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DUARTIN, AN ISOFLAVAN FROM *MACHAERIUM OPACUM**

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Key Word Index—*Machaerium opacum*; Leguminosae–Lotoideae; isoflavans; stilbenes.

Abstract—The heartwood of *Machaerium opacum* contains 2,3-dimethoxyphenol, the stilbenes pinosylvin monomethyl ether and dimethyl ether, and the isoflavans (−)-duartin and (−)-mucronulatol. The structure of (3*S*)-7,3′-dihydroxy-8,2′,4′-trimethoxyisoflavan was deduced for duartin and the constitution confirmed by synthesis of the racemate.

INTRODUCTION

The secondary metabolites of *Dalbergia* and *Machaerium* species comprise chiefly neoflavonoids, on which we reported in a previous series of papers (for part VIII see ref. [1]), and isoflavonoids, which are described in this and the subsequent papers of the present series.

Machaerium opacum Vog. is of common occurrence in the savannahs of central Brazil. Five constituents were isolated from a benzene extract of its dark violet heartwood: 2,3-dimethoxyphenol [2], the monomethyl and dimethyl ethers of pinosylvin [3], and two isoflavans. One of these, (−)-mucronulatol (**1a**, α-Ar), was identified by comparison with a sample isolated from *M. mucronulatum* Mart. [4, 5], and the other was named (−)-duartin. The name duartin was chosen to indicate our appreciation of the Brazilian botanist Apparício Pereira Duarte, who collected many of the plants whose chemical examination is reported in the two series of papers mentioned above.

RESULTS AND DISCUSSION

Duartin, an optically active solid, is devoid of carbonyl absorption in the IR. The molecular formula, $C_{18}H_{20}O_6$, was expanded to $C_{15}H_9O(OH)_2(OMe)_3$ upon inspection of the PMR spectrum. This shows, furthermore, an ABCXX′ system, assigned to the $H_ACH_B–CH_C–H_XCH_{X'}$ grouping of an isoflavan. Each aromatic ring of this skeleton is probably associated with one hydroxyl, since the MS fragments are not exceeded by those of the dimethyl ether by more than 14 mass units. The PMR spectrum of this ether shows the presence of two pairs of *ortho*-related aromatic protons but the position of the five substituents was established unequivocally only by its degradation through the classical sequence **1b** → **2a** → **3a** → **4a** → **5a**. This was supported by synthesis of the deoxybenzoin **4a** by the BF_3-catalysed reaction [6] of 2,3-dimethoxyphenol with 2,3,4-trimethoxyphenylacetic acid and the conversion of this deoxybenzoin (**4a**) by reaction with $HC(OEt)_3$ [7] into the isoflavone **3a**. Degradation of duartin diethyl ether was more informative, indicating inclusively the relative position of the OH/OMe groups on ring B of duartin.

Oxidation of duartin diethyl ether with $KMnO_4$ gave an isoflavone, whose PMR spectrum gave evidence for the presence of H-5, characteristically deshielded by an adjacent carbonyl. This isoflavone was hydrolysed to the corresponding deoxybenzoin which, upon $KMnO_4$ oxidation, gave 3-ethoxy-2,4-dimethoxybenzoic acid (**5b**), identified by comparison with a synthetic sample. This result established that the deoxybenzoin, the isoflavone and duartin diethyl ether had, respectively, the alternative constitutions **4b** or **4c**, **2b** or **2c** and **1c** or **1d**. Of the two possibilities which thus resulted for duartin itself, **1e** was shown to be the correct representation by synthesis of the racemate.

Pyrogallol 2-methyl ether reacted with 3-hydroxy-2,4-dimethoxyphenylacetic acid in the presence of BF_3–Et_2O to give the deoxybenzoin **4d** which was converted into the isoflavone **3b** by reaction with $HC(OEt)_3$. Hydrogenation of **3b** using a Pd/C catalyst in AcOH gave (±)-duartin (**1e**), having spectroscopic properties in solution identical with those of natural (−)-duartin. The reduction of isoflavones to isoflavans has previously been reported [8] to give low yields, but the conditions described in the Experimental gave good yields of isoflavans from a variety of isoflavones.

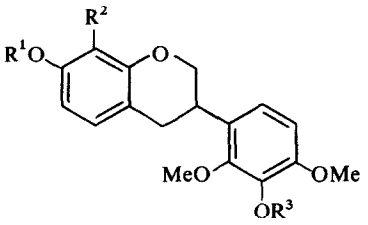
The similarity of the ORD curve of (3*S*)-5,7,3′,4′-tetramethoxyisoflavan [9–11] and of (−)-duartin [12] established the 3*S*-configuration for this compound (**1e**, α-Ar).

EXPERIMENTAL

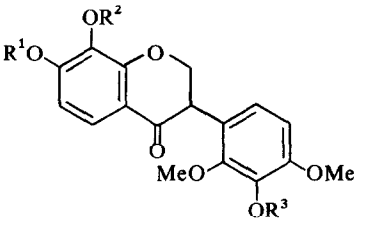
Unless otherwise stated, spectroscopic measurements were made in EtOH (UV), $CHCl_3$ (IR), $CDCl_3$ (60 MHz PMR) and MeOH (ORD). All evapns of volatile material were performed under diminished pressure.

Isolation of the constituents. A specimen of *M. opacum* was collected near Belo Horizonte, MG, Brasil, and identified by Apparício Pereira Duarte. The C_6H_6 extract (57 g) of ground heartwood (2.2 kg) was chromatographed on Si gel (1.2 kg) to

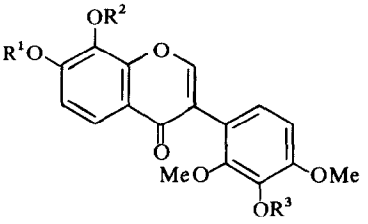
* Part 1 in the series 'Isoflavonoid constituents of *Dalbergia* and *Machaerium* species'.



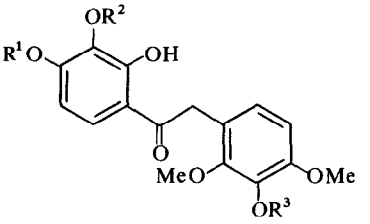
1a $R^1 = R^2 = R^3 = H$
1b $R^1 = R^3 = Me$, $R^2 = OMe$
1c $R^1 = R^3 = Et$, $R^2 = OMe$
1d $R^1 = Me$, $R^2 = OEt$, $R^3 = Et$
1e $R^1 = R^3 = H$, $R^2 = OMe$
1f $R^1 = R^3 = Ac$, $R^2 = OMe$
1g $R^1 = H$, $R^2 = OMe$, $R^3 = Me$
1h $R^1 = Et$, $R^2 = OMe$, $R^3 = Me$



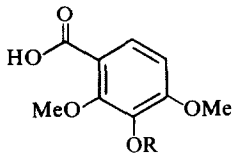
2a $R^1 = R^2 = R^3 = Me$
2b $R^1 = R^3 = Et$, $R^2 = Me$
2c $R^1 = Me$, $R^2 = R^3 = Et$



3a $R^1 = R^2 = R^3 = Me$
3b $R^1 = R^3 = H$, $R^2 = Me$



4a $R^1 = R^2 = R^3 = Me$
4b $R^1 = R^3 = Et$, $R^2 = Me$
4c $R^1 = Me$, $R^2 = R^3 = Et$
4d $R^1 = R^3 = H$, $R^2 = Me$



5a R = Me
5b R = Et

the following products (eluant, method of purif. and quantity indicated): pinosylvin dimethyl ether (C_6H_6, TLC, 30 mg), fatty material (C_6H_6–$CHCl_3$ (9:1 and 4:1) 33.4 g), a mixture (C_6H_6–$CHCl_3$ (4:1) separated by TLC into pinosylvin monomethyl ether, 100 mg, and 2,3-dimethoxyphenol, 100 mg), (−)-**1e** (C_6H_6–$CHCl_3$ (13:7) cryst. from $CHCl_3$–petrol, 7.7 g), a mixture of (−)-**1a** and (−)-**1e** (C_6H_6–$CHCl_3$ (1:3) 2.2 g), (−)-**1a** ($CHCl_3$, TLC, 100 mg).

Identifications. 2,3-Dimethoxyphenol, pinosylvin monomethyl ether, pinosylvin dimethyl ether and (−)-mucronulatol (**1a**, α-Ar) were identified by direct comparison respectively with a synthetic sample [13], a sample kindly supplied by H. Erdtman [3], a sample obtained by methylation of the former [3] and a sample isolated from *M. mucronulatum* [5].

(−)-*Duartin* (**1e**, α-*Ar*). Needles, mp 145° (MeOH), $[\alpha]_D^{20}$ *ca* −18.5° (*c* 1.68, $CHCl_3$) [Found: C, 65.06; H, 5.86; OMe, 27.86; M (MS), 332. $C_{15}H_{11}O_3(OMe)_3$ requires: C, 65.05; H, 6.07; OMe, 28.04%; M, 332]. λ_{max} (nm): 225, 278 (ε 11 400, 2150). ν_{max} (cm^{-1}): 3540, 1620. PMR (τ): 3.31, 3.48 (AB system, J_{AB} = 8.5 Hz, H-5, H-6), 3.37 (*s*, H-5′, H-6′), 4.29, 4.36 (2 *s*, 2 OH), 5.65 (*dd*, *J* = 10 and 3.5 Hz, H-2), 6.03 (*t*, *J* = 10 Hz, H-2), 6.3–6.7 (*m*, H-3), 7.08 (*br. d*, *J* = 7.5 Hz, 2 H-4), 6.07 (*s*, 2 OMe), 6.11 (*s*, OMe). ORD (*c* 0.10): $[\phi]_{333}$ −392, $[\phi]_{303}$ −975, $[\phi]_{282}$ −4680, $[\phi]_{263}$ −2330, $[\phi]_{256}$ −3720.

Diacetate (**1f**, α-Ar). Needles, mp 101° (aq. EtOH), $[\alpha]_D^{20}$ −22° (*c* 2.08, $CHCl_3$) [Found: C, 63.39; H, 5.92; M (MS), 416. $C_{22}H_{24}O_8$ requires: C, 63.45; H, 5.81; M, 416]. λ_{max} (nm): 225, 275 (ε 23 800, 2700). ν_{max} (cm^{-1}): 1760, 1600. PMR (τ): 3.11, 3.25 (AB system, J_{AB} 8.5 Hz, H-5, H-6), 3.21, 2.98 (AB system, J_{AB} = 8.5 Hz, H-5′, H-6′), 5.52 (*dd*, *J* = 10 and 3.5 Hz, H-2), 5.92 (*t*, *J* = 10 Hz, H-2), 6.3–6.8 (*m*, H-3), 7.00 (*br, d*, *J* = 7.5 Hz, 2 H-4), 6.10, 6.12, 6.15 (3 *s*, 3 OMe), 7.62, 7.65 (2 *s*, 2 OAc). *Monomethyl ether* (**1g**, α-Ar). 3*S*-**1e** (200 mg) MeI (480 mg), Me_2CO (8 ml), K_2CO_3 (200 mg) were kept at room temp. (9 days), filtered and evapd. The residue was chromatographed. Elution with C_6H_6 gave 3*S*-**1b** (100 mg) and with C_6H_6–CCl_4 gave 3*S*-**1g** (75 mg), prisms, mp 131°, $[\alpha]_D^{20}$ −16.5° (*c* 2.5, $CHCl_3$) [Found: C, 65.74; H, 6.71; M (MS), 346. $C_{19}H_{22}O_6$ requires: C, 65.88; H, 6.40%; M, 346]. ν_{max} (cm^{-1}): 3500, 1600. PMR (τ): 3.27, 3.47 (AB system, J_{AB} = 8.5 Hz, H-5, H-6), 3.32, 3.18 (AB system, J_{AB} = 8.5 Hz, H-5′, H-6′), 4.24 (*s*, OH), 5.62 (*dd*, *J* = 10 and 3.5 Hz, H-2), 5.96 (*t*, *J* = 10 Hz, H-2), 6.3–6.7 (*m*, H-3), 7.09 (*br. d*, *J* = 7.5 Hz, 2 H-4), 6.06 (*s*, 2 OMe), 6.10, 6.14 (2 *s*, 2 OMe). *Dimethyl ether* (**1b**, α-Ar). Needles, mp 120° (MeOH), $[\alpha]_D^{20°}$ −20° (*c* 3.68, $CHCl_3$) [Found: C, 66.52; H, 6.71; OMe 43.05, M (MS), 360. $C_{15}H_9O(OMe)_5$ requires: C, 66.65; H, 6.71; OMe 43.10%; M, 360]. ν_{max} (cm^{-1}). 1615. PMR (τ): 3.13, 3.42 (AB system, J_{AB} = 8.5 Hz, H-5, H-6), 3.25, 3.12 (AB system, J_{AB} = 8.5 Hz, H-5′, H-6′), 5.52 (*dd*, *J* = 10 and 4 Hz, H-2), 5.92 (*t*, *J* = 10 Hz, H-2), 6.2–6.8 (*m*, H-3), 7.02 (*br. d*, *J* = 7.5 Hz, 2 H-4), 6.03 (*s*, 4 OMe), 6.09 (*s*, OMe). *7-Ethyl-3′-methyl diether* (**1h**, α-Ar), 3*S*-**1g**, EtI and K_2CO_3 in Me_2CO gave 7-ethoxy-8,2′,3′,4′-tetramethoxyisoflavan (**1h**, α-Ar), needles, mp 105° (MeOH) [Found: C, 67.16; H, 7.02; M (MS), 374. $C_{21}H_{26}O_6$ requires: C, 67.36; H, 7.00%; M, 374]. ν_{max} (cm^{-1}): 1615. *Diethyl ether* (**1d**, α-Ar). 3*S*-**1e** (1.5 g), Et_2SO_4 (3.2 ml), K_2CO_3 (10 g), Me_2CO, reflux, 24 hr, gave 3*S*-**1d** (1.58 g), rhombs, mp 89° (MeOH) [Found: C, 68.17; H, 7.12;

M, 388. $C_{22}H_{28}O_6$ requires: C, 68.02; H, 7.27%; M, 388]. λ_{max} (nm): 225, 278 (ε 28700, 2700). ν_{max} (cm^{-1}): 1615.

Degradation of (−)-*duartin dimethyl ether* (**1b**, α-Ar), (a) *Formation of* (+)-7,8,2′,3′,4′-*pentamethoxyisoflavanone* (**2a**). Aq. 5% $KMnO_4$ (24 ml) was added at room temp. to a stirred soln of 3*S*-**1b** (200 mg) in Me_2CO. After 12 hr the soln was decolourized with SO_2, acidified, H_2O added the ppt. collected and cryst. to **2a** (130 mg), needles, mp 179°, $[\alpha]_D^{20}$ +16° (*c* 1.34, $CHCl_3$) [Found: C, 63.92; H, 5.87. $C_{20}H_{22}O_7$ requires: C, 64.16; H, 5.92%]. λ_{max} (nm): 282 (ε 16700). ν_{max} (cm^{-1}): 1685, 1605. PMR (τ): 2.22 (AB system, J_{AB} = 9 Hz, H-5, H-6), 3.36, 3.18 (AB system, J_{AB} = 9 Hz, H-5′, H-6′), 5.39 (*m*), 5.79 (*dd*) (AA′B system, average of J_{AB} and $J_{A'B}$ = 9.6 Hz, H-2, H-3, H-2), 6.05, 6.09 (2 *s*, 2 OMe), 6.13 (*s*, 3 OMe). (b) *Formation of* 7,8,2′,3′,4′-*pentamethoxyisoflavone* (**3a**). **2a** (400 mg) and active MnO_2 [14] in Me_2CO (200 ml) were heated under reflux (5 days), the mixture filtered and evapd. The residue was fractionated by TLC (Si_1 gel, $CHCl_3$) to **3a** (220 mg), prims, mp 150° (EtOH–$CHCl_3$) [Found: C, 64.35; H, 5.38. $C_{20}H_{20}O_7$ requires: C, 64.51; H, 5.41%]. λ_{max} (nm): 251, 294 (ε 36700, 9650). ν_{max} (cm^{-1}): 1650, 1630, 1610. PMR (τ): 2.03 (*s*, H-2), 1.97, 3.28 (AB system, J_{AB} = 10 Hz, H-5, H-6), 3.07, 2.80 (AB system, J_{AB} = 8.5 Hz, H-5′, H-6′), 6.00 (*s*, 2 OMe), 6.10 (*s*, 2 OMe), 6.17 (*s*, OMe). (c) *Formation of* 2,3,4-*trimethoxybenzyl* 2-*hydroxy*-3,4-*dimethoxyphenyl ketone* (**4a**). **3a** (110 mg) was heated (2 hr, N_2 atm.) under reflux with KOH (550 mg) in H_2O (2 ml) and EtOH (2 ml), the mixture diluted with H_2O, acidified and extracted with $CHCl_3$. The $CHCl_3$ was evapd and the residue (100 mg) cryst. to **4a**, prisms, mp 135° [Found: C, 63.16; H, 6.25. $C_{19}H_{22}O_7$ requires: C, 62.97; H, 6.12%. λ_{max} (nm): 225, 283, 330 infl. (ε 18800, 14700, 3500). ν_{max} (cm^{-1}): 1630. PMR (τ): −2.58 (*s*, OH), 3.36, 3.15 (AB system, J_{AB} = 8.5 Hz, H-5, H-6 of benzyl), 3.49, 2.32 (AB system, J_{AB} = 9 Hz, H-5, H-6 of phenyl), 5.83 (*s*, CH_2), 6.07 (*s*, OMe), 6.10 (*s*, 2 OMe), 6.17 (*s*, 2 OMe). **2a** gave, under the conditions of the preceding experiment, the same deoxybenzoin (**4a**). (d) *Formation of* 2,3,4-*trimethoxybenzoic acid* (**5a**). Aq. 5% $KMnO_4$ (9 ml) was added to a stirred soln of **4a** (70 ml) in Me_2CO (30 ml) at room temp. The soln was then decolourised with SO_2, acidified, boiled (30 min) and extracted with Et_2O. The Et_2O extract was shaken with aq. $NaHCO_3$. The aq. extract, after acidification and extraction with Et_2O, gave **5a** (12 mg), mp 96° (light petrol) (lit. [15] mp 99°).

Synthesis of 7,8,2′,3′,4′-*pentamethoxyisoflavone* (**3a**). (a) *Formation of* 2,3,4-*trimethoxybenzyl* 2-*hydroxy*-3,4-*dimethoxyphenyl ketone* (**4a**). 2,3-Dimethoxyphenol [13] (500 mg), 2,3,4-trimethoxyphenylacetic acid [5] (500 mg) and BF_3–Et_2O (5 ml) were heated (100°, 30 min), and the mixture evapd. The residue was treated with 2N HCl (20 ml) and extracted with $CHCl_3$. Evapn of the $CHCl_3$ gave a residue which, after purification by TLC and crystl. from MeOH, gave **4a** (350 mg), identical with the deoxybenzoin obtained by degradation of (−)-duartin dimethyl ether. (b). *Formation of* 7,8,2′,3′,4′-*pentamethoxyisoflavone* (**3a**). **4a** (35 mg), $HC(OEt)_3$ (0.2 ml), C_5H_5N (1 ml) and $C_5H_{10}N$ (0.2 ml) were heated under reflux (6 hr, N_2 atm.). Acidification, extraction with $CHCl_3$ and crystl. from MeOH gave **3a**, identical with the isoflavone obtained by oxidation of (−)-duartin dimethyl ether.

Degradation of (−)-*duartin diethyl ether* (**1d**, α-Ar). (a) *Formation of* (+)-7,3′-*diethoxy*-8,2′,4′-*trimethoxyisoflavanone* (**2b**, α-Ar). $KMnO_4$ oxidation of 3*S*-**1c** (1 g), as described above for 3*S*-**1b**, gave 3*S*-**2b** (660 mg), needles, mp 89° (Et_2O–petrol), $[\alpha]_D^{20}$ +′15.5° (*c* 0.78, $CHCl_3$) [Found: C, 65.88; H, 6.38. $C_{24}H_{26}O_7$ requires: C, 65.66; H, 6.51%]. λ_{max} (nm): 283 (ε 12200). ν_{max} (cm^{-1}): 1685, 1605. PMR (τ): 2.28, 3.35 (AB system, J_{AB} = 8.5 Hz, H-5, H-6), 3.36, 3.19 (AB system, J_{AB} = 8.5 Hz, H-5′, H-6′), 5.40 (*m*), 5.69 (*dd*) (AA′B system, average of J_{AB} and $J_{A'B}$ = 9.6 Hz, H-2, H-3, H-2), 6.09, 6.13, 6.16 (3 *s*, 3 OMe), 5.93 (*q*), 8.51 (*t*), 8.62 (*t*) (J = 7 Hz, 2 OEt). (b) *Formation of* 3-*ethoxy*-2,4-*dimethoxybenzyl* 4-*ethoxy*-2-*hydroxy*-3-*methoxyphenyl ketone* (**4b**). Hydrolysis of **2b** (200 mg), as described above for **3a**, gave **4b** (100 mg), needles, mp 105° (Et_2O–petrol) [Found: C, 64.54; H, 6.93. $C_{21}H_{26}O_7$ requires: C, 64.60; H, 6.71%]. λ_{max} (nm): 225, 285, 330 (ε 22500, 16500, 3000). ν_{max} (cm^{-1}): 1635, 1605. PMR (τ): −2.58 (*s*, OH), 3.52, 2.33 (AB system, J_{AB} = 9 Hz, H-5, H-6 of phenyl), 3.35, 3.11 (AB system, J_{AB} = 8.5 Hz, H-5, H-6 of benzyl), 5.81 (*s*, CH_2), 6.11 (*s*, 2 OMe), 6.13 (*s*, OMe) 5.81, 5.92 (2 *q*), 8.51, 8.62 (2 *t*) (J = 7 Hz, 2 OEt). (c) *Formation of* 3-*ethoxy*-2,4-*dimethoxybenzoic acid* (**5b**). Oxidation of **4b**, as described above for **4a**, gave **5b**, mp 92° (lit. [16] mp 89–90°).

Synthesis of (±)-*duartin* (**1e**). (a) *Formation of* 3-*hydroxy*-2,4-*dimethoxybenzyl* 2,4-*dihydroxy*-3-*methoxyphenyl ketone* (**4d**). 3-Hydroxy-2,4-dimethoxyphenylacetic acid [5] (212 mg), pyrogallol 2-methyl ether [17] (170 mg), treated with BF_3–Et_2O (3 ml), as described above for the formation of **4a**, gave **4d** (220 mg), prisms, mp 101° (C_6H_6–petrol). [Found: C, 61.18; H, 5.35. $C_{17}H_{18}O_7$ requires: C, 61.07; H, 5.43%]. ν_{max} (cm^{-1}): 3500, 1625. PMR (τ): −2.90 (*s*, 2 OH). 4.23 (*br. s*, 2 OH), 3.39 (*s*, H-5, H-6 of benzyl), 3.52, 2.42 (AB system, J_{AB} = 8.5 Hz, H-5, H-6 of phenyl), 5.83 (*s*, CH_2), 6.08, 6.15, 6.19 (3 *s*, 3 OMe). (b) *Formation of* 7,3′-*dihydroxy*-8,2′,4′-*trimethoxyisoflavone* (**3b**). The deoxybenzoin **4d** (230 mg), $HC(OEt)_3$ (20 ml), C_5H_5N (40 ml) and $C_5H_{10}N$ (1 ml), treated as described above for the formation of **3a**, gave **3b** (113 mg), rhombs, mp 204° (EtOH–petrol). [Found: C, 62.44; H, 5.01. $C_{18}H_{16}O_7$ requires: C, 62.79; H, 4.68%]. λ_{max} (nm): 225, 252, 303 infl. (ε 26400, 30700, 9500). ν_{max} (cm^{-1}): 3500, 1645, 1615, 1604. PMR (τ): 2.06 (*s*, H-2), 2.07, 3.00 (AB system, J_{AB} = 8.5 Hz, H-5, H-6), 3.30, 3.12 (AB system, J_{AB} = 8.5 Hz, H-5′, H-6′), 4.28 (*br. s*, 2 OH), 5.91, 6.05, 6.15 (3 *s*, 3 OMe). (c) *Formation of* (±)-7,3′-*dihydroxy*-8,2′,4′-*trimethoxyisoflavan* (**1e**). Hydrogenation (20 hr. room temp., 1 atm.) of the isoflavone **3b** (182 mg) over 10% Pd/C (100 mg) in AcOH (20 ml) gave **1e** (117 mg), prisms, mp 195° (EtOH–petrol). [Found: C, 65.04; H, 6.30. $C_{18}H_{20}O_6$ requires: C, 65.05; H, 6.07%], identical (IR and PMR) with natural (−)-duartin.

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