solvent yielded 70 g of crude syrup which was chromatographed on silica gel Elution of the column with mixtures of increasing polarity (hexane–CH_2Cl_2–EtOAc) and repeated CC of the fractions eluted from CH_2Cl_2–EtOAc (3 17) to EtOAc afforded **1** (7 mg), **2** (3 mg) and **3** (25 mg)

Dehydromelitensin (**1**). Colourless oil; IR ν_{max} cm^{-1}. 3600–3100, 1760, 1640 MS *m/z* (rel. int.) 249 $[M-15]^+$ (0.42), 246 $[M-18]^+$ (0.94), 231 (1 65).

8-(4-*hydroxymethacryloil*)-*Dehydromelitensin* (**2**) Colourless oil IR ν_{max} cm^{-1} 3600–3150, 1770, 1730 MS *m/z* (rel int.) 246 $[M-RCO_2H]^+$ (6.1), 85 $(RCO)^+$ (60).

Elemacarmanin (**3**) Colourless oil, IR ν_{max} cm^{-1} 3550–3150, 1715, 1630 MS *m/z* (rel int) 278 $[M-RCO_2H]^+$ (4 9), 85 $[RCO]^+$ (57)

Acknowledgements—Financial support by the Comisión Asesora de Investigación Cintífica y Técnica (CAICYT, Grant No 559/84) is gratefully acknowledged We thank Prof Dr J Alcover (Department of Botany, Faculty of Biological Sciences, University of Valencia, Spain) for identification of plant material.

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Phytochemistry, Vol 28, No 4, pp 1267–1268, 1989
Printed in Great Britain

0031–9422/89 $3 00 + 0 00

A DERIVATIVE OF *ENT*-13-*EPI*-MANOYL OXIDE ISOLATED FROM *SIDERITIS JAVALAMBRENSIS*

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(*Received* 5 *July* 1988)

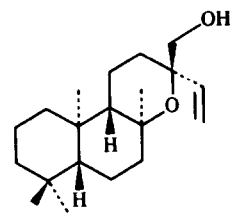
Key Word Index—*Sideritis javalambrensis*; Labiatae, diterpenoid; *ent*-13-*epi*-manoyl oxide derivative; *ent*-16-hydroxy-13-*epi*-manoyl oxide.

Abstract—*ent*-16-Hydroxy-13-*epi*-manoyl oxide, a new derivative of *ent*-13-*epi*-manoyl oxide, has been isolated from the hexanic extract of *Sideritis javalambrensis* aerial parts.

INTRODUCTION

Sideritis javalambrensis Pau is a plant endemic to Sierra Javalambre (Teruel, Spain) whose chemical content has not been previously studied. The hexanic extract obtained from the aerial parts of this species exerts anti-inflammatory effects in animals [1] In the present work, it has been studied to establish the principle responsible for the pharmacological activity thus leading to the isolation of a new diterpenoid

The diterpenoid was found to have the molecular formula $C_{20}H_{34}O_2$. The ^1H NMR spectrum showed an AB quartet centred at δ3.05 ($J = 10.8$ Hz) assigned to two protons geminal to a primary hydroxyl group, as well as a vinylic ABX system and four methyl singlet signals at 0.79 (6H), 0.71 (3H) and 0 66 (3H) The ^{13}C NMR data of C-1 to C-11 and C-17 to C-20 were identical to those of *ent*-13-epi-manoyl oxide [2] whereas the carbon resonances of C-12 to C-16 led us to place the hydroxyl function at C-16.



(1)

On the basis of its spectral data the structure of *ent*-16-hydroxy-13-*epi*-manoyl oxide (**1**), a diterpenoid isolated for the first time as a natural product, is proposed

EXPERIMENTAL

The ^{1}H NMR spectrum was measured at 200 MHz in $CDCl_3$ soln with TMS as int standard The ^{13}C NMR spectrum was determined at 50 MHz also in $CDCl_3$ soln with TMS added as int reference Plant material was collected in July 1984 in Sierra Javalambre (Teruel) and voucher specimens were deposited at the herbarium of the Faculty of Pharmacy (University of Valencia)

Extraction and isolation of the diterpenoid Dried and powdered plants of *S javalambrensis* (980 g) were extracted with hexane in a Soxhlet The extract (42 g) was chromatographed on a silica gel (Merck, 60) column (1 26 kg) Elution with CH_2Cl_2–EtOAc mixtures of increasing polarity, yielded a diterpenic fraction (2 22 g) which was chromatographed on a 10% $AgNO_3$–silica gel dry column and eluted with CH_2Cl_2–EtOAc (19 1) yielding the compound **1** (55 5 mg)

ent-16-*Hydroxy*-13-epi-*manoyl oxide* (**1**) Treatment of **1** (3 mg) with mesyl chloride (0 2 ml) for 24 hr and later reduction with $LiAlH_4$ (10 mg) for 6 hr gave a substance with $[\alpha]_D^{20}$ −21° ($CHCl_3$, *c* 1 0) ^{1}H NMR δ 5 84 (1H, *dd*, part X of an ABX system, J_{AX} = 11 0 Hz, H-14), 5 03 (2H, part AB of an ABX system, J_{BX} = 18 0 Hz, 2H-15), 3 05 (2H, *q*, *J* = 10 8 Hz, 2H-16) and C-Me singlets at 0 79 (6H), 0 71 (3H) and 0 66 (3H), ^{13}C NMR δ 15 2 (*t*, C-11), 15 9 (*q*, C-20), 18 65 (*t*, C-2), 19 9 (*t*, C-6), 21 3 (*q*, C-19), 24 0 (*q*, C-17), 28 4 (*t*, C-12), 33 3 (*q*, C-18), 33 4 (*s*, C-4), 36 9 (*s*, C-10), 39 3 (*t*, C-1), 42 2 (*t*, C-3), 43 0 (*t*, C-7), 56 5 (*s*, C-5), 58 4 (*s*, C-9), 69 6 (*t*, C-16), 76 7 (*s*, C-8), 77 2 (*s*, C-13), 113 5 (*t*, C-15) and 144 1 (*d*, C-14) MS *m/z* (rel int) M$^+$ absent, 291 [M − Me]$^+$ (0 8), 276 (6), 275 (29), 259 (2), 258 (21), 257 (100), 205 (3), 203 (2), 201 (4), 193 (3), 191 (5), 189 (2), 187 (4), 177 (2), 175 (3), 173 (2), 163 (4), 161 (4), 159 (2), 151 (6), 137 (28), 123 (15), 109 (16), 107 (11), 95 (21), 93 (11)

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Phytochemistry, Vol 28, No 4, pp 1268 1271, 1989
Printed in Great Britain

0031 9422/89 $3 00 + 0 00

CUCURBITACIN GLYCOSIDES FROM *CITRULLUS COLOCYNTHIS*

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Key Word Index—*Citrullus colocynthis*, Cucurbitaceae, cucurbitacin glycosides, hexanorcucurbitacin I glycoside

Abstract—The chloroform extract of *Citrullus colocynthis* yielded four cucurbitacin glycosides which were identified spectroscopically as 2-*O*-*β*-D-glucopyranosyl-cucurbitacin I, 2-*O*-*β*-D-glucopyranosyl-cucurbitacin E, 2-*O*-*β*-D-glucopyranosyl-cucurbitacin L and the novel glycoside, 2-*O*-*β*-D-glucopyranosyl-(22–27)-hexanorcucurbitacin I Detailed ^{1}H and ^{13}C NMR data are provided

INTRODUCTION

The fruit of *Citrullus colocynthis* L Schrad has been used medicinally since ancient times It has been suggested to possess anti-tumour activity [1–3] Phytochemical investigations of its bitter principles, cucurbitacins, are numerous, but conflicting regarding the type of cucurbitacin and their glycosides present [3–14] In this paper we describe the isolation and structural elucidation of a novel hexanorcucurbitacin glycoside in addition to three other known cucurbitacin glycosides

RESULTS AND DISCUSSION

The chloroform extract of the defatted plant was fractionated by preprative TLC (Experimental) to give four glycosides, characterized by spectral analysis as 2-*O*-*β*-D-glucopyranosyl-cucurbitacin I (**1**), 2-*O*-*β*-D-glucopyranosyl-cucurbitacin E (**2**) as the major product, 2-*O*-*β*-D-glucopyranosyl-cucurbitacin L (**3**) and a novel glycoside 2-*O*-*β*-D-glucopyranosyl-(22–27)-hexanorcucurbitacin I (**4**) No free cucurbitacin aglycones were detected in the extract which contradicts previous findings [6, 11, 13, 14], and this is in accordance with the reported presence of cucurbitacins as glycosides only in *Citrullus* due to the absence of the enzyme elaterase, the enzyme capable of hydrolysing the glycosides [15]. Cucurbitacin L glycoside (**3**) has not been previously isolated directly from the plant, although its aglycone was isolated from the enzymatic hydrolysate of the fruit extract [10], so this is the first report of its direct isolation from *Citrullus colocynthis* A following ethanolic extract yielded the glycosides **1**–**3** only, with **1** being the major product

Although ^{1}H and ^{13}C NMR spectra have been presented and used for the structural studies of cucurbitacins