

# Composition of the Essential Oil from *Kyllinga erecta* S.

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The essential oil from the rhizomes of *Kyllinga erecta* S. was analyzed and found to contain a large amount of manoyl oxide (1), with lesser amounts of 13-epimanoyl oxide, of oxo and of hydroxymanoyl oxide derivatives. The major sesquiterpene hydrocarbon was identified as cyperene, along with sativene, cyperotundone, and spatulenol.

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## INTRODUCTION

*Kyllinga erecta* S., family Cyperaceae, is an annual herb which is widespread throughout tropical and subtropical zones. In Chad, this plant is found in the south country swamps and on the riversides. The rhizomes of this herb which give off a pleasant and a strong smell are sold in town markets for domestic use and cosmetic purposes. In African traditional medicine, the use of *K. erecta* is not often referred to. However, the aqueous extract has been shown to possess some antitoxic, tonic, antifebrile, and antidiabetic properties (Variati and Rovesti, 1959). The volatile oil is used in the treatment of itching and hepatitis. The only previous work about the genus *Kyllinga* was realized by Variati and Rovesti (1959), who specified the chemical and physical properties of the essential oil of *K. triceps* and briefly noted the presence of sesquiterpene, alcohol, and ether compounds. However, there are many reports about the allied genus *Cyperus*: Couchman et al. (1964), Nerali et al. (1965, 1967), Kapadia et al. (1967), Hikino et al. (1967a,b, 1969, 1971, 1976), Satinder et al. (1984), Nyasse et al. (1988a,b), Komai and Tang (1989a,b). The main characteristic components of the genus *Cyperus* are cyperene,  $\beta$ -selinene, cyperotundone, and  $\alpha$ -cyperone.

In this study, the chemical composition of essential oil from the rhizomes of *K. erecta* S. is described.

## EXPERIMENTAL PROCEDURES

**Sample Preparation.** Rhizomes of *K. erecta* (90 g of air-dried plant materials) that grow wild in Moundou (Southern Logone, Chad) were collected. Voucher specimens were deposited in the Herbarium of "Laboratoire Vétérinaire et Zootechnique de Farcha", in N'Djaména.

The samples of crushed rhizomes were subjected to hydro-distillation for 2 h. The collected distillate, approximately 500 mL, was saturated with salt and extracted with dichloromethane. The organic layer was dried with anhydrous sodium sulfate and then concentrated at room temperature under reduce pressure. A yellow oily residue was obtained (560 mg). The yield was 0.63%. The crude essential oil was analyzed by a rapid thin layer chromatography (aluminum plates precoated with a layer of silica gel 60F254, mobile phase: hexane-diethyl ether, 9:1 v/v). Four main spots were detected at  $R_f$  0.16, 0.33, 0.38, and 0.55. Infrared

spectrum presented characteristic bands at 3288, 3040, 1710, 1640, 1460, 1380, 1260, 1100, 1080, 920, and 810  $\text{cm}^{-1}$ .

**Analysis Methods of the Essential Oil.** Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS). The sample was analyzed by GC using a Girdel Model 30 instrument. Conditions were as follows: capillary column with DB-1; detector and injector temperature, 220 and 230 °C, respectively; oven program, 70 °C at 2 min rising to 210 °C at 5 °C/min. The GC was equipped with FID and connected with an electronic integrator (Shimadzu C-R 6A). The percentage composition of the oil sample was computed from the GC peak areas without using correction factors. Combined GC-MS was performed using a Hewlett-Packard system. The GC column used was a fused silica capillary column (30 m; 0.30-mm i.d.) with DB-1 bonded phase. The oven temperature was held at 70 °C for 2 min and then programmed to increase at 5 °C/min to 250 °C, the carrier gas was helium with a flow rate at 1.0 mL/min, and the injector temperature was 220 °C. The detector of the mass spectrometry was a quadrupole system (electron energy: 70 eV).

The identity of the compounds was assigned by comparisons with authentic materials (available compounds), known essential oils (Komai and Tang, 1989b), and literature data (Stenhagen et al., 1974; Jennings and Shibamoto, 1980; MacLeod and Pieris, 1981).

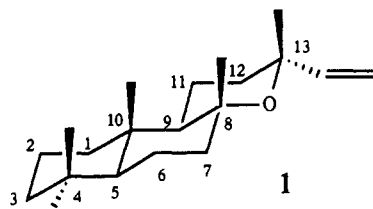
**Column Chromatography.** The essential oil (560 mg) was submitted to column chromatography over silica gel 60 (65 g, 230-400 mesh, E. Merck) using a glass column of 40 cm (5-cm i.d.) on the top of which 2.8 bar inlet pressure of nitrogen azote was applied. Elution was carried out by using a hexane-diethyl ether gradient, as follows: hexane (415 mL), hexane-diethyl ether, 98/2 v/v (200 mL), 96/4 v/v (200 mL), 94/6 v/v (200 mL), 90/10 v/v (200 mL), 85/15 v/v (200 mL), 70/30 v/v (200 mL), 50/50 v/v (200 mL), and diethyl ether (200 mL). Fractions of about 5 mL were collected in 384 test tubes. According to CCM analysis, some fractions were joined together, and three portions were obtained: fraction F1 (260 mg,  $R_f$  = 0.51, tubes 185-190), fraction F2 (95 mg,  $R_f$  = 0.38, tubes 221-277) and fraction F3 (60 mg,  $R_f$  = 0.15, tubes 278-344).

**Nuclear Magnetic Resonance Spectroscopy.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded by using Bruker AM-200 or AM-300 spectrometers. All spectra were obtained in deuteriochloroform as solvent, and the chemical shifts are recorded in  $\delta$  (ppm) units downfield from  $\text{Me}_4\text{Si}$ . Assignments of the  $^{13}\text{C}$  NMR chemical shifts were made with the aid of broad-band proton decoupling and experiments of distortionless enhancement by polarization transfer (DEPT) using a "flip angle" of 135°.

**Table I.** Composition of the Essential Oil from *K. erecta*

no.	$t_R$ , min	compound	%	identification
1	5.70	$\beta$ -pinene	0.2	a, b, c
2	6.82	1,8-cineole	0.2	a, b, c
3	12.15	methylthymol	0.3	a, b, c
4	15.33	$M = 202$	0.2	
5	15.70	capric acid	0.3	a, c
6	15.80	$\alpha$ -copaene	0.2	b, c
7	16.37	cyperene	9.4	a, c
8	17.38	$M = 194$ (aromatic)	0.6	
9	17.76	sativene	1.4	c
10	17.97	$\beta$ -selinene	0.7	a, b, c
11	19.22	spatulenol	0.8	b, c
12	19.85	$M = 220$	0.5	
13	20.44	lauric acid	1.2	a, c
14	21.15	$M = 218$	0.6	
15	21.52	unknown	0.4	
16	22.72	cyperotundone	10.2	a, c
17	23.83	$M = 218$	0.2	
18	24.90	myristic acid	0.5	a, c
19	27.06	$M = 236$	1.2	
20	27.52	unknown	0.4	
21	28.00	$M = 250$	0.5	
22	28.60	$M = 250$	0.5	
23	29.02	palmitic acid	1.7	a, c
24	29.15	$M = 250$	0.4	
25	29.38	manoyl oxide	48.0	c, d
26	29.74	13-epimanoyl oxide	4.3	d
27	29.90	unknown	1.0	
28	30.04	11-oxomanoyl oxide	3.5	d
29	30.34	11 $\alpha$ -hydroxymanoyl oxide	7.5	d
30	30.80	unknown	0.5	
31	31.11	unknown	0.4	

<sup>a</sup> Comparison with authentic material. <sup>b</sup> GC retention time. <sup>c</sup> Mass spectra. <sup>d</sup> NMR.

**Figure 1.** Manoyl oxide.

**Infrared Spectroscopy.** IR spectra were realized either neat or in chloroformic solution with a Beckman Model Acculab 2 spectrometer.

## RESULTS AND DISCUSSION

Careful analysis by GC-MS of the essential oil from *K. erecta* allowed us to identify most components (Table I), except those having retention times of 29.38, 29.74, 30.04, and 30.34 min. The latter ones with molecular weights 290, 290, 304, and 306, respectively, were the main components of the mixture. Their identification was assigned on the basis of spectroscopic data, after their isolation by repeated column chromatography over silica gel. Eluted fractions F1 corresponded to the mixture of constituents 26 and 27, while eluted fractions F2 and F3 corresponded to the constituents 28 and 29, respectively.

Examination of F1 showed that this fraction contained two constituents: manoyl oxide 1 mostly and a few of its C-13 epimer (Figure 1). They have been simultaneously identified by <sup>13</sup>C NMR spectroscopic measurements. The data for manoyl oxide (148.0, 110.3, 75.1, 73.2, 56.4, 55.6, 43.3, 42.1, 39.0, 37.0, 35.7, 33.4, 33.2, 28.5, 25.5, 21.4, 20.0, 18.6, 15.4, 15.3) and for 13-epimanoyl oxide (147.7, 109.5, 76.0, 58.5, 43.1, 42.2, 39.4, 34.8, 32.7, 23.9, 21.3, 18.7, 15.9) are in good agreement with literature [(Almqvist et al., 1975; Buckwalter et al., 1975; Werli and Nishida, 1979)

and (Werli and Nishida, 1979; Palaniappan Kulanthaivel and Benn, 1985), respectively]. Furthermore, the structure of the manoyl oxide was also confirmed by the <sup>1</sup>H NMR spectrum that showed a typical ABX system [4.92 (dd,  $J = 10.7, 1.6$  Hz, 1 H), 5.17 (dd,  $J = 17.4, 1.6$  Hz, 1 H), 5.87 (dd,  $J = 17.4, 10.7$  Hz, 1 H)] and, additionally, five signals of tertiary methyl groups [0.78 (s, Me), 0.79 (s, Me), 0.85 (s, Me), 1.27 (s, Me), 1.29 (d,  $J = 0.9$  Hz, Me)], and by the value of optical rotary power ( $\alpha_D = +21.6, c 1.55$ , ethanol) that is identical to the literature (Devon and Scott, 1972). The IR spectrum was indicative of a characteristic vinyl group (3040, 1640, 1470, 1380  $\text{cm}^{-1}$ ). The mass spectra of these two epimers matched the spectra reported in the MS libraries (Enzell and Rhyage, 1964).

Infrared spectra of the fractions F2 and F3 revealed the presence of a ketonic function (1710  $\text{cm}^{-1}$ ) and an alcohol (3400  $\text{cm}^{-1}$ ), respectively. Oxidation of F3 with Jones reagent gave the corresponding ketone in F2. The spectroscopic data of F2 [<sup>1</sup>H NMR  $\delta$  5.95 (dd,  $J = 17.3, 10.7$  Hz, 1 H), 5.24 (dd,  $J = 17.3, 1.1$  Hz, 1 H), 5.06 (dd,  $J = 10.7, 1.1$  Hz, 1 H), 2.62 (d,  $J = 17.5$  Hz, 1 H), 2.60 (s, 1 H), 2.59 (d,  $J = 17.5$  Hz, 1 H), 1.32 (s, 3 H), 1.29 (s, 3 H), 1.03 (s, 3 H), 0.87 (s, 3 H), 0.81 (s, 3 H)] and <sup>13</sup>C NMR  $\delta$  207.7, 146.7, 112.2, 77.3, 75.0, 66.8, 55.8, 50.2, 43.3, 41.9, 39.5, 37.2, 33.5, 33.3, 31.3, 28.0, 21.6, 19.7, 18.4, 15.5] were in agreement with the presence of 11-oxomanoyl oxide (De Pascual Teresa et al., 1976; Gabetta et al., 1989). Examination of <sup>1</sup>H NMR spectra of F3 [6.03 (dd,  $J = 17.1, 1.9$  Hz, 1 H), 5.43 (dd,  $J = 17.1, 1.9$  Hz, 1 H), 5.07 (dd, 10.5, 1.9 Hz, 1 H), 3.93 (t,  $J = 6.5$  Hz, 1 H), 1.28 (s, 3 H), 1.21 (s, 3 H), 0.88 (s, 3 H), 0.87 (s, 3 H), 0.81 (s, 3 H)] shows probably the presence of unknown 11 $\alpha$ -hydroxymanoyl oxide compared to its 11 $\beta$ -epimer (De Pascual Teresa et al., 1976). Confirmation of identification of this alcohol discovered in a mixture of hydroxy manoyl oxides from diethylether extract of rhizomes of *K. erecta* will be presented in another paper.

Thus, analysis of the essential oil from the rhizomes of *K. erecta* S. revealed a high content of diterpenoid family from labdanic serie (manoyl oxide and derivatives). These components have been identified for the first time in the essential oils from *Cyperus* and *Kyllinga* genera. Moreover, a new component (11 $\alpha$ -hydroxymanoyl oxide) has been isolated. Otherwise, the oil of *K. erecta* contains cyperene and cyperotundone like the *Cyperus* genus.

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**Registry No.**  $\beta$ -Pinene, 127-91-3; 1,8-cineole, 470-82-6; methylthymol, 52006-37-8; capric acid, 334-48-5;  $\alpha$ -copaene, 3856-25-5; cyperene, 2387-78-2; sativene, 6813-05-4;  $\beta$ -selinene, 17066-67-0; spathulenol, 6750-60-3; lauric acid, 143-07-7; cyperotundone, 3466-15-7; myristic acid, 544-63-8; palmitic acid, 57-10-3; manoyl oxide, 596-84-9; 13-epimanoyl oxide, 1227-93-6; 11-oxomanoyl oxide, 61242-47-5; 11 $\alpha$ -hydroxymanoyl oxide, 144900-90-3.