

A suspension of **5** (40 mg) in anhydrous CH_2Cl_2 (15 ml) was added with (*S*)-MTPA (188 mg), DMAP (26 mg) and then with DCC (176 mg). After 2 days of stirring, more (*S*)- MTPA (45 mg) and DCC (46 mg) were added. After 2 days the mixture was diluted with water and extracted with additional CH_2Cl_2. The residue of the evaporation of the organic phase was submitted to CC (silica gel, solvents cyclohexane:EtOAc=8:2) and the tetra acyl derivative **10** was obtained. Molecular formula $C_{50}H_{48}O_{12}F_{12}$, ICR-FTMS *m*/*z*: 1091.28111 $[M + Na]^+$, calcd 1091.28464. ^{1}H NMR ($CDCl_3$) *δ*: 7.47-7.37 (20H, *m*, ArH_5 × 4); 5.15 (1H, *m*, H-4″); 4.26 (1H, *dd*, *J* = 11.4, 4.9, H_b-10″); 4.22 (1H, *dd*, *J* = 12.0, 4.4, H_a-10″); 4.13, 4.11 (2H, *m*, H_2-7″); 4.08 (1H, *m*, H_b-9″); 3.93 (1H, *dd*, *J* = 11.4, 6.8, H_a-9″); 3.50, 3.47, 3.45 (12H, *s*, MeO × 4); 2.05 (1H, *m*, H-8″); 1.81 (1H, *m*, H-3″); 1.69 (1H, *m*, H_b-5″); 1.65 (1H, *m*, H-1″); 1.46 (1H, *m*, H-2″); 1.16 (1H, *m*, H_a-5″); 0.83 (3H, *d*, *J* = 6.2, H_3-6″). ^{13}C NMR *δ*: 166.2 (CO × 4); 132.2 (C Ar1 × 4); 129.8, 128.7, 127.4, 127.3 (C Ar2-6 × 4); 122.3 (CF_3 × 4); 84.3 (C-1 × 4); 79.6 (C-4″); 68.0 (C-7″); 64.3 (C-9″); 63.3 (C-10″); 55.6, 55.3 (MeO × 4); 48.9 (C-3″); 48.1 (C-2″); 40.0 (C-5″); 38.8 (C-8″); 35.2 (C-1″); 18.7 (C-6″).

3.10.1. (R)-MTPA tetra-ester of 5 (11)

Tetraol **5** was likewise treated with *(R)-MTPA* and tetra acyl derivative **11** was obtained. Molecular formula $C_{50}H_{48}O_{12}F_{12}$, ICR-FTMS *m*/*z*: 1091.27944 $[M + Na]^+$, calcd 1091.28464. ^{1}H NMR ($CDCl_3$) *δ*: 7.47–7.36 (20H, *m*, ArH_5 × 4); 5.09 (1H, *m*, H-4″); 4.36 (1H, *dd*, *J* = 11.7, 5.1, H_b-10″); 4.10 (1H, *m*, H_a-10″); 4.08, 4.06 (2H, *m*, H_2-7″); 3.98, 3.92 (2H, *m*, H_2-9″); 3.49, 3.47 (12H, *s*, MeO × 4); 2.04 (1H, *m*, H-8″); 1.81 (1H, *m*, H_b-5″); 1.74 (1H, *m*, H-1″); 1.73 (1H, *m*, H-3″); 1.54 (1H, *m*, H-2″); 1.37 (1H, *m*, H_a-5″); 0.86 (3H, *d*, *J* = 6.0, H_3-6″). ^{13}C NMR *δ*: 165.9 (CO × 4); 132.0 (C Ar1 × 4); 129.7, 128.5, 127.2 (C Ar2-6 × 4);121.4 (CF_3 × 4); 84.4 (C-1 × 4); 79.3 (C-4″); 67.9 (C-7″); 63.9 (C-9″); 63.5 (C-10″); 55.3 (MeO × 4); 48.7 (C-3″); 47.8 (C-2″); 39.8 (C-5″); 38.9 (C-8″); 35.4 (C-1″); 18.7 (C-6″).

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