

3 β ,9 α -DIHYDROXYCINNAMOLIDE: A FURTHER NOVEL DRIMANE SESQUITERPENE FROM THE STEM BARK OF *CANELLA WINTERANA*DEBORAH KIOY,¹ ALEXANDER I. GRAY,* and PETER G. WATERMAN*Phytochemistry Research Laboratories, Department of Pharmacy, University of Strathclyde, Glasgow G1 1XW, Scotland, UK*

ABSTRACT.—In continuation of our studies of the stem barks of species of *Canellaceae* we have now isolated three further compounds from *Canella winterana*. Two of these are the known helicid and clovanediol. The third is a novel drimane sesquiterpene which we have characterized, on the basis of spectroscopic analysis, as 3 β ,9 α -dihydroxycinnamolide [**2**].

In a previous paper (1) we reported the isolation of four drimane sesquiterpenes and two common phenylpropenes from the stem bark of *Canella winterana* L. (*Canellaceae*) collected on Grand Cayman. One of the isolated compounds was the novel 9 α -hydroxycinnamolide [**1**]. Continuing our investigation we have managed, using preparative hplc, to isolate two minor sesquiterpene components. One of these has proved to be a further novel drimane identified as 3 β ,9 α -dihydroxycinnamolide [**2**] on the evidence presented below, while the other is the tricyclic compound clovanediol (2). In addition, polar extracts have yielded the para *O*-glucoside of benzaldehyde (helicid).

The less polar of the two compounds purified by hplc gave $[M]^+$ analyzing for $C_{15}H_{22}O_4$. The ir spectrum indicated the occurrence of hydroxyl(s) and lactone carbonyl, and the 1H -nmr spectrum (Table 1) revealed an isolated AB quartet (for the C-11 methylene of the lactone of a 9-hydroxydrimane, e.g., **1**) and an

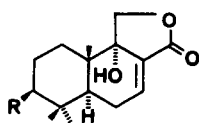
oxymethine proton at δ 3.34 with two couplings, one of which (11.5 Hz) indicated an axial configuration. The 1H -nmr spectrum of the new compound showed resonances comparable to H-5 to H-7 of **1** (Table 1). The secondary alcohol must therefore be placed at C-1 or C-3 where it is in the equatorial (β) configuration. Assignment to C-3 is supported by the deshielding of the C-4 axial methyl resonance from δ 0.97 in **1** to δ 1.07 in **2**. This is the first record of a 3-hydroxy drimane in the *Canellaceae* although an enantiomeric compound, iresin, has been reported (3) from the *Amaranthaceae*.

The second isolate purified by hplc was identified as clovanediol (2,4,5), an unusual tricyclic sesquiterpene probably derived by cyclization of caryophyllene oxide. 1H - and ^{13}C -nmr data available for clovanediol agreed closely with those published by Jarvis *et al.* (5).

EXPERIMENTAL

PLANT MATERIAL.—Stem bark of *C. winterana* was collected from the coastal bluffs at East End, Grand Cayman in August 1981. A voucher specimen. A. I. Gray, s.n., has been deposited at the Herbarium of the Botanical Garden, Edinburgh.

EXTRACTION AND ISOLATION OF COMPOUNDS.—The defatted ground stem bark (85 g) was further extracted with EtOAc and then MeOH. The combined EtOAc and MeOH extracts were subjected to cc over Si gel eluting with $CHCl_3$ and then $CHCl_3$ with increasing amounts of MeOH. This gave, in order of elution, mukadial (1), a mixture, mannitol (ca. 3 g), β -sitoserial glucoside (30 mg), and helicid (7 mg). The



- 1** R=H
2 R=OH

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TABLE 1. ¹H-nmr Chemical Shift Data (δ), Multiplicities, and Coupling Constants for α-Hydroxycinnamolide [1] and 3β,9α-Hydroxycinnamolide [2].^a

Proton	Compound	
	1	2
H-1 _{eq}	1.20 dq (12.3, 1.7)	1.25 m
H-1 _{ax}	1.94 dt (5.5, 12.3)	2.13 dt (4.1, 13.5)
H-2	1.53/1.56 m	1.66/1.73 m
H-3	1.27/1.34 m	3.34 dd (11.5, 4.2)
4-Me _{eq}	0.94 s	0.95 s
4-Me _{ax}	0.97 s	1.07 s
H-5	1.86 dd (11.3, 5.0)	1.85 dd (11.5, 5.4)
H-6 _{eq}	2.45 ddd (20.8, 5.0, 4.5)	2.46 ddd (20.9, 5.0, 4.5)
H-6 _{ax}	2.11 ddd (20.8, 11.3, 3.2)	2.20 ddd (20.9, 11.5, 4.1)
H-7	7.01 dd (4.5, 3.2)	7.06 dd (4.5, 4.1)
10-Me	0.88 s	0.89 s
CH ₂ -11	4.21/4.35 ABq (10.0)	4.23/4.36 ABq (9.9)

^aSpectra run in CDCl₃ at 360 MHz.

mixture was separated by preparative hplc [10 μ silica 250 × 10 mm; MeOH-CH₂Cl₂ (2:100)] to give **2** (6 mg, Rt 14.5 min) and clovanediol (18 mg, Rt 23.0 min).

3β,9α-DIHYDROXYCINNAMOLIDE [2].—Amorphous; [α]_D -14° (c = 0.01, MeOH); ¹H nmr see Table 1; ir ν max 3450–3350, 1745, 1675, 1460, 1240 cm⁻¹; eims *m/z* (rel. int.) [M]⁺ 266 (1), 248 (7), 233 (10), 140 (7), 127 (60), 122 (100), 107 (16), 96 (86); calcd for C₁₅H₂₂O₄, 266.1518, found (hreims) 266.1515.

CLOVANEDIOL.—Needles from CHCl₃, mp 150–152° [lit. (2) 152–153°]; [α]_D +6° (c = 0.2, CHCl₃) [lit. (2) +5°]; ir ν max (KBr) 3400, 1650, 1460, 1390, 1360, 1050 cm⁻¹; ¹H nmr (360 MHz, CDCl₃), ¹³C nmr (90.56 MHz, CDCl₃) see Jarvis *et al.* (5); eims *m/z* (rel. int.) [M]⁺ 238 (99), 220 (54), 182 (57), 164 (100), 150 (29), 135 (26), 107 (26), 105 (26), 95 (21), 93 (23); calcd for C₁₅H₂₆O₂, 238.1933, found (hreims) 238.1921.

HELICID.—Prisms from MeOH, mp 199–200° [lit. (5) 188–190°]; [α]_D -27° (c = 3.2, MeOH); uv λ max (MeOH) 268 nm; ir ν max (KBr) 3450, 1675, 1665, 1605, 1580, 1510, 820 cm⁻¹; ¹H nr (250 MHz, pyridine-*d*₅) δ 9.93 (1H, s, CHO), 7.83 (2H, d, *J* = 8.8, H-2, -6),

7.33 (2H, d, *J* = 8.8, H-3, -5), 6.13 (1H, d, *J* = 7.8 Hz, anomeric H); eims *m/z* (rel. int.) [M]⁺ 284 (3), 162 (100), 145 (39), 127 (27), 122 (75), 85 (65); calcd for C₁₃H₁₆O₇, 284.0896, found (hreims) 284.0892.

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