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FLAVONOIDS AND EUPAHAKONENIN B FROM *STEVIA SATUREIAEFOLIA*

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Key Word Index—*Stevia satureiaefolia*, Eupatorieae, Compositae, flavonoids, cirsimaritin, eupatorin, sesquiterpene lactones, guaianolide, eupahakonenin B

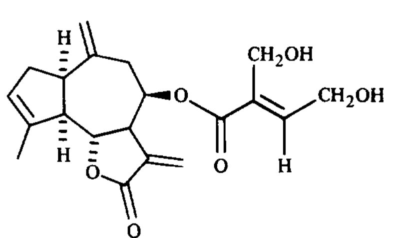
Abstract—Extraction of *Stevia satureiaefolia* furnished the flavonoids cirsimaritin and eupatorin and the guaianolide eupahakonenin B

INTRODUCTION

Nearly 20 species of the large genus *Stevia* (Compositae, tribe Eupatorieae, subtribe Piquerinae [1]) have been studied chemically A summary of the results up to 1981 has appeared [2] Since then labdanes and clerodanes have been found in *S lucida* [3], *S polycephala* [4] and *S monardaefolia* [5], the latter species also gave a heliangolide [6] while various flavonoids were reported from *S rebaudiana* [7] which is known for its diterpene glycosides

As has been pointed out [2], the chemical picture so far is not very uniform and further studies are needed to determine how chemically heterogeneous this genus really is We have recently described isolation and structure determination of two new C-8 lactonized guaianolides, a type so far unprecedented in the genus, from *S achalensis* The present brief report deals with isolation of two flavones and a guaianolide from another Argentinian *Stevia* species, *S satureiaefolia* (Lam) Schultz-Bip The flavones were cirsimaritin (scutellarein 6,7-dimethyl ether) and eupatorin (6-hydroxyluteolin 6,7,4′-trimethyl ether), while the guaianolide was identified as eupahakonenin B (1) This sesquiterpene lactone has been isolated previously only from *Eupatorium chinense* L var *hakonense* (Nakai) Kitam [9] and is a double bond isomer of a guaianolide recently isolated from *S myriadenia* [2]

A close reading of ref [2] suggests that a substance isolated in 1979 from *S setifera* and depicted then as a 1βH-guaianolide [10] is actually identical with eupahakonenin B If this is so, it may indicate a relatively close relationship between *S myriadenia*, *S setifera* and *S satureiaefolia*, but further work on the chemistry of the genus is clearly needed



1

EXPERIMENTAL

S satureiaefolia (Lam.) Schultz-Bip was collected in Copina, Córdoba, Argentina, during December 1982 and identified by Prof Luis Ariza Espinar A voucher specimen is on deposit in the Museo Botánico, Córdoba The air dried aerial parts (4 9 kg) were exhaustively extracted with $CHCl_3$ at room temp Evaporation of the solvent at red pres gave 340 g of dark green gum. 280 g of this material were dissolved in 2.1 l of EtOH and diluted with 2 1 l of a 4 % solution of lead acetate After standing overnight, the mixture was filtered, concentrated at red pres and extracted with $CHCl_3$ The washed and dried $CHCl_3$ extract on evaporation at red pres yielded 90 6 g of crude gum which gave three fractions (A, B and C) after column chromatography on silica gel Repeated chromatography of fraction A on silica gel gave cirsimaritin, mp 189–190° (C_6H_6), and eupatorin, mp 184–186° (C_6H_6–$CHCl_3$), which were identified spectroscopically and by comparison with authentic samples Fraction B was a mixture of these flavonoids and a sesquiterpene lactone which was the major constituent of fraction C Purification by column chromatography (silica gel) gave a gum which was transformed into an amorphous solid, mp 72–74°, on standing for several weeks The ^1H NMR spectrum at 270 MHz in $CDCl_3$, with extensive decoupling in $CDCl_3$ and C_6H_6 to identify the signals and the ^{13}C NMR spectrum in $CDCl_3$, had chemical shifts and coupling constants which tallied with those reported [9] for eupahakonenin B, although the latter is reported as a gum

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8-HYDROXYDOTRIACONTAN-30-ONE AND OTHER CONSTITUENTS FROM *DUBOISIA MYOPOROIDES*

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Key Word Index—*Duboisia myoporoides*, Solanaceae, leaves and stems, 8-hydroxydotriacontan-30-one, dotriacontanol, tetratriacontanoic acid, betulonic acid, ursolic acid

Abstract—In addition to the known constituents betulonic acid, ursolic acid, tetratriacontanoic acid and dotriacontanol, a new compound isolated from the leaves and stems of *Duboisia myoporoides*, has been characterized as 8-hydroxydotriacontan-30-one by spectral studies

INTRODUCTION

During a large-scale isolation of the tropane alkaloids hyoscine and hyoscyamine possessing mydriatic and antispasmodic properties, it was of interest to investigate the non-alkaloidal constituents of the leaves and stems of *Duboisia myoporoides* We have recently reported the characterization of four novel aliphatic compounds from this plant [1] We now report a new aliphatic hydroxyketone and four other constituents

RESULTS AND DISCUSSION

Silica gel column chromatography of the *n*-hexane extract of the plant furnished five crystalline compounds, A–E

Compound C, mp 76–77°, obtained in traces, had IR absorption bands at 3440 (OH), 2910, 2840, 1470, 725, 715 (long chain), 1700 (CO) and 1390 cm^{-1} (methyl) and gave a positive 2,4-dinitrophenylhydrazine test The mass spectrum of this compound displayed a $[\text{M}]^+$ ion at m/z 480 suggesting the molecular formula $C_{32}H_{64}O_2$ The location of the carbonyl group at C-30 was achieved by the prominent α-fission ions at m/z 451, 57, 423, and β-fission involving McLafferty rearrangement at m/z 72 [2] Similarly, the hydroxyl group was placed at C-8 due to significant ions at m/z 129, 351, 99 and 381 These fragmentations are shown on the structure below The absence of a $[\text{M}-15]^+$ ion indicated the straight-chain nature of the compound [3] The above data led to the characterization of this compound as 8-hydroxydotriacontan-30-one (**1**)

Compound A, mp 85–86°, was identified as dotriacontanol by IR, mass spectrometry, acetate, mp 76° and a comparison of the literature data [4] Compound B, mp 90°, was identified as tetratriacontanoic acid by IR, mass spectrometry, methyl ester, mp 75° and a comparison of the literature data [5] Compound D, mp 248–250° (dec), afforded a methyl ester, mp 165°, a sodium borohydride-reduced product, mp 285°, and was identified as betulonic acid by IR, NMR, mass spectrometry and a comparison of the literature data [6] Compound E, mp 265°, was identified as ursolic acid by comparison with an authentic specimen (mmp, IR, MS and co-TLC)

The mass spectral and IR data of **1** were in complete agreement with the assigned structure This compound has not previously been found in nature The other compounds, except ursolic acid [7], constitute the first reports from this plant

EXPERIMENTAL

Mps are uncorr IR spectra were recorded in KBr and 60 MHz ^{1}H NMR spectrum in $CDCl_3$ with TMS as int standard TLC was carried out on silica gel G in at least three different solvent systems and the spots were visualized by exposure to I_2 vapour or DNPH spray

Plant material was cultivated at the Experiment Farm,