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ISOLATION OF α-CORYMBOLOL, AN EUDESMANE SESQUITERPENE DIOL FROM *CYPERUS ARTICULATUS*

B. NYASSE, R. GHOGOMU TIH, B. L. SONDENGAM, M. T. MARTIN* and B. BODO*

Département de Chimie, Université de Yaoundé, B. P. 812, Yaoundé, Cameroun; *Laboratoire de Chimie, UA 401 CNRS, Muséum national d'Histoire naturelle, 63 rue de Buffon, 75231 Paris Cedex 05, France

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Abstract—A new sesquiterpenic alcohol, α-corymbolol has been isolated from the rhizomes of *Cyperus articulatus* along with the known corymbolone. The structure and stereochemistry was assigned on the basis of spectroscopic data and the reduction of corymbolone into α-corymbolol and β-corymbolol.

INTRODUCTION

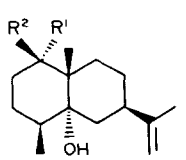
Cyperus articulatus L. is a tropical sedge widely distributed in Cameroon, where it is commonly known as mandassi and its rhizomes used in traditional medecine. The essential oils from the rhizomes of *Cyperus* species are known to contain sesquiterpenes [1–5]. During our investigations on the components of the medicinal plants from Cameroon, we have isolated a new sesquiterpene alcohol from the non-polar extract of the rhizomes of *C. articulatus* and we now report its structure determination.

RESULTS AND DISCUSSION

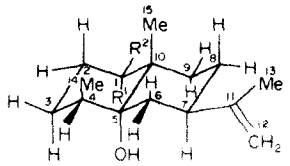
From the hexane extract of the rhizomes of *C. articulatus* two sesquiterpenes, **1** and **2** were isolated by silica gel column chromatography. Compound **1** was obtained from hexane–ethyl acetate (9:1) fraction, purified by repeated chromatography (hexane–ethyl acetate 17:13) and crystallized from hexane (mp 137°). The EIMS of **1** showed the molecular ion at *m/z* 236 in agreement with the molecular formula $C_{15}H_{24}O_2$. Its IR spectrum exhibited absorptions of hydroxyl (3430 cm^{-1}). The ^1H and ^{13}C NMR spectra (Tables 1 and 2) indicated that **1** was identical with corymbolone, isolation from *C. corymbosus* and structure elucidation of which have been recently reported [4].

Further elution of the column with hexane–ethyl acetate (8:2) afforded compound **2** which was purified by repeated column chromatography (dichloromethane–ethyl acetate 17:13) and obtained as a colourless oil, $[\alpha]_D^{25} + 43°$ ($CHCl_3$; *c* 2.9). The ion of highest mass observed at *m/z* 220 in the EIMS of **2** was shifted at *m/z* 221 ($+H^+$) and 238 ($+NH_4^+$) in the CI spectrum (ionising gas: ammonia) and assigned to a monodehydratation product $C_{15}H_{24}O$, leading to the molecular formula $C_{15}H_{26}O_2$ (M = 238) for **2**. Its IR spectrum showed hydroxyl groups (3404 cm^{-1}), a carbon–carbon double bond (1643 cm^{-1}) and no carbonyl absorption. The fifteen carbon atoms were revealed from the ^{13}C NMR spectrum with two being ethylenic (δ150.00 and 108.36), two bearing oxygen atoms (76.24 CH-O and 77.70 C-O), three methyl, six methylene, two methine groups and one quaternary carbon atom (Table 2).

Acetylation of **2** by Ac_2O–pyridine at room temperature afforded a monoacetyl derivative **3**, still containing a tertiary alcohol function. The ^1H NMR spectrum, which was similar to that of corymbolone **1**, displayed an angular methyl group (δ1.031, 3H, *s*, C-15), a secondary methyl group (δ1.039, 3H, *d*, *J* = 7.8 Hz, C-14) and an isopropenyl chain (δ4.710, 1H, *m*, H-12a; 4.724, 1H, *m*, H-12b and 1.740, 3H, *m*, Me-13). The ^1H and ^{13}C NMR spectra assignments (Tables 1 and 2), achieved by ^1H–^1H 2D COSY and ^1H–^{13}C 2D correlation techniques, enabled the distinction of two substructures *a* and *b*. The signal centred at δ3.469 (1H) was indicative of a methine proton (CH-1) geminal to an hydroxyl group that was coupled to a methylene (CH_2-2), connected itself to another methylene group (CH_2-3). The methine proton at δ1.694 (CH-4) was linked to a methyl group (δ1.039) and to this methylene-3, leading to the substructure *a*: –O–CH–CH_2–CH_2–CH–Me. The methine protons H-1 and H-4 were equatorial since their coupling constant values are low (< 5 Hz). The signal at δ2.584 was assigned to the methine proton H-7; it was coupled with an isolated methylene (CH_2-6) and with an other methylene (CH_2-8) itself coupled to methylene CH_2-9. The chemical shift of H-7 indicated that it was vicinal to a double bond (C-11, C-12) giving thus the second substructure *b*: –CH_2–CH_2–CH (iC_3H_5)–CH_2–. The H-7 was axial as it exhibited two large coupling constants (13 Hz) with vicinal protons H-6a and H-8a.



1 $R^1 = R^2 = O$
2 $R^1 = OH$ $R^2 = H$
3 $R^1 = OAc$ $R^2 = H$
4 $R^1 = H$ $R^2 = OH$
5 $R^1 = H$ $R^2 = OAc$



2 R^1 = OH R^2 = H
4 R^1 = H R^2 = OH

Hence, structure **2** was proposed for this compound, with the secondary alcohol been axial. This was confirmed by comparing it with the reduction products of corymbolone **1** with $NaBH_4$ in ethanol. This reaction gave two products A and B which were separated by column chromatography. Compound A (69% of the crude mixture) was identical to **2** (R_f, $[\alpha]_D$, IR, MS, ^{1}H NMR).

The minor compound B (31%) from the reduction of **1**, was found to be an isomer of **2**. Its ^{1}H NMR spectrum closely related to that of **2** and it was assigned by using ^{1}H–^{1}H 2D COSY which showed the H-1 geminal to an hydroxyl group at δ3.827 (1H, *dd*, J = 4.8 and 11.4 Hz). Since the coupling with one of the protons at C-2 had a high value, characteristic of a *trans*-diaxial coupling, the H-1 must be axial and the hydroxyl group equatorial, thus in the β-position. These results suggested structure **4** for the isomer B. The reaction of **4** with Ac_2O-pyridine afforded a mono acetate **5**.

Reduction of the carbonyl group of **1** by $NaBH_4$ introduced the hydride ion mainly opposite to the 5-hydroxyl group, as observed in the reduction of cholestan-5α-ol-3-one, suggesting the hydroxyl group exercises mainly a steric control [6].

The names α-corymbolol and β-corymbolol are proposed for **2** and **4**, respectively, in analogy to corymbolone (**1**).

EXPERIMENTAL

The air-dried rhizomes of *Cyperus articulatus* harvested in Kribi (South Cameroon, December 1984), were powdered and extracted with *n*-hexane. The hexane was evaporated under red.

Table 2. ^{13}C NMR spectral data of corymbolone (**1**), α-corymbolol (**2**) and β-corymbolol (**4**) (62.5 MHz, $CDCl_3$, TMS)

C	1		2		4	
	δ		δ		δ	
1	215.52	*s*	76.24	*d*	74.17	*d*
2	34.14	*t*	24.77	*t*	26.49[a]	*t*
3	30.08	*t*	22.36	*t*	26.85[a]	*t*
4	40.50	*d*	41.40	*d*	41.28	*d*
5	78.48	*s*	77.70	*s*	77.25	*s*
6	27.95	*t*	38.24	*t*	38.19	*t*
7	39.29	*d*	39.77	*d*	39.84	*d*
8	25.41	*t*	25.98	*t*	26.06	*t*
9	37.17	*t*	32.65	*t*	33.36	*t*
10	51.16	*s*	39.67	*s*	41.90	*s*
11	149.43	*s*	150.00	*s*	150.21	*s*
12	108.78	*t*	108.36	*t*	108.57	*t*
13	20.97	*q*	21.10	*q*	21.00	*q*
14	20.26	*q*	17.04	*q*	15.45[b]	*q*
15	17.66	*q*	21.77	*q*	16.78[b]	*q*

[a, b] May be reversed.

Table 1. ^{1}H NMR spectral data of corymbolone (**1**), α-corymbolol (**2**) and β-corymbolol (**4**). (500.13 MHz, $CDCl_3$, TMS)

H	1			2			4		
	δ		J (Hz)	δ		J (Hz)	δ		J (Hz)
1*a*							3.827	*dd*	11.4, 4.8
1*e*				3.469	*dd*	2.7, 2.4			
2*a*	2.675	*ddd*	16.3, 10.0, 6.3	2.087	*dddd*	14.6, 14.5, 4.6, 2.7	1.654	*dddd*	13.9, 13.7, 11.4, 4.4
2*e*	2.423	*m*		1.619	*dddd*	14.5, 4.4, 3.0, 2.4	1.573	*dddd*	13.7, 5.4, 4.8, 2.7
3*a*	1.682	*m*		2.379	*dddd*	14.6, 14.1, 4.5, 4.4	2.120	*dddd*	13.9, 13.7, 5.4, 5.4
3*e*	2.390	*m*		1.227	*dddd*	14.1, 4.6, 3.0, 1.6	1.298	*dddd*	13.7, 4.4, 2.7, 1.4
4*e*	1.860	*m*		1.694	*qdd*	7.8, 4.5, 1.6	1.453	*qdd*	7.5, 5.4, 1.4
6*a*	1.893	*dd*	13.7, 12.8	1.772	*dd*	13.6, 12.7	1.856	*dd*	13.6, 12.8
6*e*	1.438	*ddd*	13.7, 3.9, 2.0	1.221	*ddd*	13.6, 4.1, 1.6	1.158	*ddd*	13.6, 4.2, 1.7
7*a*	2.321	*dddd*	12.8, 12.8, 3.9, 3.9	2.584	*dddd*	13.1, 12.7, 4.1, 4.0	2.403	*dddd*	13.0, 12.8, 4.2, 4.2
8*a*	1.374	*dddd*	13.7, 13.7, 13.7, 3.9	1.518	*dddd*	13.1, 13.1, 13.1, 4.1	1.376	*dddd*	13.4, 13.4, 13.0, 4.0
8*e*	1.682	*m*		1.651	*ddddd*	13.1, 4.3, 4.0, 3.1, 1.6	1.573	*ddddd*	13.4, 4.5, 4.2, 2.9, 1.7
9*a*	1.900	*ddd*	14.0, 13.7, 3.2	2.380	*ddd*	13.1, 13.0, 4.3	1.682	*ddd*	13.4, 13.0, 4.5
9*e*	1.596	*ddd*	14.0, 3.6, 3.2	0.961	*ddd*	13.0, 4.1, 3.1	1.490	*ddd*	13.0, 4.0, 2.9
12*a*	4.752	*s*		4.710	*m*		4.651	*m*	
12*b*	4.752	*s*		4.724	*m*		4.662	*m*	
13	1.752	*s*		1.740	*m*		1.680	*m*	
14	1.195	*d*	7.5	1.039	*d*	7.8	0.973	*d*	7.5
15	1.240	*s*		1.031	*s*		0.956	*s*	

pres. and the oily residue remaining (60 g) was chromatographed over a silica gel column. Fractions eluted with *n*-hexane–EtOAc (9:1), yielded a simplified mixture (1 g) which was further purified over a silica gel column in a similar way. The fraction eluted with *n*-hexane–EtOAc (17:13) provided one major component which on crystallization in *n*-hexane gave 0.28 g of corymbolone (**1**).

Further elution of the first column with *n*-hexane–EtOAc (80:20) yielded a mixture, which on repeated chromatography over silica gel columns with CH_2Cl_2–EtOAc (19:1) gave 0.04 g of α-corymbolol (**2**).

The 2D ^1H–^1H COSY and ^{13}C NMR spectra were recorded on a WM 250 Bruker and the 1D ^1H NMR spectra on a WM 500 Bruker.

Corymbolone (**1**). Colourless crystals, mp 137° (*n*-hexane). IR ν_{max} cm^{-1}: 3430, 3080, 2959, 1692, 1639, 1456, 1417, 1370, 1343, 1281, 1175, 995, 887. MS (EI, 70 eV, 200°), *m/z*(rel. int.): 236 $[M]^+$ (14), 218 (12), 203 (12), 193 (7), 175 (17), 135 (27), 109 (23), 91 (17), 79 (26), 67 (53), 55 (84), 41 (100).

α-Corymbolol (**2**). Oil, $[\alpha]_D^{25}+43°$ ($CHCl_3$; *c*2.9); IR: ν_{max} cm^{-1}: 3304, 3081, 2926, 2874, 1643, 1453, 1381, 1264, 1216, 1169, 1131, 1104, 1051, 995, 911, 886. MS (EI, 70 eV, 200°), *m/z*(rel. int.): 220 $[M-H_2O]^+$ (9), 202 (64), 187 (33), 159 (17), 145 (22), 121 (23), 109 (87), 83 (100). MS(Cl, NH_4OH) *m/z*: 238 $[M-H_2O+NH_4]^+$, 221 $[M-H_2O+H]^+$.

Monoacetyl α-corymbolol (**3**). To 50 mg of **2** dissolved in dry pyridine (4 ml), 6 ml of Ac_2O were added, the mixture was kept at room temp. for 24 hr and the crude mixture was treated in the usual way. The residue was chromatographed on a silica gel column with CH_2Cl_2 as eluent to give 5 mg of **3**. Oil; IR: ν_{max} cm^{-1}: 3592, 2928, 1747, 1643, 1458, 1377, 1238, 1174, 1130, 1036, 1019, 986, 886, 800. MS (EI, 70 eV, 200°), *m/z*(rel. int.): 280 $[M]^+$ (0.5), 220 (4), 202 (100), 187 (40).

Reduction of corymbolone. To 90 mg of corymbolone dissolved in EtOH (5 ml) an excess of $NaBH_4$ was added in several portions and the mixture was stirred at room temp. for 3 hr and then worked-up as usual to give a oily residue (89 mg). TLC showed it to be composed of two products A (R_f: 0.41) **2** and B (R_f: 0.28) **4** (Silica gel, CH_2Cl_2–EtOAc, 85:15).

β-Corymbolol (**4**). Oil, $[\alpha]_D^{25}+25°$ ($CHCl_3$; *c*0.35); IR: ν_{max} cm^{-1}: 3500, 3081, 2926, 2870, 1450, 1380, 1260, 1215, 1175, 1131, 1100, 1049, 995, 911, 864. MS (EI, 70 eV, 200°), *m/z*(rel. int.): 220 $[M-H_2O]^+$ (8), 202 (12), 187 (12), 135 (56), 109 (100), 96 (60), 81 (40), 69 (44).

Monoacetyl β-corymbolol (**5**). Prepared in the same way as **3**, oil. IR: ν_{max} cm^{-1}: 3510, 3080, 2929, 2869, 1718, 1645, 1455, 1372, 1251, 1168, 1077, 1026, 981, 962, 887, 796. MS (EI, 70 eV, 200°) *m/z*: 280 $[M]^+$.

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