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Identification of TLC Markers and Quantification by HPLC-MS of Various Constituents in Noni Fruit Powder and Commercial Noni-Derived Products

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The composition of noni (*Morinda citrifolia*) products has been investigated. TLC profiles of several commercial juices and capsules were compared. 3-Methyl-1,3-butanediol was identified as a typical marker in noni juices. The presence of sorbic acid (E200) was detected in one juice declared as additive free. Quantitative data have been obtained by HPLC-MS. A method for the quantification of characteristic noni constituents, such as iridoid glucosides, scopoletin, rutin, fatty acid glucosides, and anthraquinones, was developed and validated. The separation was performed on a C18 column with a gradient of acetonitrile in water containing 0.1% formic acid. Detection was carried out with ESI-MS in the negative ion mode. Significant differences were observed between the products. Asperulosidic acid, deacetylasperulosidic acid, and rutin were present in all samples analyzed, but their concentrations differed considerably between the products. Fatty acid glucosides, noniosides B and C, were present in capsules and most juices. Scopoletin was mainly found in juices. The anthraquinone alizarin, which has been reported from roots and leaves, was not detected in the samples investigated.

KEYWORDS: Noni; *Morinda citrifolia*; Rubiaceae; 3-methyl-1,3-butanediol; HPTLC; quantitative analysis; HPLC-MS.

INTRODUCTION

Products derived from the noni fruit (*Morinda citrifolia* L., Rubiaceae) have been commercialized in the U.S. since the 1990s and are now available in health food stores and through the Internet (*1*). Noni products include capsules, teas, and juices. The popularity of noni products in the U.S. has been attributed to claims of a "cure-all" for a variety of diseases (*2*). Noni fruit juice has been legally sold in the European Community since 2003, and other products are readily available through the Internet. There have recently been some controversies on the safety of noni products after the publication of a few clinical case reports that associated consumption of noni juice with cases of acute hepatitis (*1*, *3*, *4*).

Various secondary metabolites have been reported from noni fruit. Among them, fatty alcohol and fatty acid glycosides appear quite unique with respect to their structures and contents in ripe fruits (*5*−*8*). The fruit further contains numerous iridoids, in particular asperuloside (*9*), asperulosidic acid, and deacetylasperulosidic acid (*10*). Other compound classes found in the fruit include flavonol glycosides such as rutin (*11*), lignans, and the coumarin scopoletin (*12*). Finally, the fruit contains a wide spectrum of 1-hydroxyanthraquinones (*10*, *12*), albeit in very low concentrations, and miscellaneous compounds such as β-sitosterol (*13*) and ursolic acid (*11*).

The noni market is largely uncontrolled. A survey of the quality of available products is desirable from a consumer safety perspective. In this context, there is a lack of validated analytical methods for the determination of important markers and/or putative bioactive compounds. This prompted us to investigate the composition of the noni fruit powder and various commercial juices and capsules derived from noni. In a first step, TLC profiles were compared and chromatographic markers identified. We then developed and validated a quantitative HPLC-MS assay, which was used for the determination of characteristic constituents in noni fruit powder and several commercial products.

MATERIALS AND METHODS

Chemicals and Reference Compounds. Solvents were of analytical grade (ASE) or HPLC grade and were supplied by Scharlau (Barcelona, Spain). Formic acid (98−100%) and sulfuric acid (95−97%) were purchased from Sigma-Aldrich (Buchs, Switzerland). HPLC grade water was obtained by an EASYpure II (Barnstead, Dubuque, USA) water

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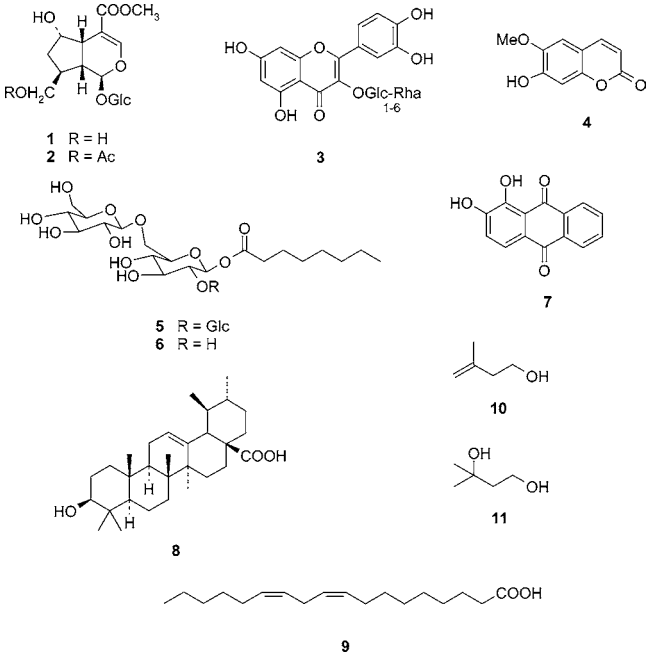

Figure 1. Structures of noni constituents.

purification system. Vanillin (>99%) was from Carl Roth GmbH + Co (Karlsruhe, Germany).

Noniosides B (**5**) and C (**6**) (*8*), asperulosidic acid (**2**), and deacetylasperulosidic acid (**1**) (**Figure 1**) were isolated from ground noni fruit powder at the Institute of Pharmaceutical Biology, University of Basel, Switzerland. Purities were ≥99% as determined by HPLC and NMR. Scopoletin (**4**), alizarin (**7**), and ursolic acid (**8**) were purchased from Extrasynthèse (Genay, France) and were >99% purity. 3-Methyl-3-buten-1-ol (**10**) (97%) was obtained from Acros Organics (Morris Plains). 3-Methyl-1,3-butanediol (**11**) (≥97%) was from Sigma-Aldrich. Rutin (**3**) and linoleic acid (**9**) were from Carl Roth GmbH + Co and were >99% purity. Sorbic acid (purum) was obtained from Siegfried Ltd. (Zofingen, Switzerland).

Plant Material. Noni fruits were harvested in December, 2005 (ripe stage) (F1) and July 2006 (unripe stage) (F2) at the Botanical Garden of the University of Basel. A voucher specimen is preserved at the Institute of Pharmaceutical Biology, University Basel, Switzerland. Ground noni fruit powder (GNFP) was obtained from Nature's Sunshine Products (Spanish Fork, Utah).

Commercial Noni Products. The following eight juices have been analyzed: Apo 1 Thai Noni (origin unknown), Pacific Noni (Percenta Ltd., London, U.K.), Tahitian Noni Juice (Tahitian Noni Int. U.K. Ltd., Milton Keynes, U.K.), Noni Wildfruchtsaft (Life Light Handels GmbH, Salzburg, Austria), Good Noni Juice (Herbex Ltd., Lautoka, Fiji), Cook Islands Noni Juice (Sunline Noni Ltd., Rarotonga, Cook Islands), Cook Island Noni des Iles Cook (GSE Vertrieb GmbH, Saarbruecken, Germany), Nature's Noni (Nature's Sunshine Products, Spanish Fork, Utah). Four Noni capsules have been analyzed: Nature's Noni Capsules (Nature's Sunshine Products), Noni Pur Noni Capsules (origin unknown), Indian Mulberry Capsules (Thanyaporn Herbs Co. Ltd., Parasamutjedi, Samutprakarn, Thailand) and Cook Islands Pure Noni Capsules (Sunline Noni Ltd.). Apo 1 Thai Noni was bought in a public pharmacy, the other products were purchased through the Internet. In the manuscript, juices are randomly referred to as J1−J8 and capsules as C1−C4.

Isolation of 3-Methyl-1,3-Butanediol (11). A total of 500 mL of Tahitian Noni Juice was evaporated under reduced pressure. The viscous residue was extracted 8 times with 1 L of EtOAc. The combined EtOAc extracts were concentrated to 100 mL and extracted twice with 100 mL of water. The water phase was concentrated to 10 mL and separated by high-speed counter current chromatograpy (HSCCC) on a P.C. Inc. instrument (P.C. Inc., Potomac, MD) equipped with a 400 mL coil. Elution was performed with *n*-BuOH−H_2O at 5 mL/min in the descending mode. Further separation of the **11**-enriched fraction by Sephadex LH-20 (MeOH), followed by medium-pressure liquid chromatography (MPLC) on SiO_2 ($CHCl_3$−MeOH, 9:1) and RP-18 (MeOH−H_2O, 5:95) afforded pure **11** (2.5 mg).

Isolation of Sorbic Acid. A total of 100 mL of juice J1 was extracted 12 times with 25 mL of $CHCl_3$. The organic phases were pooled and concentrated under reduced pressure. Upon evaporation of the solvent, colorless needles were obtained that were washed with cold Et_2O to give 21.4 mg of sorbic acid.

Sample Preparation for HPTLC. Reference compounds were dissolved in MeOH. Concentrations were 0.2 mg/mL for **1**, **2**, **3**, **4**, **8**, **9**, 0.01 mg/mL for **10**, and 0.02 mg/mL for **11**.

Capsules and fruit powder: 1 g of capsule content, GNFP or fruit powder F1 (ripe fruit, Botanical Garden University of Basel, Switzerland) were extracted twice with 20 mL of MeOH for 15 min at 40 °C in an ultrasonic bath and made up to 50 mL. After centrifugation at 3000 rpm for 5 min, the supernatant was evaporated to dryness under nitrogen and the residue redissolved in 250 μL of MeOH.

Juices: lipophilic compounds were extracted from 15 mL of juices three times with 5 mL of $CHCl_3$. An aliquot of 3 mL was evaporated to dryness under nitrogen and redissolved in 300 μL of $CHCl_3$. For comparison, extracts were also analyzed without any concentration step (no drying and redissolution). Samples used for the analysis of polar constituents were first submitted to solid-phase extraction (SPE) on Chromabond EASY 200 mg cartridges (Macherey-Nagel, Düren, Germany) to remove sugars. A total of 5 mL of juice was loaded onto the cartridges, which were washed with 10 mL of H_2O and subsequently eluted with 10 mL of MeOH. A 1 mL aliquot of the eluent was dried under N_2 and redissolved in 100 μL of MeOH. Pacific Noni, Nature's Noni, and Tahitian Noni Juice were centrifuged at 4000 rpm for 5 min before SPE.

HPTLC Analyses. For comparison of the chromatographic profiles of noni products, the samples (10 μL) were spotted as 6 mm bands onto a 20 cm × 10 cm HPTLC silica gel 60 F_{254} plate (Merck, Darmstadt, Germany) using a Linomat IV sample applicator (Camag, Muttenz, Switzerland). The plates were developed with $CHCl_3$−MeOH, 9:1 or $CHCl_3$−MeOH−H_2O, 65:30:5. Detection was performed under UV 254 and 366 nm and after spraying with Godin reagent (1% vanillin in EtOH containing 2% H_2SO_4) and heating at 105 °C. For the chromatographic identification of sorbic acid in Juice 1, 3 μL of a 0.01 mg/mL sorbic acid solution were compared to 2 μL of Juice 1 diluted 10 times with MeOH. The eluent was $CHCl_3$−MeOH, 9:1 (data not shown). HPTLC fingerprints were documented with a Reprostar 3 illumination unit (Camag) equipped with a Hitachi HV-C20AP camera.

Sample Preparation for LC/MS. Fresh fruits were lyophilized and ground in a ZM 100 centrifugal mill (Retsch GmbH, Haan, Germany) equipped with a 1 mm sieve. The fruit powder (1 g) was extracted by accelerated solvent extraction on a ASE 200 extractor (Dionex, Olten, Switzerland) in 18 mm × 75 mm cells at 60 °C and a pressure of 120 bar. After evaporation to dryness, the extract was redissolved in MeOH at concentrations of 1.0 and 0.1 mg/mL and centrifuged before analysis at 13 000 rpm for 10 min. Extracts and samples of GNFP were prepared following the same procedure. The 0.1 mg/mL extract concentration was used to quantify nonioside B (**5**) in GNFP, as well as nonioside B (**5**) and deacetylasperulosidic acid (**1**) in the unripe fruit sample (F2). All other determinations were made with the 1.0 mg/mL extract concentration.

Capsules were extracted as follows: 1 g of capsule content out of several capsules was macerated twice with 30 mL of MeOH for 15 min at 40 °C in an ultrasonic bath. The extracts were collected by centrifugation at 3000 rpm for 5 min, pooled, and made up with MeOH to 100 mL. Before analysis, the solutions were centrifuged at 13 000 rpm for 10 min and further diluted by a factor 2.5.

The juices were diluted by factors of 10 and 200 with water and cleaned through a 45 μm pore size PTFE syringe filter (Semadeni, Ostermundigen, Switzerland). The 1:200 dilution was used for the quantification of nonioside B (**5**) in juices J2 and J6, deacetylasperulosidic acid (**1**) in all juices, and asperulosidic acid (**2**) in juices J1−J6 and J8. All other determinations were made with the 1:10 dilution.

HPLC System. HPLC separations were carried out on a Agilent series 1100 system equipped with a degasser, a binary pump, a column oven, and a PDA detector (Agilent Technologies, Waldbronn, Ger-

Table 1. Noni Constituents, **1**–**7**, RSD (%) ($n = 6$), Limits of Detection (LOD), and Quantification (LOQ)[a]

compound	RSD	detection limit [ng]	quantification limit [ng]
deacetylasperulosidic acid (**1**)	5.17	1.0	4.0
asperulosidic acid (**2**)	4.14	0.4	2.0
rutin (**3**)	4.13	0.4	1.0
scopoletin (**4**)	3.75	1.0	2.0
nonioside B (**5**)	6.95	1.0	2.0
nonioside C (**6**)	6.37	0.4	1.0
alizarin (**7**)	6.03	0.4	2.0

[a] Injection volume 20 μL; RSD: the amount of compound injected was 20 ng

many). A liquid handler 215 (Gilson, Mettmenstetten, Switzerland) was used as autosampler. The HPLC was coupled over a 1:2 splitter to an Esquire 3000 Plus ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany) fitted with an ESI source. Data acquisition and processing were performed using HyStar 3.0 software (Bruker Daltonics).

HPLC-MS Analyses. Analyses were performed at 30 °C on a 125 mm × 4 mm i.d., 5 μm CC125/4 Nucleodur C18 gravity column (Macherey-Nagel, Düren, Germany), equipped with a 8 mm × 4 mm i.d., 5 μm guard column. The mobile phase consisted of water containing 0.1% formic acid (eluent A) and acetonitrile (eluent B). The gradient of B used was as follows: in 7.5 min from 5% to 25%, from 7.5 to 13 min up to 100% B, held at 100% for 2 min, 100% to 5% in 1 min, held at 5% for 4 min. The flow rate was 1.0 mL/min, the injection volume was 20 μL. ESI-MS spectra were recorded in the negative ion mode at a scan speed of 13 000 Da/s under ion charge control conditions (ICC 15000). Nitrogen was used as drying gas at a flow rate of 10 L/min and as nebulizing gas at a pressure of 30 psi. The nebulizer temperature was set at 300 °C. Spectra were recorded in the range from m/z 170 to 700; capillary voltage was set at 4500 V, end plate offset at −500 V, capillary exit at −102.5 V, skimmer voltage at −80.0 V, and trap drive at 39.2. Analyses were performed in triplicate.

Method Validation. Peak purity was established from MS data. Reproducibility was assessed with solutions of compounds **1**−**7** at 1μg/mL. Analyses were performed in six replicates, and the relative standard deviation was calculated (**Table 1**). Detection limit (S/N ratio of 3) and quantification limit (S/N ratio of 10) were determined by serial dilution of a standard solution containing **1**−**7** and are listed in **Table 1**.

Accuracy was determined by spiking the methanol extract of GNFP with defined amounts of **1**−**7**. The amounts added were selected to be in the same range as the amounts of compounds originally present in the extract. Extract concentration in analysis was 1 mg/mL. Amounts added and recovery rates of **1**−**7** are listed in Table 1, Supporting Information.

Calibration Curves. Stock solutions of 2.0 mg/mL of **1**−**7** were prepared in MeOH (**1**−**6**) or DMSO/MeOH, 1:1 (**7**). Calibration solutions containing a mixture of compounds **1**−**7** were prepared from the stock solutions by dilution with MeOH. Each standard solution was measured in triplicate. Calibration curves are shown in Table 2, Supporting Information.

RESULTS AND DISCUSSION

HPTLC Analyses. HPTLC analyses were performed to identify chromatographic markers and to compare the chromatographic fingerprints of commercial noni products with authentic materials. We observed significant differences in the chromatographic fingerprints of juices and capsules and, to a lesser extent, within a same product type (**Figure 2**). For the analysis of lipophilic compounds, juices were partitioned with chloroform, while capsules were extracted with methanol. Ursolic acid (**8**) (R_f 0.60), as well as large amounts of linoleic acid (**9**) (R_f 0.55), were found in all capsules and in some juices (J6−J8). Scopoletin (**4**) (R_f 0.53) was detected in all samples except for capsules C2, albeit only in traces in juice J1 and in all capsules. In the nonconcentrated juice extracts, a compound appeared as a characteristic bright-blue spot (R_f 0.55) after spraying with vanillin/H_2SO_4. However, this spot was absent if the extracts had been dried prior to HPTLC analysis, pointing to a volatile nature of the metabolite. The chromatographic profile of the unconcentrated extract of juice 8 is shown as a representative example in **Figure 2A**. The compound was identified as 3-methyl-3-buten-1-ol (**10**), the aglycone of nonioside A (*8*). A more polar characteristic blue spot (R_f 0.27) was observed in juices J3−J8 but was absent from the capsules. The compound was isolated from Tahitian Noni Juice and identified as 3-methyl-1,3-butanediol (**11**) by NMR and by chromatographic comparison with a commercial standard. Finally, a strongly UV absorbing compound (R_f 0.47) detected in J1 turned out to be the food additive sorbic acid (E200). This compound was identified, after isolation, by NMR and chromatographic comparison with an authentic sample. Interestingly, the product label indicated that juice J1 was free of any additive.

Polar constituents were analyzed with $CHCl_3$−MeOH−H_2O, 65:30:5 (**Figure 2B**). MeOH extracts of capsules were used. Sugars were previously removed from juices by SPE. The iridoid glucosides deacetylasperulosidic acid (**1**) and asperulosidic acid (**2**) could be identified in all samples. However, different chromatographic patterns were observed between juices and capsules. In particular, a spot (R_f 0.47) appearing blue after spraying with vanillin/H_2SO_4 was found in all juices but was absent from capsules. The compound could not be identified, but the color reaction was identical to that obtained with 3-methyl-1,3-butanediol and 3-methyl-buten-1-ol. Because of compound overlapping, no spot could be assigned to rutin in the analyzed samples.

HPLC-MS Analyses. To obtain quantitative data on the composition of noni products, we developed and validated an HPLC-MS method for analysis of characteristic constituents, including iridoid glucosides, scopoletin, rutin, fatty acid glucosides, and anthraquinones. More lipophilic constituents were not included due to carryover effects. The TLC markers **10** and **11** were also excluded because no signal for such low-molecular compounds can be obtained in ESI-MS. Separation on a reversed phase C18 column with a gradient of acetonitrile in water containing 0.1% formic acid provided a good separation of compounds **1**−**7** within 13 min. ESI-MS detection was performed in the negative ion mode. A strong $[M-H]^-$ quasimolecular ion was observed in the spectra of all compounds. The HPLC analyses of a mixture of **1**−**7,** a capsule, and a juice under optimized conditions are shown in **Figure 3**. Calibration curves were found to be linear for compound **2** ($R^2 = 0.9993$) or fitted quadratic functions for **1** and **3**−**7** ($R^2 > 0.998$) over a broad concentration range. Accuracy of the method was checked by spiking experiments. Recovery rates between 85% and 114% were obtained for compounds **1**−**7**. Compounds **1**−**7** were quantified in two fruit samples collected at different ripening states, GNFP, four commercial capsules, and eight juices. A graphic representation of the results is shown in the **Figure 4**. Values are listed in **Table 2**. Significant differences were observed among the samples. The iridoid glucosides decacetyl asperulosidic acid (**1**) and asperulosidic acid (**2**) were found in all samples, but differences of a factor up to 10 among juices (**1**: 0.23−2.42 mg/mL; **2**: 0.006−0.29 mg/mL) and up to 5 among capsules (**1**: 0.16−0.51 mg/mL; **2**: 0.022−0.12 mg/mL) were observed. In all samples, the concentration of **1** was found to be the highest of the quantified substances.

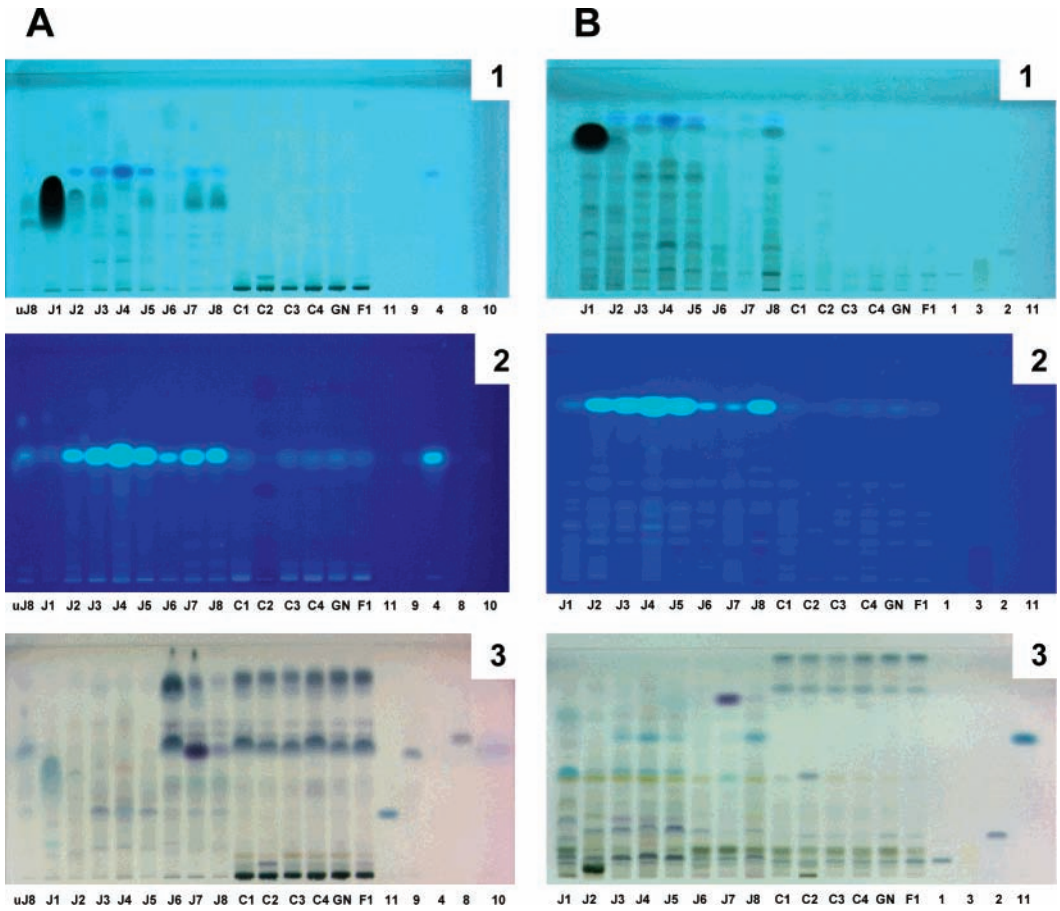

Figure 2. HPTLC profiles of noni products. (**A**) $CHCl_3$–MeOH 9:1. (**B**) $CHCl_3$–MeOH–H_2O 65:30:5. Detection: A1/B1: UV 254 nm. A2/B2: UV 366 nm. A3/B3: Vanilin/H_2SO_4. Samples: uJ8: nonconcentrated juice 8; J1–J8: Juices; C1–C4: Capsules; GN: Ground noni fruit powder; F1: ripe fruit sample; **1**: deacetylasperulosidic acid; **2**: asperulosidic acid; **3**: rutin; **4**: scopoletin; **8**: ursolic acid; **9**: linoleic acid; **10**: methyl-3-buten-1-ol; **11**: 3-methyl-1,3-butanediol.

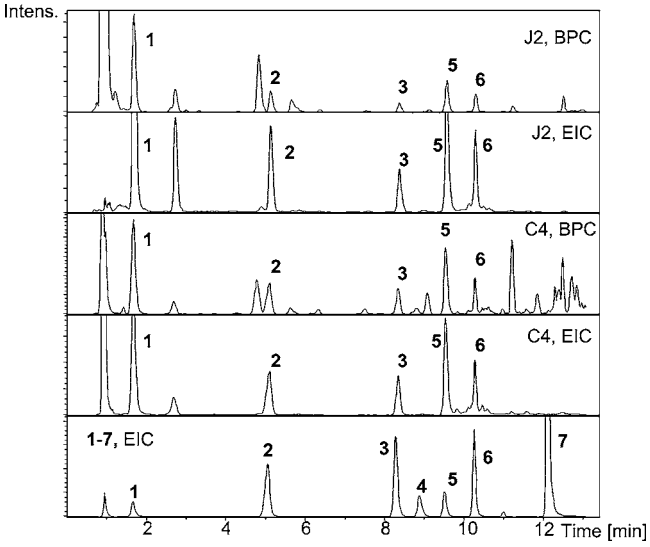

Figure 3. HPLC-MS analyses of a juice, (J2, diluted 10×), a capsule (C4), and a mixture of **1**–**7** (0.01 mg/mL). Volume of injection: 20 μL. BPC: base peak chromatogram; EIC: extracted ion chromatogram (*m*/*z* 191, 239, 389.5, 431.5, 467.5, 605.5, 629.5).

Rutin (**3**) was also present in all samples. Its content strongly differed among juices (0.0009−0.14 mg/mL), but was more similar in capsules (0.024−0.055 mg/g) and as high as 0.36 mg/mL in GNFP. Scopoletin (**4**) was mainly found in juices albeit at highly different concentrations (from undetectable to 0.023 mg/mL). GNFP contained small amounts of the coumarin (0.002 mg/g), which was detected only in traces in some capsules. The relative concentrations of scopoletin in the samples agree well with the semiquantitative data obtained by HPTLC. The fatty acid glucosides noniosides B (**5**) and C (**6**) were found in all samples but one juice. While their contents in capsules were similar (**5**: 0.13−0.22 mg/mL; **6**: 0.03−0.04 mg/mg), their concentration were much higher in two juices (**5**: 0.09 mg/mL, **6**: ca. 0.01 mg/mL) compared to the others (**5**: ≤0.015 mg/mL; **6**: ≤0.0035 mg/mL). Finally, the anthraquinone alizarin (**7**) was not detected in any of the investigated samples. The concentration of the compounds was found to be much higher in GNFP and fruit samples than in the capsules. Interestingly, large differences were also observed between the two fruit samples, in particular for the content of nonioside B (**5**), which was much higher in the less ripe fruit.

Our results revealed strong differences in the composition of noni-derived commercial products. Differences appeared not only between capsules and juices but within a same product type, in particular in the case of juices. 3-Methyl-1,3-butanediol (**11**) isolated from Tahitian Noni Juice, appears to be a specific marker of juices and is absent from capsule and fruit samples. It must be pointed out that **11** is not only found in Tahitian Noni Juice, known to contain small amounts of additional fruit juices, but also in juices claimed to be pure noni juice. The compound is possibly derived from 3-methyl-3-buten-1-ol, the aglycone of noniosoide A, and could result from a different manufacturing process for juices than for capsules. Traditionally, mature fruit are fermented and the juice is collected by drip-

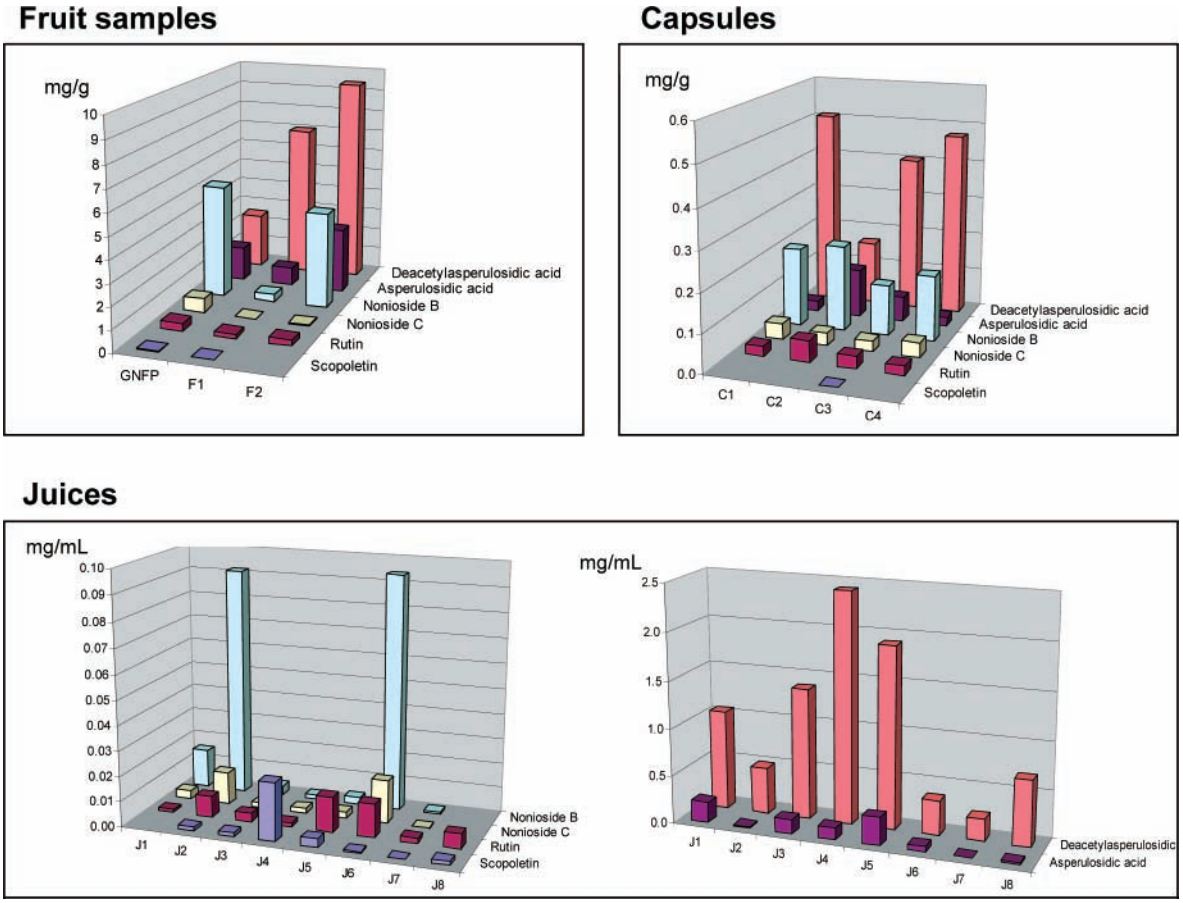

Figure 4. Comparison of the content of compounds **1**–**6** in noni fruits, capsules, and juices.

Table 2. Content of **1**–**7** in Noni Fruit and Noni-Derived Commercial Products[a]

compound/ juice	J1	J2	J3	J4	J5	J6	J7	J8
DAA (**1**)	1050.7 ± 24.2	488.8 ± 18.6	1378.2 ± 50.0	2423.5 ± 115.9	1909.7 + 70.3	360.4 ± 14.2	233.2 ± 15.2	692.7 ± 21.7
AA (**2**)	220.2 ± 7.1	11.5 ± 1.4	148.2 ± 4.5	122.1 ± 2.0	294.2 ± 5.9	55.9 ± 0.4	5.6 ± 0.3	22.2 ± 1.7
rutin (**3**)	0.85 ± 0.05	8.2 ± 0.2	3.5 ± 0.1	1.7 ± 0.1	14.0 ± 0.4	13.3 ± 0.3	2.0 ± 0.1	6.0 ± 0.9
scopoletin (**4**)	nd	1.5 ± 0.2	1.6 ± 0.9	23.2 ± 0.2	3.4 ± 0,9	(0.5)	traces	1.52 ± 0.08
nonioside B (**5**)	15.5 ± 0.4	91.7 ± 8.1	3.8 ± 0.2	1.8 ± 0.3	3.0 ± 0.2	94.2 ± 1.6	(0.9)	nd
nonioside C (**6**)	3.52 ± 0.04	12.7 ± 0.2	1.8 ± 0.2	2.05 ± 0.02	2.5 ± 0.1	17.1 ± 0.7	(0.3)	nd
alizarin (**7**)	nd	nd	nd	nd	nd	nd	nd	nd

compound/ capsule	C1	C2	C3	C4	GNFP	F1	F2
DAA (**1**)	508.6 ± 28.3	164.5 + 7.6	403.0 ± 8.2	475.7 ± 14.0	2536.5 ± 109.8	7028.7 ± 78.1	9444.0 ± 275.5
AA (**2**)	25.5 ± 0.9	124.7 ± 2.2	63.6 ± 6.8	(21.8)	1573.3 ± 64.9	847.9 ± 16.0	2984.5 ± 50.0
rutin (**3**)	24.7 ± 1.0	54.6 ± 2.2	31.4 ± 1.2	24.1 ± 1.1	362.8 ± 11.9	179.0 ± 5.1	258.3 ± 14.2
scopoletin (**4**)	nd	nd	traces	nd	(19.4)	(13.8)	nd
nonioside B (**5**)	202.4 ± 3.5	222.1 ± 3.4	130.7 ± 4.8	169.3 ± 35.0	5217.1 ± 140.0	329.5 ± 3.4	4419.9 ± 215.8
nonioside C (**6**)	41.9 ± 1.9	33.0 ± 0.9	27.1 ± 1.9	38.3 ± 5.0	659.6 ± 12.2	(19.4)	42.4 ± 0.8
alizarin (**7**)	nd	nd	nd	nd	nd	nd	nd

[a] DAA = deacetylasperulosidic acid; AA = asperulosidic acid. Juices (J): μg/mL; capsules (C) and fruit samples (F): μg/g of dry material. nd: not detected; values in parentheses: <QL, tentative determination.

extraction. Nonfermented juices, which are obtained by squeezing or pressing mature fruits and preserved by pasteurization, are also commercialized (*14*). Capsules are usually prepared from dried fruits. However, in most cases, no details are given on the preparation of commercial noni products, thus contributing to the poor characterization of noni products. In this context, the presence of large amount of sorbic acid in a juice claimed free of additives indicates the need for quality control of commercial noni products. Considering the phytochemical differences between juices and capsules, one should keep in mind that the juice is the only form approved by the European Commission as a novel food.

While the knowledge on the phytochemistry of noni fruit has considerably increased over recent years, the chemical composition of commercial products distributed mainly via the Internet is still poorly established. The significant differences among the samples underline the urgent need to establish quality

standards for noni products which allow assessment of safety and equivalence of commercial products.

ABBREVIATIONS USED

ASE, accelerated solvent extraction; PDA, photodiode array; ESI, electrospray ionization; GNFP, Ground Noni Fruit Powder; RSD, relative standard deviation; SPE, solid-phase extraction.

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Supporting Information Available: Recovery rates and calibration curves. This information is available free of charge via the Internet at http://pubs.acs.org.

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