

Cop-10(11)-en-3,12-diol (4). Viscous mass showing same tendency to crystallize. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3400 (OH), 2920, 1640, 1370, 1090, 1010. MS, m/z (rel. int.): 236 ($[\text{M}]^+$, $\text{C}_{15}\text{H}_{24}\text{O}_2$) (3), 218 ($[\text{M} - \text{H}_2\text{O}]^+$) (4), 200 ($[\text{M} - \text{H}_2\text{O}]^+$) (2), 161 (54), 109 (65), 95 (78), 45 (100), 43 (97), 41 (92). $^1\text{H NMR}$ (CDCl_3): 0.90 (s, 3H, H-14), 1.30 (s, 3H, H-15), 1.65 (s, 3H, H-13), 4.20 (d, $J = 6.0$ Hz, 2H, H-12), 0.85 (d, $J = 6.0$ Hz, 1H, H-2).

Known compounds. α -Pinene, sabinene, myrcene, β -pinene, car-3-ene, limonene, α -phellandrene, p-cymene, γ -terpinene, epoxytagetone, camphor, α -L-gurjunene, iso-humulene, eremophilene, α -humulene, allo-aromadendrene, borneol, γ -patchoulene, γ -selinene, α -copaene, myrtenol, few unidentified sesquiterpenes and sesquiterpene alcohols.

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GUAIANOLIDES AND OTHER CONSTITUENTS FROM *STEVIA* SPECIES

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Key Word Index—*Stevia eupatoria*, *S. chamaedrys*, *S. hyssopifolia*; Compositae; sesquiterpene lactones; guaianolides; diterpenes; *ent*-labdanes.

Abstract—The investigation of three *Stevia* species afforded a large variety of known sesquiterpene lactones as well as one new guaianolide, two known longipinene derivatives, two *ent*-labdanes and several other common compounds.

INTRODUCTION

In continuation of our studies on *Stevia* species [1] we have investigated two species from Chile and one from Mexico.

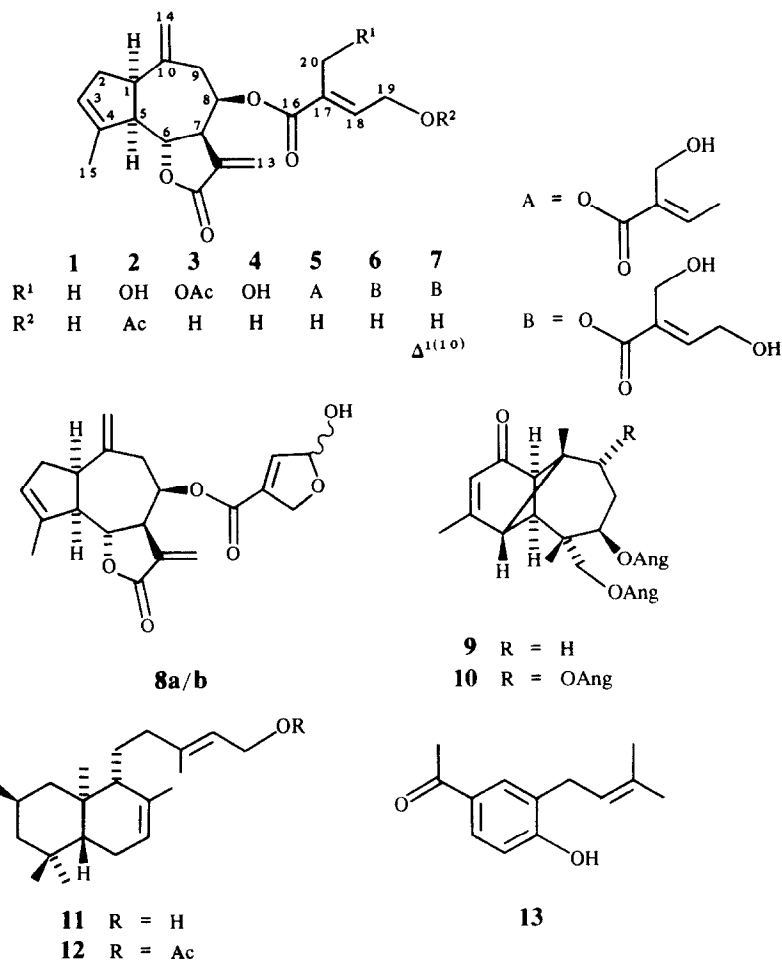
RESULTS AND DISCUSSION

The aerial parts of *Stevia eupatoria* (Spreng.) Willd. gave, in addition to germacrene D and the longipinene derivatives **9** [2] and **10** [3], the known guaianolides **5** [4] and **7** [5] as well as **6**. The $^1\text{H NMR}$ spectral data of the latter (Table 1) were as expected close to those of **5**. The olefinic methyl doublet was replaced by a hydroxymethylene doublet at δ 4.36 which was coupled with a low field triplet at δ 6.78 typical for 4,5-dihydroxytiglates. Thus, lactone **6** is an isomer of **7** which has a 1(10)-double bond.

The aerial parts of *S. chamaedrys* Griseb. gave germacrene D, costic acid, its Δ^3 and Δ^4 isomer, costunolide, reynosin, santamarin, desoxyeupatoriopicrin [6] and the guaianolides **1** [2], **2** [7], **3** [7], **4** [2] and the epimers **8a/b** [2].

The aerial parts of *S. hyssopifolia* Phil. var. *hyssopifolia* gave no sesquiterpene lactones or longipinene derivatives but in high concentration the *ent*-labdanes **11** and **12** which have been isolated from an *Ophryosporus* species [8], as well as the more widespread compounds germacrene D, bisabolene, 6,7-dimethoxy-2,2-dimethyl chromene and the *p*-hydroxyacetophenone derivative **13**.

These results again show that the chemistry of the genus *Stevia* is not uniform. However, highly oxygenated guaianolides are quite common. This is also true for the longipinene derivatives. Different diterpenes have also been reported from several species. In a previous invest-



igation of *S. eupatoria* two kaurane derivatives were isolated [9] which could not be detected in this study.

EXPERIMENTAL

The air-dried plant material was extracted with MeOH-Et₂O-petrol (1:1:1) at room temp. After treatment of the extracts with MeOH to remove long chain saturated compounds, separation was achieved by CC (silica gel), TLC (silica gel), HPLC (RP 8, 100 bar, flow rate, 3 ml min⁻¹) and in part again by TLC. Known compounds were identified by comparing the 400 MHz ¹H NMR spectra with those of authentic material.

Stevia eupatoria (130 g aerial parts, voucher RMK 9926, collected near Chihuahua, northern Mexico) gave 5 mg germacrene D, 5 mg **5**, 20 mg **6** (HPLC, MeOH-H₂O, 3:2, *R_f*, 5.0 min), 3 mg **7**, 2 mg **9** and 3 mg **10**.

Stevia chamaedrys (360 g aerial parts, voucher Niemeyer 8973, collected near Putre-Chapiquina, Region de Tarapaca, May 1989) gave 10 mg germacrene D, 100 mg costic acid, 100 mg of the Δ^3 and 100 mg of the Δ^4 isomer, 30 mg costunolide, 4 mg reynosin, 3 mg santamarin, 2 mg desoxyeupatoriopicrin, 8 mg **1**, 3 mg **2**, 3 mg **3**, 150 mg **4** and 11 mg **8a/b**.

Stevia hyssopifolia var. *hyssopifolia* (425 g aerial parts, voucher Niemeyer 89115, collected near Socoroma, Region de Tarapaca, May 1989) gave 200 mg germacrene D, 200 mg bisabolene, 1.6 g 6,7-dimethoxy-2,2-dimethylchromene, 20 mg **13**, 5 g **11** and 1 g **12**.

Table 1. ¹H NMR spectral data of compound **6** (CDCl₃, 400 MHz, δ -values)

H		H	
1	3.14 <i>ddd</i>	14	5.01 <i>br s</i>
2	2.51 <i>m</i>	14'	4.86 <i>br s</i>
2'	2.41 <i>ddq</i>	15	1.85 <i>br s</i>
3	5.58 <i>br s</i>	18	7.10 <i>t</i>
5	2.86 <i>br t</i>	19	4.49 <i>dd</i>
6	4.48 <i>dd</i>	19'	4.42 <i>dd</i>
7	3.18 <i>dddd</i>	20	4.96 <i>d</i>
8	5.69 <i>ddd</i>	20'	4.85 <i>d</i>
9	2.58 <i>dd</i>	23	6.78 <i>t</i>
9'	2.51 <i>dd</i>	24	4.36 <i>br d</i>
13	6.26 <i>d</i>	25	4.28 <i>br s</i>
13'	5.60 <i>d</i>		

J [Hz]: 1,2=8; 1,2'=4; 1,5=8; 2,2'=15; 2,3=2,3=2',15~2; 5,6=10; 6,7=9; 7,8=7,13~3; 8,9=8,9'=4; 9,9'=14; 18,19=23,24=6; 19,19'=15; 19, OH=5.5; 20,20'=12.

Ligustrin-[4-hydroxy-5-(4,5-dihydroxytigloyloxy)-tiglate] (6). Gum; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3620, 3460 (OH), 1760 (γ -lactone), 1720 ($\text{C}=\text{CCO}_2\text{R}$); MS m/z (rel. int.): 474.190 [$\text{M}]^+$ (1.5) (calc. for $\text{C}_{25}\text{H}_{30}\text{O}_9$: 474.190), 456 [$\text{M}-\text{H}_2\text{O}]^+$ (0.5), 360 (2), 342 (2), 324 (2), 306 (1.3), 246 (4), 228 (81), 213 (16), 183 (42), 143 (48), 115 (55), 97 (100), 69 (95).

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TWO DITERPENOIDS FROM LEAVES OF *JUNIPERUS SABINA*

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Key Word Index—*Juniperus sabina*; Cupressaceae; sesquiterpenoids; diterpenoids; 19-acetoxy-labd-13(*E*)-en-8,15-diol, 4-*epi*-palustric acid 9 α ,13 α -endoperoxide.

Abstract—Two new diterpenoids, 19-acetoxy-labd-13(*E*)-en-8,15-diol and 4-*epi*-palustric acid 9 α ,13 α -endoperoxide, as well as some other known sesquiterpenoids and diterpenoids have been isolated from the *n*-hexane extract of *J. sabina*.

INTRODUCTION

Continuing our research on the composition of leaves of *Juniperus sabina* L. we have examined the terpenoids isolated from the cold insoluble part of the *n*-hexane extract. Previously we reported the existence of several lignans in the same fraction [1, 2]. We have now isolated new compounds **1** and **2**, in addition to three sesquiterpenoids: oplopanone, α -cadinol and (–)-germacra-1(10),5(*E*)-dien-4 β -ol and the diterpenoids: 4-*epi*-abietal (**3**), abieta-7,13-dien-3-one (**4**), labd-13(*E*)-en-8,15-diol (**5**), 4-*epi*-abietic acid (**6**) and sandaracopimaric acid by chromatographic procedures. Oplopanone, α -cadinol, sandaracopimaric acid and compounds **3–6** were identified by direct comparison with authentic samples isolated from

this and other species of *Juniperus* [3, 4]. The germacrane derivative was determined by comparison of its ^1H NMR spectrum with that of an authentic sample [5].

The structure of compound **1** was assigned through comparison of its ^1H and ^{13}C NMR spectra (Tables 1 and 2) with those of compound **5**. Most signals were similar for both substances, showing only small differences in their chemical shifts. Nevertheless, apart from the presence of the acetate signal, the ^{13}C DEPT spectrum of **1** showed one methylene more (δ 67.1) and one methyl less (δ 21.4) than the spectrum of **4**. This indicated the presence of an acetoxymethyl group in compound **1** rather than a methyl group. This change must be located at C-19 due to the chemical shift, larger than 4.00 ppm, for the methylene supporting the acetate group in the ^1H NMR spectrum of **1** and the chemical shift for Me-18 in the ^{13}C NMR spectrum (δ 27.4), which is characteristic for an equatorial methyl group. Thus, the structure assigned for **1** corresponds to 19-acetoxy-labd-13(*E*)-en-

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