SUPPLEMENTARY MATERIAL

Glucosinolates of the only three Brassicales indigenous to French Polynesia

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The glucosinolate (GL) profiles in leaf and stem of *Rorippa sarmentosa* (G.Forst. ex DC.) J.F.Macbr., *Lepidium bidentatum* Montin var. *bidentatum*, and *Capparis spinosa* subsp. *cordifolia* (Lam.) Fici indigenous to French Polynesia were investigated for the first time using LC-MS analysis. In the present study, we have established the presence of 8 known GLs in *R. sarmentosa*: 4-(methylsulfinyl)butyl- (**1**), but-3-enyl- (**2**), 5-(methylsulfinyl)pentyl- (**3**), 6-(methylsulfinyl)hexyl- (**4**), indol-3-ylmethyl- (**6**), 2-phenylethyl- (**7**), 8-(methylsulfinyl)octyl- (**8**), and 9-(methylsulfinyl)nonyl- (**9**) GLs. We have also tentatively identified for the first time the presence in *R. sarmentosa* of 7-(methylsulfinyl)heptyl GL (**5**). In addition, we have identified two known GLs in *L. bidentatum* var. *bidentatum*: benzyl- (**10**) and 4-methoxybenzyl- (**11**) GLs. Finally, the known methyl GL (**12**) was shown to be largely predominant in *C. spinosa* subsp. *cordifolia.*

Experimental

General Experimental Procedures

All solvents were ACS grade and used as such. Formic acid was purchased from BDH (Toronto, ON, Canada). HPLC-grade MeOH and Et_3N (reagent grade) were purchased from Fisher Scientific (Whitby, ON, Canada). HPLC-grade H_2O was generated in the laboratory through a Nanopure Diamond Ultrapure water system provided by Barnstead (Dubuque, IA, USA). GLs **1**, **2** and **10** were purchased from Chromadex (Irvine, CA, USA). **7** was purchased from LKT Laboratories Inc. (St. Paul, MN). The intact GLs **3**, **4**, **6**, **8**, **9**, and **11** were identified by comparison of retention times, UV and mass spectra of authenticated standards (Blažević et al. 2013; Montaut et al. 2009; Montaut et al. 2010; Montaut et al. 2015; Montaut et al. 2018). The authenticated sample of GL **12** (Kjær and Gmelin 1956) was graciously supplied by Susanna Cinti (Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria, Centro di Ricerca per le Colture Industriali, Bologna, Italy).

Plant Material

Detailed information regarding characteristic features, collection, identification, drying of the plants, and voucher specimen information are found in Table S1. The plants were identified by the botanist Dr. J.-F. Butaud (Tahiti, French Polynesia).

LC-MS Analysis of Glucosinolates

The plant part (leaf and stem) was frozen in liquid N_2, ground in a mortar, and immediately extracted three times with boiling EtOH-H_2O (7:3, v/v) (1 mL/100 mg of sample mass) for 5 min. The hydro-ethanolic solution was filtered and concentrated to dryness. LC-MS analysis was performed by injecting 10 µL aliquot of the solution of the crude extract (15 mg/mL) into an Agilent Technologies HP 1100 (New Castle, DE, USA) high-performance liquid chromatograph equipped with a quaternary pump, automatic injector, diode-array detector (wavelength range 190-600 nm), degasser, and a Hypersil ODS column (5 µm, 4.6 × 200 mm). The two mobile phase solvents, MeOH and H_2O, were prepared with 0.15% Et_3N and 0.18% HCO_2H, added as ion-pairing reagents. Both solutions were filtered using 0.45 µm nylon membranes. The initial mobile phase was 100% HPLC-grade H_2O. After 10 min, the mobile phase was switched to a linear gradient to 100% MeOH within 60 min. After each run, the initial mobile phase conditions were set and the system was allowed to equilibrate. The flow rate was kept at a constant 1 mL/min. The column temperature was held at room temperature (Zrybko et al. 1997). The HPLC was interfaced to an Agilent model 6120 mass spectrometer (Toronto, ON, Canada) with a Chemstation LC-MSD B.03.01 data system. The electrospray interface was a standard ED source

operating with a capillary voltage of 4 kV and temperature of 350°C. Spectra were obtained with a fragmentation voltage of 200 eV. The system was operated in the negative and positive ion electrospray modes. Nitrogen was used as drying gas at a flow rate of 12 L/min (35 psig). The mass spectrometer was programmed to perform full scans between *m/z* 100 and 1,500 Da.

Table. S1. *Rorippa sarmentosa*, *Lepidium bidentatum* var. *bidentatum*, and *Capparis spinosa* subsp. *cordifolia* characteristic features (family, biological type, and biogeographical status), plant collection, drying conditions, and voucher specimen information.

	Rorippa sarmentosa	*Lepidium bidentatum* var. *bidentatum*	*Capparis spinosa* subsp. *cordifolia*
Family	Brassicaceae	Brassicaceae	Capparidaceae
Biological type	Herb	Herb	Shrub
Biogeographical status	Native or Polynesian introduction	Native	Native
Identification and harvest	J.-F. Butaud	J.-F. Butaud	J.-F. Butaud
Harvest date	February 1st 2017	January 10th 2018	January 9th 2018
Location	Papehue Valley (Tahiti, French Polynesia), 50 m above sea level	Tematahoa islet (Anaa atoll, Tuamotu archipelago, French Polynesia), 3 m above sea level	Kerito islet (Anaa atoll, Tuamotu archipelago, French Polynesia), 5 m above sea level
Drying	Air-dried in the shade	Air-dried in the shade	Air-dried in the shade
Herbarium (deposit number)	Herbarium of French Polynesia (Butaud 3512)	Herbarium of French Polynesia (Butaud 3604)	Herbarium of French Polynesia (Butaud 3600)

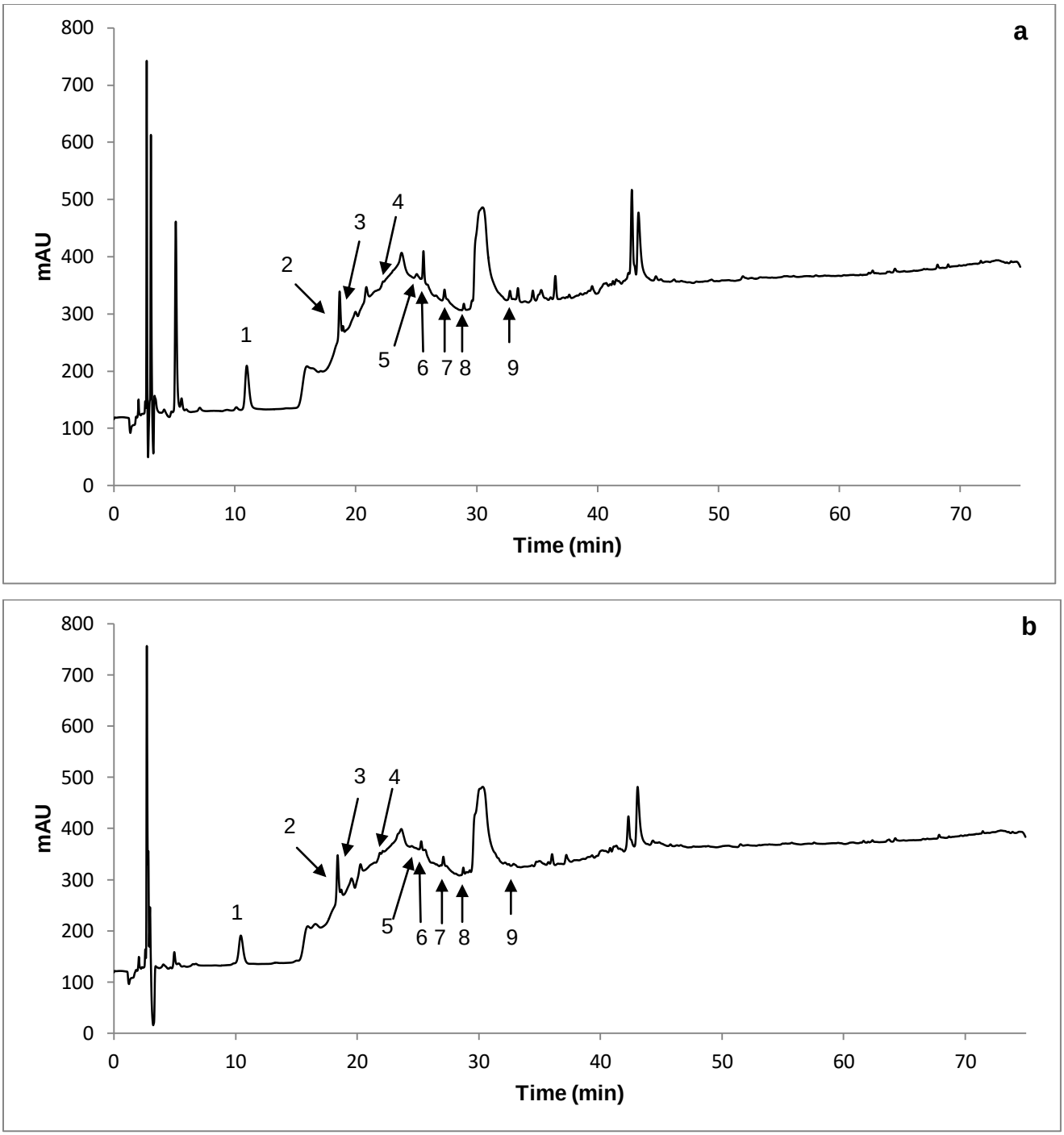

Fig. S1. HPLC chromatograms of the methanolic extracts of *Rorippa sarmentosa* a) leaf and b) stem. Detection at 220 nm. 1: 4-(methylsulfinyl)butyl GL, 2: but-3-enyl GL, 3: 5-(methylsulfinyl)pentyl GL, 4: 6-(methylsulfinyl)hexyl GL, 5: 7-(methylsulfinyl)heptyl GL (tentative identification), 6: indol-3-ylmethyl GL, 7: 2-phenylethyl GL, 8: 8-(methylsulfinyl)octyl GL, 9: 9-(methylsulfinyl)nonyl GL.

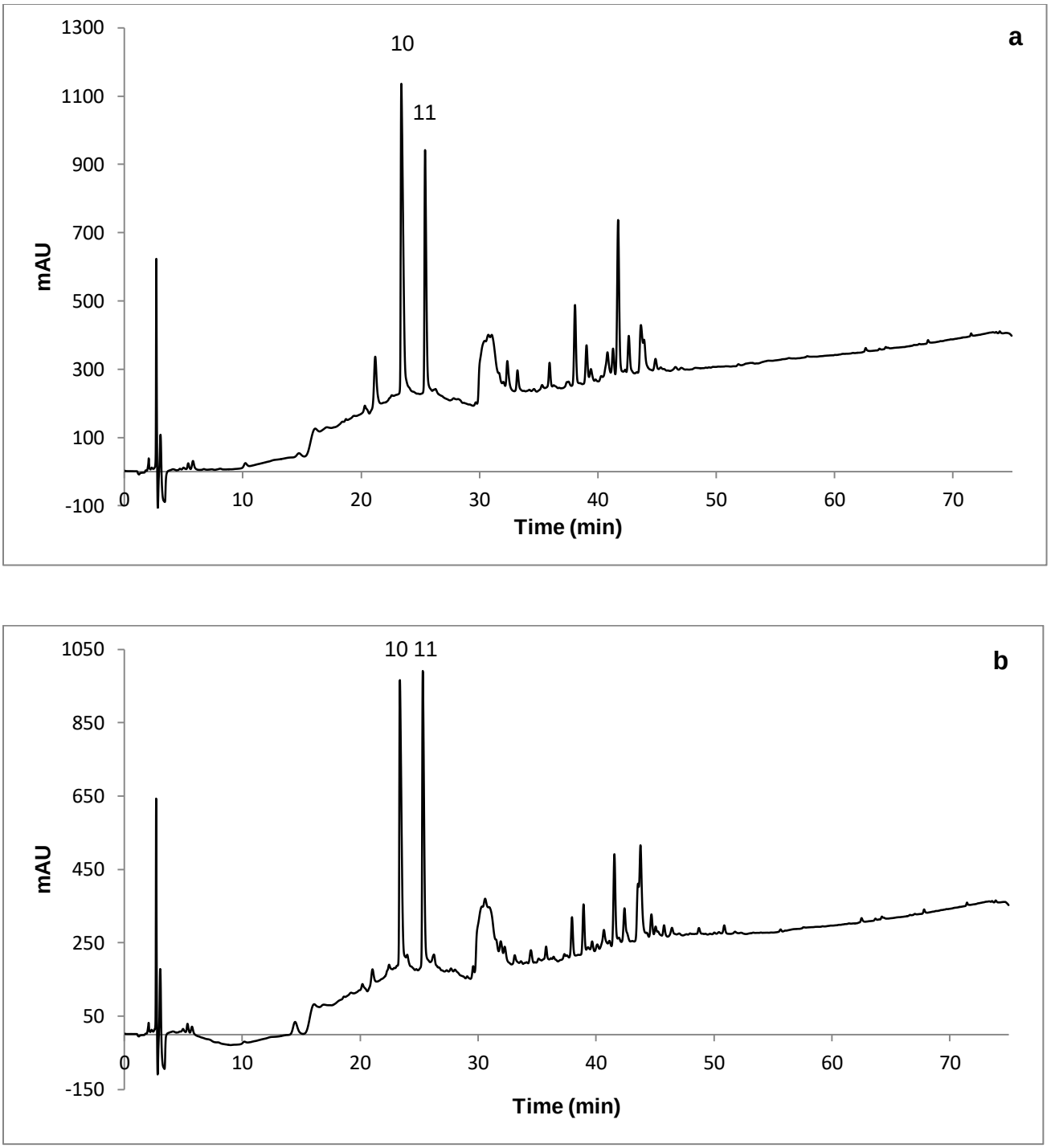

Fig. S2. HPLC chromatograms of the methanolic extracts of *Lepidium bidentatum* var. *bidentatum* a) leaf and b) stem. Detection at 220 nm. 10: benzyl GL, 11: 4-methoxybenzyl GL.

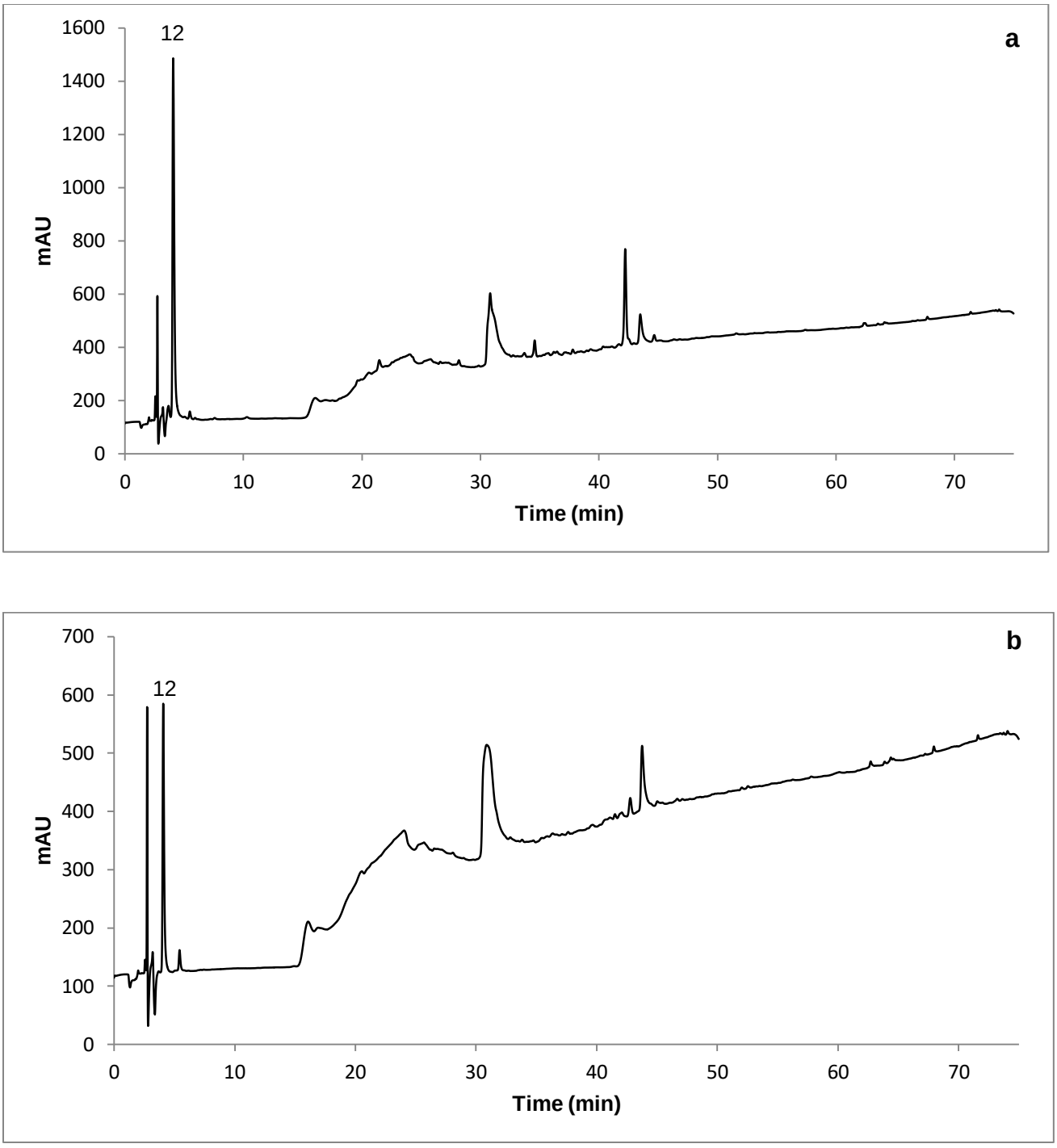

Fig. S3. HPLC chromatograms of the methanolic extracts of *Capparis spinosa* subsp. *cordifolia* a) leaf and b) stem. Detection at 220 nm. 12: methyl GL.

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