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THE DICHAPETALINS—A NEW CLASS OF TRITERPENOIDS*†

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Key Word Index—*Dichapetalum madagascariense*; Dichapetalaceae; dichapetalins A–H; cytotoxic compounds.

Abstract—Further to our recent report on dichapetalin A, we describe the isolation and structure elucidation by spectroscopic methods of dichapetalins B–H from the roots of *Dichapetalum madagascariense*. These compounds constitute a novel class of triterpenoids. Dichapetalin A shows a strong and selective cytotoxic activity. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Several members of the family Dichapetalaceae (=Chailletiaceae) are known to be highly toxic due to the presence of fluorinated compounds, mainly fluorocarboxylic acids [2, 3]. Whereas there have been many studies on these fluorinated constituents, very little is known about the fluorine-free compounds of the Dichapetalaceae: *N*-methylserine and *N*-methylalanine have been isolated from *Dichapetalum cymosum* [4] and friedelin has been found in *D. gelonioides* [5].

D. madagascariense Poir. (syn. *Dichapetalum guineense* (DC.) Keay) grows as a shrub or tree to over 20 m high in tropical Africa [6]. In folk medicine, preparations of the plant are used against jaundice and for the treatment of sores and urethritis [6].

Recently we reported the isolation and structure elucidation of dichapetalin A (**1**), a major constituent of the roots of *D. madagascariense* with cytotoxic activity [7]. Further examination of the acetone extract of the roots has resulted in the isolation of seven further members of this new class of phenylpyranotriterpenoids, which were named dichapetalins B–H (**2–8**). Biogenetically their basic structures are characterized by the addition of a C_6–C_2-unit to a cyclodammarane skeleton.

RESULTS

Chromatographic separation of the root extract of *D. madagascariense* afforded as the major constituent dichapetalin A (**1**) and the minor compounds dichapetalin B–H (**2–8**). The spectroscopic properties of **2–8** closely resembled those of **1**.

In the ^{1}H and ^{13}C NMR spectra of **2–5** (Tables 1 and 2) all the resonances of the protons and carbons of the basic ring system of **1** were discernible.

However, the signals of the side chain protons and carbons differed significantly. For compound **2**, the ^{1}H and ^{13}C NMR data suggested an additional hydroxy group at C-22, and this was demonstrated by homo- and heteronuclear COSY experiments as well as by the quasi molecular ion at *m/z* 601 in the DCI-mass spectrum of **2**, which is 16 masses higher than that of **1**. The relative configuration of **2** was determined from NOE experiments.

One of the most conspicuous features of the NMR spectra of **3** and **4** was the appearance of the resonances of methyl ester groups in the ^{1}H NMR spectrum at about δ 3.7 and in the ^{13}C NMR spectrum at about δ 52 and 175. Furthermore, the spectra of compound **4** differed from the others in having additional signals for a long chain aliphatic acid. Consequently, **4** was determined to be the stearic acid ester of **3** from its molecular mass (determined by FAB-mass spectrometry) and by identification of the acyl moiety as methyl stearate after methanolysis. The position of the stearoyloxy moiety at C-26 was deduced from the characteristic downfield shift of H-26 and C-26 and the highfield shift of C-25, respectively. Furthermore, a cross-peak between H-26 and the carbonyl carbon of the stearoyl moiety was observed in the long range heteronuclear correlation of **4** (Fig. 1). This experiment also established the structure of the side chain at C-17 in **3** and **4**.

Compound **5** was isolated in a very small amount. Comparison of the ^{1}H NMR spectral data with those of **3** and **4** suggested the same basic skeleton, as well as

*Dedicated to Prof. Dr Mutschler, Frankfurt, on the occasion of his 65th birthday.

†Part 74 in the series 'Constituents of Tropical Medicinal Plants'. For Part 73 see ref. [1].

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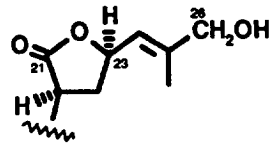
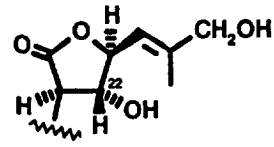
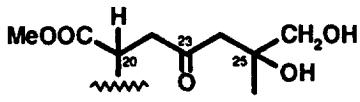
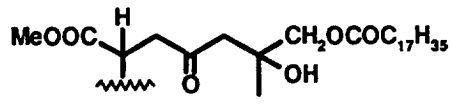
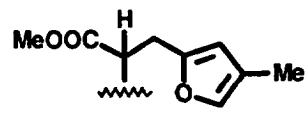
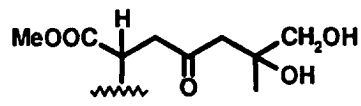
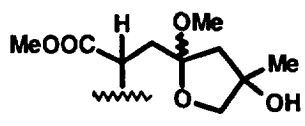
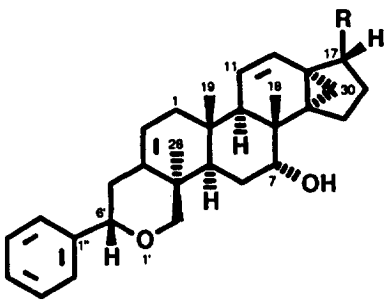
Dichapetalin (Formula)	R
A (1):	
B (2):	
C (3):	
D (4):	
E (5):	
F (6):	 11,12 - Dihydro
G and H (7, 8):	 11,12 - Dihydro



the presence of a carboxylic acid methyl ester at C-20. The protons of the side chain gave rise to three multiplets at δ 2.69, 2.78 and 2.94, a weakly coupled doublet of a methyl group at δ 1.96 and two signals at δ 5.86 and 7.04. The former three could be assigned to H-20 and the two H-22 by a COSY-experiment, and the latter three were established as the resonances of the protons of a 4-methylfuran-2-yl moiety by HMQC and HMBC measurements. These experiments also established the structure of the side chain of **5**. The most important HMB correlations are depicted in Fig. 2.

The ^{1}H NMR spectra of **6**–**8** showed only one signal of an alkenic proton. In addition, the signals of the cyclopropane hydrogens were shifted significantly to higher field, indicating a fully hydrogenated ring-C of the dichapetalin-system. Furthermore, in the DCI-mass

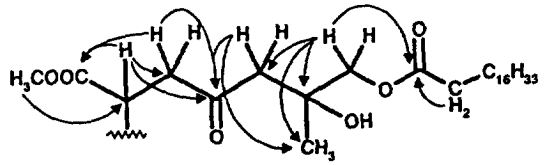


Fig. 1. Important long range heteronuclear correlations observed in the HMBC of **4** for the side chain at C-17.

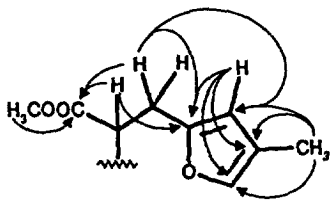


Fig. 2. Important long range heteronuclear correlations observed in the HMBC of **5** for the side chain at C-17.

spectrum of **6** all significant ions were found two masses higher compared with **3**. Since all NMR signals of **6** not directly in the neighbourhood of ring-C were very similar to those of **3**, this suggested **6** to be 11,12-dihydro-dichapetalin C. Final proof for the structure of **6** came from the HMQC and HMBC spectra (Fig. 3).

The spectroscopic properties of **7** and **8** established these compounds as isomeric methylketals with the 11,12-dihydro-dichapetalin ring system like **6**. The structures of the side chains were established from 2D NMR measurements in the same way as described for compounds **1**–**6** (see also [7]).

The absolute configuration of **1** has been determined by X-ray crystallography [8]. The very similar CD curves of **1**–**4** and **6** showed a strong positive Cotton effect around 217 nm and a considerably weaker Cotton effect around 235 nm. This suggested identical absolute configurations for these compounds as far as the cyclodammarane ring system is concerned. However, the relative configurations between C-17 and C-20 in **3** to **8** and the absolute configurations at C-25 could not be established.

DISCUSSION

The dichapetalins represent a new class of triterpenoids which could be derived from the condensation of a 13,30-cyclo-dammarane-type triterpenoid with a C_6–C_2 moiety, possibly from the shikimic acid pathway. The structural feature of a 2-phenylpyran moiety annellated to ring A is unique among the triterpenoids. Moreover, naturally-occurring 13,30-cyclo-dammaranes constitute a relatively rare class of triterpenes, which up-to-now have been isolated mainly from a few *Meliaceae* species [9–17].

In the course of isolation by HPLC, it was observed that the amounts of **5**, **7** and **8** in the fractions containing compounds **2**, **3** and **6** as the main components increased with time. Compounds **5**, **7** and **8** may therefore be artifacts. Formation of **5** might proceed by the two-fold dehydration of an intermediate hemiketal formed intramolecularly. A similar intermediate obviously might give rise to **7** and **8** by ketalization with methanol during work-up and/or chromatographic separation.

Dichapetalin A (**1**), in the brine shrimp bioassay [18] exhibited pronounced cytotoxicity, which exceeded that of podophyllotoxin about seven-fold; dichapetalin C (**3**) was also effective, but to a much smaller extent, and dichapetalins D and F were almost inactive.

In various cell systems, compound **1** inhibited the cell growth. However, the sensitivity depending on the cell systems was found to be highly different: L1210 murine leukaemia cells were extremely sensitive (EC $90 < 0.0001\ \mu g\ ml^{-1}$), but human KB carcinoma and murine bone marrow stimulated with GM-CSF were only affected by concentrations four orders of magnitude higher [7].

None of the dichapetalins tested showed any antibacterial nor antifungal activity.

EXPERIMENTAL

General. Unless otherwise stated, TLC was performed on precoated plates (Nano-Plates Sil-20 UV_{254}, Macherey-Nagel) using $CHCl_3$–MeOH (49:1) as eluent; detection: UV, anisaldehyde reagent [19]. CC

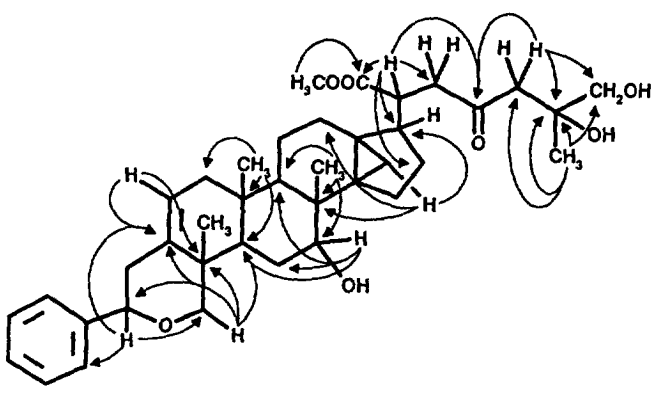


Fig. 3. Important long range heteronuclear correlations observed in the HMBC of **6**.

Table 1. ^{1}H NMR data of the isolated dichapetalins **1–8** (δ [ppm] in $CDCl_3$)

	1	**2**	**3**	**4**†	**5**	**6**	**7**	**8**
H-1	~1.7*	~1.7*	~1.65*	~1.65*	~1.65*	~1.60*	~1.60*	~1.60*
	2.12 *dd*	2.11 *dd*	2.09 *dd*	2.09 *dd*	2.08 *dd*	1.95 *dd*	1.94 *dd*	1.95 *dd*
	J = 16; 7	J = 16; 7	J = 16; 7	J = 16; 7	J = 16; 7	J = 16; 7	J = 16; 7	J = 16; 7
H-2	5.41 *brd*	5.41 *brd*	5.41*	5.40*	5.40 *brd*	5.37 *brd*	5.37 *brd*	5.37 *brd*
	J = 7	J = 7			J = 7	J = 7	J = 7	J = 7
H-5	2.00 *dd*	2.01 *dd*	2.00*	2.00*	2.00 *dd*	1.98 *dd*	1.98 *dd*	1.98 *dd*
	J = 13.5; 2.5	J = 13.5; 2.5			J = 13.5; 2.5	J = 13.5; 2.5	J = 13.5; 2.5	J = 13.5; 2.5
H-6	~1.7*	~1.7*	~1.65*	~1.65*	~1.65*	~1.55*	~1.55*	~1.55*
	1.86 *ddd*	~1.85*	1.85 *ddd*	1.85 *ddd*	1.85 *ddd*	~1.70*	~1.70*	~1.75*
	J = 14; 3; 3		J = 14; 3; 2.5	J = 14; 3; 2.5	J = 14; 3; 2.5			
H-7	3.95 *brdd*	3.97 *brdd*	3.93 *brdd*	3.93 *brdd*	3.93 *brdd*	3.80 *brdd*	3.80 *brdd*	3.80 *brdd*
	J = 2.5; 2.5	J = 2.5; 2.5	J = 2.5; 2.5	J = 2.5; 2.5	J = 2.5; 2.5	J = 2.5; 2.5	J = 2.5; 2.5	J = 2.5; 2.5
H-9	1.98*	1.99*	1.97*	1.97*	~1.97*	~1.25*	~1.25*	~1.25*
H-11	5.47 *dd*	5.51 *dd*	5.41*	5.41*	5.36 *dd*	~1.25*	~1.25*	~1.25*
	J = 10; 2.5	J = 10; 2.5			J = 10; 2.5	~1.25*	~1.25*	~1.25*
H-12	6.15 *dd*	6.14 *dd*	5.86 *dd*	5.86 *dd*	5.85 *dd*	~1.60*	~1.60*	~1.60*
	J = 10; 3	J = 10; 3	J = 10; 3	J = 10; 3	J = 10; 3	~1.60*	~1.60*	~1.60*
H-15	~1.7*	~1.7*	~1.65*'	~1.65*	~1.65*	~1.55*	~1.55*	~1.55*
	2.05*	~2.05*	~2.00*	~2.00*	~1.95*	1.90 *m*	~1.90*	1.88 *m*
H-16	1.12*	1.16 *brm*	~1.10*	~1.10*	1.16 *m*	0.92 *m*	0.88 *m*	0.88 *m*
	~1.75*	~1.85*	~1.65*	~1.65*	~1.95*	~1.55*	~1.75*	~1.75*
H-17	2.63*	~2.68*	2.36 *m*	~2.35*	2.37 *ddd*	2.27 *ddd*	2.25*	2.25*
					J = 10; 9; 8.5	J = 10.5; 6.5; 6.5		
Me-18	0.91 *s*	0.93 *s*	0.88 *s*	0.88 *s*	0.89 *s*	1.05 *s*	1.05 *s*	1.05 *s*
Me-19	1.09 *s*	1.09 *s*	1.07 *s*	1.07 *s*	1.07 *s*	1.01 *s*	1.01 *s*	1.01 *s*
H-20	3.09 *ddd*	3.12 *dd*	3.08 *m*	3.05 *m*	2.69 *ddd*	~2.98*	~2.35*	2.25*
	J = 13; 8.5; 5	J = 9.5; 5			J = 11; 8.5; 4			
H-22	1.85*	4.23 *ddd*	2.60 *m*	2.58 *m*	2.78 *dd*	~2.55*	~2.35*	2.43 *dd*
		J = 9.5; 8; 3.5			J = 15; 4			J = 13.5; 12
	2.39 *ddd*		3.03 *m*	3.00 *m*	2.94 *dd*	~2.98*	~1.55*	~1.55*
	J = 13; 8.5; 5.5				J = 15; 11			
H-23	5.14 *ddd*	4.90 *dd*	—	—	—	—	—	—
	J = 10.5; 8.5; 5.5	J = 8; 8						
H-24	5.53 *dq*	5.54 *dq*	2.52 *d*	2.54 *d*	5.86 *brs*	2.51 *d*	2.01 *d*	1.73 *d*
	J = 8.5; 1.5	J = 8; 1.5	J = 16	J = 16		J = 16	J = 14	J = 13
			2.90 *d*	2.79 *d*		2.88 *d*	2.14 *brd*	2.22 *d*
			J = 16	J = 16		J = 16	J = 14	J = 13

H-26	4.06 *m* (2H)	4.11 *m* (2H)	3.39 *d* *J* = 11 3.44 *d* *J* = 11	3.99 *s* (2H)	7.04 *dq* *J* = 1; 1	3.37 *brdd* *J* = 11 3.43 *brd* *J* = 11	3.63 *brd* *J* = 9.5; 4.5 3.68 *dd* *J* = 9.5; 2.5	3.85 *d* *J* = 9.5 3.93 *d* *J* = 9.5
Me-27	1.75 *d* *J* = 1.5	1.81 *d* *J* = 1.5	1.21 *s*	1.23 *s*	1.96 *d* *J* = 1	1.20 *s*	1.37 *s*	1.35 *s*
Me-28	1.33 *s*	1.34 *s*	1.33 *s*	1.33 *s*	1.33 *s*	1.32 *s*	1.32 *s*	1.32 *s*
H-30	0.79 *d* *J* = 5.5 1.19 *d* *J* = 5.5	0.90 *d* *J* = 5 1.24 *d* *J* = 5	0.84 *d* *J* = 5 1.30 *d* *J* = 5	0.84 *d* *J* = 5 ~1.30*	0.85 *d* *J* = 5 1.27 *d* *J* = 5	0.54 *d* *J* = 5 0.78 *d* *J* = 5	0.53 *d* *J* = 5 0.76 *d* *J* = 5	0.52 *d* *J* = 5 0.76 *d* *J* = 5
O-$\underline{CH_3}$	—	—	3.71 *s*	3.70 *s*	3.66 *s*	3.69 *s*	3.70 *s* 3.18 *s*	3.66 *s* 3.14 *s*
H-2′	3.61 *d* *J* = 10.5 3.78 *d* *J* = 10.5	3.61 *d* *J* = 10.5 3.77 *d* *J* = 10.5	3.60 *d* *J* = 10.5 3.77 *d* *J* = 10.5	3.60 *d* *J* = 10.5 3.76 *d* *J* = 10.5	3.60 *d* *J* = 10.5 3.77 *d* *J* = 10.5	3.57 *d* *J* = 10.5 3.75 *d* *J* = 10.5	3.58 *d* *J* = 10.5 3.75 *d* *J* = 10.5	3.58 *d* *J* = 10.5 3.75 *d* *J* = 10.5
H-5′	2.20 *dd* *J* = 13.5; 2.5 2.63*	2.21 *dd* *J* = 13.5; 2.5 2.68*	2.20 *dd* *J* = 13.5; 2.5 2.64 *brdd* *J* = 13.5; 11.5	2.20 *dd* *J* = 13.5; 2.5 2.63 *brdd* *J* = 13.5; 11.5	2.20 *dd* *J* = 13.5; 2.5 2.63 *brdd* *J* = 13.5; 11.5	2.18 *dd* *J* = 13.5; 2.5 2.62 *brdd* *J* = 13.5; 11.5	2.18 *dd* *J* = 13.5; 2.5 2.62 *brdd* *J* = 13.5; 11.5	2.18 *dd* *J* = 13.5; 2.5 2.62 *brdd* *J* = 13.5; 11.5
H-6′	4.27 *dd* *J* = 11.5; 2.5	4.27 *dd* *J* = 11.5; 2.5	4.27 *dd* *J* = 11.5; 2.5	4.27 *dd* *J* = 11.5; 2.5	4.27 *dd* *J* = 11.5; 2.5	4.25 *dd* *J* = 11.5; 2.5	4.25 *dd* *J* = 11.5; 2.5	4.25 *dd* *J* = 11.5; 2.5
H-2″6″	7.38 *m*	7.38 *m*	7.38 *m*	7.38 *m*	7.38 *m*	7.37 *m*	7.38 *m*	7.38 *m*
H-3″5″	7.34 *m*	7.34 *m*	7.34 *m*	7.33 *m*	7.33 *m*	7.33 *m*	7.33 *m*	7.33 *m*
H-4″	7.27 *m*	7.27 *m*	7.26 *m*	7.26 *m*	7.26 *m*	7.26 *m*	7.26 *m*	7.26 *m*

* Signal not resolved.

† Further signals at δ 0.88 *t*, *J* = 7.5; 1.25, *brs*; 2.35 *t*, *J* = 7.5.

Table 2. ^{13}C NMR data of **1–4** and **6–8** (δ [ppm] in $CDCl_3$)

C	1	2	3	4*	6	7	8
1	40.0	39.9	40.0	40.0	40.1	40.1	40.1
2	117.7	117.7	117.8	117.7	118.0	118.0	118.0
3	140.0	140.0	140.0	140.0	139.6	139.6	139.6
4	38.3	38.3	38.3	38.3	38.3	38.3	38.3
5	43.7	43.8	43.7	43.7	43.6	43.7	43.7
6	24.1	24.2	24.2	24.2	23.8	23.8	24.0
7	72.2	72.2	72.2	72.2	73.8	73.8	73.9
8	36.4	36.4	36.4	36.3	38.4	38.5	38.5
9	45.7	45.8	45.5	45.4	42.3	42.1	42.2
10	36.2	36.3	36.2	36.2	36.6	36.6	36.6†
11	124.0	124.9	123.9	123.9	16.3	16.3	16.4
12	128.9	128.2	129.0	129.1	25.2	24.8	25.0
13	30.1	29.7	29.9	30.0	26.6	27.2	27.0
14	35.2	35.5	36.2	36.4	35.2	36.9	36.7†
15	24.9	24.9	24.8	24.8	25.9	25.8	25.8
16	22.7	22.9	26.2	26.2	24.9	27.6	27.5
17	40.9	40.1	44.2	44.2	48.0	49.0	49.3
18	17.4	17.5	17.4	17.4	19.6	19.6	19.6
19	18.1	18.2	18.1	18.1	16.7	16.6	16.7
20	42.1	48.7	42.1	42.1	41.8	45.4	45.7
21	178.2	174.9	175.5	175.2	175.6	176.8	175.7
22	31.3	74.2	43.4	43.3	43.4	35.1	34.4
23	75.1	78.9	211.6	210.2	211.7	109.4	110.4
24	121.9	119.4	49.0	49.3	49.1	51.6	50.1
25	141.7	144.2	72.3	70.8	72.3	79.0	77.6
26	67.1	67.1	69.7	70.0	69.7	78.7	81.9
27	14.1	14.4	24.3	24.6	24.3	23.8†	23.8
28	23.8	23.8	23.8	23.8	23.7	23.7†	23.8
30	15.0	14.9	15.7	15.6	14.8	14.2	14.3
2′	72.5	72.5	72.5	72.5	72.6	72.6	72.6
5′	40.7	40.7	40.7	40.7	40.7	40.7	40.7
6′	81.8	81.8	81.8	81.8	81.7	81.8	81.8
1″	142.5	142.6	142.6	142.6	142.6	142.7	142.7
2″, 6″	125.8	125.8	125.8	125.8	125.8	125.8	125.8
3″, 5″	128.3	128.4	128.3	128.3	128.3	128.3	128.3
4″	127.5	127.5	127.5	127.5	127.4	127.5	127.5
O-Me	—	—	52.0	51.9	51.9	52.0	51.5
						48.5	48.3

* Further signals see Experimental section.

† Signals within the same column may be interchanged.

was carried out on silica gel 60 (Fluka). Prep. HPLC was performed on Eurospher RP 18 (7 μm, Knauer) using MeOH–H_2O mixtures; detection: UV at 220 nm. Mps: uncorr. $[\alpha]_D$ in $CHCl_3$ at 21°C. UV in EtOH, IR in KBr. ^1H NMR were run at 360 MHz and ^{13}C NMR at 90 MHz in $CDCl_3$ with TMS as int. standard. EI-MS were obtained at 70 eV; DCI-MS with isobutane; FAB-MS with xenon (8 kV) from glycerol; except for key ions, only ions with rel. int. >20% and $m/z > 100$ are given.

Plant material. Roots of *D. madagascariense* Poir. (syn. *D. guineense* (DC) Keay) were collected from the Teaching Garden of the Botany Department, University of Ghana, Legon, in October 1992 and August 1993 and identified by Mr D. K. Abbiw, Botany Department, University of Ghana. A voucher specimen is held at the Ghana National Herbarium, Botany Department, University of Ghana, under No. 47511.

Extraction and isolation. The dried, pulverized roots (3.3 kg) were extracted 3× at 28° by percolation with 7.5 l Me_2CO. Evapn of the solvent afforded 51 g extract. Chromatographic sepn of 45 g of this extract on silica gel with petrol–Me_2CO mixtures (increasing amounts of Me_2CO from 0 to 50%) yielded 6 frs, 1 to 6.

Further purification of fr. 3 by CC (petrol–Me_2CO, 4:1) and subsequent crystallization from MeOH gave **4**, and crystallization of fr. 4 afforded **1**. Fr. 6 (80 mg) was subjected to prep. HPLC (MeOH–H_2O, 17:3) to yield **2**, **3**, **5** and **6** together with a mixture of **7** and **8**, which was further sepd by prep. HPLC with MeOH–H_2O (9:1) to give pure **7** and **8**.

Dichapetalin A (**1**) (4α,6′α,7α,17α,20*S*,23*R*,24*E*)-2′,3′,5′,6′-tetrahydro-7,23,26-trihydroxy-6′-phenyl-13,30-cyclo-29-nor dammara-2,11,24-trieno[4,3-c]pyran-21-oic acid γ-lactone). Crystals (1.26 g). Mp 211–214° (from petrol). TLC: R_f 0.22; anisaldehyde: blue. $[\alpha]_D$ +35° (*c* 1.5). CD λ_{max} nm ($\Delta\varepsilon$): 217

(+9.88), 235 (−0.60), 258 (+0.07). IR ν_{max}^{KBr} cm^{-1}: 3436, 2937, 2873, 1767, 1177. UV λ_{max}^{EtOH} nm (log ε): 218 (sh, 4.74), 251 (3.80), 257 (3.75), 263 (3.70). ^1H NMR: see Table 1. ^{13}C NMR: see Table 2. EI-MS *m/z* (rel. int.): 584 $[M]^+$ (0.5), 566.3418 $[M-H_2O]^+$ (2) (calcd for $C_{38}H_{46}O_4$: 566.3396), 299 (24), 283 (27), 281 (26), 235 (26), 223 (25), 209 (35), 207 (25), 197 (41), 195 (35), 193 (21), 183 (45), 181 (34), 171 (40), 169 (38), 167 (24), 159 (25), 157 (53), 155 (42), 145 (44), 143 (70), 142 (25), 141 (26), 133 (23), 131 (42), 129 (42), 128 (25), 121 (24), 119 (36), 117 (34), 107 (30), 105 (81), 91 (100); DCI-MS *m/z* (rel. int.): 585 $[M+H]^+$ (100), 567 (39).

Dichapetalin B (**2**). Amorphous powder (5 mg). TLC: R_f 0.10; anisaldehyde: blue. $[\alpha]_D$ +73° (*c* 0.17). CD λ_{max} nm ($\Delta\varepsilon$): 218 (+6.10), 235 (−0.75). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3447, 3012, 2954, 1729. UV λ_{max}^{EtOH} (log ε): 216 (sh, 4.72), 251 (3.78), 257 (3.74), 263 (3.70). ^1H NMR: see Table 1. ^{13}C NMR: see Table 2. DCI-MS *m/z* (rel. int.): 601 $[M+H]^+$ (31), 583 (53), 487 (100).

Dichapetalin C (**3**). Crystals (22 mg). Mp 219–222° (from EtOH). TLC: R_f 0.15; anisaldehyde: violet. $[\alpha]_D$ +40° (*c* 0.26). CD λ_{max} nm ($\Delta\varepsilon$): 197 (+11.11), 218 (+10.79), 234 (−1.11), 268 (+1.03). IR ν_{max}^{KBr} cm^{-1}: 3377, 2943, 1732, 1712, 1170. UV λ_{max}^{EtOH} nm (log ε): 217 (sh, 4.25), 250 (2.50), 258 (2.55), 263 (2.51). ^1H NMR: see Table 1. ^{13}C NMR: see Table 2. DCI-MS *m/z* (rel. int.): 615 $[M+H-H_2O]^+$ (20), 597 (100), 579 (65), 559 (53), 541 (36).

Dichapetalin D (**4**). Crystals (100 mg). Mp 82–85° (from MeOH). TLC (petrol–Me_2CO, 4:1): R_f 0.26; anisaldehyde: brown-orange. $[\alpha]_D$ +28° (*c* 1.45). CD λ_{max} nm ($\Delta\varepsilon$): 1997 (+12.39), 217 (+14.30), 235 (−1.00), 258 (+0.27). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3475, 2928, 1730. UV λ_{max}^{petrol} nm (log ε): 214 (sh, 4.16), 251 (2.60), 257 (2.65), 263 (2.60). ^1H NMR: see Table 1. ^{13}C NMR: see Table 2, signals of the stearoyl moiety: 173.6 (C-1), 34.2 (C-2), 31.9 (C-16), 29.7–29.1 (C-4 − C-15), 25.2 (C-3), 22.7 (C-17), 14.1 (C-18). FAB-MS *m/z* (rel. int.): 899 $[M+H]^+$ (5), 633 (100), 427 (42).

Dichapetalin E (**5**). Amorphous powder (1.2 mg). TLC: R_f 0.71; anisaldehyde: orange. $[\alpha]_D$ +46° (*c* 0.05). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3377, 2929, 1729. UV λ_{max}^{EtOH} nm (log ε): 216 (sh, 4.25), 250 (3.29), 257 (3.25), 263 (3.21). ^1H NMR: see Table 1. DCI-MS *m/z* (rel. int.): 597 $[M+H]^+$ (100), 579 (38).

Dichapetalin F (**6**). Crystals (25 mg). Mp 210° (from EtOH). TLC: R_f 0.15; anisaldehyde: violet. $[\alpha]_D$ +38° (*c* 0.34). CD λ_{max} nm ($\Delta\varepsilon$): 201 (+27.43), 217 (+23.05), 258 (+0.58). IR ν_{max}^{KBr} cm^{-1}: 3563, 3369, 2944, 1734, 1711. UV λ_{max}^{EtOH} nm (log ε): 217 (sh, 4.05), 251 (2.50), 257 (2.58), 263 (2.50). ^1H NMR: see Table 1. ^{13}C NMR: see Table 2. DCI-MS *m/z* (rel. int.): 617 $[M+H-H_2O]^+$ (22), 599 (76), 581 (20), 561 (100), 543 (35), 529 (32), 505 (23).

Dichapetalin G (**7**). Amorphous powder (2.5 mg). TLC: R_f 0.42; anisaldehyde: orange. $[\alpha]_D$ +22° (*c* 0.07). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2929, 1730, 1677. UV λ_{max}^{EtOH} nm (log ε): 216 (sh, 4.38), 251 (3.44), 257 (3.39), 263 (3.25). ^1H NMR: see Table 1. ^{13}C NMR: see Table 2. DCI-MS *m/z* (rel. int.): 649 $[M+H]^+$ (3), 617 (38), 599 (100), 581 (27), 561 (22).

Dichapetalin H (**8**). Amorphous powder (2 mg). TLC: R_f 0.51; anisaldehyde: orange. $[\alpha]_D$ +44° (*c* 0.19). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2949, 1729, 1677. UV λ_{max}^{EtOH} nm (log ε): 218 (sh, 4.35), 251 (3.40), 257 (3.35), 263 (3.21). ^1H NMR: see Table 1. ^{13}C NMR: see Table 2. DCI-MS *m/z* (rel. int.): 649 $[M+H]^+$ (14), 617 (75), 599 (100), 581 (21).

Methanolysis of **4**. Compound **4** (5 mg) suspended in 2 ml Et_2O was treated with 1 ml of a 10% soln of NaOMe in MeOH at room temp. for 16 hr. After evapn of the solvent the residue was dissolved in *n*-pentane and the soln was subjected to GC-MS (DB 5, 25 m × 0.24 mm, 0.25 μm). Stearic acid methyl ester was identified by coinjection and EI-MS data; *m/z* (rel. int.): 298 $[M]^+$ (22), 87 (80), 74 (100), 43 (65).

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