

## Five New Ergostane-Related Compounds from *Nicandra physaloides*<sup>1)</sup>

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Five new ergostane-related compounds, nicaphysalins A (1), B (2), C (3), D (4) and E (5), were isolated from the fresh whole plants of *Nicandra physaloides* (Solanaceae). Their structures were established by spectroscopic means. Nicaphysalins D (4) and E (5) had a folmyloxy group at C-22 in the side chain.

**Keywords** *Nicandra physaloides*; Solanaceae; ergostane; withanolide; nicaphysalin; folmyloxy group

The extractive of *Nicandra physaloides* is known to inhibit the feeding of various insect species, from which many steroids were obtained by several groups.<sup>2)</sup> These steroidal constituents possessed characteristic partial structures, a 24,25-epoxy- $\delta$ -lactol group in the side chain moiety or an aromatized D-ring, which were biosynthetically related to withanolide.

In our series of studies on constituents possessing antitumor activities in solanaceous plants, we recently reported the structural characterization of several withanolides and their derivatives from *Datura metel*,<sup>3)</sup> *Datura tatura*,<sup>4)</sup> *Tubocapsicum anomalum*,<sup>5)</sup> and *Physalis angulata*.<sup>6)</sup> An extended study of the constituents of *N. physaloides* has led to the isolation and structural elucidation of five new steroids, nicaphysalins A (1), B (2), C (3), D (4) and E (5).

Nicaphysalin A (1) showed an absorption band at  $1690\text{ cm}^{-1}$  due to an  $\alpha,\beta$ -unsaturated carbonyl group in its infrared (IR) spectrum. The negative fast atom bombardment mass spectrum (FAB-MS) displayed a molecular peak  $[M-H]^-$  at  $m/z$  487, and the positive FAB-MS showed peaks at  $m/z$  511  $[M+Na]^+$ , 471  $[M-H_2O+H]^+$  and 453  $[M-2H_2O+H]^+$ . A comparative study of the proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectrum (Table I) of 1 with that of nicandrin B (6)<sup>2)</sup> led to the assignment of the respective signals due to rings A–D as follows: two angular methyl groups [ $\delta$  0.74 (s, H<sub>3</sub>-18) and 1.17 (s, H<sub>3</sub>-19)], one secondary methyl group [ $\delta$  0.99 (d,  $J=6.6\text{ Hz}$ , H<sub>3</sub>-21)], three oxygenated methine protons [ $\delta$  3.03 (d,  $J=4.0\text{ Hz}$ , H-6), 3.31 (dd,  $J=4.0, 1.8\text{ Hz}$ , H-7) and 4.01 (br s, H-12)] and two olefinic protons [ $\delta$  5.84 (dd,  $J=9.9, 2.2\text{ Hz}$ , H-2), 6.60 (ddd,  $J=9.9, 5.1, 2.2\text{ Hz}$ , H-3)]. The chemical shift and the coupling constant of the H-12 signal, which correlated with C-18, C-13 and C-14 in long range carbon-13 and proton correlated spectroscopy (<sup>13</sup>C-<sup>1</sup>H COSY), indicated the presence of a hydroxy group with an  $\alpha$  (*axial*)-orientation at C-12. The carbon-13 nuclear magnetic resonance (<sup>13</sup>C-NMR) data (Table II) for 1 coincided with those of C-1–C-21 in 6, and suggested that 1 had the structure of a 1-one-2-ene-6 $\alpha$ (7 $\alpha$ )-epoxy-5 $\alpha$ -hydroxy system. On the other hand, among the <sup>1</sup>H-NMR signals of the side chain moiety, signals due to two oxygen methine protons [ $\delta$  3.74 (dt,  $J=10.9, 3.7\text{ Hz}$ ) and 5.01 (s)], two quaternary methyl groups [ $\delta$  1.41 (s) and  $\delta$  1.42 (s)] and one secondary methyl group [ $\delta$  0.99 (d,  $J=6.6\text{ Hz}$ )] were observed and were similar to those of nicalbin A (7),<sup>7)</sup>

which possessed a side chain including an epoxy- $\delta$ -lactol system. Furthermore, since the <sup>13</sup>C-NMR signals in this side chain system were in good agreement with those in 7, the side chain structure involving the stereochemistries on the asymmetric centers at C-22, 24, 25 and 26 in 1 should be the same as those of 7. Thus, nicaphysalin A (1) could be represented as (20*S*,22*R*,24*S*,25*S*,26*R*)-6 $\alpha$ (7 $\alpha$ ),22(26),24(25)-tri epoxy-5 $\alpha$ ,12 $\alpha$ ,26-trihydroxy-5 $\alpha$ -ergost-2-ene-1-one. Nicaphysalin A is, conceivably, the biosynthetic reducing substance of the C-12 carbonyl group of Nic-7<sup>2b)</sup> isolated from the same plant.

Nicaphysalin B (2) exhibited an absorption band at  $1692\text{ cm}^{-1}$  ( $\alpha,\beta$ -unsaturated carbonyl group) in its IR

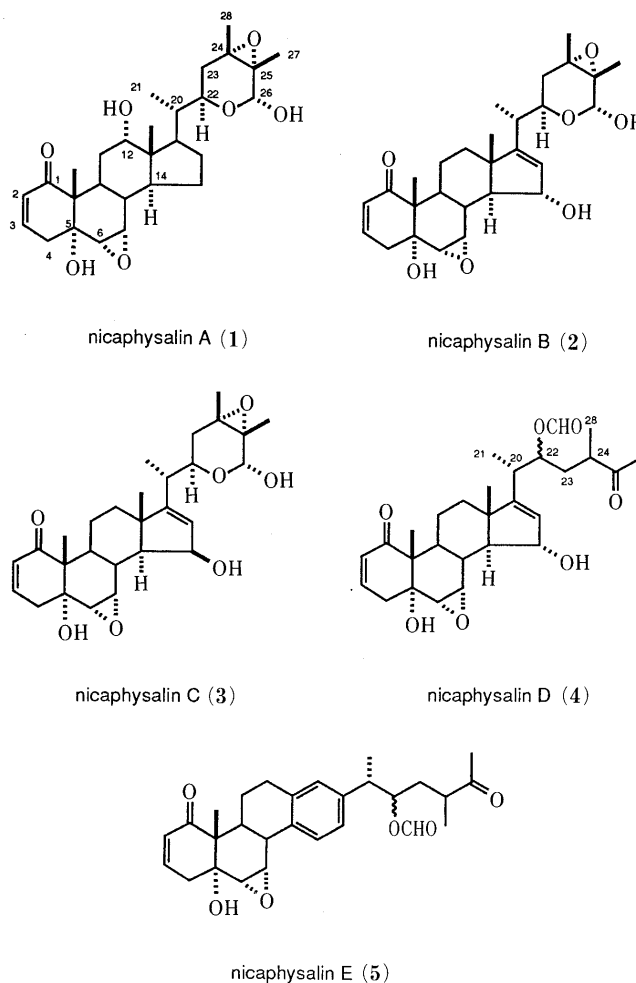


TABLE I.  $^1\text{H-NMR}$  Data ( $\delta/\text{ppm}$ , in  $\text{CDCl}_3$ ) for Nicaphysalins A(1), B(2), C(3), D(4) and E(5)

	1	2	3	4	5
H- 2	5.84 dd (9.9, 2.2)	5.81 dd (11.0, 2.4)	5.85 dd (9.9, 2.2)	5.83 dd (10.1, 2.2)	5.90 dd (10.1, 2.2)
H- 3	6.60 ddd (9.9, 5.1, 2.2)	6.63 ddd (11.0, 5.1, 2.4)	6.60 ddd (9.9, 5.1, 2.2)	6.59 ddd (10.1, 5.1, 2.2)	6.65 ddd (10.1, 5.1, 2.2)
H- 4	2.69 dd (19.0, 2.2) 2.54 dd (19.0, 5.1)	2.74 d (19.0) 2.51 dd (19.0, 5.1)	2.70 dd (19.0) 2.53 dd (19.0, 5.1)	2.69 d (18.7) 2.54 dd (18.7, 5.1)	
H- 6	3.03 d (4.0)	3.06 d (3.7)	3.07 d (3.7)	3.12 d (3.7)	3.26 d (4.0)
H- 7	3.31 dd (4.0, 1.8)	3.63 m	3.79 m	3.68 m	4.04 m
H- 9	2.09 td (12.0, 3.3)				
H-11	2.87 dt (14.7, 3.3)				
H-12	4.01 br s				
H-15		4.62 d (9.5)	4.67 dd (4.8, 2.8)	4.63 d (8.8)	7.36 d (7.7)
H-16		5.47 br s	5.61 d (2.8)	5.52 br s	7.25 dd (7.7, 1.5)
H-18	0.74 s	0.91 s	1.16 s	0.92 s	6.99 d (1.5)
H-19	1.17 s	1.25 s	1.24 s	1.21 s	1.26 s
H-21	0.99 d (6.6)	1.04 d (7.3)	0.96 d (7.0)	1.11 d (6.2)	1.27 d (7.3)
H-22	3.74 dt (10.9, 3.7)	3.87 m	3.80 m	5.04 m	5.14 m
H-26	5.01 br s	5.02 s	5.00 s	2.15 s	2.12 s
H-27	1.41 s	1.40 s	1.42 s	—	—
H-28	1.42 s	1.41 s	1.42 s	1.10 d (4.0)	1.07 d (7.3)
CHO				8.05 s	8.01 s

TABLE II.  $^{13}\text{C-NMR}$  Assignments ( $\delta/\text{ppm}$ , in  $\text{CDCl}_3$ ) of Nicaphysalin A(1), B(2), C(3), D(4) and E(5)

	1	2	3	4	5
C- 1	203.4	203.9	203.2	202.9	202.7
C- 2	128.9	128.1	129.1	128.8	128.7
C- 3	139.9	140.1	139.6	139.6	139.9
C- 4	36.7	36.3	36.7	36.7	36.9
C- 5	73.3	73.1	73.5	73.4	72.8
C- 6	56.0	55.8	55.9	56.7	56.9
C- 7	57.0	56.4	57.0	57.5	55.6
C- 8	35.9	33.5	36.5	33.9	38.6
C- 9	28.6	35.4	36.5	36.1	31.7
C-10	50.5	50.8	51.3	51.0	51.7
C-11	29.7	20.9	21.4	21.3	24.4
C-12	72.5	34.4	35.2	34.5	29.3
C-13	46.9	46.7	48.0	47.4	137.2
C-14	43.6	60.1	55.2	61.4	135.6
C-15	22.9	75.8	73.4	76.8	124.1
C-16	26.3	127.7	124.0	128.8	125.3
C-17	43.2	156.5	162.7	156.6	140.4
C-18	12.5	18.3	23.3	18.9	128.8
C-19	14.6	14.4	15.1	14.9	14.1
C-20	38.6	35.9	32.2	36.2	43.5
C-21	11.4	16.2	18.8	17.0	17.7
C-22	65.2	66.3	66.6	74.6	75.8
C-23	29.5	33.6	34.5	33.6	35.0
C-24	65.3	62.9	64.6	42.9	43.1
C-25	63.8	62.8	63.6	211.3	211.6
C-26	91.8	91.9	91.6	28.8	28.7
C-27	16.6	16.0	16.6	—	—
C-28	18.9	17.9	17.7	17.9	17.8
CHO				160.8	160.9

spectrum. The negative FAB-MS displayed a molecular ion peak at  $m/z$  485  $[\text{M}-\text{H}]^-$ , and the positive FAB-MS showed peaks at  $m/z$  509  $[\text{M}+\text{Na}]^+$ , 469  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ , 451  $[\text{M}-2\text{H}_2\text{O}+\text{H}]^+$  and 433  $[\text{M}-3\text{H}_2\text{O}+\text{H}]^+$ . Since the  $^1\text{H-NMR}$  signals of **2** showed the same pattern as those of rings A and B and the side chain moiety in **1**, the respective  $^1\text{H-NMR}$  signals could be assigned as follows:  $\delta$  5.81 (dd,  $J=11.0, 2.4$  Hz, H-2), 6.63 (ddd,  $J=11.0, 5.1, 2.4$  Hz, H-3), 2.51 (dd,  $J=19.0, 5.1$  Hz, H-4), 2.74 (d,  $J=19.0$  Hz, H-4), 3.06 (d,  $J=3.7$  Hz, H-6), 3.63

(m, H-7), 1.25 (s, H<sub>3</sub>-19), 1.04 (d,  $J=7.3$  Hz, H<sub>3</sub>-21), 3.87 (m, H-22), 5.02 (s, H-26), 1.40 and 1.41 (each s, H<sub>3</sub>-27 and 28). Therefore, **2** was found to have a 1-one-2-ene-5 $\alpha$ -hydroxy-6 $\alpha$ (7 $\alpha$ )-epoxy system in rings A and B, and a 22(26),24(25)-diepoxy-26-hydroxy- $\delta$ -lactol system in the side chain moiety. The  $^{13}\text{C-NMR}$  signals of **2** also supported this structure with the aforementioned rings A and B and the side chain moiety. Furthermore, the remaining signals in the  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of **2** suggested the presence of a hydroxy group [ $\delta_{\text{H}}$  4.62 (d,  $J=9.5$  Hz),  $\delta_{\text{C}}$  75.8] near a tri-substituted double bond group [ $\delta_{\text{H}}$  5.47 (br s),  $\delta_{\text{C}}$  127.7 (d),  $\delta_{\text{C}}$  156.5 (s)], which was analyzed by the analysis of the proton-proton ( $^1\text{H}-^1\text{H}$ ) COSY and  $^{13}\text{C}-^1\text{H}$  COSY, and the locations of these functional groups were determined to be a 15-hydroxy-16(17)-ene according to the correlations between the proton signals of H<sub>3</sub>-18 [ $\delta_{\text{H}}$  0.91 (s)], H<sub>3</sub>-21 [ $\delta_{\text{H}}$  1.04 (d,  $J=7.3$  Hz)] and the singlet  $sp^2$  carbon signal ( $\delta_{\text{C}}$  156.5), and between the olefinic proton signal [ $\delta_{\text{H}}$  5.47 (br s)] and C-13 signal ( $\delta_{\text{C}}$  46.7) in the long range  $^{13}\text{C}-^1\text{H}$  COSY. The stereo-chemistries at C-14 and C-15 were established through nuclear Overhauser effect (NOE) difference measurements. Irradiation at the signal due to H<sub>3</sub>-18 resulted in an increase in the intensities of the H-8, H-15 and H-16 signals, and the H-15 signal was irradiated to increase the intensities of the H-7, H-8, H-14 and H-16 signals. These NOE experiments led to the establishment of the 14*S* and 15*S* configurations. Thus, the structure of nicaphysalin B (**2**) could be (20*S*,22*R*,24*S*,25*S*,26*R*)6 $\alpha$ (7 $\alpha$ ),22(26),24(25)-triepoxy-5 $\alpha$ ,15 $\alpha$ ,26-trihydroxy-5 $\alpha$ -ergost-2,16-diene-1-one.

Nicaphysalin C (**3**), showed an absorption band at  $1692\text{ cm}^{-1}$  due to an  $\alpha,\beta$ -unsaturated carbonyl group in its IR spectrum. The negative FAB-MS displayed a molecular ion peak at  $m/z$  485  $[\text{M}-\text{H}]^-$  and the positive FAB-MS gave peaks at  $m/z$  469  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ , 451  $[\text{M}-2\text{H}_2\text{O}+\text{H}]^+$  and 433  $[\text{M}-3\text{H}_2\text{O}+\text{H}]^+$ . The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectral data for **3**, as listed in Tables I and II, respectively, showed good accordance with those of nicaphysalin B (**2**) except for the signals

around ring D; however, **3** also was declared to have a 15-hydroxy-16-ene system on ring D according to the  $^1\text{H}$ - $^1\text{H}$  COSY,  $^{13}\text{C}$ - $^1\text{H}$  COSY and long range  $^{13}\text{C}$ - $^1\text{H}$  COSY. The  $^1\text{H}$ -NMR signal assignable to  $\delta$  4.67 in **3** had a different coupling pattern (dd,  $J=4.8, 2.8$  Hz) from that (d,  $J=9.5$  Hz) of **2**. Furthermore, the results of the NOE experiments of **3** differed from those of **2**; namely, irradiation at the signal due to H<sub>3</sub>-18 resulted in the enhanced intensities of H-8, H-12 and H-16, and the signal of H-15 simultaneously coupled with H-7, H-14 and H-16 signals. These discriminations of the  $J$  values, combined with the result of the NOE experiments, led to the assignment of the 14*S* and 15*R* configurations, and nicaphysalin C (**3**) was shown to be an epimer at C-15 of nicaphysalin B (**2**). Thus, the structure of nicaphysalin C (**3**) was established as shown in the formula.

Nicaphysalin D (**4**), had absorption bands at  $1740\text{ cm}^{-1}$  (aldehyde),  $1718\text{ cm}^{-1}$  (ketone) and  $1690\text{ cm}^{-1}$  ( $\alpha,\beta$ -unsaturated carbonyl) in its IR spectrum. The negative FAB-MS gave peaks at  $m/z$  485  $[\text{M}-\text{H}]^-$  and 467  $[\text{M}-\text{H}_2\text{O}-\text{H}]^-$ , and the positive FAB-MS displayed peaks at  $m/z$  509  $[\text{M}+\text{Na}]^+$ , 469  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ , 451  $[\text{M}-2\text{H}_2\text{O}+\text{H}]^+$ , 423  $[\text{M}-\text{H}_2\text{O}-\text{HCOOH}+\text{H}]^+$  and 405  $[\text{M}-2\text{H}_2\text{O}-\text{HCOOH}+\text{H}]^+$ . Since the  $^1\text{H}$ -NMR spectrum indicated a signal pattern on rings A—D similar to that of nicaphysalin B (**2**), the respective signals could be assigned as follows:  $\delta$  6.59 (ddd,  $J=10.1, 5.1, 2.2$  Hz, H-3), 5.83 (dd,  $J=10.1, 2.2$  Hz, H-2), 5.52 (s, H-16), 4.63 (br d,  $J=8.8$  Hz, H-15), 3.68 (m, H-7), 3.12 (d,  $J=3.7$  Hz, H-6), 2.80 (m, H-11), 2.69 (d,  $J=18.7$  Hz, H-4), 2.54 (dd,  $J=18.7, 5.1$  Hz, H'-4), 1.21 (s, H<sub>3</sub>-19), 1.11 (d,  $J=6.2$  Hz, H<sub>3</sub>-21), 0.92 (s, H<sub>3</sub>-18). In comparing the  $^{13}\text{C}$ -NMR data (Table II) of **4** with those of **2**, they coincided well with those of C-1—21 in **2**. These assignments of the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR signals were supported by the  $^1\text{H}$ - $^1\text{H}$  COSY,  $^{13}\text{C}$ - $^1\text{H}$  COSY and long range  $^{13}\text{C}$ - $^1\text{H}$  COSY. Moreover, the NOE experiment of **4** provided the same result as that of **2**. These NMR assignments and the result of the NOE experiments indicated that **4** had the same substitutions on rings A—D, a 2,16(17)-diene-5 $\alpha$ ,15 $\alpha$ -dihydroxy-1-one system, as did **2**. On the other hand, a series of  $^1\text{H}$ - $^1\text{H}$  correlations was observed in the  $^1\text{H}$ -NMR signals related to the side chain moiety: H<sub>3</sub>-21 and H-20 [ $\delta$  2.41 (br t,  $J=6.6$  Hz)]; H-20 and H-22 [ $\delta$  5.04 (m)]; H-22 and H<sub>2</sub>-23 [ $\delta$  2.09 and 1.52]; H<sub>2</sub>-23 and H-24 [ $\delta$  2.61 (m)]; H-24 and H<sub>3</sub>-28 [ $\delta$  1.10 (d,  $J=4.0$  Hz)]. Moreover, one proton signal at  $\delta$  8.05, with no correlation to any other proton signal, was observed. In the  $^{13}\text{C}$ -NMR signals regarding the side chain moiety of **4**, a characteristic signal for C-26 in the  $\delta$ -lactol ring system (at around  $\delta$  91 ppm, in case of nicaphysalins A, B and C), and in the  $\delta$ -lactone ring system (at ca.  $\delta$  167 ppm, in case of nicandrin B and other typical withanolide) were observed, but two carbonyl carbon signals appeared at  $\delta$  160.8 and 211.0 ppm. Since the carbon signal at  $\delta$  160.8 correlated to the  $^1\text{H}$ -NMR signal at  $\delta$  8.05 in the  $^{13}\text{C}$ - $^1\text{H}$  COSY, these NMR signals indicated the presence of a formyloxy group, and its presence was also suggested by the FAB-MS. Moreover, according to the NOE experiment between the proton signal of H-22 and the signal of the proton attached to the formyloxy group, it became clear that this formyloxy

group should be located at C-22 in **4**. Since another carbonyl carbon signal at  $\delta$  211.0 ppm correlated to the singlet methyl signal at  $\delta$  2.15 (3H, s) and the signal of H<sub>3</sub>-28, which had a  $^1\text{H}$ - $^1\text{H}$  correlation in succession to the H<sub>3</sub>-21, and in the long range  $^{13}\text{C}$ - $^1\text{H}$  COSY, an acetyl group was found to be present in the side chain moiety in **4** and to be located at C-24. Thus, the structure of nicaphysalin D (**4**) could be determined as shown in the formula.

Nicaphysalin E (**5**), showed characteristic absorption bands at  $1718\text{ cm}^{-1}$  (carbonyl) and  $1694\text{ cm}^{-1}$  (an  $\alpha,\beta$ -unsaturated carbonyl) in its IR spectrum. The negative FAB-MS gave peaks at  $m/z$  465  $[\text{M}-\text{H}]^-$  and 447  $[\text{M}-\text{H}_2\text{O}-\text{H}]^-$ . By comparison of the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectral data (Tables I and II, respectively) of **5** with those of nicandrene (**8**)<sup>2a</sup> and **4**, the signal data of **5** were found to coincide with those of rings A to D in **8**, and with those of the side chain moiety in **4**. These NMR assignments showed that **5** had the same steroidal skeleton with an aromatic ring D as **8**, and the same side chain moiety which had a formyloxy group as **4**. Thus, the structure of nicaphysalin E (**5**) was established as that shown in the formula.

#### Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and were uncorrected. Optical rotations were taken with a JASCO DIP-360 automatic digital polarimeter and CD spectrum on a JASCO J-50A spectropolarimeter. The IR spectra were recorded with a Hitachi IR spectrometer, model 270-30. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were measured with a JEOL JNM-GX 400 NMR spectrometer and chemical shifts are given on a  $\delta$  (ppm) scale with tetramethylsilane (TMS) as an internal standard. The FAB-MS were measured with a JEOL DX-303 HF spectrometer and taken in a glycerol matrix containing NaI. Thin layer chromatography was performed on precoated Kieselgel 60 F<sub>254</sub> (Merck), and detection was achieved by spraying with 10% H<sub>2</sub>SO<sub>4</sub>, followed by heating. Column chromatographies were carried out on Kieselgel (70—230 mesh and 230—400 mesh, Merck) and Sephadex LH-20 (Pharmacia Fine Chem. Co.) using MeOH.

**Extraction and Separation** The fresh whole plants (5.0 kg) of *Nicandra physaloides* (Solanaceae), harvested at the Botanical Garden at Kumamoto University in July 1989, were extracted with MeOH, and the extract was partitioned between 1-BuOH and H<sub>2</sub>O. The organic layer (38.4 g) was partitioned between *n*-hexane and MeOH, and the MeOH layer (22.6 g) was subjected repeatedly to column chromatography over silica gel using CHCl<sub>3</sub>:MeOH:H<sub>2</sub>O=1:0:0→8:2:0.1→1:1:0 and Sephadex LH-20 using MeOH to give nicaphysalins A (**1**, 26.0 mg), B (**2**, 111.8 mg), C (**3**, 7.5 mg), D (**4**, 42.7 mg) and E (**5**, 23.2 mg).

**Nicaphysalin A (1)** Colorless needles, mp 228—231 °C,  $[\alpha]_D^{24} + 44.6^\circ$  ( $c=1.03$ , CHCl<sub>3</sub>). IR  $\nu_{\text{max}}^{\text{CHCl}_3}\text{ cm}^{-1}$ : 3016, 2952, 1690, 1424, 1210, 1124, 1092, 1026, 910, 850, 790, 778, 762, 746, 720, 666  $\text{cm}^{-1}$ . Negative FAB-MS ( $m/z$ ): 579  $[\text{M}+\text{glycerol}-\text{H}]^-$ , 487  $[\text{M}-\text{H}]^-$ ; positive FAB-MS ( $m/z$ ): 511  $[\text{M}+\text{Na}]^+$ , 471  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ , 453  $[\text{M}-2\text{H}_2\text{O}+\text{H}]^+$ , 397, 329, 289.

**Nicaphysalin B (2)** Colorless needles, mp 224—226 °C,  $[\alpha]_D^{24} + 75.8^\circ$  ( $c=0.46$ , CHCl<sub>3</sub>). IR  $\nu_{\text{max}}^{\text{CHCl}_3}\text{ cm}^{-1}$ : 3016, 2956, 2430, 1692, 1224, 1216. Negative FAB-MS ( $m/z$ ): 577  $[\text{M}+\text{glycerol}-\text{H}]^-$ , 485  $[\text{M}-\text{H}]^-$ ; positive FAB-MS ( $m/z$ ): 509  $[\text{M}+\text{Na}]^+$ , 469  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ , 451  $[\text{M}-2\text{H}_2\text{O}+\text{H}]^+$ , 433  $[\text{M}-3\text{H}_2\text{O}+\text{H}]^+$ , 377, 325, 291, 263, 171, 143, 99.

**Nicaphysalin C (3)** A white powder,  $[\alpha]_D^{24} + 22.6^\circ$  ( $c=0.61$ , CHCl<sub>3</sub>). IR  $\nu_{\text{max}}^{\text{CHCl}_3}\text{ cm}^{-1}$ : 3556, 3520, 1692, 1224, 784, 780, 764, 740, 728, 674. Negative FAB-MS ( $m/z$ ): 577  $[\text{M}+\text{glycerol}-\text{H}]^-$ , 559  $[\text{M}+\text{glycerol}-\text{H}_2\text{O}-\text{H}]^-$ , 517  $[\text{M}+\text{MeOH}-\text{H}]^-$ , 485  $[\text{M}-\text{H}]^-$ ; positive FAB-MS ( $m/z$ ): 543  $[\text{M}+\text{glycerol}-2\text{H}_2\text{O}+\text{H}]^+$ , 469  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ , 451  $[\text{M}-2\text{H}_2\text{O}+\text{H}]^+$ , 433  $[\text{M}-3\text{H}_2\text{O}+\text{H}]^+$ , 325, 291.

**Nicaphysalin D (4)** Colorless needles, mp 173—175 °C,  $[\alpha]_D^{24} + 57.8^\circ$  ( $c=0.25$ , CHCl<sub>3</sub>). IR  $\nu_{\text{max}}^{\text{CHCl}_3}\text{ cm}^{-1}$ : 3016, 2930, 2410, 1740, 1718, 1690,

1234, 1210. Negative FAB-MS ( $m/z$ ): 577  $[M + \text{glycerol} - H]^-$ , 485  $[M - H]^-$ , 467  $[M - H_2O - H]^-$ ; positive FAB-MS ( $m/z$ ): 509  $[M + Na]^+$ , 469  $[M - H_2O + H]^+$ , 451  $[M - 2H_2O + H]^+$ , 423  $[M - HCOOH - H_2O + H]^+$ , 405  $[M - HCOOH - 2H_2O + H]^+$ , 379, 351, 299.

**Nicaphysalin E (5)** A white powder,  $[\alpha]_D^{26} + 15.9^\circ$  ( $c = 1.72$ ,  $\text{CHCl}_3$ ). IR  $\nu_{\text{max}}^{\text{CHCl}_3} \text{ cm}^{-1}$ : 3016, 2980, 2932, 1740, 1718, 1694, 1220, 1180. Negative FAB-MS ( $m/z$ ): 465  $[M - H]^-$ , 447  $[M - H_2O - H]^-$ , 339, 289, 137, 123, 59; positive FAB-MS ( $m/z$ ): 559  $[M + \text{glycerol} + H]^+$ , 467  $[M + H]^+$ , 421  $[M - HCOOH + H]^+$ , 333, 241, 150, 75, 57.

#### References and Notes

- 1) This work is Part 28 in a series of studies on the constituents of solanaceous plants.
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