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EPIPHORELLIC ACIDS 1 AND 2, TWO DIARYL ETHERS FROM THE LICHEN *CORNICULARIA EPIPHORELLA**

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Key Word Index—*Cornicularia epiphorella*; Usneaceae; lichen; diaryl ethers; epiphorellic acid 1; epiphorellic acid 2.

Abstract—From the lichen *Cornicularia epiphorella* two new diaryl ethers, epiphorellic acids 1 and 2, were isolated besides the known compound atranorin. The structures of the new compounds were established by spectroscopic evidence and chemical transformations. The structure of epiphorellic acid 1 was also confirmed by correlation with a known compound.

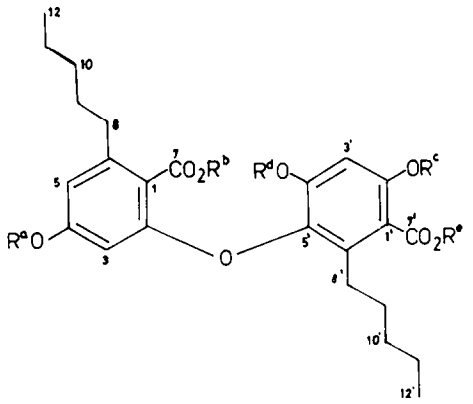
INTRODUCTION

In the course of systematic research on lichen substances from the Chilean flora, we have examined *Cornicularia epiphorella*. This lichen is distributed in the southern part of South America and in continental Chile it is associated with *Nothofagus* spp. and *Araucaria araucana* forests [2, 3]. In previous work on this species, using specimens collected in Tierra del Fuego, protolichesterinic acid was reported [4]. This paper describes the isolation and characterization of two new diaryl ethers, epiphorellic acid 1 (**1**) and epiphorellic acid 2 (**2**), present in *C. epiphorella*.

RESULTS AND DISCUSSION

A chloroform extract of *C. epiphorella* revealed a mixture of two main compounds by TLC. Chromatography of this extract afforded **1** and **2**.

The pure compound **1**, white crystals, mp 158–160°, analysed for $C_{26}H_{34}O_8$ by both mass spectral and ^{13}C NMR methods. The nature of this lichen substance was evident from the ^1H NMR spectrum, which showed signals due to the presence of two C_5-side chains (δ0.90, 6H; 1.37, 12H; 2.57, 2H; and 2.90, 2H), two methoxy groups (δ3.70 and 3.90), and three aromatic protons (δ5.83, *d*, J = 2.5 Hz; 6.40, *d*, J = 2.5 Hz; and 6.50, *s*). Since a doublet aromatic proton occurs at an unusually upfield position [5], a depside or depsidone structure for **1** was tentatively discarded. The ^{13}C NMR spectrum (Table 1) confirmed the presence of two C_5 units, established the two methoxy groups as Ar–COOMe (168.7, *s*; 51.7, *q* and Ar–OMe, 56.0, *q*) and a carbon singlet at δ173.6 was assigned to an Ar–COOH group. Treatment of epiphorellic acid 1 (**1**) with ethereal diazomethane gave **1a**, whose ^1H NMR spectrum showed the characteristics of a new carbomethoxyl function (δ3.90, *s*) with an *ortho*-hydroxy group (δ11.60, *s*). The presence of this system was also evident from the mass spectrum of **1** and **1a** which exhibited peaks at *m/z* 456 due to loss of water and methanol, respectively. Because the carboxy groups of epiphorellic acid 1 (**1**) and its methyl derivative **1a** do not participate in the linkage between the two aromatic moieties, it was suggested that **1** possessed a diaryl ether structure.



	R^a	R^b	R^c	R^d	R^e
1	H	Me	H	Me	H
1a	H	Me	H	Me	Me
1c	Me	Me	Me	Me	Me
1d	Me	Me	H	Me	Me
1e	Me	H	H	H	Me
1f	Me	Me	H	H	Me

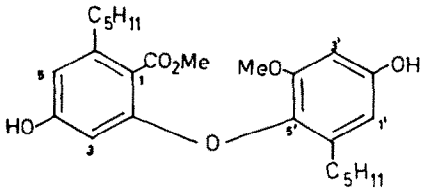
In order to determine the position of the carboxylic function in **1**, it was partially decarboxylated to afford, after treatment of the mixture with diazomethane and

*Part 9 in the series "Studies on Chilean Lichens". For part 8 see ref. [1].

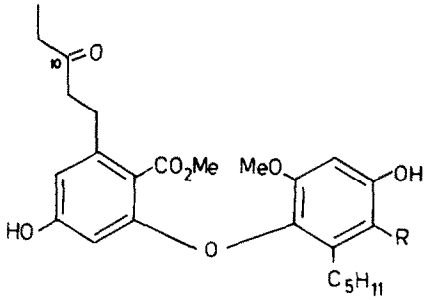
Table 1. ^{13}C NMR spectra of compounds **1**, **1a**, **2** and **2a**

Carbon	1*	1a†	2*	2a†
1	115.1 *s*	114.6	115.2	114.3
2	163.8 *s*	162.2	163.9	162.2
3	99.3 *d*	98.7	99.5	98.7
4	158.5 *s*	157.7	158.5	157.4
5	109.6 *d*	109.2	109.8	109.3
6	143.7 *s*	143.4	142.8	141.6
7	168.7 *s*	169.2	168.5	168.7
1′	104.5 *s*	104.1	104.7	104.2
2′	159.4 *s*	157.9	159.7	157.4
3′	98.5 *d*	98.1	98.9	98.7
4′	157.8 *s*	157.1	158.0	158.5
5′	140.6 *s*	139.7	140.6	139.6
6′	134.4 *s*	134.1	134.4	133.8
7′	173.6 *s*	171.8	173.4	171.6
8	30.3 *t*	33.6	28.3	28.0
9	29.6 *t*	30.7	43.9	43.6
10	32.0 *t*	31.7	209.5 *s*	211.8 *s*
11	22.7 *t*	22.4	35.9	36.0
12	14.0 *q*	14.0	8.0	7.7
8′	31.3 *t*	30.4	31.2	30.4
9′	28.8 *t*	28.5	28.7	28.4
10′	32.5 *t*	32.2	32.8	32.2
11′	22.7 *t*	22.4	23.0	22.4
12′	14.0 *q*	14.0	14.3	14.1
MeO (C-4′)	56.0 *q*	55.7	56.3	55.7
MeO (C-7)	51.7 *q*	52.1	52.0	52.1
MeO (C-7′)	—	52.1 *q*		52.1

*In Me_2CO-d_6.
†In $CDCl_3$.



1b



R	
2	CO_2H
2a	CO_2Me
2b	H

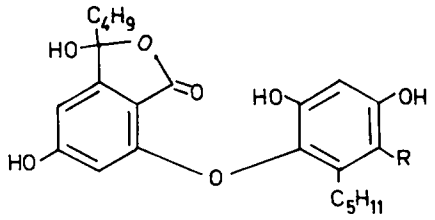
chromatographic separation, **1a** and **1b**. From the ^1H NMR spectrum of **1b** it was readily deduced that the Ar–COOMe group is situated in the same aromatic moiety as the two doublet aromatic protons, since in the new substance (**1b**) signals were exhibited corresponding to four aromatic protons. A doublet at δ5.80 (1H, J = 2.5 Hz) was assigned to H-3 and a broadened singlet centred at δ6.30 (3H) was due to H-5, H-1′ and H-3′ of **1b**.

On the basis of data mentioned above and from a biogenetic point of view, methyl epiphorellate 1 (**1a**) could have either of the alternative structures **1a** or **1f**. However, the mp of **1f** (85–87°) [6] is significantly different from **1a** (135–137°). On the other hand, the ^1H NMR spectrum of 2-(4′,6′-dihydroxy-3′-methoxycarbonyl-2′-pentylphenoxy)-4-methoxy-6-pentylbenzoic acid (**1e**) (sample supplied by M. V. Sargent) showed clearly that the two doublet aromatic protons (H-3 and H-5) are shifted more downfield (*ca* 0.4 ppm) in comparison with those of **1**, thus indicating that the position of methylation was the 4′-hydroxyl group in **1**, instead of the 4-hydroxyl group such as occurs in **1e**.

Finally, to confirm the structure **1** previously proposed for epiphorellic acid 1, **1** was converted into its permethylated derivative (**1c**). The spectral and physical data of **1c** were in full agreement with those from the permethylated derivative of **1e**.

Epiphorellic acid 2 (**2**), mp 146–148°, $C_{26}H_{32}O_9$, exhibited a ^1H NMR spectrum very similar to that of **1**. The chemical shifts of the aromatic protons in **2** attached to C-3 (δ5.78, 1H, *d*, J = 2.5 Hz), C-5 (δ6.36, 1H, *d*, J = 2.5 Hz) and C-3′ (δ6.52, 1H, *s*) were almost identical to those of **1**, which suggested that **2** had the same framework of the diaryl ether structure **1**. The proton signals of **2** were markedly different from those of **1** at one C_5 unit, because the ^1H NMR spectrum showed the following signals: δ1.00 (3H, *t*, J = 7.0 Hz, H-12), 2.45 (2H, *q*, J = 7.0 Hz, H-11) and 2.79 (4H, *br s*, H-8 and H-9), which were tentatively attributable to an Ar–CH_2CH_2COEt sequence. This suggestion was consistent with the ^{13}C NMR spectrum of **2** (Table 1), which contained one additional carbonyl function at C-10 (209.5, *s*) relative to that of **1**. The remaining signals of this side chain were assigned as follows: 28.3, C-8; 43.9, C-9; 35.9, C-11; and 8.0, C-12. Additionally, the ^{13}C NMR spectrum exhibited the characteristics of another C_5-side chain (C_5H_{11}), one Ar–OMe group (56.3, *q*), one carbomethoxy function (168.5, *s* and 52.0, *q*) and one carboxylic group (173.4, *s*). Methylation of **2** gave the corresponding derivative (**2a**), which showed a new carbomethoxy function with an *ortho*-hydroxy group, such as occurs in **1a**. Compound **2** was also partially decarboxylated to afford, after addition of diazomethane and chromatographic separation **2a** and **2b**. Again, the ^1H NMR spectrum of this new decarboxylated derivative (**2b**), showed that the carbomethoxy function is situated in the same aromatic moiety as the two doublet aromatic protons. Therefore, the unique difference between epiphorellic acids 1 (**1**) and 2 (**2**) is the additional carbonyl group in one of the C_5-side chains of **2**.

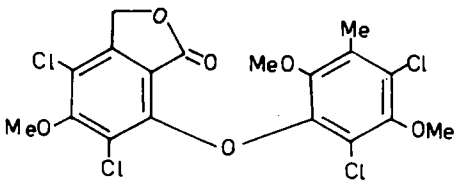
The position of the carbonyl C_5-side chain of **2** and **2a** was elucidated by comparison of ^{13}C NMR spectral data (Table 1) with those of **1** and **1a**, respectively. The



R

3 H

3a CO_2Me



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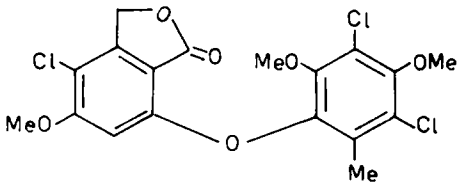

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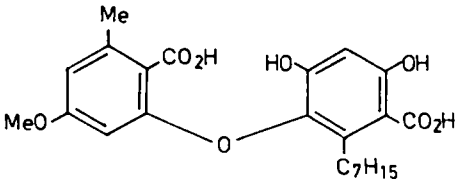

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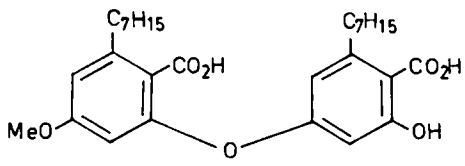
assignments of the ^{13}C NMR spectral signals of **1**, **1a**, **2** and **2a** were made on the basis of the observed multiplicities, empirical shift rules [7] and comparison with reported ^{13}C NMR spectral data of known derivatives [8, 9]. On going from **1** to **2** and **1a** and **2a**, it could be appreciated that the signal due to C-6 was displaced upfield by 0.9 and 1.8 ppm, respectively. The differences observed in chemical shift could be rationalized by considering the γ effects of the carbonyl function [7]. The other carbon resonances remained almost unshifted, leading to the assignment of the structure of **2** and **2a** as epiphorellic acid 2 and its methyl derivative.

Diphenyl ethers constitute a relatively rare group of lichen metabolites with eight examples known prior to the present work. They are norlobariol (**3**) [10], loxodinol (**3a**) [11], buellolide (**4**) [12], canesolide (**5**) [12], congrayanic acid (**6**) [13], micareic acid (**7**) [14], methoxymicareic acid (**8**) [14] and leprolomin [15]. Compounds **3**, **3a**, **4**, **5** and **6** have been postulated as biogenetic depsidone cleavage products [12], whereas **7** and **8** have a distinctly different substitution pattern, and presumably, biogenetic origin [14]. On the other hand, leprolomin apparently arises by direct oxidative coupling of two molecules of C-methylphloroacetophenone [15]. Therefore, epiphorellic acid 1 (**1**) and epiphorellic acid 2 (**2**) probably arise biogenetically by catabolism of their congeneric depsidones.



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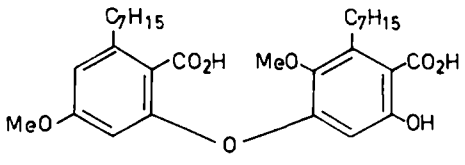

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EXPERIMENTAL

Mps are uncorr. ^1H NMR were recorded at 60 and 100 MHz in Me_2CO-d_6 or $CDCl_3$ soln with TMS as int. standard. ^{13}C NMR were recorded in Me_2CO-d_6 or $CDCl_3$ with TMS as int. standard. MS were recorded by direct inlet with 70 eV ionization. IR spectra were recorded in KBr pellets.

Cornicularia epiphorella (Nyl.) Du Rietz, collected on *Araucaria araucana*, Parque Nacional Conguillío, IX Región, Chile, in December 1983, was identified by G. Guzmán (Academia Superior de Ciencias Pedagógicas, Valparaíso); voucher specimens are deposited at the herbarium of Universidad F. Santa María.

Air dried lichen thalli (530 g) were triturated and extracted at room temp., successively with petrol (40–60°) and $CHCl_3$. The petrol extract was concd in vacuum and the residue subjected to fractional crystallization from $CHCl_3$–EtOH (1:1). On standing

a white solid deposited (31 mg), which was removed by filtration and identified as atranorin by direct comparison (mp, TLC, IR, ^{1}H NMR) with an authentic sample. The $CHCl_3$ extract (14.3 g) was also concd and showed a mixture of two components by TLC (R_f 0.53 and 0.41, silica gel, toluene–EtOAc–HCO_2H, 81:16:3). This crude material (2 g) was subjected to silica gel CC (80 g, HF_{254} for TLC) using a mixture of C_6H_6–EtOAc–HCO_2H (45:3:2). Fractions of 40 ml were taken and combined based upon TLC monitoring. Fractions 26–42, containing a pure compound, were mixed and afforded **1**. Fractions 48–53, containing another pure compound, were mixed and afforded **2**.

Epiphorellic acid 1 (**1**). Compound **1** (1.15 g) was isolated as white crystals; mp 158–160° (Me_2CO–*n*-heptane). IR ν_{max}^{KBr} cm^{-1}: 3420, 2960–2860, 1710, 1700, 1625, 1610, 1430, 1370, 1280, 1250, 1150. ^{1}H NMR ($CDCl_3$): δ0.90 (6H, *m*, H-12 and H-12'), 1.37 (12H, *m*, H-9, H-10, H-11, H-9', H-10' and H-11'), 2.57 (2H, *t*, *J* = 7.0 Hz, H-8), 2.90 (2H, *t*, *J* = 7.0 Hz, H-8'), 3.70 (3H, *s*, Ar–OMe), 3.90 (3H, *s*, Ar–COOMe), 5.83 (1H, *d*, *J* = 2.5 Hz, H-3), 6.40 (1H, *d*, *J* = 1.5 Hz, H-5), 6.50 (1H, *s*, H-3'). ^{13}C NMR see Table 1. MS *m/z* (rel. int.): 474 $[M]^+$ (15.3; $C_{26}H_{34}O_8$), 456 $[M-H_2O]^+$ (20), 430 $[M-CO_2]^+$ (100), 399 $[430-OMe]^+$ (25), 355 (5), 285 (5), 271 (6.5), 193 (10), 192 (9), 137 (5.3).

Methyl epiphorellate 1 (**1a**). After addition of CH_2N_2, **1** (200 mg) was transformed to **1a**, which was purified by crystallization from Me_2CO–petrol (160 mg). White crystals, mp 135–137°. IR ν_{max}^{KBr} cm^{-1}: 3400, 2950–2860, 1730, 1700, 1650, 1610, 1590, 1440, 1375, 1325, 1240, 1210, 1145. ^{1}H NMR ($CDCl_3$): δ0.90 (6H, *m*, H-12 and H-12'), 1.33 (12H, *m*, H-9, H-10, H-11, H-9', H-10' and H-11'), 2.63 (4H, *m*, H-8 and H-8'), 3.67 (3H, *s*, Ar–OMe), 3.85 (3H, *s*, Ar–COOMe), 3.90 (3H, *s*, Ar–COOMe), 5.40 (1H, *br s*, OH-4), 5.73 (1H, *d*, *J* = 2.5 Hz, H-3), 6.27 (1H, *d*, *J* = 2.5 Hz, H-5), 6.40 (1H, *s*, H-3'), 11.60 (1H, *s*, OH-2'). ^{13}C NMR: see Table 1. MS *m/z* (rel. int.): 488 $[M]^+$ (100), 456 $[M-MeOH]^+$ (81.3), 355 (7), 353 (5), 251 (9), 250 (8), 219 (10), 191 (8), 163 (5).

Decarboxylated epiphorellic acid 1 (**1b**). A soln of **1** (200 mg) in 20 ml of EtOH was heated under reflux for 96 hr. After evapn of solvent the residue was treated with CH_2N_2. This crude material showed two components by TLC. The substances were isolated by prep. TLC (silica gel, toluene–EtOAc–HCO_2H, 78:19:3) and yielded **1a** (40 mg, R_f 0.77) and **1b** (140 mg, R_f 0.45). Compound **1b**, prisms, mp 66–67° (petrol). IR ν_{max}^{KBr} cm^{-1}: 3320, 2960–2860, 1725, 1715, 1610, 1470, 1280, 1160, 1100. ^{1}H NMR ($CDCl_3$): δ0.90 (6H, *m*, H-12 and H-12'), 1.30 (12H, *m*, H-9, H-10, H-11, H-9', H-10' and H-11'), 2.45 (4H, *m*, H-8 and H-8'), 3.60 (3H, *s*, Ar–OMe), 3.90 (3H, *s*, Ar–COOMe), 5.80 (1H, *d*, *J* = 2.5 Hz, H-3), 6.30 (3H, *br s*, H-5, H-3' and H-1'). MS *m/z* (rel. int.): 430 $[M]^+$ (100), 399 $[M-OMe]^+$ (13), 355 (12), 341 (5), 285 (5), 271 (5), 193 (7), 192 (6), 137 (8), 43 (49), 41 (52).

Methyl epiphorellate 1-2',4-*dimethyl ether* (**1c**) *and methyl epiphorellate* 1-4-*methyl ether* (**1d**). A soln of **1** (200 mg) in dry Me_2CO (20 ml) was heated with anhydrous K_2CO_3 (1 g) and MeI (2 ml) for 48 hr. After filtration and evapn of solvent, the residue showed two components by TLC. The substances were isolated by prep. TLC (silica gel; toluene–EtOAc–HCO_2H; 22:2:1) and yielded **1c** (100 mg, R_f 0.53) and **1d** (50 mg, R_f 0.76). Compound **1c**, white crystals, mp 73–74° (petrol). IR ν_{max}^{KBr} cm^{-1}: 2980–2860, 1730, 1620, 1590, 1490, 1470, 1440, 1380, 1330, 1270, 1160, 1100, 950, 820. ^{1}H NMR ($CDCl_3$): δ0.87 (5H, *m*, H-12 and H-12'), 1.30 (12H, *m*, H-9, H-10, H-11, H-9', H-10' and H-11'), 2.50 (4H, *m*, H-8 and H-8'), 3.71 (3H, *s*, OMe), 3.80 (3H, *s*, OMe), 3.88 (3H, *s*, OMe), 3.93 (6H, *s*, OMe), 5.87 (1H, *d*, *J* = 2.5 Hz, H-3), 6.40 (1H, *d*, *J* = 2.5 Hz, H-5), 6.47 (1H, *s*, H-3'). MS *m/z* (rel. int.): 516 $[M]^+$ (100), 485 $[M-OMe]^+$ (13), 453 $[485-MeOH]^+$ (5), 441 (9), 425 (10), 386 (6), 265 (10), 233 (8), 205 (5), 191 (5), 149 (5), 91 (5), 69 (5), 59 (7), 43 (12), 41 (13). Compound **1d**, white crystals, mp 95–96° (petrol). IR ν_{max}^{KBr} cm^{-1}: 2960–2860, 1730, 1650, 1610, 1690, 1490, 1470, 1440, 1380, 1335, 1210, 1160, 1100, 1050, 950, 840, 810. ^{1}H NMR ($CDCl_3$): δ0.87 (6H, *m*, H-12 and H-12'), 1.33 (12H, *m*, H-9, H-10, H-11, H-9', H-10' and H-11'), 2.70 (4H, *m*, H-8 and H-8'), 3.70 (3H, *s*, OMe), 3.78 (3H, *s*, OMe), 3.94 (3H, *s*, OMe), 3.97 (3H, *s*, OMe), 5.83 (1H, *d*, *J* = 2.5 Hz, H-3), 6.40 (1H, *d*, *J* = 2.5 Hz, H-5), 6.46 (1H, *s*, H-3'), 11.80 (1H, *s*, OH-2'). MS *m/z* (rel. int.): 502 $[M]^+$ (100), 470 $[M-MeOH]^+$ (48), 440 (10), 411 (6), 369 (4), 251 (9), 250 (10), 192 (6), 164 (3), 135 (5), 43 (8), 41 (10).

Methylation of 2-(4',6'-*dihydroxy*-3'-*methoxycarbonyl*-2'-*pentylphenoxy*)-4-*methoxy*-6-*pentylbenzoic acid* (**1e**) *to* **1d** *and* **1c**. A soln of **1e** (100 mg) in $CHCl_3$ (5 ml) was treated with freshly prepared CH_2N_2 for 5 min. Evapn of solvent and crystallization from petrol provided **1g** as white crystals (85 mg). The spectral and physical data (TLC, mp, IR, ^{1}H NMR, MS) of this compound were in complete agreement with those of **1d**. Compound **1g** was treated with excess MeI in Me_2CO and K_2CO_3, as described above. After filtration and evapn of solvent, the residue showed two components by TLC. The substances were isolated by prep. TLC, as described above and provided **1g** = **1d** (30 mg) and **1h** (45 mg). The spectral and physical data (TLC, mp, IR, ^{1}H NMR, MS) of **1h** were in full agreement with those of **1c**.

Epiphorellic acid 2 (**2**). Compound **2** (280 mg) was isolated as white crystals; mp 146–148° (Me_2CO–*n*-heptane). IR ν_{max}^{KBr} cm^{-1}: 3360, 2960, 2860, 1740, 1700, 1655, 1625, 1610, 1485, 1450, 1440, 1415, 1370, 1280, 1240, 1215, 1150, 1100, 830, 740. ^{1}H NMR (Me_2CO-d_6): δ0.82 (3H, *t*, *J* = 7.0 Hz, H-12'), 1.00 (3H, *t*, *J* = 7.0 Hz, H-12), 1.32 (4H, *m*, H-10' and H-11'), 1.48 (2H, *m*, H-9'), 2.45 (2H, *q*, *J* = 7.0 Hz, H-11), 2.79 (4H, H-8 and H-9), 2.93 (2H, *m*, H-8'), 3.80 (3H, *s*, Ar–OMe), 3.86 (3H, *s*, Ar–COOMe), 5.78 (1H, *d*, *J* = 2.5 Hz, H-3), 6.36 (1H, *d*, *J* = 2.5 Hz, H-5), 6.52 (1H, *s*, H-3'), 9.70 (2H, *m*, OH). ^{13}C NMR: see Table 1. MS *m/z* (rel. int.): 444 $[M-CO_2]^+$ (72.9), 413 $[444-OMe]^+$ (13.5), 381 (33.7), 355 (100), 337 (20.8), 285 (96.6), 271 (17.5), 193 (50.4), 192 (54.8), 163 (22.2), 138 (21.8), 137 (67.7), 57 (58.6).

Methyl epiphorellate 2 (**2a**). After addition of CH_2N_2, **2** (100 mg) was transformed to **2a**, which was purified by crystallization from $CHCl_3$–*n*-heptane (90 mg). White crystals, mp 108–109°. IR ν_{max}^{KBr} cm^{-1}: 3440, 3220, 2960, 2860, 1730, 1685, 1660, 1610, 1440, 1380, 1325, 1270, 1240, 1210, 1150, 1090, 1050, 950, 840. ^{1}H NMR ($CDCl_3$): δ0.84 (3H, *t*, *J* = 7.0 Hz, H-12'), 1.00 (3H, *s*, Ar–OMe), 3.86 (3H, *s*, Ar–COOMe), 3.91 (3H, *s*, (2H, *q*, *J* = 7.0 Hz, H-11), 2.75 (6H, *m*, H-8', H-8 and H-9), 3.66 (3H, *s*, Ar, OMe), 3.86 (3H, *s*, Ar–COOMe), 3.91 (3H, *s*, Ar–COOMe), 5.80 (1H, *d*, *J* = 2.5 Hz, H-3), 6.25 (1H, *d*, *J* = 2.5 Hz, H-5), 6.36 (1H, *s*, H-3'), 11.73 (1H, *s*, OH-2'). ^{13}C NMR: see Table 1. MS *m/z* (rel. int.): 502 $[M]^+$ (100), 470 $[M-MeOH]^+$ (88), 355 (25), 285 (10), 192 (5), 191 (6), 137 (15), 57 (20).

Decarboxylated epiphorellic acid 2 (**2b**). A soln of **2** (150 mg) in 20 ml of EtOH was heated under reflux for 70 hr. After evapn of solvent, the residue was treated with CH_2N_2. This crude material showed two components by TLC. The substances were isolated by prep. TLC (silica gel; toluene–EtOAc–HCO_2H, 15:4:1) and yielded **2a** (70 mg, 0.65) and **2b** (65 mg, R_f 0.40). Compound **2b**, white crystals, mp 145–146° (petrol). IR ν_{max}^{KBr} cm^{-1}: 3370, 2960–2860, 1725, 1690, 1600, 1490, 1450, 1270, 1200, 1140, 1110, 1090, 1070, 1030, 1010, 990, 950, 840. ^{1}H NMR ($CDCl_3$): δ0.80 (3H, *t*, *J* = 8.0 Hz, H-12'), 1.00 (3H, *t*, *J* = 7.0 Hz, H-12), 1.27 (6H, *m*, H-9', H-10' and H-11'), 2.40 (4H, *m*, H-11, H-8'), 2.77 (4H, *br s*, H-8 and H-9), 3.67 (3H, *s*, Ar–OMe), 3.90 (3H, *s*, Ar–COOMe), 5.90 (1H, *d*, *J* = 2.5 Hz, H-3), 6.30 (1H, *d*, *J* = 2.5 Hz, H-5), 6.37 (2H, *s*, H-1' and H-3'). MS *m/z* (rel. int.): 444 $[M]^+$ (100), 413 (10), 381 (8), 355 (100), 285 (60), 193 (45), 192 (55), 137 (38), 57 (65).

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