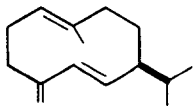

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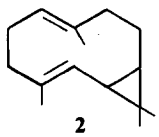

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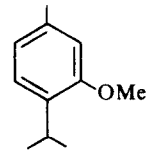

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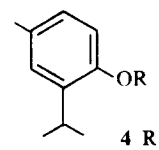
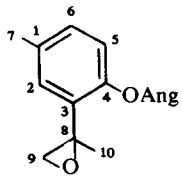


4 R = Me [6]
5 R = Ang



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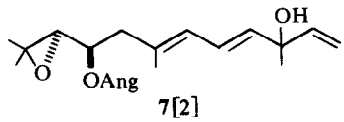
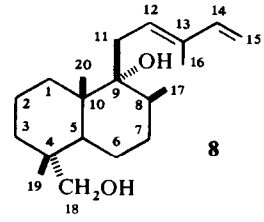


7[2]



8

$-O{=}C{=}(Me)CH{=}CH_2$ 150(15); $C_4H_7CO^+$ 83(100); 83 $-CO$ 55(61).

8,9-Dehydro-8,9-epoxythymolangelicat(**6**). Farbloses Öl, IR: Ph OCOC=C 1740, 1650 cm^{-1}. MS: M^+ *m/e* 246.126 (1%) ($C_{15}H_{18}O_3$); $C_4H_7CO^+$ 83(100); 83 $-CO$ 55(77).

9α,18-Dihydroxy-labda-12(E),14-dien(**8**). Farbloses Öl, IR: OH 3630; C=C 3090, 1640, 1610, 900 cm^{-1}. MS: M^+ *m/e* 306. 256 (0.5%), ($C_{20}H_{34}O_2$); $-H_2O$ 288(1); $-{}^{\cdot}CH_2CH{=}C(Me)$-$CH{=}CH_2$ 225(12); 225 $-H_2O$ 207(82); 207 $-CH_2O$ 177(75); $H_2C{=}CHC(Me){=}CHCH_2^+$ 81(100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\ nm}{+11.9 \quad +12.4 \quad +14.5} \quad (c = 4.7).$$

Danksagung—Der Deutschen Forschungsgemeinschaft danken wir für die Förderung dieser Arbeit.

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SESQUITERPENOIDS AND FLAVONOIDS FROM *FLOURENSIA OOLEPIS*

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Key Word Index—*Flourensia oolepis*; Compositae; sesquiterpenoids; flavonoids; 2′,4′-dihydroxychalcone; 7-hydroxyflavanone; euparin; ilicic acid; ilicol.

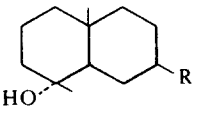
INTRODUCTION

In continuation of our studies on constituents of the Compositae from the central-west region of Argentina [1–4], we now report the work done on *Fluorensia oolepis* (common name 'chilca melosa') which is most abundant in the San Luis province.

RESULTS AND DISCUSSION

From the petrol extract, euparin [5] was isolated by means of chromatography. The ethyl acetate extract was fractionated by alkaline extraction and column chromatography giving ilicic acid [6], and the rest of the extract after chromatography on Si gel gave 2′,4′-

dihydroxychalcone [7], 7-hydroxyflavanone [7], and a sesquiterpenic alcogol which was identified as 4α-H-eudesm-11(13)-en-4,12-diol (**1**); this substance has not been previously reported in the literature and from its relationship to ilicic acid it was named ilicol.



1 R = $HOH_2C-\underset{|}{\overset{|}{C}}=CH_2$

2 R = $Me-\underset{|}{CH}-Me$

3 R = $OHC-\underset{|}{\overset{|}{C}}=CH_2$

4 R = $AcOH_2C-\underset{|}{\overset{|}{C}}=CH_2$

5 R = $HO_2C-\underset{|}{\overset{|}{C}}=CH_2$

Compound **1**, $C_{15}H_{26}O_2$, showed in the IR spectrum the presence of primary and tertiary hydroxyl groups (3500–3100, 1170, 1050 cm^{-1}) and an end vinyl group (1640, 890 cm^{-1}). The ^1H NMR ($CDCl_3$) spectrum had two singlets at δ 0.90 and 1.10 assigned to tertiary methyl groups, the latter having an oxygenated function at the α-carbon; a singlet at 2.13 that disappeared on exchange with D_2O; a wide singlet at 4.10 (2H, $=C-CH_2OH$) and two multiplets at 4.90 and 5.01 (terminal vinyl group). Addition of trichloroacetylisocyanate [8] shifted the δ 1.10 and 4.10 signals to 1.61 and 4.82 respectively, indicating the presence of primary and tertiary alcohol groups. The MS (70 eV) showed the molecular ion at *m/e* 238 and typical ions at *m/e* 223 (M − 15), 220 (M − 18), 205 (M − 15 − 18), 202 (M − 2 × 18), 187 (M − 15 − 2 × 18), 162 ($C_{12}H_{18}$) [9], 147 (162 − 15) [9] and 135 ($C_{10}H_{15}$, base peak) [9]. Acetylation of **1** afforded a monoacetate, $C_{17}H_{28}O_3$, whose IR, ^1H NMR and MS spectra were in accord with structure **4**. Catalytic hydrogenation of **1** resulted in hydrogenolysis and reduction of the double bond affording compound **2**, whose ^1H NMR spectrum had a doublet at δ 0.88 (6H, *iso*propyl group). Compound **1** on oxidation with Jones' reagent yielded **3** which was characterized as an α,β-unsaturated aldehyde by UV, IR, ^1H NMR and MS. Final proof of the structure of compound **1** came from $LiAlH_4$ reduction of ilicic acid (**5**) which afforded an alcohol identical to the one named ilicol.

As far as we know, this is the first example where both ilicic acid and ilicol are present in the same plant and this result could give an indirect proof of the intermediary role of the new alcohol in the biosynthetic pathway to ilicic acid [10].

EXPERIMENTAL

Mps were determined on a Kofler block and are uncorr. UV spectra were recorded in MeOH, IR in KBr, ^1H NMR at 60 MHz in $CDCl_3$–TMS, and MS at 70 eV by direct probe insertion. Microanalyses were performed by Dr. B. B. de Deferrari.

Plant material. Leaves and stems of *F. oolepis* were collected in Cuesta del Gato, San Luis province, in December; voucher specimens have been deposited in the collection of Instituto Nacional de Tecnología Agropecuaria (INTA) under No. VM-2329.

Extraction of plant and isolation procedure. Leaves and stems (2.5 kg) were extracted with petrol and then with EtOAc. From the petrol extract euparin was isolated by chromatography. $C_{13}H_{12}O_3$, mp 120°; UV λ_{max}^{MeOH} nm: 259, 286 sh, 299 sh, 350; MS (*m/e*): 216 (M^+), 201 (M − 15), 173 (M − 43). A portion of the residue obtained from evapn of the EtOAc was dissolved in Et_2O and extracted with 10% $NaCO_3H$ soln. The aq. soln was acidified and extracted with Et_2O; the residue obtained was chromatographed on Si gel and elution with C_6H_6–EtOAc (8:2) afforded ilicic acid (**5**) mp 181–182°. IR ν_{max}^{KBr} cm^{-1}: 3420–2300, 1695, 945 (—COOH), 1625, 895 ($R_2C=CH_2$); ^1H NMR: δ 0.93 (3H, *s*, C-10 Me), 1.06 (3H, *s*, C-4 Me), 5.63 and 6.27 (1H each, C-11=CH_2); MS (*m/e*): 252 (M^+), 237 (M − 15), 234 (M − 18), 219 (M − 15 − 18), 206 (M − 18 − 28), 191 (M − 15 − 18 − 28). The rest of the EtOAc extract was chromatographed on Si gel. Elution with C_6H_6 produced 2',4'-dihydroxychalcone, mp 147–148°; UV λ_{max}^{MeOH} nm: 264, 319, 345 [7]. Elution with C_6H_6–EtOAc (9:1) gave 7-hydroxyflavanone, mp 178–179°; UV λ_{max}^{MeOH} nm: 278, 310 [7]. The fractions eluted with C_6H_6–EtOAc (8:2) afforded ilicol (**1**), mp 134–135°; $[\alpha]_D$ −43.3° (*c* 1.9, $CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 3500–3100, 1170, 1050 (—OH), 1640, 890 ($R_2C=CH_2$); ^1H NMR: δ 0.90 (3H, *s*, C-10 Me), 1.10 (3H, *s*, C-4 Me), 2.13 (1H, —OH), 4.10 (2H, *s*, $-CH_2OH$), 4.90 and 5.01 (1H each, C-11 $=CH_2$). After addition of trichloroisocyanate the spectrum showed signals at 0.94 (3H, *s*), 1.51 (3H, *s*), 4.82 (2H, *AB* quartet, J = 12 Hz, —CH_2OOCNH), 5.10 and 5.17 (1H each, vinyl group), 8.56 and 8.58 (1H each, —NH.COOC-4 and —NH.COOC-13); MS (*m/e*): 238 (M^+), 223, 220, 205, 202, 187, 162, 147, 135 (base peak). (Found: C, 75.68; H, 10.99. $C_{15}H_{26}O_2$ requires: C, 75.63; H, 11.01%).

Hydrogenation of compound **1**. A soln of **1** (150 mg) in EtOAc (2.5 ml) was hydrogenated over 10% Pd/C at 3 Torr and room temp. for 12 hr. Compound **2**, purified by chromatography, had IR ν_{max}^{KBr} cm^{-1}: 3500–3200, 1105 (—OH), 3367, 1385 (—$CHMe_2$); ^1H NMR: δ 0.85 (3H, *s*, C-16 Me), 0.88 (6H, *d*, J = 7 Hz, gem-dimethyl group), 1.10 (3H, *s*, C-4 Me), 1.31 (1H, —OH); MS (*m/e*): 224 (M^+), 209 (M − 15), 206 (M − 18), 191 (M − 15 − 18), 163 (M − 18 − C_3H_7).

Oxidation of compound **1**. Compound **1** (240 mg) dissolved in Me_2CO (5 ml) was treated with Jones' reagent for 10 min at room temp. After usual work-up, compound **3** was isolated. The crystalline product (180 mg) had mp 83–84°; IR ν_{max}^{KBr} cm^{-1}: 3600, 1170 (—OH), 2705, 1690 (—CHO); ^1H NMR: δ 0.88 (3H, *s*, C-10 Me), 1.04 (3H, *s*, C-4 Me), 5.92 and 6.24 (1H each, vinyl group), 9.50 (1H, *s*, —CHO); MS (*m/e*): 236 (M^+), 221 (M − 15), 218 (M − 18), 203 (M − 15 − 18), 185 (M − 15 − 2 × 18), 175 (M − 18 − 28).

Acetylation of compound **1**. Compound **1** (150 mg) in Py (1.5 ml) was treated with Ac_2O (1.5 ml) and the soln was left at room temp. overnight. After usual work-up, compound **4** was isolated and purified by chromatography. IR ν_{max}^{KBr} cm^{-1}: 3420 (—OH), 3090, 1645, 910 ($R_2C=CH_2$), 1740, 1240 (—OCOMe); ^1H NMR: δ 0.90 (3H, *s*, C-10 Me), 1.09 (3H, *s*, C-4 Me), 2.06 (3H, *s*, C-13 OCOCH_3), 4.60 and 5.03 (1H each, vinyl group); MS (*m/e*): 280 (M^+), 265 (M − 15), 262 (M − 18), 247 (M − 15 − 18), 220 (M − 60), 205 (M − 15 − 60), 202 (M − 18 − 60).

Reduction of ilicic acid with $LiAlH_4$. A soln of **5** (80 mg) in THF (1 ml) was gradually added to a soln of $LiAlH_4$ (40 mg) in THF (8 ml). The mixture was refluxed for 3 hr, treated with EtOAc and satd Na_2SO_4 soln, and filtered. Evapn of the solvent gave a residue that after chromatographic purification afforded a compound identical (mp, mmp, IR, MS) to natural ilicol (**1**).

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ACNISTOFERIN, A NEW WITHANOLIDE FROM *ACNISTUS BREVIFLORUS*

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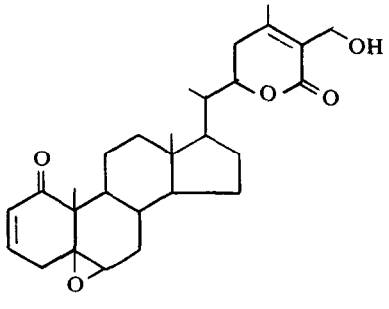
Key Word Index—*Acnistus breviflorus*; Solanaceae; withanolide; withaferin A; 3-methoxy-2,3-dihydro-withaferin A; jaborosalactone A; acnistoferin.

INTRODUCTION

Previous investigation on the plant *Acnistus breviflorus* (Griseb.) has resulted in the isolation and identification of withaferin A [1]. From the same source we have now isolated, besides withaferin A, three other withanolides. Two of them were identified as jaborosalactone A (**1**) [2, 3] and 3-methoxy-2,3-dihydro-withaferin A [4]; the third withanolide was characterized as the 1-oxo-5α,6β,27-trihydroxy-witha-2,24-dienolide (**2**) and named acnistoferin.

RESULTS AND DISCUSSION

The methanolic extract of dry leaves of the plant was diluted with water and extracted with petrol; it was then extracted with ether and the residue obtained by evaporation of the ether was chromatographed on Si gel. The fractions eluted with CH_2Cl_2–MeOH (96:4) gave a product to which the 1-oxo-5α,6β,27-trihydroxy-witha-2,24-dienolide structure was assigned from the following evidence. Compound **2**, $C_{28}H_{40}O_6$, mp 285–288°, presented in its IR spectrum bands at 3300, 1700, 1050, 960



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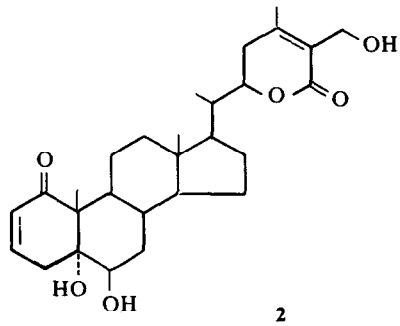

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