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EUDESMANE DERIVATIVES FROM *CYPERUS CORYMBOSUS*

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Key Word Index—*Cyperus corymbosus*; Cyperaceae; sesquiterpenes; eudesmanes.

Abstract—From the rhizomes of *Cyperus corymbosus* a new eudesmane sesquiterpenoid, isocorymbolone, was isolated besides the known compounds corymbolone and (+)-α-cyperone. The structure of the new compound was established by means of spectroscopic methods.

INTRODUCTION

The members of the *Cyperus* genus are widespread throughout the temperate and tropical zones. Some species of this genus have been used in traditional medicine as abortifacients [1], and as remedies for women's diseases [2 and references therein]. *Cyperus corymbosus*, commonly known as 'piri-piri', is a sedge which grows in the Amazon Region. A crude drug, prepared from the rhizomes of this grass, is used in indigenous medicines in birth control processes [1].

In a previous paper [3], the characterization of corymbolone (**1**) from the petrol ether extract of the rhizomes of *C. corymbosus* was described. Further examination of the eluates from the chromatography of this extract resulted in the isolation of two additional eudesmane sesquiterpenoids. One of these terpenoids was identified as (+)-α-cyperone (**2**), a plant growth retardant [4]. The other compound, isocorymbolone (**3**), is new, and the present study deals with its structural determination.

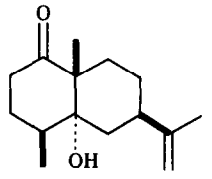
RESULTS AND DISCUSSION

The petrol ether extract from the rhizomes of *C. corymbosus* was subjected to column chromatography on silica gel, using increasing proportions of ethyl acetate in petrol ether as the solvent, to afford some sesquiterpene-enriched fractions [3]. Repeated chromatography of the petrol–ethyl acetate (19:1) fraction led to the isolation of (+)-α-cyperone (**2**) which was identified by direct comparison (IR, ^{1}H NMR, MS, $[\alpha]_D$) with an authentic sample. The petrol–ethyl acetate (4:1) eluate, after treatment with acetic anhydride in pyridine and preparative TLC, gave **3a**.

Isocorymbolone (**3**), was characterized as its acetate (**3a**), mp 102–103°; $[\alpha]_D^{25}$ −17.9°. The MS of **3a** suggested a molecular formula $C_{17}H_{26}O_3$ ($[M]^+$ at *m/z* 278) and gave a typical ^{1}H NMR spectrum for an eudesmane skeleton with an angular methyl group (δ0.98, C-14) a secondary methyl group (δ0.96, *d*, *J* = 6.0 Hz, C-15), an isopropenyl group (δ4.62, *m*, H_2-12) and a methyl group (δ1.67, *s*, C-13). Additionally, a doublet of a doublet (*J* = 2.0 and 3.0 Hz) centred at δ5.10 (1H) indicated a geminal proton to an acetoxyl group, because this signal appeared shifted to upper field (*ca* 1.20 ppm) in the natural product **3** (see Experimental).

The C-9 α-position for the acetoxyl group was deduced from the splitting and coupling constant values of its geminal proton (β-orientation) in the ^{1}H NMR spectrum and because the ^{13}C NMR spectrum showed that **3a** lacked the unsubstituted methylene group at C-9 (*ca* 37 ppm) [3, 5]. Furthermore, from the ^{13}C NMR spectrum the presence of a β-oriented isopropenyl group was confirmed (39.5, *d*, C-7; 108.5, *t*, C-12; 150.6, *s*, C-11). The ^{13}C NMR spectrum also contained a signal due to a carbonyl group at C-1 (215.3, *s*, IR: 1708 cm^{-1}) which produced a deshielding effect on C-10 (51.2, *s*) [3].

Finally, the α-orientation of Me-15 in **3a** was unambiguously established by comparison of its ^{13}C NMR spectral data with those of α- and β-dihydroeudesmol (α-isomer: 31.5, *d*, C-4 and 51.3, *d*, C-5; β-isomer: 33.7, *d*, C-4 and 47.0, *d*, C-5) [6]. The acetate **3a** was then hydrolysed with potassium carbonate in methanol and purified by preparative TLC, to give the pure natural product iso-



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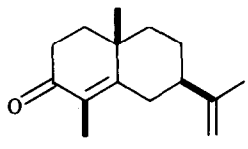

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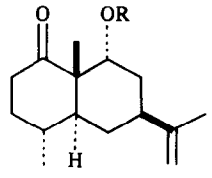

3 R = H
3a R = Ac

corymbolone (3) (^{1}H NMR: δ3.90, *dd*, J = 2.0, 3.0 Hz, Hβ-9).

From the IR spectrum of 3 an absorption band at 1695 cm^{-1}, a saturated ketone-carbonyl frequency, suggested a spatial relationship between the 9α-OH and CO at C-1 such as occurs in corymbolone (1) [3] and in other related systems [7]. Therefore, on the basis of these data, isocorymbolone is shown to be 4β(H)-eudesm-11-en-1-one-9α-ol.

Besides the aforementioned compounds, a mixture of δ-cadinene, β-selinene and eight unidentified sesquiterpenoids and a mixture of stigmasterol, campesterol and β-sitosterol were detected in the petrol–ethyl acetate (19:1 and 9:1, respectively) fractions by GC/MS analysis.

EXPERIMENTAL

Mps: uncorr; ^{1}H NMR: 60 MHz and 100 MHz in $CDCl_3$ with TMS as int. standard; ^{13}C NMR: 100 MHz, $CDCl_3$ with TMS as int. standard; MS: direct inlet, 70 eV; IR: film on NaCl or KBr pellets; GC/MS: Varian-Mat model CH7-A mass spectrometer coupled to a Varian 1440 gas chromatograph and interfaced to a Varian Mat Data System 166. The mixture of sesquiterpenoids was analysed with a 6 m × 2 mm i.d. column packed with Emulphor, 175°; the steroids were analysed with a 1.8 m × 2 mm i.d. column packed with 3% OV-17, 150–290° at a rate 4°/min with He as carrier gas at 30 ml/min.

Cyperus corymbosus Rottboll, collected in Santa María de los Guaicas, 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. General details of extraction and chromatographic separation of the petrol extract from the rhizomes of *C. corymbosus* have been described previously [3].

(+)-α-Cyperone (2). A fraction (200 mg) eluted with petrol–EtOAc (93:7) contained one major component (R_f 0.74, silica gel, 9:1). It was rechromatographed on a silica gel column (20 g) which was eluted with petrol–EtOAc (97:3). Fractions 10–18, containing a pure compound, were mixed (oil, 110 mg) and afforded (+)-α-cyperone (2), which was identified by comparison (TLC, IR, ^{1}H NMR, MS and $[\alpha]_D^{25}$) with an authentic sample.

Isocorymbolone acetate (3a). The ^{1}H NMR spectrum of the fraction eluted with petrol–EtOAc (4:1) suggested the presence of one major compound with a secondary OH group. This fraction (80 mg) was treated with Ac_2O (2.5 ml) and C_5H_5N (0.5 ml) at room temp. for 24 hr. The reaction mixture was then worked up as usual to give an oily residue, which was submitted to prep. TLC (silica gel, petrol–EtOAc, 17:3, R_f 0.60). Pure isocorymbolone acetate (3a, 60 mg) was obtained as colourless crystals; mp 102° (petrol–EtOAc); $[\alpha]_D^{25}$ −17.9° ($CHCl_3$, *c* 0.728); IR ν_{max}^{KBr} cm^{-1}: 3080, 1640, 890 (CH_2=$\overset{|}{C}$–Me), 1740, 1240 (OAc), 1710 (CO); ^{1}H NMR: δ0.96 (3H, *d*, J = 6 Hz, H-15), 0.98 (3H, *s*, H-14), 1.67 (3H, *s*, H-13), 2.02 (3H, *s*, OAc), 2.63 (1H, *m*, Hβ-2), 4.62 (2H, *m*, H-12), 5.10 (1H, *dd*, J = 2.0, 3.0 Hz, Hβ-9); ^{13}C NMR: δ215.3 (*s*, C-1), 169.9 (*s*, OAc), 150.6 (*s*, C-11), 108.5 (*t*, C-12), 79.0 (*d*, C-9), 53.7 (*d*, C-5), 51.2 (*s*, C-10), 39.5 (*d*, C-7), 33.0 (*t*, C-2), 31.7 (*d*, C-4), 30.5 (*t*, C-3), 26.7 (*t*, C-8), 25.6 (*t*, C-6), 21.0 (*q*, C-13), 19.9 (*q*, C-15 or OAc), 19.6 (*q*, C-15 or OAc), 17.4 (*q*, C-14); MS *m/z* (rel. int.): 278 $[M]^+$ (10.7), 236 $[M-CH_2=C=O]^+$ (6.5), 219 $[M-OAc]^+$ (14.3), 218 $[M-HOAc]^+$ (70.2), 203 $[218-Me]^+$ (23.2), 175 $[203-CO]^+$ (33.4), 147 (38.9), 136 (44.7), 123 (100), 122 (48.8), 95 (40.6), 43 (80.7).

Isocorymbolone (3). Compound 3a (20 mg) was hydrolysed with K_2CO_3 in MeOH at room temp. under N_2. After 1 hr the mixture was filtered, concd and purified by prep. TLC (R_f 0.65, silica gel, petrol–EtOAc, 7:3) to give 3 (8 mg), colourless oil. IR ν_{max}^{film} cm^{-1}: 3450 (OH), 3080, 1645, 890 (CH_2=$\overset{|}{C}$–Me), 1695 (C=O); ^{1}H NMR: δ1.00 (3H, *d*, J = 6 Hz, H-15), 1.12 (3H, *s*, H-14), 1.68 (3H, *br s*, H-13), 2.62 (1H, *m*, Hβ-2), 3.90 (1H, *dd*, J = 2.0, 3.0 Hz, Hβ-9), 4.62 (2H, *m*, H-12); MS *m/z* (rel. int.): 236 $[M]^+$ (60.3), 221 $[M-Me]^+$ (15.1), 218 $[M-H_2O]^+$ (32.4), 203 $[218-Me]^+$ (11.3), 193 (34.9), 180 (58.7), 175 (25.6), 167 (62.4), 136 (64.0), 123 (75.1), 110 (100), 97 (98.3), 95 (76.7), 84 (80.7), 81 (58.3), 55 (54.6), 43 (53.5), 41 (55.7).

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