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LONGIPINENE DERIVATIVES FROM *STEVIA LUCIDA* AND *S. TRIFLORA**

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Key Word Index—*Stevia lucida*, *S. triflora*, Compositae, Eupatorieae, sesquiterpenes, longipinene derivatives.

Abstract—The aerial parts of *Stevia lucida* afforded longipin-2-ene-7β-angeloyloxy-9α-acetyloxy-1-one, while the aerial parts of *S. triflora* gave rastevione, 2-dehydrorastevione and the new natural longipinene, triflorestevione. The structure of triflorestevione was established on the basis of chemical and spectral evidences. Single crystal X-ray analysis of longipin-2-ene-7β-angeloyloxy-9α-hydroxy-1-one confirmed the structure of the constituent of *S. lucida*.

INTRODUCTION

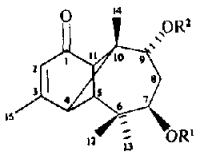
In the course of our chemical research on species from the Andean flora of Venezuela, we have already reported [1, 2] the isolation and identification of pectolinaringenin, eupatolitin and labdan-13(*Z*)-en-8α-ol-15-oic acid from *Stevia lucida*. In this paper we report the isolation of longipin-2-ene-7β-angeloyloxy-9α-acetyloxy-1-one (**1**) [3] from *S. lucida* and of 2-dehydrorastevione (**6**) [4–6], rastevione (**8**) [7] and the new natural longipinene, triflorestevione (**9**) from *S. triflora*. The relevant literature about longipinenes has been recently reviewed [8].

RESULTS AND DISCUSSION

Chromatography of the ethanolic extracts of the aerial parts of *S. lucida* yielded a compound which was identified as longipin-2-ene-7β-angeloyloxy-9α-acetyloxy-1-one (**1**) [3] from its spectral properties, although it was obtained as white needles with mp 123–125° instead of the colourless oil previously reported [3].

Furthermore, treatment of **1** with methanolic potassium hydroxide under reflux gave longipin-2-ene-7β,9α-diol-1-one (**2**) [6], while controlled alkaline hydrolysis of **1** gave the monoester **3**. That the angeloyl group is at C-7 is readily deduced from its ^{1}H NMR spectrum where the multiplicity of H-7 corresponds to a double doublet, while that of H-9 corresponds to a triplet [6]. When **3** was converted by Jones' reagent to the diketone **5**, the presence of the C-9 keto group was further evidenced since the ^{13}C NMR signals of C-8 and C-10 were shifted to lower fields (Table 1). A sample of **3** was directly compared by Bohlmann *et al.* with a longipinene to which they assigned structure **4** [4, 9], but it seems that is more properly represented by **3** [6, 7, 10].

Cogent evidence that confirms the structure of **1** was obtained from a single crystal X-ray diffraction analysis of **3**. The results also corroborate the relative stereochemistry, and from the known absolute stereochemistry



1 R^1 = Ang R^2 = Ac
2 R^1 = R^2 = H
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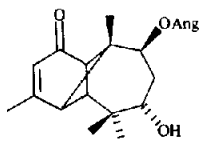

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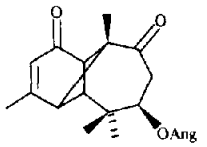

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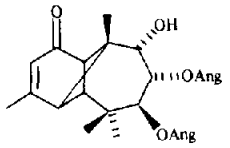

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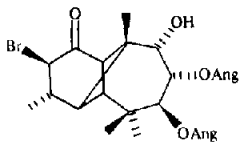

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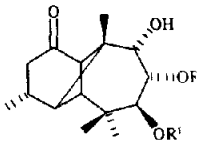

8 R^1 = R^2 = Ang
9 R^1 = R^2 = Tigl
10 R^1 = R^2 = Mebut

[11] of **2**, the correct molecular perspective can be drawn as shown in Fig. 1. The molecular conformation is essentially equal to that of rastevione (**8**), which has already been discussed in detail [7, 11].

Repeated chromatography of the methanolic extracts of the aerial parts of *S. triflora* yielded 2-dehydrorastevione (**6**), rastevione (**8**) and triflorestevione (**9**). Bromination of **8** with TBDC [12] afforded 2β-bromorastevione (**7**) in almost quantitative yields. Treatment of **7** with DBU [13] gave synthetic 2-dehydrorastevione (**6**), ident-

*Part 5 in the series 'Phytochemical Studies on the Venezuela Andean Flora'. For Parts 3 and 4 see refs [1, 2].

ical to the natural product. Since the structure of rastevione (**8**) is known [7], this chemical transformation allows us to assign the structure of **6**, previously formulated as longipin-2-ene-8β,9α-diangeloyloxy-7β-hydroxy-1-one [5] and later as longipin-2-ene-8α,9β-diangeloyloxy-7α-hydroxy-1-one [4].

The spectral properties of **9** closely resembled those of rastevione (**8**) [7]. Comparison of the ^{1}H NMR and ^{13}C NMR of both compounds (see Table 1 and Experimental) indicates [14] the only difference being the replacement of the angeloyl groups of **8** by tigloyl groups. Thus, **9** is the ditiglate analogue of rastevione and in accordance with its origin it has been named triflorestevione. Direct correlation between **8** and **9** was established through the derivative **10** (isomeric mixture), independently obtained by catalytic hydrogenation of both **8** and **9**.

EXPERIMENTAL

Mps uncorr. UV spectra were recorded in MeOH and IR spectra in films or KBr pellets. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as int. standard. EIMS were recorded at 70 eV. TLC was carried out on 0.25 mm layers of silica gel PF_{254} (Merck). CC as performed with silica gel 60 (70–230 mesh).

Plant material. *S. lucida* Lagasca was collected at Páramo de La Negra, near El delgadito (Mérida, Venezuela) in November, 1978. *S. triflora* DC at Gavidia, Distrito Rangel (Merida, Venezuela) in November, 1982. Voucher specimens of both (JMA 1503 and JMA 1511, respectively) are deposited at the Herbarium MERF of the Faculty of Pharmacy (ULA).

Extraction and isolation of compounds. Aerial parts of *S. lucida* were extracted and chromatographed as reported previously [1]. Fractions eluted with petrol–EtOAc (9:1) yielded **1** (1.6 g). Aerial parts of *S. triflora* (*ca* 7 kg) were air-dried, ground and extracted exhaustively with MeOH in a Soxhlet. The residue (470 g) left after removal of the solvent *in vacuo* was chromatographed over silica gel (1.7 kg) and eluted with petrol–EtOAc mixts. of increasing polarity. Fractions of 500 ml were taken and combined based upon TLC monitoring, affording the following combinations: Fractions 1–5 (petrol), 6–18 (petrol–EtOAc, 9:1), 19–25 (petrol–EtOAc, 4:1), 26–43 (petrol–EtOAc, 7:3), 44–56 (petrol–EtOAc, 3:2), 57–70 (petrol–EtOAc, 1:1), 71–81 (petrol–EtOAc, 1:4), 82–90 (EtOAc, 100%), 91–110 (EtOAc–MeOH, 1:4). Fractions 26–43 (12 g, four spots on TLC) were rechromatographed by (CC C_6H_6–EtOAc, 9:1) giving crude rastevione (*ca* 7 g) and a mixt. of **6** and **9**. Prep. TLC of this mixt. (C_6H_6–EtOAc, 19:1, multiple development) yielded pure **6** (*ca* 400 mg) and **9** (*ca* 250 mg).

Longipin-2-ene-7β-angeloyloxy-9α-acetyloxy-1-one (**1**) [3]. White needles from EtOAc, mp 123–125°, $[\alpha]_D$ +19.4° (EtOAc, *c* 1.7). IR ν_{max}^{KBr} cm^{-1}: 1730, 1710, 1675, 1615, 1240, 860. UV λ_{max}^{MeOH} nm: 216, 251. ^{1}H NMR (300 MHz): δ 0.93 (3H, *s*, H-13), 1.00 (3H, *s*, H-14), 1.07 (3H, *s*, H-12), 1.88 (3H, *quin*, J = 1.5 Hz, Me-5 angelate), 1.97 (3H, *dq*, J = 6.5 and 1.5 Hz, Me-4 angelate), 2.06 (3H, *d*, J = 1.5 Hz, H-15), 2.13 (1H, *m*, H-8α), 2.16 (1H, *ddd*, $J_{-,8\beta}$ = 12, $J_{8\alpha,8\beta}$ = 15, $J_{8\beta,9}$ = 3 Hz, H-8β), 2.18 (3H, *s*, Ac), 2.32 (1H, *s*, H-5), 2.64 (1H, *d*, $J_{4,11}$ = 7 Hz, H-4), 3.18 (1H, *dd*, $J_{2,11}$ = 1.5 and $J_{4,11}$ = 7 Hz, H-11), 4.99 (1H, *t*, J = 3.5 Hz, H-9), 5.05 (1H, *dd*, J = 11 and 3 Hz, H-7), 5.81 (1H, *m*, J = 1.5 Hz, H-2) and 6.05 ppm (1H, *qq*, J = 6.5 and 1.5 Hz, H-3 angelate). ^{13}C NMR, see Table 1. EIMS *m/z* (rel. int.): 374 [M]$^+$ (4.8), 314 (1.2), 291 (9.3), 274 (4.0), 249 (2.2), 232 (18.3), 214 (22.4), 199 (22.1),

Table 1. ^{13}C NMR chemical shifts (20 MHz, $CDCl_3$-TMS) for compounds **1**, **3**, **5**–**7** and **9**

C	1	3	5	6	7	9
1	202.7 (*s*)	203.4 (*s*)	200.8 (*s*)	201.3 (*s*)	202.4 (*s*)	211.0 (*s*)
2	122.6 (*d*)	122.6 (*d*)	122.1 (*d*)	122.9 (*d*)	52.0 (*d*)†	42.0 (*t*)
3	170.5 (*s*)	170.6 (*s*)	169.4 (*s*)	169.5 (*s*)	30.8 (*d*)	27.0 (*d*)
4	48.4 (*d*)	48.8 (*d*)	49.9 (*d*)	48.3 (*d*)	45.7 (*d*)	44.5 (*d*)
5	65.7 (*d*)	66.1 (*d*)	65.4 (*d*)	65.7 (*d*)	46.7 (*d*)	46.6 (*d*)
6	37.2 (*s*)	37.4 (*s*)	38.3 (*s*)	36.5 (*s*)	35.2 (*s*)	35.2 (*s*)
7	72.5 (*d*)	72.5 (*d*)	75.0 (*d*)	71.0 (*d*)*	70.9 (*d*)*	71.6 (*d*)*
8	32.1 (*t*)	35.7 (*t*)	42.8 (*t*)	70.2 (*d*)*	70.4 (*d*)*	71.2 (*d*)*
9	75.1 (*d*)	73.1 (*d*)	208.2 (*s*)	75.2 (*d*)	75.1 (*d*)	75.3 (*d*)
10	55.5 (*s*)	57.3 (*s*)	64.3 (*s*)	55.4 (*s*)	44.0 (*s*)	45.9 (*s*)
11	53.6 (*d*)	52.9 (*d*)	56.5 (*d*)	52.4 (*d*)	51.9 (*d*)†	51.7 (*d*)
	26.1 (*q*)	26.2 (*q*)	25.5 (*q*)	26.4 (*q*)	26.9 (*q*)	27.0 (*q*)
methyl	23.3 (*q*)	23.3 (*q*)	24.6 (*q*)	22.9 (*q*)	20.9 (*q*)	20.3 (*q*)
signals	21.3 (*q*)	21.7 (*q*)	20.4 (*q*)	21.5 (*q*)	20.1 (*q*)‡	19.8 (*q*)
	19.0 (*q*)	19.2 (*q*)	17.4 (*q*)	20.2 (*q*)†	20.1 (*q*)‡	19.6 (*q*)
1′	166.8 (*s*)	167.2 (*s*)	166.2 (*s*)	166.2 (*s*) 166.0 (*s*)	166.0 (*s*) 165.8 (*s*)	166.5 (*s*) 166.4 (*s*)
2′	137.6 (*d*)	137.9 (*d*)	138.0 (*d*)	139.4 (*d*) 139.1 (*d*)	140.1 (*d*) 139.3 (*d*)	138.3 (*d*) 137.2 (*d*)
3′	127.8 (*s*)	127.9 (*s*)	127.4 (*s*)	127.2 (*s*) 127.1 (*s*)	127.5 (*s*) 127.3 (*s*)	128.6 (*s*) 127.9 (*s*)
4′	15.7 (*q*)	15.8 (*q*)	15.6 (*q*)	15.6 (2*q*)	15.7 (*q*) 15.6 (*q*)	14.1 (2*q*)
5′	20.5 (*q*)	20.6 (*q*)	20.4 (*q*)	20.0 (2*q*)†	20.3 (2*q*)‡	11.6 (2*q*)
OAc	170.1 (*s*)					
	21.0 (*q*)					

*†‡Assignments bearing the same sign may be interchanged

177 (25 1), 173 (18 5), 145 (11.7), 135 (24.4), 122 (22.8), 83 (100), 69 (15 9), 55 (9.7), 43 (10.2).

Alkaline hydrolysis of **1** A soln of **1** (300 mg) in hot MeOH was refluxed with 1.8 g of KOH dissolved in H_2O. After 1 hr, the mixt was dild with H_2O and extracted with $CHCl_3$. The organic layer was washed with HCl (5%) and H_2O, dried over $MgSO_4$, filtered and evapd to dryness. The residue was crystallized from petrol–EtOAc yielding 70 mg of longipin-2-ene-7β,9α-dihydroxy-1-one (**2**) [6], mp 184–186°, $[\alpha]_D$ +41.8 (EtOH, *c* 0.32). EIMS *m/z* (rel. int.) 232 (4.0), 189 (23 1), 173 (22 5), 161 (27.6), 149 (40.9), 135 (64 9), 122 (100), 107 (25.7), 91 (31.4), 55 (30 7), 41 (45 4), 28 (77.9).

Partial alkaline hydrolysis of **1**. To a soln of **1** (400 mg) in cold MeOH (20 ml) was added 2 4 g of aq KOH and the mixt stirred for 5 min at 0° (the time and temp of this reaction was previously monitored by TLC with smaller amounts of **1**). The reaction mixt was treated as previously and the residue crystallized from petrol–EtOAc, giving 290 mg of longipin-2-ene-7β-angeloyloxy-9α-hydroxy-1-one (**3**), mp 147–149°, $[\alpha]_D$ +45 3 (EtOAc, *c* 0 64). IR ν_{max}^{KBr} cm^{-1}: 3445, 1700, 1660, 1625, 840. UV λ_{max}^{MeOH} nm: 216, 251. ^{1}H NMR (300 MHz): δ0 93 and 1 07 (3H each, 2*s*, *gem*-dimethyl group), 1 12 (3H, *s*, H-14), 1.90 (3H, *quin* J = 1.5 Hz, Me-5 angelate), 1 96 (1H, *d*, $J_{9,OH}$ = 3 Hz, OH), 2 00 (1H, *ddd*, $J_{7,8\alpha}$ = 2, $J_{8\alpha,8\beta}$ = 15 and $J_{8\alpha,9}$ = 3 Hz, H-8α), 2 02 (3H, *dq*, J = 6 5 and 1.5 Hz, Me-4 angelate), 2 04 (3H, *d*, J = 1.5 Hz, H-15), 2.27 (1H, *ddd*, $J_{7,8\beta}$ = 12, $J_{8\alpha,8\beta}$ = 15 and $J_{8\alpha,9\beta}$ = 3 Hz, H-8), 2 29 (1H, *s*, H-5), 2.57 (1H, *d*, $J_{4,11}$ = 7 5 Hz, H-4), 3.13 (1H, *dd*, $J_{2,11}$ = 1.5 and $J_{4,11}$ = 7.5 Hz, H-11), 3 88 (1H, *q*, $J_{8\alpha,9} \simeq J_{8\beta,9} \simeq J_{9,OH}$ = 3 8 Hz, H-9), 5 10 (1H, *dd*, $J_{7,8\beta}$ = 12 Hz and $J_{7,8\alpha}$ = 2 Hz, H-7), 5 80 (1H, *m*, J = 1.5 Hz, H-2) and 6.10 ppm (1H, *qq*, J = 6 5 and 1 5 Hz, H-3 angelate. ^{13}C NMR, see Table 1. EIMS *m/z* (rel. int.) 332 $[M]^+$ (0 4), 249 (2 7), 232 (5 5), 135 (22 1), 122 (24.7), 83 (100), 55 (49.3), 28 (39 7).

X-Ray analysis. Single crystals of **3** were grown by slow crystallization from CH_2Cl_2–hexane. They were orthorhombic, space group $p2_12_12_1$ with a = 8.8746 (40), b = 13 5999 (81), c = 15 6960 (68) Å, and d_{calc} = 1.17 g/cm^3 for Z = 4 (M, 332.48). The intensity data were measured on a Nicolet R3m four-circle diffractometer with CuK_α monochromated radiation in the θ:2θ scan mode. The size of the crystal used for data collection was *ca* 0 58 × 0 28 × 0 24 mm^3. No absorption correction was necessary (μ = 6 5 cm^{-1}). A total of 1414 reflections was measured for 3° ≤ θ ≤ 110°, of which 1342 reflections were considered to be observed [$I \geq 3(I)$]. The structure was solved by the direct method using the software provided by the manufacturer and refined by full-matrix least-squares assuming the anisotropic temperature factors for non-hydrogen atoms and the isotropic ones for hydrogen atoms. The final discrepancy indices were R = 7 38% using a unit weight for 1339 reflections. The final difference Fourier map was essentially featureless, the highest residual peaks having densities of 0.4 e/Å^3. Lists containing atomic coordinates and thermal parameters, bond distances, bond angles, anisotropic temperature factors, hydrogen atom coordinates and comparison of the observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre.

Oxidation of **3** *with Jones' reagent*. Compound **3** (250 mg) was dissolved in Me_2CO (20 ml) at 0° and Jones' reagent (8 ml) added dropwise. The soln was stirred for 1 hr at 0° and then stored at room temp. overnight. Excess reagent was destroyed with MeOH, the soln filtered and concd at red pres. The residue was extracted with EtOAc, dried (Na_2SO_4), evapd to dryness and chromatographed on a silica gel column C_6H_6–EtOAc, 19:1). Crude **5** was purified by prep. TLC (C_6H_6) and crystallized from C_6H_6–hexane, giving 190 mg of longipin-2-ene-7β, angeloyloxy-1,9-dione (**5**), mp 118–120°. IR ν_{max}^{KBr} cm^{-1}: 3050, 1720, 1700, 1678, 1625, 1235, 858. UV λ_{max}^{MeOH} nm: 204, 218, 254. ^{1}H NMR (80 MHz). δ0 85 and 0 93 (each 3H, *s*, *gem*-dimethyl), 0 95 (3H, *s*, H-14), 1 70 (3H, *qd*, J = 1 5 Hz, Me-5 angelate), 1 75 (3H, *dd*, J = 6 5 and 1 5 Hz, Me-4 angelate), 1 90 (3H, *d*, J = 1 5 Hz, H-15), 2 18 (1H, *s*, H-5), 2 50–3 20 (4H, *br*, H-4, H-8, H-8′ and H-11), 4 85 (1H, *dd*, J = 11 and 1.5 Hz, H-7), 5 60 (1H, *m*, J = 1 5 Hz, H-2) and 5 90 ppm (1H, *dq*, J = 6 5 and 1 5 Hz, H-3 angelate). ^{13}C NMR, see Table 1.

2-Dehydrorastevione (**6**) [4–6]. Colourless oil. IR ν_{max}^{film} cm^{-1}: 3450, 1750, 1680, 865. UV λ_{max}^{MeOH} nm: 217, 252. ^{1}H NMR (80 MHz) δ0.85 and 1.18 (each 3H, *s*, *gem*-dimethyl), 1 10 (3H, *s*, H-14), 1 73 (6H, *m*, J = 1 5 Hz, Me-4 angelate), 1 80 (6H, *dq*, J = 6.5 and 1 5 Hz, Me-5 angelate), 2 00 (3H, *d*, J = 1 5 Hz, H-15), 2.25 (1H, *s*, H-5), 2 62 (1H, *d*, J = 6 Hz, H-4), 3 18 (1H, *d*, J = 6 Hz,

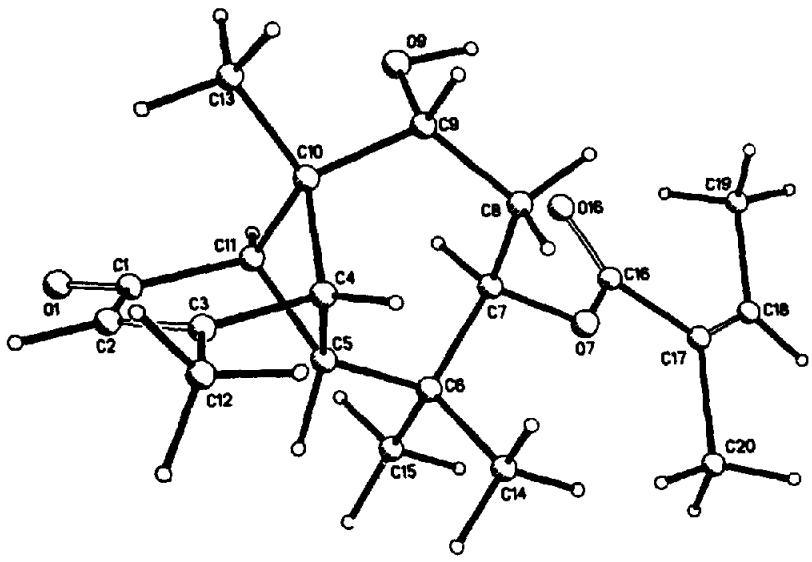

Fig. 1.

H-11), 3 78 (1H, *d*, $J = 1$ 5 Hz, H-9), 5.46 (2H, *br s*, H-7 and H-8), 5 74 (1H, *m*, $J = 1$ 5 Hz, H-2) and 6 02 ppm (2H, *dq*, $J = 6$ 5 and 1 5 Hz, H-3 angelate) ^{13}C NMR, see Table 1. EIMS *m/z* (rel int) 330 (1 4), 247 (1 0), 230 (2 8), 219 (2 5), 202 (2 7), 201 (6 3), 187 (3 6), 175 (4 0), 149 (3 1), 135 (3 9), 122 (337), 109 (4 2), 83 (100), 55 (56 2)

Bromination of **8** *with TBDC* To a soln of **8** (350 mg) in dry Et_2O were added 340 mg of TBDC (2,4,4,6-tetrabromocyclohexan-2,5-dienone) and the mixt stirred for 3 hr at room temp The Et_2O soln was extd with aq Na_2CO_3, washed and dried (Na_2SO_4) The residue obtained after evapn of solvent was purified by prep TLC (C_6H_6–EtOAc, 9 1, double development) yielding 250 mg of 2*β-bromorastevione* (**7**), colourless oil IR ν_{max}^{film} cm^{-1} 3440, 1680, 1640, 765 UV λ_{max}^{MeOH} nm 205, 230 ^{1}H NMR (80 MHz) δ0 95 and 1 10 (each 3H, *s*, *gem*-dimethyl), 1 02 (3H, *s*, H-14), 1 24 (3H, *d*, $J = 7$ Hz, H-15), 1 75 (6H, *m*, $J = 1$ 5 Hz, Me-5 angelates), 1 90 (6H, *qd*, $J = 6$ 5 and 1 5 Hz, Me-4 angelates), 2 10 2 80 (2H, *m*, H-3 and H-4), 2 45 (1H, *s*, H-5), 3 30 (1H, *d*, $J = 6$ Hz, H-11), 3 75 (1H, *s*, H-9), 4 53 (1H, *d*, $J = 8$ Hz, H-2), 5 46 (2H, *br s*, H-7 and H-8) and 6 05 ppm (2H, *dq*, $J = 6$ 5 and 1 5 Hz, H-3 angelates) ^{13}C NMR, see Table 1

Dehydrobromination of **7** *with DBU* A soln of compound **7** (200 mg) in DMSO was treated with an equimolecular amount of DBU (1,5-diazabicyclo[5 4 0]undecen-5-ene) and heated at 85° during 3 hr The residue left after *in vacuo* removal of solvent was chromatographed by prep TLC (C_6H_6–EtOAc, 4 1) yielding 150 mg of an oil identical to natural 2-dehydrorastevione (**6**)

Triflorestevione (**9**) Colourless oil IR ν_{max}^{film} cm^{-1} 3450, 1725, 1710, 1630, 1270, 750 UV λ_{max}^{MeOH} nm 208, 230 ^{1}H NMR (80 MHz) δ0 76, 0 89 and 0 97 (each 3H, *s*, *gem*-dimethyl and H-14), 1 09 (3H, *d*, $J = 7$ Hz, H-15), 1 66 (12H, apparent *br s*, tigloyl Me's hydrogens), 2 98 (1H, *d*, $J = 6$ Hz, H-11), 3 70 (1H, *d*, $J = 1$ 5 Hz, H-9), 5 38 (6H, *br s*, H-7 and H-8) and 6 67 ppm (2H, *qq*, $J = 7$ and 1 5 Hz, H-3 tiglates) ^{13}C NMR see Table 1. EIMS *m/z* (rel int) 332 (0 8), 309 (0 4), 281 (0 6), 249 (0 5), 232 (1 9), 217 (2 1), 203 (3 4), 189 (2 8), 177 (3 2), 165 (3 0), 137 (3 5), 109 (4 5), 83 (100), 55 (58 0)

Catalytic hydrogenation of **8**. A soln of 150 mg of **8** in EtOAc (8 ml) was stirred in the presence of 30 mg of prehydrogenated 10% Pd on activated charcoal catalyst under an H_2 atmosphere at room temp and at 30 atm press The reaction mixt was stored for 48 hr and then centrifuged and filtered over silica gel The residue obtained after evapn of solvent was subjected to CC giving 150 mg of a isomeric mixt of longipin-7β,8α-di(2-methyl-butyroyloxy)-9α-hydroxy-1-one (**10**), colourless oil, IR ν_{max}^{film} cm^{-1} 3480, 1730, ^{1}H NMR (80 MHz) δ0 60–1 50 (signals corresponding to methyls), 3 62 (1H, *s*, H-9) and 5 43 ppm (2H, *m*, H-7 and H-8) ^{13}C NMR δ210 1 (*s*, C-1), 175 0 and 175 3 (*s*, esters C=O)

Catalytic hydrogenation of **9** This was performed as described above, to yield an oil identical (TLC and NMR) to **10** above

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