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Flavonoids from *Ulex airensis* and *Ulex europaeus* ssp. *europaeus*

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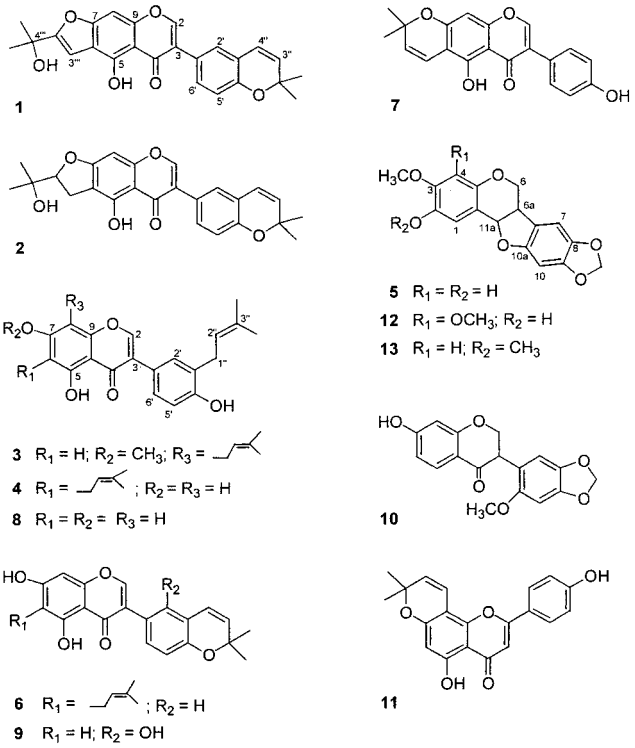
From the dichloromethane extract of *Ulex airensis* three new isoflavonoids, ulexin C (**1**), ulexin D (**2**), and 7-*O*-methylisolupalbigenin (**3**), were isolated and characterized by spectroscopic methods. Ulexin D (**2**) was also identified from the dichloromethane extract of *Ulex europaeus* ssp. *europaeus*. Together with these new metabolites, 18 compounds of previously known structures were isolated and identified from both species. The antifungal activity of these compounds was tested against *Cladosporium cucumerinum* by a bioautographic TLC assay.

The genus *Ulex* L. (Leguminosae, subfamily Papilionoideae) is well represented in Portugal, where 10 species are recognized, and some of them are endemic. These plants are shrubs and have been used in rural areas for different purposes.[1] In folk medicine, the flowers of certain species have become commercialized and are used as infusions in the treatment of liver disease.

Ulex species are rich in flavonoids, particularly isoflavones and pterocarpans.[2−8] Some of these are phytoalexins and have insecticide or cytotoxic effects.[9,10] In continuation of our search for bioactive compounds in this genus we have investigated the flavonoid fractions of *Ulex airensis* Espírito-Santo, Cubas, Lousã, Pardo & Costa and *Ulex europaeus* L. ssp. *europaeus*. From the first species, the three new isoflavones ulexin C (**1**), ulexin D (**2**), and 7-*O*-methylisolupalbigenin (**3**) were identified, together with the known lupalbigenin (**4**),[11] isochandalone (**6**),[12] and alpinumisoflavone (**7**)[13] and the chalcone 4-hydroxylonchocarpin.[14] From the second species, ulexin D (**2**) was also isolated together with the isoflavones isowighteone (**8**),[15,16] isolupalbigenin,[17] and licoisoflavone B (**9**),[18,19] the isoflavanone onogenin (**10**),[20] the flavone atalantoflavone (**11**),[21] and the pterocarpans (6a*R*,11a*R*)-(−)-2-hydroxypterocarpin (**5**),[22,23] (6a*R*,11a*R*)-(−)-2-hydroxy-4-methoxypterocarpin (**12**),[3] and (6a*R*,11a*R*)-(−)-2-methoxypterocarpin (**13**).[24] The isoflavonoids isoderrone,[7,12] ulexin A,[8] and ulexin B[8] and the pterocarpans (6a*R*,11a*R*)-(−)-maackiain,[25,26] (6a*R*,11a*R*)-(−)-2-methoxymaackiain,[7,27] and (6a*R*,11a*R*)-(−)-4-methoxymaackiain[7,28,29] were identified in both species. The structures of the new compounds (**1**−**3**) were established by the analysis of their spectroscopic data. The known compounds were identified by comparison with literature data and in certain cases by comparison with authentic samples.

For the first time the ^{13}C NMR data of lupalbigenin (**4**) and (6a*R*,11a*R*)-(−)-2-hydroxypterocarpin (**5**) are also presented.

Compounds **1**−**13** were tested against the fungus *Cladosporium cucumerinum* by a bioautographic TLC bioassay.[30] The other compounds have previously been tested,[8] and the overall structure/activity relations are discussed herein.



Results and Discussion

Ulexin C (**1**), isolated from *Ulex airensis*, $C_{25}H_{22}O_6$ ([M]$^+$ *m*/*z* 418, confirmed by HREIMS), was obtained as a colorless oil. The ^{1}H NMR and ^{13}C NMR spectra (Tables 1 and 2, respectively) showed characteristic signals of a 5-hydroxyisoflavone structure (proton signals at δ_{OH-5} 13.59 s, δ_{H-2} 7.95 s and carbon signals at δ_{C-2} 153.5 d, δ_{C-3} 122.8 s, δ_{C-4} 182.6 s).[31,32] The IR spectrum showed the corresponding carbonyl absorption ($\nu_{C=O}$ 1659 cm^{-1}) of the α,β-unsaturated ketone of the isoflavone ring C, establishing a hydrogen bond with the hydroxyl group at C-5 ($\nu_{C=O}$ 1622 cm^{-1}). The UV spectrum of **1** was characteristic of an isoflavone system[33] (see Experimental Section). The addition of NaOAc confirmed the absence of a hydroxyl group at C-7, and the bathochromic shift observed after addition of $AlCl_3$ was in agreement with the presence of the hydroxyl group at C-5. The ^{1}H NMR spectrum of **1** also showed the presence of a dimethylchromene system ($\delta_{H-2'}$ 7.20 d, $J_{2',6'} = 1.9$ Hz, $\delta_{H-5'}$ 6.85 d, $J_{5',6'} = 8.1$ Hz, $\delta_{H-6'}$ 7.26

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Table 1. ^{1}H NMR Spectral Data of Compounds **1**−**3**[a]

proton(s)	1	2	3
2	7.95 s	7.84 s	7.90 s
O*H*-5	13.59 s	13.09 s	12.94 s
6			6.42 s
OCH$_3$-7			3.90 s
8	7.03 s	6.37 s	
2′	7.20 d (1.9)	7.17 d (1.7)	7.29−7.27 m
O*H*-4′			5.24 bs
5′	6.85 d (8.1)	6.84 d (8.3)	6.87 d (8.7)
6′	7.26 dd (8.1, 1.9)	7.23 dd (8.4, 2.0)	7.29−7.27 m
1″A			3.40 d (5.9)
1″B			3.40 d (5.9)
2″	-		5.35 tq (7.2, 1.9)
3″	5.65 d (9.9)	5.64 (9.7)	
4″	6.37 d (9.9)	6.35 d (10.2)	
C*H*$_3$-4″			1.80 s
C*H*$_3$-5″	1.46 s	1.45 s	1.78 d (1.1)
C*H*$_3$-6″	1.46 s	1.45 s	
1‴A			3.41 d (5.9)
1‴B			3.41 d (5.9)
2‴		4.79 t (8.7)	5.16 tq (7.1, 1.9)
3‴A	6.80 s	3.20 dd (15.7, 9.4)	
3‴B		3.12 dd (15.7, 8.1)	
C*H*$_3$-4‴			1.80 s
C*H*$_3$-5‴	1.70 s	1.36 s	1.68 d (1.1)
C*H*$_3$-6‴	1.70 s	1.24 s	

[a] Chemical shifts are referenced to the signal of residual $CHCl_3$ (δ 7.26). Coupling constants are expressed in Hz and are presented in parentheses.

dd, $J_{6',5'} = 8.1$ Hz and $J_{6',2'} = 1.9$ Hz, $\delta_{H-3''}$ 5.65 d, $J_{3'',4''} = 9.9$ Hz, $\delta_{H-4''}$ 6.37 d, $J_{4'',3''} = 9.9$ Hz, $\delta_{CH3-5''}$ 1.46 s, $\delta_{CH3-6''}$ 1.46 s). This system was confirmed by the corresponding ^{13}C NMR signals (C-2′−C-6′ and C-2″−C-4″; see Table 2). The presence of a 2,2-dimethylpyrano substituent was further confirmed by the mass fragment at *m/z* 403 $[M - CH_3]^+$ (Figure 1, Supporting Information).[12,34] These signals corresponded to an isoflavone structure hydroxylated at C-5 with a 2,2-dimethylpyrano system on ring B. Compound **1** was also shown to possess one additional aromatic proton, a vinyl proton, and two methyl groups geminal to a hydroxyl group. The chemical shifts of the aromatic proton (δ 7.03, s) and of δ_{OH-5} 13.59 ppm were in agreement with an aromatic proton at C-8. Both methyl groups exhibited the same chemical shifts ($\delta_{CH3-5''}$ and $\delta_{CH3-6''}$ 1.70 s) indicative of the presence of a cyclized isoprenyl group on ring A on C-6 and C-7 positions. The chemical shift of the vinyl proton ($\delta_{H-3'''}$ 6.80 s) was characteristic of a proton of a furan system. These data were in agreement with a 2-(1-hydroxy-1-methylethyl)furan system on ring A of the isoflavone structure. The 1-hydroxy-1-methylethyl substituent was confirmed by the presence of the mass fragments at *m/z* 385 $[M - CH_3 - H_2O]^+$ and *m/z* 345 $[M - CH_3 - H_3CC(O)CH_3]^+$. Final confirmation of structure **1** was given by the presence of the mass fragments at *m/z* 235 and 169, both resulting from the retro Diels−Alder cleavage of the isoflavone as indicated in Figure 1 (Supporting Information).

All the ^{13}C NMR spectrum signals of compound **1** were assigned from the HMQC and HMBC spectra (Table 2). From the above data it was established that ulexin C (5-hydroxy-6,7-(2-(1-hydroxy-1-methylethyl)furan)-3′,4′-(2,2-dimethylpyrano)isoflavone) has structure **1**.

Ulexin D (**2**), isolated from both *Ulex* species, $C_{25}H_{24}O_6$ ($[M]^+$ *m/z* 420, confirmed by HREIMS), was obtained as a colorless oil. The structure of this isoflavone was assigned by spectral data interpretation by the same procedures as described for ulexin C (**1**). The molecular weight of the two metabolites differed by 2 amu, and the ^{1}H NMR and ^{13}C NMR data of rings B and C of both ulexins C (**1**) and D (**2**) were identical, leading to the conclusion that structures **1** and **2** differed in their substitution on ring A. The ^{1}H NMR spectrum of ulexin D (**2**) lacked the olefinic proton and showed three upfield signals at δ 4.79 (t, $J_{2''',3'''} = 8.7$ Hz, H-2‴), at δ 3.20 (dd, $J_{3'''A,3'''B} = 15.7$ Hz, $J_{3'''A,2'''} = 9.4$ Hz, H-3‴A), and at δ 3.12 (dd, $J_{3'''B,3'''A} = 15.7$ Hz, $J_{3'''B,2'''} = 8.1$ Hz, H-3‴B). The ^{13}C NMR spectrum also exhibited two upfield signals corresponding to C-2‴ and C-3‴ ($\delta_{C-2'''}$ 91.9 d and $\delta_{C-3'''}$ 26.7 t), demonstrating that ulexin D (**2**) did not possess unsaturation between these two carbon atoms. The presence of the 2-(1-hydroxy-1-methylethyl)-2,3-dihydrofuran substituent on ring A of ulexin D (**2**) was further confirmed by the mass fragment at *m/z* 361 amu $[M - 59]^+$, typical of this substituent.[12,34] Subsequent retro Diels−Alder cleavage of ring C gave rise to the fragments at 177 and 169 amu, as indicated in Figure 2 (Supporting Information). From these data it was established that ulexin D {5-hydroxy-6,7-[2-(1-hydroxy-1-methylethyl)-2,3-dihydrofuran)]-3′,4′-(2,2-dimethylpyrano)isoflavone} has structure **2**.

7-*O*-Methylisolupalbigenin (**3**), isolated from *U. airensis*, $C_{26}H_{28}O_5$ ($[M]^+$ *m/z* 420, confirmed by HREIMS), was obtained as a yellow amorphous solid. The ^{1}H NMR and ^{13}C NMR spectra (Tables 1 and 2, respectively) showed characteristic signals of a 5-hydroxyisoflavone structure (proton signals at δ_{OH-5} 12.94 s, δ_{H-2} 7.90 s and carbon signals at δ_{C-2} 152.9 d, δ_{C-3} 123.2 s, and δ_{C-4} 181.0 s). The IR spectrum showed the corresponding carbonyl absorption of an isoflavone unit ($\nu_{C=O}$ 1651 cm^{-1}) in accordance with the presence of the α,β-unsaturated ketone of ring C, establishing a hydrogen bond with the C-5 hydroxyl group ($\nu_{C=O}$ 1609 cm^{-1}). The mass spectrum showed fragments at *m/z* 377 $[M - 43]^+$ and *m/z* 365 $[M - 55]^+$, indicating the presence of the 3,3-dimethylallyl substituent.[35] The ^{1}H NMR spectrum of 7-*O*-methylisolupalbigenin (**3**) also showed the presence of two 3,3-dimethylallyl systems (see Table 1), which must be located on rings A and B due to the aromatic signals present in the spectrum. This structural factor was confirmed by a singlet at δ 6.42 that was assigned to H-6 due to the correlations observed with C-5 and to the chemical shift value of O*H*-5 that was observed below 13 ppm (unpublished results and literature data).[4,13,27,29,36,37] The other two aromatic signals at δ 7.29−7.27 (m, 2H) and δ 6.87 (d, $J = 8.7$ Hz, 1H) were assigned to H-2′ and H-6′, and H-5′, respectively, from the HMBC experiment (Table 2). The remaining methoxyl group signal at δ 3.90 (s, 3H) was assigned to C-7 from UV (NaOMe and NaOAc), HMBC, and EIMS observations. This structure was further confirmed by the mass fragments at *m/z* 179 and 131, which corresponded to the retro Diels−Alder rupture of the ring C of the isoflavone, together with the loss of C_4H_7 of both 3,3-dimethylallyl substituents on rings A and B. From the HMQC and HMBC data all the ^{13}C NMR spectrum signals of **3** were assigned (Table 2). From the analysis of the above data it was established that 7-*O*-methylisolupalbigenin [5,4′-dihydroxy-7-methoxy-3′,8-bis-(3,3-dimethylallyl)isoflavone] has structure **3**.

The antifungal activity of flavonoids **1**−**13** identified in these two *Ulex* species was tested against *Cladosporium cucumerinum* (Table 3). The results for the remaining compounds were previously reported.[8] From these data some structure/activity comments can be drawn for all the isoflavones and pterocarpans tested.

For the various isoflavones, the 3,3-dimethylallyl substituents seem to determine the antifungal activity. The presence of these substituents at C-8 and C-3′ confers activity to the isoflavones, whereas the C-6-substituted compounds are inactive. A 2,2-dimethylpyran substituent

Table 2. ^{13}C NMR Spectral Data of Compounds **1**−**5**[a]

	1[b]		**2**[b]		**3**[c]		**4**[b]	**5**[b]
carbon	δ_C	HMBC	δ_C	HMBC	δ_C	HMBC	δ_C	δ_C
1								114.9 d
1a								111.9 s
2	153.5 d		152.7 d		152.9 d		152.8 d	140.5 s
3	122.8 s	H-2, H-2′, H-6′	123.7 s	H-2	123.2 s[e]	H-2	123.7 s[f]	147.8 s
O*C*H$_3$-3								56.0 q
4	182.6 s	H-2	181.7 s	H-2	181.0 s	H-2	181.2 s	100.0 d
4a								149.2 s
5	155.7 s	O*H*-5	157.3 s	O*H*-5	161.2 s	O*H*-5, H-6	159.8 s	
6	113.8 s	O*H*-5, H-8, H-3‴	109.2 s[d]	O*H*-5, H-8	95.2 d	O*H*-5, H-6	110.1 s	66.7 t
6a								40.5 s
7	159.0 s	H-8, H-3‴	158.4 s	H-8	162.9 s	H-6, H-1‴, *OCH*$_3$-7,	161.6 s	104.6 d
O*C*H$_3$-7					56.0 q			
7a								117.8 s
8	90.6 d		88.9 d		107.0 s	H-1‴	94.0 d	141.6 s
9	154.4 s	H-2, H-8	158.4 s	H-2, H-8	154.7 s	H-2	156.3 s	148.0 s
10	106.6 s	O*H*-5, H-8	106.7 s[d]	O*H*-5	107.9 s	O*H*-5, H-6	106.0 s	93.8 d
10a								154.2 s
11a								78.5 s
1′	123.0 s	H-2, H-2′, H-5′, H-6′	123.0 s	H-5′	123.3 s[e]	H-2, H-5′	123.2 s[f]	
2′	127.1 d		127.0 d		130.6 d	H-1″	130.7 d	
3′	121.5 s	H-5′, H-3″, H-4″	121.4 s	H-5′, H-3″	127.0 s	H-5′, H-1″	127.2 s	
4′	153.2 s	H-2′, H-5′, H-6′, H-4″	153.5 s	H-2′, H-4″	154.7 s	H-2′, H-5′, H-6′, H-1″	154.9 s	
5′	116.6 d		116.6 d		116.0 d		116.0 d	
6′	129.7 d		129.7 d		128.2 d		128.3 d	
1″					29.9 t		29.7 t	
2″	76.8 s	H-3″, H-4″, C*H*$_3$-5″, C*H*$_3$-6″	76.5 s	H-3″, H-4″, C*H*$_3$-5″, C*H*$_3$-6″	121.6 d	H-1″	121.6 d	
3″	131.2 d		131.2 d		136.0 s	H-1″	135.2 s	
4″	122.2 d		122.2 d					
*C*H$_3$-4″					17.9 q		25.7 q[f]	
*C*H$_3$-5″	25.0 q		28.0 q		25.7 q		25.7 q[f]	
*C*H$_3$-6″	25.0 q		28.0 q					
1‴					21.5 t		21.4 t	
2‴	163.2 s	H-3‴, C*H*$_3$-5‴, C*H*$_3$-6‴	91.9 d		122.0 d	H-1‴	121.2 d	
3‴	98.1 d		26.7 t		131.9 s	H-1‴	136.1 s	
4‴	69.1 s	C*H*$_3$-5‴, C*H*$_3$-6‴	71.8 s	C*H*$_3$-5‴, C*H*$_3$-6‴				
*C*H$_3$-4‴					17.9 q		17.8 q[f]	
*C*H$_3$-5‴	28.5 q		25.8 q		25.7 q		25.7 q[f]	
*C*H$_3$-6‴	28.5 q		23.8 q					
O*C*H$_2$O								101.2 t

[a] Chemical shifts are referenced to the signal of residual $CHCl_3$ (δ 77.0). [b] Spectrum obtained at 100 MHz. [c] Spectrum obtained at 50 MHz. [d−f] Assignments interchangeable in any one column.

Table 3. Bioautographic TLC Assay of Flavonoids **1**−**13** with *Cladosporium cucumerinum*[a]

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
−	−	+	−	↑	−	−	+	+	+	−	↑	+

[a] Activity at 100 μg. +, inhibition of growth; −, no inhibition of growth; ↑, induction of growth.

at C-3′/C-4′ is also important for activity since ulexin B[8] and isoderrone[8] were slightly active, and alpinumisoflavone (**7**) showed no activity. Comparison of the antifungal activity of isoderrone[8] and isowighteone (**8**) shows that substitution of the 2,2-dimethylpyran substituent at C-3′/C-4′ by a 3,3-dimethylallyl substituent at C-3′ increases the antifungal activity of the isoflavones. In both cases (2,2-dimethylpyran substituent at C-3′/C-4′ or 3,3-dimethylallyl substituent at C-3′), the presence of an extra 3,3-dimethylallyl substituent at C-8 (ulexone A[8] and isolupalbigenin[8]) must contribute to the antifungal activity since the presence of this substituent at C-6 [isochandalone[8] and lupalbigenin (**4**)] renders the compounds inactive. The fact that compounds **1**, **2**, and **7** are inactive can be justified by the fact that they are all C-6 substituted. The presence of a hydroxyl group at C-7 does not seem to be required for activity since isolupalbigenin[8] and 7-*O*-methylisolupalbigenin (**3**) are both active. Finally, the increased activity of licoisoflavone B (**9**) with respect to isoderrone[8] must be due to the presence of a hydroxyl group at C-2′.

For all the pterocarpans tested there is no particular structural feature that can be assigned as responsible for the antifungal activity. However it is important to mention that the presence of a hydroxyl group at C-2 (compounds **5** and **12**) seems to be important for the induction of growth of the fungus.

Experimental Section

General Experimental Procedures. Melting points (for known compounds) were measured in a Reichert thermovar apparatus and are uncorrected. A Perkin-Elmer 241MC polarimeter was used to obtain specific optical rotation values. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer and UV spectra on a Milton Roy Spectronic 1201 instrument. ^{1}H NMR spectra were recorded on a Bruker ARX400 NMR spectrometer at 400 MHz, and ^{13}C NMR were recorded on Bruker ARX400 and Bruker AM200 NMR spectrometers at 100 and 50 MHz, respectively. All NMR spectra were recorded in $CDCl_3$ solution and referenced by the residual chloroform signal (δ 7.26 and 77.0 ppm); δ values are expressed in ppm and *J* couplings in Hz. The EIMS were performed on Kratos MS 25RF and Hewlet Packard LC/MS HP 1100 instruments at 70 eV and the HREIMS on a Finnigan FT/MS 2001-DT at 20 eV.

Plant Material. *Ulex airensis* Espírito-Santo, Cubas, Lousã, Pardo & Costa was collected at Ramalhal, Torres Vedras, Portugal, in 1998 and *Ulex europaeus* L. ssp. *europaeus* was collected at Peninha, Sintra, Portugal, in 1994. Voucher specimens, [LISU171667] and [ASCE2595], respectively, are deposited in the herbarium of Herbário, Museu, Jardim Botânico, Faculdade de Ciências, Universidade de Lisboa.

Extraction and Isolation. Dried and finely powdered aerial parts of *U. airensis* (2 kg) were extracted successively with petroleum ether and dichloromethane at room temperature. The dried dichloromethane extract (21.4 g) was chromatographed on a Si gel 60 column (Merck) eluted with *n*-hexane−EtOAc mixtures (9:1, 8:2, 7:3, and 6:4, v/v) to obtain fractions a−d, respectively. Fraction a was separated on a Si gel column and eluted with *n*-hexane−EtOAc mixtures. After purification on Si gel 60 F_{254} TLC (Merck) with *n*-hexane−EtOAc (9:1) pure ulexin B (8.2 mg) was obtained. Fraction c was successively fractionated on Si gel 60 columns and on Si gel 60 TLC plates using *n*-hexane−EtOAc, *n*-hexane−Et_2O, or $CHCl_3$−MeOH mixtures. Final purification on Si gel 60 TLC plates using *n*-hexane−EtOAc (6:4) or $CHCl_3$−MeOH (99.4:0.6 or 98,75:1.25) mixtures as eluents afforded pure isochandalone (**6**, 4.7 mg), (6a*R*,11a*R*)-(−)-2-methoxymaackiain (1.7 mg), (6a*R*,11a*R*)-(−)-4-methoxymaackiain (5.0 mg), 7-*O*-methylisolupalbigenin (**3**, 4.4 mg), ulexin A (14.6 mg), ulexin C (**1**, 1.0 mg), 4-hydroxylonchocarpin (0.1 mg), and (6a*R*,11a*R*)-(−)-maackiain (38.2 mg), in order of increasing chromatographic polarity. Fraction d was successively fractionated on Si gel 60 columns and on Si gel 60 TLC plates using *n*-hexane−EtOAc, *n*-hexane−Et_2O, or $CHCl_3$−MeOH mixtures. Final purification on Si gel 60 TLC plates using *n*-hexanes−Et_2O (6:4) or $CHCl_3$−MeOH (97,5:2.5) afforded pure ulexin D (**2**, 0.4 mg), isoderrone (21.2 mg), lupalbigenin (**4**, 10.1 mg), and alpinumisoflavone (**7**, 0.6 mg), in order of increasing chromatographic polarity.

Dried and finely powdered aerial parts of *Ulex europaeus* ssp. *europaeus* (1.2 kg) were treated in the same way as the preceding plant, to obtain 16.0 g of a dichloromethane extract. This extract was fractionated using the same chromatographic procedures as described above, and final purification on Si gel 60 TLC plates using *n*-hexane−EtOAc (9:1), $CHCl_3$, or $CHCl_3$−MeOH (99.7:0.3, 98.75:1.25, 97,5:2.5, 95:5, or 92.5:7.5) afforded pure ulexin B (1.6 mg), (6a*R*,11a*R*)-(−)-2-methoxypterocarpin (**13**, 8.6 mg), (6a*R*,11a*R*)-(−)-2-methoxymaackiain (36.2 mg), (6a*R*,11a*R*)-(−)-4-methoxymaackiain (21.1 mg), (6a*R*,11a*R*)-(−)-2-hydroxypterocarpin (**5**, 7.3 mg), ulexin A (3.2 mg), ulexin D (**2**, 0.1 mg), 4-hydroxylonchocarpin (2.5 mg), (6a*R*,11a*R*)-(−)-maackiain (194.2 mg), isoderrone (41.2 mg), (6a*R*,11a*R*)-(−)-2-hydroxy-4-methoxypterocarpin (**12**, 2.9 mg), licoisoflavone B (**9**, 1.8 mg), onogenin (**10**, 2.5 mg), atalantoflavone (**11**, 4.4 mg), isolupalbigenin (8.3 mg), and isowighteone (**8**, 1.5 mg) in order of increasing chromatographic polarity.

Ulexin C (1): colorless oil; UV (MeOH) λ_{max} (log ϵ) 213 (4.11), 258 (4.32), 317 (sh), 341 (sh) nm; +NaOMe 230 (sh), 268, 314, 361 nm; +NaOAc 258, 315 (sh), 347 nm; +$AlCl_3$ 231, 277, 403 nm; IR (NaCl) ν_{max} 3400, 2976, 2921, 1659, 1622, 1585, 1491, 1464, 1264, 1187, 1094, 956 cm^{-1}; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2); EIMS *m*/*z* 418 $[M]^+$ (23), 403 (100), 385 (28), 345 (20), 235 (1), 194 (20), 169 (14), 139 (5), 115 (11); HREIMS *m*/*z* 418.13990 $[M]^+$ (calcd for $C_{25}H_{22}O_6$, 418.14109).

Ulexin D (2): colorless oil; $[\alpha]_D$ 20−16.7° (*c* 0.06; $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 213 (4.00), 260 (4.03), 303 (sh), 345 (sh) nm; +NaOMe 234 (sh), 272, 328 (sh) nm; +NaOAc 260, 280 (sh), 337 nm; +$AlCl_3$ 221, 227 (sh), 271, 334 (sh), 360 nm; IR (NaCl) ν_{max} 3433, 2916, 2846, 1665, 1622, 1578, 1490, 1460, 1272, 1185, 1064, 959 cm^{-1}; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2); EIMS *m*/*z* 420 $[M]^+$ (20), 405 (100), 387 (13), 361 (5), 345 (13), 177 (1), 166 (4); HREIMS *m*/*z* 420.15538 $[M]^+$ (calcd for $C_{25}H_{24}O_6$, 420.15674).

7-*O*-Methylisolupalbigenin (3): yellow amorphous solid; UV (MeOH) λ_{max} (log ϵ) 266 (4.40), 320 (sh) nm; +NaOMe 271, 347 (sh) nm; +NaOAc 266, 314 (sh) nm; +$AlCl_3$ 272, 303 (sh), 355 nm; IR (NaCl) ν_{max} 3417, 2969, 2921, 1651, 1609, 1578, 1494, 1446, 1376, 1263, 1202, 1044, 827 cm^{-1}; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2); EIMS *m*/*z* 420 $[M]^+$ (47), 405 (48), 403 (35), 379 (44), 377 (51), 365 (100), 349 (16), 321 (22), 309 (22), 297 (15), 284 (23), 267 (11), 179 (20), 167 (17), 155 (12), 149 (33), 145 (11), 131 (14), 129 (14), 115 (17), 105 (26); HREIMS *m*/*z* 420.19395 $[M]^+$ (calcd for $C_{26}H_{28}O_5$, 420.19312).

Bioautographic TLC Bioassay. The fungus *Cladosporium cucumerinum* CCMI 206 was obtained from the Culture Collection of Industrial Microorganisms (CCMI) at INETI, Lisbon, Portugal. The bioassay was performed according to Homans and Fuchs.[8,30]

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Supporting Information Available: Figures showing proposed EIMS fragmentation patterns of ulexin C (**1**) and ulexin D (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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