while fraction 8 gave 3'-OMe-chrysosplenol (8 mg) and 6,7,4'-tri-OMe-3,5,3'-trihydroxyflavone (12 mg). Fraction 9 afforded chrysosplenol (22 mg).

*Arteannuin C* (3). Colourless crystals, mp 128°; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1770 (γ-lactone), 1250, 930, 860, (epoxide), MS *m/z* (rel. int.): 248 $[M]^+$ (5), 230 $[M-H_2O]^+$ (7), 206 [M − ketene]$^+$ (70), 190 $[M-OCOCH_2]^+$ (67), 177 (75), 169 (100), 55 (35), 43 (58), 41 (42); $^1$H NMR ($CDCl_3$): δ2.05 (*ddd*, H-1α, *J* = 12, 3, 3 Hz), 2.65 (*s*, H-5α), 2.66 (*dddd*, H-7, *J* = 12, 6, 3, 3 Hz), 6.20 (*d*, H-13, *J* = 3 Hz), 5.40 (*d*, H-13', *J* = 3 Hz), 0.95 (*brd*, H-14, *J* = 6 Hz), 1.30 (*s*, H-15). $[\theta]_{270} - 1249$.

$$\alpha_{26}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 435}{-26.04 \quad -27.36 \quad -36.04 \quad -55.6} \text{ (MeOH; } c \text{ 0.53).}$$

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# A *NOR*-DITERPENE AND OTHER CONSTITUENTS FROM *ISOCOMA CORONOPIFOLIA*

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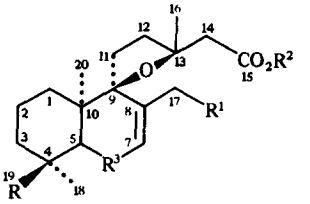
**Key Word Index**—*Isocoma coronopifolia*; Astereae; grindelanes; diterpenes; *nor*-labdane; sesquiterpenes; endoperoxide; renecraviotonic acid, a cedrene derivative.

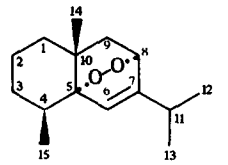
**Abstract**—The aerial parts of *Isocoma coronopifolia* afforded several known compounds including diterpenes related to grindelic acid, one of them being a new *nor*-diterpene. Furthermore a new eudesmene endoperoxide and a derivative of α-cedrene were isolated.

The aerial parts of *Isocoma coronopifolia* Greene, tribe Astereae, afforded, in addition to the widespread compounds β-seseline, caryophyllene, δ-cadinene and β-phytene (see Experimental), the diterpene grindelic acid **1** [1–6], and its analogs **2** [7], **3** [8] and **4** [9] as well as the *nor*-diterpene **5**. The structure of the latter was deduced from the molecular formula and the $^1$H NMR spectrum (see Experimental) which was in part close to that of the corresponding 6-desoxo derivative [9]. The presence of a singlet at δ2.91 and the downfield shifts of H-7 and H-17 indicated the presence of 6-keto group. From a W-coupling between H-14 and H-16 the quasi-axial orientation of the 13-methyl group was deduced. Furthermore, the endoperoxide **6** and the cedrene derivative renecraviotonic acid (**7**) were present. The structure of **6** was deduced from the spectral data. The presence of an endoperoxide was indicated by the mass spectrum, which showed loss of oxygen from the molecular ion. The $^1$H NMR spectrum (see Experimental) showed that an eudesmane derivative was present. Spin decoupling allowed the assignment of most signals. The stereochemistry followed from the presence of a W-coupling between H-1α and H-14α, from the NOE between H-15 and from biogenetic considerations. The necessary precursor would be eudesm-5,7-diene which should react with oxygen from the α-side as the β-side is hindered by the methyl groups at C-4 and C-10.

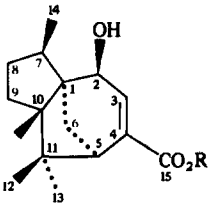
The structure of renecraviotonic acid (**7**), which was transformed to the methyl ester **7a**, was deduced from the $^1$H NMR spectrum (see Experimental) which was very similar to that of α-cedrene and the corresponding 15-aldehyde. Spin decoupling allowed the assignment of



| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| R | Me | Me | $CH_2OH$ | $CO_2H$ | OH |
| $R^1$ | H | OH | H | H | H |
| $R^2$ | H | H | H | Me | Me |
| $R^3$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | C=O |



6



7 R = H
7a R = Me

most signals and NOE difference spectroscopy established the stereochemistry. Clear effects were obtained between H-12, H-10 (12%) and H-5 (4%), between H-13, H-6 (10%) and H-5 (8%), between H-14 and H-2 (6%) as well as between H-2, H-3 (10%), H-6′ (6%) and H-14 (5%).

The chemistry of this species indicated a relationship with the genus *Haplopappus* by the co-occurrence of grindelic acid derivatives [2–6]. The only other *Isocoma* species which has been investigated chemically, *I. wrightii*, gave no diterpenes but several derivatives of δ-seseline [10] and some widespread compounds [11–16].

## EXPERIMENTAL

The air dried aerial parts (500 g, voucher 7986, collected in Cuatro Ciénegas, Coah. México, deposited in the herbarium of the Instituto Tecnológico de Monterrey) were extracted with $Et_2O$–petrol–MeOH (1:1:1) and the extract obtained was defatted with MeOH and separated first by CC (silica gel) into six fractions (1: petrol, 2: $Et_2O$–petrol, 1:9; 3: $Et_2O$–petrol, 3:7; 4: $Et_2O$–petrol, 1:1; 5: $Et_2O$ and 6: $Et_2O$–MeOH, 9:1). Prep. TLC (silica gel–$AgNO_3$ coated, $Et_2O$–petrol, 9:1) gave 5 mg β-seseline, 1.5 mg caryophyllene, 3 mg δ-cadinene, 5 mg β-phytene, 4.5 mg α-seseline and 9 mg δ-seseline. Prep. TLC (petrol) of fraction 2 gave 5 mg squalene and 1 mg **6**. Prep. TLC of fraction 3 ($Et_2O$–petrol, 1:9) afforded 4 mg friedelin, 70 mg bisabolol and 135 mg *trans*-toxol angelate. Flash chromatography of fraction 4 ($Et_2O$–petrol, 1:1, $Et_2O$) gave 15 mg 5-hydroxy-3,7,4′-trimethoxyflavone and a mixture which gave by HPLC (RP 8, MeOH–$H_2O$, 7:3, *ca* 3 ml/min) 2.6 mg **5** ($R_t$ 7.2 min), 6 mg **4**, 265 mg **3**, 5 mg oplapanone and 2 mg grindelic acid prep. TLC of fraction 5 ($Et_2O$–petrol, 4:1) afforded 6.5 mg sukuranetin, 10 mg kumatakenin and a crude product which gave by HPLC (MeOH–$H_2O$, 7:3) 1 mg **7** ($R_t$ 7.8 min). Prep. TLC of fraction 6 ($C_6H_6$–$CH_2Cl_2$–$Et_2O$, 1:1:1) gave 12 mg **2** and 31 mg **3**. Known compounds were identified by comparing the 400 MHz $^1$H NMR spectra with those of authentic material.

*Methyl-4β-hydroxy-6-oxo-18-nor-grindelate* (**5**). Colourless oil, MS *m/z* (rel. int.): 350 $[M]^+$ (61) ($C_{20}H_{30}O_5$), 332 $[M-H_2O]^+$ (36), 259 $[333-CH_2CO_2Me]^+$ (26), 109 (66), 15 (100); $^1$H NMR (400 MHz, $CDCl_3$): δ2.91 (*s*, H-5), 5.73 (*q*, H-7), 2.76 (*d*, H-14), 2.59 (*br d*, H-14), 1.36 (*s*, H-16), 1.99 (*d*, H-17), 1.41 (*s*, H-19), 1.39 (*s*, H-20), 3.68 (*s*, OMe) [*J* (Hz): 7,17 = 1.5:14,14′ = 14].

*Eudesm-6-ene-5α,8β-endoperoxide* (**6**). Colourless oil; MS *m/z* (rel. int.): 236 $[M]^+$ (2) ($C_{15}H_{24}O_2$), 204 $[M-O_2]^+$ (12), 189 $[204-Me]^+$ (4), 161 $[204-C_3H_7]^+$ (18), 85 (100); $^1$H NMR ($CDCl_3$): δ1.98 (*br ddd*, H-1), 2.05 (*m*, H-4), 6.06 (*dd*, H-6), 4.47 (*ddd*, H-8), 1.89 and 1.17 (*dd*, H-9), 2.62 (*dqq*, H-11), 1.13 (*d*, H-12), 1.07 (*d*, H-13), 0.95 (*br s*, H-14), 1.20 (*d*, H-15) [*J* (Hz): 1α,1β = 1α,2β = 13; 1α,2α = 4; 4,15 = 7,6,8 = 6,11 ~ 1.5; 8,9 = 3.5; 8,9′ = 2.5; 9,9′ = 13; 11,12 = 11,13 = 7].

*Renecraviotonic acid* (*2β-hydroxy-α-cedrene-15-oic acid*, **7**). Colourless oil; MS *m/z* (rel. int.): 250 $[M]^+$ (48) ($C_{15}H_{22}O_3$), 232 $[M-H_2O]^+$ (34), 217 $[232-Me]^+$ (16), 189 (52), 162 (74), 123 (88), 109 (68), 81 (62), 69 (96), 55 (100); $^1$H NMR ($CDCl_3$): δ4.60 (*br d*, H-2), 6.68 (*d*, H-3), 2.67 (*d*, H-5), 1.78 (*dd*, H-6), 1.60 (*d*, H-6′), 1.80 (*m*, H-7), 2.27 (*br dd*, H-10), 0.97 (*s*, H-12), 1.06 (*s*, H-13), 1.10 (*d*, H-14) [*J* (Hz): 2,3 = 2.5; 5,6 = 3.5; 6,6′ = 12; 7,14 = 7; 9,10 = 9′,10 = 9].

Addition of $CH_2N_2$ afforded the methyl ester **7a**; colourless oil; $^1$H NMR ($CDCl_3$): δ4.58 (*br dd*, H-2), 6.55 (*d*, H-3), 2.68 (*d*, H-5), 1.78 (*dd*, H-6), 1.57 (*d*, H-6′), 1.75 (*m*, H-7), 2.25 (*dd*, H-10), 0.92 (*s*, H-12), 1.05 (*s*, H-13), 1.09 (*d*, H-14), 3.74 (*s*, OMe) [*J* (Hz): 2,3 = 2.5; 2,OH = 6; 5,6 = 4; 6,6′ = 11.5; 7,14 = 7; 9,10 = 9′,10 = 9].

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# A SPIROSTANOL GLYCOSIDE FROM *AGAVE CANTALA*

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**Key Word Index**—*Agave cantala*; Agavaceae; rhizomes; saponin; spirostanol glycoside; tigogenin; $^{13}$C INEPT and $^{1}$H decoupled NMR.

**Abstract**—A new spirostanol glycoside, cantalasaponin-3, isolated from the methanolic extract of the rhizomes of *Agave cantala*, has been characterized.

## INTRODUCTION

*Agave* species have been used for medicinal purposes and various saponins have been reported from *A. cantala* Roxb. [1]. This communication deals with the structure elucidation of cantalasaponin-3 (**2**) isolated from the rhizomes of this plant.

## RESULTS AND DISCUSSION

Saponin **2**, a 25*R*-spirostane derivative (IR) was found to have an $M_r$ of 1034, as indicated from the pseudomolecular ions at $m/z$ 1073, 1057 and 1035 corresponding to $[M+K]^+$, $[M+Na]^+$ and $[M+H]^+$ ions, respectively, in its FD-mass spectrum. The peaks at $m/z$ 925/903 and at 895/873 arise from the loss of terminal pentose and hexose, respectively, from $[M+Na]^+/[M+H]^+$ ions.

Acidic hydrolysis of **2** gave tigogenin, and D-galactose, D-glucose and D-xylose in the ratio 1:2:1.

The interglycosidic linkages in **2** were established by means of $^{13}$C NMR spectroscopy. $^{13}$C chemical shifts of methyl pyranosides of β-D-galactose, β-D-glucose and β-D-xylose in pyridine-$d_5$ [2–4] and those of tigogenin [5] are available and the signals in **2** were assigned by the application of glycosylation shifts [2, 3]. In the $^{13}$C INEPT spectrum, by setting the delay time Δ as 3/4$J$ [6], CH and Me signals were in phase, $CH_2$ out of phase, and quaternary carbons and carbons of the solvent were absent. In the $^{1}$H decoupled mode the signals in the sugar region of **2** and **1** [1], the 12-oxo analogue of **2**, were almost superimposable. This observation was further supported when the permethylation products of **2** and its partial hydrolysis product, $PS_2$, gave methylated sugars identical to those obtained after permethylation of **1** and $PS_3$ [1], respectively.

The anomeric linkages were deduced as β from the $^{1}$H NMR spectrum of **2** and by the application of Klyne's rule [7].

Thus, **2** was characterized as 3-*O*-[{β-D-glucopyranosyl(1 → 3)-β-D-glucopyranosyl(1 → 2)}{β-D-xylopyranosyl(1 → 4)}-β-D-galactopyranosyl]-(25*R*)-5α-spirostan-3β-ol, a 12-deoxo analogue of **1** [1]. This provides an example of the co-occurrence of hecogenin and tigogenin glycosides with identical sugar chains.

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