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RETRODIHYDROCHALCONES FROM *DRACAENA LOUREIRI*

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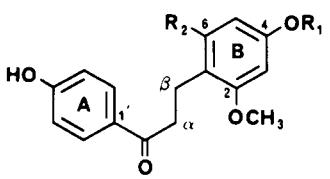
ABSTRACT.—The first four members of a new class of natural products, the retrodihydrochalcones, have been isolated from the leaves of *Dracaena loureiri*. The structures of the loureirins **1–4** were elucidated through interpretation of their spectroscopic data, with particular use being made of the selective INEPT nmr technique.

In a previous phytochemical study of *Dracaena loureiri* Gagnep (Agavaceae), we reported the isolation and structure elucidation of two members of the dracaenone skeleton (1), in which phenolic oxidation of a preformed homoisoflavan has occurred, a reaction that can be reproduced experimentally (2). We now report on the isolation and structure determination of the first four members of a new group of natural products, the loureirins, **1–4**, having the retrodihydrochalcone skeleton.

The molecular formula of $C_{17}H_{18}O_4$ for loureirin A [**1**] was deduced from the eims in combination with the ^{1}H- and ^{13}C-nmr spectra. A uv maximum at 279 nm, showing a bathochromic shift when NaOAc was added, suggested a free 4′-hydroxyl group (3), and the absence of a phenolic hydroxyl group ortho to the carbonyl group was demonstrated from the lack of a hypsochromic shift on the addition of $AlCl_3$. The ^{1}H-nmr and APT spectra displayed two sets of methylene, two methoxyl, and seven aromatic protons, in addition to a carbonyl resonance in the latter spectrum. In the proton spectrum, three of the aromatic protons appeared as an ABX pattern at 6.40 (dd, $J = 8.1$, 2.1 Hz), 6.43 (d, $J = 2.1$ Hz), and 7.05 ppm (d, $J = 8.1$ Hz) assigned to H-5, H-3, and H-6, respectively, with the remaining four protons as an AA′XX′ pattern at 6.92 (d, $J = 8.5$ Hz) and 7.91 ppm (d, $J = 8.5$ Hz), assigned to H-3′/5′ and H-2′/6′, respectively. The downfield resonance of the latter protons implied that they were attached ortho to the carbonyl group, in agreement with a 4-hydroxyacetophenone (7.9 ppm) derivative. The dominant peaks in the eims spectrum, at *m/z* 121 and 151 from α and β cleavage (3–6), respectively, revealed the existence in loureirin A of a monohydroxybenzoyl group in which ring A bore no oxygen function at C-2′ or C-6′, and an oxygenated benzyl group. Thus, loureirin A was deduced to be 4′-hydroxy-2,4-dimethoxydihydrochalcone [**1**].

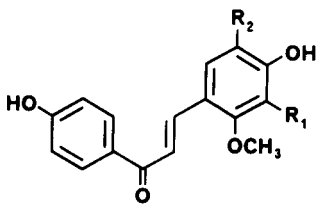
From the available literature data on related compounds (7–9), it appeared that assignment of the ^{1}H- and ^{13}C-nmr chemical shifts of the aliphatic α and β positions was ambiguous. In the present studies, evidence to assign H-α and H-β was obtained from the homonuclear COSY spectrum which revealed the presence of long range coupling between the signals at 7.05 (H-6) and 2.96 ppm. The latter resonance could, therefore,



	R_1	R_2
1	Me	H
2	Me	OMe
3	H	H
4	H	OH

be assigned to H-β, leaving the methylene triplet at 3.19 ppm to be assigned to H-α. In addition, the long range coupling and nOe effects between the methoxy group singlet at 3.77 ppm and H-3, H-5, as well as between the singlet at 3.76 ppm and H-3, were observed in the COSY and 2D-nOe spectra. Consequently, these methoxy group singlets were assigned to positions 4 and 2, respectively. An nOe effect between the 2-OMe and H-α was also observed, in substantiation of these attributions.

Recently, the structure elucidation of 2,4-dihydroxy-6,4′-dimethoxychalcone, isolated from *Pancratium biflorum* (10), was not confirmed when comparison of the chemical shift of H-2′/6′ was made among this compound (δ 7.32), echinatin [**5**] (δ 8.00) (11), licochalcone A [**6**] (δ 7.97) and licochalcone B [**7**] (δ 8.07) (12), and 4-methoxyacetophenone (δ 7.95). Furthermore, analysis of the H-2′/6′ resonance, considering the normal numbering system of natural dihydrochalcones (13,14), of the diacetate of 2,4-dihydroxy-4′-methoxydihydrochalcone (δ 6.70), isolated from *Artemisia palustris* (15), and compound **1** (δ 7.91), indicated no close similarity. Consequently, it was necessary to establish independently the position of the carbonyl in the dihydrochalcone moiety of **1**.



	R_1	R_2
5	H	H
6	H	$C(CH_3)_2CH=CH_2$
7	OH	H

Previous studies suggested that the selective INEPT technique would be an appropriate spectroscopic tool (1, 16–21). Polarization transfer from H-2′/6′ ($J=9$ Hz) enhanced a carbonyl resonance at 200.86 ppm, an oxygenated carbon at 161.33 ppm (C-4′), and a protonated resonance at 130.96 ppm (C-2′/6′) (Figure 1). Hence, the carbonyl is attached to the para-hydroxy benzoyl moiety. In addition, transfer from H-β ($J=4$ Hz) enhanced the carbonyl resonance at 200.86 ppm, a protonated carbon at 130.20 ppm (C-6) as well as two quaternary carbons at 158.21 (C-2) and 121.57 (C-1) ppm. This also confirmed that the ethylene bridge was connected to the 2,4-dimethoxy benzene moiety. Assignment of the protonated carbons was confirmed by two-dimensional heteronuclear ^{1}H-^{13}C shift correlation.

Loureirin B displayed an intense molecular ion in the eims at *m/z* 316, which in combination with the ^{1}H- and ^{13}C-nmr spectral data was consistent with a molecular formula of $C_{18}H_{20}O_5$. Comparison of the methanolic uv, eims and ^{1}H-nmr spectra of this isolate with those of loureirin A [**1**] indicated a close similarity. Two intense fragments at *m/z* 121 and 181 arising from α and β cleavage were present, and the aromatic protons still contained an AA′XX′ type quartet for ring A at 6.93 and 7.93 ppm. An additional methoxyl singlet (3.77 ppm) was located at position 6 of ring B leading to the meta protons being observed as a two-proton singlet (6.11 ppm) as expected for a symmetrically substituted ring. Ortho-dimethoxy substitution of the phenylpropanone moiety introduced some restriction to rotation resulting in enhanced complexity and line broadening of both the H-α (3.07 ppm) and H-β (2.99 ppm) systems at ambient temperature. The presence of three methoxyl groups in ring B of loureirin B

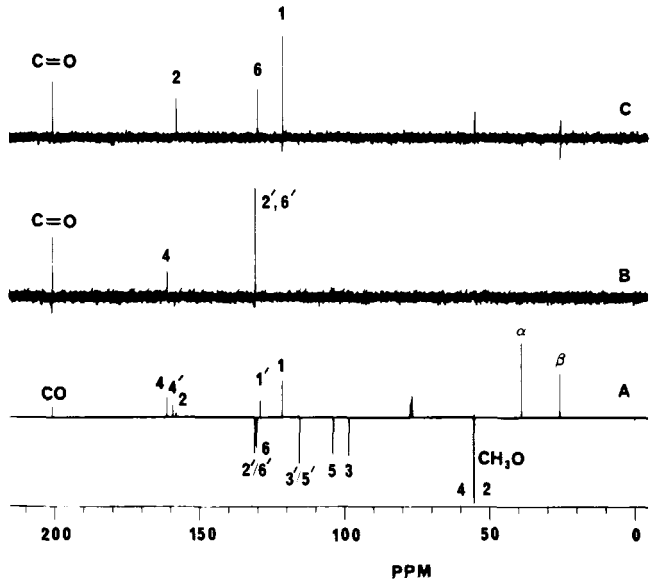


FIGURE 1. Carbon-13 nmr spectra of loureirin A [**1**]. (A) APT; (B,C) Selective INEPT spectra through irradiation of H-2′/6′ and H-β, respectively.

forced the two magnetically-equivalent proton resonances, H-3 and H-5, to move to higher field than in **1**, whereas H-2′/6′ and H-3′/5′ were similarly located as in **1**. It was, therefore, concluded that loureirin B was 4′-hydroxy-2,4,6-trimethoxydihydrochalcone [**2**]. Assignment of the quaternary carbons was established through selective INEPT experiments.

Loureirin C [**3**] showed an intense molecular ion at *m/z* 272, for which the molecular formula $C_{16}H_{16}O_4$ could be deduced from the ^{1}H- and ^{13}C-nmr spectra. As in the preceding two compounds, the fragment ions at *m/z* 121 and 137 suggested the presence of para-hydroxybenzoyl and hydroxymethoxy-tropylium ions from α and β cleavage. Comparison of the methanolic uv, eims, ^{1}H and ^{13}C-nmr spectra of this isolate with those of loureirin A [**1**] suggested that loureirin C differed by the replacement of a methoxyl group by a hydroxyl group.

Comparison of the methanolic uv spectra of **1** and **3** after NaOMe addition did not show any significant difference of bathochromic shift indicating the presence of a para-hydroxy group in ring B as in other flavonoids. Location of a methoxy group either at position 2 or 4 was determined through two selective INEPT experiments. Transfer from H-β ($J = 4$ Hz) enhanced a carbonyl resonance (201.60 ppm), an oxygenated sp^2 carbon (C-2, 159.57 ppm), and a protonated sp^2 carbon (C-6, 131.21 ppm). When the methoxy group singlet at 3.75 ppm was irradiated, enhancement of the same oxygenated sp^2 carbon (C-2) was observed as in the preceding SINEPT experiment. Loureirin C was, therefore, concluded to have the structure 4,4′-dihydroxy-2-methoxydihydrochalcone [**3**].

The ^{1}H- and ^{13}C-nmr spectra of loureirin D, together with a weak molecular ion at *m/z* 288, were consistent with a molecular formula of $C_{16}H_{16}O_5$, and this was confirmed by high resolution mass measurement. The predominant peaks at *m/z* 120 and 152 in the mass spectrum revealed the existence of monohydroxybenzoyl and oxygenated tropylium ions in the structure. Similarly to loureirin A, there was no significant difference on the addition of NaOMe to the methanolic uv spectra; this indicated the

presence of a free 4-hydroxyl group in ring B. Analysis of the spectroscopic data obtained for **4** indicated a close similarity to those of loureirin B [**2**]. The two-proton singlet for the meta protons (H-3 and H-5) in **2** had become an AB spin system in **4**, indicating that the three substituents in ring B were not identical. One must be a methoxyl group (3.70 ppm) and the other two must be hydroxyl groups as indicated by the number of oxygenated quaternary resonances in the low field region of the APT spectrum. The location of the methoxyl group was solved through the application of nOe difference spectroscopy. Irradiation of the methoxy group resulted in nOe enhancement of only the resonance at 5.99 ppm (14%), which was, therefore, assigned to H-3. Loureirin D, therefore, has the structure 4,6,4′-trihydroxy-2-methoxydihydrochalcone [**4**].

With the proton assignments available, all of the ambiguous assignments of the oxygenated quaternary carbons of compound **4** could be solved with the aid of selective INEPT experiments. Irradiation of H-2′/6′ ($J = 9$ Hz) enhanced a carbonyl resonance (202.86 ppm), an oxygenated sp^2 resonance (163.51 ppm, C-4′), and a protonated resonance (132.01 ppm, C-2′/6′). Selective INEPT transfer from H-β ($J = 6$ Hz) enhanced the same carbonyl resonance, two oxygenated sp^2 resonances at 160.34 ppm (C-2) and 157.28 ppm (C-6), and a nonprotonated carbon at 108.11 ppm (C-1). When the 2-OMe was irradiated ($J = 4$ Hz), the same resonance as that previously assigned to C-2 was enhanced, thereby confirming the result of the nOe experiment.

Comparison of the carbon assignments among compounds **1–4** revealed that the carbon resonances of C-1, C-3, and C-5 of **2** and **4** were moved further upfield by the ortho and para shielding effect of the additional oxygenated substituent at C-6. In addition, the carbon resonances of C-β of **2** and **4** also moved upfield by the γ-gauche shielding effect to a hetero atom of this additional oxygenated substituent at C-6.

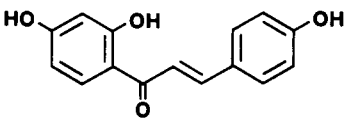
It was noted in the mass spectrum that the fragment ions due to $[M - OMe]^+$ and $[M - Me]^+$, which are characteristic of 2-methoxyretrochalcones **11** and **12**, were not observed for the 2-methoxyretrodihydrochalcones **1–4**, probably due to the lack of a driving force from the conjugated carbonyl linked between two aromatic moieties to expel a methoxy as in echinatin [**5**] (11), licochalcone A [**6**] and licochalcone B [**7**] (12). Interestingly, the major fragment ions of loureirin D occurred at 1 mass unit less than the anticipated fragments resulting from the simple α and β cleavage of other loureirin derivatives. It is thought that in this case the intramolecular rearrangement might involve internal ketal formation prior to retro-Diels-Alder fragmentation to afford *m/z* 152, or β cleavage in other loureirins, and rearrangement leading to α cleavage and *m/z* 120.

Loureirin D appeared white after recrystallization in MeOH but turned red in $CHCl_3$ solution. This observation suggested that traces of acid in the $CHCl_3$, together with a catalytic effect of the light, caused some degradation or rearrangement of loureirin D, because it also rapidly turned yellow, then orange, after addition of HCl, and became red and finally melted to a deep red liquid after warming. The red color in this instance might possibly be due to the formation of a flavylium cation or a quinoidal base (22–25). A greater tendency to form the stable retrodihydrochalcone in basic solution (25,26) was observed, inasmuch as there was no color change after addition of alkali to a MeOH solution of loureirin D.

Conformational information regarding the retrodihydrochalcones was achieved through the aid of a 2D-nOe experiment. NOe effects were observed between H-β and H-2′/6′ and between the 2-OMe and H-α, H-3′/5′, H-2′/6′ in loureirin A. It was, therefore, concluded that the active conformation in solution of the retrodihydrochalcones was preferably a bent form. The probable mechanism for the intramolecular cyclization of loureirin D in acidic MeOH could be explained by a general acid attack to the

ionized form of loureirin D and rotation through the CO-Cα bond, followed by nucleophilic addition of the phenolate anion to form the final product (27).

Echinatin [**5**], a constituent of the tissue culture of *Glycyrrhiza echinata*, has been shown by feeding experiments to be the first retrochalcone in which the biosynthetic origins of the two aromatic rings are reversed compared with those of a normal flavonoid, i.e., ring A of echinatin originates from cinnamyl CoA while ring B is formed via the acetate-malonate pathway (28–30). Incorporation of the ^{14}C label at the carbonyl carbon in isoliquiritigenin [**8**] and licodione [**9**] has suggested that the biosynthetic process involved the 1,3 functional group transposition of an α,β-unsaturated ketone via an epoxide or peroxide to licodione which could be converted intact to label the β position of echinatin. The last steps of echinatin biosynthesis would then consist of the following steps: 2′-*O*-methylation of licodione catalyzed by LMT (*S*-adenosyl-L-methionine/licodione 2′-*O*-methyltransferase), subsequent reduction of the 1-keto group of 2′-*O*-methyl licodione to a benzyl alcohol, and dehydration to yield the retrochalcone (31). Biogenetically, it is proposed that the loureirin series, having a similar hydroxylation pattern and, therefore, a corresponding mechanistic pathway in which reduction takes the place of dehydration, can thus be designated as retrodihydrochalcones. Loureirins A, B, C, and D (compounds **1**–**4**, respectively) represent the first naturally occurring representatives of this compound class.



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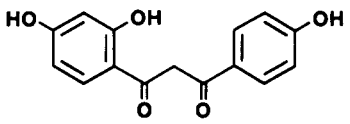

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EXPERIMENTAL

GENERAL EXPERIMENTAL METHODS.—The general methods used in these studies have been described previously (1).

PLANT MATERIAL.—Dried stem material of *D. loureiri* was collected at Prachuab-kirikhan Province, Thailand, in January 1982. The plant material was identified by the Botany Section, Technical Division, Department of Agriculture, Ministry of Agriculture and Cooperatives, Thailand. A herbarium specimen is deposited in the herbarium of the Department of Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok, Thailand.

EXTRACTION AND ISOLATION.—The chipped and ground dried stems (630 g) were successively extracted with petroleum ether, $CHCl_3$, and EtOH in a Soxhlet apparatus for 48 h. Evaporation of the solvents gave residues of 11.8, 152.7, and 104.4 g, respectively.

The petroleum ether, $CHCl_3$, and EtOH extracts were tested for antibacterial activity against *Staphylococcus aureus* ATCC 25923, *Bacillus subtilis* ATCC 6633, and *Escherichia coli* ATCC 25922, which are representatives of Gram positive, spore producing, and Gram negative bacteria, respectively, by the Kirby-Bauer disc diffusion technique (32). Only the $CHCl_3$-soluble fraction displayed antibacterial activity against *S. aureus* and *B. subtilis*. Using a bioautographic method (33), we localized antibacterial activity of the $CHCl_3$ extract between R_f 0.5 and 0.6 on Si gel tlc plate developed with petroleum ether-EtOAc (6:1) at the 250-μg level. The active extract (152 g) was subjected to Si gel-60 cc (8 × 100 cm), collecting 1-liter fractions and eluting with mixtures of petroleum ether and EtOAc, EtOAc, and MeOH of increasing polarity. Full details of the remaining isolates together with their biological properties have appeared elsewhere (34).

PURIFICATION OF LOUREIRIN A [**1**].—Fractions 28–32, eluted from the Si gel-60 column with petroleum ether and EtOAc (3:1), were further subjected to Si gel-60 PF 254 chromatography (5.5 × 47 cm), collecting 50-ml fractions and eluting with mixtures of $CHCl_3$ and MeOH of increasing polarity. Fractions 29–40 afforded yellow rhombic crystals of **1** (1.7 g, 0.276% dry wt), mp 124°, $[\alpha]^{21}D$ 0° ($c = 0.082$, MeOH); R_f [$CHCl_3$-MeOH (92:8)] 0.42; uv λ max (MeOH) 218 (log ε 4.31), 279 nm (4.27); λ max

(+ NaOMe) 217 (log ε 4.35), 228 (sh) (4.14), 285.5 (sh) (3.89), 315 (4.32), 334 (sh) nm (4.26); λ max (+ $AlCl_3$) 216.5 (log ε 4.35), 278 nm (4.25); λ max (+ $AlCl_3$/HCl) 219 (log ε 4.30), 279 nm (4.24); λ max (+ NaOAc) 233 (log ε 4.40), 282 (4.24), 323 nm (4.00); λ max (+ NaOAc/H_3BO_3) 233 (log ε 4.40), 280 nm (4.34); ir ν max (KBr) 3360, 3075, 3005, 2954, 2936, 2909, 2868, 2833, 1655, 1616, 1605, 1578, 1507, 1300, 1275, 1209, 1175, 1155 cm^{-1}; ^1H nmr (360 MHz, $CDCl_3$) δ 8.05 (1H, br s, exchangeable with D_2O, OH), 7.91 (2H, d, J = 8.5 Hz, H-2′ and H-6′), 7.05 (1H, d, J = 8.1 Hz, H-6), 6.92 (2H, d, J = 8.5 Hz, H-3′ and H-5′), 6.43 (1H, d, J = 2.1 Hz, H-3), 6.40 (1H, dd, J = 8.1, 2.1 Hz, H-5), 3.77 (3H, s, 4-OMe), 3.76 (3H, s, 2-OMe), 3.19 (2H, t, J = 7.6 Hz, H-α), 2.96 (2H, t, J = 7.6 Hz, H-β); ^{13}C nmr (90.8 MHz, $CDCl_3$) δ 200.86 (C=O), 161.33 (C-4′), 159.32 (C-4), 158.21 (C-2), 130.96 (C-2′ and C-6′), 130.20 (C-6), 129.08 (C-1′), 121.57 (C-1), 115.49 (C-3′ and C-5′), 103.86 (C-5), 98.48 (C-3), 55.35 (4-OMe), 55.16 (2-OMe), 38.91 (C-α), 25.70 (C-β); eims *m/z* (rel. int.) $[M]^+$ 286 (77%), 166 (3), 165 (26), 152 (31), 151 (100), 150 (4), 138 (71), 122 (13), 121 (100), 107 (6), 93 (25), 77 (18).

PURIFICATION OF LOUREIRIN B [**2**].—Fractions 36–39, eluted from the Si gel-60 column with petroleum ether-EtOAc (2:1), were further subjected to Si gel-60 PF 254 chromatography (5.5 × 43 cm), collecting 50-ml fractions and eluting with mixtures of $CHCl_3$ and MeOH of increasing polarity. Fractions 54–68 afforded glassy, square yellow crystals in $CHCl_3$ and white needles in MeOH of **2** (918.7 mg, 0.146% w/w), mp 132–133° (MeOH); $[\alpha]^{21}D$ 0° (*c* = 0.073, MeOH); R_f [$CHCl_3$-MeOH (92:8)] 0.39; uv λ max (MeOH) 215 (log ε 4.31), 277 nm (4.21); λ max (+ NaOMe) 216 (log ε 4.32), 233 (4.17), 315 (sh) (4.30), 324 nm (4.31); λ max (+ $AlCl_3$) 215 (log ε 4.30), 277 nm (4.20); λ max (+ $AlCl_3$/HCl) 215 (log ε 4.30), 277.5 nm (4.17); λ max (+ NaOAc) 229 (log ε 4.38), 280.5 (4.15), 322.5 nm (3.84); λ max (+ NaOAc/H_3BO_3) 218 (sh) (log ε 4.37), 232 (4.39), 279.5 nm (4.21); ir ν max (KBr) 3115, 3057, 2942, 2835, 2629, 1647, 1613, 1603, 1592, 1574, 1291, 1227, 1206, 1178, 1152, 1127 cm^{-1}; ^1H nmr (360 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 8.7 Hz, H-2′ and H-6′), 6.93 (2H, d, J = 8.7 Hz, H-3′ and H-5′), 6.11 (2H, s, H-3 and H-5), 3.78 (3H, s, 4-OMe), 3.77 (6H, s, 2-OMe and 6-OMe), 3.07 (2H, m, H-α), 2.99 (2H, m, H-β); ^{13}C nmr (90.8 MHz, $CDCl_3$) δ 201.48 (C=O), 161.26 (C-4′), 159.50 (C-2 and C-6), 158.63 (C-4), 130.03 (C-2′ and C-6′), 129.15 (C-1′), 115.40 (C-3′ and C-5′), 109.51 (C-1), 90.40 (C-3 and C-5), 55.52 (2-OMe and 6-OMe), 55.31 (4-OMe), 38.48 (C-α), 18.90 (C-β); eims *m/z* (rel. int.) $[M]^+$ 316 (76%), 196 (3), 195 (22), 182 (46), 181 (100), 168 (50), 136 (30), 122 (10), 121 (98), 107 (6), 93 (21), 91 (12), 77 (12).

PURIFICATION OF LOUREIRIN C [**3**].—Fractions 44–45, eluted from the Si gel-60 column with petroleum ether-EtOAc (2:1), were further subjected to Si gel-60 PF 254 chromatography (5 × 47 cm), collecting 200-ml fractions, and eluting with mixtures of $CHCl_3$ and MeOH of increasing polarity. Fractions 149–182 afforded a yellow foam of **3** (498.4 mg, 0.079% dry wt), mp 157–158°; $[\alpha]^{21}D$ 0° (*c* = 0.054, MeOH); R_f [$CHCl_3$-MeOH (87:13)] 0.41; uv λ max (MeOH) 219 (log ε 3.89), 279.5 nm (3.90); λ max (+ NaOMe) 215 (log ε 4.09), 238 (3.85), 324 nm (4.03); λ max (+ $AlCl_3$) 219.5 (log ε 3.88), 279 nm (3.87); λ max (+ $AlCl_3$/HCl) 219.5 (log ε 3.84), 279.5 nm (3.84); λ max (+ NaOAc) 227 (log ε 4.13), 281.5 (3.81), 324 nm (3.64); λ max (+ NaOAc/H_3BO_3) 229 (log ε 4.13), 280.5 nm (3.88); ir ν max (KBr) 3409, 3137, 2942, 2829, 2709, 1657, 1598, 1579, 1511, 1290, 1247, 1212, 1199, 1177, 1154 cm^{-1}; ^1H nmr (360 MHz, CD_3OD) δ 7.85 (2H, d, J = 8.7 Hz, H-2′ and H-6′), 6.91 (1H, d, J = 8.0 Hz, H-6), 6.81 (2H, d, J = 8.7 Hz, H-3′ and H-5′), 6.38 (1H, d, J = 2.1 Hz, H-3), 6.28 (1H, dd, J = 8.0, 2.1 Hz, H-5), 3.75 (3H, s, 2-OMe), 3.09 (2H, t, J = 7.7 Hz, H-α), 2.84 (2H, t, J = 7.7 Hz, H-β); ^{13}C nmr (90.8 MHz, CD_3OD) δ 201.60 (C=O), 163.53 (C-4′), 159.57 (C-2), 158.05 (C-4), 131.83 (C-2′ and C-6′), 131.21 (C-6), 129.84 (C-1′), 121.21 (C-1), 116.10 (C-3′ and C-5′), 107.58 (C-5), 99.64 (C-3), 55.52 (2-OMe), 39.88 (C-α), 26.78 (C-β); eims *m/z* (rel. int.) $[M]^+$ 272 (46%), 152 (2), 151 (14), 138 (9), 137 (100), 136 (6), 124 (30), 122 (6), 121 (72), 107 (24), 93 (13), 77 (11).

PURIFICATION OF LOUREIRIN D [**4**].—Fractions 120–122, eluted from the Si gel-60 column with EtOAc, were further subjected to Si gel-60 column chromatography (3 × 30 cm), collecting 100-ml fractions and eluting with mixtures of petroleum ether, $CHCl_3$, and EtOAc of increasing polarity. Fractions 6–11 afforded red needles in $CHCl_3$ and a white powder in MeOH of **4** (90.5 mg, 0.014% dry wt), mp 176–178° (MeOH); $[\alpha]^{21}D$ 0° (*c* = 0.078, MeOH); R_f [EtOAc-MeOH (9:1)] 0.56; uv λ max (MeOH) 225 (sh) (log ε 4.26), 278 nm (4.25); λ max (+ NaOMe) 235.5 (sh) (log ε 4.20), 294.5 (sh) (4.03), 324.5 nm (4.43); λ max (+ $AlCl_3$) 225 (sh) (log ε 4.32), 275 nm (4.00); λ max (+ NaOAc) 281 (log ε 4.17), 322.5 nm (3.98); λ max (+ NaOAc/H_3BO_3) 279.5 nm (log ε 4.23); ir ν max (KBr) 3320, 3195, 3116, 2997, 2959, 2838, 2697, 1658, 1597, 1513, 1484, 1289, 1168, 1150, 1101 cm^{-1}; ^1H nmr (360 MHz, CD_3OD) δ 7.90 (2H, d, J = 8.7 Hz, H-2′ and H-6′), 6.84 (2H, d, J = 8.7 Hz, H-3′ and H-5′), 6.03 (1H, d, J = 2.0 Hz, H-5), 5.99 (1H, d, J = 2.0 Hz, H-3), 3.70 (3H, s, 2-OMe), 3.08 (2H, t, J = 7.4 Hz, H-α), 2.91 (2H, t, J = 7.4 Hz, H-β); ^1H nmr (360 MHz, DMSO-d_6) δ 10.32 (1H, s, OH), 9.17 (1H, s, OH), 9.07 (1H, s, OH), 7.86 (2H, d, J = 8.7 Hz, H-2′ and H-6′), 6.84 (2H, d, J = 8.7 Hz, H-3′ and H-5′), 5.97 (1H, d, J = 2.0 Hz, H-5), 5.89 (1H, d, J = 2.0 Hz, H-3), 3.66 (3H, s, OMe-2), 2.90 (2H, t,

J = 7.1 Hz, H-α), 2.71 (2H, t, J = 7.1 Hz, H-β); ^{13}C nmr (90.8 MHz, CD_3OD) δ 202.86 (C=O), 163.51 (C-4′), 160.34 (C-2), 157.72 (C-4), 157.28 (C-6), 132.01 (C-2′ and C-6′), 129.68 (C-1′), 116.05 (C-3′ and C-5′), 108.11 (C-1), 96.48 (C-5), 91.87 (C-3), 55.73 (2-OMe), 39.47 (C-α), 19.79 (C-β); eims *m/z* (rel. int.) $[M]^+$ 288 (4%), 287 (23), 269 (11), 268 (15), 166 (12), 153 (10), 152 (100), 151 (4), 150 (4), 148 (6), 139 (71), 135 (5), 134 (3), 121 (5), 120 (60), 106 (6), 93 (4), 92 (14), 76 (6); mass measurement found 288.1003; calcd for $C_{16}H_{16}O_5$, 288.0998.

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