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Resorcinol Derivatives and Flavonoids of *Ononis natrix* Subspecies *ramosissima*

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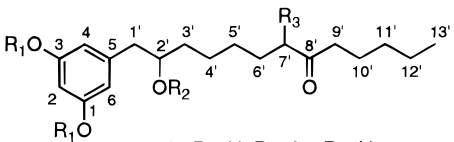
From extracts of *Ononis natrix* subsp. *ramosissima* two new resorcinol derivatives, 5-(2-acetoxy-8-oxotridecyl)resorcinol (**1**) and 5-(2-acetoxy-7-hydroxy-8-oxotridecyl)resorcinol (**2**) were isolated and identified, as well as chavicol β-D-glucoside, betulaprenol 6 (**13**), two steroids, four chalcones, six dihydrochalcones, two flavanones, and three pterocarpans.

The more polar extracts of *Ononis* species (Leguminosae) contain mainly phenolic compounds such as flavonoids and phenylpropanoids, while the less polar extracts of these species may include among their components resorcinol derivatives with an alkyl chain at position C-5. This chain may be saturated or unsaturated and may have several oxygenated functions.[1−8]

The botanical classification of the species *Ononis natrix* comprises three subspecies that grow in the Iberian Peninsula: *O. natrix*, *O. hispanica*, and *O. ramosissima*. We have previously studied the chemical composition of the *O. natrix* subsp. *natrix*[3,4] and *hispanica*.[5] In order to get a chemotaxonomic differentiation of these three subspecies we present here the results obtained with *O. natrix* L. subsp. *ramosissima* (Desf.) Batt., a plant that grows in coastal zones of southern Spain and Portugal.

Results and Discussion

Ononis natrix subsp. *ramosissima* was extracted with *tert*-butyl methyl ether and then with EtOH. Two new natural alkylresorcinols were isolated, 5-(2-acetoxy-8-oxotridecyl)resorcinol (**1**) and 5-(2-acetoxy-7-hydroxy-8-oxotridecyl)resorcinol (**2**). Additionally, the following known compounds were identified: the steroids β-sitosterol and β-sitosterol β-D-glucoside;[9−11] four chalcones, 2′,4′-dihydroxychalcone (**3**),[12−14] 2′-hydroxy-4′-methoxychalcone (**4**),[15] 4,2′,4′-trihydroxychalcone (**5**),[16] and 4,2′-dihydroxy-4′-methoxychalcone (**6**);[17] six dihydrochalcones, 2′,4′,6′-trihydroxydihydrochalcone (**7**),[18] 2′,6′-dihydroxy-4′-methoxydihydrochalcone (**8**),[18] 2′,4′-dihydroxy-6′-methoxydihydrochalcone (**9**),[19] 4,2′,6′-trihydroxy-4′-methoxydihydrochalcone (**10**),[20,21] 4,2′,4′-trihydroxy-6′-methoxydihydrochalcone (**11**),[21] and 2′,6′-dihydroxy-4,4′-dimethoxydihydrochalcone (**12**);[15] two flavanones, 7-hydroxyflavanone[13] and 5,7-dihydroxyflavanone;[22,23] three pterocarpans, medicarpin,[24] homopterocarpin,[24] and trifolirhizin;[25] the phenylpropanoid, chavicol β-D-glucoside;[26−28] and the polyprene, betulaprenol 6 (**13**).[29] The structures of the known compounds were determined by comparison of their physical and spectroscopic features with those reported in the literature. Table 1 shows previously unpublished ^{13}C-NMR data of the above-mentioned chalcones and dihydrochalcones.



1 R_1=H, R_2=Ac, R_3=H
1a R_1=Ac, R_2=Ac, R_3=H

2 R_1=H, R_2=Ac, R_3=OH

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Table 1. ^{13}C-NMR (75 MHz) Data for Chalcones and Dihydrochalcones **3**, **3a**, **4**, **5a**, **6a**, **8a**, **9a**, **10**, **11**, **12a**[a]

carbon	**3**[b]	**3a**[b]	**4**[b]	**5a**[b]	**6a**[b]	**8a**[b]	**9a**[b]	**10**[c]	**11**[c]	**12a**[b]
CO	192.8	190.4	191.8	191.1	190.8	199.3	201.3	205.8	204.0	199.4
Cα	121.7	119.2	120.3	126.8	126.7	45.5	45.6	46.6	45.6	45.8
C*β*	144.8	145.4	144.3	146.2	146.4	29.8	30.3	30.3	29.5	28.9
1	135.9	134.4	134.7	134.2	134.3	141.2	141.3	132.7	131.4	133.2
2	129.8[d]	128.5[d]	128.9[d]	129.1[d]	129.3[d]	128.7[d]	128.6[d]	130.2	129.1	129.3
3	129.6[e]	129.1[e]	128.4[e]	128.6[e]	128.5[e]	128.6[e]	128.4[e]	116.2	115.1	113.9
4	131.4	130.8	130.5	131.1	131.0	126.2	125.1	156.5	155.4	158.0
5	129.6[e]	129.1[e]	128.4[e]	128.6[e]	128.5[e]	128.6[e]	128.4[e]	116.2	115.1	113.9
6	129.8[d]	128.5[d]	128.9[d]	129.1[d]	129.2[d]	128.7[d]	128.6[d]	130.2	129.1	129.3
1′	114.5	129.7	114.0	118.3	119.6	119.3	121.6	105.9	104.4	120.2
2′	165.9	149.6	166.2	149.7	151.7	149.3	148.4	165.6	163.0	149.2
3′	103.8	117.1	101.0	108.7	108.9	106.8	109.1	94.1	95.8	106.7
4′	167.7	153.4	166.6	159.4	159.2	161.4	152.4	166.6	164.9	161.3
5′	108.9	125.0	107.6	108.7	108.9	106.8	103.0	94.1	91.4	106.7
6′	133.6	130.8	131.2	149.7	151.7	149.3	158.0	165.6	166.1	149.2
OCH_3			55.5		61.7	55.9	56.1	56.3	55.8	55.8
OCH_3										55.3
CH_3COO		169.0		169.6	169.3	168.6	169.4			168.6
CH_3COO		168.6					168.9			
$\boldsymbol{C}H_3COO$		21.1		20.9	21.1	21.2	21.2			20.9
CH_3COO		20.9					20.4			

[a] Assignments were made by the use of DEPT experiments and the application of additivity rules. [b] $CDCl_3$. [c] DMSO-d_6. [d,e] May be interchanged.

Compound **1** was isolated as an oily product; its molecular formula was established by HRCIMS as $C_{21}H_{32}O_5$. The IR spectrum had absorption bands indicative of hydroxyl (3370 cm^{-1}), acetoxyl (1741 cm^{-1}), aliphatic ketone (1703 cm^{-1}), and aromatic ring (1603, 1512, 838 cm^{-1}) functionalities. Its ^{13}C-NMR spectrum showed signals for a ketone (*δ* 213.4), an acetoxyl (*δ* 172.0, 21.3), four signals due to an aromatic ring 1,3,5-symmetrically substituted (*δ* 157.1, 2C; 140.1, 1C; 108.7, 2C; 101.3, 1C), and twelve signals of a linear chain in which one carbon atom was attached to oxygen by a single bond (*δ* 75.2). All of these data corresponded to a 5-alkylresorcinol skeleton with two oxygenated functions in the side chain, namely an acetoxyl and a carbonyl. The acetoxyl group was positioned at C-2′ because the signal in the ^{1}H-NMR spectrum due to the proton geminal to this group (*δ* 5.00, dddd, J = 6.5 Hz) was coupled to the signals of the benzylic protons (*δ* 2.69, dd, J = 13.7, 6.5 Hz; *δ* 2.59, dd, J = 13.7, 6.5 Hz). Study of the chemical shifts in the ^{13}C-NMR spectrum of the carbons in the side chain, as well as analysis of the prominent peaks of the mass spectrum, served to locate the carbonyl group at C-8′ in the side chain. Thus, the ^{13}C-NMR signals could only be rationalized if the keto group were at either the C-7′ or the C-8′ position. However, the EIMS peaks corresponding to deacetylation and subsequent α-fragmentation from the carbonyl would occur only if this functionality were at C8′, hence the fragment ions at m/z 71 $[C_5H_{11}]^+$, 99 $[COC_5H_{11}]^+$, 205 $[M - AcOH\text{-}COC_5H_{11}]^+$, and 233 $[M - AcOH - C_5H_{11}]^+$ appeared at relative abundances ranging between 8 and 58%, while fragment peaks due to the same pattern of fragmentation but with the keto group at C-7′ at m/z 85 $[C_6H_{13}]^+$, 111 $[COC_6H_{13}]^+$, 191 $[M - AcOH - COC_6H_{13}]^+$ and 233 $[M - AcOH - C_6H_{13}]^+$ were not present in the CIMS or were of extremely low relative abundance. Compound **1** is a new natural product, and its other physical and spectroscopic features, as well as those of its acetylated derivative **1a**, were in agreement with the proposed structure.

Compound **2**, with a molecular formula of $C_{21}H_{32}O_6$ as deduced from its HRCIMS, differed from compound **1** by the presence of an additional hydroxyl group which must be in an α- position to the carbonyl, because the proton geminal to the OH group appeared in the ^{1}H-NMR spectrum as a multiplet was somewhat deshielded (*δ* 4.08), and the carbon that bore it also gave a signal in the ^{13}C-NMR spectrum at lower field than the usual values for hydroxyls in linear chains (*δ* 77.4). The location of this CO−CHOH substructure in the side chain could be made through the analysis of its ^{13}C-NMR and EIMS spectra. In the latter, the fragmentation peaks due to the cleavage of the C7−C8 bond—considering that the OH was at C-7′ and the keto function was at C-8′—were of high relative abundances (m/z 221 (82) $[M - AcOH - COC_5H_{11}]^+$ and 99 (19) $[COC_5H_{11}]^+$), while the peaks due to the same fragmentation pattern—but considering that the OH was at C-8′ and the keto function was at C-7′ (m/z 219 $[M - AcOH - CHOHC_5H_{11}]^+$ and 99 (19) $[CHOHC_5H_{11}]^+$)—were not present in the CIMS. Other spectroscopic features of **2** were in agreement with the proposed structure for this new natural product.

Among the three subspecies of *O. natrix* (subsp. *natrix*, subsp. *hispanica*, and subsp. *ramosissima*) three main phytochemical differences were found: (a) a quantitative difference between the ratio of more polar compounds (flavonoids) to less polar compounds (alkylresorcinols) [The alkylresorcinols were the main components in subsp. *natrix* and subsp. *hispanica*, while in subsp. *ramosissima* the flavonoids were the major components.]; (b) the absence of alkylbenzoates and alkylisocoumarins in subsp. *ramosissima*; and (c) the absence of chalcones and dihydrochalcones in subsp. *natrix* and subsp. *hispanica*.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. UV spectra were recorded on a Bausch and Lomb Spectronic 2000 UV-vis spectrometer and IR spectra on a Perkin-Elmer 983G spectrometer. HRMS were determined on a VG-Analytical (Fisons) Autospec-Q mass spectrometer, and LRMS were determined on a Hewlett-Packard 5988A mass spectrometer. NMR spectra were

recorded on a Bruker ARX 400 spectrometer, a Bruker AMX 300 spectrometer, or a Bruker WP 80 SY spectrometer (δ values given in ppm relative to internal Me_4Si (= 0) and J values in Hz). Assignments of ^{13}C-NMR signals were made with the aid of additivity rules and DEPT experiments. Column chromatography was carried out using Si gel Merck 60 (70−230 mesh), eluting with mixtures of hexane−*tert*-butylmethyl ether or $CHCl_3$−Me_2CO of increasing polarity. Analytical TLC was performed on Si gel Merck 60 G layers of 0.25 mm thickness, using a 7% phosphomolybdic acid solution (EtOH) for compound visualization.

Plant Material. *O. natrix* subsp. *ramosissima* was collected at Barbate, Cádiz, Spain, in June 1993. The plant material was identified by Professor F. Valle, Department of Botany, University of Granada. A voucher specimen is available for inspection at the Herbarium of the Faculty of Sciences of the University of Granada.

Extraction and Isolation. The air-dried aerial parts (8 kg) of *O. natrix* subsp. *ramosissima* were submerged in *t*-butylmethyl ether (15 min) and subsequently extracted in a Soxhlet with EtOH (24 h). From the *t*-butylmethyl ether extract (250 g, 3.1% of dried plant) fatty acids (81 g, 32% of extract) were removed by precipitation in MeOH at low temperature. The defatted extract (169 g, 68%) was then column chromatographed, eluting with hexane−*t*-butylmethyl ether mixtures of increasing polarity. Acetyl derivatives of some of these fractions were prepared to improve the chromatographic behavior of the products. From the nonacetylated fractions, the following compounds were isolated: β-sitosterol (1.2 g, 0.5% of the extract); 5-(2-acetoxy-8-oxotridecyl)resorcinol (**1**) (6.3 g, 2.5%); 2′,4′-dihydroxychalcone (**3**) (29.4 g, 11.8%), 2′-hydroxy-4′-methoxychalcone (**4**) (44 mg, 0.02%), 2′,4′,6′-trihydroxydihydrochalcone (**7**) (250 mg, 0.1%); 7-hydroxyflavanone (6.1 g, 2.4%); 5,7-dihydroxyflavanone (12.9 g, 5.2%); homopterocarpin (75 mg, 0.03%), and (2*E*,6*E*,10*E*,14*E*,18*E*,22*E*)-3,7,11,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaen-1-ol (**13**) (500 mg, 0.2%). From the acetylated fractions, the following compounds were isolated: 2′,4′,4-triacetoxychalcone (**5a**) (2.8 g, 1.1%); 4,2′-diacetoxy-4′-methoxychalcone (**6a**) (2.5 g, 1.0%); 2′,6′-diacetoxy-4′-methoxydihydrochalcone (**8a**) (5.6 g, 2.2%); 2′,4′-diacetoxy-6′-methoxydihydrochalcone (**9a**) (10.4 g, 4.2%); 2′,6′-diacetoxy-4,4′-dimethoxydihydrochalcone (**12a**) (1.4 g, 0.6%), and medicarpin acetate (375 mg, 0.2%).

The EtOH extract (120 g, 1.5%) was column chromatographed eluting with mixtures of $CHCl_3$−Me_2CO of increasing polarity. Acetyl derivatives of some of the fractions obtained were prepared to improve their chromatographic behavior. In order of increasing polarity, the following compounds were isolated from the nonacetylated fractions: 4,2′,6′-trihydroxy-4′-methoxydihydrochalcone (**10**) (350 mg, 0.3%), 2′,4′,4-trihydroxy-6′-methoxydihydrochalcone (**11**) (350 mg, 0.3%); and 5-(2-acetoxy-7-hydroxy-8-oxotridecyl)resorcinol (**2**) (690 mg, 0.6%). From the acetylated fractions, the following compounds were isolated: 5,7-diacetoxydihydroflavanone (750 mg, 0.6%); 2′,4′-diacetoxychalcone (**3a**) (610 mg, 0.5%); β-D-glucopyranosyl-β-sitosterol tetraacetate (160 mg, 0.1%); β-D-glucopyranosyl-4-(2-propenyl)phenol tetraacetate (chavicol tetra-*O*-acetyl-β-D-glucoside) (200 mg, 0.2%), and trifolirhizin tetraacetate (480 mg, 0.4%).

5-(2-Acetoxy-8-oxotridecyl)resorcinol (1): colorless oil; $[\alpha]^{20}_D$ −1.5° (*c* 0.65, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 224 (3.72), 272 (3.30), 282 (3.30) nm; IR (film) ν_{max} 3370 (OH), 2930, 2857, 1741 (OAc), 1703 (CO), 1603 (Ar), 1512, 1454, 1375, 1267, 1160, 1025, 838 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.23 (3H, br s, H-2, H-4, H-6), 5.00 (1H, dddd, J = 6.5 Hz, H-2′), 2.69 (1H, dd, J = 13.7, 6.5 Hz, H-1′A), 2.59 (1H, dd, J = 13.7, 6.5 Hz, H-1′B), 2.37 (2H, t, J = 7.4 Hz, H-7′), 2.36 (2H, t, J = 7.4 Hz, H-9′), 1.97 (3H, s, AcO−C-2′), 1.55 (2H, m, $W_{1/2}$ = 3 Hz, H-3′), 1.23 (14H, m, $W_{1/2}$ = 2 Hz, H-4′-H-7′, H-10′-H-12′), 0.85 (3H, t, J = 6.7 Hz, H-13′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 213.4 (C, C-8′), 172.0 (C, AcO-2′), 157.1 (C, C-1, C-3), 140.1 (C, C-5), 108.7 (CH, C-4, C-6), 101.3 (CH, C-2), 75.2 (CH, C-2′), 42.9, 42.6 (CH_2, C-7′, C-9′), 40.5 (CH_2, C-1′), 33.2 (CH_2, C-3′), 31.4 (CH_2, C-11′), 28.9 (CH_2, C-5′), 25.1 (CH_2, C-4′), 23.6, 23.6 (CH_2, C-6′, C-10′), 22.5 (CH_2, C-12′), 21.3 (CH_3, AcO-2′), 14.1 (CH_3, C-13′); EIMS (70 eV) *m*/*z* $[M]^+$ 364 (8), 322 (2) $[M - CH_2CO]^+$, 304 (27) $[M - AcOH]^+$, 233 (8) $[M - AcOH - C_5H_{11}]^+$, 205 (9) $[M - AcOH - COC_5H_{11}]^+$, 181 (77), 163 (62), 149 (69), 137 (88), 124 (100) $[C_7H_8O_2]^+$, 99 (46) $[COC_5H_{11}]^+$, 71 (58) $[C_5H_{11}]^+$; HRCIMS (CH_4) *m*/*z* $[MH]^+$ 365.2319 (calcd for $C_{21}H_{33}O_5$ 365.2328).

1,3-Di-*O*-acetyl-5-(2-acetoxy-8-oxotridecyl)resorcinol (1a): colorless oil; $[\alpha]^{20}_D$ −1.4° (*c* 1.05, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 220 (3.40), 263 (2.85) nm; IR (film) ν_{max} 2928, 2863, 1769 (OAc), 1734 (OAc), 1715 (CO), 1615, 1592 (Ar), 1452, 1370, 1239, 1197, 1124, 1024, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 6.78 (3H, br s, H-2, H-4, H-6), 5.03 (1H, dddd, J = 6 Hz, H-2′), 2.81 (2H, br d, J = 6 Hz, H-1′), 2.36 (4H, t, J = 7 Hz, H-7′, H-9′), 2.23 (6H, s, AcO−Ar), 1.99 (3H, s, AcO−C-2′), 1.68−1.13 (14H, br s, H-3′−H-6′, H−10′-H-12′), 0.88 (3H, m, $W_{1/2}$ = 6 Hz, H-13′); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 211.0 (C, C-8′), 170.8 (C, AcO-2′), 169.0 (C, AcO-1, AcO-3), 151.0 (C, C-1, C-3), 140.0 (C, C-5), 120.0 (CH, C-4, C-6), 113.6 (CH, C-2), 74.1 (CH, C-2′), 42.9, 42.67 (CH_2, C-9′, C-7′), 40.4 (CH_2, C-1′), 33.5 (CH_2, C-3′), 31.5 (CH_2, C-11′), 29.1 (CH_2, C-5′), 25.3 (CH_2, C-4′), 23.7, 23.7 (CH_2, C-10′, C-6′), 22.5 (CH_2, C-12′), 19.3 (CH_3, AcO-1, AcO-3, AcO-2′), 14.0 (CH_3, C-13′); EIMS (70 eV) *m*/*z* $[M]^+$ 448 (0.2), 406 (0.3) $[M - CH_2CO]^+$, 388 (1) $[M - AcOH]^+$, 346 (2) $[M - AcOH - CH_2CO]^+$, 304 (6) $[M - AcOH - 2(CH_2CO)]^+$, 233 (4) $[M - AcOH - 2(CH_2CO) - C_5H_{11}]^+$, 205 (3) $[M - AcOH - 2(CH_2CO) - COC_5H_{11}]^+$, 199 (2), 181 (28), 124 (21), 99 (8) $[COC_5H_{11}]^+$, 71 (9) $[C_5H_{11}]^+$, 43 (100).

5-(2-Acetoxy-7-hydroxy-8-oxotridecyl)resorcinol (2): white powder; $[\alpha]^{20}_D$ +3.7° (*c* 2.03, Me_2CO); UV (MeOH) λ_{max} (log ϵ) 208 (4.16), 276 (3.30), 284 (3.29), 327 (3.09) nm; IR (film) ν_{max} 3364 (OH), 2933, 2861, 1711 (OAc), 1605 (Ar), 1516, 1506, 1499, 1455, 1376, 1341, 1268, 1247, 1161, 1073, 1048, 1025, 999, 842, 830, 806, 706, 675 cm^{-1}; ^1H NMR (Me_2CO-d_6, 300 MHz) δ 6.21 (3H, s, H-2, H-4, H-6), 4.96 (1H, dddd, J = 6.5 Hz, H-2′), 4.08 (1H, m, $W_{1/2}$ = 9 Hz, H-7′), 2.69 (1H, dd, J = 13.6, 6.5 Hz, H-1′A), 2.61 (1H, dd, J = 13.6, 6.5 Hz, H-1′B), 2.54 (2H, t, J = 7.1 Hz, H-9′), 1.94 (3H, s, AcO−C-2′), 1.55 (4H, m, $W_{1/2}$ = 13 Hz, H-3′, H-6′), 1.27 (10H, m, $W_{1/2}$ = 17 Hz, H-4′, H-5′, H-10′, H-11′, H-12′), 0.86 (3H, t, J = 7.5 Hz, H-13′); ^{13}C NMR (Me_2CO-d_6, 75 MHz) δ 213.7 (C, C-8′), 170.7 (C, AcO-2′), 159.20 (C, C-1, C-3), 140.8 (C, C-5), 108.6 (CH, C-4, C-6), 101.6 (CH, C-2),

77.4 (CH, C-7′), 74.9 (CH, C-2′), 41.0 (CH_2, C-1′), 37.9 (CH_2, C-9′), 34.3 (CH_2, C-3′), 33.9, 32.3 (CH_2, C-6′, C-11′), 25.4 (CH_2, C-4′, C-10′), 23.8, 23.12 (CH_2, C-5′, C-12′), 21.1 (CH_3, AcO-2′), 14.3 (CH_3, C-13′); EIMS (70 eV) *m*/*z* $[M]^+$ 380 (8), 320 (8) $[M - AcOH]^+$, 270 (13), 249 (1) $[M - AcOH - C_5H_{11}]^+$, 235 (10), 222 (13), 221 (82) $[M - AcOH - COC_5H_{11}]^+$, 203 (40) $[M - AcOH - COC_5H_{11} - H_2O]^+$, 201 (10), 193 (13), 192 (83) $[M - AcOH - CHOHCOC_5H_{11}]^+$, 191 (6), 177 (12), 175 (11), 163 (19), 161 (15), 150 (10), 149 (26), 137 (17), 136 (14), 124 (100) $[C_7H_8O_2]^+$, 123 (73) $[C_7H_7O_2]^+$, 99 (19) $[COC_5H_{11}]^+$, 83 (11), 71 (13) $[C_5H_{11}]^+$, 67 (12), 55 (27), 43 (81); HRCIMS (CH_4) *m*/*z* $[MH]^+$ 381.2272 (calcd for $C_{21}H_{33}O_6$ 381.2277).

(2*E*,6*E*,10*E*,14*E*,18*E*,22*E*)-3,7,11,15,19,23-Hexamethyl-2,6,10,14,18,22-tetracosahexaen-1-ol (13): colorless oil; IR (film) ν_{max} 3353 (OH), 2960, 2924, 2840, 1666 (C=C), 1448, 1380, 1101 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.42 (1H, t, J = 6.9 Hz, H-2), 5.12 (5H, t, J = 6.9 Hz, H-6, H-10, H-11, H-18, H-22), 4.15 (2H, d, J = 6.9 Hz, H-1), 2.08 (10H, m) and 1.99 (10H, m) (H-4, H-5, H-8, H-9, H-12, H-13, H-16, H-17, H-20, H-21), 1.68 (3H, s, Me-24), 1.60 (18H, s, C-3-Me, C-7-Me, C-11-Me, C-15-Me, C-19-Me, C-23-Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.9 (C, C-3), 135.0, 135.0, 135.0, 135.0 (C, C-7, C-11, C-15, C-19), 131.3 (C, C-23), 124.5, 124.4, 124.3, 124.3, 123.8, 123.4 (CH, C-2, C-6, C-10, C-14, C-18, C-22), 59.45 (CH_2, C-1), 39.81, 39.79, 39.63 (CH_2, C-5, C-9, C-13, C-17, C-21), 26.85, 26.78, 26.75, 26.41 (CH_2, C-4, C-8, C-12, C-16, C-20), 25.74 (CH_3, C-24), 17.73, 16.35, 16.05, 16.06 (CH_3, C-25, C-26, C-27, C-28, C-29, C-30); EIMS (70 eV) *m*/*z* $[M]^+$ 426 (1), 409 (8), 167 (16), 143 (24), 141 (10), 127 (18), 125 (15), 113 (11), 111 (14), 109 (13), 101 (100), 99 (25), 95 (13), 85 (18).

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