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FLAVONOIDS AND ISOFLAVONOIDS FROM *TEPHROSIA FULVINERVIS* AND *TEPHROSIA PENTAPHYLLA*

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Key Word Index—*Tephrosia fulvinervis*; *T. pentaphylla*; Papilionoideae; Leguminosae; isoflavone derivatives; rotenoids.

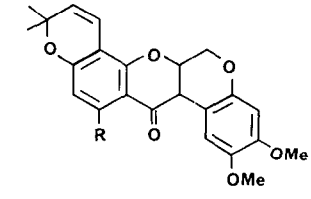
Abstract—From the roots, leaves and pods of *Tephrosia pentaphylla* three new 6-oxygenated rotenoids (dihydrostemonal, 9-demethyldihydrostemonal and 6-acetoxydihydrostemonal) were isolated and characterized. In addition six known rotenoids (villosin, sumatrol, rotenone, *cis*-12a-hydroxyrotenone, 6-hydroxyrotenone and α-toxicarol) and the flavanone obovatin were obtained. A similar analysis of the roots of *T. fulvinervis* yielded only known rotenoids (α-toxicarol, deguelin, munduserone, *cis*-12a-hydroxymunduserone) and the common pterocarpan (−)-maackiain.

INTRODUCTION

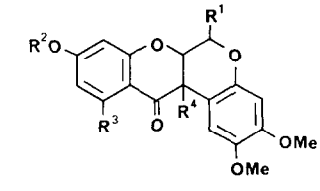
The genus *Tephrosia* Pers. is well known for elaborating flavonoids and isoflavonoids [1]. As part of a continuing study of *Tephrosia* species found in Ethiopia [2] we have investigated the roots, pods and leaves of *T. pentaphylla* (Roxb.) G. Don. and the roots of *T. fulvinervis* Hochst *ex* A. Rich. *Tephrosia pentaphylla* is an annual or short-lived perennial known to occur in many parts of East Africa, Arabia and South India whereas *T. fulvinervis* is endemic to the south-western provinces of Ethiopia [3]. Previous investigations of the seeds and pods of *T. fulvinervis* have revealed the presence of flavones and flavanones fully substituted in ring-A [4, 5]. No previous studies have been reported for *T. pentaphylla*.

RESULTS AND DISCUSSION

TLC examination of the crude chloroform extracts of the pods, leaves and roots of *T. pentaphylla* showed the plant to be rich in flavonoids. It proved possible by a combination of column chromatographic and PTLC techniques to isolate 10 compounds of which three are novel. Similar analysis of *T. fulvinervis* roots yielded only five known compounds, the rotenoids α-toxicarol (**1**), deguelin (**2**), munduserone (**3**) and *cis-12a-hydroxymunduserone* (**4**) and the common pterocarpan, (−)-maackiain. Compounds **1**–**4** were characterized by comparison of physical and spectral data with those reported previously (see Experimental). ^{1}H NMR data for these and other rotenoids isolated in this study are given in Table 1. The *cis* stereochemistry of the B/C ring junction of **4** was established from the ^{1}H NMR spectrum (Table 1, H-1 is strongly deshielded in *trans* substituted compounds [6]). As **4** was not obtained pure an accurate measurement of optical activity was not possible but a chloroform solution was dextrorotatory, comparable to **3**.



1 R = OH
2 R = H



	R^1	R^2	R^3	R^4
3	H	Me	H	H
4	H	Me	H	OH
6	OH	Me	OH	H
7	OH	H	OH	H
8	OAc	Me	OH	H

The pods of *T. pentaphylla* yielded three rotenoids of which one proved to be the known compound villosin (**5**). Methylation of **5** gave two products, in both cases this being accompained by oxidation across the C-6a–C-12a bond to give dehydrorotenoids, **5a** and **5b** respectively. Compound **5b** is known (trivial name villinol [7]). A series of NOE studies were performed on **5b** (Experimental) to allow the four methoxyl resonances to be assigned unambiguously. Acetylation of **5** again yielded two products, the monoacetate (**5c**) and the diacetate (**5d**). ^{13}C NMR data was obtained for the first time for **5** and **5d** and are listed in Table 2.

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Table 1. ^{1}H NMR shift data for rotenoids

Position	1	2	3	4	5	5a	5b	5c	5d	6	7	8	9	10	11	12
Rotenoid nucleus																
H-1	6.86	6.79	6.76	6.54	6.86	8.46	8.58	6.84	6.59	6.83	6.81	6.82	6.86	6.75	6.54	6.77
H-4	6.46	6.46	6.46	6.50	6.48	6.68	6.81	6.53	6.49	6.48	6.46	6.54	6.46	6.49	6.48	6.48
H-6	4.16	4.18	4.18	4.50	5.76	5.75	5.71	6.64	6.61	5.76	5.73	6.64	4.15	4.16	4.48	5.79
	4.62	4.64	4.62	4.50	—	—	—	—	—	—	—	—	4.59	4.60	4.48	—
H-6a	4.87	4.92	4.94	4.50	4.77	—	—	4.76	4.77	4.77	4.89	4.75	4.88	4.91	4.59	4.82
H-8	—	—	6.41	6.38	—	—	—	—	—	5.95	5.87	5.97	—	—	—	—
H-10	5.96	6.46	6.57	6.59	6.02	6.36	6.52	6.03	6.18	6.04	5.92	6.06	6.01	6.49	6.54	6.51
H-11	—	7.75	7.87	7.85	—	—	—	—	—	—	—	—	—	7.82	7.82	7.85
11-OH	12.2	—	—	—	12.4	13.1	—	12.6	—	12.1	12.2	12.0	12.4	—	—	—
H-12a	3.80	3.83	3.86	—	3.92	—	—	3.89	3.80	4.00	3.80	3.89	3.84	3.82	—	3.93
Dihydrofuranoid system																
H-2′	—	—	—	—	5.18	5.36	5.42	5.19	5.21	—	—	—	5.20	5.22	5.24	5.24
H-3a′	—	—	—	—	2.81	3.07	3.13	2.83	2.88	—	—	—	2.85	2.93	2.94	2.95
H-3b′	—	—	—	—	3.19	3.47	3.58	3.19	3.22	—	—	—	3.23	3.30	3.29	3.28
1″-Me	—	—	—	—	1.74	1.79	1.75	1.74	1.74	—	—	—	1.75	1.75	1.76	1.76
1″=CH_2	—	—	—	—	4.93	4.95	4.97	4.95	4.92	—	—	—	4.93	4.91	4.94	4.93
	—	—	—	—	5.05	5.11	5.10	5.05	5.04	—	—	—	5.06	5.10	5.07	5.07
Pyran system																
H-3′	4.46	5.56	—	—	—	—	—	—	—	—	—	—	—	—	—	—
H-4′	6.55	6.64	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2′-Me	1.37	1.38	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1.44	1.45	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Substituents																
OMe		3.77	3.76	3.72	3.78	3.96	3.94	3.80	3.78	3.78	3.66	3.79	3.79	3.75	3.33	3.77
		3.81	3.80	3.79	3.82	3.91	3.93	3.82	3.79	3.80	3.74	3.82	3.82	3.79	3.82	3.81
	—	—	3.80	3.81	—	3.60	3.65	—	—	3.76	—	3.78	—	—	—	—
	—	—	—	—	—	—	3.96	—	—	—	—	—	—	—	—	—
OAc	—	—	—	—	—	—	—	2.18	2.09	—	—	2.12	—	—	—	—
	—	—	—	—	—	—	—	—	2.39	—	—	—	—	—	—	—

Spectra recorded run at 250 MHz; $CDCl_3$ except **8** which was run in Me_2CO-d_6.

J values (i) for rotenoid skeleton, 6-6 = 12.2 Hz, 6-6a = 2.8 and *ca* 1Hz, 6a-12a = 3.6 Hz, 8-10 = 2.4 Hz, 10-11 = 8.5 Hz; (ii) for dihydrofuran skeleton, 2′-3a′ = 9.8 Hz, 2′-3b′ = 8.3 Hz, 3a′-3b′ = 15.9 Hz; 1″=CH_2 = two broad singlets; (iii) pyran skeleton, 3′-4′ = 10.0 Hz.

The second isolate from the pods analysed for $C_{19}H_{18}O_8$. The ^{1}H NMR spectrum (Table 1) revealed the presence of three methoxyl substituents, a chelated 11-hydroxyl and oxygenation at C-6. EIMS fragmentation showed major ions for fission across ring-C; **6a** for ring-D and **6b** for rings A and B, thus indicating that one methoxyl must be at C-9 with the others presumably at C-2 and C-3, leaving C-6 substituted with an hydroxyl. On this basis the compound was assigned structure **6** and given the trivial name dihydrostemonal, based on the known dehydrorotenoid stemonal [8]. Acetylation of **6** afforded the 6-acetoxy derivative (**8**) which showed the anticipated deshielding of the H-6 oxymethine proton (Table 1). The ^{13}C NMR data for **6** (Table 2) was in agreement with that anticipated for the proposed structure.

The final compound from the pods analysed for $C_{18}H_{16}O_8$, 14 mass units less than **7**. The ^{1}H NMR spectrum (Table 1) was similar to **6** but revealed one less methoxyl resonance. As the EIMS revealed ion **6b** as a major fragment and also fragment **7a**, the loss of the methoxyl must be from C-9, allowing assignment of structure **7** (trivial name 9-demethyldihydrostemonal).

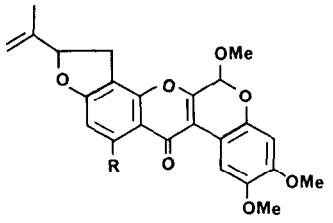
From the leaves four rotenoids were obtained, **1, 5, 6** and a further new compound which analysed for $C_{21}H_{20}O_9$. Spectral data for this compound established it as 6-acetoxydihydrostemonal (**8**) which had previously been prepared during the identification of **6**. The ^{13}C NMR data for **8** was obtained and is given in Table 2.

The roots proved to be the most productive part of the plant yielding eight compounds including the already identified **5, 6** and **8**. The remaining five were characterised as the flavanone obovatin and the rotenoids sumatrol (**9**), rotenone (**10**), *cis*-12a-hydroxyrotenone (**11**) and 6-hydroxyrotenone (**12**).

EXPERIMENTAL

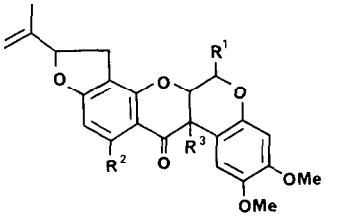
Plant material. Tephrosia fulvinervis was collected from the Ghibey Valley and *T. pentaphylla* from the Blue Nile Gorge in September 1986. Voucher specimens, Masresha 142 and 140 respectively, are kept at the National Herbarium, Biology Department, Addis Ababa University.

Extraction and isolation of compounds from T. fulvinervis. Powdered roots (600 g) were successively extracted with petrol



5a R = OH

5b R = OMe

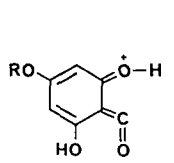


	R^1	R^2	R^3
5	OH	OH	H
5c	OAc	OH	H
5d	OAc	OAc	H
9	H	OH	H
10	H	H	H
11	H	H	OH
12	OH	H	H

Table 2. ^{13}C NMR shift data for compounds **5**, **5b**, **6** and **8**

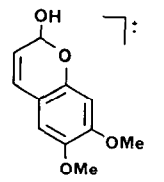
C	5	5d	6	8
1a	104.0 *s*	104.4 *s*	104.9 *s*	104.0 s
1	110.1 *d*	109.7 *d*	110.2 *d*	109.5 *d*
2	144.0 *s*	144.7 *s*	144.5 *s*	144.7 *s*
3	144.1 *s*	143.7 *s*	144.3 *s*	143.8 *s*
4	101.7 *d*	101.3 *d*	101.9 *d*	101.5 *d*
4a	149.6 *s*	149.7 *s*	150.0 *s*	149.8 *s*
6	87.9 *d*	87.6 *d*	90.1 *d*	87.6 *d*
6a	72.6 *d*	71.1 *d*	72.9 *d*	71.2 *d*
7a	155.5 *s*	156.7 *s*	161.5 *s*	160.9 *s*
8	104.9 *s*	106.7 *s*	95.6 *d*	95.5 *d*
9	165.5 *s*	166.3 *s*	165.0 *s*	164.7 *s*
10	91.8 *d*	100.2 *d*	94.4 *d*	94.1 *d*
11	169.1 *s*	152.9 *s*	168.1 *s*	168.3 *s*
11a	101.7 *s*	111.0 *s*	104.8 *s*	101.7 *s*
12	193.6 *s*	186.3 *s*	194.5 *s*	193.4 *s*
12a	39.8 *d*	41.7 *d*	40.2 *d*	40.2 *d*
2′	89.7 *d*	88.3 *d*	—	—
3′	31.1 *t*	31.0 *t*	—	—
1″	142.6 *s*	142.4 *s*	—	—
1″=CH_2	112.5 *t*	112.8 *t*	—	—
1″-Me	16.8 *q*	16.9 *q*	—	—
OMe	55.7 *q*	56.0 *q*	55.4 *q*	55.6 *q*
	56.2 *q*	55.8 *q*	56.2 *q*	55.8 *q*
	—	—	56.6 *q*	56.6 *q*
Ac(CO)	—	168.9 *s*	—	168.7 *s*
	—	169.1 *s*	—	—
Ac(Me)	—	20.8 *q*	—	20.8 *q*
	—	21.1 *q*	—	—

All spectra run in $CDCl_3$, at 22.5 MHz except for **5b** which was run at 90.56 MHz.



6a R = Me

7a R = H



6b

(bp 60–80°), $CHCl_3$ and EtOH. The petrol extract was concd to an oil and the Me_2CO soluble portion subjected to chromatography over silica gel eluting with petrol containing increasing amounts of EtOAc. A total of forty 50 ml fractions were collected. Further purification of the contents of fractions 27, 28 and 37 by PTLC on silica gel (solvent: C_6H_6–petrol–EtOAc 3:5:3) yielded **1** (9 mg) and **2** (20 mg), respectively. The $CHCl_3$ extract was treated similarly to give (−)-maackiain (20 mg) from fractions 19, 20 and then further **2** (13 mg) from fractions 24, 25. Fractions 27–30 gave a mixture which was separated by PTLC using the same solvent system as above to yield **3** (27 mg) and **4** (15 mg).

Extraction and isolation of compounds from T. pentaphylla. *Pods.* Powdered pods (1 kg) were extracted successively (Soxhlet) with petrol (bp 60–80°), $CHCl_3$ and EtOH. Concn of the $CHCl_3$ extract under red. pres. yielded a residue (98 g) which was chromatographed on Sephadex LH-20, eluting with $CHCl_3$–MeOH (1:1) to remove chlorophyll and fatty materials, The partially purified mixture was applied to a silica gel column (100 g) and was eluted with petrol containing increasing amounts of EtOAc. A total of fifty 50 ml fractions were collected. Fractions 11–13 (15% EtOAc) yielded compound **5** (95 mg), fractions 23–25 (15% EtOAc) **6** (50 mg), fractions 26–32 (20% EtOAc) showed one major spot on TLC which was purified by PTLC (petrol–C_6H_6–EtOAc 1:1:1) to give **7** (8.0 mg).

Leaves. Powdered leaves (1 kg) were extracted as above. After removal of $CHCl_3$ an oily residue was obtained. The residue was chromatographed on Sephadex LH-20 and then silica gel (100 g), as above. From the silica gel column fractions 22–23 (5% EtOAc) yielded compound **1** (7 mg), fractions 28, 29 (5% EtOAc) **8** (95 mg), fractions 30–32 (10% EtOAc) **5** (200 mg), and fractions 37–39 **6** (130 mg).

Roots. Powdered roots (800 g) were extracted as above. Concn of the petrol extract yielded an oily residue which was taken up with Me_2CO. The Me_2CO-soluble part was chromatographed on silica gel (90 g) eluting with increasing amounts of EtOAc in petrol (50 ml fractions). Fractions 4/8 (3% EtOAc) contained a mixture of two compounds, separated by PTLC (petrol–C_6H_6–EtOAc 4:3:3) to give compounds **8** (10 mg) and β-sitosterol (300 mg). Comparable treatment of the $CHCl_3$ extract yielded from fractions 14/16 (5% EtOAc) a mixture of three compounds which were separated by circular PTLC (silica gel, petrol–C_6H_6–EtOAc 2:1:1) to give **9** (20 mg) and obovatin (6 mg). Fractions 18–20 (5% EtOAc) also showed the presence of two compounds and through circular PTLC **10** (145 mg) and **11** (25 mg) were obtained. Fractions 24–26 (10% EtOAc) yielded **5** (16 mg) and **6** (9 mg) and fractions 27, 28 (10% EtOAc) **12** (7 mg).

Known rotenoids. α-Toxicarol (**1**). Amorphous solid (UV, IR [9]). Found: $[M]^+$ 410.1358; $C_{23}H_{22}O_7$ requires 410.1365. *Deguelin* (**2**). Amorphous solid (UV, IR [7, 10]). Found: $[M]^+$ 394.1403; $C_{23}H_{22}O_6$ requires 394.1103. *Munduserone* (**3**). Plates from MeOH, mp 125–128° (lit. [11] 162°), $[\alpha]_D$ +77° ($CHCl_3$; *c* 0.15) (lit. [8] +103°). Found: $[M]^+$ 342.1093; $C_{19}H_{18}O_6$ requires 342.1103. UV λ_{max} nm (log ε): 275 (4.13). IR ν_{max} cm^{-1}:

1660. cis-12*a*-*Hydroxymunduserone* (**4**). Amorphous solid (IR [12]). Found: $[M]^+$ 358.1069; $C_{19}H_{18}O_7$ requires 358.1052. *Sumatrol* (**9**). Needles from $CHCl_3$, mp 179–182°, (lit [9] 174–177°). Found: $[M]^+$ 420.1326; $C_{23}H_{22}O_7$ requires 410.1365. UV, IR, identical to [7]. *Rotenone* (**10**). Plates from MeOH, mp 159–161°, (lit [9] 162–164°), $[\alpha]_D$ −199° ($CHCl_3$, *c* 1) (lit. [10] −225°). Found: $[M]^+$ 394.1382; $C_{23}H_{22}O_6$ requires 394.1416. UV, IR, identical to [9].

cis-12*a*-*Hydroxyrotenone* (**11**). Oil, $[\alpha]_D$ −133° ($CHCl_3$, *c* 0.05) (lit [6] −145°). Found: $[M]^+$ 410.1362; $C_{23}H_{22}O_7$ requires 410.1365. IR, NMR identical to [6, 13]. 6-*Hydroxyrotenone* (**12**). Amorphous solid, mp 112–115°. Found: $[M]^+$ 410.1376; $C_{23}H_{22}O_7$ requires 410.1365. UV λ_{max} nm (log ε): 240 (4.34), 272 (4.69), 292 (4.47).

Villosin (**5**). Yellow plates from MeOH, mp 134–136°, (lit. [7] 133°), $[\alpha]_D$ +38° ($CHCl_3$; *c*. 1). UV, IR identical to [7]. Found: $[M]^+$ 426.1318; $C_{23}H_{22}O_8$ requires 426.1315. ^{1}H NMR (Table 1). ^{13}C NMR (Table 2). EIMS *m/z* (rel. int.): 426 $[M]^+$ (45), 219 (48), 208 (100), 191 (54). *Methylation of* **5**. A mixture of **5** (30 mg), MeI (1 ml) and Ag_2O in $CHCl_3$ was refluxed on a water bath for 6 hr. The mixture was cooled to room temp., filtered, concd and separated by PTLC on silica gel (solvent, petrol–C_6H_6–EtOAc 2:1:1) to give **5a** and **5b**. 11-*Demethylvillinol* (**5a**). Oil. Found: $[M]^+$ 438.1276; $C_{24}H_{22}O_8$ requires 438.1315. ^{1}H NMR (Table 1). EIMS *m/z* (rel. int.): 438 $[M]^+$ (90), 407 $[M-Me]^+$ (100), 222 (44), 191 (71). *Villinol* (**5b**). Found: $[M]^+$ 452.1479; $C_{25}H_{24}O_8$ requires 452.1471. ^{1}H NMR (see Table 1); NOE experiment (360 MHz): irradiation of OMe δ3.96 causes 18% enhancement of H-10, of δ3.94 21% of H-1, of δ3.93 17% of H-4, of δ3.65 8% of H-6. EIMS *m/z* (rel. int.): 452 $[M]^+$ (21), 421 (60), 238 (37), 233 (79), 222 (21), 207 (30), 191 (33). *Acetylation of* **5**. A mixture of **5** (120 mg), acetic anhydride (0.5 ml) and dimethylaminopyridine (5 mg) was stirred for 2 days. The crude product was poured over crushed ice and shaken, filtered and subjected to PTLC (petrol–C_6H_6–EtOAc 2:1:1) to give the 6-*monoacetate* **5c** (20 mg), identical to **8**, and the 6,11-*diacetate* (**5d**) (85 mg). Found: $[M]^+$ 510.1525; $C_{27}H_{26}O_{10}$ requires 510.1526. ^{1}H NMR (Table 1). EIMS *m/z* (rel. int.): 510 $[M]^+$ (21), 468 $[M-CH_2CO]^+$ (17), 450 $[M-MeCOOH]^+$ (42), 408 (23), 250 (60), 208 (20), 191 (95), 43 (100).

Dihydrostemonal (**6**). Amorphous, mp 184–186°, $[\alpha]_D$ +233° ($CHCl_3$; *c* 0.25). Found: $[M]^+$ 374.0975; $C_{19}H_{18}O_8$ requires 374.1002. UV λ_{max} nm (log ε): 258sh (4.04), 290 (4.50), 324sh (4.11). IR ν_{max} cm^{-1}: 3400, 3025, 2955, 1650, 1590, 1520. ^{1}H NMR (Table 1). ^{13}C NMR (Table 2). EIMS *m/z* (rel. int.): 374 $[M]^+$ (94), 356 (27), 345 (16), 343 (31), 331 (16), 219 (22), 208 $[C_{11}H_{12}O_4]^+$ (100), 191 (60), 167 $[C_8H_7O_4]^+$ (57). *Acetylation of* **6**. A mixture of **6** (15 mg), acetic anhydride and pyridine (0.1 ml) was stirred for 2 days. After work-up and PTLC purification the monoacetate **8** was obtained.

9-*Demethyldihydrostemonal* (**7**). Amorphous solid, mp 180° (dec.). $[\alpha]_D$ +225° ($CHCl_3$; *c* 0.15). Found: $[M]^+$ 360.0840; $C_{18}H_{16}O_8$ requires 360.0845. UV λ_{max} nm (log ε): 256sh (4.04), 288 (4.50), 324sh (4.09). ^{1}H NMR (Table 1). EIMS *m/z*. (rel. int.): 360 $[M]^+$ (81), 342 (100), 331 (15), 299 (74), 208 $[C_{11}H_{12}O_4]^+$ (68), 191 (27), 153 $[C_7H_5O_4]^+$ (14).

6-*Acetoxydihydrostemonal* (**8**). Plates from $CHCl_3$, 154–157°, $[\alpha]_D$ +308° ($CHCl_3$; *c* 0.5). Found: $[M]^+$ 416.1082; $C_{21}H_{20}O_9$ requires 416.1107. UV λ_{max} nm (log ε): 258sh (4.07), 286 (4.47), 325 (4.11). IR ν_{max} cm^{-1}: 3100, 2950, 1760, 1640, 1585, 1520, 1454. ^{1}H NMR (Table 1). ^{13}C NMR (Table 2). EIMS *m/z* (rel. int.): 416 $[M]^+$ (83), 345 (82), 250 $[C_{13}H_{14}O_5]^+$ (50), 208 (38), 191 $[C_{11}H_{11}O_3]^+$ (100).

(−)-*Maackiain*. Amorphous. Found: $[M]^+$ 284.0696; $C_{16}H_{12}O_5$ requires 284.0685. UV, IR, EIMS, ^{1}H NMR in agreement with lit. [14]. ^{13}C NMR (22.5 MHz, $CDCl_3$) ppm: *s* at 158.4, 156.6, 154.3 (C-3, -4a, -10a), 148.1, 141.6 (C-8, -9), 112.0, 111.7 (C-6b, -11b); *d* at 131.9 (C-1), 110.0 (C-7), 104.9, 103.6 (C-2, -10), 93.7 (C-4), 78.7 (C-11a), 40.2 (C-6a); *t* at 101.3 (O–CH_2–O), 66.4 (C-6).

Obovatin. Amorphous, mp 123–125° (lit [15] 126°). Found: $[M]^+$ 322.1167; $C_{20}H_{18}O_4$ requires 322.1205. UV, IR, ^{1}H NMR identical to [15]. EIMS *m/z* (rel. int.): 322 $[M]^+$ (79), 307 $[C_{19}H_{15}O_4]^+$ (100), 203 (80), 104 (20).

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