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AN EPI-13-MANOYLOXIDE DITERPENOID FROM *KYLLINGA ERECTA*

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Key Word Index—*Kyllinga erecta*; Cyperaceae; diterpenoid; 16-hydroxy-13-epi-manoyloxide.

Abstract—16-Hydroxy-13-epi-manoyloxide, a new derivative of 13-epi-manoyloxide, has been isolated from the ethyl acetate extract of *Kyllinga erecta* rhizomes.

INTRODUCTION

In a previous paper, we described the isolation of 16-hydroxy-manoyloxide from ethyl acetate extracts of *Kyllinga erecta* rhizomes [1]. In a continuation of our studies [2, 3] on the diterpenoids of *K. erecta* S., we have identified a new compound, isolated previously [1] from the fraction F_{45}, as (+)-16-hydroxy-13-epi-manoyloxide (**1**). Its structure has been established by spectroscopic means and by comparison with literature data.

The ^{13}C NMR spectra of **1** were recorded using broad band and gated decoupling, DEPT and HETCOR sequences. The data were identical to those described for *ent*-16-hydroxy-13-epi-manoyloxide [4], a compound which differs from **1** by having a specific rotation of opposite sign ($[\alpha]_D = -20°$, *c* 1.0, chloroform) Valvuole, S., personal communication. A similar concordance was observed between the mass spectra of the two compounds.

The ^1H NMR spectrum of **1** has been partially analysed. It contains the signals of four tertiary methyl groups at $\delta 1.240$ (*d*, $J = 0.9$ Hz), 0.858, 0.782 and 0.728 (*d*, $J = 0.9$ Hz), which are correlated with carbon signals at $\delta 23.96$, 33.31, 21.25 and 15.89, respectively. The ^1H NMR also shows an ABX system corresponding to a vinyl group attached to a quaternary sp^3. This system is not first-order and has been analysed using the BRUKER PANIC program: $\delta_X 5.901$; $\delta_A 5.105$, $\delta_B 5.102$; $J_{AB} = 0.9$ Hz, $J_{AX} = 18.0$ Hz, $J_{BX} = 11.1$ Hz, H_X (H-14) and H_B (H-15 *cis* to H-14) show long-range couplings of 1.0 and 0.6 Hz, respectively, couplings which have not been assigned unambiguously. Finally, the signals of two anisochronous methylene protons of a CH_2OH group are observed at $\delta 3.313$ (*d*, $J = 10.6$ Hz) and 2.971 (*t*, $J = 10.6$ Hz) and are correlated with the carbon signal at $\delta 69.59$, the hydroxyl proton being at $\delta 2.206$ (*d*, $J = 10.6$ Hz).

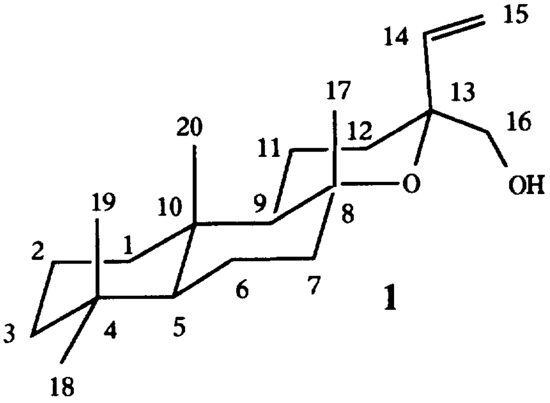
EXPERIMENTAL

Plant material; extraction and isolation of the diterpenoid. Rhizomes of *K. erecta*, growing wild in Moundou (southern Chad) were collected in July 1990 and authenticated. A voucher specimen is available at the herbarium of 'Laboratoire Vétérinaire et Zootechnique de Farcha', N'Djamena, Chad.

Extraction and isolation of **1** from fr. F_{45} is described in ref. [1].

MS studies. Hewlett Packard chromatograph type 5890 equipped with capillary DB1 column (25 m × 0.23 mm) (carrier gas He), mass quadrupole detector type 5970 A series, mass selective detector (EI to 70 eV), 60° (2 min) and then 10° min^{-1} until 200°.

16-*Hydroxy*-13-*epi-manoyloxide* (**1**). 5 mg; mp 94° (uncorr.); $[\alpha]_D + 34.7°$ (*c* 0.60, $CHCl_3$); IR ν_{max} cm^{-1}: 3450–3350, 3040, 1640 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$, TMS): see text; ^{13}C NMR (TMS): $\delta 144.09$ (C-14), 113.42 (C-15), 76.67 (C-13), 76.07 (C-8), 69.59 (C-16), 58.39 (C-9), 56.45 (C-5), 42.92 (C-7), 42.12 (C-3), 39.27 (C-1), 36.88 (C-10), 33.31 (C-4, C-18), 28.36 (C-12), 23.96 (C-17), 21.25 (C-19), 19.83 (C-6), 18.60 (C-2), 15.89 (C-20), 15.23 (C-11); EIMS *m/z* (rel. int.): 306 ($[M]^+$ absent), 291 (1), 276 (6), 275 (26), 259 (2), 258 (22), 257 (100), 215 (1), 205 (3), 203 (2), 201 (3), 193 (3), 191 (4), 189 (2), 187 (4), 177



1

(2), 175 (4), 173 (3), 163 (4), 161 (4), 159 (2), 151 (5), 149 (5), 147 (5), 137 (24), 123 (11), 121 (9), 109 (11), 107 (9), 95 (17), 93 (10), 81 (18), 69 (20), 55 (39).

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