

Supporting Information

A New Benzopyranyl Cadenane Sesquiterpene and Other Antiplasmodial and Cytotoxic Metabolites from *Cleistochlamys kirkii*

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1. NMR and Mass Spectra of Cleistonol (1)

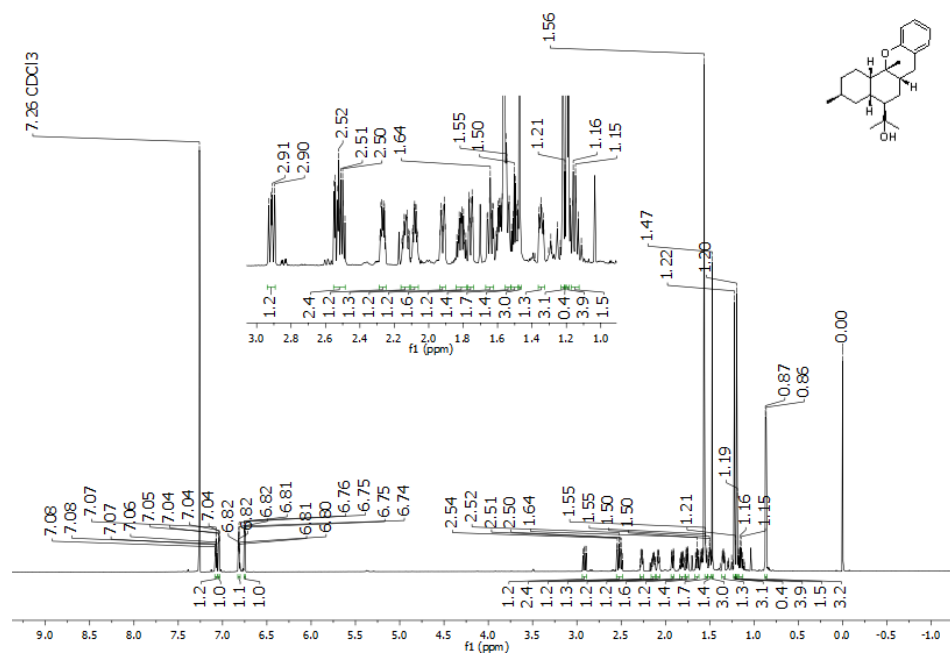


Figure S1. The ^1H NMR Spectrum of Cleistonol (1) Measured at 800 MHz and Acquired in CDCl_3 .

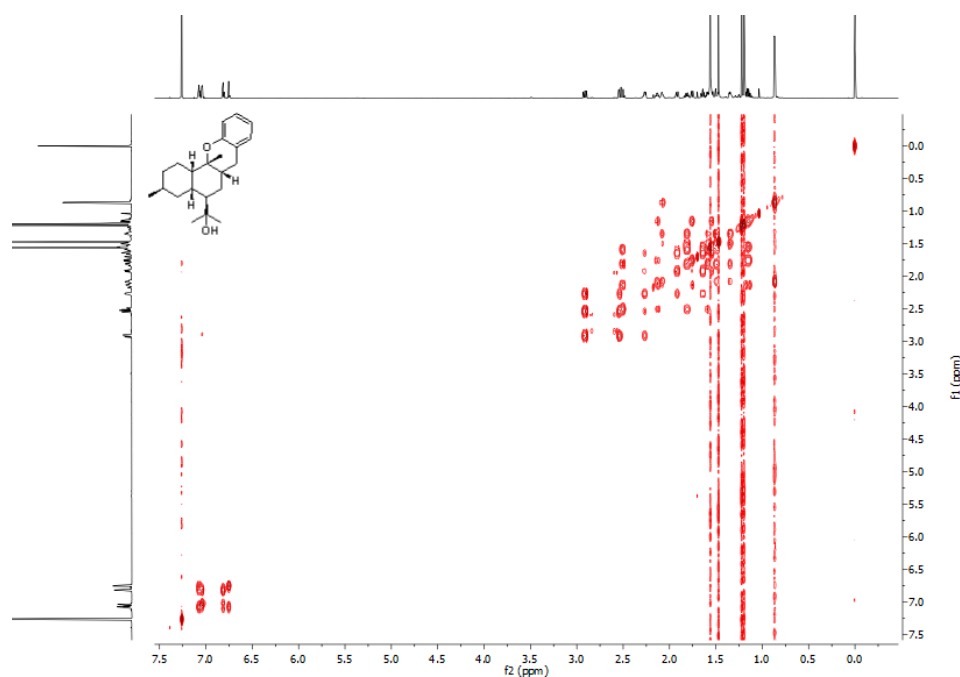


Figure S2. The $^1\text{H}/^1\text{H}$ COSY Spectrum of Cleistonol (1) Measured at 800 MHz and Acquired in CDCl_3 .

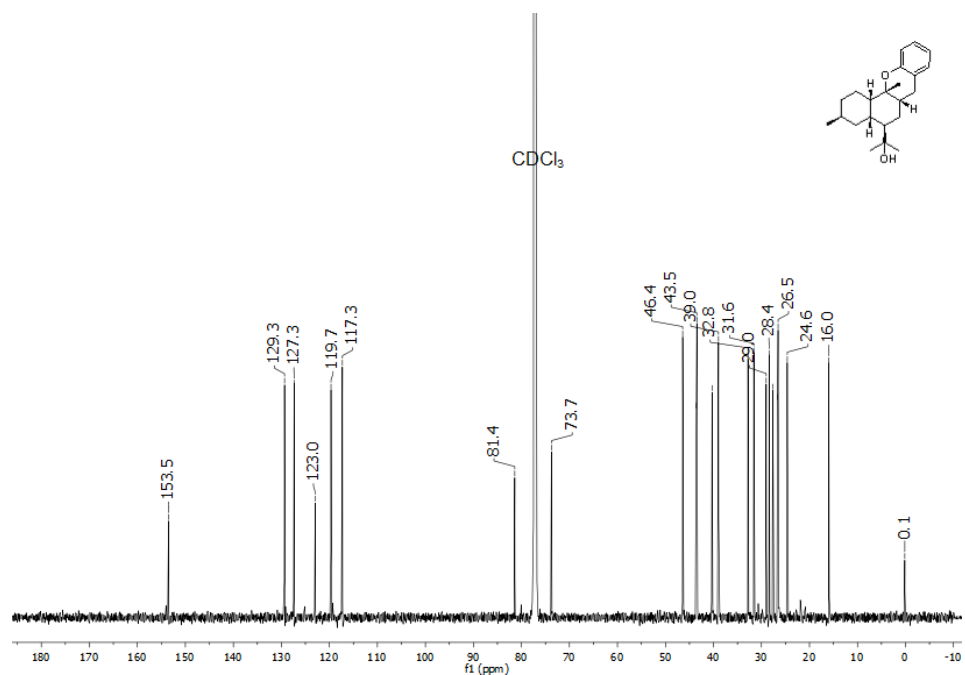


Figure S3. The ^{13}C NMR Spectrum of Cleistonol (**1**) Measured at 800 MHz and Acquired in CDCl_3 .

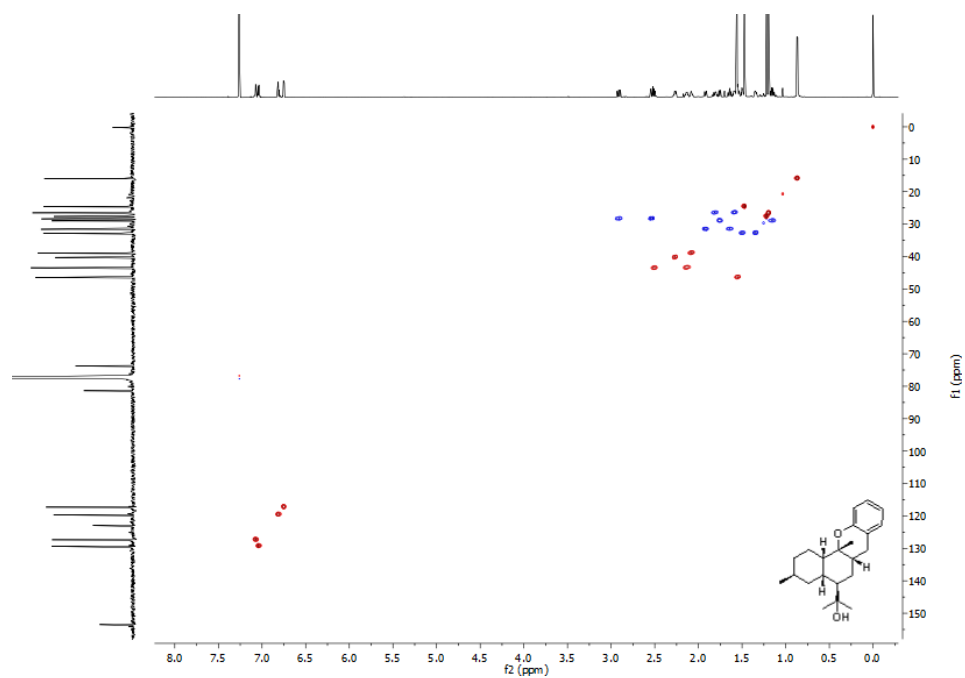


Figure S4. The HSQC Spectrum of Cleistonol (**1**) Measured at 800 MHz and Acquired in CDCl_3 .

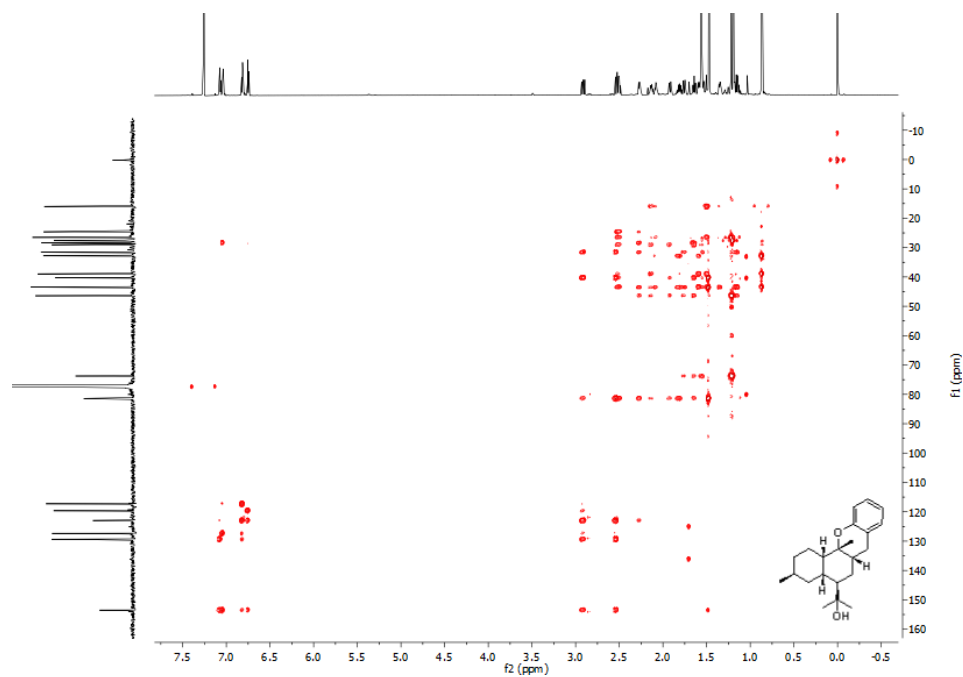


Figure S5. The HMBC Spectrum of Cleistonol (1) Measured at 800 MHz and Acquired in CDCl₃.

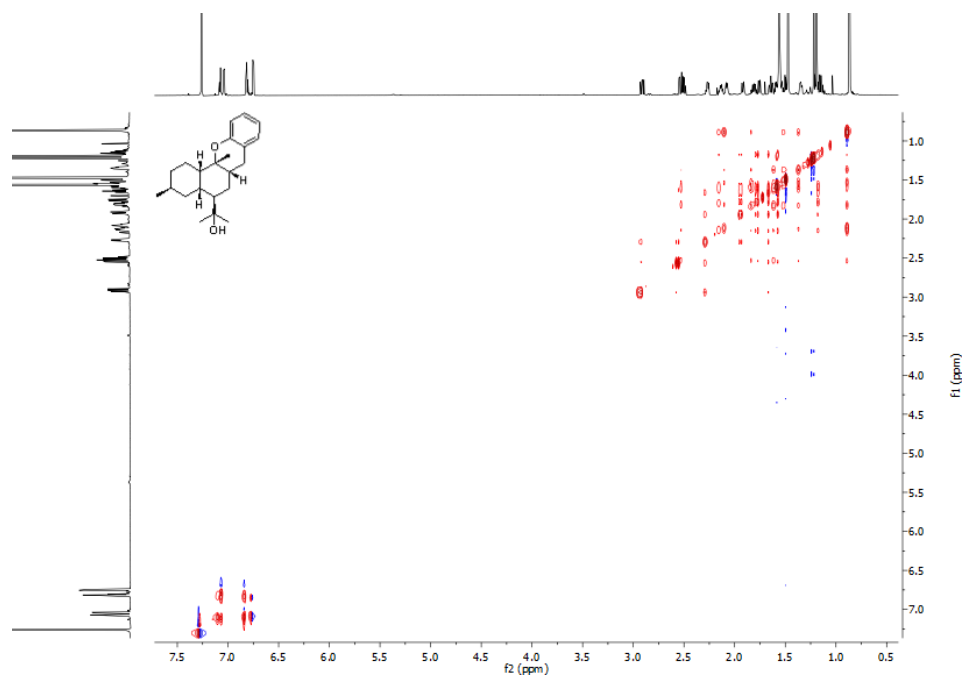


Figure S6. The TOCSY Spectrum of Cleistonol (1) Measured at 800 MHz and Acquired in CDCl₃.

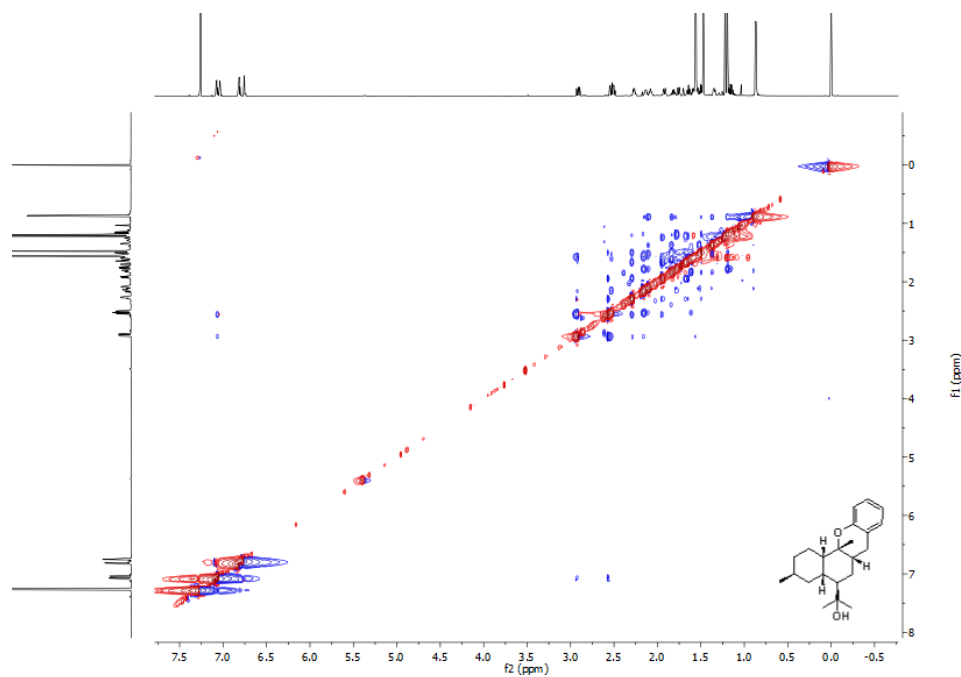


Figure S7. The NOESY Spectrum of Cleistonol (1) Measured at 800 MHz and Acquired in CDCl₃.

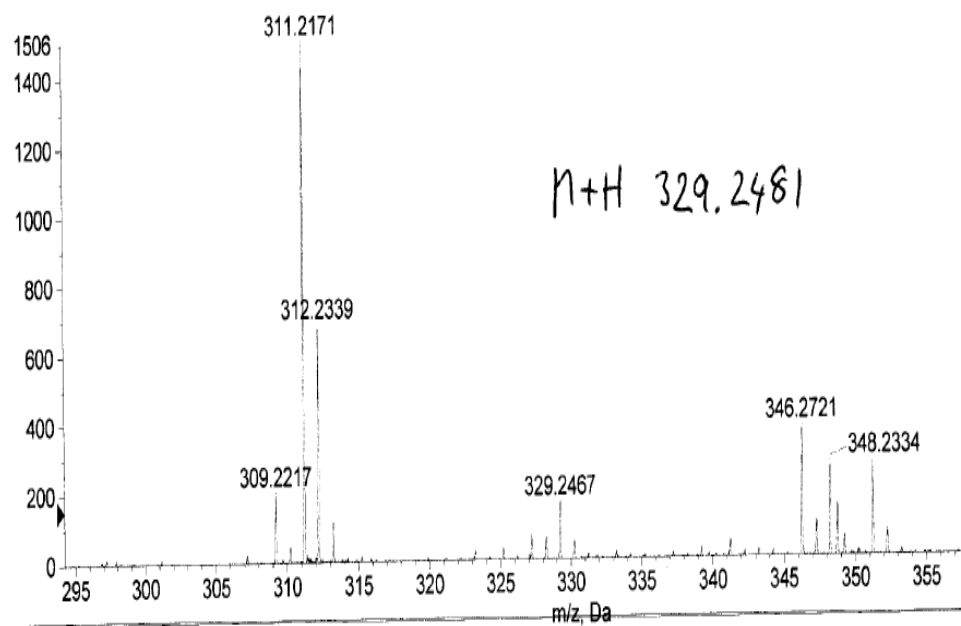
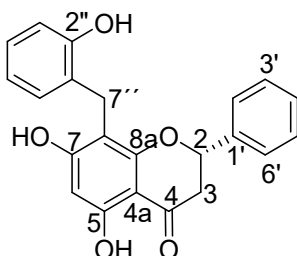
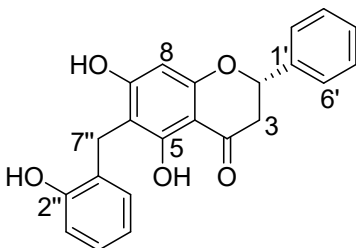


Figure S8. The HRESIMS of Cleistonol (1).

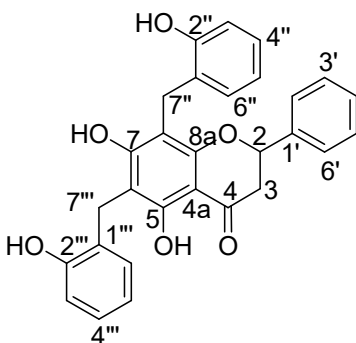
2. Spectroscopic Data of Known Compounds 2-13.



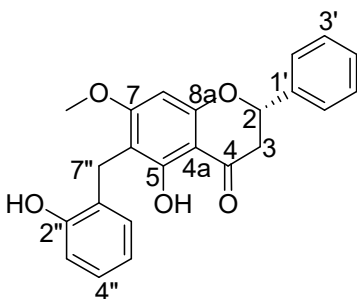
Chamaneitin (2): [1, 2] Yellow crystals. mp 200 - 204 °C; $[\alpha]_D^{20} - 16.1$ (c, 5.3, MeOH), UV (MeOH) λ_{\max} 290, 325 nm; CD (MeOH, λ_{nm} ($\Delta\epsilon$; $M^{-1}\text{cm}^{-1}$): (- 7.67) $_{290}$; (+ 3.47) $_{216}$; IR (KBr) ν_{\max} 3056, 1423, 1265, 895, 739 cm^{-1} ; LC-MS m/z 363.5 $[M+H]^+$, 269.6, 257.5, 165.4, 149.6, 102.2, 74.1, 60.2; $^1\text{H-NMR}$ (CDCl_3 , 25 °C) δ (800 MHz, ppm): 5.52 (1H, *dd*, $J = 12.9, 3.1$ Hz, H-2), 3.10 (1H, *dd*, $J = 17.1, 12.9$ Hz, H-3 α), 2.81 (1H, *dd*, $J = 17.1, 3.1$ Hz, H-3 β), 12.08 (1H, *s*, 5-OH), 6.03 (1H, *s*, H-6), 3.78 (2H, *s*, H-11), 7.39 - 7.50 (2H, *m*, H-2'/6'), 7.39 - 7.50 (2H, *m*, H-3'/5'), 7.50 (1H, *m*, H-4'), 6.79 (1H, *dd*, $J = 8.0, 0.9$ Hz, H-3''), 7.02, (1H, *m*, H-4''), 6.74 (1H, *td*, $J = 7.5, 1.0$ Hz, H-5''), 7.04 (1H, *dd*, $J = 7.5, 1.6$ Hz, H-6''); $^{13}\text{C-NMR}$ (CDCl_3 , 25 °C) δ (200 MHz, ppm): 80.1 (C-2), 43.4 (C-3), 197.6 (C-4), 103.6 (C-4a), 163.3 (C-5), 97.0 (C-6), 164.7 (C-7), 107.3 (C-8), 161.3 (C-8a), 139.9 (C-1'), 127.3 (C-2'/6'), 129.7 (C-3'/5'), 129.6 (C-4'), 154.7 (C-2''), 115.9 (C-3''), 128.2 (C-4''), 121.1 (C-5''), 130.9 (C-6''), 22.9 (C-7'').



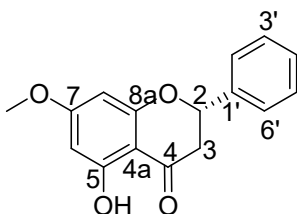
Isochamanetin (3): [1, 2] Yellow powder. mp 212 - 214 °C; $[\alpha]_D^{20}$ - 4.3 (c, 0.7, MeOH), UV (MeOH) λ_{\max} 290, 335 nm; CD (MeOH, λ_{nm} ($\Delta\epsilon$; $\text{M}^{-1}\text{cm}^{-1}$): (+9.23) $_{331}$; (- 40.16) $_{288}$; (+ 45.07) $_{222}$; IR (KBr) ν_{\max} 3418, 1638, 1265, 740 cm^{-1} ; LC-MS m/z 363.5 $[\text{M}+\text{H}]^+$, 271.6, 269.4, 259.6, 257.5, 241.3, 175.5, 165.3, 149.5, 147.0, 123.2, 107.4, 98.9, 81.1, 60.1; $^1\text{H-NMR}$ (CDCl_3 , 25 °C) δ (800 MHz, ppm): 5.45 (1H, *dd*, $J = 12.9, 3.0$ Hz, H-2), 3.08 (1H, *dd*, $J = 17.0, 13.0$ Hz, H-3 α), 2.76 (1H, *dd*, $J = 17.0, 3.0$ Hz, H-3 β), 6.01 (1H, *s*, H-8), 3.83, 3.81 (2H, *q*, $J = 3.9$ Hz, H-7''), 7.50 (2H, *d*, $J = 7.3$ Hz, H-2'/6'), 7.41 (2H, *t*, $J = 7.7$ Hz, H-3'/5'), 7.36 (1H, *m*, H-4'), 6.75 (1H, *dd*, $J = 8.0, 1.0$ Hz, H-3''), 6.98 (1H, *dt*, $J = 7.8, 1.6$ Hz, H-4''), 6.69 (1H, *dt*, $J = 7.6, 1.2$ Hz, H-5''), 7.05 (1H, *dd*, $J = 7.6, 1.2$ Hz, H-6'); $^{13}\text{C-NMR}$ (CDCl_3 , 25 °C) δ (200 MHz, ppm): 80.4 (C-2), 44.3 (C-3), 197.2 (C-4), 103.1 (C-4a), 162.8 (C-5), 109.0 (C-6), 162.8 (C-7), 96.3 (C-8), 155.7 (C-8a), 140.6 (C-1'), 127.3 (C-2'/6'), 129.7 (C-3'/5'), 129.6 (C-4'), 128.4 (C-1''), 155.7 (C-2''), 116.0 (C-3''), 127.8 (C-4''), 120.7 (C-5''), 130.8 (C-6''), 22.7 (C-7'').



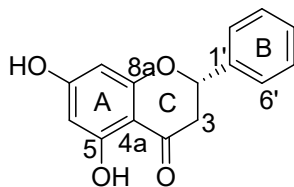
Dichamanetin (4): [1, 2] Yellow gum. $[\alpha]_D^{20} - 12.8$ (c, 9.2, MeOH), UV (MeOH) $_{\lambda_{\max}}$ 335, 295 nm; CD (MeOH, λ_{nm} ($\Delta\epsilon$; $\text{M}^{-1}\text{cm}^{-1}$): (- 5.01) $_{380}$; (- 3.35) $_{253}$; (+ 1.11) $_{223}$; IR (KBr) ν_{\max} 3054, 1630, 1420, 1265, 896, 739 cm^{-1} ; LC-MS m/z 469.4 $[\text{M}+\text{H}]^+$, 429.1, 377.5, 375.5, 365.6, 363.5, 296.9, 281.5, 271.6, 269.6, 253.3, 213.3, 177.3, 149.5, 114.3; $^1\text{H-NMR}$ (CDCl_3 , 25 °C) δ (800 MHz, ppm): 5.54 (1H, *dd*, $J = 12.8, 3.0$ Hz, H-2), 3.16 (1H, *dd*, $J = 17.2, 12.8$ Hz, H-3 α), 2.86 (1H, *dd*, $J = 17.2, 3.0$ Hz, H-3 β), 3.87 (2H, *d*, $J = 6.9$ Hz, H-7''), 3.84 (2H, *s*, H-7'''), 7.53 (2H, *d*, $J = 7.3$ Hz, H-2'/6'), 7.47 (2H, *t*, $J = 7.5$ Hz, H-3'/5'), 7.43 (1H, *m*, H-4'), 6.85 (1H, *dd*, $J = 8.1, 0.9$ Hz, H-3''), 7.08 (1H, *m*, H-4''), 6.82 (1H, *m*, H-5''), 7.26 (1H, *dd*, $J = 7.6, 1.3$ Hz, H-6''), 6.83 (1H, *m*, H-3'''), 7.05 (1H, *m*, H-4'''), 6.77 (1H, *m*, H-5'''), 7.09 (1H, *m*, H-6'''), 12.71 (1H, *s*, 5-OH), 8.16 (1H, *brs*, 7-OH), 8.16 (1H, *brs*, 2''-OH), 8.16 (1H, *brs*, 2'''-OH); $^{13}\text{C-NMR}$ (CDCl_3 , 25 °C) δ (200 MHz, ppm): 79.9 (C-2), 43.0 (C-3), 197.6 (C-4), 103.2 (C-4a), 160.7 (C-5), 108.1 (C-6), 161.9 (C-7), 107.3 (C-8), 159.2 (C-8a), 139.5 (C-1'), 127.0 (C-2'/6'), 129.3 (C-4'), 127.2 (C-1''), 154.0 (C-2''), 115.7 (C-3''), 128.0 (C-4''), 121.1 (C-5''), 131.1 (C-6''), 22.3 (C-7''), 127.1 (C-1'''), 153.8 (C-2'''), 115.5 (C-3'''), 128.0 (C-4'''), 121.1 (C-5'''), 130.9 (C-6'''), 22.9 (C-7''').



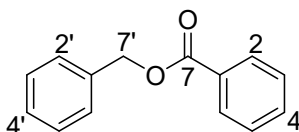
7-Methoxyisochamanetin (5): [3] White crystals. $[\alpha]_D^{20} - 5.6$ (c, 2.1, MeOH), UV (MeOH) λ_{max} 285, 330 nm; CD (MeOH, λ_{nm} ($\Delta\epsilon$; $M^{-1}cm^{-1}$): (+18.25) $_{334}$; (- 3.91) $_{302}$; (+ 2.49) $_{279}$; (- 8.41) $_{265}$; IR (KBr) ν_{max} 3424, 1638, 1265, 739 cm^{-1} ; LC-MS m/z 377.5 $[M+H]^+$, 318.3, 283.7, 271.7, 241.5, 205.2, 179.1, 167.5, 149.5, 125.2, 102.1; 1H -NMR ($CDCl_3$, 25 °C) δ (800 MHz, ppm): 5.40 (1H, *dd*, $J = 13.1, 3.1$ Hz, H-2), 3.09 (1H, *dd*, $J = 17.3, 13.1$ Hz, H-3 α), 2.84 (1H, *dd*, $J = 17.3, 3.1$ Hz, H-3 β), 12.82 (1H, *s*, 5-OH), 6.13 (1H, *s*, H-8), 3.85 (2H, *s*, H-7''), 7.43-7.44 (2H, *m*, H-2'/6'), 7.43-7.44 (2H, *m*, H-3'/5'), 7.43-7.44 (1H, *m*, H-4'), 6.86 (1H, *dd*, $J = 8.1, 1.0$ Hz, H-3''), 7.10 (1H, *td*, $J = 8.0, 1.7$ Hz, H-4''), 6.82 (1H, *td*, $J = 7.5, 1.1$ Hz, H-5''), 3.92 (3H, *s*, 7-OCH₃); ^{13}C -NMR ($CDCl_3$, 25 °C) δ (200 MHz, ppm): 79.7 (C-2), 43.3 (C-3), 196.3 (C-4), 103.0 (C-4a), 159.0 (C-5), 109.1 (C-6), 165.4 (C-7), 92.1 (C-8), 162.0 (C-8a), 138.2 (C-1'), 126.3 (C-2'/6'), 129.1 (C-3'/5'), 129.2 (C-4'), 125.9 (C-1''), 154.7 (C-2''), 116.6 (C-3''), 128.0 (C-4''), 120.1 (C-5''), 131.8 (C-6''), 22.8 (C-7''), 56.3 (-OCH₃).



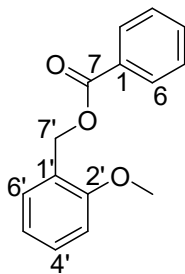
5-Hydroxy-7-methoxyflavanone (Pinostrobin, 6): [4] Yellow powder. $[\alpha]_D^{20}$ - 37.5 (c, 1.3, MeOH), UV (MeOH) λ_{\max} 275nm; CD (MeOH, λ_{nm} ($\Delta\epsilon$; $M^{-1}\text{cm}^{-1}$): (+13.45) $_{356}$; (- 2.33) $_{335}$; (- 6.85) $_{257}$; (+ 3.03) $_{246}$; IR (KBr) ν_{\max} 3429, 1640, 1423, 1265, 738 cm^{-1} ; LC-MS m/z 271.6 $[M+H]^+$, 251.6, 229.5, 187.4, 167.3, 149.6, 131.1, 144.4, 102.4, 74.1, 55.5; $^1\text{H-NMR}$ (CDCl_3 , 25 °C) δ (800 MHz, ppm): 5.43 (1H, *dd*, $J = 13.2, 3.0$ Hz, H-2), 3.09 (1H, *dd*, $J = 17.2, 13.2$ Hz, H-3 α), 2.83 (1H, *dd*, $J = 17.1, 3.0$ Hz, H-3 β), 6.07 (1H, *d*, $J = 2.3$ Hz, H-6), 6.09 (1H, *d*, $J = 2.3$ Hz, H-8), 7.38-7.47 (2H, *m*, H-2'/6'), 7.38-7.47 (2H, *m*, H-3'/5'), 7.38-7.47 (1H, *m*, H-4'), 3.82 (3H, *s*, 7-OCH₃), 12.02 (1H, *s*, 5-OH); $^{13}\text{C-NMR}$ (CDCl_3 , 25 °C) δ (200 MHz, ppm): 79.4 (C-2), 43.6 (C-3), 195.9 (C-4), 103.3 (C-4a), 164.3 (C-5), 95.3 (C-6), 168.1 (C-7), 94.4 (C-8), 162.9 (C-8a), 138.5 (C-1'), 126.3 (C-2'/6'), 129.0 (C-3'/5'), 129.0 (C-4'), 55.9 (-OCH₃).



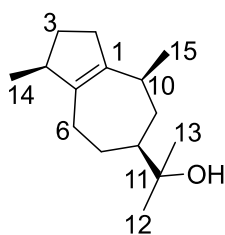
Pinocebrin (7): [5] White powder. mp 205 – 208 °C; $[\alpha]_D^{20}$ - 20.8 (c, 1.5, MeOH), UV (MeOH) $_{\lambda_{\max}}$ 295, 210 nm; IR (KBr) ν_{\max} 3430, 1640, 1265, 740 cm^{-1} ; LC-MS m/z 257.6 $[\text{M}+\text{H}]^+$, 237.1, 233.1, 223.5, 207.4, 183.1, 166.3, 151.3, 149.5, 145.2, 129.0; $^1\text{H-NMR}$ (CDCl_3 , 25 °C) δ (800 MHz, ppm): 12.04 (1H, s, H-5-OH), 7.45 (4H, m, H-2'/6' and H-3'/5'), 7.40 (1H, m, H-4'), 6.00 (2H, s, H-6 and H-8), 5.43 (1H, dd, $J = 13.1$ and 3.1 Hz, H-2), 3.09 (1H, dd, $J = 17.1, 13.1$, H-3 α), 2.83 (1H, dd, $J = 17.1, 3.1$ Hz, 3 β); $^{13}\text{C-NMR}$ (CDCl_3 , 25 °C) δ (200 MHz, ppm): 79.4 (C-2), 43.5 (C-3), 195.9 (C-4), 103.4 (C-4a), 164.5 (C-5), 96.9 (C-6), 164.5 (C-7), 95.6 (C-8), 163.3 (C-8a), 138.4 (C-1'), 129.1 (C-4'), 129.0 (C-3'/5'), 126.3 (C-2'/6').



Benzylbenzoate (8): [6] Colourless oil. UV (MeOH) $_{\lambda_{\max}}$ 225nm; IR (KBr) ν_{\max} 3425, 3056, 1641, 1423, 1265, 894, 739 cm^{-1} ; LC-MS m/z 213.1 $[\text{M}+\text{H}]^+$, 189.4, 181.1, 175.4, 160.3, 149.4, 137.4, 129.0, 121.0, 114.2, 122.3, 98.9, 91.3.; $^1\text{H-NMR}$ (CDCl_3 , 25 °C) δ (800 MHz, ppm): 8.08 (2H, d, $J = 8.1$ Hz, H-2/6), 7.45 (2H, m, H-3/5), 7.56 (1H, m, H-4), 7.46 (2H, m, H-2'/6'), 7.39 (2H, t, $J = 7.4$ Hz, H-3'/5'), 7.40 (1H, d, $J = 7.4$ Hz, H-4'), 5.37 (2H, s, H-7'); $^{13}\text{C-NMR}$ (CDCl_3 , 25 °C) δ (200 MHz, ppm): 132.7 (C-1), 132.3 (C-2/6), 131.0 (C-3/5), 135.7 (C-4), 131.2 (C-2'/6'), 130.8 (C-3'/5'), 130.9 (C-4'), 138.7 (C-1'), 169.1 (C-7), 69.3 (C-7').

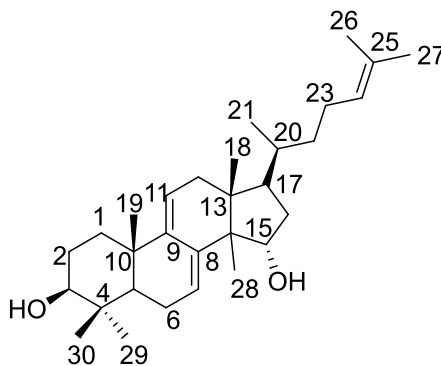


2-Methoxybenzylbenzoate (**9**): [6] Colourless oil. UV (MeOH) λ_{max} 225, 275nm; LC-MS m/z 265.2 [M+Na] $^+$, 243.7, 241.4, 218.5, 196.2, 175.4, 149.5, 129.0, 125.2, 121.5, 120.7, 114.4, 98.4, 91.2, 79.2, 60.3; 8.11; $^1\text{H-NMR}$ (CDCl_3 , 25 °C) δ (800 MHz, ppm): (2H, *dd*, $J = 8.1, 0.9$ Hz, H-2/6), 7.55 (1H, *m*, H-1), 7.44 (2H, *m*, H-3'/5'), 7.42 (1H, *m*, H-4'), 7.33 (1H, *m*, H-6'), 6.97 (1H, *t*, $J = 7.4$ Hz, H-5'), 6.92 (1H, *d*, $J = 8.2$ Hz, H-3'), 5.42 (2H, *s*, H-7'), 3.86 (3H, *s*, -OCH $_3$); $^{13}\text{C-NMR}$ (CDCl_3 , 25 °C) δ (200 MHz, ppm): 124.9 (C-1'), 130.6 (C-1), 157.7 (C-2'), 129.9 (C-2/6), 133.0 (C-4), 128.5 (C-3/5), 166.7 (C-7), 124.9 (C-1'), 157.7 (C-2'), 110.6 (C-3'), 129.6 (C-4'), 120.6 (C-5'), 129.6 (C-6'), 62.3 (C-7'), 55.6 (-OCH $_3$).



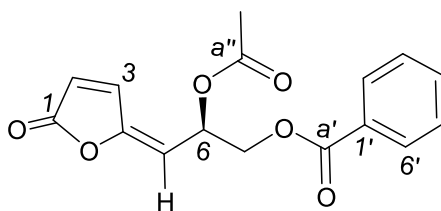
Guaiol (**10**): [7] White crystals. mp 91 – 92 °C; $[\alpha]_{\text{D}}^{20} + 97.5$ (c, 0.15, CHCl_3); UV (CHCl_3) λ_{max} 205 nm; CD (MeOH, λ_{nm} ($\Delta\epsilon$; $\text{M}^{-1}\text{cm}^{-1}$): (- 7.31) $_{242}$; (+ 1.26) $_{210}$; IR (KBr) ν_{max} 3429, 1641, 1423, 1265, 739 cm^{-1} ; LC-MS m/z 245.7 [M+Na] $^+$, 228.7, 223.5, 205.4, 163.7, 150.2, 149.5, 135.6, 114.2, 109.4, 107.2, 95.4, 93.2, 81.4, 72.2. $^1\text{H-NMR}$ (CDCl_3 , 25 °C) δ (800 MHz,

ppm): 2.53 (1H, *m*, H-4), 2.43 (1H, *m*, C-2a), 2.30 (1H, *m*, H-10), 2.15 (1H, *d*, $J = 15.7$ Hz, H-6a), 2.12 (1H, *m*, H-2b), 1.95 (2H, *m*, H-6b and H-3a), 1.81 (1H, *dddd*, $J = 13.0, 9.6, 4.0, , 1.7$ Hz, H-7a), 1.72 (1H, *m*, $J = 13.7, 9.4, 7.6, 3.4$ Hz, H-9a), 1.56 (2H, *m*, H-9b and H-8), 1.45 (1H, *dddd*, $J = 13.0, 10.6, 7.5, 3.4$ Hz, H-7b), 1.29 (1H, *ddd*, $J = 12.6, 9.0, 5.0$, Hz, H-3b), 1.20 (1H, *s*, OH), 1.19 (3H, *s*, CH₃-12), 1.16 (3H, *s*, CH₃-13), 0.99 (3H, *d*, $J = 7.2$ Hz, CH₃-15), 0.95 (3H, *d*, $J = 6.9$ Hz, CH₃-14); ¹³C-NMR (CDCl₃, 25 °C) δ (200 MHz, ppm): 140.2 (C-1), 139.0 (C-5), 73.7 (C-11), 49.8 (C-8), 46.5 (C-4), 35.5 (C-2), 33.9 (C-9), 33.8 (C-10), 31.1 (C-3), 28.0 (C-6), 27.6 (C-12), 27.5 (C-7), 26.2 (C-13), 20.1 (C-14), 19.9 (C-15).



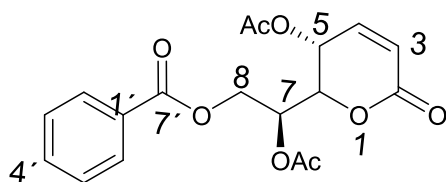
Polycarpol (11): [2, 5, 8] White crystals. mp 184 – 185 °C; $[\alpha]_D^{20} + 97.5$ (c, 5.8, CH₂Cl₂), UV (CH₂Cl₂) $_{\lambda_{max}}$ 245nm; CD (MeOH, λ_{nm} ($\Delta\epsilon$; M⁻¹cm⁻¹): (- 7.67)₂₉₀; (+ 3.61)₂₁₂; IR (KBr) ν_{max} 3418, 3055, 1640, 1423, 1265, 895, 739 cm⁻¹; LC-MS m/z 463.5 [M+Na]⁺, 428.9, 416.6, 377.4, 371.6, 343.2, 320.9, 302.5, 259.4, 251.4, 227.1, 175.5, 149.6, 142.0, 125.1, 123.3, 98.1, 83.3, 60.3; ¹H-NMR (CDCl₃, 25 °C) δ (800 MHz, ppm): 1.98 (1H, *m*, H-1 α) 1.43 (1H, *m*, H-1 β), 1.72 (1H, *m*, H-2 α), 1.65 (1H, *m*, H-2 β), 3.24 (1H, *dd*, $J = 11.6, 3.9$ Hz, H-3 α), 1.45 (1H, *dd*, J

= 13.3, 3.9 Hz, H-5), 2.16 (1H, *m*, H-6 α), 2.07 (1H, *m*, H-6 β), 5.85 (1H, *d*, *J* = 6.2 Hz, H-7), 5.30 (1H, *d*, *J* = 6.2 Hz, H-11), 2.29 (1H, *m*, H-12 α), 2.05 (1H, *m*, H-12 β), 4.27 (1H, *m*, H-15), 1.96 (1H, *m*, H-16 α), 1.72 (1H, *m*, H-16 β), 1.35 (1H, *m*, H-17), 0.61 (3H, *s*, 18-CH₃), 0.93 (3H, *s*, 19-CH₃), 1.86 (1H, *m*, H-20), 0.88 (3H, *s*, 21-CH₃), 1.35 (1H, *m*, H-22 α), 1.03 (1H, *m*, H-22 β), 2.03 (1H, *m*, H-23), 1.85 (1H, *m*, H-23), 5.08 (1H, *t*, *J* = 6.9 Hz, H-24), 1.60 (3H, *s*, H-26), 1.68 (3H, *s*, H-27), 0.88 (3H, *s*, H-28), 0.98 (3H, *s*, H-29), 1.00 (3H, *s*, H-30); ¹³C-NMR (CDCl₃, 25 °C) δ (200 MHz, ppm): 35.9 (C-1), 27.9 (C-2), 79.0 (C-3), 38.8 (C-4), 49.1 (C-5), 23.1 (C-6), 121.4 (C-7), 141.0 (C-8), 146.2 (C-9), 37.6 (C-10), 116.2 (C-11), 38.6 (C-12), 44.5 (C-13), 51.9 (C-14), 74.9 (C-15), 40.3 (C-16), 49.0 (C-17), 16.1 (C-18), 23.0 (C-19), 36.4 (C-20), 18.5 (C-21), 35.9 (C-22), 25.0 (C-23), 125.1 (C-24), 131.3 (C-25), 25.9 (C-26), 17.8 (C-27), 17.3 (C-28), 28.3 (C-29), 16.0 (C-30).



(*E*)-Acetylmelodorinol (**12**): [5] Colourless oil. [α]_D²⁰ - 2.8 (c, 1.1, MeOH), UV (MeOH) λ_{max} 265, 225 nm; CD (MeOH, λ_{nm} ($\Delta\epsilon$; M⁻¹cm⁻¹): (- 0.99)₃₂₉; (+ 1.31)₃₁₁; (- 1.56)₃₀₁; (+1.34)₂₈₁; IR (KBr) ν_{max} 3430, 2082, 1640, 1265, 739 cm⁻¹; LC-MS *m/z* 303.4 [M+H]⁺ 291.1, 274.6, 273.4, 251.4, 231.3, 175.8, 149.5, 129.0, 109.5, 105.1, 91.3, 81.4, 79.1, 73.9, 60.1; ¹H-NMR (CDCl₃, 25 °C) δ (800 MHz, ppm): 6.34 (1H, *d*, *J* = 5.7 Hz, H-2), 7.90 (1H, *d*, *J* = 5.7 Hz, H-3), 5.72

(1H, *dd*, $J = 10.0, 1.1$ Hz, H-5), 5.98 (1H, *ddd*, $J = 10.8, 6.7, 4.2$ Hz, H-6), 4.53 (1H, *dd*, $J = 11.8, 4.2$ Hz, H-7 α), 4.47 (1H, *dd*, $J = 11.6, 6.7$ Hz, H-7 β), 8.01 (2H, *dd*, $J = 8.1, 1.1$ Hz, H-2'/6'), 7.46 (2H, *t*, $J = 7.8, 7.8$ Hz, H-3'/5'), 7.60 (1H, *m*, H-4'), 2.10 (3H, *s*, -CH₃), ¹³C-NMR (CDCl₃, 25 °C) δ (200 MHz, ppm): 168.7 (C-1), 122.6 (C-2), 140.2 (C-3), 153.5 (C-4), 107.5, (C-5), 66.8 (C-6), 65.1 (C-7), 129.3 (C-1'), 129.7 (C-2'/6'), 128.6 (C-3'/5'), 133.5 (C-4'), 166.0 (C- α'), 170.1 (C- α'').



Cleistenolide (**13**): [2, 5] White needles. Green upon spraying with anisaldehyde reagent; mp 128-130 °C; IR 2965 cm⁻¹, 1749.72 cm⁻¹, 1601.20 cm⁻¹; ¹H-NMR (CDCl₃, 25 °C) δ (800 MHz, ppm): 6.31 (*d*, 9.6, H-3), 7.02 (*dd*, 9.6, 6.4, H-4), 5.44 (*dd*, 6.4, 3.2, H-5), 4.82 (*dd*, 10.4, 2.4, H-6), 5.52 (*ddd*, 10.4, 4.4, 2.4, H-7), 4.56 (*dd*, 12.8, 4.8 H-8 α), 4.95 (*dd*, 12.8, 2.4, H-8 β), 2.06 (H-11), 2.11 (*s*, H-13), 8.04 (*dd*, 8.8, 0.8, H-2'), 7.48 (*dd*, 8.0, 8.0, H-3'), 7.60 (*t*, 8.0, H-4') 7.48, (*dd* (8.0, 8.0, H-5'), 8.04 (*dd* 8.8, 0.8 H-6'); ¹³C-NMR (CDCl₃, 25 °C) δ (200 MHz, ppm): 161.2 (C-2), 125.5 (C-3), 139.9 (C-4), 75.6 (C-5), 170.0 (5-O \underline{C} OCH₃), 20.6 (5- \underline{C} H₃COO), 59.9 (C-6), 67.8 (C-7), 169.6 (7-O \underline{C} OCH₃), 20.8 (7- \underline{C} H₃COO) 62.2 (C-8), 166.9 (7'-O \underline{C} OPh), 129.7 (C-1'), 129.8 (C-2'/6'), 128.6 (C-3'/5'), 133.4 (C-4')

3. X-Ray crystallography for 7-methoxyisochamanetin (5) and guaiol (10)

X-Ray data for single crystals of **5** and **10** were collected on an Agilent SuperNova Dual source diffractometer, equipped with an Atlas detector, at $T = 120.0$ K for **5** and $T = 123.0$ K for **10** using mirror-monochromatized Cu-K α radiation ($\lambda = 1.54184$ Å). The data collection and reduction were performed using the program *CrysAlisPro*, [9] and the intensities were corrected using Gaussian face index absorption correction method [9] for **5** and **10**. The structure was solved by Intrinsic Phasing method with SHELXT [10] and refined by full-matrix least-squares using SHELXL-2015^[11] within OLEX2 package.^[12] All non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were refined using riding models with $U_{\text{eq}}(\text{H})$ of $1.5U_{\text{eq}}(\text{parent})$ for terminal groups and $1.2 U_{\text{eq}}(\text{parent})$ for non-terminal groups.

Compound **5**: $0.335 \times 0.085 \times 0.066$ mm, $\text{C}_{23}\text{H}_{20}\text{O}_5$, $M = 376.39$, orthorhombic, space group $P2_12_12_1$, $a = 5.27836(4)$ Å, $b = 15.81290(14)$ Å, $c = 21.27803(16)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1776.00(2)$ Å³, $Z = 4$, $\rho = 1.408$ g cm⁻³, $\mu = 0.811$ mm⁻¹, $F(000) = 792$, 25733 reflections ($\theta_{\text{max}} = 66.746^\circ$) measured (3154 unique, $R_{\text{int}} = 0.0338$, completeness = 99.89%), Final R indices ($I > 2\sigma(I)$): $R_1 = 0.0275$, $wR_2 = 0.0709$, R indices (all data): $R_1 = 0.0279$, $wR_2 = 0.0713$. GoF = 1.081 for 256 parameters and 0 restraints, largest diff. peak and hole 0.140/−0.186 eÅ⁻³. Absolute structure parameter $x = -0.07(5)$. CCDC number - 1937081 contains the supplementary data for this structure.

Compound **10**: $0.188 \times 0.081 \times 0.075$ mm, $\text{C}_{15}\text{H}_{26}\text{O}$, $M = 222.36$, trigonal, space group $P3_2$, $a = 13.02112(10)$ Å, $b = 13.02112(10)$ Å, $c = 7.05780(5)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 1036.327(18)$ Å³, $Z = 3$, $\rho = 1.069$ g cm⁻³, $\mu = 0.483$ mm⁻¹, $F(000) = 372$, 16437 reflections ($\theta_{\text{max}} = 76.545^\circ$) measured (2884 unique, $R_{\text{int}} = 0.0254$, completeness = 99.99%), Final R indices ($I > 2\sigma(I)$): $R_1 = 0.0370$, $wR_2 = 0.0986$, R indices (all data): $R_1 = 0.0371$, $wR_2 = 0.0988$. GOF = 1.089 for 150 parameters and 1 restraint, largest diff. peak and hole 0.334/−0.290 eÅ⁻³. Absolute structure parameter $x = 0.01(6)$. CCDC number - 1937082 contains the supplementary data for this structure.

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