LIGNANS FROM WOOD OF CALOCEDRUS FORMOSANA

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Abstract—Hinokinin, savinin, calocedrin, matairesinol and three new lignans, 7-oxohinokinin, 4',5-dihydroxy-3,3',4-trimethoxy lign-7-en-9,9'-olide and 4,4'-dihydroxy-3,3',5-trimethoxy lign-7-en-9,9'-olide, were isolated from an acetone extract of the wood of Calocedrus formosana. The structures of new lignans were determined by spectral methods.

INTRODUCTION

The constituents of the heartwood of Calocedrus formosana, a member of Cupressaceae indigenous to Taiwan [1], have been extensively investigated in our laboratory [2-7]. In addition to a large quantity of terpenoid acids, such as shonanic, thujic and chaminic acids, the wood also contains tropolones, monoterpenes, naphthalene-type sesquiterpenes, diterpenoid phenols and lignans, viz. (-)-hinokinin (1), (-)-savinin (hibalactone, 2), and (+)-calocedrin (3). On continuing a study of the chemical constituents, we have now isolated (-)-matairesinol (4) [8, 9] and three new lignans 5-7 from an acetone extract of the wood of C. formosana.

RESULTS AND DISCUSSION

Compound 5, [M]+ m/z 368, showed resonances of 20 carbons in its 13C NMR spectrum. The resonances of δ172.7 (s) and 190.9 (s) are ascribed to two carbonyl carbons. The IR absorptions at 1765 and 1660 cm⁻¹ indicate the presence of γ-butyrolactone and conjugated ketone moieties. By comparison of the 1H and 13C NMR data with those of hinokinin [3, 10], the structure of compound 5 is determined to be 7-oxohinokinin. The H-8 resonance appears at δ4.19 as a doublet (J = 5.7 Hz). On treatment with a strong base (t-BuOK, t-BuOH, THF) at room temperature for 34 hr. no epimerization took place. Thus, this lignan is considered to have the thermodynamically stable 8,8'-trans-configuration. The absolute configuration (8$8/R) of (-)-7-oxohinokinin is tentatively assigned by analogy to (-)-hinokinin and other lignan constituents found in the same plant.

Compounds 6 and 7, both of them showing [M]+ at m/z 386, must be isomeric compounds because they have similar IR and UV spectra. The presence of a cinnamic acid γ-lactone moiety is inferred from IR absorptions at 1740 and 1640 cm⁻¹ as well as from UV absorption at 320 nm. In the 1H NMR spectrum, 6 displayed five aromatic protons, two phenolic hydroxy protons and resonances at δ3.86, 3.87 and 3.95 attributable to three anisole methyl groups. The positions of hydroxyl and methoxy groups are readily deduced by comparison with the literature [10]. Thus, the structure of 6 is assigned as (7E)-4',5-dihydroxy-3,3',4-trimethoxy lign-7-en-9,9'-olide. On the other hand, the 1H and 13C NMR spectra of 7 (C24H22O3) revealed that it has symmetry on a phenyl ring; there were only 18 peaks visible in the 13C NMR spectrum. The three methoxy groups appeared at two positions, δ55.8 and 56.3 (two superimposed carbons). The corresponding proton signals occurred at δ3.80 (3H) and 3.85 (6H) in the 1H NMR spectrum. The aromatic protons H-2 and H-6 had the same chemical shift of δ6.77 (s). The structure of 7 is thus (7E)-4,4'-dihydroxy-3,3',5-trimethoxy lign-7-en-9,9'-olide.

EXPERIMENTAL

Plant material. Calocedrus formosana (Florin) Florin was collected in the campus of the National Taiwan University. A
voucher specimen is deposited in the herbarium of the Department of Botany. The skinning and air-dried wood (660 g) from branches 6–8 cm in diameter was selected for study. After extraction with warm Me2CO, the combined extracts were concentrated in vacuo to 20 g of residue. Components were seeded by CC on silica gel (230 g) and elution with hexane–EtOAc gradients. Compound 1 was eluted first, followed by 6, 7, 2, 5, 4, and 3.

7-Oxohinokinin (5). C28H17O7N3, needle-like crystals (from CHCl3–MeOH), mp 105.9–111.1°C,[α]D25° +10° (CHCl3, c 0.82). λmax nm (ε): 313 (7.570), 281 (8.620), 240 (8.250). IR νmax cm−1: 1765, 1660. EIMS m/z (rel. int.): 368 [M]+ (13), 260 (5), 242 (6), 235 (9), 227 (5), 201 (9), 178 (10), 160 (100), 149 (68), 135 (33), 131 (69), 121 (40). 1H NMR (CDCl3, 300 MHz): δ 2.75 (1H, dd, J = 13.6, 8.2 Hz, H-7), 2.79 (1H, dd, J = 13.6, 7.8 Hz, H-7), 3.31 (1H, m), 4.12 (1H, dd, J = 9.0, 7.0 Hz, H-9), 4.19 (1H, d, J = 5.7 Hz, H-8), 4.51 (1H, dd, J = 9.0, 5.3 Hz, H-9), 3.93 (2H, s), 6.05 (2H, s), 6.61 (1H, dd, J = 7.8 Hz, 1.2 Hz, H-6), 6.63 (1H, d, J = 1.2 Hz, H-2), 6.72 (1H, d, J = 7.8 Hz, H-5), 6.82 (1H, d, J = 8.1 Hz, H-5), 7.30 (1H, d, J = 1.7 Hz, H-2), 7.42 (1H, dd, J = 8.1, 1.7 Hz, H-6). 13C NMR (CDCl3, 75 MHz, DEPT): δ 38.1 (t, C-7), 41.4 (d, C-8), 53.6 (d, C-8), 71.9 (t, C-9), 101.1 (t, OCH2O), 102.1 (t, OCH2O), 107.9 (d, C-2), 108.5 (d, C-2), 108.6 (d, C-5), 109.1 (d, C-5), 122.0 (d, C-6), 126.2 (d, C-6), 130.1 (s, C-1), 131.1 (s, C-1), 146.6 (s, C-4), 148.1 (s, C-3), 148.3 (s, C-3), 152.6 (s, C-4), 172.7 (s, C-9), 190.9 (s, C-7).

(7E)-4,5-Dihydroxy-3,5-trimethoxylignan-7-en-9,9'-alide (6). C24H16O7, needle-like crystals (obtained from HPLC), mp 130–131°C,[α]D25° −94° (CHCl3, c 0.15). UV λmax nm (ε): 322 (21.620), 299 (17.300), 280 (21.700), 238 (27.410). IR νmax cm−1: 3440, 1735, 1540, 1600, 1510. MS m/z (rel. int.): 386 [M]+ (8), 249 (23), 205 (3), 193 (7), 189 (7), 161 (12), 137 (100), 122 (23), 105 (6).
1H NMR (CDCl3): 52.7 (H, dd, J = 14.1, 10.2 Hz, H-7), 3.02 (H, dd, J = 14.1, 3.9 Hz, H-7), 3.82 (1H, m, H-8), 3.86 (3H, s, OMe), 3.87 (3H, s, OMe), 3.95 (3H, s, OMe), 4.25 (2H, m, H-9), 5.50 (1H, s, OH), 5.86 (1H, s, OH), 6.61 (1H, d, J = 1.8 Hz, H-6), 6.69 (1H, br, d, J = 8.4 Hz, H-5), 6.70 (1H, br, s, H-2), 6.83 (1H, d, J = 8.4 Hz, H-5), 6.95 (1H, d, J = 1.8 Hz, H-2), 7.45 (1H, d, J = 1.8 Hz, H-7). 13C NMR (CDCl3, 75 MHz, DEPT): δ 37.6 (t, C-7), 40.1 (d, C-9), 55.9 (q, OMe), 56.0 (q, OMe), 61.1 (q, OMe), 70.0 (s, C-9), 107.6 (d, C-2), 108.7 (d, C-6), 111.4 (d, C-2), 114.5 (d, C-5), 121.5 (d, C-6), 127.7 (s, C-1), 129.8 (s, C-1' and C-8), 137.0 (s, C-4), 137.1 (d, C-7), 144.6 (s, C-4'), 146.7 (s, C-3'), 149.5 (s, C-5), 152.3 (s, C-3), 172.5 (s, C-9).

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