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TETRONIC ACID AND DIARYLPROPANES FROM *IRYANTHERA ELLIPTICA**

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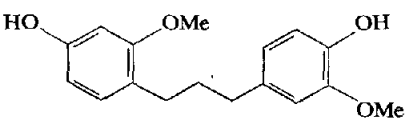
Key Word Index—*Iryanthera elliptica*; Myristicaceae; spiro-cyclohexadien-1,1′-tetralin-4-one; flavan; diarylpropane; 2-(ω-piperonyltridecyl)-4-methylidenetetronic acid.

Abstract—The trunk wood of *Iryanthera elliptica* Ducke (Myristicaceae) contains, besides 2-(ω-piperonyltridecyl)-4-methylidenetetronic acid (iryelliptin), three biogenetically related compounds: (±)-7,4′-dihydroxy-3′-methoxyflavan, 1-(4′-hydroxy-2′-methoxyphenyl)-3-(4″-hydroxy-3″-methoxyphenyl)-propane and spiro-[3-methoxy-2,5-cyclohexadien-1.1′-6′,7′-dihydroxy-5′-methoxy-1′,2′,3′,4′-tetrahydronaphthalen]-4-one-(spiroelliptin). Spiroelliptin rearranges upon methylation to 2,2′-trimethylene-3,4,5,4′,5′-pentamethoxybiphenyl.

INTRODUCTION

Iryanthera elliptica Ducke, a slender tree which grows 20 m high, occurs in the Brazilian region of the Amazon [2]. Fractionation of the EtOH extract of its trunk wood gave, besides aliphatic esters and sitosterol, a 1,3-diarylpropane **1**, previously isolated from *I. coriacea* Ducke [3], together with three novel compounds: **2** (spiroelliptin), **3** and **4** (iryelliptin).



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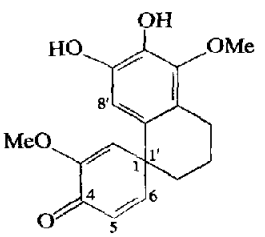

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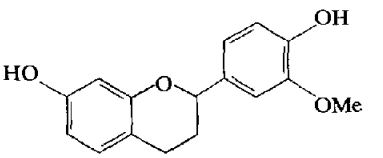

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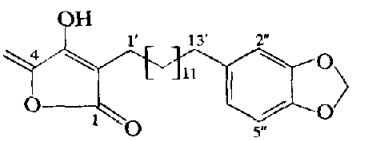

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RESULTS

Compound **1** belongs to the 1,3-diarylpropanes, a flavonoid type [4] which can be characterized by the easily discernible $ArCH_2CH_2CH_2Ar$ ^1H NMR signals at δ 1.7–2.2 (*m*, 2H) and 2.57 (*t*, $J = 7$ Hz, 4H). Spiroelliptin (**2**), $C_{15}H_{10}O(OH)_2(OMe)_2$, also shows a $(CH_2)_3$ chain, and thus, presumably, is also a $C_6{\cdot}C_3{\cdot}C_6$-type compound. In contradistinction with **1**, however, only one of the trimethylene terminals is benzylic (δ 1.85–2.20, 4H, vs 2.55–3.00, 2H). The other terminal must be linked to a sp^3-carbon and the additional hexacycle can thus not be aromatic. Indeed, the ^1H NMR signals (δ 6.02, *d*, $J = 9$ Hz; 6.09, *d*, $J = 3$ Hz; 6.99, *dd*, $J = 9$, 3 Hz) associated with this unit are compatible with either α′,β′,γ,δ-unsaturated (substituted by OMe at C-γ) or α,β,α′,β′-unsaturated (substituted by OMe at C-α) carbonyl systems (ν_{max} 1653 cm^{-1}). In both cases pairs of protons are situated at vicinal positions ($J = 9$ Hz) and in *W*-configurations ($J = 3$ Hz) [5]. Since only 2 hydroxyls, one methoxyl and an isolated proton (δ 6.2, *s*) remain

*Part 12 in the series "The Chemistry of Brazilian Myristicaceae". For Part 11 see ref. [1]. Based on part of the Doctorate thesis presented by P.P.D.D., on leave of absence from Universidad Nacional de Colombia, Bogotá, to Universidade de São Paulo (1978).

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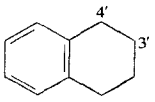
available for substitution of the benzyl moiety, a direct link must connect the aromatic ring and the sp^3-C of the aliphatic ring. The compound thus possesses the basic skeleton of a spiro-cyclohexan-1.1′-tetralin, which is consistent with the ^{13}C NMR spectrum which includes three triplets due to three methylenes (δ 34.4, 22.7, 18.6; cf. 30.3, 24.1 in tetralin **5** [6]), a singlet and two doublets (respectively δ 44.3, 125.0, 156.7; cf. 50.7, 126.6, 154.3 for C-1, C-5 and C-6 in model **6** [7]).



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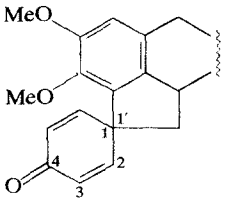

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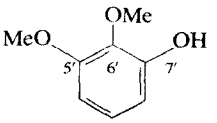
Two alternative oxygenation patterns were considered above for the aliphatic ring. A similar problem exists with respect to the aromatic ring. The two hydroxyls are vicinal (UV H_3BO_3 + NaOAc shift) and the methoxyl is flanked by two substituents (^{13}C NMR δ 59.2; cf. OMe-6′ and 5′ in model **7** respectively δ 60.4, 55.4 [8]). This evidence is consistent



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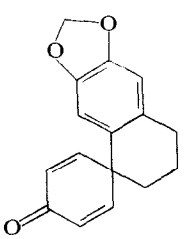
with the formulation of tetralins either with OMe-5′ as shown (**2**) or with OMe-8′. Both problems were solved by analysis of the methylation product, $C_{15}H_9(OMe)_5$, of spiroelliptin. Its ^1H NMR spectrum was suprisingly simple, showing besides the $(CH_2)_3$ proton multiplet (δ 1.9–2.7), one singlet for all 5 methoxyls (δ 3.94) and 3 singlets for 3 aromatic protons. The acid-catalysed rearrangement of synthetic dienones (e.g. **8**) into phenols (e.g. **9**) has been described [9, 10], and the methylation product of spiroelliptin may again be a dibenzocycloheptane. Indeed **10a** is compatible with the ^1H NMR data. While there is doubt concerning the assignment of the three ArH signals, it is, nevertheless, clear that the tetralin ArH suffered an at least 0.5 ppm downfield shift upon rearrangement of spiroelliptin. This fact is incompatible with its location at C-5′ whose vicinity suffered little modification



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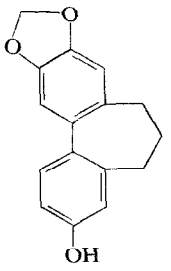

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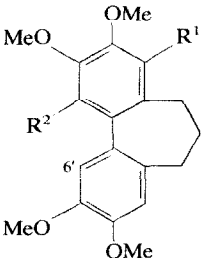


10a R^1 = OMe, R^2 = H
10b R^1 = H, R^2 = OMe

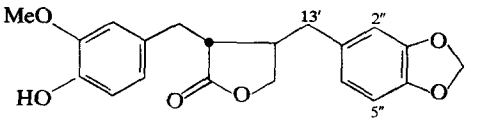
by the reaction. Corroborating this conclusion, a methoxyl at the highly shielded C-6 of the biphenyl would not be expected to share with the other four an identical ^1H NMR frequency. Indeed, in the spectrum of synthetic **10b** [9] the methoxyl signal assigned to OMe-6 appears at δ 3.57, while all other methoxyl signals appear close to 3.95. Constitution **2** is thus proposed for spiroelliptin.

The ^1H NMR of compound **3**, $C_{15}H_{11}O(OH)_2OMe$, $[\alpha]_D$ 0°, includes the typical signals indicative of a cyclic $ArCH(O)CH_2CH_2Ar$ chain and thus is a flavan. The distribution of the substituents among the rings was shown by the retro Diels–Alder MS fragments at *m/e* 123 (19%) and 150 (100%). Indeed ring B either sustains *para* related OH and OMe groups or, more probably for biosynthetic reasons, is a guaiacyl unit as shown by a negative Gibbs test and the broad 60 MHz ^1H NMR singlet, representing all its protons, around δ 6.9. A partly superimposed *ortho* split doublet on the low field side of this signal (δ 6.98), together with a *d* (δ 6.42, J = 3 Hz) and a *dd* (δ 6.29, J = 8, 3 Hz) are conclusive evidence for a 7-hydroxyl. ^1H NMR and MS of the diacetate are also consistent with structure **3**.

^1H NMR evidence reveals the existence in iryelliptin, $C_{25}H_{34}O_5$, of a $[CH_2]_{11}$ chain. Two further methylenes, represented by two partly superimposed triplets, and thus possibly flanking this chain at either terminal, are benzylic or allylic. One of the unsaturated groups is represented by a piperonyl unit. The presence of this 3,4-methylenedioxybenzyl group is not only shown by the characteristic ^1H NMR signals, but also by the base peak of the MS at *m/e* 135. The other unsaturated group must contain all the hitherto undefined atoms $C_5H_3O_3$. The 3 protons belong to an exocyclic methylene (δ 5.09, 5.20, 2*d*, J = 3 Hz) and an enolic hydroxyl (ν_{max} 3165 cm^{-1}), and the remaining C_4O_2 to a γ-lactone (ν_{max} 1730 cm^{-1}).

The ^1H NMR of dihydroelliptin gives evidence for a MeCHOR group (δ 1.50, 4.85, respectively *d* and *q*, J = 7 Hz), a fact which allows unambiguous assignment of the exocyclic CH_2 to C-4 of the lactone in **4**. Transformation into the acetate (ν_{max} 1779 cm^{-1}) causes considerable shielding of the vinylic protons (Δδ 0.32, 0.13) and the enolic OH must thus occupy C-3. This leaves only C-2 for the allylic methylene and leads to the tetronic acid structure **4** for iryelliptin.

Assignment of ^{13}C signals of **4** was based on fully and single frequency off-resonance decoupled NMR spectra and standard chemical shift theory [6]. Carbon shifts of models **11** [11], **12** [12] and **13** [6] are in good agreement with these assignments and hence corroborate the structural proposal **4** for irryelliptin.



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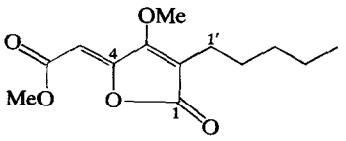

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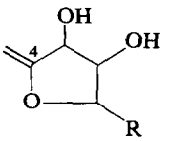

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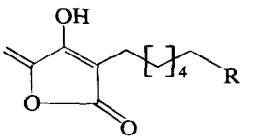
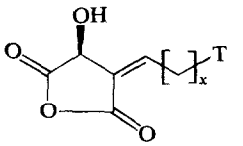
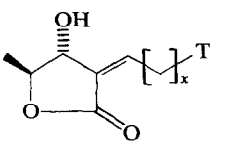


14a R = $(CH{=}CH)_3(CH_2)_2T$; T = T^1; T^2
14b R = $CH\overset{c}{=}CHCH_2CH\overset{c}{=}CH(CH_2)_4CH_3$
14c R = $CH\overset{c}{=}CH(CH_2)_7CH_3$



15a x = 9, T = T^2
15b x = 11, T = T^1
15c x = 13, T = T^1, T^2, T^3
15d x = 15, T = T^1

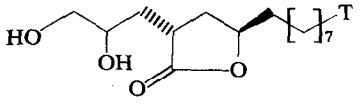


16a x = 9, T = T^2, T^3
16b x = 11, T = T^1
16c x = 13, T = T^1, T^2, T^3
16d x = 15, T = T^1

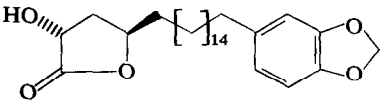
DISCUSSION

The natural interconversion of **3** into **1** was proposed previously in connection with a general discussion on flavonoids of Myristicaceae [4]. The distribution of the OH/OMe functions in **1** and **2** is such as to make their relation also highly probable.

The tetronic acid nucleus occurs in a number of natural products. These include not only mould metabolites [13], but also, more significantly with respect to the present work, compounds **14a–14c** from Umbelliferae [14] whose biosynthesis was postulated to involve condensation of fatty acid with pyruvate. Such a condensation may proceed not only through the interaction involving the α-methylene of fatty acid and the carboxyl of pyruvate leading to **4** and **14**, as well as to the obtusilactones (**15a**, **b**) [15], litsenolides (**16a**, **b**) [16], mahuba lactones (**15c**, **d**; **16c**, **d**) [17] and rubre(y)nolides (**17**) [18], all from Lauraceae, but also through the interaction involving the carboxyl of fatty acid and the methyl of pyruvate leading to juruenolide (**18**) [19] from Myristicaceae, as well as the avocatins (e.g. **19**, **20**) [20] from Lauraceae. As additional phenomena, condensation involving the carboxyl of cinnamate and the methyl of fatty acid would be required for the formation of **4** and **18**, while in all other cases the terminal ethyl, ethenyl and ethynyl groups may be generated as shown in Scheme 1.



17 T = T^2, T^3



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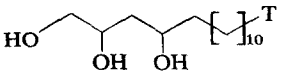
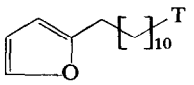


19 T = T^2, T^3



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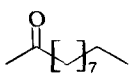

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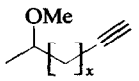
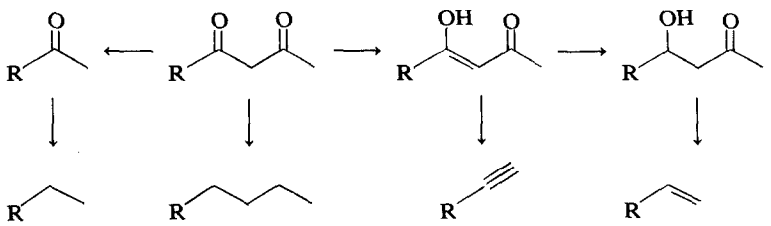


22 x = 7, 9

$T^1 = CH_2Me$, $T^2 = CH{=}CH_2$, $T^3 = C{\equiv}CH$



Scheme 1. Possible biosynthetic derivation of terminal ethyl, ethenyl and ethynyl groups of polyketides.

This postulate would explain satisfactorily why in *Lindera obtusiloba* Blume [15], *Litsea japonica* (Thumb.) Jus. [16] *and Licaria mahuba* (Samp.) Kosterm. ([17], Martinez V., J. C., Yoshida, M. and Gottlieb, O. R., unpublished results) C_n compounds with ethenyl and ethynyl terminals (respectively **15a**, **16a**, **15c** and **16c**) co-occur with C_{n+2} compounds with ethyl terminals (respectively **15b**, **16b**, **15d** and **16d**). In contradistinction, for the rationalization of the biosynthesis of **21** and **22**, again from Lauraceae, decarboxylation of a polyketide precursor seems to be a more straightforward postulate [21]. Such a pathway, which precludes the involvement of pyruvate, has been advocated previously also to explain the biosynthesis of the rubre(y)nolides (**17**) and the avocatins (e.g. **19**, **20**) [22]. Since it is likely that iryelliptin (**4**) and the compounds **14–22** belong to a biosynthetically homogeneous group of natural compounds, both biogenetic postulates must at present be considered.

EXPERIMENTAL

Isolation of the constituents. Trunk wood of a specimen (voucher herbarium INPA, Manaus, 58732) identified by Dr. W. A. Rodrigues, collected near km 145 of the Manaus–Itacoatiara highway, was dried and its powder (1.5 kg) was percolated with EtOH. The extract (40 g) was washed exhaustively with C_6H_6–$CHCl_3$, 1:1. The solvents were evapd and the residue (25 g) was chromatographed on a silica column (400 g). Elution with the following solvents gave the indicated fractions: C_6H_6 (A, B), C_6H_6–$CHCl_3$ 9:1 (C), $CHCl_3$ (D). Fraction A (675 mg) was composed of aliphatic esters. Fraction B (135 mg) was cryst. from MeOH to sitosterol. Fraction C (2 g) was cryst. from MeOH to **4** (350 mg) and the mother-liquor purified by TLC (Si gel, $CHCl_3$–Me_2CO, 19:1) to **1** (120 mg). Fraction D (1.5 g) was cryst. from C_6H_6 to **3** (80 mg) and the mother-liquor cryst. from EtOAc to **2** (50 mg).

spiro-[3-Methoxy-2,5-cyclohexadien-1-1′-6′,7′-dihydroxy-5′-methoxy-1′,2′,3′,4′-tetrahydronaphthalen]-4-one (**2**). Mp 149–151° (EtOAc). Found: C, 66.70; H, 6.26. $C_{17}H_{18}O_5$ requires: C, 67.54; H, 5.96%). λ_{max}^{EtOH} nm: 242, 275 (ε 5750, 2700); NaOH and $NaOAc + H_3BO_3$ shifts. ν_{max}^{KBr} cm^{-1}: 3470, 3100, 1653, 1629, 1224, 1087. ^1H NMR (60 MHz, $(CD_3)_2CO$): δ 1.85–2.20 (*m*, 4H-2′, 3′), 2.55–3.05 (*m*, 2H-4′), 3.55, 3.75 (2*s*, 2 OMe-3, 5′), 6.02 (*d*, *J* = 3 Hz, H-2), 6.09 (*d*, *J* = 9 Hz, H-5), 6.20 (*s*, H-8′), 6.63, 6.80 (2 *br. s*, 2 OH), 6.99 (*dd*, *J* = 9, 3 Hz, H-6). ^{13}C NMR **2** (DMSO-d_6)/**5**/**6**/**7**: δ 44.3/—/50.7/—(*s*, C-1), 124.7* /—/—/— (*d*, C-2), 144.4/—/—/— (*s*, C-3), 180.1/—/185.3/— (*s*, C-4), 125.0* /—/126.6/— (*d*, C-5), 156.7/—/154.3/— (*d*, C-6), 34.4/—/—/— (*t*, C-2′), 18.6/24.1/—/— (*t*, C-3′), 22.7/30.3/—/— (*t*, C-4′), 120.8/—/—/— (*s*, C-4′a), 146.1/—/143.7/152.5 (*s*, C-5′), 137.6/—/—/135.4 (*s*, C-6′), 148.1/—/152.7/149.0 (*s*, C-7′), 109.8/—/111.9/107.9 (*d*, C-8′), 124.1/—/—/— (*s*, C-8′a), 54.4/—/—/— (*q*, OMe-3), 59.2/—/—/60.4 (*q*, OMe-5′). MS (*m/e*): 302 (100%) M^+, 287 (5), 274 (2), 259 (19), 152 (3). *Acetate*, oil. ν_{max}^{film} cm^{-1}: 1764, 1658, 1634, 1605, 1215, 1186. ^1H NMR (60 MHz, $CDCl_3$): δ 1.8–2.10 (*m*, 4 H-2′, 3′), 2.23, 2.30 (2*s*, 2 OAc), 2.7–3.0 (*m*, 2H-4′), 3.64, 3.80 (2*s*, 2 OMe-3, 5′), 5.94 (*d*, *J* = 3 HZ, H-2), 6.25 (*d*, *J* = 9 Hz, H-5), 6.54 (*s*, H-8′), 6.99 (*dd*, *J* = 9, 3 Hz, H-6). MS (*m/e*): 386 (10%) M^+, 344 (18), 302 (46), 287 (1), 274 (2), 259 (6), 252 (4), 43 (100).

(±)-*7,4′-Dihydroxy-3′-methoxyflavan* (**3**). Mp 157–159° (C_6H_6) (Found: C, 70.56; H, 5.80. $C_{16}H_{16}O_4$ requires: C, 70.58; H, 5.88%). λ_{max}^{EtOH} nm: 228, 278 (ε 4400, 4750); $\lambda_{max}^{EtOH+NaOH}$ nm: 248, 288 (ε 6600, 4550); no $AlCl_3$ and H_3BO_3 + NaOAc shifts. ν_{max}^{KBr} cm^{-1}: 3367, 3322, 1626, 1613, 1595, 1527, 1515, 1311, 1290, 1163, 1119, 1053, 1010. ^1H NMR (60 MHz, $CDCl_3$); δ 1.9–2.3 (*m*, 2H-3), 2.6–2.9 (*m*, 2H-4), 3.92 (*s*, OMe), 4.85 (*s*, OH-7), 4.95 (*dd*, *J* = 8.5, 3.5 Hz, H-2), 5.62 (*s*, OH-4′), 6.29 (*d*, *J* = 3 Hz, H-8), 6.42 (*dd*, *J* = 8, 3 Hz, H-6), 6.93 (*br. s*, 3H-2′, 5′, 6′), 6.98 *d*(*J* = *ca* 8 Hz, H-5). MS (*m/e*): 272 (76%) M^+, 151 (11), 150 (100), 135 (32), 107 (18), 123 (19). *Diacetate*, mp 126–128° (EtOH). ν_{max}^{KBr} cm^{-1}: 3049, 1745, 1613, 1608, 1603. ^1H NMR (60 MHz, $CDCl_3$): δ 2.0–2.4 (*m*, 2H-3), 2.30, 2.34 (2*s*, 2 OAc), 2.8-3.2 (*m*, 2H-4), 3.87 (*s*, OMe), 5.09 (*dd*, *J* = 8.5, 3.5 Hz, H-2), 6.57 (*d*, *J* = 3 Hz, H-8), 6.67 (*dd*, *J* = 8, 3 Hz, H-6), 6.9–7.2 (*m*, 4 H-5, 2′, 5′, 6′). MS (*m/e*): 356 (10%) M^+, 314 (33), 272 (30), 151 (56), 150 (7), 135 (19), 123 (15), 107 (12), 43 (100).

2-(ω-Piperonyltridecyl)-4-methylidenetetronic acid (iryelliptin. **4**). Crystals, mp 81–83° (C_6H_6) (Found: C, 72.40; H, 8.19. $C_{25}H_{34}O_5$ requires: C, 72.44; H, 8.27%). λ_{max}^{EtOH} nm: 237, 281, 337 inf. (ε 16 100, 10 650, 1250); $\lambda_{max}^{EtOH+NaOH}$ nm: 235 inf., 291, 317 (ε 21 600, 11 150, 10 850). ν_{max}^{KBr} cm^{-1}: 3165, 1730, 1640, 1623, 1502, 1490, 1239, 1220, 1042. ^1H NMR (60 MHz, $CDCl_3$): δ 1.27 (*s*, CH_2-2′ to 12′) 1.28, 1.52 (2*t*, *J* = 7 Hz, CH_2-1′, 13′), 5.09, 5.20 (2*d*, *J* = 3 Hz, $=CH_2$), 5.90 (*s*, O_2CH_2), 6.67 (*s*, H-2″, 5″, 6″). ^{13}C NMR **4**/**13**/**14**/**15** (20 MHz, $CDCl_3$): δ 161.9/—/161.1/— (*s*, C-1), 105.7/—/110.6/— (*s*, C-2), 169.0/—/168.7/— (*s*, C-3), 162.0/—/—/162.9 (*s*, C-4), 91.9/—/—/86.4 (*t*, $=CH_2$), 21.5/—/22.3/— (*t*, C-1′), 29.7/—/29.7/— (*t*, C-2′), 29.7/—/—/— (*t*, C-3′-11′), 38.1/—/—/— (*t*, C-12′), 35.7/38.1/—/— (*t*, C-13′), 133.3/131.1/—/— (*s*, C—1″), 109.0/109.2/—/— (*d*, C-2″), 150.0/147.5/—/— (*s*, C-3″), 150.0/146.4/—/— (*s*, C-4″), 108.1/107.9/—/— (*d*, C-5″), 121.1/122.0/—/— (*d*, C-6″), 100.7/100.8/—/— (*t*, O_2CH_2). MS (*m/e*): 414 (26%) M^+, 386 (6), 344 (1), 149 (5), 135 (100), 125 (2). *Acetate*, oil ν_{max}^{Film} cm^{-1}: 1779, 1737, 1650, 1513, 1495, 1258, 1182. ^1H NMR (60 MHz, $CDCl_3$): δ 2.34 (*s*, OAc), 4.77, 5.07 (2*d*, *J* = 3 Hz, $=CH_2$), all other signals as for **4**. MS (*m/e*): 456 (1%) M^+, 414 (2), 149 (7), 135 (100), 125 (2). *Dihydroiryelliptin.* A soln. of **4** (155 mg) in MeOH (20 ml) was hydrogenated over 10% Pd/C (20 mg), filtered and evapd. The residue was purified by TLC (Si gel, C_6H_6–EtOAc 4:1). Oil, ν_{max}^{Film} cm^{-1}: *ca* 3000 (*br*, 1710, 1635, 1500, 1490, 1250, 1090, 1055. ^1H NMR (60 MHz, $CDCl_3$): δ 1.25 (*s*, CH_2-2′ to 12′), 1.50 (*d*, *J* = 6 Hz, Me-4), 2.10, 2.52 (2*t*, *J* = 7 Hz, CH_2-1′, 13′), 4.85 (*q*, *J* = 6 Hz, H-4), 5.90 (*s*, O_2CH_2), 6.68 (*s*, H-2″, 5″, 6″). MS (*m/e*): 416 (6%) M^+, 149 (100), 135 (60), 127 (4).

2,2′-Trimethylene-3,4,5,4′,5′-pentamethoxybiphenyl (**10a**). Me_2SO_4 (1.5 ml) and K_2CO_3 (130 mg) were added to a soln of **2** (130 mg) in Me_2CO (20 ml). The mixture was maintained under reflux (24 hr), cooled, filtered and evapd. Residue in $CHCl_3$ was washed, dried and purified by TLC (Si gel, C_6H_6–EtOAc 17:3) to **12a** (80% yield), mp 155–156° (EtOAc) (Found: C, 70.04; H, 6.90. $C_{20}H_{24}O_5$ requires: C, 69.73; H, 7.03%). ν_{max}^{KBr} cm^{-1}: 1600, 1565, 1515, 1485, 1470, 1455, 1410, 1272, 1121, 1100. ^1H NMR (60 MHz, $CDCl_3$): δ 1.9–2.3 (*m*, 2H), 2.3–2.6 (*m*, 4H), 3.94 (*s*, 5 OMe), 6.70, 6.80, 6.94 (3*s*, 3H-3′, 6′, 6). MS (*m/e*): 344 (11%) M^+, 329 (3), 301 (3), 167 (25), 150 (9), 43 (100).

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