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Natural 2,6-Dialkyl-3-piperidinols. 9. Total Synthesis of (±)-Prosafrinine and ^{13}C NMR Studies of Some Analogous Compounds

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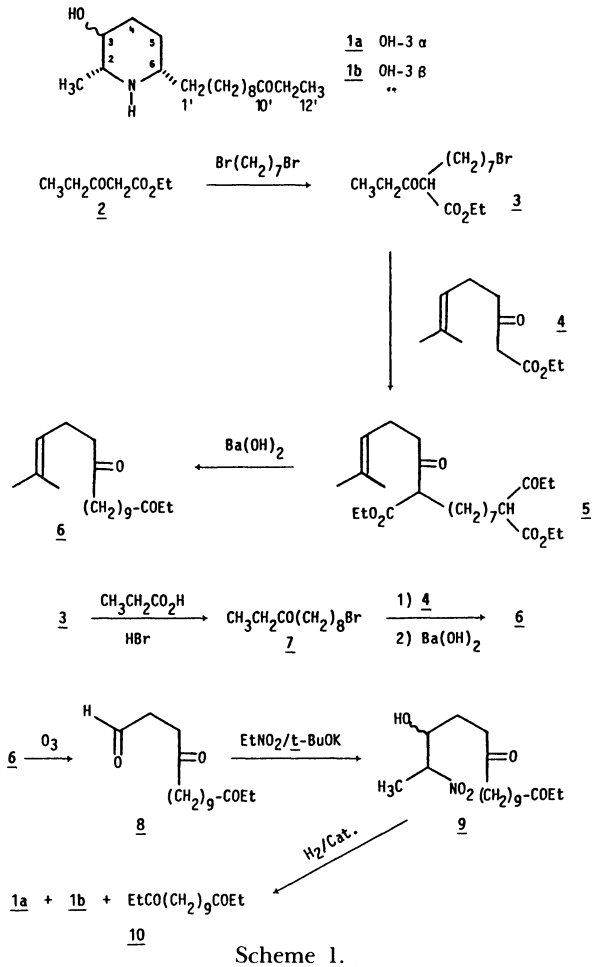
1,7-Dibromoheptane was used to alkylate both ketoesters **2** and **4** successively. Hydrolysis and decarboxylation of the resulting intermediate afforded the ethylenic diketone (**6**). Ozonolysis of the double bond of **6** gave the diketonic aldehyde (**8**). Alkaline condensation of nitroethane on the aldehydic carbonyl of the latter, followed by hydrogenation using a Pd–Pt catalyst, afforded 3-*r*-hydroxy-6-*c*-(10-oxododecyl)-2-*c*-methylpiperidine [(±)-prosafrinine] (**1a**) and (±)-3-epiprosafrinine (**1b**). The structures of **1a**, **1b**, and some analogues were confirmed by ^{13}C NMR studies.

The alkaloid prosafrinine (**1a**) was isolated from the leaves of *Prosopis africana*, and its structure was established in 1972.[1] Prosafrinine (**1a**) is a 2,6-dialkyl-3-piperidinol in which the three substituents are cis. We describe here a racemic total synthesis of the alkaloid (**1a**) following a general reaction scheme previously developed in our laboratory for the synthesis of 2,6-dialkyl-3-piperidinols.[2] We have confirmed or established the relative stereochemistry of prosafrinine (**1a**) and some related compounds, more particularly by ^{13}C NMR studies, and by comparison with the data published in a recent paper.[3]



Scheme 1.

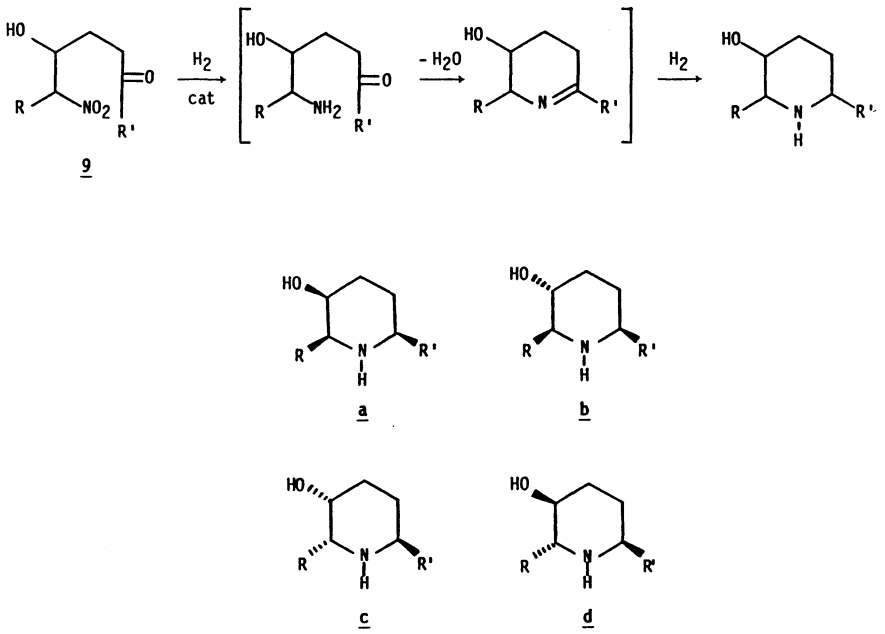
γ,δ-Unsaturated ketones are key-intermediates in our synthetic scheme for 2,6-dialkyl-3-piperidinols. In the present case, we needed to prepare 17-methyl-16-octadecene-3,13-dione (**6**), which contains the carbon atoms at the positions 3 to 6 of the final piperidine ring, as well as the twelve carbon substituent at the position 6 of the same ring. Thus, ethyl 3-oxopentanoate (**2**), prepared from Meldrum's acid,[4] was alkylated with 1,7-dibromoheptane and afforded the monobromo intermediate (**3**) (Scheme 1). Alkylation of the β-keto ester **4**[5] with the bromide **3** gave the diketonic diester **5**, which was next hydrolyzed and decarboxylated in refluxing aqueous barium hydroxide, thus leading to the ethylenic diketone **6** in about 40% yields of purified product, with regards to the starting 1,7-dibromoheptane. Another route to the ethylenic diketone **6** consisted in the decarboxylation of the intermediate **3**, in order to obtain 11-bromo-3-undecanone (**7**) following a known analogous method.[6] Next, the alkylation of the β-keto ester **4** with the bromide **7**, followed by hydrolysis and decarboxylation, afforded the ethylenic diketone **6**. However, this route was found less satisfactory than the former one, which was less toilsome and gave higher yields of **6**.

Ozonolysis of the double bond of **6** in dichloromethane (in the presence of pyridine) at low temperature, followed by reduction of the intermediate ozonide with zinc in acetic acid, afforded the dioxo aldehyde **8** in about 80% yields of purified product. Selective condensation of nitroethane with the aldehydic carbonyl of **8** using potassium *t*-butoxide in a THF/ethanol mixture, gave the β-nitro alcohol **9** as a crystalline mixture of both erythro and threo diastereomers, and in about 80% yields of recrystallized product. The hydrogenation of the mixture of diastereomers **9** was next carried out in ethanol under a pressure of 3 bar, using a mixed catalyst composed of palladium (8%) and platinum (2%) deposited on charcoal. Thin-layer chromatography of the crude reaction product revealed the presence of compounds of high R_f values, together with the piperidinols **1a** and **1b** whose R_f's are very different. By column chromatography on silica

gel, we isolated 3,13-pentadecanedione (**10**) (30%) as well as a mixture of the 3-piperidinols **1a** and **1b** (40—50% yields). The dione **10** probably resulted from a palladium-catalyzed decarbonylation of the γ-keto aldehyde **8** liberated by retrocondensation of the β-nitro alcohols **9**. The above mixture of epimers **1a** and **1b** was easily separated by high-pressure liquid chromatography on an inversed-phase column and using aqueous methanol for the elution. This afforded (±)-prosafrinine (**1a**), mp 69—72 °C and (±)-3-epiprosafrinine (**1b**), mp 76—80 °C, whose structures were confirmed as indicated below.

In principle, four racemic diastereomers could be formed by reduction-cyclization of the mixture of the epimeric β-nitro alcohols **9** (Scheme 2). According to former studies from our laboratory,[7] the catalytic hydrogenation of compounds such as **9** generally yields 2,6-dialkyl-3-piperidinols of types **a** and **b** in which the groups at the positions 2 and 6 are *cis*-diequatorial. In the case of the epimer **a**, the axial hydroxyl can be intramolecularly bound with the lone pair of electrons on the nitrogen atom by hydrogen bonding, which is not possible in the case of the epimer **b** where the hydroxyl is equatorial. Until quite recently, both structures **a** and **b** could be identified essentially by two spectroscopic methods. The infrared spectrum of a dilute carbon tetrachloride solution shows, for the hydroxyl at the position 3, two absorption bands (free and associated OH) for **a** and a single band (free OH) for **b**.[8] On the other hand, the ^{1}H NMR signal of the equatorial carbinolic proton of **a** shows up as a peak whose half-height width is about 6 Hz, whereas the axial carbinolic proton of **b** gives a much flatter peak having a half-height width of about 20 Hz.[9]

Additional information was gained from the examination of the 300 MHz ^{1}H NMR spectra of the isomers **1a** and **1b**. In the case of prosafrinine (**1a**), the H-3 proton shows up as a peak at δ 3.71 whose half-height width is about 5 Hz. This poorly resolved signal having the coupling constants $J_{3\text{-}2,\,4ax,\,4eq} < 2$ Hz is characteristic of an equatorial proton, and its selective irradiation allowed the signals at δ 2.99 and 2.76 to be assigned to the H-2 and H-6 protons respectively.



Scheme 2.

Table 1. Characteristic ^{13}C NMR Data of Various 2,6-Dialkyl-3-piperidinols

		δ/ppm			
		C-2	C-3	C-6	C-7
a	**11a** R′=-CH_3	55.80	67.52	52.67	18.48
	12a R′=-$(CH_2)_{12}$-CO-CH_3 (±)-spectaline	57.24	67.90	55.81	18.61
	1a R′=-$(CH_2)_9$-CO-Et (±)-prosafrinine	57.27	67.59	55.92	18.16
b	**11b** R′=-CH_3	58.50	73.61	51.87	18.85
	1b R′=-$(CH_2)_9$-CO-Et (±)-3-epiprosafrinine	58.74	73.72	56.62	19.16

In the case of the epimer (**1b**), the H-3 proton shows up at δ 3.17 as a multiplet whose high coupling constants J_{3-2}=8.8 Hz and J_{3-4}=10.4 Hz are characteristic of trans-diaxal couplings. The selective irradiation of H-3 allowed the signals at δ 2.49, 2.04, and 1.32 to be assigned to the H-2, H-4eq, and H-4ax protons respectively, and made it possible the complete attribution of all the remaining protons of the piperidine ring. However, the H-6 proton at δ 2.52 could not be analyzed because of the overlap with the H-2 signal. The signals and chemical shifts we observed for **1a** and **1b** are in agreement with those reported for (−)-deoxocassine and 3-epideoxocassine, respectively.[3]

The information provided by the infrared and ^1H NMR spectra were confirmed and completed by the study of ^{13}C NMR spectra (see Table 1).

In the case of prosafrinine (**1a**), it can be seen that the C-3 carbon atom, which bears an axial hydroxyl, gives a signal at δ 67.59 whereas in the 3-epimer (**1b**) the same carbon atom (bearing an equatorial hydroxyl) gives a signal at δ 73.72 which corresponds to a difference $\Delta\delta$ =6.13 ppm. This difference has almost the same value in the case of the 2,6-dimethyl-3-piperidinols (**11a** and **11b**) ($\Delta\delta$ =6.09 ppm).[7] It can also be noticed that the C-7 carbon atom of the methyl groups (at the position 2 of the ring) has δ values ranging from 18.16 to 19.16 and which are therefore very close, in all the cases where this methyl group and the substituent at position 6 are cis-diequatorial. These various data confirm the all-cis structure of the epimers of type **a**.[10]

Experimental

The IR spectra were recorded with a Nicolet 5DX spectrophotometer. The NMR spectra were recorded with Varian EM 390 and Bruker 300 spectrometers for the proton, and Varian FT 80 or Jeol FX 90 Q spectrometers for ^{13}C. NMR spectra were run with samples in $CDCl_3$ solutions. TMS was the internal standard. Chemical shifts are expressed in ppm values (δ scale). Elemental analyses were carried out by the "Centre de Microanalyse du CNRS" (Lyon). Melting points were taken with a Reichert microscope. Thin layer chromatographies (TLC) were carried out using precoated silica gel plates. Preparative column chromatographies were carried out under pressure (1—3 bar) using Merck silica gel (Kieselgel 60). The following abbreviations are used: RP, reduced pressure; RT, room temperature; THF, tetrahydrofuran.

11-Bromo-4-ethoxycarbonyl-3-undecanone (3). To a solution of sodium ethoxide (2.42 g of sodium in 300 ml of anhydrous ethanol) cooled to 0 °C, ethyl 3-oxopentanoate (**2**; 14.4 g) was added dropwise, followed by NaI (100 mg). 1,7-Dibromoheptane (25.8 g) was then added and the mixture was refluxed under stirring for 24 h. The ethanol was removed under RP, the residue was acidified with 0.5 M H_2SO_4 (1 M=1 mol dm^{-3}) and was extracted with ether. The ethereal phase was washed with water until neutral, dried ($MgSO_4$) and evapored under RP. The crude compound (**3**; 29.2 g) was thus obtained in 91% yield, having bp 155—165 °C/0.1 mmHg (1 mmHg≈133.322 Pa). It was used without further purification in the next step; ^1H NMR δ=1.06 (6H, mult., $C\underline{H}_3$-CH_2), 1.33 (12H, -CH_2-), 2.56 (2H, -CH_2-CO), 3.30 (3H, -CH< and -CH_2Br), 4.26 (2H, q, CH_2-O-CO-); IR (film) 1743, 1713, 1186, 1028 cm^{-1}.

4,12-Bis(ethoxycarbonyl)-17-methyl-16-octadecene-3,13-dione (5). To a solution of sodium ethoxide (2.1 g of sodium in 100 ml of anhydrous ethanol) cooled to 0 °C, ethyl 7-methyl-3-oxo-6-octenoate (**4**; 18.01 g)[2] was added, followed by NaI (200 mg). After stirring for 30 min, a solution of crude 11-bromo-4-ethoxycarbonyl-3-undecanone (**3**; 29.2 g) in anhydrous ethanol (150 ml) was added dropwise, and the mixture was refluxed under stirring for 24 h. The ethanol was removed under RP, the residue was acidified with 0.5 M H_2SO_4 and was extracted with ether. The ether phase was washed with water until neutral, dried ($MgSO_4$) and evaporated under RP. The crude compound (**5**; 39.1 g) was thus obtained in 98% yield. It was used without purification in the next step; ^1H NMR δ=1.65 (6H, d, $(CH_3)_2$ C=C), 2.33 (4H, -CH_2-CO-), 3.46 (2H, tertiary CH), 4.20 (4H, q, -CH_2-OCO-), 5.05 (1H, ethylenic proton); IR (film) 1737, 1717, 1180, 1034 cm^{-1}.

17-Methyl-16-octadecene-3,13-dione (6). Crude 4,12-bis-(ethoxycarbonyl)-17-methyl-16-octadecene-3,13-dione (**5**; 39.4 g) was treated with barium hydroxide octahydrate (70 g) in water (1200 ml). After refluxing for 16 h under vigorous stirring, the mixture was cooled down, then acidified with HCl and stirred until complete dissolution of the barium salts. The mixture was then extracted with ether, the organic phase was washed with water, and was dried ($MgSO_4$) and evaporated under RP. The residue was crystallized from pentane, thus giving the purified diketone (**6**; 12.2 g) in 46% yield and as white crystals, mp 71—72 °C (pentane); ^1H NMR δ=1.05 (3H, t, $C\underline{H}_3$-CH_2-), 1.25 (14H, methylenes), 1.65 (6H, d, $(CH_3)_2$C=C-), 2.45 (10H, -CH_2-CO- and $C\underline{H}_2$-CH=C-), 5.0 (1H, ethylenic proton); IR (film) 1716 cm^{-1}; HRMS Found: 294.481; Calcd for $C_{19}H_{34}O_2$: 294.530.

11-Brom-3-undecanone (7). Crude 11-bromo-4-ethoxycarbonyl 3-undecanone (**3**; 14 g) in a mixture of propionic acid (35 ml) and 48% aqueous hydrobromic acid (50 ml) was refluxed for 2.5 h. After cooling, the mixture was added to ice and extracted with toluene. The organic phase was washed with water, dried ($MgSO_4$) and evapored under RP. Crystallization of the residue from pentane afforded the bromide (**7**; 6.5 g) in 60% yield and as white crystals, mp 17—18 °C (pentane); **7** is unstable and should be kept in the refrigerator; ^1H NMR δ=1.0 (3H, t, CH_3-), 1.33 (12H, -CH_2-), 2.30 (4H, -CH_2-CO-), 3.40 (2H, t, -CH_2-Br); IR (film) 1716, 1110, 731 cm^{-1}.

4,14-Dioxohexadecanal (8). Ozone was bubbled through a solution of 17-methyl-16-octadecene-3,13-dione (**6**; 2 g) in dichloromethane (500 ml) at −70 °C until persistence of a blue colour in the ozonolysis reactor. After purging for 5 min, the solution was added to zinc powder (3.4 g), followed by a slow addition of acetic acid (6.8 g) and the resulting mixture was magnetically stirred at RT for 3 h, at which time the peroxide test was found to be negative. The solids were filterd through celite and the filtrate was washed with water. The solution was dried ($MgSO_4$) and evapored under RP and the crystalline residue was chromatographed over silica gel. Elution with 95:5 CH_2Cl_2/ether afforded the dioxo aldehyde (**8**; 1.46 g) in 80% yield, mp 67—69 °C (ether/pentane); ^1H NMR δ=1.03 (2H, t, $C\underline{H}_3$-CH_2), 1.26 (14H, CH_2), 2.43 (8H, CH_2CO), 2.69 (4H, s HCO-$C\underline{H}_2C\underline{H}_2$CO-),

9.95 (1H, s, CHO); ^{13}C NMR δ=211.59 (C-14), 208.67 (C-4), 200.27 (C-1), 42.75 (C-5), 42.40 (C-13), 37.54 (C-2), 35.85 (C-15), 34.70 (C-3), 29.29 (C-7 to C-11), 23.94 (C-6 and C-12), 7.87 (C-16); IR (film) 1712, 1420, 823 cm^{-1}; HRMS Found: 268.2033; Calcd for $C_{16}H_{28}O_3$: 268.2038; Found: C, 71.25; H, 10.29; O, 17.84%. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.51; O, 17.88%.

16-Hydroxy-17-nitro-3, 13-octadecanedione (9). (Erythro and Threo Isomers). To a solution of potassium *t*-butoxide (0.446 g) in anhydrous ethanol (1 ml) and anhydrous THF (10 ml), a solution of nitroethane (0.343 g) in anhydrous THF (20 ml) was added dropwise. Then a solution of 4,14-dioxohexadecanal (**8**; 0,97 g) in anhydrous THF (20 ml) was added dropwise and the reaction mixture was stirred at RT for 14 h. The potassium salt was destroyed by addition of acetic acid (0.24 g) in THF (5 ml), followed by water (1 ml). The solids were removed by filtration and the solution was dried ($MgSO_4$) and evapored under RP at RT, thus leaving a white crystalline product in quantitative yield. Recrystallization of the latter from ether afforded the mixture of isomers **9** (1 g) in 80% yield, mp 75—76 °C (ether); ^{1}H NMR δ=1.04 (3H, t, C$\underline{H}_3$-CH_2), 1.27 (14H, broad peak, -CH_2-), 1.56 (3H, d, C$\underline{H}_3$-CH-), 2.26 to 2.83 (8H, -CH_2-CO-), 3.0 (1H, -OH), 4.1 (1H, m, -C$\underline{H}$OH), 4.6 (1H, CH-NO_2); IR (film) 3849, 1709, 1559, 1116, 972, 822 cm^{-1}; Found: C, 62.67; H, 9.84; O, 23.35; N, 4.14%. Calcd for $C_{18}H_{33}NO_5$: C, 62.94; H, 9,68; O, 23.29; N, 4.07%.

Hydrogenation of β-Nitro Alcohols (9). (±)-Prosafrnine (1a) and (±)-3-Epiprosafrinine (1b). The hydrogenation was carried out in a Parr apparatus. 16-Hydroxy-17-nitro-3,13-octadecanedione (**9**; 0.73 g) in 95% ethanol (80 ml), and in the presence of a mixed palladium (8%)-platinum (2%) on charcoal catalyst, was hydrogenated under 3 bars at 30 °C for 14 h. After filtration of the catalyst through Celite and evaporation of the solvent under RP, a crude product (0.63 g) was obtained, and whose IR spectrum did not contain a nitro band. TLC over silica gel using 30 : 9 : 1 AcOMe/MeOH/15 M aqueous NH_3 as eluent revealed the presence of compounds of high R_f values and two distinct spots at R_f 0.72 and 0.41 corresponding to **1a** and **1b** respectively. The product was chromatographed on a column of silica gel (Merck, 230—400 mesh) using CH_2Cl_2/EtOH/15 M aqueous NH_3 (100 : 10 : 1) as eluent, to give a mixture (0.23 g) of (±)-prosafrinine (**1a**) and (±)-3-epiprosafrinine (**1b**) after elimination of less polar head fractions; HRMS of the mixture $[M-C_2H_5]^+$: Found: 268.2287; Calcd: 268.2276; among the head fractions, 3,13-pentadecanedione (**10**) was isolated as a white crystalline solid, mp 78—80 °C (ether), which was characterized as follows; ^{1}H NMR δ=1.06 (6H, t, C$\underline{H}_3$-CH_2), 1.27 (10H, broad peak, -CH_2-), 1.60 (4H, -CH_2CH_2CO-), 2.40 (8H, m, -CH_2-CO-): ^{13}C NMR δ=211.35 (C-3 and C-13), 42.38 (C-4 and C-12), 35.82 (C-2 and C-14), 29.43 and 29.33 (C-6 to C-10), 23.97 (C-5 and C-11), 7.84 (C-1 and C-15): IR (film) 1708, 1701, 1420, 1104, 823 cm^{-1}; HRMS Found: 240.2112; Calcd: 240.2089.

The separation of the mixture of epimers **1a** and **1b** was carried out by high-pressure liquid chromatography on an inversed-phase column (Bondapack Waters C_{18}, 7.8 mm×30 cm, 2 ml min^{-1}) and using MeOH/H_2O (90 : 10) for the elution. Thus, starting from a solution of the mixture of **1a** and **1b** (250 mg in 1 ml of 90 : 10 MeOH/H_2O), each 100 µl injection afforded (±)-3-epiprosafrinine (**1b**; 12 mg) and (±)-prosafrinine (**1a**; 9 mg). (±)-3-Epi-prosafrinine (**1b**): mp 76—80 °C (acetone/pentane); ^{1}H NMR (300 MHz) δ=1.05 (3H, t, $J_{12'-11'}$=7.4 Hz, CH_3-12'), 1.18 (1H, m, $J_{5ax-4eq}$=3.6 Hz, $J_{5ax-6ax}\approx$11.5 Hz, $J_{ab}\approx J_{5ax-4ax}$=13.1 Hz, H-5ax), 1.21 (3H, d, J_{7-2}=6.2 Hz, CH_3-7), 1.28 (14H, s, CH_2-1' to 7'), 1.32 (1H, m, $J_{4ax-5eq}$=3.8 Hz, J_{4ax-3}=10.5 Hz, $J_{AB}\approx J_{4ax-5ax}$=13.4 Hz, H-4ax), 1.56 (1H, m, CH_2-8'), 1.75 (1H, dq, $J_{5eq-4eq,\,4ax,\,6}\approx$3.0 Hz, J_{AB}=12.5 Hz, H-5eq), 1.81 (2H, large s, OH and NH), 2.04 (1H, dq, $J_{4eq-3,\,5eq,\,5ax}\approx$3.5 Hz, J_{AB}=12.0 Hz, H-4eq), 2.39 (2H, t, $J_{9'-8'}$=7.4 Hz, CH_2-9'), 2.42 (2H, q, $J_{11'-12'}$=7.4 Hz, CH_2-11'), 2.49 (1H, m, H-2), 2.52 (1H, m, H-6), 3.17 (1H, ddd, J_{3-4eq}=4.4 Hz, J_{3-2}=8.8 Hz, J_{3-4ax}=10.4 Hz, H-3); ^{13}C NMR δ=212.13 (C-10'), 73.72 (C-3), 58.74 (C-2), 56.62 (C-6), 42.54 (C-9'), 36.64 (C-1'), 35.96 (C-11'), 34.28 (C-4), 31.79 (C-5), 29.85, 29.59, 29.51, 29.37 (C-3' to C-7'), 26.34 (C-2'), 24.07 (C-8'), 19.16 (C-7), 8.01 (C-12'); IR (film) 3261, 3120, 1713, 1113, 1044 cm^{-1}. (±)-Prosafrinine (**1a**): mp 69—72 °C (acetone/pentane); ^{1}H NMR (300 MHz) δ=1.05 (3H, t, $J_{12'-11'}$=7.3 Hz, CH_3-12'), 1.26 (18H, s, CH2-1' to 7'), 1.32 (3H, d, J_{7-2}=6.5 Hz, CH_3-7), 1.56 (m, CH_2-8'), 1.45 to 1.8 (m, H-4ax and CH_2-5), 1.99 (1H, m, H-4eq), 2.39 (2H, t, $J_{9'-8'}$=7.4 Hz, H-9'), 2.42 (2H, q, $J_{11'-12'}$=7.3 Hz, H-11'), 2.76 (1H, m, H-6), 2.99 (1H, q, J_{2-7}=6.3 Hz, H-2), 3.71 (1H, s, H-3), in agreement with the literature;[1,3] ^{13}C NMR δ=211.83 (C-10'), 67.59 (C-3), 57.27 (C-2), 55.92 (C-6), 42.35 (C-9'), 36.34 (C-1'), 35.79 (C-11'), 31.84 (C-4), 29.64, 29.45, 29.32, and 29.11 (C-3' to C-7'), 25.69 (C-5), 25.39 (C-2'), 23.90 (C-8'), 18.16 (C-7), 7.71 (C-12'); IR (film) 3302, 1713, 1107, 1000, 913, 863 cm^{-1}; IR (in dilute CCl_4 solution) 3640 (free OH), 3540 (bound OH) cm^{-1}, $\varepsilon_{ass}/\varepsilon_{free}$: 2.

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