

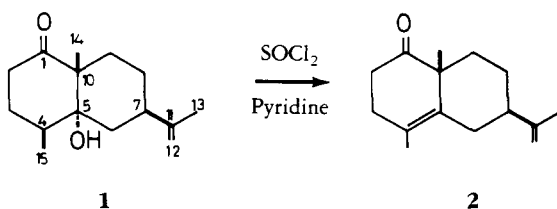
THE STRUCTURE OF CORYMBOLONE, AN EUDESMANE SESQUITERPENOID KETO-ALCOHOL FROM *CYPERUS CORYMBOSUS*

JUAN A. GARBARINO,* VICENTE GAMBARO, and MARÍA C. CHAMY

Departamento de Química, Facultad de Ciencia, Universidad Federico Santa María,
Casilla 110-V, Valparaíso, Chile

Cyperus corymbosus Rottboll (Cyperaceae), commonly known as "piri-piri," is a sedge that grows in the Amazon Region. A crude drug prepared from the rhizomes of this grass is used in indigenous medicine for abortive purposes (1). Several chemical investigations have been reported for members of this genus for ethnobotanical considerations (2). From one of them, *Cyperus rotundus*, a crude drug is also obtained in the same way and is used in Oriental medicine as a remedy for women's diseases (2). Several sesquiterpenoids have been reported from this drug, and most of them possess structures of the cyperane and eudesmane types (2-4). In view of these observations, we wish to report the structure elucidation of the major compound, a novel eudesmane sesquiterpenic keto-alcohol, corymbolone (**1**), from the rhizomes of *C. corymbosus*.

and analyzed for $C_{15}H_{24}O_2$ by both mass spectral and ^{13}C -nmr methods. The molecular formula of **1** requires four sites of unsaturation. The ^{13}C -nmr spectrum (Table 1) reveals one double bond (149.6, s, and 109.0, t), typical of an isopropenyl group (C-11 and C-12), and one carbonyl function (214.0, s, C-1; ir: 1695 cm^{-1}). Hence, **1** is bicyclic. The 1H -nmr spectrum (360 MHz, Table 1) confirmed the presence of an isopropenyl group: a two proton singlet at δ 4.74 and a methyl singlet at δ 1.75, and displayed signals due to an angular methyl group at δ 1.24, and a secondary methyl group, a doublet ($J=7.4\text{ Hz}$) at δ 1.20. The tertiary nature of the alcohol (ir: 3420 and 1175 cm^{-1}) is disclosed by the ^{13}C -nmr off-resonance multiplicity (78.7, singlet) of this signal and by the failure of **1** to form an acetate with pyridine and Ac_2O .



The petroleum ether extract from the rhizomes of *C. corymbosus* was chromatographed on a silica gel column with a mixture of petroleum ether-EtOAc. Corymbolone, **1**, was obtained from the petroleum ether-EtOAc (85:15) eluate as the major component and was purified by crystallization from *n*-hexane.

The pure sesquiterpenoid **1**, colorless needles, mp 136.5 - 137° (*n*-hexane), showed $[\alpha]_D^{25} + 57.9^\circ$ (c 0.84, $CHCl_3$)

On dehydration with thionyl chloride in pyridine, **1** afforded one main product. The ir spectrum of this derivative showed a band at 1715 cm^{-1} , indicating the presence of a ketonic function on a six-membered ring. The 1H -nmr spectrum (60 MHz) of this product does not show any signals due to the presence of vinyl protons; thus, the new double bond in the bicyclo-sesquiterpene ketone is tetrasubstituted. It was further deduced that the tertiary hydroxyl group

TABLE 1. NMR Data for Corymbolone (1)

C #	¹ H nmr		J (Hz)	¹³ C nmr	
	δ	m		δ	m ^a
1	—	—	—	214.0	s
2	2.68(ax)	ddd	(15.9, 9.9, 6.1)	34.4	t
	2.42(eq)	ddd	(15.9, 6.6, 5.2)		
3	1.69(ax)	dddd ^b	(9.4, 9.9, 6.6, 5.9)	30.3	t
	2.39(eq)	dddd	(9.4, 6.1, 5.2, 6.2)		
4	1.86(eq)	ddq	(5.9, 6.2, 7.4)	40.8	d
5	—	—	—	78.7	s
6	1.89(ax)	dd	(13.8, 12.8)	28.2	t
	1.44(eq)	ddd	(13.8, 3.9, 2.0)		
7	2.32(ax)	dddd	(12.8, 3.9, 13.2, 3.9)	39.6	d
8	1.38(ax)	dddd ^c	(14.3, 13.2, 13.1, 3.8)	25.7	t
	1.69(eq)	dddd	(14.3, 3.9, 4.8, 3.0, 2.0)		
9	1.90(ax)	dddd	(13.9, 13.1, 4.8, 1.2)	37.5	t
	1.60(eq)	ddd	(13.9, 3.8, 3.0)		
10	—	—	—	51.4	s
11	—	—	—	149.6	s
12	4.74	s	—	109.0	t
13	1.75	s	—	21.1	q
14	1.24	s	—	17.8	q
15	1.20	d	(7,4)	20.4	q

^aMultiplicities were determined by single frequency off-resonance decoupling.

^bObtained by iterative simulation of the five-spin system.

^cObtained by iterative simulation of the seven-spin system.

in **1** was adjacent to the secondary methyl group because the signal due to this appeared shifted to lower field (ca. 0.5 ppm) in the dehydrated compound **2**.

Based on the above data, it is suggested that corymbolone (**1**) contains an eudesmane skeleton, and hence the OH group must be placed at C-5. It was evident (¹³C nmr) that the carbonyl group is situated at C-1 in **1** on the basis of a deshielding effect on C-10 (51.4, S), which is well documented in other related systems (5). Finally, the 1,2-diaxial relationship between 4-Me (40.8, d) and 5-OH was also deduced from the ¹³C-nmr spectrum, which indicated a β-effect on C-4 of **1** such as occurs in agarofuran (6).

The minor components from the petroleum ether extract are being investigated.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—All mps were uncorrected. Optical rotation was

measured in CHCl₃. ¹H-nmr spectra were recorded at 60 MHz and 360 MHz, and ¹³C-nmr spectrum at 90.5 MHz in CDCl₃ solution with TMS as internal standard. The ms were measured at 70 eV with a direct inlet system. Ir spectra were recorded as KBr pellets. Elemental analysis was performed at the microanalytical laboratory of Dr. F. Pascher, Bonn, West Germany.

Cyperus corymbosus Rottboll, collected in Santa María de los Guacicas, Orinoco, Venezuela, in November 1979, was identified by Dr. J.A. Steyermark (Herbario Nacional, Venezuela); a voucher specimen (#80524) is deposited at the Herbario Nacional, Caracas, Venezuela.

The air-dried rhizomes (1.0 kg) of *C. corymbosus* were triturated and extracted with petroleum ether in a Soxhlet extractor for 40 h, affording 20.5 g of syrup. This syrup (10 g) was chromatographed on a silica gel column (300 g) that was eluted with a petroleum ether-EtOAc gradient system. Fractions eluted with this mixture (85:15) giving a major spot on tlc (Rf 0.37) were combined and evaporated. This fraction (0.8 g) gave, after crystallization from *n*-hexane, corymbolone, **1**.

CORYMBOLONE (**1**).—Corymbolone was isolated as colorless needles; mp 136.5–137° (*n*-hexane). C₁₅H₂₄O₂. Found: C, 76.12; H, 10.27; requires: C, 76.22; H, 10.24%. Ir ν (max) cm⁻¹ 3430, 3070, 3015, 2980, 2960, 2880, 1695,

1640, 1175, 890. ^1H nmr and ^{13}C nmr see Table 1. Eims (probe) 70 eV m/z (rel. int.) 236 (M^+ , 18), 218 ($\text{M}-\text{H}_2\text{O}$, 21), 203 (218-Me, 25), 175 (203-CO, 23), 135 (36), 124 (30), 109 (86), 107 (50), 93 (56), 69 (75), 55 (80), 43 (72), 41 (100); $[\alpha]^{25}_{\text{D}} +57.9^\circ$ (c 0.84, CHCl_3); uv (EtOH) λ max (log ϵ) 211 (2.45), 264 (1.99).

DEHYDROCORYMBOLONE (2).—To a solution of **1** (50 mg) in pyridine (0.5 ml) was added SOCl_2 (1.0 ml) at 0° . After 30 min, the mixture was poured into ice-cold aqueous 10% NaHCO_3 and extracted with Et_2O . The ethereal solution was washed with 10% H_2SO_4 , H_2O , NaHCO_3 solution and H_2O , and dried with Na_2SO_4 .

The residue after removal of the solvent was purified by preparative tlc (silica gel, petroleum ether-EtOAc, 90:10) and showed one main band (Rf 0.52). Elution of this band with CHCl_3 gave **2** (oil). Ir ν (max) cm^{-1} 3070, 2960, 2930, 1715, 1640, 890; ^1H nmr δ 1.30 (3H, s, Me-14), 1.70 (6H, s, Me-15 and Me-13), 2.45 (2H, m, H-2), 4.73 (2H, bs, H-12); eims (probe) 70 eV m/z (rel. int.) 218 (M^+ , 42), 203 (M^+-Me , 35), 175 (203-CO, 32), 161 (62), 109 (68), 69 (71), 55 (84), 41 (100).

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