Acetate: mp 80°C; Found: C, 54.31; H, 5.15; C_{12}H_{10}O_{14} requires C, 54.2; H, 5.15; 1H NMR (CDCl₃): δ 6.26 (1H, d, J = 10 Hz, H-3), 7.65 (1H, d, J = 10 Hz, H-4), 7.40 (1H, d, J = 9 Hz, H-5), 6.90 (1H, dd, J = 9 and 2 Hz, H-6), 6.90 (1H, dd, J = 2 Hz, H-8), coumarin protons 5.2 (4H, m), 4.92 (1H, s), 4.64 (1H, q, J = 12, 6 Hz), 4.13 (2H, d, J = 1.8 Hz); sugar protons and acetoxyl chemical shifts given in the text.

REFERENCES


Phytochemistry, Vol 24, No 8, pp 1863–1864, 1985
Printed in Great Britain

1863

(+)-CALOCE DRIN, A LIGNAN DIHYD ROAN HYDRIDE FROM CALOCEDRUS FORMOSANA

JIM-MIN FANG, SHYI-TAI JAN and YU-SHIA CHENG

Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

(Revised received 28 November 1984)

Key Word Index—Calocedrus formosana; Cupressaceae; calocedrin; lignan dihydroanhydride; hibalactone.

Abstract—A novel lignan dihydroanhydride, (+)-calocedrin, was isolated from the wood of Calocedrus formosana. Its structure was determined to be trans-a-(3,4-methylenedioxybenzylidene)-β-(3,4-methylenedioxybenzyl)-γ-hydroxybutanoid by spectroscopic methods. Reduction of (+)-calocedrin resulted in an optically inactive lignan lactone, (±)-hibalactone.

INTRODUCTION

Calocedrus formosana, a member of the Cupressaceae, is an economically important tree indigenous to Taiwan [1]. Previous investigations [2, 3] on the heartwood have shown that it contains essential oil and a large quantity of terpenoid acids, such as shonanic, thujic and chaminic. Lignan components, such as hinokinin and hibalactone (savvinin), have also been found.

RESULTS AND DISCUSSION

On continuing a study of the chemical constituents, the wood of C. formosana was collected in our campus and subjected to extraction with acetone. The combined extracts were concentrated and the residual contents separated on a silica gel column eluting with hexane-ethyl acetate gradients. After (±)-hibalactone 1 (R₇ 0.30, hexane-acetone, 7:3) [4, 5], a novel lignan, namely (+)-calocedrin, was eluted (R₇ 0.16). Calocedrin was re-crystallized from ethanol, mp 187–188°C, [α]D²⁵ +6° (c 0.9; acetone). The mass spectrum displayed the parent peak at m/z 368 and the base peak at m/z 135, ascribable to the 3,4-methylenedioxybenzyl fragment. The IR spectrum showed the presence of hydroxyl (3560 cm⁻¹), lactone (1745 cm⁻¹) and olefin (1640 cm⁻¹) groups. Analyses of

![Structural formula of (+)-calocedrin](image)

1 R = H
2 R = OH

REFERENCES

the \(^1\)H and \(^{13}\)C NMR spectra (Tables 1 and 2) revealed that the structure of (+)-calocedrin (2) was related to that of hibalactone. Calocedrin contained an unusual hemiacetal lactone (–CO\(_2\)-CHOH–) moiety as characterized in the \(^1\)H NMR spectrum [6]. The hydroxyl proton, coupled by H-9', exhibited as a doublet (\(J = 5.5\) Hz) at \(\delta 6.49\) that was shifted by change of concentration or temperature. Similarly, the hemiacetal proton (H-9') was coupled by the hydroxyl proton, displaying as a doublet (\(J = 5.5\) Hz) at \(\delta 5.67\). Since irradiation at the resonance of H-8' (\(\delta 3.71\)) did not cause any apparent effect on the signal pattern of H-9', these two protons should orient nearly orthogonally (trans configuration) according to the Karplus empirical rule.

The structures of calocedrin and hibalactone are chemically correlated. (+)-Calocedrin was reduced by sodium borohydride in the presence of sodium hydroxide [7]. The product (66 % yield) exhibited compatible physical and spectroscopic properties (mp, mmp, HPLC, UV, IR and \(^1\)H NMR) with those of (–)-hibalactone, except optical activity. An intermediate aldehyde 3, obtained from hemiacetal opening, was presumed to undergo epimerization prior to reduction under the alkaline conditions.

**EXPERIMENTAL**

**Plant material.** Calocedrus formosana (Florin) Florin was collected in the campus of the National Taiwan University. The skinned and air-dried wood (600 g) from branches 6–8 cm in diam. was selected for study. After extraction \(\times 3\) with Me\(_2\)CO, the combined extracts were condensed in vacuo to give 20 g of residue. Components were separated by CC on silica gel (230 g) and elution with hexane–EtOAc gradients.

(+)-Calocedrin. Crystals (105 mg) \(R_\ell 0.16\) (hexane–Me\(_2\)CO, 7:3). Recrystallization samples from EtOH exhibited mp 187–188 °C; \([\alpha]_D^{25} + 0.0\) (c 0.9; Me\(_2\)CO). UV \(\lambda_{max}^{E1OH}\) nm (\(e\)): 237 (10400), 294 (10800), 332 (11600). IR \(\nu_{max}^{cm^{-1}}\): 3560 (OH), 1745 (C=O), 1640 (C=C), 1600 (aromatic). MS m/z (rel. int.): 368 (15) [M\(^+\)], 350 (9), 310 (10), 135 (100).

Reduction of (+)-calocedrin. NaOH (21 mg, 0.53 mmol) was added to a soln of (+)-calocedrin (49 mg, 0.13 mmol) in MeOH. After stirring for 10 min, NaBH\(_4\) (6.5 mg, 0.17 mmol) was added and the mixture refluxed (80 °C) for 1 hr under N\(_2\). The mixture was cooled, acidified (pH 2) with HCl and extracted with CHCl\(_3\). The combined extracts were dried over Na\(_2\)SO\(_4\), filtered, and purified by TLC (R\(_f\) 0.30, hexane–Me\(_2\)O, 7:3) to afford a 66 % yield of (–)-hibalactone (30 mg, 0.085 mmol); mp 141.5–143 °C. Recrystallization samples from EtOH exhibited mp 187–188 °C; \([\alpha]_D^{25} + 6°\) (c 0.9; Me\(_2\)CO). UV \(\lambda_{max}^{E1OH}\) nm (\(e\)): 237 (10400), 294(10800), 332 (11600). IR \(\nu_{max}^{cm^{-1}}\): 3560 (OH), 1745 (C=O), 1640 (C=C), 1600 (aromatic). MS m/z (rel. int.): 352 (12) [M\(^+\)], 217 (18), 135 (100).

**Acknowledgement.** The authors thank the National Science Council (ROC) for financial support.

**REFERENCES**