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5-ALKYLRESORCINOLS FROM *ONONIS NATRIX*

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Key Word Index—*Ononis natrix*; Fabaceae; resorcinol derivatives.

Abstract—From a *n*-hexane extract of aerial parts of *Ononis natrix*, nine new 5-tridecylresorcinol derivatives were isolated. The identification of all these compounds was achieved by spectroscopic means. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

Previous work on the chemical constituents of *Ononis natrix*, yielded a number of 3,4-dihydroisocoumarins and two resorcinol derivatives [1–3]. Other 5-alkylresorcinols and related compounds were identified as the major components of extracts from *O. especiosa* [4], *O. viscosa* [5] and *O. pubescens* [6]. In the present paper, we report the isolation and characterization of nine resorcinol derivatives, **2–3** and **5–11**, isolated from a less-soluble fraction of the *n*-hexane extract of the aerial parts of *O. natrix*.

RESULTS AND DISCUSSION

The structure of the new natural product **2** was established by comparison of its spectral data with those previously reported for 1-*O*-methyl-5(2-acetoxy tridecyl) resorcinol (**1**) [1]. Compound **2** differed from **1** by the presence of an additional carbonyl group which absorbed at 1710 cm^{-1} in the IR spectrum and produced one signal at δ 210.9 in the ^{13}C NMR spectrum (Table 2). Its $[M]^+$ at *m/z* 378 also agreed for a ketoderivative of **1**. The analysis of prominent peaks in the mass spectrum served to locate the carbonyl group at position 8′ on the side-chain. Before the loss of an acetate group, some fragments corresponding to fragmentations α and β to the carbonyl (*m/z* 71 $[C_5H_{11}]^+$ and 99 $[C_5H_{11}CO]^+$) appeared in the mass spectrum with relative abundances of 9% and 18%, respectively. These data supported structure **2** for this substance. Comparison of its optical rotation ($[\alpha]_D$ −1.2°) with those reported for similar compounds [1], suggested that C-2′ has the *R*-configuration.

The ^{13}C NMR spectrum of **3** differed from that of **2** in the absence of carbonyl signal and the presence of on oxygenated methine (δ72.2 CH) and two methylenes (δ37.4 CH_2 and 37.3 CH_2) deshielded by the presence of an oxygenated vicinal group, indicating structure **3** for this compound.

Compounds **4–6** were isolated as the corresponding acetyl derivatives **4a–6a** to facilitate their chromatographic purification. Compounds **4** and **4a** have been described previously [1]. Compound **5a**, by saponification with refluxing Na_2CO_3 in methanol, yielded the natural product **5**. Compound **6a**, by saponification with KOH in methanol yielded resorcinol. Compounds **5** and **6** showed spectroscopic features similar to those of **2** and **3**, respectively. The ^1H and ^{13}C NMR spectra (Tables 1 and 2) showed no signals for acetoxyl groups, this was the only difference from **2** and **3**.

The spectral properties of compounds **7–9** compared with those of **1–3** clearly demonstrated their respective structural relationships, which was the presence of a phenolic group instead of a methoxyl group at position 3 of the resorcinol moiety in each case.

Finally, compounds **10** and **11** were also isolated as their acetyl derivatives **10a** and **11a**. Compound **10a** was treated with Na_2CO_3 in methanol under conditions that allowed the selective hydrolysis of phenolic acetates; the derivative obtained was the compound previously described, **8**. Furthermore, **10a** was treated with Na_2CO_3 in methanol under reflux to yield the new natural resorcinol, **10**. Saponification of **11a** with Na_2CO_3–methanol under reflux yielded the natural resorcinol, **11**. The spectral properties of compounds **10** and **11**, compared with those of **5** and **6**, demonstrated their respective structural relationships,

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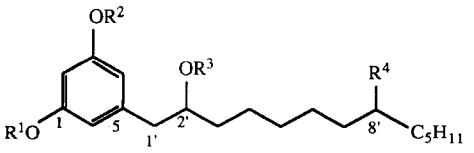
Table 1. ^{13}C NMR spectral data for compounds **1–11**, **4a–6a**, **10a** and **11a** (50.3 MHz, $CDCl_3$, TMS as internal standard)

C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11†***	**4a**	**5a**	**6a**	**10a**	**11a**
1	157.2	157.2	157.3	157.4	157.3	157.6	156.8	157.2	157.2	157.1	159.2	151.5	151.5	151.5	150.9	150.9
2	99.9	99.9	99.9	100.0	99.8	99.9	101.6	101.5	101.6	101.5	101.7	105.7	105.7	105.6	113.3	113.2
3	160.9	161.0	160.9	161.3	161.2	161.1	157.0	157.2	157.2	157.1	159.2	160.4	160.4	160.3	150.9	150.9
4	107.6	107.6	107.5	107.6	107.8	107.3	109.1	108.9	108.9	109.1	109.1	112.9	112.8	112.8	119.8	119.8
5	140.2	140.1	140.1	141.3	141.1	141.1	140.6	140.2	140.2	141.3	142.7	140.1	140.0	140.0	139.9	139.9
6	109.1	109.1	109.1	109.2	109.0	109.2	109.1	108.9	108.9	109.1	109.1	115.0	115.0	114.9	119.8	119.8
1′	40.8	40.6	40.6	44.2	44.2	44.1	40.8	40.6	40.5	43.7	45.2	40.6	40.6	40.5	40.2	40.2
2′	75.1	74.7	74.8	72.9	72.5	72.7	75.6	75.3	75.4	72.9	73.9	74.4	74.3	74.3	73.8	74.1
3′	33.7	33.3	33.3	37.0	36.6	36.6	33.9	33.3	33.2	36.5	37.6	33.6	33.4	33.5	33.3	33.4[b]
4′	25.4	25.1	25.3	25.8	25.5	25.4	25.5	25.0	25.0	25.4	26.4	25.4	25.2	25.2	25.0	25.1[a]
5′	29.5[a]	29.0	29.3	29.7[a]	29.2	29.5	29.4[a]	28.9	29.2	29.1	30.7	29.5[a]	29.0	29.3	28.9	19.1
6′	29.6[a]	23.6	25.3	29.7[a]	23.9[a]	25.5	29.6[a]	23.7	25.3	23.8[b]	26.7	29.7[a]	23.7[a]	24.9	23.5[a]	24.8[a]
7′	29.6[a]	42.8[a]	37.5[a]	29.7[a]	42.9[a]	37.5[a]	29.6[a]	42.6[a]	37.3[a]	42.9[a]	38.3	29.3[a]	42.8[b]	34.0	42.6[b]	33.9[b]
8′	29.6[a]	210.9	72.2	29.7[a]	212.0	72.3	29.6[a]	213.2	72.5	213.8	72.5	29.4[a]	211.3	74.3	211.0	73.9
9′	29.5[a]	42.6[a]	37.3[a]	29.7[a]	42.8[a]	37.3[a]	29.6[a]	42.9[a]	37.1[a]	42.7[a]	38.3	29.3[a]	42.6[b]	34.0	42.4[b]	33.5[b]
10′	29.3[a]	23.6	25.3	29.4[a]	23.7[a]	25.5	29.4[a]	23.7	25.3	23.7[b]	26.7	29.6[a]	23.6[a]	25.2	23.4[a]	25.1[a]
11′	31.9	31.5	31.9	32.1	31.5	32.0	31.9	31.4	31.9	31.5	33.1	31.9	31.5	31.7	31.4	31.6
12′	22.7	22.4	22.6	22.7	22.5	22.6	22.7	22.4	22.8	22.4	23.7	22.7	22.5	22.5	22.5	22.3
13′	14.0	13.8	14.0	14.1	13.9	14.0	14.1	13.9	14.0	13.9	14.4	14.0	13.9	13.9	13.9	13.8
OMe	55.2	55.3	55.3	55.4	55.3	55.3	–	–	–	–	–	55.4	55.4	55.4	–	
OCO	–	–		–	–		–	–		–	–	170.6	170.6	170.8	170.4	170.5
												169.2	169.2	170.5	168.6	170.3
														169.1	168.6	168.5
																168.5
Me	–	–	–	–	–	–	–	–	–	–	–	21.1	21.1	21.2	20.9	20.9
												21.1	21.1	21.1		20.8
														21.1		
Ac	171.4	170.9	171.1	–	–	–	172.2	172.0	172.1	–	–	–	–		–	–
	21.4	21.2	21.2				21.2	21.2	21.2							

[a, b] Interchangeable assignments.

*In CD_3OD.



	R1	R2	R3	R4
1	CH_3	H	Ac	H
2	CH_3	H	Ac	O=
3	CH_3	H	Ac	OH
4	CH_3	H	H	H
4a	CH_3	Ac	Ac	H
5	CH_3	H	H	O=
5a	CH_3	Ac	Ac	O=
6	CH_3	H	H	OH
6a	CH_3	Ac	Ac	AcO
7	H	H	Ac	H
8	H	H	Ac	O=
9	H	H	Ac	OH
10	H	H	H	O=
11	H	H	H	OH
10a	Ac	Ac	Ac	O=
11a	Ac	Ac	Ac	AcO

the most important difference being the presence of a phenolic group instead of a methoxyl group at position 3 in both cases.

EXPERIMENTAL

General. Mps uncorr. Optical rotations: $CHCl_3$. UV: EtOH. IR: $CHCl_3$ and film. EI-MS: 70 eV. ^1H NMR (200 MHz), ^{13}C NMR (50.3 MHz): $CDCl_3$ with TMS as int. standard. Flash CC: silica gel (Merck no. 9385).

Extraction and isolation. Flowering plant material was collected in July at Aldealengua (Salamanca, Spain) and a voucher specimen is deposited in the Botany Department, Faculty of Pharmacy, Salamanca (SALAF N° 16052). Air-dried material (4.2 kg) was extracted with hexane and the resulting extract cooled at room temp. to give 16.4 g of an insoluble fr., which was successively defatted with MeOH and a satd soln of urea in MeOH. This fr. (12.2 g) was chromatographed on silica gel and compounds **1** (80 mg), **2** (50 mg), **3** (57 mg), **4** (130 mg), **7** (50 mg), **8** (109 mg), **9** (89 mg) and a mixt. (2.6 g) from which, after acetylation, **4a** (42 mg), **5a** (47 mg), **6a** (230 mg), **10a** (617 mg) and **11a** (472 mg) were isolated.

1-O-*Methyl*-5-(2-*acetoxytridecyl*)*resorcinol* (**1**). Eluted with *n*-hexane–EtOAc (9:1). [α](λ) −4.0° (589), −4.2°(578), −5.0°(546), −10.6°(436), −19.5°(365) (*c* 0.75). UV: 212(ε 12400), 274(ε 3000), 281(ε 2600) nm. IR: 3400, 1735, 1705, 1615, 1600, 1500, 1270, 1160, 840, 705 cm^{-1}. EI-MS *m/z* (rel. int.): 364(2), 304(2), 177(10), 138(100), 137(32). ^1H NMR (Table 2); ^{13}C NMR (Table 1).

1-O-*Methyl*-5-(2-*acetoxy*-8-*oxotridecyl*)*resorcinol* (**2**). Eluted with *n*-hexane–EtOAc (9:1). [α] (λ) −1.1°(589), −1.3°(578), −1.6°(546), −4.4°(436) (*c* 0.60). UV: 214 (ε 10400), 275 (ε 2300), 281 (ε 2300) nm. IR: 3600, 3400, 1730, 1710, 1620, 1605, 1505, 1165, 900, 840 cm^{-1}. EI-MS *m/z* (rel. int.): 378(9), 318(13), 204(9) 181(26), 138(68), 137(27), 99(13), 71(17), 55(18), 43(100). ^1H NMR (Table 2). ^{13}C NMR (Table 1).

1-O-*methyl*-5-(2-*acetoxy*-8-*hydroxytridecyl*)*resorcinol* (**3**). Eluted with *n*-hexane–EtOAc (4:1). [α] (λ) −1.6°(589), −1.9°(578), −2.3°(546), −5.6° (436) (*c* 0.79). UV: 211 (ε 18700), 275 (ε 2500), 281 (ε 2500) nm. IR: 3600, 3400, 1725, 1715, 1665, 1610, 1605, 1500, 1255, 1165, 950, 840 cm^{-1}. ^1H NMR (Table 2). ^{13}C NMR (Table 1).

1-O-*Methyl*-5-(2-*acetoxytridecyl*)*resorcinol acetate* (**4a**). Eluted with *n*-hexane–EtOAc (49:1). [α] (λ) −1.2°(589), −1.3°(578), −1.7°(546), −3.0° (346), −5.4°(365) (*c* 0.94). UV: 227 (ε 3100), 272 (ε 1700), 278 (ε 1700)nm. IR: 1775, 1740, 1620, 1610, 1600, 1240, 1155, 900 cm^{-1}. EI-MS *m/z* (rel. int.) 406(1), 346(27), 304(52), 180(38), 177(31), 163(33), 138(100), 137(59). ^1H NMR (Table 2); ^{13}C NMR (Table 1).

1-O-*Methyl*-5-(2-*acetoxy*-8-*oxotridecyl*)*resorcinol acetate* (**5a**). Eluted with *n*-hexane–EtOAc (9:1). $[\alpha]_D 0°$ (*c* 0.79). UV: 225 (ε 4300), 227 (ε 2000), 278 (ε 1900)nm. IR: 1760, 1735, 1710, 1610, 1595, 1230,

Table 2. ^{1}H NMR data for compounds **1**–**11**, **4a**–**6a**, **10a**

H	1	2	3	4	5	6	7	8
Ar-H	6.30 *m*	6.30 *m*	6.29 *m*	6.28 *m*	6.31 *s*	6.28 *m*	6.25 *m*	6.27 *s*
1′	2.67 *dd*(13.7, 6.30)*	2.66 *dd*(13.6, 6.5)	2.66 *dd*(13.7, 6.6)	2.51 *dd*(13.6, 6.5)	2.53 *dd*(13.7, 8.3)	2.51 *dd*(13.5, 8.1)	2.68 *d*(6.5)	2.61 *dd*(13.7, 6.1)
	2.79 *dd*(13.7, 7.0)	2.79 *dd*(13.7, 6.6)	2.79 *dd*(13.7, 6.6)	2.73 *dd*(13.6, 3.9)	2.72 *dd*(13.6, 4.4)	2.67 *dd*(13.6, 4.4)		
2′	5.04 *q*(6.3)	5.05 *q*(6.3)	5.58 *q*(6.3)	3.80 *m*	3.77 *m*	3.70 *m*	5.07 *q*(6.3)	5.02 *m*
7′	–	2.38 *t*(7.4)	–	–	2.38 *t*(7.3)	–	–	2.38 *t*(7.2)
8′	–	–	3.61 *m*	–		3.57 *m*	–	–
9′	–	–	–	–	2.40 *t*(7.3)	–	–	2.39 *t*(7.4)
13′	0.87 *t*(6.0)	0.88 *t*(6.0)	0.88 *t*(6.0)	0.88 *t*(6.3)	0.88 *t*(6.3)	0.87 *t*(6.3)	0.87 *t*(6.4)	0.87 *t*(6.7)
OCH_3	3.73 *s*	3.75 *s*	3.74 *s*	3.73 *s*	3.75 *s*	3.70 *s*	–	–
OAc-1	–	–	–	–	–	–	–	
OAc-3		–	–	–	–	–	–	–
OAc-2′	2.01 *s*	2.01 *s*	2.00 *s*	–		–	1.98 *s*	1.99 *s*
OAc-8′	–		–	–	–		–	

*J (Hz) in parentheses.
†In CD_3OD.

1210, 900, 725 cm^{-1}. EI-MS *m/z* (rel. int.) 420(0.2), 318(26), 180(20), 177(20), 138(91), 137(41), 43(100). ^{1}H NMR (Table 2); ^{13}C NMR (Table 1).

1-O-*Methyl*-5-(2, 8-*diacetoxytridecyl*)*resorcinol acetate* (**6a**). Eluted with *n*-hexane–EtOAc (9:1). [α] (λ) −2.3°(589), −2.5°(578), −2.6°(546), −4.5° (436), −7.7°(365) (*c* 0.53). UV: 227 (ε 7900), 272 (ε 1800), 272 (ε 1800) nm. IR: 1.775, 1740, 1620, 1615, 1600, 1250, 900, 730 cm^{-1}. EI-MS *m/z* (rel. int.): 464(3), 444(12), 302(25), 180(20), 177(18), 150(33), 138(95), 137(31), 43(100). ^{1}H NMR (Table 2); ^{13}C NMR (Table 1).

1-O-*Methyl*-5-(2-*hydroxytridecyl*)*resorcinol* (**4**). Eluted with *n*-hexane–EtOAc (7:3). [α](λ) −6.8°(589), −8.1°(578), −9.2°(546), −18.0°(436), −27.3°(365)(*c* 0.60). UV: 214 (ε 10400), 275 ε 2000), 282 (ε 2000) nm. IR: 3600, 3330, 2620, 1605, 1500, 835 cm^1. EI-MS *m/z* (rel. int.): 322(4), 304(8), 177(18), 167(14), 163(21), 138(100), 137(75), 109(24), 77(23), 55(64), 43(93), 28(43). ^{1}H NMR (Table 2); ^{13}C NMR (Table 1).

1-O-*Methyl*-5-(2-*hydroxy*-8-*oxotridecyl*)*resorcinol* (**5**). To a soln of **5a** (20 mg) in MeOH (2 ml) was added a satd soln of Na_2CO_3 (1 ml). The mixt. was refluxed for 4 hr and the resulting product chromatographed on silica gel to give 15 mg of **5**. [α] (λ) −2.7°(589), −8.6°(5768), −93°(546), −18,6°(436) (*c* 0.29). UV: 214 (ε 7400), 274 (ε 1600) 281 (ε = 1.600) nm. IR: 3600, 3570, 1710, 1610, 840 cm^1. ^{1}H NMR (Table 2); ^{13}C NMR (Table 1).

1-O-*Methyl*-5-(2-8-*dihydroxytridecyl*)*resorcinol* (**6**). Compound **6a** (122 mg) was dissolved in 4% KOH in MeOH (3 ml) and the mixt. stirred for 24 hr at room temp. The reaction product was purified by chromatography, yielding 79 mg of **6**. [α] (λ) −10.1°(589), −11.3°(578), −13.1°(546), −25.1°(436) (*c* 1.05). UV: 227 (ε 4600), 275 (ε 2100), 281 (ε 2100) nm. IR: 3600, 3320, 1615, 1600, 1500, 940, 935 cm^1. EI-MS *m/z* (rel. int.): 338(3), 139(10), 138(100), 137(14). ^{1}H NMR (Table 2); ^{13}C (Table 1).

5-(2-*Acetoxytridecyl*)*resorcinol* (**7**). Eluted with $CHCl_3$–MeOH (49:1). [α] (λ) −3.8°(589), −4.2°(578), −4.5°(546), −3.8°(436), −17.6° (365) (*c* 0.72). UV: 212 (ε 14300), 276 (ε 2100), 282 (ε 2100) nm. IR: 3400, 1745, 1710, 1610, 1515, 1490, 1275 845 cm^1. EI-MS *m/z* (rel. int.): 350(3), 290(32), 124(73), 123(30), 43(100). ^{1}H NMR (Table 2); ^{13}C NMR (Table 1).

5-(2-*Acetoxy*-8-*oxotridecyl*)*resorcinol* (**8**). Eluted with $CHCl_3$–MeOH (49:1). [α](λ) −1.5°(589), −1.8°(578), −2.1°(546), −4.4°(436), −11.1°(365) (*c* 0.60). UV: 224 (ε 5300), 272 (ε 2000), 282 (ε 2000) nm. IR: 3740, 3600, 3680, 1710, 1605, 1260, 1205, 950, 840 cm^{-1}. EI-MS *m/z* (rel. int.): 364(4), 181(22), 124(50), 123(27), 43(100). ^{1}H NMR (Table 2); ^{13}C NMR (Table 1).

5-(2-*Acetoxy*-8-*hydroxytridecyl*)*resorcinol* (**9**). Eluted with $CHCl_3$–MeOH (49:1). [α](λ) −1.5° (589), −1.5°(578), −2.0°(546), −5.0°(436) (*c* 0.65). UV: 222 (ε = 5.0), 277 (ε 1600), 282 (ε 1600) nm. IR: 3590, 3310, 1720, 1605, 1620, 1160, 840 cm^{-1}. EI-MS *m/z* (rel. int.): 336(7), 306(8), 149(19), 136(25), 121(100), 43(89). ^{1}H NMR (Table 2); ^{13}C NMR (Table 1).

5-(2-*Hydroxy*-8-*oxotridecyl*)*resorcinol* (**10**). To a soln of **10a** (105 mg) in MeOH (7 ml) was added a satd soln of Na_2CO_3 in H_2O (4 ml). The mixt. was refluxed for 14 hr and the resulting product chromatographed on silica gel with $CHCl_3$–MeOH (49:1) to give 63 mg of **10**. [α](λ) −24.0°(589), −26.1°(578), −30.0°(546) (*c* 1,04). UV: 211 (ε 16000), 276 (ε 1700), 281 (ε = 1700) nm. IR: 3.600, 3540, 1710, 1610, 1455, 1345, 840 cm^{-1}. EI-MS *m/z* (rel. int.): 322(4), 199(18), 163(14), 124(100), 43(32). ^{1}H NMR (Table 2); ^{13}C NMR (Table 1).

5-(2-*Acetoxy*-8-*oxotridecyl*)*resorcinol diacetate* (**10a**). Eluted with $CHCl_3$–MeOH (49:1). [α](λ) −1.4°(589), −1.6°(578), −2.0°(546), −3.1°(436), −6.2°(365) (*c* 1.05). UV: 216 (ε 7300), 263 (ε 400) nm. IR: 1775, 1735, 1710, 1620, 1600, 1500, 1355, 1235, 920, 840 cm^{-1}. ^{1}H NMR (Table 2); ^{13}C NMR (Table 1).

and **11a** (200 MHz, $CDCl_3$, TMS as internal standard)

9	10	11†	4a	5a	6a	10a	11a
6.25 *s*	6.20 *sa*	6.13	6.54 *m*	6.55 *m*	6.55	6.76 *m*	6.76 *m*
2.63 *m*	–	2.51 *dd*(13.4, 6.4)	2.73 *dd*(13.7, 6.2)	2.73 *dd*(13.7, 6.1)	2.74 *dd*(13.8, 6.1)	2.76 *d*(6.0)	2.77 *d*(6.4)
		2.61 *dd*(13.4, 6.0)	2.85 *dd*(13.7, 6.7)	2.83 *dd*(13.7, 6.8)	2.82 *dd*(13.8, 6.8)	2.77 *d*(7.2)	–
4.99 *m*	3.68 *sa*	3.71 *m*	5.03 *q*(6.5)	5.03 *q*(6.3)	5.04 *q*(6.3)	–	4.98 *q*(6.2)
–	2.35 *m*						
3.58 *m*	–	3.47 *m*	–		4.84 *q* (6.3)	–	4.80 *q* (6.2)
–	2.35 *m*	–	–	–	–		–
0.85 *t*(6.2)	0.85 *t*(6.6)	0.88 *t*(6.6)	0.88 *t*(6.7)	0.88 *t*(6.7)	0.88 *t*(6.3)	0.84 *t*(6.7)	0.83 *t*(6.4)
–	–	–	3.77 *s*	3.77 *s*	3.77 *s*	–	–
–	–	–	–	–		2.21 *s*	2.20 *s*
–	–	–	2.27 *s*	2.27 *s*	2.27 *s*	2.21 *s*	2.20 *s*
1.97 *s*	–	–	2.00 *s*	2.00 *s*	1.99 *s*	1.95 *s*	1.97 *s*
–	–	–	–	–	2.02 *s*	–	1.94 *s*

5-(2,8-*Diacetoxytridecyl*)*resorcinol diacetate* (**11a**). Eluted with $CHCl_3$–MeOH (49:1). [α](λ) −2.5° (589), −2.7°(578), −3.1°(546), −5.7°(436), −10.2°(365) (*c* 1.0). UV: 211 (ε 13,400), 263 (ε 4000) nm. IR: 1770, 1730, 1625, 1600, 1375, 900 cm^{-1}. ^1H NMR (Table 2); ^{13}C NMR (Table 1).

5-(2,8-*Dihydroxytridecyl*)*resorcinol* (**11**). To a soln of **11a** (160 mg) in MeOH (8 ml) was added a satd aq. soln of Na_2CO_3 (4 ml). The mixt. was refluxed for 6 hr and the resulting product chromatographed on silica gel with $CHCl_3$–MeOH (49:1) to give 85 mg of **11**. Viscous oil. [α](λ) +2.4°(589), +2.9°(578), +3.2°(546), +3.6°(436) (MeOH; *c* 1.22). UV: 211(ε = 12 200), 276(ε = 1700), 282(ε = 1700) nm. IR: 3300, 1605, 1510, 1340, 840 cm^{-1}. ^1H NMR (Table 2); ^{13}C NMR (Table I).

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