Phytochemistry, Vol. 27, No. 2, pp. 473–477, 1988.
Printed in Great Britain.

0031-9422/88 $3.00 + 0.00

SESQUITERPENES FROM *ORTHOSPHENIA MEXICANA*

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(*Received* 4 *March* 1987)

Key Word Index—*Orthosphenia mexicana*, Celastraceae, sesquiterpene esters of the dihydro-β-agarofuran type.

Abstract—The new sesquiterpenes 1α-benzoyloxy-9β-acetoxy-4β,6β-dihydroxydihydro-β-agarofuran, 1α-benzoyloxy-6β,9β-diacetoxy-4β-hydroxydihydro-β-agarofuran, 1α-benzoyloxy-6β,9β,15-triacetoxy-4β-hydroxydihydro-β-agarofuran, 1α-benzoyloxy-6β,8β,9α-triacetoxy-4β-hydroxydihydro-β-agarofuran, 1α-benzoyloxy-6β,9α-diacetoxy-4β,8β-dihydroxydihydro-β-agarofuran and 1α-cinnamoyloxy-2β,6β,9β-triacetoxy-4β-hydroxydihydro-β-agarofuran were isolated from the aerial part of *Orthosphenia mexicana* and their structures determined by spectroscopic and chemical studies.

INTRODUCTION

In our continuing studies on the constituents of the plants of the Celastraceae family, six new esters of sesquiterpenes often found in this botanical family [1] were isolated from *Orthosphenia mexicana* Standley [2]. This is a plant endemic to north-eastern Mexico, which had already yielded, among other products, three new triterpenes [3–5] and alkaloids [6].

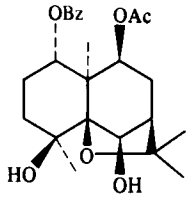
RESULTS

Compound **2** was assigned the structure 1α-benzoyloxy-6β,9β-diacetoxy-4β-hydroxydihydro-β-agarofuran. It was isolated as a crystalline solid, mp 202°, molecular formula $C_{26}H_{34}O_8$. The IR spectrum showed hydroxyl and ester group bands; the alcohol grouping was tertiary since it could not be acetylated under normal conditions. The mass spectrum suggested the presence of a benzoate with a fragment at *m/z* 105 and an acetate fragment at *m/z* 42. The ^{1}H NMR spectrum showed signals corresponding to the protons of two acetate methyl groups as singlets at δ1.63 and 2.13 with the geminal protons centred at 5.05 (1H, *d*, $J = 6$ Hz) and 5.50 (1H, *s*). Two multiplets corresponding to a benzoate grouping were found centred at 7.52 and 8.06 with the geminal proton centred at 5.31 (*dd*, $J = 4$, 12 Hz). The above data characterizes a polyester dihydro-β-agarofuran sesquiterpene. Comparison of the ^{1}H NMR data of **2** with that of celorbicol ester A (**3**) [7], which had its structure establishd by X-ray analysis, sited a benzoate at C-1α, an acetate at C-9β and the remaining acetate at C-6β. The assignments were confirmed by double resonance experiments and chemical reactions. Thus, hydrolysis of **2** with sodium bicarbonate under reflux [8] produced a deacetyl derivative with physical constants and spectral properties identical to those of the natural product (**1**). Total hydrolysis of **2** with potassium carbonate under reflux afforded the tetraol (**4**). When compound **2** was dehydrated with thionyl chloride in pyridine it yielded a product (**5**) with an exocyclic methylene, only possible in this skeleton if the tertiary hydroxyl is on C-4β. These data were all confirmed by ^{13}C NMR and two-dimensional ^{13}C–^{1}H, (Tables 1 and 2).

The natural product (**6**) had one more acetate grouping than **2**, assigned to C-15 since two AB protons of an acetoxy methylene system were shown in ^{1}H NMR spectrum as a double doublet centred at δ4.53. The chemical shift of the axial proton H-6 moved from 5.50 in the spectrum of **2** to 6.07 in the spectrum of **6** and the equatorial proton H-9 moved from 5.05 in **2** to 5.40. These data, and the ^{13}C NMR spectrum established the structure of **6** as 1α-benzoyloxy-6β,9β,15-triacetoxy-4β-hydroxydihydro-β-agarofuran, (Tables 1 and 2).

Product **9** was obtained as a crystalline solid, mp 194–198°, molecular formula $C_{25}H_{34}O_9$, suggesting that it would have one more hydroxyl group than **2**. The ^{1}H NMR spectrum showed data indicating the 8β-9α diacetoxy stereochemistry like that of isoeunyminol [9] and this was confirmed by an NOE experiment [10]. Thus when H-6 was irradiated, the signal of the proton geminal to the substituent on C-8 increased by 51%. The $J_{9-8} = 9.6$ Hz indicates a *trans*-diaxial position. Acetylation of compound **9** afforded an acetyl derivative identical to natural product **7** and the preparation of derivatives **8**, **10** and **11** confirmed the structures proposed (Tables 1 and 2).

The mass spectrum of compound (**12**) showed the presence of fragments indicative of acetate and cinnamate at *m/z* 131. The ^{1}H NMR spectra showed the clear relation of **12** with the products described above, the most marked differences being a cinnamate grouping at C-1α with its vinyl protons as two doublets at δ6.42 and 7.74 and the geminal proton at 5.36, just as in isocelorbicol ester B [7] and a secondary hydroxyl group at C-2β with the geminal proton as a multiplet at 3.64. The 2β-position was confirmed when **12** was oxidized to yield **14** which, when dehydrated, gave the α,β-unsaturated ketone **16** as the principal product together with **15** which has an exocyclic methylene. Also, the acetate **13** was prepared (see Tables 1 and 2).



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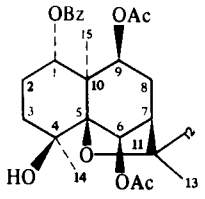

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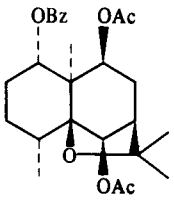

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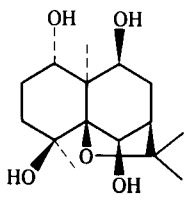

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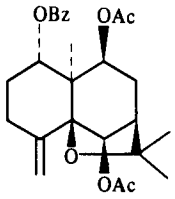

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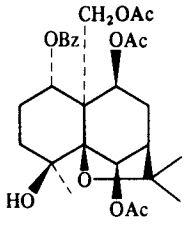

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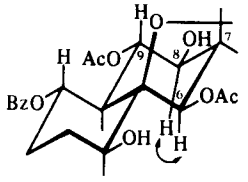


9

NOE experiment

EXPERIMENTAL

Mps: uncorr. IR spectra were taken in $CHCl_3$, unless otherwise stated. ^1H NMR spectra were obtained using $CDCl_3$ as solvent. Dry chromatography was carried out on silica gel 0.05–0.2 mm. The plant was gathered in spring 1981 near Matamoros, Tamaulipas, in north-east Mexico and identified by the Biology Dept of the ITESM, Monterrey Mexico. A voucher specimen no. 7723 is lodged there. From the aerial part of *Orthosphenia mexicana* a MeOH extract (26 g) was obtained. This was repeatedly chromatographed on silica gel and eluted with hexane–EtOAc mixtures of increasing polarity yielding in order of elution: **1** (12 mg), **2** (550 mg), **6** (40 mg), **7** (480 mg), **9** (1 g) and **12** (500 mg).

1α-*Benzoyloxy-9β-acetoxy-4β,6β-dihyroxydihydro-β-agarofuran* (**1**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3510, 3000, 2940, 1730, 1705, 1595, 1445, 1380, 1100, 975. ^1H NMR (200 MHz): δ 1.31 (3H, *s*), 1.48 (3H, *s*), 1.54 (3H, *s*), 1.56 (3H, *s*), 3.23 (1H, *s*, H-OH), 7.46 (3H, *m*), 8.01 (2H, *m*), other values see Table 1. EIMS *m/z* (rel. int.): 432 $[M]^+$ (2), 417 (5), 372 (6), 295 (28), 250 (17), 192 (19), 181 (37), 175 (17), 135 (15), 121 (17), 105 (100).

1α-*Benzoyloxy-6β,9β-diacetoxy-4β-hydroxydihydro-β-agarofuran* (**2**). Mp 202°. $[M]^+$ at *m/z* 474.2229 (calc. for $C_{26}H_{34}O_8$ 474.2253). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530, 3000, 1725, 1450, 1380, 1090, 1025, 970. ^1H NMR (360 MHz): δ 1.34 (3H, *s*), 1.48 (3H, *s*), 1.53 (3H, *s*), 2.91 (1H, *s*, H-OH), 7.52 (3H, *m*), 8.06 (2H, *m*) other values see Table 1. EIMS *m/z* (rel. int.): 474 $[M]^+$ (1), 459 (2), 432 (8), 414 (6), 354 (6), 337 (8), 250 (12), 232 (13), 217 (8), 204 (9), 192 (15), 181 (20), 175 (17), 138 (18), 121 (13), 109 (27), 105 (100).

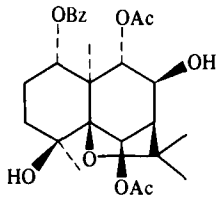
A soln of **2** (193 mg, 0.407 mmol) in MeOH (15 ml) was treated with 0.05 M $NaHCO_3$ (8 ml) and heated under reflux for 28 hr. After work-up and chromatography, **2** (100 mg) and **1** (81 mg) were obtained.

1α,4β,6β,9β-*Tetrahydroxydihydro-β-agarofuran* (**4**). A soln of **1** (67 mg, 0.155 mmol) in MeOH (10 ml) was treated with 0.36 M K_2CO_3 (3.5 ml) and heated under reflux for 72 hr. After work-up and chromatography, **3** (13 mg) was obtained. ^1H NMR (200 MHz): δ 1.08 (3H, *s*), 1.51 (6H, *s*), 1.61 (3H, *s*) other values see Table 1.

1α-*Benzoyloxy-6β, 9β-diacetoxy-4*(14)-*dehydro-dihydro-β-agarofuran* (**5**). A soln of **2** (159 mg, 0.335 mmol) in dry pyridine (1 ml) was treated for 20 min with $SOCl_2$ at 0°. After work-up, the resulting residue was chromatographed and crystallized in hexane–EtOAc (1:1), yielding **4** (56 mg). Mp 179–183°. $[M-15]^+$ at 441.1903 (calc. for $C_{25}H_{29}O_7$ 441.1913). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3020, 2950, 1720, 1445, 1380, 1280, 1145, 1105, 965. ^1H NMR (60 MHz): δ 1.20 (3H, *s*), 1.42 (3H, *s*) other values see Table 1. EIMS *m/z* (rel. int.): 441 $[M-15]^+$ (1), 414 (62), 454 (9), 292 (13), 277 (7), 232 (13), 217 (13), 204 (45), 189 (20), 176 (11), 161 (13), 148 (9), 122 (14), 105 (100).

1α-*Benzoyloxy-6β-9β,15-triacetoxy-4β-hydroxydihydro-β-agarofuran* (**6**). Mp 188–190°. $[M-15]^+$ at *m/z* 517.2073 (calc. for $C_{27}H_{33}O_{10}$ 517.2032). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3670, 3650, 3000, 2940, 1725, 1595, 1445, 1365, 1170, 1090, 1020. ^1H NMR (200 MHz): δ 1.31 (3H, *s*), 1.50 (3H, *s*), 1.53 (3H, *s*), 4.42, 4.62 (each 1H, *d*, J_{AB} = 12 Hz), 7.50 (3H, *m*), 8.02 (2H, *m*), other values see Table 1. EIMS *m/z* (rel. int.): 517 $[M-15]^+$ (1), 490 (5), 430 (2), 412 (3), 370 (1), 248 (8), 202 (11), 148 (8), 131 (17), 105 (100).

1α-*Benzoyloxy-6β,8β,9α-triacetoxy-4β-hydroxydihydro-β-agarofuran* (**7**). Mp 76–80°. $[M-15]^+$ at *m/z* 517.2073 (calc. for $C_{27}H_{33}O_{10}$ 517.2042). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3650, 3530, 3000, 2970, 1725, 1595, 1445, 1365, 1170, 1105, 1040, 960. ^1H NMR (90 MHz):



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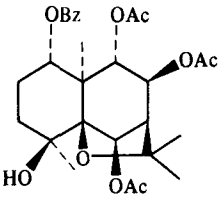

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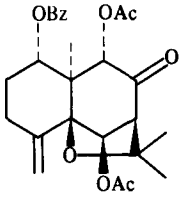

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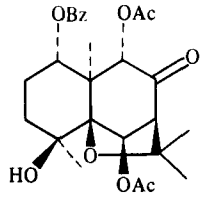

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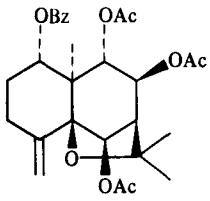

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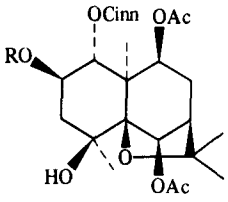
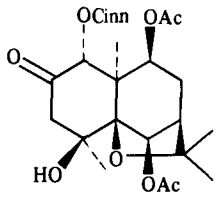


12 R = H
13 R = OAc



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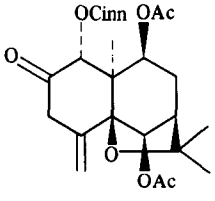

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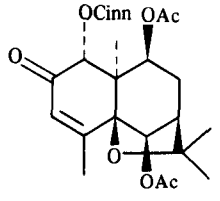

16

δ1.32 (3H, *s*), 1.43 (3H, *s*), 1.48 (3H, *s*), 1.52 (3H, *s*), 7.51 (3H, *m*), 8.02 (2H, *m*), other values see Table 1. EIMS *m/z* (rel. int.): 517 $[M-15]^+$ (1), 472 (7), 430 (6), 412 (1), 248 (7), 202 (13), 166 (16), 148 (10), 131 (23), 105 (100).

1α-*Benzoyloxy-6β,8β,9α-triacetoxy-4(14)-dehydro-dihydro-β-agarofuran* (**8**). A soln of **7** (124 mg, 0.233 mmol) in dry pyridine (1 ml) was treated with $SOCl_2$ for 25 min at 0°. After work-up, the resulting residue was chromatographed yielding **8** (70 mg). $[M]^+$ at *m/z* 514.2208 (calc. for $C_{28}H_{34}O_9$ 514.2202). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3010, 2970, 1725, 1595, 1445, 1380, 1080, 910. ^1H NMR (60 MHz): δ1.23 (3H, *s*), 1.43 (3H, *s*), 1.56 (3H, *s*), 7.55 (3H, *m*), 8.04 (2H, *m*), other values see Table 1. EIMS *m/z* (rel. int.) 514 $[M]^+$ (0.5), 499 (2), 498 (2), 472 (7), 412 (34), 272 (15), 230 (7), 202 (13), 131 (15), 105 (100).

1α-*Benzoyloxy-6β,9α-diacetoxy-4β,8β-dihydroxydihydro-β-agarofuran* (**9**). Mp 194–198°. $[M-15]^+$ *m/z* at 475.1962 (calc. for $C_{25}H_{31}O_9$ 475.1968). IR ν_{max}^{KBr} cm^{-1}: 3590, 3550, 3000, 1722, 1705, 1450, 1095, 950. ^1H NMR (200 MHz): δ1.30 (3H, *s*), 1.39 (3H, *s*), 1.48 (3H, *s*), 2.77 (1H, *s*), 7.49 (3H, *m*), 8.04 (2H, *m*), other values see Table 1. EIMS *m/z* (rel. int.): 475 $[M-15]^+$ (2), 472 (3), 430 (3), 248 (5), 202 (10), 105 (100). NOE difference experiments show H-8, 51.4% enhancements for H-6 irradiation.

1α-*Benzoyloxy-6β,9α-diacetoxy-8-oxo-4β-hydroxydihydro-β-agarofuran* (**10**). A soln of **9** (103 mg, 0.210 mmol) in Me_2CO (25 ml) was treated with freshly prepared Jones reagent (10 drops) at room temp. The reaction was halted by adding 3 drops of *i*-PrOH and, after usual work-up and chromatography, the mixture yielded **10** (100 mg). $[M]^+$ at *m/z* 448.1986 (calc. for $C_{26}H_{32}O_9$ 488.2046): IR ν_{max}^{KBr} cm^{-1}: 3460, 2945, 1725, 1365, 1170, 1095. ^1H NMR (90 MHz): δ1.38 (6H, *s*), 1.53 (6H, *s*), 7.04 (3H, *m*), 8.08 (2H, *m*), other values see Table 1. EIMS *m/z* (rel. int.): 488 $[M]^+$ (1), 446 (3), 428 (2), 386 (3).

1α-*Benzoyloxy-6β,9α-diacetoxy-8-oxo-4(14)-dehydrodihydro-β-agarofuran* (**11**). A soln of **10** (130 mg, 0.266 mmol) in dry

Table 1. ^{1}H NMR spectra of compounds **1**, **2**, **4–16**

H	H-1	H-6	H-7	H-8	H-9	H-14			
1‡	5.31 *dd*	4.43 *s*			4.97 *d*			Ac-9	
	J=4, 12 Hz				*J*=6 Hz			1.57 *s*	
2‖	5.31 *dd*	5.50 *s*	2.47 *m*		5.05 *d*		Ac-6	Ac-9	
	J=4, 12 Hz				*J*=6 Hz		2.13 *s*	1.63 *s*	
	4.21 *dd*	4.31 *s*			3.50 *d*				
4‡	*J*=4, 12 Hz				*J*=6 Hz				
5*	5.59 *dd*	5.37 *s*			5.18 *d*	4.79 *s*	Ac-6	Ac-9	
	J=5, 11 Hz				*J*=6.6 Hz	5.04 *s*	2.08 *s*	1.53 *s*	
6‡	5.37, *dd*	6.07 *s*			5.40 *d*		Ac-6	Ac-9	Ac-15
	J=4, 12 Hz				*J*=6 Hz		2.09 *s*	1.55 *s*	2.24 *s*
7†	5.13 *dd*	5.69 *s*	2.47 *d*	5.30 *dd*	5.96 *d*		Ac-6	Ac-9	Ac-8
	J=3.5, 11.7 Hz		*J*=3.5 Hz	*J*=3, 10 Hz	*J*=10 Hz		2.12 *s*	1.67 *s*	1.86 *s*
8*	5.44 *m*	5.52 *s*	2.54 *d*	5.44 *m*	6.03 *d*	4.73 *s*	Ac-6	Ac-9	Ac-8
			J=3 Hz		*J*=10 Hz	5.10 *s*	2.11 *s*	1.68 *s*	1.89 *s*
9‡	5.09 *dd*	5.44 *s*	2.37 *d*	4.13 *d*	5.76 *d*		Ac-6	Ac-9	
	J=4, 12 Hz		*J*=3 Hz	*J*=3, 9.6 Hz	*J*=9.6 Hz		2.11 *s*	1.69 *s*	
10†	5.31 *dd*	5.67 *s*‖	2.99 *s*		5.78 *s*‖		Ac-6	Ac-9	
	J=4, 10.8 Hz						2.15 *s*	1.61 *s*	
11‡	5.52 *dd*	5.51 *s*‖	3.04 *s*		5.83 *s*‖	4.74 *s*	Ac-6	Ac-9	
12§	*J*=4, 14 Hz					5.14 *s*	2.11 *s*	1.57 *s*	
	5.36 *d*	5.45 *s*			4.82 *dd*		Ac-6	Ac-9	
	J=10.5 Hz				*J*=1, 6.6 Hz		2.13 *s*	1.93 *s*	
13*	5.65 *d*	5.50 *s*			4.81 *dd*		Ac-6	Ac-9	Ac-2
	J=10.6 Hz				*J*=1.8, 5.4 Hz		2.10 *s*	1.95 *s*	1.83 *s*
14*	5.90 *s*	5.59 *s*	2.63 *s*		4.96 *dd*		Ac-6	Ac-9	
					J=5 Hz		2.14 *s*	1.95 *s*	
15†	6.04 *s*	5.42 *s*			5.05 *d*	4.95 *s*	Ac-6	Ac-9	
					J=7 Hz	5.17 *s*	2.14 *s*	1.93 *s*	
16‡	5.98 *s*	5.60 *s*			4.92 *d*	2.15 *d*	Ac-6	Ac-9	
					J=6 Hz	*J*=1.3 Hz	2.13 *s*	1.95 *s*	

*60 MHz, †90 MHz, ‡200 MHz, §360 MHz, ‖may be interchanged.

Table 2. ^{13}C NMR spectra of compounds **1**, **2**, **5–9**, **11**, **12** and **16**

C	**1**	**2**	**5**	**6**	**7**	**8**	**9**	**11**	**12**	**16**
1	72.55	72.59	71.31	9.37*	73.43	73.95	73.72	75.10	72.64	70.53*
2	23.35	23.32	27.66	23.70	24.01	28.02	24.23	28.68	67.81	192.88
3	37.18	38.50	32.73	38.21	38.12	31.50	38.33	31.84	48.67	129.19
4	73.03	70.33	143.11	70.24	70.38	142.11	70.51	141.81	70.96	153.59
5	91.53	91.49	88.76	91.35	92.59	90.26	92.52	91.23	91.10	87.85
6	79.68	79.71	79.40	78.19	78.07	78.09	78.19	77.38*	79.56	81.65
7	50.23	49.02	48.47	49.05	52.05	52.20	54.20	65.58	49.04	49.28
8	31.99	31.80	31.84	34.51	77.23*	72.22*	7.28*	199.26	31.61	31.98
9	73.27	72.94	73.01	72.39*	76.45*	75.91*	80.19*	81.20*	76.32	74.93*
10	50.32	51.40	51.55	54.09	47.85	48.82	48.07	50.29	51.56	51.48
11	84.58	84.30	82.69	84.34	84.11	82.36	84.33	82.70	84.67	84.97
12	30.22	29.56	31.19	29.40	29.65	31.32	29.96	31.04	29.72	29.91
13	26.65	25.74	26.24	25.72	25.47	26.30	25.72	25.73	25.74	25.65
14	23.86	24.00	112.26	23.80	23.70	112.76	23.92	113.59	24.85	21.98
15	19.93	19.61	19.31	65.08	13.31	13.30	13.61	13.06	20.16	20.18

*May be interchanged.

pyridine (1 ml) was treated with $SOCl_2$ (10 drops) for 15 min. After usual work-up and chromatography **11** (20 mg) was obtained. $[M]^+$ at *m/z* 470.1923 (calc. for $C_{26}H_{30}O_8$ 470.1941). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3020, 3000, 1735, 1600, 1365, 865. ^{1}H NMR (200 MHz): δ1.18 (3H, *s*), 1.50 (3H, *s*), 1.53 (3H, *s*), 7.54 (3H, *m*), 8.04 (2H, *m*), other values see Table 1. EIMS *m/z* (rel. int.): 470 $[M]^+$, 428, 410, 368, 348, 337.

1α-Cinnamoyloxy-6β,9β-diacetoxy-2β,4β-dihydroxydihydro-β-agarofuran (**12**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300, 2950, 1725, 1590, 1368, 1240, 1090. ^{1}H NMR (360 MHz): δ1.37 (6H, *s*), 1.50 (3H, *s*), 1.53

(3H, *s*), 6.40 (1H, *d*, J = 16 Hz), 7.40 (3H, *m*), 7.56 (2H, *m*), 7.69 (1H, *d*, J = 16 Hz) other values see Table 1. EIMS *m/z* (rel. int.): 501 $[M-15]^+$ (0.2), 483 (4), 441 (2), 48 (12), 381 (0.4). 290 (11), 228 (12), 168 (21), 131 (100), 121 (10), 103 (47).

1α-Cinnamoyloxy-2β,6β,9β-triacetoxy-4β-hydroxydihydro-β-agarofuran (**13**). A soln of **12** (55 mg, 0.106 mmol) was treated with Ac_2O in pyridine at room temp. After usual work-up and chromatography **13** (35 mg) was obtained. $[M]^+$ at *m/z* 558.2493 (calc. for $C_{30}H_{38}O_{10}$ 558.2465). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3332, 3000, 1735, 1595. ^1H NMR (60 MHz): δ1.39 (6H, *s*), 1.49 (6H, *s*), 3.01 (1H, *s*, H-OH), 4.97 (1H, *m*), 6.44 (1H, *d*, J = 16 Hz), 7.45 (5H, *m*), 7.72 (1H, *d*, J = 16 Hz), other values see Table 1. EIMS *m/z*: (rel. int.): 558 $[M]^+$ (3), 516 (10), 498 (14), 395 (38), 308 (23), 290 (29), 248 (20), 230 (23), 209 (20), 168 (25), 149 (20), 131 (100), 103 (91).

1α-Cinnamoyloxy-6β,9β-diacetoxy-2-oxo-4β-hydroxydihydro-β-agarofuran (**14**). A soln of **12** (122 mg, 0.236 mmol) in Me_2CO (25 ml) was treated with Jones reagent (9 drops) at room temp. while stirring. The reaction was halted by the addition of *i*-PrOH and, after work-up and chromatography, **14** (114 mg) was obtained. $[M]^+$ at *m/z* 514.2202 (calc. for $C_{28}H_{34}O_9$ 514.2251). IR ν_{max}^{KBr} cm^{-1}: 3500, 2920, 1750, 1730, 1630. ^1H NMR (60 MHz): δ1.28 (6H, *s*), 1.60 (6H, *s*), 6.38 (1H, *d*, J = 16 Hz), 7.45 (5H, *m*), 7.74 (1H, *d*, J = 16 Hz) other values see Table 1. EIMS *m/z* (rel. int.): $[M]^+$ 514 (1), 472 (11), 324 (6).

Products **15** *and* **16**. A soln of **14** (92 mg, 0.179 mmol) in dry pyridine (1 ml) was treated with $SOCl_2$ (10 drops) at 0°. After 15 min, the reaction mixture was extracted and chromatographed, yielding **15** (25 mg) and **16** (50 mg). Compound **15** was identified as 1α-cinnamoyloxy-6β,9β-diacetoxy-2-oxo-4(14)dehydro-dihydro-β-agarofuran. ^1H NMR (90 MHz): δ1.13 (3H, *s*), 1.52 (3H, *s*), 1.59 (3H, *s*), 6.35 (1H, *d*, J = 16 Hz), 7.44 (5H, *m*), 7.70 (1H, *d*, J = 16 Hz) (other values see Table 1). Compound **16** was identified as 1α-cinnamoyloxy-6β,9β-diacetoxy-2-oxo-3-ene-dihydro-β-agarofuran. $[M]^+$ at *m/z* 496.2062 (calc. for $C_{28}H_{32}O_8$ 496.2097). ^1H NMR (200 MHz): δ1.26 (3H, *s*), 1.51 (3H, *s*), 1.55 (3H, *s*), 5.96 (1H, *d*, J = 1.4 Hz), 6.31 (1H, *d*, J = 16 Hz), 7.35 (3H, *m*), 7.49 (2H, *m*), 7.66 (1H, *d*, J = 16 Hz) other values see Table 1. EIMS *m/z* (rel. int.): $[M]^+$ 454 (3), 436 (5), 349 (28), 307 (8), 289 (45).

Acknowledgements—This research has been partly subsidized by CAICYT Grant no. 0694-84 and by the AIETI Foundation (Madrid).

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