Absolute Configuration of Two New 6-Alkylated α-Pyrones (=2*H*-Pyran-2-ones) from *Ravensara crassifolia*

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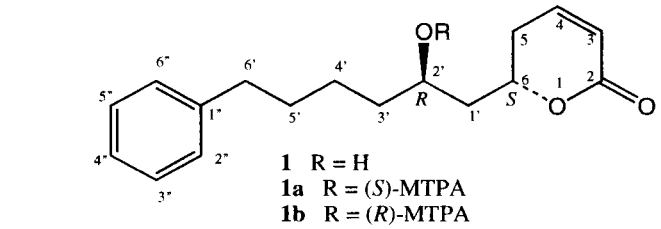
The stem bark CH_2Cl_2 extract of *Ravensara crassifolia* showed antifungal activity against the phytopathogenic fungus *Cladosporium cucumerinum* in a bioautographic TLC assay. Activity-guided fractionation afforded two new α-pyrones : (6*S*)-5,6-dihydro-6-[(2*R*)-2-hydroxy-6-phenylhexyl]-2*H*-pyran-2-one (**1**) and (6*R*)-6-[(4*R*,6*R*)-4,6-dihydroxy-10-phenyldec-1-enyl]-5,6-dihydro-2*H*-pyran-2-one (**2**). Their structures and absolute configurations were established by NMR spectroscopy, chemical methods, and CD spectroscopy. The antifungal activity against *C. cucumerinum* was determined for both compounds.

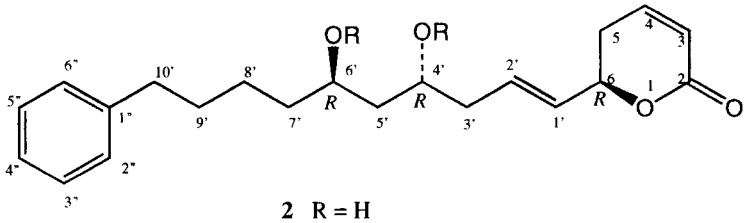
Introduction. – As part of our search for new antifungal lead compounds from plants, we investigated *Ravensara crassifolia* DANGUY (Lauraceae) (syn. *Cryptocarya crassifolia* BAKER), a tree up to 18–20 m growing in the eastern region of Madagascar. The genus *Ravensara* is considered as endemic to Madagascar [1]. In a series of preliminary screenings, the stem bark CH_2Cl_2 extract of *R. crassifolia* displayed antifungal activity against the phytopathogenic fungus *Cladosporium cucumerinum* in a bioautographic TLC assay [2]. Although no ethnomedical use is reported for *R. crassifolia,* other *Ravensara* species are used in traditional medicine, and some of their essential oils have shown antimicrobial activity [3][4]. Activity-guided fractionation of the CH_2Cl_2 extract yielded two new 6-alkylated α-pyrones. These results support the fact that plants from the Lauraceae family represent an excellent source of this chemical class [5].

Results and Discussion. – Crude extracts of *R. crassifolia* were obtained by successive extraction at room temperature by CH_2Cl_2 and MeOH. Both extracts were submitted to the bioautographic TLC assays against *Cladosporium cucumerinum*. The CH_2Cl_2 extract exhibited antifungal activity, while the MeOH extract was inactive. The active extract was fractionated by a combination of silica-gel open-column chromatography, gel filtration on *Sephadex LH-20*, and MPLC on reversed phase to afford compounds **1** and **2**.

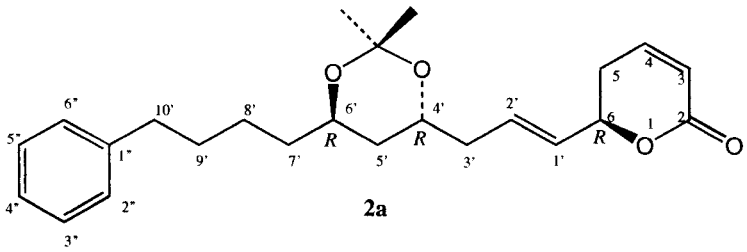
The EI-MS of compound **1** displayed a molecular ion at *m/z* 275 ($[M+H]^+$), which, together with ^{13}C-NMR data suggested a molecular formula $C_{17}H_{22}O_3$. This was confirmed by the peak at *m/z* 292 ($[M+NH_4]^+$) recorded in the D/CI-MS. The IR spectrum showed absorption bands at 1691, 2924, and 3840 cm^{-1}, revealing the presence



1 R = H
1a R = (*S*)-MTPA
1b R = (*R*)-MTPA



2 R = H
2b R = (*S*)-MTPA
2c R = (*R*)-MTPA



2a

of an α,β-unsaturated lactone ring, a monosubstituted phenyl ring and an OH group, respectively [6][7]. Full assignment of the ^{1}H- and ^{13}C-NMR chemical shifts (*Tables 1* and *2*) was achieved on the basis of 2D-NMR experiments including COSY, HSQC, and HMBC. The absolute configuration of the secondary alcohol was established by preparation of the *Mosher* esters **1a** and **1b** [8]. The ^{1}H-NMR spectra of the two esters revealed a slight difference of the δ(H) due to the diamagnetic effect of the benzene ring of the MTPA moiety (MTPA = α-methoxy-α-(trifluoromethyl)phenylacetyl). Calculation of the $\Delta\delta_{(H)} = \delta_S - \delta_R$ by *Mosher*'s method [9] allowed assignment of the (*R*)-configuration to C(2′) of compound **1** (*Fig.*).

The ^{1}H-NMR spectrum of **1** showed signals at δ 7.15 (*m*, 3 H) and 7.25 (*m*, 2 H) attributed to the aromatic protons H–C(3″), H–C(4″), and H–C(5″), and H–C(2″) and H–C(6″), respectively, of the monosubstituted benzene ring; this was confirmed by the presence of two pairs of superimposed aromatic C-atoms, *i.e.* C(3″) and C(5″) at δ 128.2 and C(2″) and C(6″) at δ 128.1, and by the signal at *m/z* 91 corresponding to the C_7H_7 fragment in the EI-MS. ^{1}H-NMR Signals at δ 3.96 and 4.71 were attributable to H–C(2′) and H–C(6), respectively, both being located at oxygenated C-atoms. This was in agreement with the observation of two C-atoms at δ 74.9 (C(6)) and 66.5 (C(2′)) in the ^{13}C-NMR spectrum. Moreover, the EI-MS fragment ion at *m/z* 256 ($[M - H_2O]^+$) corresponded to a dehydration due to the presence of an OH function. The single OH substituent was confirmed by the presence of signals for one MeO in the ^{1}H-NMR spectra of the two *Mosher* esters **1a** (δ 3.67) and **1b** (δ

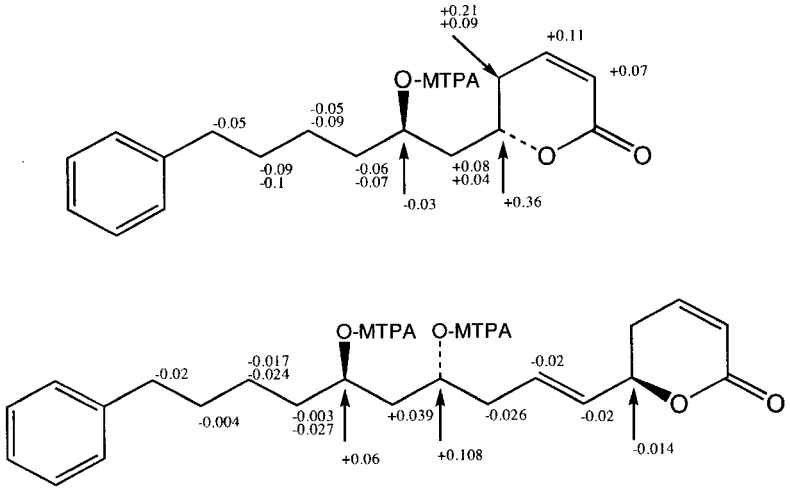


Figure. $\Delta\delta_{(H)}$ ($\Delta\delta_{(H)} = \delta_S - \delta_R$) *of* Mosher *esters of compounds* **1** *and* **2**. MTPA = PhC(MeO)(CF_3)CO.

Table 1. ^{1}*H-NMR Data* (500 MHz, $CDCl_3$) *of compounds* **1**, **2**, *and Their Derivatives* **1a,b** *and* **2a**–**c**[a])

	1	**2**	**1a**	**1b**	**2a**	**2b**	**2c**
H–C(3)	5.97 (*dd*, *J* = 1.95, 9.77)	6.03 (*dd*, *J* = 1.95, 9.77)	6.00 (*dd*, *J* = 1.95, 9.77)	5.93 (*dd*, *J* = 1.95, 9.77)	6.04 (*dd*, *J* = 1.95, 9.77)	6.028 (*dd*, *J* = 1.95, 9.77)	6.032 (*dd*, *J* = 1.95, 9.77)
H–C(4)	6.85 (*m*)	6.85 (*m*)	6.82 (*m*)	6.71 (*m*)	6.86 (*m*)	6.832 (*m*)	6.837 (*m*)
H–C(5)	2.30 (*m*)	2.43 (*m*)	2.25 (*m*)	2.04–2.16 (*m*)	2.42 (*m*)	2.297 (*m*)	2.281 (*m*)
H–C(6)	4.71 (*m*)	4.89 (*dd*, *J* = 7, 14.5)	4.33 (*m*)	3.97 (*m*)	4.88 (*dd*, *J* = 7, 14.5)	4.772 (*dd*, *J* = 7, 14.5)	4.786 (*dd*, *J* = 7, 14.5)
H–C(1′)	1.83–1.65 (*m*)	5.68 (*dd*, *J* = 7, 15.5)	1.89–2.02 (*m*)	1.81–1.98 (*m*)	5.66 (*dd*, *J* = 7, 15.5)	5.56 (*dd*, *J* = 7, 15.5)	5.58 (*dd*, *J* = 7, 15.5)
H–C(2′)	3.96 (*m*)	5.85 (*ddd*, *J* = 8, 8, 15.5)	5.30 (*m*)	5.33 (*m*)	5.81 (*ddd*, *J* = 8, 8, 15.5)	5.56 (*ddd*, *J* = 8, 8, 15.5)	5.58 (*ddd*, *J* = 8, 8, 15.5)
H–C(3′)	1.47 (*m*)	2.28 (*m*)	1.7-1.75 (*m*)	1.77–1.81 (*m*)	2.22–2.28 (*m*)	2.346 (*m*)	2.372 (*m*)
H–C(4′)	1.38–1.47 (*m*)	3.91 (*m*)	1.30–1.6 (*m*)	1.39–1.65 (*m*)	3.84 (*m*)	5.036 (*m*)	4.928 (*m*)
H–C(5′)	1.59 (*m*)	1.58 (*m*)	1.3–1.6 (*m*)	1.39–1.7 (*m*)	1.58 (*m*)	1.808 (*m*)	1.769 (*m*)
H–C(6′)	2.61 (*t*)	4.00 (*m*)	2.55 (*t*)	2.60 (*t*)	3.76 (*m*)	4.98 (*m*)	4.92 (*m*)
H–C(7′)		1.46–1.59 (*m*)			1.46–1.56 (*m*)	1.5–1.624 (*m*)	1.503–1.651 (*m*)
H–C(8′)		1.35–1.46 (*m*)			1.38 (*m*)	1.172–1.192 (*m*)	1.196–1.209 (*m*)
H–C(9′)		1.65 (*m*)			1.65 (*m*)	1.547 (*m*)	1.551 (*m*)
H–C(10′)		2.62 (*t*)			2.60 (*t*)	2.51 (*t*)	2.53 (*t*)
Arom. H	7.15–7.25 (*m*)	7.11–7.27 (*m*)	7.14–7.51 (*m*)	7.13–7.50 (*m*)	7.15–7.25 (*m*)	7.10–7.52 (*m*)	7.11–7.56 (*m*)
MeO			3.67 (*s*)	3.57 (*s*)		3.50 (*s*), 3.50 (*s*)	3.57 (*s*), 3.54 (*s*)
Me					1.33 (*s*), 1.32 (*s*)		

[a]) For convenience, derivatives of **1** and **2** are numbered like **1** and **2**, respectively; for systematic names, see *Exper. Part*.

3.57). Chemical shifts of protons and C-atoms of the lactone ring were assigned on the basis of literature data [10]. Six additional ^{13}C-NMR signals were detected, one quaternary C-atom being attributed to the C(1″) (142.3) of the monosubstituted benzene ring and the other five arising from CH_2 groups.

Molecule **1** possesses a noncoplanar six-membered α,β-unsaturated lactone chromophore (A), in addition to a monosubstituted benzene one (B) with a four-C

Table 2. ^{13}C-*NMR Data* (125 MHz, $CDCl_3$) *of Compounds* **1**, **2**, *and* **2a**[a])

	1	**2**	**2a**
C(2)	164.6	164.1	164.0
C(3)	120.7	121.0	121.6
C(4)	145.6	144.8	144.6
C(5)	29.8	29.7	29.8
C(6)	74.9	77.8	78.0
C(1′)	42.0	129.6	129.1
C(2′)	66.5	131.4	131.0
C(3′)	37.6	40.3	38.5
C(4′)	25.0	68.2	66.0
C(5′)	31.2	42.0	38.2
C(6′)	35.7	69.1	66.5
C(7′)		37.2	35.7
C(8′)		25.4	25.1
C(9′)		31.3	31.4
C(10′)		35.8	35.9
C(1″)	142.3	142.4	142.7
C(2″), C(6″)	128.1	128.2	128.2
C(3″), C(5″)	128.2	128.3	128.3
C(4″)	125.5	125.6	125.6
Me			24.9, 24.7
Me_2C			100.25

[a]) See *Footnote a* of *Table 1*.

distance from the chirality center at C(2′). The characteristic absorption bands of these chromophores, such as the $n \rightarrow \pi^*$ transition of the carbonyl group in *A* and the ^1L_b transition of the monosubstituted benzene ring (*B*), can be expected to appear at *ca.* 260 nm in the CD spectrum of **1**. Since the conjugated δ-lactone moiety of **1** is fixed in a chiral arrangement by the absolute configuration of the chirality center at C(6), it is reasonable to assume that the chiroptical properties of **1** are determined rather by this chromophore *A* than by *B*. Thus, the freely rotating chromophore *B* can induce only a weak ^1L_b transition ($\Delta\varepsilon < 0.3 - 0.5$) due to the long distance of the chirality centers (C(2′) and C(6)) from *B*. Moreover, this *Cotton* effect cannot be influenced at all by changing the polarity of the solvent, while an influence should be observed for the $n \rightarrow \pi^*$ transition of a carbonyl group, allowing an unequivocal assignment of the latter one. These considerations are confirmed by the observation of a relatively strong negative *Cotton* effect ($\Delta\varepsilon = -3.08$) at 256 nm in the CD spectra of **1** in MeOH, which showed a significant bathochromic shift (9 nm) in hexane. It clearly indicated that this *Cotton* effect belongs to the $n \rightarrow \pi^*$ transition of the chromophore *A* in **1**, and it is in good agreement with the prediction [11].

The thermodynamically favored equatorial position of the bulky side chain of **1** also indicated that the absolute configuration at C(6) was (*S*) on the basis of the helicity rule first proposed by *Snatzke* and *Hänsel* [12] and later modified by *Beecham* [13] for α,β-unsaturated lactones. The validity of this rule is well-documented in the literature [14–16][5]. Thus, compound **1** was identified as (6*S*)-5,6-dihydro-[(2*R*)-2-hydroxy-6-phenylhexyl]-2*H*-pyran-2-one.

Compound **2** showed a molecular ion M^+ at *m/z* 344 and the ammonium adduct $[M+NH_4]^+$ at *m/z* 362 in the D/CI-MS. This was supported by the presence of the molecular ion peak at *m/z* 344 in the EI-MS corresponding to the molecular formula $C_{21}H_{28}O_4$. The IR spectrum of **2** is comparable to that recorded for **1**, suggesting that compound **2** also possesses an α,β-unsaturated lactone ring, a monosubstituted benzene ring, and an OH group. The structure of **2** was suggested by its ^{1}H- and ^{13}C-NMR data (*Tables 1* and *2*) and confirmed by 2D-NMR spectroscopy including HSQC, HMBC, and COSY experiments. The relative configuration of the proposed vicinal-diol moiety in **2** was deduced from the ^{13}C-NMR analysis of the acetonide derivative **2a** (*Table 2*). The observed chemical shifts of the two Me groups (δ 24.9 and 24.7) at the ketal C-atom (δ 100.25) were attributed to an '*anti*'-diol conformation in **2** ('*syn*'-diol conformation: 2 Me at δ *ca.* 30 and 19 and ketal C-atom at higher fields) [17][18]. *Mosher* esterification [9] at the stereogenic atoms C(4′) and C(6′) of **2** yielding the esters **2b** and **2c** established the absolute configuration as (*R*) for both chiral centers (*Fig.*), while an (*R*) absolute configuration was assigned to C(6) of **2** on the basis of the positive *Cotton* effect measured both in MeOH and in hexane at 254 and 265 nm, respectively. Compound **2** was established as (6*R*)-[(4*R*,6*R*)-4,6-dihydroxy-10-phenyldec-1-enyl]-5,6-dihydro-2*H*-pyran-2-one.

Comparison of the ^{1}H-NMR spectrum of **2** with that of **1** (see *Table 1*) allowed some proton assignments. In fact, signals at δ 7.11–7.27 (*m*, 5 H) corresponding to the aromatic protons of the monosubstituted benzene ring were observed, together with signals at δ 6.03 (*dd*, J = 1.95, 9.77 Hz) and 6.85 (*m*), which were attributed to the olefinic protons H–C(3) and H–C(4) of the α,β-unsaturated lactone ring. Differences were detected in the ^{1}H-NMR spectrum of **2** arising from the presence of an additional double bond carrying H–C(1′) (δ 5.68) and H–C(2′) (δ 5.85), their coupling constant $J(1',2)$ = 15.5 Hz indicating a *trans*-configuration at C(1′)=C(2′). The protons at δ 4.89, 4.00, and 3.91 were attributed to H–C(6) of the lactone ring, H–C(6′), and H–C(4′), respectively. A peak at *m/z* 308 [$M-2\,H_2O$] in the EI-MS suggested the presence of two OH groups in **2**; this was confirmed by the acetonide derivative **2a** implicating vicinal-diol functionalities and by the *Mosher* esters with the appearance of two MeO groups in the ^{1}H-NMR spectrum of **2b** (both at δ 3.50 ppm) and **2c** (δ 3.54 ppm and 3.57 ppm).

The minimum amount of compounds **1** and **2** required to inhibit *C. cucumerinum* fungal growth on TLC plates was 1 μg for compound **1** and 3 μg for **2**. These amounts were comparable to the minimum quantities in the same assays of miconazole (1 μg) and propiconazole (0.1 μg), two commercially available reference antifungal compounds.

Experimental Part

General. TLC: *Merck* silica gel *60 F_{254}* Al sheets. Open-column chromatography (CC): *Pharmacia Sephadex LH-20* and *Merck* silica gel (40–63 and 70–200 μm). Medium-pressure liquid chromatography (MPLC): home-packed *Lichroprep RP-18* (*Merck*) column (45 × 4 cm, 15–25 μm). Anal. HPLC: *HP 1090* instrument equipped with a photodiode-array detector (*Agilent Technologies*); *Novapak RP-18* (4 μm; 150 × 3.9 mm i.d.); MeCN/H_2O 10:90 → 100:0 in 40 min, 0.05% CF_3COOH, 1 ml/min. Prep. HPLC: *Shimadzu LC-10AD* pump, radial compression module (RCM) 8 × 100 mm with a μ*Bondapak C_{18}* prepacked column (10 μm) (*Waters*). M.p.: *Mettler FP-80/82* hot-stage apparatus; uncorrected. Optical rotation: *Perkin-Elmer 241* polarimeter. UV Spectra: *Perkin-Elmer Lambda-20* spectrophotometer; λ_{max} (log ε) in nm. CD: *Jasco J-715/150S* spectrometer; in MeOH (c = 0.22–0.35 mmol l^{-1}; cell length 0.2 cm) at 24°; λ ($\Delta\varepsilon$) in nm. IR Spectra: *Perkin-Elmer 781* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Varian Unity-Inova-500* spectrometer, at 500 and 125 MHz, resp.; δ in ppm rel. to Me_4Si, J in Hz. EI-MS, D/CI-MS (NH_3, pos.-ion mode): *Finnigan-MAT TSQ-700* triple-stage quadrupole instrument; *m/z* (rel. int. in %).

Plant Material. The aerial parts of *R. crassifolia* were collected in Mandraka, eastern region of Madagascar. A voucher specimen was deposited at the Institute of Pharmacognosy and Phytochemistry in Lausanne (Voucher No 2000076).

Extraction and Isolation. The powdered stem bark (600 g) was extracted at r.t. successively with CH_2Cl_2 and MeOH to afford 45 and 125 g of extract, resp. A portion (25 g) of the CH_2Cl_2 extract was fractionated by CC (silica gel) with a stepwise gradient elution (petroleum ether/AcOEt 2:1; 1:1; 1:2, 0:1) to give 8 fractions (*I–VIII*). *Fr. III* was separated by MPLC (*RP-18*, MeCN/H_2O 3:7) to yield 3 fractions. Compound **1** was obtained from *Fr. 3* as a pale yellow powder after gel filtration (*Sephadex LH-20*, $CHCl_3$/MeOH 1:1). *Fr. V* was fractionated by CC (silica gel) followed by MPLC (*RP-18*, MeCN/H_2O 3:7). Compound **2** was obtained as a white powder after gel filtration (*Sephadex LH-20*, $CHCl_3$/MeOH 1:1).

*(6*S*)-5,6-Dihydro-6-[(2*R*)-2-hydroxy-6-phenylhexyl]-2*H*-pyran-2-one* (**1**). Pale yellow powder. M.p. 37°. $[\alpha]_D = -66$ ($c = 2$, $CHCl_3$). UV: 208 (4.2), 256 (2.6). CD ($c = 0.36$ mM): 256 (−3.08). IR: 3480, 2924, 1691, 1495, 1396, 1259, 1110, 1018, 813, 695, 489. EI-MS: 275 (2, $[M+H]^+$), 274 (8, $M^{+\bullet}$), 256 (3, $[M-H_2O]^+$), 196 (2), 189 (5), 171 (14), 143 (100), 104 (51), 117 (25), 91 (65, $C_7H_7^+$), 67 (11). D/CI-MS: 292 ($[M+NH_4]^+$), 275 ($[M+H]^+$).

Mosher *Esters* **1a** *and* **1b**. Compound **1** (5 mg in 2 ml of CH_2Cl_2) was sequentially treated with pyridine (0.2 ml), and 100 mg of (−)-(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride ((*R*)-MTPA chloride). The mixture was stirred at r.t. under N_2 for 5 h (HPLC monitoring). The mixture was evaporated, the residue dried and dissolved in CH_2Cl_2, and the soln. washed with 1% $NaHCO_3$ soln. (5 ml) and H_2O (2 × 5 ml). The org. layer was evaporated and the residue purified by prep. HPLC (RCM 8 × 10, MeCN/H_2O 60:40) affording the (*S*)-*Mosher* ester **1a** (5 mg, 67.1%).

The (*R*)-*Mosher* ester **1b** (6 mg, 56%) was prepared with (−)-(*S*)-α-methoxy-α-(trifloromethyl)phenylacetyl chloride under the same conditions as described above.

*(1*R*)-1-{[2*S*)-3,6-Dihydro-6-oxo-2*H*-pyran-2-yl]methyl}-5-phenylpentyl (α*S*)-α-Methoxy-α-(trifluoromethyl)benzeneacetate* (**1a**). EI-MS: 491 (1, $[M+H]^+$), 256 (49, $[M+H-H_2O-PhC(MeO)(CF_3)CO]^+$), 189 (60), 171 (49), 144 (100), 104 (38), 91 (71, $C_7H_7^+$). D/CI-MS: 508 ($[M+NH_4]^+$).

*(1*R*)-1-{[(2*S*)-3,6-Dihydro-6-oxo-2*H*-pyran-2-yl]methyl}-5-phenylpentyl (α*R*)-α-Methoxy-α-(trifluoromethyl)benzeneacetate* (**1b**). EI-MS: 490 (3, $M^{+\bullet}$), 256 (42, $[M+H-H_2O-PhC(MeO)(CF_3)CO]^+$), 189 (57), 171 (49), 144 (100), 104 (38), 91 (68, $C_7H_7^+$). D/CI-MS: 508 ($[M+NH_4]^+$).

*(6*R*)-6-[(4*R*,6*R*)-4,6-Dihydroxy-10-phenyldec-1-enyl]-5,6-dihydro-2*H*-pyran-2-one* (**2**). White powder. M.p. 74°. $[\alpha]_D = +59$ ($c = 2$, $CHCl_3$). UV: 207 (4.5), 254 (2.7). CD ($c = 0.22$ mM): 254 (+2.62). IR: 3325, 2929, 1718, 1497, 1384, 1236, 1047, 1023, 972, 821, 740, 700, 577. EI-MS: 345 (26, $[M+H]^+$), 344 (28, $M^{+\bullet}$), 327 (18, $[M+H-H_2O]^+$), 326 (71, $[M-H_2O]^+$), 309 (33, $[M+H-2H_2O]^+$), 308 (100, $[M-2H_2O]^+$), 291 (6), 290 (16). D/CI-MS: 262 ($[M+NH_4]^+$), 345 ($[M+H]^+$), 344 ($M^{+\bullet}$), 308 ($[M-2H_2O]^+$), 224.

*(6*R*)-6-{3-[(4*R*,6*R*)-2,2-dimethyl-6-(4-phenylbutyl)-1,3-dioxan-4-yl]prop-1-enyl}-5,6-dihydro-2*H*-pyran-2-one* (**2a**). To **2** (25 mg) in C_6H_6 (2 ml) were added 2,2-dimethoxypropane (10 ml) and traces TsOH. The mixture was stirred under reflux for 1 h. K_2CO_3 (0.2 mg) was added and the mixture stirred for 4 h at r.t. and then extracted with CH_2Cl_2 to afford **2a** (15 mg, 53.7%). EI-MS: 369 (28), 308 (8), 247 (10), 223 (12), 201 (8), 171 (73), 158 (23), 130 (41), 91 (100), 68 (16), 59 (23). D/CI-MS: 402 ($[M+NH_4]^+$), 385 ($[M+H]^+$), 362, 344 ($[M+2H-C_3H_6]^+$), 180.

Mosher *Esters* **2b** *and* **2c**. As described above for **1a** and **1b**, with **2** (5 mg). Prep. HPLC (RCM 8 × 10, MeCN/H_2O 75:25) afforded (*S,S*)-*Mosher* ester **2b** (7 mg, 63.2%) and the (*R,R*)-*Mosher* ester **2c** (7.5 mg, 68.6%), resp.

*(1*R*,3*R*)-1-{3-[(2*R*)-3,6-Dihydro-6-oxo-2*H*-pyran-2-yl]prop-2-enyl}-3-(4-phenylbutyl)propane-1,3-diyl Bis[(α*S*)-α-methoxy-α-(trifluoromethyl)benzeneacetate]* (**2b**). EI-MS: 776 (0.8, $M^{+\bullet}$), 498 (9), 308 (22, $[M-PhC(MeO)(CF_3)COOH]^+$), 264 (86), 223 (7), 189 (100), 131 (28), 106 (35), 91 (60, $C_7H_7^+$). D/CI-MS: 794 ($[M+NH_4]^+$).

*(1*R*,3*R*)-1-{3-[(2*R*)-3,6-Dihydro-6-oxo-2*H*-pyran-2-yl]prop-2-enyl}-3-(4-phenylbutyl)propane-1,3-diyl Bis[(α*R*)-α-methoxy-α-(trifluoromethyl)benzeneacetate]* (**2c**). EI-MS: 776 (0.8, $M^{+\bullet}$), 498 (0.8), 308 (30, $[M-2\,PhC(MeO)(CF_3)COOH]^+$), 223 (8), 190 (12), 189 (100), 170 (17), 118 (19), 104 (45), 91 (47, $C_7H_7^+$). D/CI-MS: 794 ($[M+NH_4]^+$).

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