

column and three were identified by comparison with authentic specimens. From unsaponifiable portion, *Triacontane*,  $C_{30}H_{62}$  m.p. 63–65° IR, NMR.  $\alpha$ -*Spinasterol*,  $C_{29}H_{48}O$  ( $M^+412$ ) m.p. 166°  $[\alpha]_{D_{20}} -3.0^\circ$  ( $CHCl_3$ ) UV, IR, NMR, MS fragmentation as expected, peak base 271  $m/e$ . co-TLC. Acetate, m.p.  $[\alpha]$  IR, NMR,  $\beta$ -*amyrin*  $C_{30}H_{50}O$  ( $M^+426$ ) m.p. 192–195°  $[\alpha]$  79.6° ( $CHCl_3$ ) IR, NMR, MS fragmentation, co-TLC and m.m.p. Acetate  $C_{32}H_{52}O_2$  m.p. 240°,  $[\alpha]$ , IR, NMR and m.m.p.

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*Key Word Index*—*Conyza filaginoides*; Compositae; triacontane;  $\alpha$ -spinasterol;  $\beta$ -amyrin.

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### KAURENIC ACIDS IN *ESPELETIA* SPECIES\*

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In the course of our investigation on *Espeletia* species from the Venezuelan Andes, we have isolated (–)-kaur-16-en-19-oic (I) and (–)-kaur-15-en-19-oic acid (II) from three different species, *E. floccosa*, *E. figueirasii* and *E. moritziana*.

Aerial parts of the plants were dried and extracted with light petroleum. The acidic extract of the resin thus obtained was chromatographed on  $SiO_2$ . The fractions were monitored by TLC and all those containing I and II were pooled and methylated with diazomethane. The methyl esters were separated by elution from a column of  $SiO_2$  plus 10%  $AgNO_3$ , but a small portion of each mixture of esters was saved for GLC. Light petroleum– $Et_2O$  (3%) eluted methyl kaur-16-en-19oate (III), m.p. 84–85°,  $[\alpha]_D^{25} -96.5$  (EtOH; C, 3.7). The MS of III shows a molecular ion at  $m/e$  316 ( $C_{21}H_{32}O_2$ ). IR (KBr pellet): 1720  $cm^{-1}$  (C=O), 1655 and 875  $cm^{-1}$  (C=CH<sub>2</sub>). NMR spectrum (60 MHz,  $CDCl_3$ ): 0.88  $\delta$  (s, *t*-Me), 1.09  $\delta$  (s, *t*-Me), 2.0  $\delta$  (d,  $J = 1.5$  Hz, 2H), 2.57  $\delta$  (broad, 1H), 3.58  $\delta$  (s, OCH<sub>3</sub>), 4.70  $\delta$  (m, C=CH<sub>2</sub>). The alcohol obtained by reduction of III with  $LiAlH_4$  (m.p. 140–141°), shows a characteristic AB quartet centered at 3.57  $\delta$  in the NMR spectrum. Such evidence is indicative of a tetracyclic kauren-like diterpenoid with the carbonyl function on C-4 in an axial position.

By increasing the  $Et_2O$  concentration to 10% methyl kaur-15-en-19oate (IV) was eluted, m.p. 78–80°. IR spectrum: 1722  $cm^{-1}$  (C=O), 813  $cm^{-1}$  (CH=C). NMR spectrum: 0.85  $\delta$  (s, *t*-Me), 1.14  $\delta$  (s, *t*-Me), 1.68  $\delta$  (d,  $J = 1.5$  Hz, 3H), 2.25  $\delta$  (broad, 1H), 3.62  $\delta$  (s, OCH<sub>3</sub>), 5.05  $\delta$  (m, CH=C). This compound is identical (m.p. m.m.p., TLC, IR and NMR)

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to the methyl ester obtained from *Espeletia tenore*.<sup>1</sup> Reduction of IV with LiAlH<sub>4</sub> affords an alcohol which also shows in the NMR spectrum an AB quartet at 3.56  $\delta$ . Hydrogenation of III and IV with PtO<sub>2</sub> as a catalyst renders the same product, m.p. 77–79°. The IR spectra of both hydrogenated compounds are identical.

The relative amounts of (–)-kaur-16-en-19-oic and (–)-kaur-15-en-19-oic acid in each of the three species was determined by GLC<sup>2</sup> (2% XE-60 on silanized Chromosorb W, 190°, He at 40 ml/min). The areas under the peaks were measured and showed 25%, 20% and 25% of I in *E. figureirasii*, *E. floccosa*, and *E. moritziana* respectively. *E. floccosa* exhibits the highest content of kaurenic acids (0.1%), *E. figureirasii* is also relatively rich (0.02%), but *E. moritziana* gave a very poor yield (0.001%). The life cycle of the plant could be responsible for this wide difference in kaurenic acids content, since *E. floccosa* was harvested at a budding stage while the other two were sterile when gathered.

<sup>1</sup> A. USUBILLAGA and A. MORALES, *Rev. Latinoam. Quimica* **1**, 128 (1970).

<sup>2</sup> A. USUBILLAGA and K. DE AROCHA, unpublished results.

*Key Word Index*—*Espeletia* spp.; Compositae; kaurenic acids.

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## FLAVONOIDS OF *HELENIUM BREVIFOLIUM*

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*Plant.* *Helenium brevifolium* (Nutt.) A. Wood. *Source.* Collected by Dr. R. I. Godfrey, West of Tallahassee, Florida, Spring 1958. *Previous work.* Pseudoguaianolides from CHCl<sub>3</sub> extract.<sup>1</sup>

*Compounds isolated.* After prior extraction with CHCl<sub>3</sub>, vitexin, orientin and small quantities of swertisin and saponaretin were isolated from the methanolic extract of the aerial portion of the plant by the methods described in an earlier paper<sup>2</sup> and identified by direct comparison with authentic materials by m.m.p., co-chromatography (TLC, 3 solvents) and IR analysis.

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<sup>2</sup> H. WAGNER, M. A. IYENGAR, E. MICHAHELLES and W. HERZ, *Phytochem.* **10**, 2547 (1971).

*Key Word Index*—*Helenium brevifolium*; Compositae; vitexin; orientin; swertisin; saponaretin.