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NEOLIGNANS FROM LEAVES OF *OCOTEA CATHARINENSIS**

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Key Word Index—*Ocotea catharinensis*; Lauraceae; leaves; bicyclo[3.2.1]octane neolignans; hexahydrobenzofuran neolignans.

Abstract—A hexane extract of *Ocotea catharinensis* leaves afforded, by chromatographic fractionation, 11 neolignans, eight of the benzofuran-type (including three new compounds) and three of the bicyclo[3.2.1]octane-type (including two new compounds). © 1997 Elsevier Science Ltd

INTRODUCTION

Ocotea catharinensis, a tree popularly known as 'canela preta', occurs in the 'Mata Atlantica'. Previous phytochemical study on the petrol extract of trunk barks from a specimen collected near Cunha-SP, Brazil, carried out by Haraguchi *et al.* [1] reported the occurrence of the neolignans **1**, **2**, **6a–c** and **7a–b**. Ishige *et al.* [2], after careful re-examination of the petrol extract of the trunk barks, isolated additionally **3a–b** and **5c**, while petrol extraction of the wood yielded **1**, **2**, **3a**, **4a–d**, **5c–d**, **6a–c** and **7a–c**. The petrol extract of leaves afforded **4d**. Chemical variability has been observed in the trunk wood of different specimens of *O. porosa* and has been described in several papers [3–6]. This phenomenon prompted us to carry out phytochemical analysis of leaves from different lauraceous specimens. Moreover, there is little work on the constituents of their leaves [2, 4].

The present work describes the isolation of six known neolignan, **4b–d**, **5c–d** and **6e**, and five new ones, **5b**, **5e–f**, **6d** and **6f**, besides spatulenol (**8**), from hexane extracts of leaves harvested during July 1993, near São Paulo-SP, at Instituto Florestal Reserve (Cantareira Mountain), Brazil. The nomenclature and numbering follow the rules introduced by Gottlieb [2].

RESULTS AND DISCUSSION

The alcoholic phase obtained after partitioning the hexane extract from *O. catharinensis* leaves with 90% MeOH, was submitted to flash chromatography, followed by preparative TLC. This procedure yielded spatulenol (**8**) [14], five new neolignans **5b**, **5e–f**, **6d** and **6f**, besides the six known neolignans, canelin-B (**4b**) [2, 8], (**4c**) [1, 2, 9], 5′-methoxyporosin (**4d**) [2], ferrearin-B (**5c**) [9–12], ferrearin-E (**5d**) [2] and **6e** [13, 14].

Compound **5b** ($C_{20}H_{24}O_5$) differs from **5a** ($C_{19}H_{20}O_5$), previously isolated from *O. catharinensis* [2, 11, 12], only by the substituents of the aromatic ring, 3,4-dimethoxyphenyl group in **5b**, instead of 3,4-methylenedioxyphenyl group in **5a**. Compound **5b** possesses the same constitution as **5d** (ferrearin-E) [2], but differs in the configuration of aryl groups, β-aryl for **5d** and α-aryl for **5b**. The stereochemistry of compounds **5c–f** was determined by inspection of ^{1}H NMR spectra, that showed shielding of the C-methyl protons (δ 0.7 $\pm$ 0.06) by the aromatic ring due to the *cis*-relationship. This protection is absent in **5a–b** with a *trans*-relationship between aryl and methyl groups (δ 0.9 $\pm$ 0.06).

Compound **5e** ($C_{21}H_{26}O_6$) is 5-methoxy ferrearin-E as evidenced by ^{1}H NMR data that show a 3,4,5-trimethoxyphenyl group in **5e**, instead of the 3,4-dimethoxyphenyl group in **5b**. Compound **5f** ($C_{20}H_{22}O_5$) is the *O*-methyl ketal of ferrearin-B (**5c**, $C_{19}H_{20}O_5$), assigned by ^{13}C NMR data of **5f** that showed C-2′ (δ 102.3) more deshielded than C-2′ (δ 99.6) of **5c** due to the β-effect of the methyl group on C-2′. The configurations of new compounds are *rel* (7*S*, 8*S*, 1′*R*, 2′*S*) for **5b** and *rel* (7*R*, 8*S*, 1′*R*, 2′*S*) for **5e–f**.

Spectral data of **6d** ($C_{21}H_{24}O_6$) and **6f** are close related to **6e** ($C_{22}H_{26}O_7$) [13, 14]. The difference between **6d** and **6e** consists only in the oxygenation pattern of the aromatic ring, 3,4-methylenedioxyphenyl in **6d**, instead of 5-methoxy-3,4-methylenedioxyphenyl in **6e**. Careful inspection of ^{1}H and ^{13}C NMR spectra showed that the structures of

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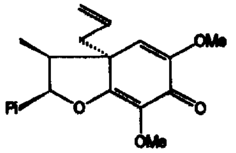

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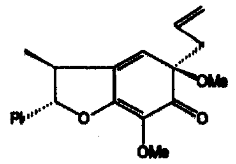

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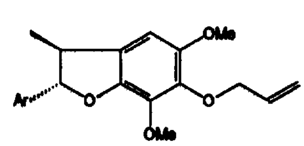

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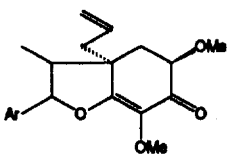
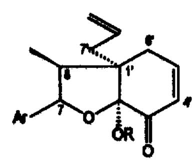
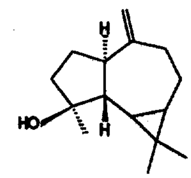
3b Ar = Mp



4a Ar = α - Pi, β - Me
4b Ar = β - Pi, α - Me
4c Ar = β - Pi, β - Me
4d Ar = β - Ve, β - Me



5a Ar = α - Pi, R = H
5b Ar = α - Ve, R = H
5c Ar = β - Pi, R = H
5d Ar = β - Ve, R = H
5e Ar = β - Tp, R = H
5f Ar = β - Pi, R = Me



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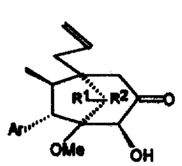
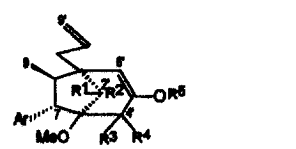


7a Ar = Pi, R1 = OH, R2 = H
7b Ar = Mp, R1 = OH, R2 = H
7c Ar = Pi, R1 = H, R2 = OH



6a Ar = Pi, R1 = OH, R3 = α - OH, R5 = Me, R2 = R4 = H
6b Ar = Pi, R1 = OH, R3 = β -OH, R5 = Me, R2 = R4 = H
6c Ar = Pi, R1 = OH, R3,R4 = O, R2 = R5 = H
6d Ar = Pi, R1,R2 = O, R3 = α - OH, R5 = Me, R4 = H
6e Ar = Mp, R1,R2 = O, R3 = α - OH, R5 = Me, R4 = H
6f Ar = Pi, R1,R2 = O, R3 = β - OH, R5 = Me, R4 = H

Pi = 3,4-methylenedioxyphenyl
Ve = 3,4-dimethoxyphenyl
Mp = 5 -methoxy-3,4-methylenedioxyphenyl
Tp = 3,4,5-trimethoxyphenyl

6d and **6f** differ in the configuration at C-4′. The *endo*-hydroxyl group at C-4′ of **6f** explains the deshielding of H-7 and the relative protection (γ-effect) of C-7.

The specific rotations of **6d** and **6f** are analogous to those of the oxidation products of **6a** and **6b**, respectively. This led us to conclude the absolute configuration of **6d** as 7*S*,8*R*,1′*R*,3′*R*,4′*S* and of **6f** as 7*S*,8*R*,1′*R*,3′*R*,4′*R*.

EXPERIMENTAL

General. Prep. TLC was carried out on silica gel PF-254 (Merck) and CC on silica gel 60H (0.005–0.045 mm) (Merck). ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) were recorded in $CDCl_3$ with TMS as int. standard. EIMS were obtained at 70 eV.

Plant material. Leaves of the *O. catharinensis* Mez. were collected in July 1993 at Horto Florestal Reserve in Serra da Cantareira, São Paulo-SP, Brazil. The species was identified by Dr João Batista Baitello (Instituto Florestal de São Paulo). A voucher is deposited in the herbarium of Instituto Florestal of São Paulo under the number SPSF 12.335.

Extraction. Dried and powdered leaves (240 g) were exhaustively extracted with hexane at room temp. Evapn of the solvent under red. pres. gave a residue which was partitioned between hexane and MeOH 90%. The hydroalcoholic phase was evapd and yielded 2.4 g of extract.

Isolation of constituents. The alcoholic phase extract (2.4 g) was submitted to flash CC (silica gel, 150 g) and eluted with hexane–EtOAc mixts of increasing polarities to yield six frs: A (40 mg), B (356 mg), C (204 mg), D (512 mg), E (440 mg) and F (339 mg). Fr. A recrystallized from hexane–EtOAc (9:1) yielded **8** (17 mg). Fr. B was purified by prep. TLC [silica gel, hexane–$CHCl_3$ *iso*-PrOH, 15:2:3)] followed by prep. TLC [silica gel, $CHCl_3$–EtOAc–*iso*-PrOH (179:19:1)] gave **5d** (100 mg). Fr. C was submitted to successive prep. TLC [silica gel, $CHCl_3$–EtOAc–*iso*-PrOH (179:19:1) and gave **5e** (3.0 mg), **5c** (39.0 mg), **5b** (5.1 mg) and **5f** (4.0 mg). Fr. D was submitted to flash CC (silica gel, $CHCl_3$–EtOAc–*iso*-PrOH, 89:9:1). Prep. TLC of D2 (50 mg) (silica gel, benzene–Me_2CO, 19:1) gave **4c** (10 mg) and **5d** (6.6 mg). Fr. D3 (30 mg) (silica gel, benzene–Me_2CO, 19:1) gave **4c** (5 mg). Fr. D5 (73 mg) was submitted by prep. TLC (silica gel, $CHCl_3$–MeOH, 97:3) and yielded **6e** (11.5 mg) and **6f** (38 mg). Fr. E was submitted to flash CC, (silica gel, $CHCl_3$–EtOAc–*iso*-PrOH, 89:9:1) and yielded pure **6d** (19.7 mg), **5d** (5.1 mg) and **4c** (5.0 mg). Fr. E6 (75 mg) was submitted to multiple prep. TLC (silica gel, $CHCl_3$–EtOAc–*iso*-PrOH, 179:20:1) and gave **4b** (10 mg), **4c** (5.0 mg) and (4.0 mg). Fr. F by prep. TLC (silica gel, $CHCl_3$–EtOAc–*iso*-PrOH, 179:20:1) yielded **4d** (12 mg).

(7R,8R,1′R,3′R)-3′,5′-*Dimethoxy*-3,4-*methylenedioxy*-4′-*oxo*-$\Delta^{1,3,5,5',8}$-8.1′,7.O.6′-*neolignan* (**4b**). Viscous oil. $[\alpha]_D^{21} = +178°$ (MeOH, *c* 0.45). For other data see refs [2, 8].

(7R,8S,1′R,3′R)-3′,5′-*Dimethoxy*-3,4-*methylenedioxy*-4′-*oxo*-$\Delta^{1,3,5,5',8}$-8.1′,7.O.6′-*neolignan* (**4c**). Viscous oil. $[\alpha]_D^{21} = +179°$ (MeOH, *c* 0.50). For other data see refs [2, 10].

(7R,8S,1′R,3′R)-3,4,3′,5′-*Tetramethoxy*-4′-*oxo*-$\Delta^{1,3,5,5',8}$-8.1′7.O.6′-*neoglignan* (**4d**). Viscous oil. $[\alpha]_D^{21} = +178°$ (MeOH, *c* 0.61). For other data see ref. [2].

rel(7S,8S,1′R,2′S)-2′-*Hydroxy*-3,4-*dimethoxy*-3′-*oxo*-$\Delta^{1,3,5,4',8'}$-8.1′,7.O.2′-*neolignan* (**5b**). Viscous oil. ($C_{20}H_{24}O_5$ requires 69.76% C, 6.97% H, found 70.45% C, 7.02% H). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.18 (*br s*, H-2), 6.66 (*d*, *J* = 7.9 Hz, H-5), 6.76 (*d*, *J* = 7.9 Hz, H-6), 4.55 (*d*, *J* = 9.7 Hz, H-7), 2.50 (*dq*, *J* = 9.7 and 6.8 Hz, H-8), 0.89 (*d*, *J* = 6.8 Hz, 3H-9), 6.06 (*dd*, *J* = 10.2 and 2.9 Hz, H-4′), 6.87–6.95 (*m*, H-5′), 2.00–2.45 (*m*, H-6′ and H-7′), 5.45–5.66 (*m*, H-8′), 4.86 (*br d*, *J* = 10.2 Hz, 1H-9′), 4.96 (*br d*, *J* = 15.9 Hz, 1H-9′), 3.85 (*s*, OMe-3), 3.81 (*s*, OMe-4), 5.00 (*br s*, OH-2′). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 134.9 (C-1), 107.4 (C-2), 147.7 (C-3), 147.2 (C-4), 107.4 (C-5) 120.6 (C-6), 88.4 (C-7), 50.1 (C-8), 9.1 (C-9), 53.2 (C-1′), 99.8 (C-2′), 192.5 (C-3′), 125.1 (C-4′), 151.1 (C-5′), 29.4 (C-6′), 39.3 (C-7′), 133.9 (C-8′), 117.4 (C-9′), 55.8 (OMe-3 and 4). EIMS (70 eV) *m/z* (rel. int.): 344 ([M]$^+$ 27), 316 (17), 271 (12), 189 (100), 179 (26), 178 (76), 166 (25), 165 (66), 151 (59), 137 (19), 115 (15), 107 (27), 91 (35), 77 (33).

rel(7R,8S,1′R,2′S)-2′-*Hydroxy*-3,4,-*methylenedioxy*-3′-*oxo*-$\Delta^{1,3,5,4',8'}$-8.1′,7.O.2′-*neolignan* (**5c**). Viscous oil. $[\alpha]_D^{21} = -22°$ (MeOH, *c* 1.38). For other data see ref. [9].

rel(7R,8S,1′R,2′S)-2′-*Hydroxy*-3,4-*dimethoxy*-3′-*oxo*-$\Delta^{1,3,5,4',8'}$-8.1′,7.O.2′-*neolignan* (**5d**). Viscous oil. $[\alpha]_D^{21} = -58°$ (MeOH, *c* 0.33). For other data see ref. [2].

rel(7R,8S,1′R,2′S)-2′-*Hydroxy*-3,4,5-*trimethoxy*-3′-*oxo*-$\Delta^{1,3,5,4',8'}$-8.1′,7.O.2′-*neolignan* (**5e**). Viscous oil. ($C_{21}H_{26}O_6$ requires 67.37% C, 6.95% H, found 68.03% C, 7.19% H). $[\alpha]_D^{21} = -51°$ (MeOH, *c* 0.15). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.44 (*s*, H-2; H-6), 5.36 (*d*, *J* = 9.6 Hz, H-7), 2.87 (*dq*, *J* = 9.6 and 7.4 Hz, H-8), 0.76 (*d*, *J* = 7.4 Hz, 3H-9), 6.25 (*dd*, *J* = 10.3 and 2.5 Hz, H-4′), 6.91 (*m*, H-5′), 2.05 (*dd*, *J* = 13.0 and 5.0 Hz, 1H-6′), 2.56 (*dt*, *J* = 13.0 and 3.0 Hz, 1H-6′), 2.11–2.47 (*m*, 2H-7′), 5.4–5.6 (*m*, 1H-8′), 4.90–5.05 (*m*, 2H-9′), 3.79 (*s*, OMe-3), 3.81 (*s*, OMe-4) 3.79 (*s*, OMe-5). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 135.19 (C-1), 103.0 (C-2), 152.9 (C-3), 133.9 (C-4), 152.9 (C-5), 103.0 (C-6), 82.0 (C-7), 44.6 (C-8), 10.8 (C-9), 52.5 (C-1′), 99.8 (C-2′), 192.9 (C-3′), 125.6 (C-4′), 150.8 (C-5′), 31.1 (C-6′), 40.6 (C-7′), 133.8 (C-8′), 117.8 (C-9′), 56.0 (OMe-3 and OMe-5), 60.8 (OMe-4). EIMS (70 eV) *m/z* (rel. int.): 374 ([M]$^+$, 23), 208 (19), 207 (15), 197 (28), 196 (52), 195 (58), 169 (20), 167 (15), 149 (100), 137 (22), 97 (31), 91 (38), 77 (40), 71 (49), 57 (67), 55 (72).

rel(7R,8S,1′R,2′S)-2′-*Methoxy*-3,4-*methylenedioxy*-3′-*oxo*-$\Delta^{1,3,5,4',8'}$-8.1′,7.O.2′-*neolignan* (**5f**). Viscous oil. ($C_{20}H_{22}O_5$ requires 70.17% C, 6.43% H, found 70.68% C, 6.72% H). $[\alpha]_D^{21} = -93°$ (MeOH, *c* 0.46). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.61–6.72 (*m*, H-2, H-5, H-6), 5.12 (*d*, *J* = 9.5 Hz, H-7), 2.65 (*m*, H-8), 0.60 (*d*, *J* = 7.4 Hz, 3H-9) 6.01 (*dd*, *J* = 10.3 and 2.2 Hz, H-4′), 6.61–6.72 (*m*, H-5′), 1.97–2.08 (*m*, 2H-6′), 2.28–2.58 (*m*, 2H-7′), 5.53–5.62 (*m*, H-8′), 4.93 (*br d*, *J* = 16.6 Hz, 1H-9′), 4.86 (*br d*, *J* = 9.8 Hz, 1H-9′), 5.87 (*s*, O_2CH_2), 3.63 (*s*, OMe-2′). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 133.2 (C-1), 107.9 (C-2), 146.6 (C-3), 147.5 (C-4), 106.6 (C-5), 119.3 (C-6), 83.4 (C-7), 44.2 (C-8), 11.2 (C-9), 54.8 (C-1′), 102.3 (C-2′), 194.0 (C-3′), 128.0 (C-4′), 147.6 (C-5′), 31.1 (C-6′), 39.7 (C-7′), 134.5 (C-8′), 117.4 (C-9′), 100.9 (O_2CH_2), 52.4 (OMe-2′). EIMS (70 eV) *m/z* (rel. int.): 342 ([M]$^+$ 4), 314 (12), 300 (12), 259 (19), 188 (19), 173 (79), 162 (100), 149 (24), 121 (17), 103 (21), 91 (39), 77 (31).

(7S,8R,1′R,3′R,4′S)-4′-*Hydroxy*-3′,5′-*dimethoxy*-3,4-*methylenedioxy*-2′-*oxo*-$\Delta^{1,3,5,5',8'}$-8.1′,7.3′-neolignan (**6d**). Viscous oil. ($C_{21}H_{24}O_6$ requires 67.74% C, 6.45% H, found 67.7% C, 6.63% H). $[\alpha]_D^{21} = +6°$ (MeOH, *c* 1.0). IR ν_{max}^{film} cm^{-1}: 3450, 1760, 1660, 1600, 1509, 1460. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.58 (*d*, *J* = 1.5 Hz, H-2), 6.71 (*d*, *J* = 8.2 Hz, H-5), 6.60 (*dd*, *J* = 8.2 and 1.5 Hz, H-6), 2.51 (*d*, *J* = 8.9 Hz, H-7), 2.31–2.35 (*m*, H-8), 0.92 (*d*, *J* = 6.9 Hz, 3H-9), 4.65 (*d*, *J* = 1.5 Hz, H-4′), 4.52 (*d*, *J* = 1.5 Hz, H-6′), 2.27 (*dd*, *J* = 13.8 and 7.4 Hz, 1H-7′), 2.31–2.35 (*m*, 1H-7′), 5.92 (*m*, H-8′), 5.02 (*br s*, 1H-9′), 5.09 (*d*, *J* = 1.9 Hz, 1H-9′), 5.92 (*br s*, O_2CH_2), 3.62 (*s*, OMe-3′), 2.94 (*s*, OMe-5′). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 132.0 (C-1), 107.8 (C-2), 147.6 (C-3), 146.6 (C-4), 109.8 (C-5), 122.5 (C-6), 052.4 (C-7), 048.6 (C-8), 012.2 (C-9), 049.1 (C-1′), 209.9 (C-2′), 083.1 (C-3′), 078.1 (C-4′), 154.4 (C-5′), 100.3 (C-6′), 035.2 (c-7′), 133.8 (C-8′), 118.1 (C-9′), 101.2 (O_2CH_2), 055.7 (OMe-3′), 051.1 (OMe-5′). EIMS (70 eV) *m/z* (rel. int.): 372 ([M]$^+$, 6), 331 (14), 170 (10), 169 (100), 162 (22), 149 (13), 135 (16), 103 (10), 77 (14).

rel(7S,8R,1′R,3′R,4′R)-4′-*Hydroxy*-3′,5′-*dimethoxy*-3,4-*methylenedioxy*-2′-*oxo*-$\Delta^{1,3,5,5',8'}$-8.1′,7.3′-neolignan (**6f**). Viscous oil ($C_{21}H_{24}O_6$ requires 67.74% C, 6.45% H, found 66.98% C, 6.65% H). $[\alpha]_D^{21} = -10°$ (MeOH, *c* 1.91). IR ν_{max}^{film} cm^{-1}: 3470, 3010, 1740, 1650, 1500, 1440, 930. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.59 (*s*, H-2), 6.64 (*d*, *J* = 8.7 Hz, H-5), 6.59 (*d*, *J* = 8.7 Hz, H-6) 3.23 (*d*, *J* = 9.3 Hz, H-7), 2.22–2.32 (*m*, H-8 and H-7′), 0.90 (*d*, $J = 6.9$ Hz, 3H-9), 4.70 (*s*, H-4′), 4.39 (*s*, H-6′), 5.80–5.88 (*m*, H-8′), 5.05 (*dd*, $J = 10.0$ and 2.0 Hz, 1H-9′), 5.09 (*dd*, $J = 16.8$ and 2.1 Hz, 1H-9′), 5.84 (*d*, $J = 1.0$ Hz, O_2CH_2), 3.14 (*s*, OMe-3′), 3.57 (*s*, OMe-5′). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 133.8 (C-1), 110.2 (C-2), 147.7 (C-3), 146.5 (C-4), 107.9 (C-5), 122.3 (C-6), 48.9 (C-7), 46.6 (C-8), 12.3 (C-9), 49.1 (C-1′), 208.9 (C-2′), 85.2 (C-3′), 76.8 (C-4′), 153.9 (C-5′), 98.8 (C-6′), 35.3 (C-7′), 133.8 (C-8′), 118.9 (C-9′), 101.0 (O_2CH_2), 55.7 (OMe-5′), 54.7 (OMe-3′). EIMS (70 eV) m/z (rel. int.): 372 ($[M]^+$, 8), 331 (18), 170 (10), 169 (100), 163 (10), 162 (12), 149 (10), 135 (15), 91 (11), 79 (11), 77 (15).

Spatulenol (**8**). Solid amorphous. For other data see ref. [7]. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 53.3 (C-1), 26.6 (C-2), 41.7 (C-3), 80.9 (C-4), 54.3 (C-5), 29.9 (C-6), 27.4 (C-7), 24.7 (C-8), 38.8 (C-9), 153.4 (C-10), 20.2 (C-11), 16.3 (C-12), 28.6 (C-13), 26.0 (C-14), 106.2 (C-15).

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