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RESORCINOL DERIVATIVES AND OTHER COMPONENTS OF *ONONIS SPECIOSA*

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Key Word Index—*Ononis speciosa*; Leguminosae; Trifoliae; resorcinol derivatives; flavonoids.

Abstract—From the flowers of *Ononis speciosa*, flavonoids, terpenoids, sterols phenolic acids, cardol monoene and methyl 6-(pentadec-8*Z*-enyl)-2,4-dimetoxybenzoate, as well as the three new compounds: 5-(10-acetoxy-pentadec-8*Z*-enyl)-resorcinol, methyl 6-(10-acetoxy-pentadec-8*Z*-enyl)-2,4-dimetoxybenzoate and 6″-*O*-acetylononin have been isolated.

INTRODUCTION

Ononis speciosa lag is an endemic shrub of the south of Spain which can reach 1.5 m in height. Although there are some reports on the chemical constituents of *Ononis* species, the components of *O. speciosa* have not been reported.

RESULTS AND DISCUSSION

Ononis speciosa was found to contain the known compounds, phytol, β-sitosterol, penduletin, formononetin, salicylic acid, *p*-hydroxybenzoic acid, quercetin, ononitol and the resorcinol derivative cardol monoene (**1a**). All of these compounds were characterized either by direct comparison with authentic samples or by comparison of their physical and spectroscopic properties with published data [1–4]. The shrub also yielded the flavonoïd glycosides **5a** and **5b** and three resorcinol derivatives, **2a**, **3a** and **4a**. **3a** is reported for the second time in plants, having been identified previously through its derivative methyl 6-(pentadec-8*Z*-enyl)-2,4-dimethoxybenzoate (**3b**) [5].

Compound **1a** is an oily liquid whose spectroscopic and physical properties (IR, UV, ^{1}H NMR, ^{13}C NMR and MS) are identical to those for cardol monoene [1, 2]. We confirmed its structure by preparing some derivatives, i.e. the diacetate (**1b**) and the methyl ether (**1c**) which was transformed into **1d** by hydrogenation.

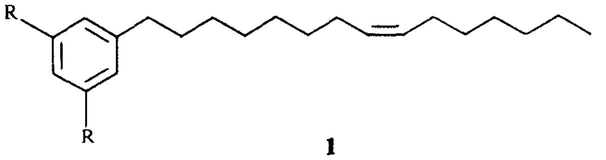
Compound **2a** has a similar ^{1}H NMR spectrum to that of **1**, except for a new signal at δ 2.05 corresponding to an acetoxy group. Its ^{13}C NMR spectrum also shows signals due to this group (δ 172.0 and 21.4), as well as those due to the methine bonded to the acetoxy function (δ 71.4) and to two olefinic methines (δ 127.8 and 134.5). The other signals were similar to those of cardol monoene. This substance, therefore, must have a cardol monoene skeleton with an additional aliphatic acetoxy group, which is located in an allylic position. The ^{13}C NMR spectra of **1a**–**1c** show only one signal corresponding to the two olefinic carbons; however, **2a** shows two ^{13}C NMR signals for methine carbons with olefinic character, whose intensities are noticeably smaller than those of compound **1**. Moreover, in these substances the two allylic methylenes give one signal with an intensity markedly higher than that corresponding to one carbon atom. In the spectrum of **2a**, however, the allylic methylene absorption has an intensity equivalent to one carbon atom.

Saponification of **2a** leads to **2b**, the mass spectrum of which places the hydroxyl group at C-10. Thus ions are observed at *m/z* 287 $[M-C_2H_5-H_2O]^+$, 273 $[M-C_3H_7-H_2O]^+$, 259 $[M-C_4H_{10}-H_2O]^+$ whereas ions corresponding to 305 $[M-C_2H_5]^+$, 291 $[M-C_3H_7]^+$, 277 $[M-C_4H_9]^+$ are not detectable. The appearance of a peak of relatively high intensity (7.3) at *m/z* 263, corresponding to the loss of C_5H_{11} from the non-dehydrated molecular ion, is attributed to the formation of a relatively stable ion like **6**. As expected, a peak at *m/z* 141 corresponding to the ion (**7**) which would be formed if the hydroxyl was at C-7 of the chain, is not observed.

Compound **2c** was obtained by methylation of **2a**. Its saponification and subsequent oxidation yielded the ketone **2d**. The mass spectrum of this substance confirms the previous assignment, since it gives an ion at *m/z* 289 $[M-C_5H_{11}]^+$ which corresponds to the α-ketone fragmentation of **2d**. The absence of an ion at *m/z* 139 (**8**) confirmed that the keto group was not at C-7.

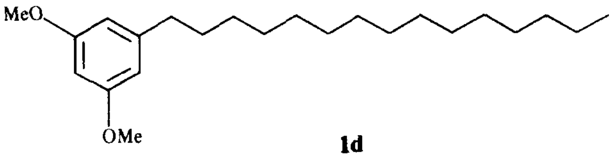
The new natural product **4a** was characterized through its derivative **4b**, $[M]^+ = m/z$ 462 ($C_{27}H_{42}O_6$), which gave a similar IR spectrum to that of **3b**, apart from the presence of absorptions attributable to the presence of an acetoxy function. The ^{1}H and ^{13}C NMR spectra reveal that the acetoxy group is linked to an allylic position of methyl 6-(pentadec-8*Z*-enyl)-2,4-dimethoxybenzoate. This position is C-10 by analogy with compound **2**.

Compound **5b** is a new natural product with similar spectroscopic features to those of ononin (**5a**) [4], although it has an acetoxy group which appears in the IR spectrum at 1737 cm^{-1} and in the ^{1}H NMR at δ 2.04. The acetoxy group is located at C-6″ as can be deduced from the ^{1}H NMR data (δ 4.18, *dd*, *J* = 12 Hz, *J* = 6 Hz; δ 4.50 *dd*, *J* = 12 Hz, *J* = 2 Hz) and from the observed chemical shift of the single methylene group in the ^{13}C NMR spectrum (δ 63.3).



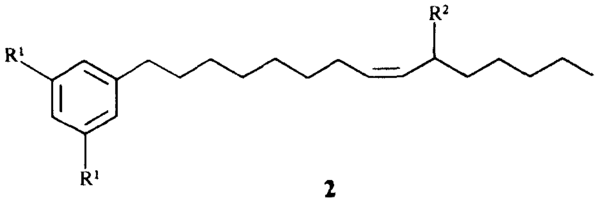
1

1a R = OH
1b R = OAc
1c R = OMe



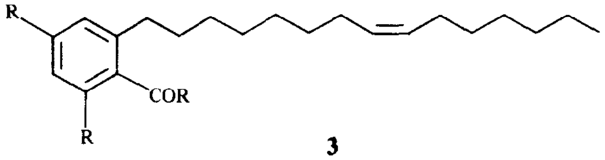
1d

1d



2

2a R^1 = OH, R^2 = OAc
2b R^1 = OH, R^2 = OH
2c R^1 = OMe, R^2 = OAc
2d R^1 = OMe, R^2 = O$=$



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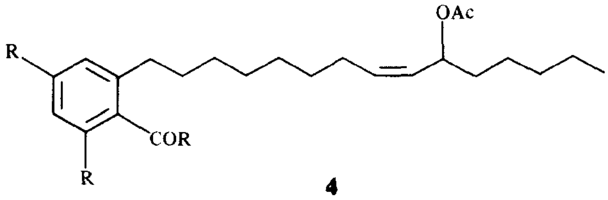
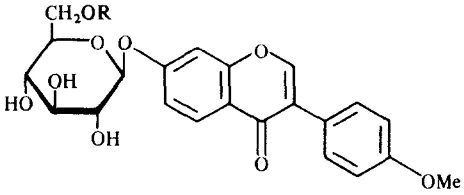
3a R = OH
3b R = OMe



4

4a R = OH
4b R = OMe



5

5a R = H
5b R = Ac

EXPERIMENTAL

Plant material was collected in May at Izbor (Granada, Spain) and has been identified by Professor F. Valle (Department of Botany, Granada University). A voucher specimen is available for inspection at the herbarium of the Faculty of Sciences of the University of Granada. The flowers were air-dried (1.55 kg) and then extracted with $CHCl_3$ followed by EtOH in a Soxhlet apparatus. The $CHCl_3$ extract was defatted and extracted with a 4% NaOH soln giving 8.99 g of a neutral fraction and 62.58 g of an acid one. The former was chromatographed on a silica gel column eluting with $CHCl_3$–MeOH mixtures, affording phytol (16 mg) and β-sitosterol (18 mg). The acid extract gave, upon chromatography, penduletin (2.19 g), formononetin (4.03 g), cardol monoene (**1a**) (675 mg), **2a** (4.7 g), and a mixture from which, after methylation with Me_2SO_4, K_2CO_3 and Me_2CO, **3b** (477 mg) and **4b** (613 mg) were isolated. The EtOH extract, after removal of the solvent, was mixed with 1.5 l of H_2O and extracted with $CHCl_3$ and EtOAc. From the former soln, ononin (22.01 g) was isolated. The EtOAc extract was chromatographed to give salicylic acid (22 mg), *p*-hydroxybenzoic acid (83 mg), **5b** (249 mg) and quercetin (288 mg). Finally, ononitol (160 mg) crystallized from the aq. liquor.

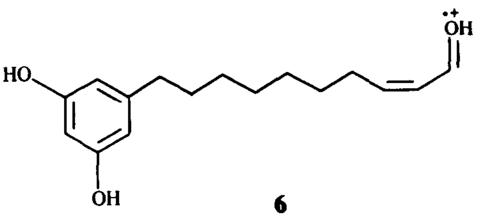
5-(*10-acetoxy-pentadec-8Z-enyl*)-*Resorcinol* (**2a**). Eluted with $CHCl_3$–MeOH (99:1) on silica gel CC. Oil. ^1H NMR ($CDCl_3$): δ0.90 (3H, *t*, $J = 6$ Hz, Me), 1.31 [16H, *m*, $(CH_2)_8$], 1.52 (2H, *m*, $-CH_2-CH_2-Ar$), 2.00 (2H, *m*, $-\underline{CH_2}-CH{=}CH-$), 2.05 (3H, *s*, –OAc), 2.43 (2H, *m*, CH_2–Ar), 5.33 (2H, *t*, $J = 7$ Hz, CH=CH) (1H, *m*, H_{gem}–OAc), 6.22 (3H, *s*, H-Ar), 6.50 (2H, *m*, HO–Ar).

5-(*10-hydroxy-pentadec-8Z-enyl*)-*Resorcinol* (**2b**). Obtained by saponification of **2a** (2M KOH/MeOH, room temp.) Mp 87–88° ($CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3412, 2929, 1599, 1158, 997, 839;

Table 1. ^{13}C NMR spectral data of the alkenylresorcynols **1–4** (20.15 MHz, Cl_3CD, TMS as internal standard)

C	**1a**	**1b**	**1c**	mult.	**2a**	**2b**	mult.	**3b**	mult.	**4b**	mult.
1	156.29	150.93	160.73	C	156.70	160.56	C	116.39	C	116.34	C
2	100.38	112.54	97.52	CH	100.37	97.48	CH	158.05	C	157.99	C
3	156.29	150.93	160.73	C	156.70	160.56	C	96.19	CH	96.19	CH
4	108.12	118.71	106.43	CH	108.00	106.33	CH	161.41	C	161.37	C
5	146.09	145.22	145.20	C	145.84	145.04	C	105.89	CH	105.85	CH
6	108.12	118.71	106.43	CH	108.00	106.33	CH	143.06	C	143.03	C
1′	35.82	35.64	36.23	CH_2	35.84	36.08	CH_2	33.94	CH_2	34.73	CH_2
2′	31.68**	31.74**	31.75**	”	31.74**	31.42**	”	31.15**	”	31.07**	”
3′	30.97*	30.81*	31.17*	”	30.62*	31.00*	”	29.74*	”	29.61*	”
4′	29.66*	29.69*	29.71*	”	29.70*	29.32*	”	29.48*	”	29.14*	”
5′	29.35*	29.23*	29.49*	”	29.32*	29.10*	”	29.74*	”	29.47*	”
6′	29.24*	29.12*	29.34*	”	28.96*	29.10*	”	29.30*	”	29.26*	”
7′	27.14	27.14	27.15	”	27.18	27.68	”	27.20	”	27.86	”
8′	129.76	129.82	129.84	CH	129.89	128.06	CH	129.84	CH	128.17	CH
9′	129.76	129.73	129.73	CH	134.41	133.79	CH	129.93	”	133.98	”
10′	27.14	27.14	27.15	CH_2	71.36	70.25	CH	27.20	CH_2	70.44	”
11′	29.66*	28.95*	29.19*	”	34.71	34.58	CH_2	29.30*	”	33.89	CH_2
12′	29.35*	29.12*	28.96*	”	24.64	24.53	”	28.99*	”	24.65	”
13′	31.85**	31.74**	31.75**	”	31.54**	31.77**	”	31.78**	”	31.57**	”
14′	22.54	22.60	22.60	”	22.45	22.33	”	22.64	”	22.45	”
15′	13.97	13.97	13.98	Me	13.89	13.72	Me	14.04	Me	13.87	Me
MeOAr			55.00			54.93		55.88		55.83	
MeOAr			55.00			54.93		55.32		55.29	
MeCOOAr		20.91								21.21	
MeCOOAr		168.69								170.23	
MeCOOR					21.32	20.99					
MeCOOR					171.91	170.01					
MeOCOAr								51.93		51.85	
MeOCOAr								167.90		167.87	

**, * Interchangeable values



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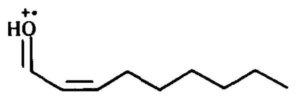

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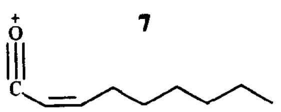

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^{1}H NMR (Me_2CO-d_6): δ0.89 (3H, *t*, $J = 6$ Hz, Me), 1.34 [18H, *m*, $(CH_2)_9$], 1.34 [18H, *m*, $(CH_2)_9$], 2.00 (2H, *m*, $-CH_2-CH=CH$), 2.44 (2H, *t*, $J = 7$ Hz, CH–Ar), 4.36 (1H, *m*, H_{gem}–OH), 5.34 (2H, *m*, CH=CH), 6.16 (3H, *s*, H–Ar), 7.95 (2H, *s*, OH–Ar); UV λ_{max}^{MeOH} nm (log ε): 272 (3.51); $[\alpha]_D^{20} + 7.47°$ ($CHCl_3$; $c = 0.49$); EIMS *m/z* (rel. int.): 334 (1.9) $[M]^+$, 316 (9.7), 287 (1.7), 274 (1.9), 263 (7.3), 193 (2.0), 191 (3.7), 177 (5.5), 179 (2.7), 163 (15.7), 165 (2.0), 149 (8.9), 151 (2.8), 137 (11.8), 139 (2.1), 124 (100), 123 (42.5).

5-(10-*acetoxy-pentadec*-8Z-*enyl*)-*Resorcinol dimethyl ether* (**2c**) was obtained upon methylation (Me_2SO_4, Me_2CO and K_2CO_3) of **2a**. Oil. IR ν_{max}^{film} cm^{-1}: 2930, 2860, 1740, 1600, 1465, 1240, 1210, 1155, 1060, 1020, 830, 700; ^{1}H NMR ($CDCl_3$): δ0.86 (3H, *t*, $J = 6$ Hz, Me), 1.31 [16H, *m*, $(CH_2)_8$], 1.65 (2H, *m*, $-\underline{CH_2}-CH_2-Ar$), 2.00 (3H, *s*, AcO–), 2.00 (2H, *m*, $-CH_2-CH=CH$), 2.54 (2H, *t*, $J = 7$ Hz, $-CH_2-Ar$), 3.77 (6H, *s*, 2MeO–Ar), 5.37–5.56 (2H, *m*, $-\underline{CH}=\underline{CH}-CH-OAc$) (1H, *m*, H_{gem}–OAc), 6.33 (3H, *br s*, H–Ar); UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 270.9 (3.23). $[\alpha]_D^{20} - 5.25°$ ($CHCl_3$; *c* 0.98); EIMS *m/z* (rel. int.) : 404 (6.9) $[M]^+$, 389 (0.9), 362 (1.2), 344 (8.9), 301 (1.0), 291 (2.0), 273 (2.0), 259 (1.6), 245 (3.5), 233 (2.3), 221 (1.2), 177 (3.6), 165 (12.9), 152 (100), 151 (22.7).

5-(10-*oxo-pentadec*-8Z-*enyl*)-*Resorcinol dimethylether* (**2d**) was obtained by saponification of **2c** (2M KOH–MeOH) and oxidation (pyridinium dichromate) of the resulting alcohol. Oil. IR ν_{max}^{film} cm^{-1}: 2925, 2840, 1683, 1590, 1450, 1200, 1140, 1050, 820, 690; ^{1}H NMR (Me_2CO-d_6): δ0.89 (3H, *t*, $J = 6$ Hz, Me), 1.32 [14H, *m*, $(CH_2)_7$], 1.62 (2H, *m*, $-CH_2-CH_2-Ar$) (2H, *m*, $-\underline{CH_2}-CH=CH-CO$), 2.09–2.55 (4H, *m*, $-\underline{CH_2}-Ar$, $-\underline{CH_2}-CO$), 3.75 (6H, *s*, 2MeO-Ar), 6.08 (2H, *m*, CH=CH), 6.32 (3H, *m*, H–Ar); EIMS *m/z* (rel. int.): 360 (14.8) $[M]^+$, 345 (3.0), 317 (2.2), 289 (1.8), 221 (2.1), 207 (2.1), 193 (1.7), 165 (17.4), 152 (100), 151 (21.3).

Table 2. ^{13}C NMR spectral data of ononin (**5a**) and 6″-*O*-acetilononin (**5b**)

C	5a	5b	mult.
2	153.6	153.5	CH
3	124.1	124.0	C
4	174.9	175.8	C
5	127.2	127.0	CH
6	115.8	115.5	CH
7	167.1	164.1	C
8	103.7	103.5	CH
9	157.2	156.9	C
10	118.7	118.6	C
1′	123.6	123.4	C
2′	130.2	130.0	CH
3′	113.8	113.6	CH
4′	159.2	159.1	C
5′	113.8	113.6	CH
6′	130.2	130.0	"
1″	100.4	99.7	"
2″	73.4	73.0	"
3″	76.7	76.2	"
4″	69.9	69.8	"
5″	77.4	73.8	"
6″	61.5	63.3	CH_2
OMe	55.3	55.1	Me
C=O	—	170.1	C
MeCOO	—	20.5	Me

Methyl 6-(10-acetoxy-pentadec-8Z-enyl)-2,4-dimethoxybenzoate (**4b**). Eluted with hexane–Et_2O (7:3) on silica gel CC. Oil. IR ν_{max}^{film} cm^{-1}: 2925, 2830, 1735, 1610, 1590, 1490, 1460, 1260, 1240, 1200, 1160, 1100, 1045, 1020, 940, 835, 760, 730; ^{1}H NMR ($CDCl_3$): δ0.89 (3H, *t*, $J = 6$ Hz, Me), 1.31 [16H, *m*, $(CH_2)_8$], 1.45 (2H, *m*,–CH_2–CH_2–Ar), 2.00 (3H, *s*, –OAc), 2.05 (2H, *m*, –CH_2–CH=CH–), 2.55 (2H, *t*, $J = 8.3$ Hz, –CH_2–Ar), 3.78 (3H, *s*, MeO–Ar), 3.79 (3H, *s*, Me–OAr), 3.87 (3H, *s*, MeO–CO–Ar), 5.37–5.56 (2H, *t*, $J = 5$ Hz, CH=CH–C–OAc) (1H, *m*, H_{gem}–OAc), 6.31 (2H, *s*, H–Ar); UV λ_{max}^{MeOH} nm (log ε): 275 (3.40); EIMS *m/z* (rel. int.): 462 (29.8) $[M]^+$, 431 (15.0), 430 (32.0), 402 (75.8), 387 (81.9), 371 (76.0), 359 (6.9), 343 (16.6), 317 (24.8), 245 (8.4), 223 (4.9), 210 (100), 179 (8.8), 178 (8.2), 151 (21.4), 370 (40.4).

Acetylation of ononin (**5a**) gives *tetraacetylononin*. Mp 89–90 ($CHCl_3$–MeOH, 9:1). IR ν_{max}^{KBr} cm^{-1}: 2962, 1760, 1645, 1624, 1515, 1446, 1374, 1239, 1181, 1070, 1034, 886, 834; ^{1}H NMR ($CDCl_3$): δ2.09 (12H, 4*s*, –OAc), 3.84 (3H, *s*, MeO), 4.23 (2H, *m*, CH_2), 5.30 (4H, *m*, glucosidic CH), 6.91–7.09 (4H, *m*, H-3′, H-5′, H-6, H-8), 7.5 (2H, *d*, $J_{2'-3'} = J_{5'-6'} = 8.5$ Hz, H-2′, H-6′), 7.93 (1H, *s*, H-2), 8.24 (1H, *d*, $J_{5-6} = 9$ Hz, H-5); UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 255 (5.15), 302 sh (4.80). Formononetin was obtained by hydrolysis of **5a**.

6″-O-*Acetylononin* (**5b**). Mp 175–180° ($CHCl_3$–MeOH, 19:1). IR ν_{max}^{KBr} cm^{-1}: 3410, 2928, 1737, 1625, 1515, 1447, 1374, 1251, 1224, 1073, 834, 809; ^{1}H NMR (Me_2CO-d_6): δ2.04 (3H, *s*, -OAc), 2.79 (5H, *br s*, glucosidic-H and OH), 3.55 (2H, *m*, glucosidic-H), 3.83 (3H, *s*, MeO), 4.18 (1H, *dd*, $J_{a-b} = 12$ Hz, $J_{a-x} = 6$ Hz, H-6″a), 4.50 (1H, *dd*, $J_{a-b} = 12$ Hz, $J_{b-x} = 2$ Hz, H-6″b), 5.21 (1H, *br d*, $J = 7$ Hz, H-1″), 6.99 (2H, *d*, $J_{2'-3'} = J_{5'-6'} = 8.5$ Hz, H-3′, H-5′), 7.15 (1H, *dd*, $J_{5-6} = 8$ Hz, H-6), 7.21 (1H, *s*, H-8), 7.58 (2H, *d*, $J_{2'-3'} = J_{5'-6'} = 8.5$ Hz, H-2′, H-6′), 8.13 (1H, *d*, $J_{5-6} = 8$ Hz, H-5), 8.24 (1H, *s*, H-2).

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