TROPANE ALKALOIDS FROM *SCHIZANTHUS PINNATUS*

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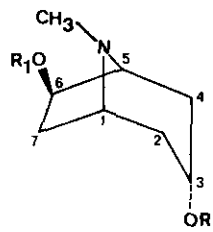
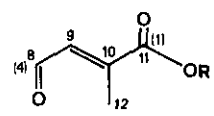
Abstract —— *From Schizanthus pinnatus Ruiz et Pav. we have isolated seven new tropan-3α,6β-diol diesters, schizanthines F (1), G (2), H (3), I (4), K (8), L (9), and M (10), together with tropine, (-)-6β-angeloyloxytropan-3α-ol (5), (-)-6β-tigloyloxytropan-3α-ol (6), and (-)-3α-senecioyloxytropan-6β-ol (7). The structures of the new alkaloids were determined mainly by spectroscopic methods comprising 2-D and 1-D nmr long-range heteronuclear correlations.*

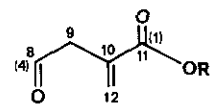
Schizanthus, an endemic genus of Chile,[1] has been included in the Solanacea family because of the isolation of tropane alkaloids.[2-5] Continuing our work on that genus[5] we report here on the structure determination of schizanthines F (1), G (2), H (3), I (4), K (8), L (9), and M (10), new tropan-3α,6β-diol diesters, isolated from plants of *Schizanthus pinnatus* Ruiz et Pav.[6]

The new bases were 3α,6β-diacyloxytropanes, as inferred from the distinctive ^{1}H nmr signals for H-1, H-3, H-5, and H-6,[3-5,7] at δ 3.04-3.20 (br s, $W\frac{1}{2}$ = 8-8.5 Hz), 4.95-5.10 (t, J=4.5-5.2 Hz), 3.18-3.32 (m, $W\frac{1}{2}$ = 15 Hz), and 5.34-5.47 (dd, J_1 = 7.5-7.7 Hz, J_2 = 3.1-3.2 Hz), respectively, and the typical ms fragments at m/z 96, 95, 94, 82, and 81.[8,9] The nature of the esters was also evident from their characteristic signals in the ^{1}H nmr spectra: δ 6.62-6.72 (1H, q, J = 1.6 Hz, H-9) and 2.15-2.29 (3H, d, J = 1.5-1.7 Hz, H-12) for mesaconic esters;[10] 3.27-3.34 (2H,





MM R=CH_3; ME R=C_2H_5



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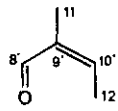
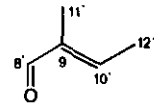


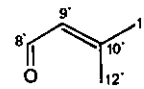
A

1 R= MM, R_1=T
2 R= IM, R_1=T
3 R= IM, R_1=A
4 R= MM, R_1=A



I

5 R=H, R_1=A
6 R=H, R_1=T
7 R=S, R_1=H
8 R=ME, R_1=T



S

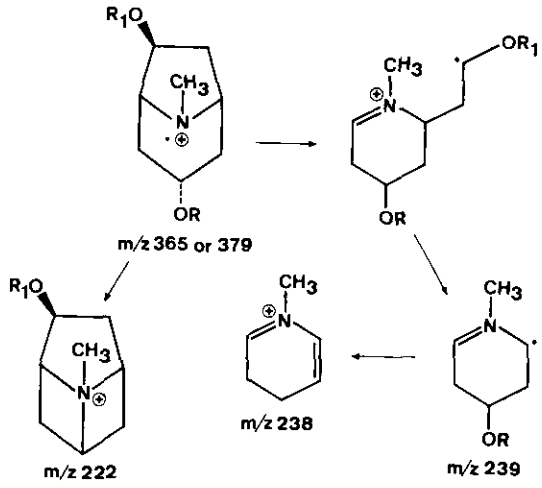
9 R=IE, R_1=A
10 R=IE, R_1=T
11 R=R_1=H

s, H-9) and 5.69-5.74 and 6.29-6.36 (1H each, s, H-12) for itaconic esters,[11] 1.82-1.86 (3H, m, $W\frac{1}{2}$ = 4-4.5 Hz, H-11'), 1.94-1.98 (3H, dq, J_1 = 7-7.2 Hz, J_2 = 1.4-1.5 Hz, H-12'), and 6.03 (1H, q, J = 7.1-7.3 Hz, H-10') for angelic esters,[12] and 1.64-1.78 (3H, d, J = 7 Hz, H-12'), 1.66-1.83 (3H, br s, H-11'), and 6.68-6.77 (1H, q, J = 6.9-7.2 Hz, H-10') for tiglic esters.[12]

The peculiarities of the ms fragmentation of 3,6-diacyloxytropane derivatives (Scheme 1)[7b,c] let us establish the position of the esters without difficulty. The intensities of the ions at m/z 222,239, 238, showed that schizanthine F (1) was a methyl-6β-tigloyloxytropan-3α-yl mesaconate, schizanthine G (2) a methyl-6β-tigloyloxytropan-3α-yl itaconate, schizanthine H (3) a methyl-6β-angeloyloxytropan-3α-yl itaconate, schizanthine I (4) a methyl-6β-angeloyloxytropan-3α-yl mesaconate, schizanthine K (8) an ethyl-6β-tigloyloxytropan-3α-yl mesaconate, schizanthine L (9) an ethyl-6β-angeloyloxytropan-3α-yl itaconate, and schizanthine M (10) an ethyl-6β-tigloyloxytropan-3α-yl itaconate.

The structures of schizanthines F (1), G (2), H (3), and I (4) were also inferred from ^{13}C-nmr spectroscopy. The assignments listed in Table 1 were made taking

into account those reported for related tropane alkaloids,[5] angelic and tiglic acids,[12] and dimethyl mesaconate and itaconate.[13]



Scheme 1

From the above evidence it was not possible to locate the tropanyl and methoxyl groups in the diesters. To solve these uncertainties, long-range ^{13}C-^{1}H chemical shift correlation experiments were carried out (Table 2). The observed connectivities allowed us to establish that schizanthine F was 1-methyl-4-(6-tigloyloxytropan-3-yl) mesaconate (1) and schizanthine G 1-methyl-4-(6-tigloyloxytropan-3-yl) itaconate (2).

The structures depicted for schizanthines H (3) and I (4) can be considered the most likely. The ^{13}C-nmr spectra were close to those of schizanthines G (2) and F (1), respectively. With respect to their carbonyl carbon resonances, compared with those of dimethyl itaconate (C-8 171.1 ppm and C-11 166.6 ppm) and mesaconate (C-8 166.2 ppm and C-11 167.5 ppm), the C-11 resonances in schizanthines H (166.4 ppm), G (166.7 ppm), I (167.2 ppm), and F (167.6 ppm) were almost identical, and the C-8 resonances at δ 169.8, 169.8, 165.0, and 165.1, respectively, were shifted 1.3-1.1 ppm upfield, as expected for a more alkyl substituted alcohol residue.[14]

The basic hydrolysis of schizanthines F (1) and G (2) yielded (+)-(3R,6R)-tropan-

Table 1. ^{13}C-Nmr chemical shifts and assignments for schizanthines F (1), G (2), H (3), and I (4), 6β-angeloyloxytropan-3α-ol (5), 6β-tigloyloxytropan-3α-ol (6), and 3α-senecioyloxytropan-6β-ol (7).

Carbon	1	2	3	4	5	6	7
1	59.9	59.9	60.1	60.3	60.4	60.3	58.5
2	33.0	33.3	33.3	33.3	36.7	36.4	28.9
3	67.5	67.8	67.7	67.0	64.2	64.3	67.2
4	34.7	34.6	34.8	35.4	37.6	37.3	30.3
5	66.1	66.0	66.2	66.5	66.6	66.5	66.2
6	79.5	79.5	79.1	78.5	79.7	80.1	76.1
7	35.6	35.7	35.6	34.9	35.8	35.8	40.8
8	165.1	169.8	169.8	165.0			
9	126.9	38.6	38.6	126.7			
10	144.2	133.8	133.8	144.1			
11	167.6	166.7	166.4	167.2			
12	14.5	129.0	129.0	14.2			
OCH_3	52.7	52.3	52.3	52.7			
8'	168.1	167.9	167.5	168.2	168.2	168.2	165.9
9'	128.8	129.0	126.9	127.4	128.1	129.0	116.4
10'	137.3	137.2	137.9	138.7	137.7	137.0	157.2
11'	12.1	12.5	20.7	20.7	20.7	12.0	20.3
12'	14.5	14.5	15.8	14.5	15.8	14.4	27.5
$N-CH_3$	40.2	40.2	40.4	40.3	40.6	40.3	36.5

Chemical shifts in ppm downfield from TMS.

Table 2. $^{13}C-^{1}H$ Long-range connectivities in schizanthine F (1)[a] and schizanthine G (2)[b]

(1) H	δ	C	(2) H	δ	C
H-9	6.62	C-10, C-11, C-12	H-3	4.97	C-1, C-2, C-5, C-8
H-12	2.15	C-9, C-10, C-11	H-6	5.35	C-1, C-8'
H-11'	1.66	C-8', C-9', C-10'	H-12	5.56	C-9, C-11
OCH_3	3.63	C-11	H-12	6.29	C-10, C-11
			OCH_3	3.69	C-11

a) HETCOR 2-D nmr experiment.[14] b) INAPT 1-D nmr experiments.[15]

3α,6β-diol (11)[17] which set their absolute configurations.

Schizanthines K (8), and M (10), as well as schizanthine A,[2] may be artifacts produced in the treatment of the vegetable material with ethanol, and from the spectral data available it was not possible to locate the sites of esterification in mesaconic and itaconic acids.

The ^{13}C-nmr spectra and assignments for 6β-angeloyloxytropan-3α-ol (5), 6β-tigloyloxytropan-3α-ol (6), and 3α-senecioyloxytropan-6β-ol (7), also isolated from this plant together with tropine, are presented in Table 1.

EXPERIMENTAL

The plant material was collected near Santiago de Chile in loco dicto Laguna de Los Cristales at an altitude of 2500 m. Voucher specimens were deposited at the Faculty of Sciences Herbarium, Universidad de Chile.

Optical rotations were measured in EtOH with a Perkin-Elmer 137 polarimeter. Infrared spectra were taken on a Perkin-Elmer 681 spectrophotometer. ^{1}H- and ^{13}C-nmr spectra were recorded on a Bruker WP-2000SY spectrometer in $CDCl_3$. Mass spectra were determined on a VG Micromass ZAB-2F instrument.

Alumina Merck, Art. 1077, 5581, and 1092, was used for cc, tlc, and ptlc, respectively.

Isolation of alkaloids. The plant material (7 kg) was extracted with ethanol in a Soxhlet for 72 h. After removing the solvent under vacuum, the ethanolic extract was partitioned between acid and base, in the usual manner, to give the crude alkaloid mixture (7 g). The basic material was chromatographed over alumina with mixtures of hexane-ethyl acetate (85:15 and 50:50) and ethyl acetate-methanol (90:10) to furnish three main fractions, F_1 (1.5 g), F_2 (0.37 g), and F_3 (4.8 g).

Further cc and ptlc, when necessary, yielded the purified alkaloids. Schizanthines F, G, H, and I were isolated from F_1; (-)-6β-angeloyloxytropan-3α-ol and (-)-6β-tigloyloxytropan-3α-ol from F_2; tropine (-)-3α-senecioyloxytropan-6β-ol, and schi-

zanthines K, L, and M from F_3.

Schizanthine F (1) —— Isolated as a colourless oil (105 mg), $[\alpha]_D$ -13.3° (c 0.16); M^+, M6z 365.1837 for $C_{19}H_{27}NO_6$, Δ 0.1 mmu. Ir ($CHCl_3$), 3005, 1725, 1640, and 1140 cm^{-1}. ^{1}H-Nmr, δ 1.53 (1H, d, J = 15 Hz, H-2β), 1.64 (3H, J = 7.0 Hz, H-12′), 1.66 (3H, br s, H-11′), 2.15 (3H, d, J = 1.6 Hz, H-12), 2.36 (3H, s, N-CH_3), 2.46 (1H, dd, J_1 = 16.1 Hz, J_2 = 6.8 Hz, H-7α), 3.04 (1H, br s, $W\frac{1}{2}$ = 8.5 Hz, H-1), 3.18 (1H, m, $W\frac{1}{2}$ = 15 Hz, H-5), 3.63 (3H, s, OCH_3), 4.95 (1H, t, J = 5 Hz, H-3), 5.34 (1H, dd, J_1 = 7.5 Hz, J_2 = 3.1 Hz, H-6), 6.62 (1H, q, J = 1.6 Hz, H-9), and 6.68 (1H, qq, J_1 = 6.9 Hz, J_2 = 1.3 Hz, H-10′). Ms, m/z 365 (11%) M^+, 239 (12%), 238 (22%), 222 (24%), 138 (34%), 122 (85%), 96 (39%), 95 (100%), 94 (100%), 83 (42%), 82 (30%), and 81 (34%). For the ^{13}C-nmr spectrum see Table 1.

Hydrolysis of Schizanthine F (1) —— An aqueous ethanol (1:1) solution (5 ml) of 1 (10 mg) and $Ba(OH)_2$ (50 mg) was refluxed for 3 h. After cooling, the reaction mixture was acidified and extracted with ether. The aqueous layer was then basified and extracted with ethyl acetate to give (-)-6β-tigloyloxytropan-3α-ol (6)[4] (4.5 mg, 70%). The treatment of 1 (25 mg) under the same conditions, by refluxing for 6 h, yielded (+)-(3R,6R)-tropan-3α,6β-diol (11)[17] (8 mg, 75%); mp 210°C, $[\alpha]_D$ = +15° (c 0.16). These compounds were identified by comparison with authentic samples.

Schizanthine G (2) —— Isolated as a colourless oil (90 mg), $[\alpha]_D$ -11.4° (c 0.23); M^+, m/z 365.1821 for $C_{19}H_{27}NO_6$, Δ 1.7 mmu. Ir ($CHCl_3$), 3005, 1715, 1640, and 1145 cm^{-1}. ^{1}H-Nmr, δ 1.55 (1H, d, J = 15.1 Hz, H-2β), 1.71 (3H, d, J = 7 Hz, H-12′), 1.75 (3H, br s, H-11′), 2.42 (3H, s, N-CH_3), 3.09 (1H, br s, $W\frac{1}{2}$ = 8 Hz, H-1), 3.23 (1H, m, $W\frac{1}{2}$ = 15 Hz, H-5), 3.27 (2H, s, H-9), 3.69 (3H, s, OCH_3), 4.97 (1H, t, J = 5.2 Hz, H-3β), 5.35 (1H, dd, J_1 = 7.6 Hz, J_2 = 3.1 Hz, H-6α), 5.69 and 6.29 (each 1H, s, H-12), and 6.77 (1H, q, J = 7.6 Hz, H-10′). Ms, m/z 365 (4%) M^+, 239 (12%), 238 (10%), 222 (19%), 138 (19%), 122 (63%), 96 (24%), 95 (97%), 94 (100%), 83 (22%), 82 (17%), and 81 (19%). For the ^{13}C-nmr spectrum see Table 1. Hydrolysis of 2 as above also afforded (3R,6R)-tropan-3α,6β-diol (11).

Schizanthine H (3) —— Isolated as a colourless oil (30 mg), $[\alpha]_D$ -12.5° (c 0.1); M^+, m/z 365.1821 for $C_{19}H_{27}NO_6$, Δ 1.7 mmu. Ir ($CHCl_3$), 3005, 1725, 1640, and

1150 cm^{-1}. ^1H Nmr, δ 1.60 (1H, d, J = 14 Hz, H-2β), 1.82 (3H, m, $W\frac{1}{2}$ = 4 Hz, H-11′), 1.94 (3H, dq, J_1 = 7.2 Hz, J_2 = 1.5 Hz, H-12′), 2.45 (3H, s, N-CH_3), 3.15 (1H, br s, $W\frac{1}{2}$ = 8.2 Hz, H-1), 3.28 (1H, m, $W\frac{1}{2}$ = 15 Hz, H-5), 3.31 (2H, s, H-9), 3.72 (3H, s, OCH_3), 5.01 (1H, t, J = 5 Hz, H-3β), 5.41 (1H, dd, J_1 = 7.6 Hz, J_2 = 3.1 Hz, H-6α), 5.72 and 6.32 (1H each, s, H-12), and 6.03 (1H, q, J = 7.1 Hz, H-10′). Ms, m/z 365 (20%) M^+, 239 (18%), 238 (18%), 222 (64%), 138 (46%), 122 (100%), 96 (40%), 95 (100%), 94 (100%), 83 (39%), 82 (28%), and 81 (32%). For the ^{13}C-nmr spectrum see Table 1.

Schizanthine I (4) —— Isolated as a colourless oil (15 mg), $[\alpha]_D$ -13.2° (c 0.18); M^+, m/z 365.1813 for $C_{19}H_{27}NO_6$, Δ 2.5 mmu. Ir ($CHCl_3$), 3020, 1715, 1640, and 1140 cm^{-1}. ^1H Nmr, δ 1.66 (1H, d, J = 15 Hz, H-2β), 1.83 (3H, m, $W\frac{1}{2}$ = 4 Hz, H-11′), 1.96 (3H, dq, J_1 = 7.1 Hz, J_2 = 1.4 Hz, H-12′), 2.27 (3H, d, J = 1.5 Hz, H-12), 2.49 (3H, s, N-CH_3), 3.20 (1H, br s, $W\frac{1}{2}$ = 8 Hz, H-1), 3.31 (1H, m, $W\frac{1}{2}$ = 15 Hz, H-5), 3.78 (3H, s, OCH_3), 5.08 (1H, t, J = 4.5 Hz, H-3β), 5.47 (1H, dd, J_1 = 7.6 Hz, J_2 = 3.2 Hz, H-6α), 6.03 (1H, q, J_1 = 7.2 Hz, H-10′), and 6.71 (1H, q, J = 1.6 Hz, H-9). Ms, m/z, 365 (10%) M^+, 239 (11%), 238 (22%), 222 (24%), 138 (32%), 122 (66%), 96 (31%), 95 (100%), 94 (100%), 83 (32%), 82 (30%), and 81 (31%). For the ^{13}C-nmr spectrum see Table 1.

(-)-6β-Angeloyloxytropan-3α-ol (5)[3] —— Isolated as an oil (70 mg), $[\alpha]_D$ -12.5° (c 0.16). Ir ($CHCl_3$), 3550, 3100, 3020, 1700, 1640, and 1160 cm^{-1}. ^1H-Nmr, δ 1.60 (1H, d, J = 14.6 Hz, H-2β), 1.82 (3H, m, $W\frac{1}{2}$ = 4 Hz, H-11′), 1.93 (3H, dq, J_1 = 7.8 Hz, J_2 = 1.4 Hz, H-12′), 2.44 (3H, s, N-CH_3), 2.67 (1H, dd, J_1 = 13.7 Hz, J_2 = 7.6 Hz, H-7α), 3.13 (1H, br s, $W\frac{1}{2}$ = 8 Hz, H-1), 3.25 (1H, m, $W\frac{1}{2}$ = 15 Hz, H-5), 4.02 (1H, t, J = 5 Hz, H-3β), 5.65 (1H, dd, J_1 = 7.7 Hz, J_2 = 3.2 Hz, H-6α), and 6.01 (1H, dq, J_1 = 7.4 Hz, J_2 = 1.3 Hz, H-10′). M^+, m/z for 239.1539 for $C_{13}H_{21}NO_3$, Δ -2.0 mmu. For the ^{13}C-nmr spectrum see Table 1. This compound was identified by comparison with an authentic sample.

(-)-6β-Tigloyloxytropan-3α-ol (6)[4] —— Isolated as a colourless oil (200 mg), $[\alpha]_D$ - 21.1° (c 0.35). Ir ($CHCl_3$), 3600, 3100, 3020, 1690, 1640, and 1170 cm^{-1}. ^1H-Nmr, δ 1.60 (1H, d, J = 14.6 Hz, H-2β), 1.75 (3H, d, J = 7.2 Hz, H-12′), 1.78 (3H, br s, H-11′), 2.47 (3H, s, N-CH_3), 2.66 (1H, dd, J_1 = 13.7 Hz, J_2 = 2.1 Hz, H-7α), 3.10 (1H, br s, $W\frac{1}{2}$ = 8 Hz, H-1), 3.26 (1H, m, $W\frac{1}{2}$ = 15 Hz, H-5), 4.03 (1H, t, J = 5 Hz,

H-3β), 5.62 (1H, dd, J_1 = 7.4 Hz, J_2 = 3.1 Hz, H-6α), and 6.81 (1H, qq, J_1 = 7.2 Hz, J_2 = 1.3 Hz, H-10′). M^+, m/z 239.1520 for $C_{13}H_{21}NO_3$, Δ 0.0 mmu. For the ^{13}C-nmr spectrum see Table 1. This compound was identified by comparison with an authentic sample.

(-)-3α-Senecioyloxytropan-6β-ol (7)[3] —— Isolated as a solid (250 mg), mp 88-90°C, crystallized from hexane-ethyl acetate, $\{\alpha\}_D$ -10.1° (c 0.14). Ir (KBr), 3400, 3180, 1706, 1643, and 1145 cm^{-1}. ^{1}H-Nmr, δ 1.42 (1H, d, J = 15 Hz, H-2β), 1.56 (1H, d, J = 15.4 Hz, H-4β), 1.86 (3H, d, J_1 = 1.2 Hz, H-11′), 2.10 (3H, d, J = 1.2 Hz, H-12′), 2.49 (3H, s, N-CH_3), 2.55 (1H, dd, J_1 = 13.6 Hz, J_2 = 7.3 Hz, H-7α), 2.90 (1H, s, OH), 2.97 (1H, br s, $W_{\frac{1}{2}}$ = 9 Hz, H-1), 3.23 (1H, m, $W_{\frac{1}{2}}$ = 14 Hz, H-5), 4.52 (1H, dd, J_1 = 7.3 Hz, J_2 = 2.6 Hz, H-6α), 4.97 (1H, t, J = 5.3 Hz, H-3β), and 5.60 (1H, m, $W_{\frac{1}{2}}$ = 3 Hz, H-9′). M^+, m/z 239.1519 for $C_{13}H_{21}NO_3$, Δ 0.1 mmu. For the ^{13}C-nmr spectrum see Table 1. This compound was identified by comparison with an authentic sample.

Schizanthine K (8) —— Isolated as a colourless oil (7 mg), $\{\alpha\}_D$ -12.1° (c 0.24); M^+, m/z 379.1990 for $C_{20}H_{29}NO_6$, Δ 0.3 mmu. Ir ($CHCl_3$), 1710, 1640, and 1150 cm^{-1}. ^{1}H-Nmr, δ 1.33 (3H, t, J = 7 Hz, $OCH_2\underline{CH_3}$), 1.78 (3H, d, J = 7 Hz, H-12′), 1.81 (3H, br s, H-11′), 2.29 (3H, d, J = 1.7 Hz, H-12), 2.49 (3H, s, N-CH_3), 3.17 (1H, br s, $W_{\frac{1}{2}}$ = 8.5 Hz, H-1), 3.32 (1H, m, $W_{\frac{1}{2}}$ = 15 Hz, H-5), 4.26 (2H, q, J = 7 Hz, $O\underline{CH_2}CH_3$), 5.10 (1H, t, J = 5.3 Hz, H-3β), 5.47 (1H, dd, J_1 = 7.7 Hz, J_2 = 3.2 Hz, H-6α), 6.72 (1H, q, J = 1.6 Hz, H-9), and 6.82 (1H, qq, J_1 = 7 Hz, J_2 = 1.4 Hz, H-10′). Ms, m/z 379 (3%) M^+, 334 (3%), 253 (4%), 239 (2%), 238 (9%), 222 (15%), 138 (21%), 122 (67%), 96 (26%), 95 (100%), 94 (100%), 83 (32%), 82 (20%), and 81 (20%).

Schizanthine L (9) —— Isolated as a colourless oil (6 mg), $\{\alpha\}_D$ -7.7° (c 0.1); M^+, m/z 379.1990 for $C_{20}H_{29}NO_6$, Δ 0.3 mmu. Ir ($CHCl_3$), 1710, 1640, and 1150 cm^{-1}. ^{1}H-Nmr, 1.28 (3H, t, J = 6.3 Hz, $OCH_2\underline{CH_3}$), 1.86 (3H, m, $W_{\frac{1}{2}}$ = 4.5 Hz, H-11′), 1.98 (7H, dq, J_1 = 7 Hz, J_2 = 1.4 Hz, H-12′), 2.48 (3H, s, N-CH_3), 2.53 (1H, dd, J_1 = 7.6 Hz, J_2 = 2.9 Hz, H-7α), 3.17 (1H, br s, $W_{\frac{1}{2}}$ = 8.5 Hz, H-1), 3.29 (1H, m, $W_{\frac{1}{2}}$ = 15 Hz, H-5), 3.34 (2H, d, J = 0.8 Hz, H-9), 4.21 (2H, q, J = 6 Hz, $O\underline{CH_2}CH_3$), 5.03 (1H, t, J = 4.7 Hz, H-3β), 5.45 (1H, dd, J_1 = 7.5 Hz, J_2 = 3.1 Hz, H-6α), 5.74 and 6.36 (each 1H, s, H-12), and 6.03 (1H, dq, J_1 = 7.3 Hz, J_2 = 1.4 Hz, H-10′). Ms, m/z 379 (17%) M^+, 334 (1%), 253 (9%), 239 (2%), 238 (11%), 222 (57%), 138 (42%),

122 (94%), 96 (33%), 95 (100%), 94 (100%), 83 (31%), 82 (24%), and 81 (28%).

Schizanthine M (10) —— Isolated as a colourless oil (5 mg), $[\alpha]_D$ -8.5° (c 0.06); M^+, m/z 379.1997 for $C_{20}H_{29}NO_6$, Δ -0.4 mmu. Ir ($CHCl_3$), 3010, 1710, 1650, and 1150 cm^{-1}. ^{1}H-Nmr, δ 1.23 (3H, t, J = 7.2 Hz, $OCH_2\underline{CH}_3$), 1.78 (3H, d, J = 7 Hz, H-12′), 1.83 (3H, br s, H-11′), 2.44 (3H, s, N-CH_3), 3.10 (1H, br s, $W\frac{1}{2}$ = 8.5 Hz, H-1), 3.25 (1H, m, $W\frac{1}{2}$ = 15 Hz, H-5), 3.29 (2H, d, J = 0.7 Hz, H-9), 4.17 (2H, q, J = 7 Hz, $O\underline{CH}_2CH_3$), 5.0 (1H, t, J = 5 Hz, H-3β), 5.37 (1H, dd, J_1 = 7.5 Hz, J_2 = 3.1 Hz, H-6α), 5.70 and 6.31 (each 1H, s, H-12), and 6.77 (1H, qq, J_1 = 7.2 Hz, J_2 = 1.4 HZ, H-10′). Ms, m/z, 379 (5%) M^+, 334 (1%), 253 (4%), 239 (2%), 238 (3%), 222 (27%), 138 (19%), 122 (52%), 96 (19%), 95 (75%), 94 (100%), 83 (15%), 82 (21%), and 81 (16%).

Tropine (12)[18] —— Isolated as a solid (2.20 g), mp 63°C, hygroscopic crystals from hexane-ethyl acetate (subl. 190°C, 0.9 mm). Ir (nujol), 3350, 1300, 1225, 1110, 1063, 1040, 970, 946, 900, and 765 cm^{-1}. ^{1}H-Nmr, δ 1.52 (2H, d, J = 14.2 Hz, H-2β and H-4β), 1.80-1.98 (6H), 2.10 (3H, s, N-CH_3), 2.92 (2H, br s, $W\frac{1}{2}$ = 10 Hz, H-1 and H-5), 3.6 (1H, br s, OH), and 3.83 (1H, t, J = 5 Hz, H-3β). Ms, m/z, 141 (28%), 124 (38%), 113 (22%), 112 (15%), 97 (29%), 96 (83%), 83 (64%), 82 (100%), 57 (27%), and 112 (70%). This compound was identified by comparison with an authentic sample.

Dimethyl Esters of Mesaconic and Itaconic Acids[19] —— A mixture of the acid (2 g), methanol (10 ml), p-toluenesulfonic acid (20 mg), and hydroquinone (2 mg) was heated, under pressure, at 150°C for 1 h. The reaction mixture was then distilled under vacuum (20 mm) to give the corresponding diester. Dimethyl mesaconate (2.94 g, 80%). ^{1}H-Nmr, δ 2.21 (3H, d, J = 1.5 Hz, H-12), 3.69 (3H, s, C_8-OCH_3), 3.73 (3H, s, C_{11}-OCH_3), and 6.70 (1H, d, J = 1.7 Hz, H-9). ^{13}C-Nmr, δ 14.2 (q, C-12), 51.6 (q, C′-8), 52.5 (q, C′-11), 126.4 (d, C-9), 143.7 (s, C-10), 166.2 (s, C-8), and 167.5 (s, C-11). Dimethyl itaconate (2.2 g, 90%). ^{1}H-Nmr, δ 3.45 (2H, s, H-9), 3.70 (3H, s, C_8-OCH_3), 3.77 (3H, s, C_{11}-OCH_3), 5.71 and 6.33 (1H each, s, H-12). ^{13}C-Nmr, δ 37.4 (t, C-9), 51.8 (q, C′-8), 52.0 (q, C′-11), 128.5 (t, C-12), 133.7 (s, C-10), 166.6 (s, C-11), and 171.1 (s, C-8). The ^{1}H and ^{13}C assignments are given taking into account the connectivities observed in long-range HETCOR 2D nmr experiments.

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