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FURTHER ISOCEDRENE DERIVATIVES AND OTHER CONSTITUENTS FROM *PEREZIA* SPECIES

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Key Word Index—*Perezia multiflora*; *P. runcinata*; Compositae; sesquiterpenes; isocedrene derivatives; germacranes; eudesmanes; unusual monoterpene derivative.

Abstract—The investigation of the aerial parts of two *Perezia* species afforded in addition to known isocedrene derivatives 10 new ones, 10 sesquiterpene esters and a pair of epimeric diesters. The structures were elucidated by high field NMR spectroscopy.

INTRODUCTION

The South American genus *Perezia* (tribe Mutisieae, subtribe Nassauviinae) with about 30 species and the North American genus *Acourtia* (previously a section of *Perezia*) with *ca* 40 species have already been studied in some detail chemically. Most common are perezone derivatives [1–4] but also 5-methyl coumarins [3, 6–9] and some less common sesquiterpenes have been reported [2, 3]. Both *P. multiflora* (H. et B.) Less [6, 8] and the roots of *P. runcinata* Lag. ex D. Don. [5] have been studied previously. We have now reinvestigated both species.

RESULTS AND DISCUSSION

The extract of the aerial parts of *P. multiflora* afforded in addition to the known isocedrenes **2e–g** [9, 10] seven new ones (**1a**, **1e**, **2a–d** and **3**). Furthermore, a complex mixture of sesquiterpene esters was present which finally gave the germacradiene derivatives **4a–c** as well as the eudesmane derivatives **5a–c** and **6a–d**.

The extract of the aerial parts of *P. runcinata* afforded in addition to the perezones reported previously [5], the isocedrenes, **1a–d** and **2a** as well as the epimeric diesters **8a/b**.

The ^{1}H NMR spectrum of **1a** (Table 1) was in part close to that of the corresponding methyl senecioate [10]. The characteristic signals of the angelate residue indicated the nature of the ester group and the observed couplings showed that the configuration was the same as in the methyl senecioate [10].

The ^{1}H NMR spectrum of **1b** (Table 1) differed from that of **1a** by the presence of a further low field signal (δ5.22 *dt*) and a second set of angelate signals. Spin decoupling allowed the assignment of all signals. The chemical shift of H-8 required an oxygen function at C-8. Accordingly, a 3,8-diangeloyloxy derivative was present. The configuration followed from the observed couplings which nicely agreed with those of the corresponding 8α-acetoxy derivative [10]. The spectrum of **1c** (Table 1) clearly showed that this compound only differed from **1b** by the replacement of one angelate by a tiglate group. However, the relative position of the unsaturated esters could not be determined from the observed chemical shifts which were almost identical with those in the spectrum of **1b**. This excluded the possibility that one of the unsaturated ester groups was at C-14. The relative position of these groups could be determined by NOE difference spectroscopy. Clear effects were obtained between H-13, H-12 (10%), H-9 (10%) and H-2 (8%), between H-12, H-10 (15%), H-4 (6%), H-13 (10%), the tiglate methyl (10%) and the tiglate proton at C-3′ (10%). These effects required a tiglate group at C-3. Further NOEs were present between methoxy, H-15 (10%) and H-14 (4%), between H-8, H-14 (6%) and H-10 (3%), between H-4, H-3 (5%) and H-15 (20%), between H-14 and H-8 (5%) as well as between H-3, H-4 (6%) and H-2 (6%). These effects again also established the configuration at all chiral centres.

The ^{1}H NMR spectrum of **1d** (Table 1) differed from that of **1c** by the absence of the angelate signals and by the upfield shift of H-8. Accordingly, the corresponding 8-desacyl derivative was present. The spectrum of **1e** (Table 1) showed some similarities with that of **1a**. However, the acetate methyl signal was missing and the corresponding H-14 signal at δ5.90 was replaced by a broadened triplet at δ4.95. Spin decoupling showed that the corresponding proton was coupled with a hydroxy proton (δ2.50 *br d*). The remaining coupling ($J = 8$ Hz) indicated the 14β-orientation of the hydroxy group. The nature of the function at C-8 changes the conformation as follows from the coupling $J_{7,14}$.

The ^{1}H NMR spectrum of **2a** (Table 1) differed from that of **1c** mainly by the couplings of H-14 and by the chemical shift of some signals. These differences are typical for isocedrenes with the opposite configurations at C-14 and C-15 as in **2f** [9, 10]. The spectrum of **2a** therefore also was close to that of **2f**. Again the H-15 signal was shifted upfield due to the replacement of the acetoxy by a methoxy group. Similar the ^{1}H NMR of **2b** (Table 1) indicated that it was an isomer of **1a** with the opposite configuration at C-14 and C-15.

The ^{1}H NMR spectra of **2c** and **2d** (Table 1) only differed by the signals of one ester group. While the typical signals of an isobutyrate were duplicated in the case of **2c**

Table 1. ^{1}H NMR data of compounds **1a–1e**, **2a–2d** and **3** (400 MHz, $CDCl_3$, δ-values)

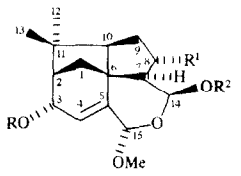
H	1a	1b	1c	1d	1e†	2a	2b	2c	2d	3	Multiplicity
2	2.21 *t*	2.28	2.25	2.25	2.21 *t*	2.30	2.29 *t*	2.20	2.27 *t*	2.25 *t*	*m*
3	5.79	5.84	5.83	5.84	5.83	5.89	5.88 *dt*	5.79 *dt*	5.83 *dt*	5.13	*dd*
4	5.38	5.45	5.43	5.39 *br s*	5.43	5.50 *dt*	5.49 *dt*	5.30 *dt*	5.35 *dt*	6.01 *dd*	*br t*
7	2.41	2.28 *m*	2.25 *m*	2.25 *m*	*	2.30 *m*	*	*	*	2.04 *m*	*br t*
8	1.95 *m*	5.22	5.23	4.31	*	5.10	*	4.99	4.98	*	*dt*
10	2.49	2.54	2.55	2.41 *dd*	2.42	2.17 *m*	*	*	*	*	*br t*
12	1.19	1.29	1.31	1.30	1.27	1.30	1.27	1.28	1.28	1.32	*s*
13	0.91	1.04	1.04	1.04	1.02	1.04	1.03	1.05	1.04	1.04	*s*
14	5.90	6.05	6.05	6.12	4.95 *t*	6.03	5.84	5.99	6.00	5.93	*d*
15	4.94	5.02	5.02	5.00	5.05	5.23 *t*	5.22 *t*	6.69 *t*	6.69 *t*	5.88 *d*	*s*
OAc	2.10	2.10	2.10	2.09		2.04	2.04	2.08	2.08	2.10	*s*
								2.07	2.05	2.07	*s*
OMe	3.45	3.46	3.46	3.43	3.41	3.42	3.42				
OCOR	6.06	6.07	6.07	6.87	6.06	6.86	6.05	2.54	2.51	6.08	*qq*
			6.87			6.08		2.51	5.66		*qq*
	1.99	2.01	1.99	1.80	2.01	1.81	2.00	1.19 *d*	1.16 *d*	1.99	*dq*
	1.86	1.99	1.80	1.84	1.90	1.98	1.89	1.16 *d*	2.18 *d*	1.87	*dq*
		1.90	1.90			1.85			1.91 *d*		*dq*
		1.89	1.85			1.88					*dq*

*Overlapped multiplet.

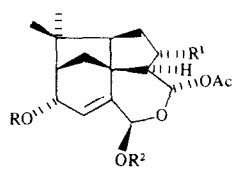
†OH: 2.50 *br d*.

J[Hz]: Compounds **1a–1e**: 1,2 = 2,3 ~ 5; 2,4 = 1.5; 3,4 = 2; 7,14 = 8.5; 9,10 = 9; [Compounds **1b**/**1d**: 7,14 = 6; 7,8 = 8,9 = 8,9′ ~ 6.5; (compound **1d**: 7,14 = 4); compound **1e**: 7,14 = 14, OH ~ 7]; compounds **2a–2d**: 1,2 = 2,3 = 4.5; 3,4 = 3,15 = 4,15 = 7,14 = 2; (compounds **2c** and **2d**: 7,8 = 8,9 = 9; 8,9′ = 5); compound **3**: 1,2 = 4; 2,3 = 3.5; 3,4 = 9; 4,15 = 2; 7,14 = 3; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5; O*i*Bu: 2,3 = 2,4 = ; OSen: 2,4 = 2,5 = 1.

in the spectrum of **2d** one isobutyryloxy was replaced by a senecioyloxy group. The position of the ester groups followed from the results of spin decoupling. The relative position of the ester groups in the isocedrene derivative **2d** was deduced from the shift differences of H-3. As in similar cases, the unsaturated ester group causes a small downfield shift.



	1a	1b	1c	1d	1e
R	Ang	Ang	Tigl	Tigl	Ang
R^1	H	OAng	OAng	OH	H
R^2	Ac	Ac	Ac	Ac	H



	2a	2b	2c	2d	2e	2f	2g
R	Tigl	Ang	*i*Bu	Sen	Ang	Ang	Ang
R^1	OAng	H	O*i*Bu	O*i*Bu	H	OAng	OH
R^2	Me	Me	Ac	Ac	Ac	Ac	Ac

The ^{1}H NMR spectrum of **3** (Table 1) differed markedly from those of **2a–g**. The molecular formula indicated that an isomer of **2e** was present. While several signals were similar in the spectra of both isomers several were typically different. In particular the lowfield signals indicated a changed substitution pattern. Spin decoupling showed that the pair of double doublets at δ5.13 and 6.01 were due to the protons at C-3 and C-4. The vicinal coupling of 9 Hz required a *trans*-orientation of the oxygen functions at these carbons while the coupling of H-14 indicated an α-orientation of the acetoxy group. The presence of an enolether was deduced from the chemical shift of H-15 (δ5.88). Thus compound **3** was an isomer formally formed by allylic rearrangement of **2e**.

The structures of **4a–c** followed from the molecular formulae and the ^{1}H NMR spectra (Table 2) which showed the typical highly broadened signals of a germacra-4,1(10)-diene. Even at elevated temperature no clear signals could be observed. At −30° the presence of different conformers could be detected. Cope rearrangement of **4a** afforded the elemane derivative **7** where the ^{1}H NMR signals (Table 2) were clear and could be assigned by spin decoupling. The corresponding alcohol has been reported previously [11]. The ^{1}H NMR data are very similar. The esters **4b** and **4c** could not be separated, but the nature of the esters clearly followed from the ^{1}H NMR signals.

The ^{1}H NMR spectra of **5a–c** (Table 2) showed that the corresponding eudesma-4(15),11(13)-dienes were present. Accordingly, the spectra were close to that of costol. Again the mixture of the isovalerate and the methyl butyrate could not be separated.

The spectra of **6a–d** (Table 2) clearly indicated that the

Table 2. ^{1}H NMR spectral data of compounds **4a–4c**, **5a–5c**, **6a–6d** and **7** (400 MHz, $CDCl_3$, δ-values)

H	4a	4b 4c	5a	5b 5c	6a	6b	6c 6d	7*
1	4.78 *br d*	4.79 *br d*						5.82 *dd*
3	2.25 *m*	2.15 *m*	2.31 *br d* 2.01 *m*	2.31 *br d* 2.11 *m*	5.32 *br s*	5.32 *br s*	5.33 *br s*	4.83 *br s* 4.59 *br s*
5	4.50 *br d*	4.50 *br d*	1.83 *br d*	1.82 *br d*	1.82 *br d*	1.83 *br d*	1.82 *br d*	2.00 *m*
12	4.67 *br s*	4.60 *br s*	4.66 *br s*	4.61 *br s*	4.69 *br s*	4.61 *br s*	4.61 *br s*	4.67 *br s*
13	4.97 *br s*	4.94 *br s*	5.08 *br s*	5.05 *br s*	5.08 *br s*	5.05 *br s*	5.05 *br s*	5.08 *br s*
13′	4.94 *br s*	4.93 *br s*	5.02 *br s*	5.01 *br s*	5.02 *br s*	5.00 *br s*	5.01 *br s*	5.02 *br s*
14	1.41 *br s* 1.49 *br s*	1.40 *br s* 1.49 *br s*	0.75 *s*	0.75 *s*	0.83 *s*	0.82 *s*	0.82 *s*	1.02 *s*
15	1.54 *br s* 1.56 *br s*	1.54 *br s* 1.56 *br s*	4.72 *q* 4.44 *q*	4.72 *q* 4.44 *q*	1.61 *br s*	1.61 *br s*	1.61 *br s*	1.71 *br s*
OCOR	6.10 *br q* 2.02 *br d* 1.94 *br s*	2.23 *m* 2.42 *m* 2.14 *m* 0.94 *t* 0.99 *d* 1.19 *d*	6.09 *qq* 2.01 *dq* 1.92 *dq*	2.24 *d* 2.40 *tq* 2.11 *m* 0.93 *t* 0.98 *d* 1.15 d	6.09 *qq* 2.01 *dq* 1.93 *dq*	2.60 *qq* 1.21 *d*	2.24 *d* 2.42 *tq* 2.05 *m* 0.93 *t* 0.98 *d* 1.18 *d*	6.09 *qq* 2.00 *dq* 1.92 *dq*

*H-2 4.92 and 4.91 *d*.

J[Hz]: Compounds **4a–c**: 1,2 = 11;, 5,6 = 10; compounds **5a–c**: 3,3′ = 5,6 = 13; 3,15 = 5,15 = 1.5; compounds **6a–d**: 5,6 = 13; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5; OiVal: 2,3 = 3,4 = 3,5 = 7; OMeBu: 2,3 = 2,5 = 3,4 = 7.

isomeric Δ^3eudesmanes were present. While **6a** and **6b** could be obtained pure again **6c** and **6d** were obtained as a mixture which could not be separated.

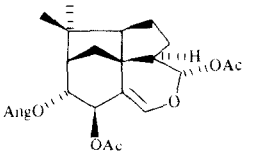
The spectral data of the last epimeric mixture (**8a/b**) indicated the presence of an unusual type. The molecular formula was $C_{16}H_{28}O_6$. As, however, the fragmentation pattern indicated the presence of two methoxy groups a norsesquiterpene structure had to be proposed. The ^{1}H NMR spectrum (Table 3) showed sets of doubled signals: four methoxy singlets, four olefinic methyl singlets, two methyl singlets at δ 1.65 and 1.64 as well as two methyl doublets. Also several other signals seemed to be doubled. Similar in the ^{13}C NMR spectrum (Table 3) nearly two sets of 16 carbons were visible. Spin decoupling in the ^{1}H NMR spectrum allowed the assignment of all signals. The resulting sequence clearly indicated the presence of a side chain derived from citronellol where the first carbon was missing. The remaining signals together with those from the ^{13}C NMR spectrum required the presence of a methyl succinate substituted with two hydroxy-, a methyl group and a norcitronellol residue. The relative configuration followed from the absence of a NOE between H-13 and H-2 as well as from a long range coupling of H-2 in both epimers with a hydroxy group. As followed from the IR spectrum all hydroxy groups were hydrogen bonded. Inspection of a model showed that this leads to a nice chair–chair-conformation. As the chemical shifts of H-10 and H-2 showed the largest differences most likely the epimers differed at C-11 and C-12. This would explain the observed shift differences as H-10 would be close to the carbonyl group in one epimer and close to hydroxy in the other. Most likely the epimers are derived from 2,3-dihydrogeranic acid by condensation with a hydroxy ketone derived from mesaconic acid followed by decarboxylation.

This investigation again shows that isocedrenes are typical for the subtribe Nassauviinae. Sesquiterpene esters of typs **4a–c**, **5a–c** and **6a–d** so far have not been reported. Perhaps they are more widespread, as they are easily overlooked when present in low concentration. As pointed out previously [7] there are indications that the North American *Perezias* (Sect. Acourtia [12], now separated as genus *Acourtia* [13]) contain perezone derivatives while the South American species [14] mostly afforded 5-methyl coumarins.

EXPERIMENTAL

The air-dried plant material was extracted with MeOH–Et_2O–petrol (1:1:1), and the extracts obtained were worked-up as reported previously [15]. The extract from 760 g of aerial parts of *P. multiflora* (voucher Solomon 16318, collected in Bolivia in February 1987, deposited in the National Herbarium of Bolivia) was separated first by CC (silica-gel) into three fractions (1: Et_2O–petrol, 3:1 and 1:1,2: Et_2O–petrol, 3:1 and 3: Et_2O). Fraction 1 was separated by TLC (silica gel), Et_2O–petrol, 1:3) affording two bands (1/1 and 1/2). Fraction 1/1 was further separated by TLC (silica gel, $AgNO_3$ coated, Et_2O–petrol, 1:9) which gave four bands (1/1/1–1/1/4). HPLC (MeOH–H_2O, 9:1, always RP 18, *ca* 100 bar) of 1/1/1 gave 2 mg **6a** (R_t 15.6 min.). HPLC of 1/1/2 (same solvent) afforded 0.5 mg **6b** (R_t 12.0 min.) and 2 mg **6c/d** (*ca* 3:1) (R_t 14.3 min.). HPLC of 1/1/3 (same solvent) gave 2 mg **5b/c** (*ca* 2:1) (R_t 13.3 min.) and 2 mg **5a** (R_t 14.5 min.). HPLC of 1/1/4 (same solvent) afforded 4 mg **4b/c** (*ca* 1:1) R_t 11.4 min.) and 4 mg **4a** (R_f 12.0 min.). TLC of fraction 1/2 (Et_2O–petrol, 1:3) gave 140 mg **1a** (R_t 0.45) and 30 mg **2b** (R_f 0.35). CC fraction 2 gave by TLC (Et_2O–petrol, 1:1) 30 mg of a mixture of **1a** and **2b** (*ca* 1:1) and a complex mixture which was separated by HPLC (MeOH–H_2O, 17:3) affording a mixture (3/1, R_t 2.3 min.), 500 mg **2e** (R_t 3.2 min.), a further mixture (3/3, R_t 3.5 min.) and 500 mg **2f** (R_t 4.2 min.). TLC of 3/1 (Et_2O–petrol, 1:1) gave 1 mg **3** (R_f 0.65), 3 mg **2c** (R_f 0.50) and 1 mg **1e** (R_f 0.25). Repeated HPLC of 3/3 (MeOH–H_2O, 4:1) gave 5 mg **1a** and a mixture which afforded by TLC (Et_2O–petrol, 1:1) 1 mg **2d** (R_f 0.42). TLC of CC fraction 3 gave by TLC (Et_2O–petrol, 3:1) 1.9 g **2g** (R_f 0.30).

The extract of the aerial parts of *P. runcinata* (300 g, collected near Apodaca, N. L. in July 1986, voucher 8120, deposited in the Herbarium of the Instituto Tecnologico y de Estudios Superiores de Monterrey, Mexico) was separated by CC. The two



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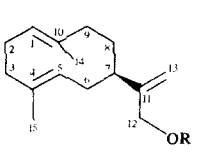
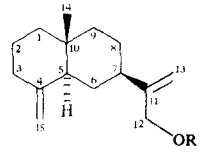
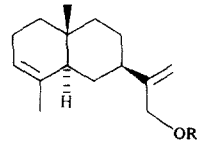


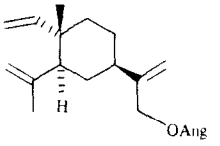
4a R = Ang
4b R = *i*Val
4c R = MeBu



5a R = Ang
5b R = *i*Val
5c R = MeBu



6a R = Ang
6b R = *i*Bu
6c R = *i*Val
6d R = MeBu



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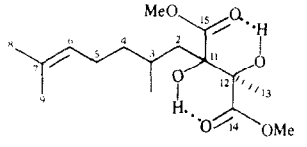

8a
8b (11,12-*epi*)

Table 3. ^{1}H and ^{13}C NMR spectral data of **8a**/**b** (400 MHz, C_6D_6, δ-values)

H	**8a**	**8b**	^{13}C	**8a**/**b***	
2	1.94 *br dd*	2.05 *m*	C-2	38.9 *t*	39.2 *t*
2′	2.38 *dd*	2.21 *br dd*	C-3	28.1 *d*	29.3 *d*
3	1.86 *m*	1.63 *m*	C-4	38.1 *t*	38.4 *t*
4	1.38 *m*	1.38 *m*	C-5	25.4 *t*	25.3 t
4′		1.27 *m*	C-6	125.5 *d*	124.7 *d*
5	2.13 *m*	2.05 *m*	C-7	131.3 *s*	131.2 *s*
5′	2.05 *m*		C-8	25.7 *q*	
6	5.28 *br t*	5.21 *br t*	C-9	17.6 *q*	
8	1.73 *br s*	1.71 *br s*	C-10	20.3 *q*	19.8 *q*
9	1.62 *br s*	1.59 *br s*	C-11	80.0 *s*	79.0 *s*
10	0.91 *d*	1.18 *d*	C-12	82.4 *s*	81.4 *s*
13	1.65 *s*	1.64 *s*	C-13	21.4 *q*	20.3 *q*
OH	4.04 *s*	4.02 *s*	C-14	175.4 *s*	175.3 *s*
	3.91 *d*	3.88 *d*	C-15	175.0 *s*	175.0 *s*
OMe	3.40 *s*	3.34 *s*	OMe	52.9 *q*	53.0 *q*
	3.39 *s*	3.33 *s*			

*Some of the quartets may be interchangeable.
J[Hz]: 2,2′ = 14; 2,3 = 4; 2′,3 = 7; 2′$_1$, OH = 2′$_1$, OH = 1; 3,10 = 5,6 = 7.

Table 4. Spectral data of compounds **1a–1e, 2a–2d, 3, 4a–4c, 5a–5c, 6a–6d, 7 and 8a/b**

OH		CO_2R	M⁺ MS *m/z* (rel. int.)
1a	—	1755, 1710	372.194 (1.5) ($C_{22}H_{28}O_5$)*, 344 (25), 290 (6), 262 (22), 83 (100)
1b	—	1755, 1710	442.236 (34) ($C_{26}H_{34}O_6$)†, 360 (26), 261 (17), 228 (51), 83 (100)
1c	—	1755, 1715	442.236 (12) $C_{26}H_{34}O_6$)†, 360 (10), 260 (16), 228 (6), 83 (100)
1d	3600	1755, 1705	360.194 (3) ($C_{21}H_{28}O_5$)†, 278 (10), 260 (3), 83 (100)
1e	3600	1715	330.183 (2.5) ($C_{20}H_{26}O_4$)*, 248 (28), 230 (2), 83 (100)
2a	—	1755, 1705	442.236 (11) ($C_{26}H_{34}O_6$)†, 360 (11), 260 (8), 228 (6), 83 (100)
2b	—	1755, 1715	344.199 (22) ($C_{21}H_{28}O_4$)†, 262 (23), 231 (9), 83 (100)
2c	—	1755, 1730	418.199 (7) ($C_{23}H_{30}O_7$)‡, 376 (100), 334 (48), 290 (63), 248 (19)
2d	—	1760, 1735, 1715	458.230 (3) ($C_{26}H_{34}O_7$)†, 418 (2.5), 376 (4), 262 (5), 83 (100)
3	—	1750, 1715	373.202 (6) ($C_{22}H_{29}O_5$)§, 332 (8), 290 (12), 230 (10), 83 (100)
4a	—	1715	302.225 (2) ($C_{20}H_{30}O_2$), 202 (41), 187 (53), 83 (100)
4b/c	—	1735	304.240 (2) ($C_{20}H_{32}O_2$), 202 (29), 187 (50), 145 (53), 57 (100)
5a	—	1715	302.225 (3) ($C_{20}H_{30}O_2$), 203 (27), 202 (24), 187 (29), 83 (100)
5b/c	—	1730	304.240 (8) ($C_{20}H_{32}O_2$), 202 (87), 187 (100), 85 (37)
6a	—	1715	302.225 (10) ($C_{20}H_{30}O_2$), 202 (88), 187 (100), 83 (86)
6b	—	1730	290.225 (5) ($C_{19}H_{30}O_2$), 202 (66), 187 (100), 71 (44)
6c/d	—	1730	304.240 (3.5) ($C_{20}H_{32}O_2$), 202 (67), 187 (100), 85 (23)
7		1715	302.225 (0.5) ($C_{20}H_{30}O_2$), 202 (22), 187 (30), 83 (100)
8a/b	3500	1735	316.189 (0.5) ($C_{16}H_{28}O_6$), 298 (2), 266 (6), 239 (4), 207 (2), 179 (7), 104 (100)

*M – MeOH.
†M – AcOH.
‡M – RCO_2H.
§M – OAc.

polar fractions (1:Et_2O–petrol, 1:1 and 2: Et_2O and Et_2O–MeOH, 9:1) were separated by TLC. Fraction 1 (Et_2O–petrol, 1:1) gave two bands (1/1 and 1/2) and fraction 2 (Et_2O–petrol, 3:1) also two bands (2/1 and 2/2). HPLC of 1/1 (MeOH–H_2O, 9:1, always RP 8, *ca* 100 bar) gave 6 mg **1a** (R_t 2.5 min). HPLC of 1/2 (same solvent) gave a mixture which was separated by TLC (Et_2O–petrol, 1:3, two developments) affording 5 mg **1b** (R_f 0.45), 5 mg **1c** (R_f 0.38) and 3 mg **2a** (R_f 0.28). HPLC of 2/1 (MeOH–H_2O, 4:1) gave 3 mg **8a/b** (R_t 3.2 min). and HPLC of 2/2 (same solvent) afforded 5 mg **1d** (R_t 3.2 min). Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material. The IR and MS data are summarized in Table 4.

Cope reaction of **4a**. 4 mg **4a** were heated in a sealed tube (evacuated) for 1 hr at 180°. The ^{1}H NMR spectrum indicated complete transformation to **7**, colourless oil, ^{1}H NMR: Table 2.

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