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Phytochemistry, Vol. 24, No. 8, pp 1845–1847, 1985
Printed in Great Britain

0031-9422/85 \$3.00 + 0.00
Pergamon Press Ltd.

STRUCTURE OF A GUAIANE FROM *CURCUMA ZEDOARIA*

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(Received 2 October 1984)

Key Word Index—*Curcuma zedoaria*; Zingiberaceae; sesquiterpene ketone; guaiane.

Abstract—A new guaiane, zedoarondiol, was isolated from fresh rhizomes of *Curcuma zedoaria* and its structure was elucidated from spectral evidence.

INTRODUCTION

The rhizome of *Curcuma zedoaria* Roscoe (Zingiberaceae) has long been used as a gastrointestinal remedy. Many kinds of sesquiterpenoids such as dehydrocurdione [1], zederone [2] and furanogermenone [3] have been isolated from the plant. Recently, we examined the constituents of the same plant and isolated a new sesquiterpenoid, zedoarondiol (1) from fresh rhizomes. This report describes the structure elucidation of the new compound.

RESULTS AND DISCUSSION

Zedoarondiol (1) was obtained as colourless needles, mp 133–134°, and the molecular formula was determined as $C_{15}H_{24}O_3$ by high resolution mass spectrometry. It showed an absorption maximum at 255 nm (ϵ 3300, EtOH) in the UV spectrum and absorptions at 3470, 3400 (OH), 1665 (conjugated ketone) and 1603 (double bond) cm^{-1} in the IR spectrum, suggesting the presence of hydroxyl groups and an α,β -unsaturated ketone.

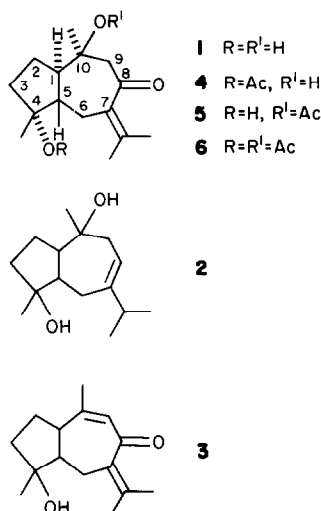
The 1H NMR spectrum (in $CDCl_3$) showed four tertiary methyl signals (δ 1.19, 1.21, 1.83 and 1.93), indicating two methyl groups attached to oxygenated carbon and the other two groups attached to unsaturated carbon. The ^{13}C NMR spectrum (in C_5D_5N) showed the signals due to one carbonyl (δ 203.12), a tetrasubstituted double bond (δ 139.84 and 136.10) and two tertiary carbinol carbons (δ 79.16 and 71.95), together with those due to two methine (δ 56.73 and 52.34), four methylene (δ 61.12, 40.26

29.09 and 22.76) and four methyl (δ 23.03, 22.76, 21.89 and 20.75) carbons.

Two proton signals at δ 2.59 (*d*, $J = 12.5$ Hz) and 2.96 (*dd*, $J = 12.5$ and 1.0 Hz) were assignable to a methylene group, adjacent to the ketone group. A long-range coupling between the proton signal (δ 2.96) and a tertiary methyl signal (δ 1.19, *d*, $J = 1.0$ Hz) was demonstrated by a decoupling experiment. This closely located relation of these protons was confirmed also by NOE experiments on the proton signals at δ 2.59 and 2.96, when irradiated at the methyl signal of δ 1.19.

These spectral data led us to consider a partial structure, $Me-C(OH)-CH_2-CO-C=CMe_2$ in the molecule of 1. Judging from the structures of sesquiterpenoids previously isolated from the same plant, we deduced a guaiane skeleton for the structure of zedoarondiol such as those of curcumadiol (2) [4] and procumumenol (3) [5].

The 1H NMR signal at δ 1.39 (*td*, $J = 11.5$ and 2.0 Hz) changed into a triplet signal and at the same time another change was observed in the proton signals at δ 1.94–2.03 (2H, *m*), assignable to H-1 and H-6 α , when irradiated at a proton signal (δ 2.82, *dd*, $J = 15.0$ and 2.0 Hz), assignable to H-6 β . These observations indicated a coupling constant of 11.5 Hz between H-1 and H-5 (δ 1.39) from a consideration of $J_{1,5} = J_{5,6\alpha} = 11.5$ Hz, indicating a *trans*-junction of the two rings of the new guaiane. In a reverse decoupling experiment the proton signal of δ 2.82 was changed into a singlet-like signal when irradiated near 2 ppm.



The stereochemistry of C-4 and C-10 was deduced from the following experiments. When irradiated at δ 1.21 (4-Me), 25% NOE was observed at the proton signal of δ 1.39 (H-5), indicating that 4-Me should be located close to H-5. On a restricted acetylation of 1 three kinds of acetates were obtained: 4-acetate (4), 10-acetate (5) and 4,10-diacetate (6). A comparison of the ^1H NMR spectrum (Table 1) of 5 with that of 1 revealed that the two proton signals due to H-9 of 1 showed downfield shifts (δ 2.59 \rightarrow 2.90; 2.96 \rightarrow 3.72) in the case of 5. Moreover, the H-5 signal of 1 showed an upfield shift (δ 1.39 \rightarrow 1.09) in the case of 5. These observations established the configuration of C-10 as 10 β -OH because the 10-OH should be located on the same side of the ring system as the 5 β -H. Therefore, the structure of zedoarondiol was elucidated as 1.

EXPERIMENTAL

Mps are uncorr. ^1H NMR were recorded at 90, 360 and 400 MHz and ^{13}C NMR at 22.5 MHz using TMS as internal standard.

Extraction and isolation. The plant was cultivated at Yakushima, Japan and the rhizomes were collected in June 1980. The fresh rhizomes (10.5 kg) were finely ground and extracted with MeOH. The MeOH extract (214 g) dissolved in water (1 l.) was extracted with Et₂O (300 ml) and *n*-BuOH (300 ml) successively. The *n*-BuOH soln was evaporated and passed through Amberlite XAD-2 CC eluted with H₂O, H₂O-MeOH (1:1) and MeOH successively. The latter two eluants were combined, evaporated to dryness (11 g) and chromatographed over silica gel CC (Merck Art. 7734; solvent: CHCl₃-MeOH, 4:1), 50 ml fractions being collected. Fr. nos. 10-15, each of which showed the same major spot on TLC, were combined and rechromatographed over silica gel CC (EtOAc-MeOH, 9:1), 30 ml fractions being collected. Fr. nos. 10-13 were combined and recrystallized from CHCl₃ to give zedoarondiol (324 mg) as colourless needles, mp 133-134° (from CHCl₃); UV $\lambda_{\text{max}}^{\text{EtOH}}$ 255 nm (ϵ 3300); IR $\nu_{\text{max}}^{\text{Nujol}}$ cm⁻¹: 3470, 3400 (OH), 1665 (CO), and 1603; MS m/z : 252.1702 [M]⁺ (Calc. for C₁₅H₂₄O₃ 252.1725); ^1H NMR (90 MHz, C₃D₃N): δ 1.39 (3H, s), 1.47 (3H, s), 1.77 (3H, s), 2.04 (3H, s), 3.07 (1H, d, J = 12 Hz), 3.15 (1H, d, J = 14 Hz), and 3.41 (1H, d, J = 12 Hz). The other NMR data are given in the text and Table 1. (Found: C, 70.43; H, 9.95. Calc. for C₁₅H₂₄O₃ · $\frac{1}{4}$ H₂O: C, 70.14; H, 9.42%.)

Acetates 4, 5 and 6. Acetylation of compound 1 (53 mg) with pyridine (3 ml) and Ac₂O (2 ml) for 20 hr at room temp. followed by usual work-up and separation by silica gel CC (*n*-hexane-EtOAc, 1:1) gave three kinds of colourless liquids together with recovered 1: diacetate 6 (5 mg), MS m/z 336 [M]⁺ and monoacetates 4 and 5 (10 and 11 mg), MS m/z both 294 [M]⁺. ^1H NMR data are listed in Table 1.

Acknowledgements—The authors wish to express their sincere thanks to Dr. Y. Ohfuné, Suntory Institute for Bioorganic Research for 360 MHz (Nicolet) ^1H NMR spectra and decoupling.

Table 1. Comparison of ^1H NMR data for compound 1, 4, 5 and 6 (CDCl₃)

	1	4 (4-Ac)	5 (10-Ac)	6 (4,10-Ac ₂)
10-Me	1.19 d (1)	1.18 d (1)	1.32 d (1)	1.29 d (1)
4-Me	1.21 s	1.42 s	1.22 s	1.42 s
Me	1.83 d (1)	1.86 br s	1.84 br s	1.86 br s
Me	1.93 d (1)	1.97 br s	1.96 br s	1.97 br s
H-5	1.39 td (11.5, 2.0)	*	1.09 m	*
H-9 α	2.59 d (12.5)	2.61 d (14)	2.90 d (14)	2.90 d (13)
H-6 β	2.82 dd (15.0, 2.0)	2.86 d (13)	2.81 d (15)	2.86 d (14)
H-9 β	2.96 dd (12.5, 1.0)	3.00 d (14)	3.72 d (14)	3.75 d (13)
H-1 } H-6 α }	1.94-2.03	*	2.34†	*
4-Ac		1.99 s		{ 1.99 s
10-Ac			1.97 s	{ 1.97 s

Compound 1: 400 MHz, 4, 5 and 6: 90 MHz. J values (Hz) are given in parentheses

*Not assigned.

†Centre δ value.

ling experiments and Mr. M. Nishi, Faculty of Pharmaceutical Sciences, Setsunan University, Osaka for 400 MHz (Jeol) ^1H NMR spectra and NOE measurements.

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Phytochemistry, Vol. 24, No. 8, pp. 1847–1848, 1985
Printed in Great Britain

0031-9422/85 \$3.00 + 0.00
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EUDESMANE SESQUITERPENES FROM *EUPATORIUM QUADRANGULARE*

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(Revised received 15 January 1985)

Key Word Index—*Eupatorium quadrangulare*; Compositae; sesquiterpene lactones; eudesmanolides.

Abstract—The aerial part of *Eupatorium quadrangulare* afforded in addition to known compounds, a possible biosynthetic intermediate, quadrangulin A, of the eudesmanolides found in this species.

INTRODUCTION

As part of our research into sesquiterpene lactones from the Compositae, we have studied the composition of *Eupatorium quadrangulare*. This paper describes the isolation and structural determination of a new biosynthetic intermediate of the eudesmanolides, quadrangulin A.

RESULTS AND DISCUSSION

The aerial parts of *Eupatorium quadrangulare* afforded a complex mixture of four eudesmane sesquiterpenes, which were separated by repeated TLC. Three of these compounds are already known: arbusculin B (1) [1], β -cyclocostunolide (2) [2] and α -cyclocostunolide (3) [3].

