Sucrose Esters from the Fruits of *Physalis nicandroides* var. *attenuata*

Emma Maldonado,*,† Fernando R. Torres,† Mahinda Martínez,‡ and Ana L. Pérez-Castorena†

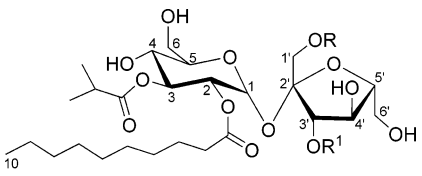
Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, 04510, D. F., México, and Facultad de Ciencias Naturales, Universidad Autónoma de Querétaro, Cerro de las Campanas s. n., Querétaro, México

Received June 9, 2006

Three 2,3,1′,3′-tetraacyl- and two 2,3,3′-triacylsucroses, nicandroses A−E (**1**−**5**), were isolated from the fruits of *Physalis nicandroides* var. *attenuata*. The acyl groups in these new compounds were identified as decanoyl, isobutyryl, 2-methylbutanoyl, and acetyl. The structures of **1**−**5** were determined on the basis of NMR and MS analyses.

Physalis and other Solanaceae genera (e.g., *Acnistus*, *Datura*, *Iochroma*, *Withania*, *Nicandra*) are known to produce withasteroids, a group of polyoxygenated C_{28}-ergostane lactone derivatives with a diversity of biological activities.[1] In *Physalis* species withasteroids have been mainly isolated from leaves and stems and occasionally from roots,[2] fruits,[3] and calices.[4] This is probably due to the fact that phytochemical studies have been focused on foliage, neglecting other parts of the plants, or due to a poor presence of withasteroids in other organs. Reports on the composition of *Physalis* fruits describe the presence of disaccharides[5,6] and calystegins[7] in *P. peruviana* and withanolides in *P. philadelphica*.[3] Recently, the first acyl sucrose in the genus was isolated from *P. viscosa*.[8] As part of our systematic studies on *Physalis* species,[9,10] we describe herein the isolation and characterization of five new acyl sucroses, nicandroses A−E (1−**5**), from the fruits of *P. nicandroides* Schltdl. var. *attenuata* Waterf., a plant used as an insecticide in some regions of Mexico.[11] Sucrose esters have been isolated from the Solanaceae genera *Nicotiana*,[12] *Petunia*,[13] *Solanum*,[14] and *Lycopersicon*,[15] as well as from the Asteraceae,[16] Cannaceae,[17] and Polygalaceae[18] families. This is the second report on its occurrence in *Physalis*. Sucrose esters of the Solanaceae have exhibited aphicidal,[19] molluscicidal,[13] and antibacterial[10,13] activities.

Chromatographic purification of the EtOAc-soluble fraction of the methanolic extract of the blended fruits of *P. nicandroides* provided sucrose ester mixtures I and II. Preparative reversed-phase TLC led to the isolation of nicandroses A (**1**), B (**2**), and C (**3**) from mixture I and nicandroses D (**4**) and E (**5**) from mixture II. The known compounds 4′,5-dihydroxy-3,7-dimethoxyflavone (kumatakenin)[20,21] and 1-*O*-(*p*-hydroxybenzoyl)-*β*-D-glucopyranose[22] were also isolated.



1 R = R^1 = 2-methylbutanoyl
2 R = Ac, R^1 = isobutyryl
3 R = Ac, R^1 = 2-methylbutanoyl
4 R = H, R^1 = isobutyryl
5 R = H, R^1 = 2-methylbutanoyl

Nicandrose A (**1**) was isolated as an amorphous powder. The positive FABMS showed a quasi-molecular ion peak at *m*/*z* 757 $[M + Na]^+$, consistent with the molecular formula $C_{36}H_{62}O_{15}$. The IR spectrum exhibited strong absorptions for hydroxyl (3455 cm^{-1}) and saturated ester functions (1749 cm^{-1}). Twelve signals between *δ* 59 and 103 in the ^{13}C NMR spectrum, which were assigned (by DEPT) to seven oxymethynes, three oxymethylenes, one anomeric methyne (*δ* 89.6), and one nonprotonated anomeric carbon (*δ* 102.2), were indicative of a disaccharide. The ^{1}H NMR signals and the connectivities observed in the ^{1}H−^{1}H COSY spectrum revealed both a pyranose and a furanose as the monomers of the disaccharide. The pyranose was identified as α-glucopyranose by the observed coupling constants ($J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10 Hz, $J_{3,4} = J_{4,5}$ = 9.5 Hz), while the $J_{3',4'} = J_{4',5'}$ = 8.5 Hz and the respective AB and ABX patterns for CH_2-1′ and CH_2-6′ characterized the furanose as a *β*-fructofuranose. The HMBC correlation from H-1 of glucose (*δ* 5.55) to C-2′ of fructose (*δ* 102.2) completed the identification of the disaccharide as sucrose. The low-field shifts of the H-2, H-3, CH_2-1′, and H-3′ signals and the presence of carbonyl signals at *δ* 178.3, 176.9, 175.6, and 173.0 were consistent with a 2,3,1′,3′-tetra-*O*-acylsucrose. FABMS, ^{1}H, ^{13}C, COSY, and HMBC spectra allowed identification of the acyl groups as decanoyl (*m*/*z* 155), isobutyryl (*m*/*z* 71), and two 2-methylbutanoyls (*m*/*z* 85). The positions of these groups were established by the HMBC correlations from H-2 to C-1 (*δ* 173.0) of decanoyl, H-3 to C-1 (*δ* 178.3) of isobutyryl, CH_2-1′ to C-1 (*δ* 175.6) of one of the 2-methylbutanoyl groups, and H-3′ to C-1 (*δ* 176.9) of the other one. The FABMS fragment at *m*/*z* 387 supported the proposed substitution of the pyranose, while the fragment at *m*/*z* 331 was consistent with two 2-methylbutanoyl moieties at the furanose ring, thus confirming nicandrose A (**1**) as 2-*O*-decanoyl-3-*O*-isobutyryl-1′,3′-di-*O*-2-methylbutanoylsucrose.

The molecular formulas $C_{32}H_{54}O_{15}$ for nicandrose B (**2**) and $C_{33}H_{56}O_{15}$ for nicandrose C (**3**) derived from the quasi-molecular ion peaks, $[M + Na]^+$, at *m*/*z* 701 (**2**) and *m*/*z* 715 (**3**), which were observed in their respective FABMS. A fragment at *m*/*z* 387 was present in both mass spectra, thus indicating, as in compound **1**, isobutyryl and decanoyl moieties attached to the pyranose rings of **2** and **3**. Analysis of the NMR data led us to identify the acetyl and isobutyryl moieties as the acyl groups bonded to the furanose of compound **2**, and the acetyl and 2-methylbutanoyl moieties in compound **3**. Finally, on the basis of the observed HMBC correlations, the structure of nicandrose B (**2**) was formulated as 1′-*O*-acetyl-2-*O*-decanoyl-3,3′-di-*O*-isobutyrylsucrose and that of nicandrose C (**3**) as 1′-*O*-acetyl-2-*O*-decanoyl-3-*O*-isobutyryl-3′-*O*-2-methylbutanoylsucrose. Supporting the above-mentioned, the alkaline hydrolysis of mixture I gave sucrose (identified by TLC, $[\alpha]_D$, ^{1}H and ^{13}C NMR) and a mixture of acids.

The more polar of the new compounds were nicandroses D (**4**) and E (**5**). The molecular formulas of **4** ($C_{30}H_{52}O_{14}$) and **5** ($C_{31}H_{54}O_{14}$) were determined from the positive FABMS ion peaks at *m*/*z* 659 $[M + Na]^+$ and 673 $[M + Na]^+$, respectively. Both compounds showed three carbonyl signals in their ^{13}C NMR spectra, and in their ^{1}H NMR spectra the CH_2-1′ signals appeared at higher

* Corresponding author. Phone: + 52-55-56224412. Fax: + 52-55-56162217. E-mail: emmaldon@servidor.unam.mx.
† Instituto de Química, Universidad Nacional Autónoma de México.
‡ Facultad de Ciencias Naturales, Universidad Autónoma de Querétaro.

10.1021/np060274l CCC: $33.50
Published on Web 10/12/2006

Table 1. ^{1}H NMR Data (δ, 500 MHz, $CDCl_3$) for Nicandroses A−E (**1**−**5**)

H	1	2	3[a]	4	5
1	5.55 d (3.5)	5.56 d (3.5)	5.55 d (3.7)	5.55 d (3.5)	5.55 d (4)
2	4.96 dd (10, 3.5)	4.92 dd (10, 3.5)	4.93 dd (10, 3.7)	4.88 dd (10.5, 3.5)	4.91 dd (10.5, 4)
3	5.14 dd (10, 9.5)	5.18 dd (10, 9.5)	5.15 dd (10, 9.5)	5.22 dd (10.5, 9.5)	5.18 dd (10.5, 9.5)
4	3.54 t (9.5)	3.55 t (9.5)	3.52 t (9.5)	3.54 t (9.5)	3.53 t (9.5)
5	4.06 m[b]	4.05 m[b]	4.02 m[b]	4.04 ddd (10, 6, 2.5)	4.05 ddd (9.5, 6, 2)
6a	3.97 br d (12.5)	3.96 dd (12, 2)	3.95 m[b]	3.97 dd (12, 2)	3.98 br d (12)
6b	3.75 dd (12.5, 6)	3.75 dd (12, 6)	3.74 m[b]	3.75 dd (12, 6)	3.75 dd[b] (12, 6)
1a′	4.04 d (11.5)	4.06 d (12)	4.05 d (11.7)	3.58 d (12.5)	3.56 d (12)
1b′	3.91 d (11.5)	3.93 d (12)	3.89 d (11.7)	3.49 d (12.5)	3.46 d[b] (12)
3′	5.27 d (8.5)	5.24 d (9)	5.28 d (8.7)	5.19 d (8)	5.21 d (8.5)
4′	4.62 t (8.5)	4.60 t (9)	4.60 t (8.7)	4.52 t (8)	4.58 t (8.5)
5′	3.90 m[b]	3.93 m[b]	3.95 m[b]	3.94 m[b]	3.93 m[b]
6a′	3.93 br d[b] (11.5)	3.93 m[b]	3.95 m[b]	3.91 br d[b] (13)	3.92 d[b] (12.5)
6b′	3.72 d (11.5)	3.72 d (13.5)	3.74 m[b]	3.75 d[b] (13)	3.74 d[b] (12.5)
2-O-			decanoyl		
2a	2.37 dt (16, 7.5)	2.36 dt (16, 7.5)	2.35 dt (16, 7.5)	2.28 dt (16, 8)	2.28 dt (16, 7.5)
2b	2.29 dt (16, 7.5)	2.29 dt (16, 8)	2.27 dt (16, 7.5)	2.23 dt (16, 8)	2.23 dt (16, 7.5)
3	1.58 m[b]	1.57 m	1.56 m[b]	1.55 qnt[c] (7.5)	1.57 m[b]
4−9	1.27 m[b]	1.25 m[b]	1.25 m[b]	1.26 m[b]	1.25 m[b]
10	0.88 t (7)	0.88 t (7)	0.88 t (7)	0.88 t (7)	0.88 t (7)
3-O-			isobutyryl		
2	2.57 hept[d] (7)	2.57 hept (7)	2.56 hept (7)	2.56 hept (7)	2.56 hetp (7)
3	1.17 d (7)	1.16 d (7)	1.16 d (7)	1.15 d (7)	1.15 d (7)
4	1.16 d (7)	1.15 d (7)	1.14 d (7)	1.13 d (7)	1.14 d (7)
1′-O-	2-methylbutanoyl	acetyl	acetyl		
2	2.43 hept (7)	2.10 s	2.11 s		
3a	1.70 dqnt[c] (14, 7.5)				
3b	1.52 dqnt[c] (14, 7.5)				
4	0.93 t (7.5)				
5	1.14 d (7)				
3′-O-	2-methylbutanoyl	isobutyryl	2-methylbutanoyl	isobutyryl	2-methylbutanoyl
2	2.58 sext[e] (7)	2.74 hept (7)	2.58 sext (7)	2.74 hept (7)	2.58 sext (7.5)
3a	1.78 dqnt (14, 7.5)	1.30 d (7)	1.78 dqnt (14, 7)	1.28 d (7)	1.78 dqnt (14, 7)
3b	1.62 dqnt (14, 7.5)	1.26 d (7)	1.60 dqnt (14, 7.5)	1.25 d (7)	1.60 dqnt (14, 7.5)
4	0.97 t (7.5)		0.97 t (7.5)		0.97 t (7.5)
5	1.24 d[b] (7)		1.23 d[b] (7)		1.24 d[b] (7)

[a] Determined at 300 MHz. [b]Superimposed signal. [c] qnt = quintuplet. [d] hept = heptuplet. [e] sext = sextet.

field (**4**: δ 3.58 and 3.49; **5**: δ 3.56 and 3.46) than the corresponding CH_2-1′ signals of **1**−**3** (δ ~4.05 and ~3.91). Analysis of their NMR data, including the HMBC spectra, together with the FABMS fragments at *m*/*z* 387 and 233 for **4** and *m*/*z* 387 and 247 for **5**, allowed us to formulate **4** as 2-*O*-decanoyl-3,3′-di-*O*-isobutyrylsucrose and **5** as 2-*O*-decanoyl-3-*O*-isobutyryl-3′-*O*-2-methylbutanoylsucrose.

We have observed, after preliminary analysis of several *Physalis* species, that acylsucroses are the main constituents of the resin covering fruits and inner parts of the calices, whereas in other parts of the plant they are scarce. This and the aphicidal, molluscicidal, and antifeedant activities exhibited by other known sucrose esters suggest a protective role for these compounds.

Experimental Section

General Experimental Procedures. Vacuum column chromatography (VCC) was performed on silica gel 60 (Merck G), while silica gel 230−400 mesh (Macherey-Nagel) was used for flash chromatography. TLC was carried out on precoated Macherey-Nagel Sil G/UV_{254} plates of 0.25 mm thickness or Alugram RP-18 W/UV_{254} plates of 0.15 mm thickness. Spots were visualized by spraying with 3% $CeSO_4$ in 2 N H_2SO_4 followed by heating. Preparative TLC was carried out on precoated Macherey-Nagel Sil RP-18W/UV_{254} plates of 1.0 mm thickness. Optical rotations were measured on a Perkin-Elmer 343 polarimeter. The IR spectra were recorded on a Bruker Tensor 27 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded either on a Varian Unity Plus 500 (^{1}H at 500 MHz; ^{13}C at 125 MHz) or on a Varian Unity (^{1}H at 300 MHz; ^{13}C at 75 MHz) spectrometer, with TMS as internal standard. Positive mode FABMS (*m*-nitrobenzyl alcohol−sodium matrix) and HRFABMS (polyethylene glycol 600 as standard) were measured on a JEOL JMS-SX102A spectrometer.

Plant Material. Ripe fruits of *Physalis nicandroides* var. *attenuata* Waterf. were collected in Tlayacapan, State of Morelos, Mexico, in November 2003. A voucher specimen of the plant (M. Martínez s/n) was identified by one of us (M.M.) and deposited at the Herbarium of the Universidad Autónoma de Querétaro.

Extraction and Isolation. The fruits (without calices) were blended and extracted with MeOH to give 137 g of extract. This extract was partitioned with MeOH−H_2O (4:1) (1 L), hexane (300 mL, × 3), and then H_2O (1 L)−EtOAc (300 mL, × 3) to obtain the hexane (9.6 g), EtOAc (44 g), and H_2O (70 g) fractions. The EtOAc fraction was fractionated by VCC (column A) eluted with hexane−EtOAc (4:6 fractions A1−A50; 3:7 fractions A51−A54; 0:10 fractions A55−A60). VCC (hexane−EtOAc 3:1) of fractions A1−A3 yielded 16.2 mg of kumatakenin (mp 254−257 °C, MeOH, uncorrected; lit.[20] mp 253−254 °C). Fractions A4−A9 contained a mixture (I), as deduced from an elonged and nonhomogeneous spot (R_f 0.32) on TLC (silica gel, hexane−Me_2CO, 7:3, 3 runs). A similar spot (R_f 0.22) was exhibited by fractions A18−A32, indicating the presence of a more polar mixture (II). Fractions A10−A17 contained both mixtures, which were purified by VCC (hexane−Me_2CO, 7:3). A total of 11.8 g of I and 9.21 g of II were obtained. Mixture I, obtained after VCC (hexane−Me_2CO−MeOH, 75:25:2) of fractions A4−A9, was fractionated on a silica gel column eluted with hexane−Me_2CO−MeOH, 7:3:0.1 (column B, fractions B1−B26). Fraction B4 contained mixture I enriched with the less polar constituent (**1**). A portion of this fraction (81.1 mg) was subjected to preparative TLC (RP-18, EtOH−H_2O, 1:1, 8 runs) to afford **1** (12 mg). Fractions B10−B16 contained mixture I enriched with **2** and **3**. Preparative TLC (RP-18, MeOH−H_2O, 3:2, 5 runs) of this mixture (83.7 mg) gave **2** (18.2 mg) and **3** (12.9 mg). Mixture II was purified by flash chromatography (hexane−Me_2CO−MeOH, 6:4:0.1). Then 117.9 mg of this mixture was subjected to preparative TLC (RP-18, MeOH−H_2O, 3:2, 3 runs), to obtain pure **4** (19.9 mg) and **5** (33.8 mg). 1-*O*-(*p*-Hydroxybenzoyl)-β-D-glucopyranose (16.2 mg) was obtained after crystallization from fractions A55−A58 (mp 234 °C, MeOH, uncorrected; lit.[22] mp 228 °C, MeOH).

Nicandrose A (1): amorphous solid; $[\alpha]^{20}_D$ +17.04 (*c* 0.27, $CHCl_3$); IR (film) ν_{max} 3455, 1749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) see Table

Table 2. ^{13}C NMR Data (δ, 125 MHz, $CDCl_3$) for Nicandroses A−E (**1**−**5**)

position	**1**	**2**	**3**[a]	**4**	**5**
1 CH	89.6	89.7	89.8	89.7	89.6
2 CH	69.2	69.4	69.4	69.8	69.6
3 CH	73.3	73.0	73.3	72.7	73.0
4 CH	70.0	69.9	70.1	71.2	70.0
5 CH	74.7	74.5	74.5	73.9	74.2
6 CH_2	62.3	62.3	62.3	62.3	62.3
1′ CH_2	63.8	64.5	64.4	64.3	64.4
2′ C	102.2	102.1	102.2	103.9	103.7
3′ CH	78.3	78.6	78.4	79.0	78.6
4′ CH	70.4	70.7	70.7	69.9	70.7
5′ CH	82.3	82.3	82.4	82.3	82.2
6′ CH_2	59.4	59.5	59.6	60.1	59.8
2-O-			decanoyl		
1 C	173.0	173.1	173.0	173.0	172.9
2 CH_2	34.0	33.9	34.0	33.9	34.1
3 CH_2	24.6	24.6	24.6	24.6	24.6
4 CH_2	29.1[b]	29.1[b]	29.1[b]	29.1[b]	29.1[b]
5,6 CH_2	29.2[b]	29.2[b]	29.2[b]	29.2[b]	29.2[b]
7 CH_2	29.4[b]	29.3[b]	29.4[b]	29.3[b]	29.4[b]
8 CH_2	31.8	31.8	31.8	31.8	31.8
9 CH_2	22.6	22.6	22.6	22.6	22.6
10 CH_3	14.1	14.0	14.0	14.1	14.1
3-O			isobutyryl		
1 C	178.3	178.1	178.1	177.9	178.1
2 CH	34.1	34.1	34.1	34.05	34.1
3 CH_3	18.9	18.9	18.9	18.9	18.9
4 CH_3	18.7	18.7	18.8	18.8	18.7
1′-O-	2-MeBu[c]	Ac	Ac		
1	175.6, C	170.0, C	170.0, C		
2	40.9, CH	20.6, CH_3	20.6, CH_3		
3	26.7, CH_2				
4	11.5, CH_3				
5	16.5, CH_3				
3′-O-	2-MeBu	*i*-Bu[d]	2-MeBu	*i*-Bu	2-MeBu
1	176.9, C	177.4, C	176.9, C	178.0, C	177.7, C
2	40.8, CH	33.9, CH	40.9, CH	33.9, CH	40.8, CH
3	26.9, CH_2	19.2, CH_3	26.9, CH_2	19.2, CH_3	26.9, CH_2
4	11.46, CH_3	18.7, CH_3	11.4, CH_3	18.7, CH_3	11.4, CH_3
5	16.4, CH_3		16.3, CH_3		16.3, CH_3

[a] Determined at 75 MHz. [b] Signals may be interchanged. [c] 2-MeBu = 2-methylbutanoyl. [d] *i*-Bu = isobutyryl.

1; ^{13}C NMR ($CDCl_3$, 125 MHz) see Table 2; FABMS (positive) *m*/*z* 757 $[M + Na]^+$ (7), 387 $[C_{20}H_{35}O_7]^+$ (5), 331 $[C_{16}H_{27}O_7]^+$ (29), 181 $[C_6H_{13}O_6]^+$ (16), 155 $[C_{10}H_{19}O]^+$ (28), 127 $[C_9H_{19}]^+$ (18), 85 $[C_5H_9O]^+$ (55), 71 $[C_4H_7O]^+$ (56), 57 $[C_4H_9]^+$ (100), 43 $[C_3H_7, CH_3CO]^+$ (82); HRFABMS *m*/*z* 757.3997 $[M + Na]^+$ (calcd for $C_{36}H_{62}O_{15}$ + Na, 757.3986).

Nicandrose B (2): amorphous solid; $[\alpha]^{20}_D$ +36.96 (*c* 0.23, $CHCl_3$); IR (film) ν_{max} 3456, 1746 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz) see Table 2; FABMS (positive) *m*/*z* 701 $[M + Na]^+$, (77), 387 $[C_{20}H_{35}O_7]^+$ (10), 275 $[C_{12}H_{19}O_7]^+$ (47), 215 $[275 - AcOH]^+$ (8), 181 $[C_6H_{13}O_6]^+$ (8), 155 $[C_{10}H_{19}O]^+$ (56), 127 $[C_9H_{19}]^+$ (22), 71 $[C_4H_7O]^+$ (63), 57 $[C_4H_9]^+$ (58), 43 $[C_3H_7, CH_3CO]^+$ (100); HRFABMS *m*/*z* 701.3359 $[M + Na]^+$ (calcd for $C_{32}H_{54}O_{15}$ + Na, 701.3360).

Nicandrose C (3): amorphous solid; $[\alpha]^{20}_D$ +41.43 (*c* 0.28, $CHCl_3$); IR (film) ν_{max} 3459, 1746 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz) see Table 2; FABMS (positive) *m*/*z* 715 $[M + Na]^+$, (9), 387 $[C_{20}H_{35}O_7]^+$ (12), 289 $[C_{13}H_{21}O_7]^+$ (8), 247 $[C_{11}H_{19}O_6]^+$ (97), 181 $[C_6H_{13}O_6]^+$ (57), 155 $[C_{10}H_{19}O]^+$ (77), 127 $[C_9H_{19}]^+$ (33), 85 $[C_5H_9O]^+$ (80), 69 $[C_4H_5O]^+$ (43), 57 $[C_4H_9]^+$ (100), 43 $[C_3H_7, CH_3CO]^+$ (63); HRFABMS *m*/*z* 715.3522 $[M + Na]^+$ (calcd for $C_{33}H_{56}O_{15}$ + Na, 715.3517).

Nicandrose D (4): amorphous solid; $[\alpha]^{20}_D$ +55.0 (*c* 0.22, $CHCl_3$); IR (film) ν_{max} 3422, 1740 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz) see Table 2; FABMS (positive) *m*/*z* 659 $[M + Na]^+$ (19), 387 $[C_{20}H_{35}O_7]^+$ (7), 233 $[C_{10}H_{17}O_6]^+$ (52), 215 $[C_{10}H_{15}O_5]^+$ (8), 155 $[C_{10}H_{19}O]^+$ (40), 127 $[C_9H_{19}]^+$ (18), 71 $[C_4H_7O]^+$ (73), 57 $[C_4H_9]^+$ (37), 43 $[C_3H_7]^+$ (100); HRFABMS *m*/*z* 659.3248 $[M + Na]^+$ (calcd for $C_{30}H_{52}O_{14}$ + Na, 659.3255).

Nicandrose E (5): amorphous solid; $[\alpha]^{20}_D$ +30.56 (*c* 0.23, $CHCl_3$); IR (film) ν_{max} 3401, 1764 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz) see Table 2; FABMS (positive) *m*/*z* 673 $[M + Na]^+$, (75), 387 $[C_{20}H_{35}O_7]^+$ (12), 247 $[C_{11}H_{19}O_6]^+$ (29), 181 $[C_6H_{13}O_6]^+$ (57), 155 $[C_{10}H_9O]^+$ (27), 85 $[C_5H_9O]^+$ (50), 71 $[C_4H_7O]^+$ (54), 69 $[C_4H_5O]^+$ (63), 57 $[C_4H_9]^+$ (100), 43 $[C_3H_7]^+$ (85); HRFABMS *m*/*z* 673.3401 $[M + Na]^+$ (calcd for $C_{31}H_{54}O_{14}$ + Na, 673.3411).

Alkaline Hydrolysis of Mixture I. A solution of mixture I (105.1 mg) in 2 M NH_4OH (4 mL) was heated at 45 °C for 4 h. The reaction mixture was acidified (pH 4) with 2 M formic acid and extracted with EtOAc to give 53.5 mg of the acid mixture. The aqueous phase was dried in vacuo to afford 45.4 mg of syrup identified as sucrose.

Acknowledgment. We are very grateful to H. Ríos and B. Quiroz for the NMR experiments. We also thank E. García for the IR and polarimetric determinations, L. Velasco and J. Pérez for the MS, and G. Salcedo for her assistance. We thank CONACyT for financial support (Project 34993-N).

Supporting Information Available: ^1H NMR spectra of nicandroses A−E (**1**−**5**) are available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ray, A. B.; Gupta, M. In *Progress in the Chemistry of Organic Natural Products*; Herz, W., Kirby, G. W., Moore, R. E., Steglich, W., Tamm, Eds.; Springer-Verlag: Wien, 1994; Vol. 63, pp 1−106.
(2) Neogi, P.; Sahai, M.; Ray, A. B. *Phytochemistry* **1987**, *26*, 243−247.
(3) Kennelly, E. J.; Gerhäuser, C.; Song, L. L.; Graham, J.; Beecher, C. W. W.; Pezutto, J. M.; Kinghorn, D. A. *J. Agric. Food Chem.* **1997**, *45*, 3771−3777.
(4) Dinan, L. N.; Sarker, S. D.; Šik, V. *Phytochemistry* **1997**, *44*, 509−512.
(5) Latza, S.; Gansser, D.; Berger, R. G. *Phytochemistry* **1996**, *43*, 481−485.
(6) Mayorga, L.; Duque, C.; Knapp, H.; Winterhalter, P. *Phytochemistry* **2002**, *59*, 439−445.
(7) Asano, N.; Kato, A.; Matsui, K.; Watson, A. A.; Nash, R. J.; Molyneux, R. J.; Hackett, L.; Topping, J.; Winchester, B. *Glycobiology* **1997**, *7*, 1085.
(8) Ovenden, S. P. B.; Yu, S.; Bernays, J.; Wan, S. S.; Christophidis, L. J.; Sberna, G.; Murray Tait, R.; Wildman, H. G.; Lebeller, D.; Lowther, J.; Walsh, N. G.; Meurer-Grimes, B. M. *J. Nat. Prod.* **2005**, *68*, 282−284.
(9) Maldonado, E.; Alvarado, V. A.; Torres, F. R.; Martínez, M.; Pérez-Castorena, A. L. *Planta Med.* **2005**, *71*, 548−553.
(10) Pérez-Castorena, A. L.; Oropeza, R. F.; Vázquez, A. R.; Martínez, M.; Maldonado, E. *J. Nat. Prod.* **2006**, *69*, 1029−1033.
(11) Casas, A.; Viveros, J. L.; Caballero, J. *Etnobotánica Mixteca*; Sociedad, Cultura y Recursos Naturales en la Montaña de Guerrero; Dirección General de Publicaciones del Consejo Nacional para la Cultura y las Artes/Instituto Nacional Indigenista: México, D. F., 1994; p 306.
(12) Wahlberg, I.; Walsh, E. B.; Forsblom, I.; Oscarson, S.; Enzell, C. R.; Ryhage, R.; Isaksson, R. *Helv. Chim. Acta* **1986**, *B 40*, 724−730.
(13) Kraus, W. *J. Toxicol. Toxin Rev.* **2003**, *22*, 495−508.
(14) King, R. R.; Singh, R. P.; Calhoun, L. A. *Carbohydr. Res.* **1988**, *173*, 235−241.
(15) King, R. R.; Calhoun, L. A.; Singh, R. P.; Boucher, A. *J. Agric. Food Chem.* **1993**, *47*, 469−473.
(16) Tschinda, A. T.; Tane, P.; Ayafor, J. F.; Connolly, J. D. *Phytochemistry* **2003**, *63*, 841−846.
(17) Yun, Y. S.; Satake, M.; Katzuki, S.; Kunugi, A. *Phytochemistry* **2004**, *65*, 2167−2171.
(18) Kobayashi, W.; Miyase, T.; Suzuki, S.; Nogushi, H.; Chen, X. M. *J. Nat. Prod.* **2000**, *63*, 1066−1069.
(19) Severson, R. F.; Eckel, R. V. W.; Jackson, D. M.; Sisson, V. A.; Stephenson, M. G. In ACS Symposium Series; Hedin, P. A., Menn, J. J., Hollingworth, R. M., Eds.; American Chemical Society: Washington, DC, 1994; Vol. 551, Chapter 12, pp 172−179.
(20) Jefferies, P. R.; Payne, T. G. *Aust. J. Chem.* **1965**, *18*, 1441−1450.
(21) Wang, Y.; Hamburger, M.; Gueho, J.; Hostettmann, K. *Phytochemistry* **1989**, *28*, 2323−2327.
(22) Tabata, M.; Umetani, Y.; Ooya, M.; Tanaka, S. *Phytochemistry* **1988**, *27*, 809−813.

NP060274L