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Studies on Terpenoids and Steroids, 25. Complete H- and C-Nmr Spectral Assignments of Salaciquinone, a New 7-Oxo-quinonemethide Dinortriterpenoid

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STUDIES ON TERPENOIDS AND STEROIDS, 25.[1] COMPLETE ^{1}H- AND ^{13}C-NMR SPECTRAL ASSIGNMENTS OF SALACIQUINONE, A NEW 7-OXO-QUINONEMETHIDE DINORTRITERPENOID

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ABSTRACT.—A new 7-oxo-quinonemethide dinortriterpenoid, salaciquinone [**1**], and a known quinonemethide dinortriterpenoid, isoiguesterin [**3**], were isolated from the root bark of *Salacia reticulata* var. β-*diandra* (Celastraceae). The structure elucidation of salaciquinone was based on detailed 2D and nOe-difference nmr spectroscopy, leading to the complete assignment of the ^{1}H- and ^{13}C-nmr spectra and revision of some ^{1}H-nmr spectral assignments made previously for the related 7-oxo-quinonemethide nortriterpenoid, dispermoquinone [**2**]. Complete ^{1}H- and ^{13}C-nmr spectral assignments of isoiguesterin were also made, also leading to revision of some ^{13}C-nmr assignments previously made for this compound.

In our continuing interest in the triterpenoids of Celastraceae (2–4) and their nmr spectral studies (5–7), we have carried out a complete ^{1}H- and ^{13}C-nmr assignment of salaciquinone [**1**], a new 7-oxo-quinonemethide dinortriterpenoid encountered in the outer root bark of *Salacia reticulata* Wight var. β-*diandra*. Although the related 7-oxo-quinonemethide nortriterpenoid, dispermoquinone [**2**], has been reported previously, only partial assignment of the 100 MHz ^{1}H-nmr spectrum has been made (8) and, to our knowledge, no ^{13}C-nmr spectral data have been published. ^{1}H-^{1}H COSY, ^{1}H-^{13}C HETCOR, HMBC (proton-detected long-range heteronuclear chemical shift correlation spectroscopy) and nOe difference spectra, recorded at 400 MHz, enabled us to assign completely the ^{1}H- and ^{13}C-nmr spectra of salaciquinone [**1**] and to revise some ^{1}H-nmr assignments made previously for the related 7-oxo-quinonemethide, dispermoquinone [**2**] (8). The isolation of **1** constitutes the second report of the natural occurrence of a 7-oxo-quinonemethide. Also isolated was isoiguesterin [**3**], which has previously been reported from *Salacia madagascariensis* (9). Detailed ^{1}H- and ^{13}C-nmr analysis with the aid of 2D techniques and comparison with the nmr data recently reported for pristimerin [**4**] led to the complete assignment of the ^{1}H-nmr data and the revision of some ^{13}C-nmr assignments previously made for **3**. Previous studies on *S. reticulata* have resulted in the isolation of gutta-percha (10), sitosterol (10), pristimerin (10), mangiferin (11), 21α,26-dihydroxy-D:A-friedo-oleanan-3-one (*epi*-kokoondiol) (12) and 3-hydroxy-2-oxo-29-nor-D:A-friedo-oleana-3(4),20(30)-dien-4-al (salacenonal) (13) from the root bark, and iguesterin, pristimerin and *epi*-kokoondiol from the stem bark (14).

RESULTS AND DISCUSSION

Chromatographic fractionation of the hot hexane extract of the outer root bark of *S. reticulata* var. β-*diandra* afforded salaciquinone [**1**], isoiguesterin [**3**], and β-amyrin. The molecular formula of salaciquinone was determined to be $C_{28}H_{36}O_3$ by hrms. The 11 degrees of unsaturation consisted of six multiple bonds {^{13}C-nmr peaks of two C=O [δ

[1]For Part 24, see Premakumara *et al.* (1).

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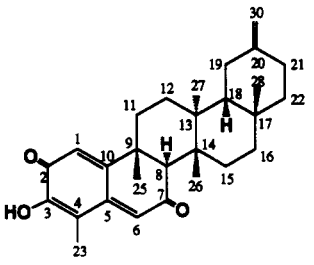

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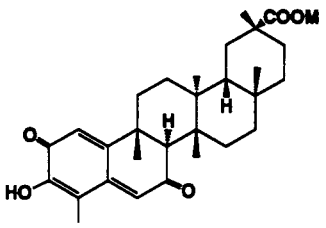

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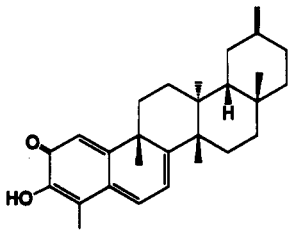

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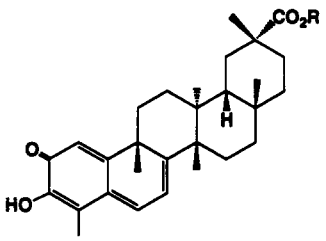


4 R=Me
5 R=H

200.7 (s), 181.2 (s)] and four C=C [δ 162.2 (s), 148.8 (s), 146.6 (s), 140.9 (s), 131.8 (d), 119.7 (d), 117.2 (s), 107.8 (t)]}; consequently five rings were present. The uv spectrum of salaciquinone suggested the presence of a chromophore different from pristimerin [**4**] (15)[3] but similar to that reported for dispermoquinone [**2**] (8). The ir spectrum showed absorption bands characteristic for H-bonded OH (3420 cm^{-1}), quinonoid CO (1672 cm^{-1}) and H-bonded quinonoid CO (1626 cm^{-1}) groups. Based on ^{1}H-^{1}H COSY, ^{1}H-^{13}C HETCOR, HMBC and nOe-difference nmr experiments, the structure **1** was established for salaciquinone. The ^{1}H- and ^{13}C-nmr spectral assignments for salaciquinone are summarized in Table 1.

In contrast to pristimerin-type quinonemethides (5), and phenolic nortriterpenoids (6), salaciquinone had two doublets at δ 6.36 and 6.39 ppm (J=1.5 Hz) in the low-field region of its ^{1}H-nmr spectrum. These signals were due to the protons of the quinonemethide system and were assigned to H-1 and H-6, respectively with the aid of the HMBC spectrum (see below). The two broad singlets at δ 4.61 and 4.60 ppm suggested the presence of an exomethylene group in ring E (see below) as in isoiguesterin [**3**] (9). Further evidence for this structural moiety came from the ^{13}C-nmr spectrum, which had signals at δ 107.8 (t) and 148.8 (s) ppm. The high-field region of the ^{1}H-nmr spectrum consisted of five methyl singlets at δ 2.10, 1.30, 1.29, 1.14, and 1.00 ppm in addition to a complex pattern at δ 1.00–2.40 ppm due to methylene and methine protons. The 3H singlet at δ 2.10 ppm was assigned to the C-4-Me on the quinonemethide system (5). All the remaining signals, including the signals due to α- and β-protons in the ring system, were analyzed with the help of the ^{1}H-^{1}H COSY spectrum (which displayed all the correlation peaks corresponding to geminal, vicinal and long-range couplings) and by comparison with the data reported by us for pristimerin [**4**] (5). The coupling constant(s) for each proton was obtained from the 1D-spectrum and by careful analysis

[3]The structure proposed for prostimerin in this reference was later corrected to [**4**] (16).

TABLE 1. ^{1}H-, ^{13}C- and Two-Dimensional Nmr Spectral Data for Salaciquinone [**1**].[a]

Position	^{1}H[b]	^{13}C[c]	^{1}H-^{1}H COSY	HMBC (^{1}H)
1	6.36 (1H, d, 1.5)	119.7 (d)	H-6	
2	—	181.2 (s)	—	3-OH
3	—	146.6 (s)	—	H-1, 3-OH, H-23
4	—	117.2 (s)	—	3-OH, H-6, H-23
5	—	140.9 (s)	—	H-1, H-23
6	6.39 (1H, d, 1.5)	131.8 (d)	H-1	—
7	—	200.7 (s)	—	H-8
8	2.91 (1H, s)	57.8 (d)	H-25	H-6, H-25, H-26
9	—	41.9 (s)	—	H-1, H-8, H-25
10	—	162.2 (s)	—	H-6, H-8, H-25
11α	2.21 (1H, td, 13.5, 4)	31.9 (t)	H-11β, H-12α, H-12β, H-25	H-25
11β	1.74 (1H, ddd, 13.5, 4, 2.5)		H-11α, H-12α, H-12β	—
12α	1.72 (1H, ddd, 13.5, 4, 2.5)	28.5 (t)	H-11α, H-11β, H-12β	H-27
12β	1.55 (1H, td, 13.5, 4)		H-11α, H-11β, H-12α, H-27	—
13	—	40.5 (s)	—	H-8, H-19α/β, H-26, H-27
14	—	39.6 (s)	—	H-8, H-26, H-27
15α	1.32 (1H, td, 13.5, 6)	27.0 (t)	H-15β, H-16α, H-16β	H-26
15β	2.04 (1H, ddd, 13.5, 6, 2)		H-15α, H-16α, H-16β	—
16α	1.25 (1H, ddd, 13.5, 6, 2)	35.7 (t)	H-15α, H-15β, H-16β	H-28
16β	1.87 td, (13.5, 6)		H-15α, H-15β, H-16α	—
17	—	31.3 (s)	—	H-16β, H-22α, H-28
18β	1.63 (1H, t, 4)	44.4 (d)	H-19α/β, H-27	H-19α/β, H-27, H-28
19α/β	2.37 (2H, br d, 4)	29.9 (t)	H-18, H-30	H-30
20	—	148.8 (s)	—	H-19α/β
21α	2.19 (1H, ddd, 13.5, 5, 2.5)	30.7 (t)	H-21β, H-22α, H-22β	H-19α/β, H-30
21β	2.34 (1H, br td, 14, 6)		H-21α, H-22α, H-22β, H-30	—
22α	2.01 (1H, td, 13.5, 5)	37.9 (t)	H-21α, H-21β, H-22β	H-28, H-16β
22β	1.14 (1H, br dd, 13.5, 5.5)		H-21α, H-21β, H-22α	—
23	2.10 (3H, s)	10.4 (q)	—	—
25	1.30 (3H, s)	29.9 (q)	H-8, H-11α	H-8
26	1.29 (3H, s)	14.7 (q)	H-27	H-8
27	1.00 (3H, s)	18.0 (q)	H-12β, H-18, H-26	—
28	1.14 (3H, s)	31.2 (q)	—	H-16β, H-22α
30	4.61, 4.60 (2×1H, br s)	107.8 (t)	H-19α/β, H-21β	H-19α/β
OH	6.94 (1H, s)			

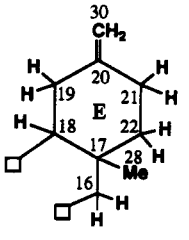
[a]Spectra were recorded in $CDCl_3$ at 399.78 MHz (^{1}H nmr) and 100.54 MHz (^{13}C nmr); chemical shifts are reported in ppm relative to TMS.

[b]Multiplicity and coupling constant(s) in Hz in parentheses.

[c]Multiplicity of carbon signals (in parentheses) were determined by the DEPT method.

of the fine structures of the correlation peaks in the ^{1}H-^{1}H COSY spectrum. The diagnostic correlations observed are summarized in Table 1.

The HMBC spectrum of salaciquinone along with the detailed analysis of the ^{1}H-^{1}H COSY spectrum indicated a partial structure **A** (Figure 1) where the exomethylene group was present in ring E of the triterpenoid skeleton. The placement of the exomethylene group at C-20 was further supported by biogenetic arguments as quinonemethide triterpenoids isolated thus far contain at least one carbon residue attached to C-20 (see **2** and **3**).



A

FIGURE 1. Partial Structure for Ring E of Salaciquinone [**1**].

The 2D nmr experiments (HETCOR and HMBC) along with the chemical shift arguments and signal multiplicities were useful in the assignments of the ^{13}C-nmr spectrum of salaciquinone (Table 1). The protonated carbons in rings C, D, and E were assigned with the aid of ^{1}H-^{13}C correlations in the HETCOR spectrum whereas the quaternary carbons in these rings were assigned with the help of the HMBC spectrum. The diagnostic HMBC correlations observed are summarized in Table 1.

Both ^{1}H- and ^{13}C-nmr assignments in the 3-hydroxy-2,7-dioxo-3,5,10(1)-triene substructure (A and B rings) were aided by careful HMBC correlations, which are represented in Figure 2. Only some important correlations are discussed here. In the HMBC spectrum of salaciquinone, the 3-OH proton (δ 6.94 ppm, exchangeable with D_2O) shows correlations with C-2 (δ 181.2 ppm), C-3 (δ 146.6 ppm) and C-4 (δ 117.2 ppm). The presence of a cross-peak between C-3 and the ^{1}H-nmr signal at δ 6.36 ppm (J=1.5 Hz) suggests that the latter signal should be assigned to H-1. As expected, the ^{1}H-nmr signal at δ 6.36 shows a HMBC correlation with C-5 (δ 140.9 ppm). The ^{1}H-nmr doublet at δ 6.39 ppm (J=1.5 Hz) coupled to H-1 exhibits correlation peaks with C-4 (δ 117.2 ppm) and C-10 (δ 162.2 ppm). Therefore, this proton should be assigned to H-6. Thus, unambiguous assignments of H-1 (δ 6.36 ppm) and H-6 (δ 6.39 ppm) were possible suggesting that the assignments made by Martin (8) for these protons in dispermoquinone [**2**] should be reversed. The ^{1}H- and ^{13}C-nmr signals due to the methylene and methyl groups in rings C and D were also assigned in a similar manner by the application of 2D nmr experiments. The relative dispositions of the methyl groups with respect to some methylene protons were determined with the help of nOe difference spectra, the results of which are summarized in Figure 3.

The physical and spectral data of the second isolated pigment compared well with those reported (9) for isoiguesterin [**3**]. The previous report of isoiguesterin contained only partial assignments of the ^{1}H- and ^{13}C-nmr spectra. Further, the ^{13}C-nmr assignments were based purely on comparisons made with the ^{13}C-nmr spectral data obtained for celastrol [**5**] and the literature data for pristimerin [**4**]. As some ^{13}C-nmr assignments for **4** have since been revised, it was thought desirable to carry out complete analysis of the ^{1}H- and ^{13}C-nmr spectra of isoiguesterin [**3**] with the aid of 2D experiments.

The ^{1}H-nmr spectrum of isoiguesterin [**3**] showed signals due to an OH at δ 7.01 ppm (br s, exchangeable with D_2O, OH-3), five olefinic protons at δ 7.01 (dd, J=7, 1 Hz, H-6), 6.53 (d, J=1 Hz, H-1), 6.33 (d, J=7 Hz, H-7), 4.59 (br s, H-29), and 4.58 (br s, H-29), and five methyl groups at δ 2.21 (s, H_3-23), 1.47 (s, H_3-25), 1.29 (s, H_3-26), 1.16 (s, H_3-28), and 0.70 (s, H_3-27). These signals were readily assigned based on their chemical shift values and/or coupling constants. However, the remaining resonances in the region δ 1.1–2.4 ppm required more rigorous analysis which was done by the application of COSY and HETCOR experiments. These assignments are depicted in Table 2. The carbon chemical shifts of isoiguesterin [**3**], except for the quaternary

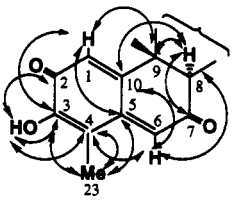


FIGURE 2. Selected HMBC Correlations of Salaciquinone [**1**].

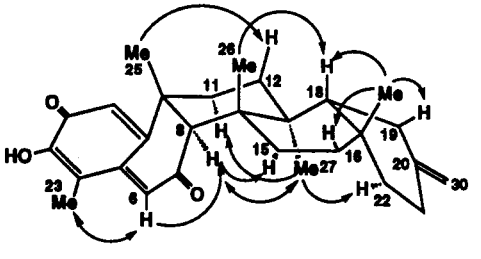


FIGURE 3. Conformation of Salaciquinone [**1**] and Main Observed nOe's.

TABLE 2. ^{1}H- and ^{13}C-Nmr Data for Isoiguesterin [**3**].[a]

Position	^{1}H[b]	^{13}C[c]	Position	^{1}H[b]	^{13}C[c]
1	6.53 d (1)	119.6 (d)	16α	1.43 ddd (13.5, 5, 2)	36.0 (t)
2	—	178.3 (s)	16β	1.87 td (13.5, 5)	
3	—	146.0 (s)	17	—	31.6 (s)
4	—	117.1[k] (s)	18	1.59[e] t (4)	44.9 (d)
5	—	127.4[k] (s)	19α	2.41[h] d (4)	30.4[k] (t)
6	7.01 dd (7, 1)	133.9 (d)	19β		
7	6.33 d (7)	117.9 (d)	20	—	147.9[k] (s)
8	—	170.1[k] (s)	21α	2.19 ddd (13.5, 5, 2)	30.5[k] (t)
9	—	42.9 (s)	21β	2.35[i] br td (13.5, 6)	
10	—	165.0[k] (s)	22α	2.02[g] td (13.5, 5)	36.9 (t)
11α	1.97[d] td (13.5, 6)	33.9[k] (t)	22β	1.14 br dd (13.5, 5.5)	
11β	2.20 ddd (13.5, 5, 2)		23	2.21 s	10.2 (q)
12α	1.84 ddd (13.5, 6, 2)	29.7 (t)	25	1.47 s	38.9 (q)
12β	1.74[e] td (13.5, 6)		26	1.29[j] s	21.3 (q)
13	—	41.3 (s)	27	0.70[j] s	19.7 (q)
14	—	44.8 (s)	28	1.16 s	31.1 (q)
15α	1.74[f] td (13.5, 5)	28.4[k] (t)	30	4.58, 4.59[h,i] each br s	108.2 (t)
15β	1.52 ddd (13.5, 5, 2)		3-OH	7.01 br s	

[a]Spectra were recorded in $CDCl_3$ at 399.78 MHz (^{1}H nmr) and 100.54 MHz (^{13}C nmr); chemical shifts are reported in ppm relative to TMS.

[b]Figures in parentheses are coupling constants in Hz.

[c]Multiplicity of carbon signals (in parentheses) were determined by the DEPT method.

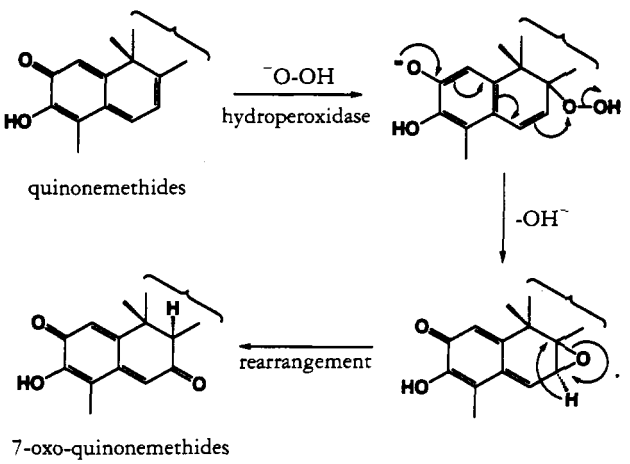
[d–g]Long-range coupling was observed with H-25, H-27, H-26, and H-28, respectively, in the ^{1}H-^{1}H COSY.

[h–i]Long-range coupling was observed between each other in the ^{1}H-^{1}H COSY.

[k]Previous assignments by Sneden (9) were revised.

carbons, were unambiguously assigned by the HETCOR experiment; quaternary carbons were assigned by comparison with our data (5) for pristimerin [**4**]. The resulting ^{13}C-nmr assignments for isoiguesterin [**3**] are presented in Table 2. Our data suggest that the assignments made by Sneden (9) for C-3, C -4, C-5, C-8, C-10, C-11, C-15, C-16, C-19, and C-21 of isoiguesterin [**3**] need revision.

The biosynthetic origin of salaciquinone [**1**] may be of some interest. The co-occurrence of 7-oxo-quinonemethides with quinonemethides in some Celastraceae and Hippocrateaceae species prompts us to suggest their biosynthetic interrelationship as depicted in Scheme 1. As such, isoiguesterin [**3**] may be considered as the biosynthetic precursor of salaciquinone [**1**].



SCHEME 1. Possible Biosynthetic Relationship Between Quinonemethides and 7-Oxo-quinonemethides.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps were determined on a Kofler hot stage and are uncorrected. Tlc involved Si gel 60 GF; visualization was by uv (254 nm) and by spraying with acidified anisaldehyde followed by charring with heat. Flash chromatography involved Si gel of mesh 230–400 ASTM. Plc used 0.25 mm layers of Si gel GF_{254}. Optical rotations were measured in $CHCl_3$ solution at 27° with a Perkin-Elmer 241 polarimeter. Uv spectra were recorded for EtOH with a Shimadzu UV 160 spectrometer and ir spectra with a Shimadzu IR 408 spectrometer. The ms were recorded on a JEOL JMS-D 300 mass spectrometer with a direct inlet system.

NMR MEASUREMENTS.—Unless otherwise stated, instrumentation and conditions used for nmr measurements and processing were the same as those described previously (5). The nmr spectra were recorded as ca. 10% solutions in $CDCl_3$ at ambient temperature. NOe difference spectra were obtained with JEOL standard pulse sequence with 5 sec irradiation. HMBC spectra were measured using a pulse sequence (JEOL VHMBC sequence, J_{CH}=140 Hz, long-range J_{CH}=8.3 Hz) reported by Bax and Summers (17). The free-induction decays were acquired over 2048 data points and 2500 Hz for each of 128 values of evolution time. The raw data were zero-filled from 128 to 256 W in the second dimension (F_1) before double Fourier transformation.

PLANT MATERIAL.—Roots of *S. reticulata* var. β-*diandra* were collected at the Sinharaja Forest in Sri Lanka by Prof. S. Balasubramaniam of the Department of Botany, University of Peradeniya, Sri Lanka, where a voucher specimen has been deposited.

EXTRACTION AND ISOLATION.—Dried and powdered root bark (375.0 g) of *S. reticulata* var. β-*diandra* was sequentially extracted with hot hexane and C_6H_6. Evaporation of the hexane extract afforded a red solid (35.0 g). A portion (25.0 g) of this extract was subjected to flash chromatography over Si gel with solvent gradients ranging from hexane to hexane containing increasing amounts of EtOAc. A total of 75 fractions were collected and combined based on their tlc patterns. The combined fraction 6–7 (0.7 g) was further fractionated by flash chromatography with solvent gradients of C_6H_6/EtOAc to obtain a mixture of two compounds which were separated by prep. tlc (5% EtOAc in C_6H_6) yielding salaciquinone [**1**] (10 mg) and β-amyrin (122 mg). β-Amyrin, mp 193–195°; $[\alpha]_D$ +88° (c=0.5) {lit. (18) mp 197–200°; $[\alpha]_D$ +88°} was identified by comparison with an authentic sample (mmp, co-tlc, and co-ir). On standing the combined fractions 8–9 from the original flash chromatography precipitated an orange solid (2.3 g), which was further purified by repeated prep. tlc (20% Me_2CO in hexane) to afford isoiguesterin [**3**] (52 mg). The remaining column fractions contained complex mixtures of compounds, and further separation of these is currently being attempted.

SALACIQUINONE [**1**].—Orange crystals, mp 252–254° (CH_2Cl_2-MeOH); $[\alpha]_D$ −130° (c=1.0); uv λ max (EtOH) 246 (log ε 3.50), 321 (3.92), 328 (3.88), 409 (3.50) nm; ir ν max ($CHCl_3$) 3420, 1672, 1654, 1626, 1461, 1453, 1423, 1301, 1251, 1196 cm^{-1}; ^1H and ^{13}C nmr see Table 1; hreims, m/z $[M]^+$ 420.2655 (calcd for $C_{28}H_{36}O_3$, 420.2664) (43), 286.1584 (calcd for $C_{18}H_{22}O_3$, 286.1569) (20), 231.1069 (calcd for $C_{14}H_{15}O_3$, 231.1021) (18), 218.0932 (calcd for $C_{13}H_{14}O_3$, 218.0943) (28), 216.0765 (calcd for $C_{13}H_{12}O_3$, 216.0786) (100).

ISOIGUESTERIN [**3**].—Orange plates, mp 198–200° (CH_2Cl_2) [lit. (9) 203–205°]; $[\alpha]_D$ −100° (c=0.1); uv and ir spectral data identical with those reported (9); ^1H and ^{13}C nmr see Table 2; eims m/z $[M]^-$ 404 (100), 389 (11), 253 (21), 241 (67), 202 (62), 201 (69), 200 (30), 187 (19), 147 (17), 107 (24), 95 (21).

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