

**Supplementary material 1. Patients with biliary obstruction (adapted from [24]).**

Seventeen patients (8 men and 9 women) with clinical and biochemical features of cholestasis were recruited [24]. In all cases, dilatation of the biliary tree was first confirmed with abdominal ultrasound. Final clinical diagnoses in patients included were as follows: common bile duct stones, 8 patients; pancreatic tumor, 5 patients; bile duct tumor, 1 patient; benign common bile duct stenosis, 1 patient and chronic pancreatitis, 1 patient. The endoscopic retrograde cholangiopancreatography (ERCP) procedure involved placement of plastic 10F stents which were removed or replaced at a median of 5 weeks after initial procedure, depending on the diagnosis.

	Normal Range	Before stenting	After stenting
AST (U/L)	5 - 43	219.67 ± 36.12	33.30 ± 6.28***
ALT (U/L)	5 - 60	290.17 ± 55.04	44.90 ± 12.03***
AP (U/L)	20 - 140	715.23 ± 189.91	157.10 ± 23.73***
γGT (U/L)	5 – 80	1154.58 ± 225.31	238.90 ± 91.74**
Total bilirubin (mg/dl)	0.1 - 1.2	15.06 ± 1.65	1.60 ± 0.32***

Liver biochemistries were determined before and after an endoscopic stenting of the bile duct. Values represent the mean ± SEM. Statistically significant differences between pre- and post-stenting samples were determined by the Wilcoxon/Mann-Whitney rank-sum test: \*\*:  $p < 0.01$ ; \*\*\*:  $p < 0.001$ . ALT: alanine aminotransferase; AST: aspartate aminotransferase; AP: alkaline phosphatase, γGT: γ-glutamyltranspeptidase.

**Supplementary material 2. Changes in the urine profile of bile acid-glucuronides and in their metabolic ratios before and after a biliary stenting procedure in patients with biliary obstruction (n=12).**

<i>Urine levels</i>	Pre-stenting (nM)	Post-stenting (nM)
CDCA-3G	135.2 ± 52.2	31.7 ± 8.3*
CDCA-24G	1.8 ± 0.2	7.3 ± 2.6*
CA-24G	293.1 ± 199.2	40.0 ± 12.6
LCA-3G	3.7 ± 1.8	13.0 ± 3.3*
LCA-24G	0.3 ± 0.2	2.0 ± 0.6**
DCA-3G	22.7 ± 8.7	24.2 ± 6.9
DCA-24G	3.0 ± 1.4	17.8 ± 3.9**
HDCA-6G	311.7 ± 271.1	431.4 ± 120.7
HDCA-24G	0.4 ± 0.2	0.6 ± 0.3
HCA-6G	3,995.1 ± 2,962.3	679.0 ± 162.2
HCA-24G	2.9 ± 0.9	0.3 ± 0.1**
<i>Metabolic ratios</i>		
CDCA-3G/CDCA	6.9 ± 1.2	4.2 ± 0.8
CDCA-24G/CDCA	0.2 ± 0.1	1.1 ± 0.3
CA-24G/CA	4.4 ± 1.2	0.8 ± 0.3**
LCA-3G/LCA	NA	NA
LCA-24G/LCA	NA	NA
DCA-3G/DCA	4.3 ± 2.8	2.1 ± 0.5
DCA-24G/DCA	0.7 ± 0.6	1.7 ± 0.2
HDCA-6G/HDCA	5.0 ± 2.5	41.4 ± 11.3
HDCA-24G/HDCA	0.0 ± 0.0	0.0 ± 0.0
HCA-6G/HCA	4,159.1 ± 3,745.9	295.4 ± 235.3
HCA-24G/HCA	1.5 ± 0.7	0.1 ± 0.1

Bile acid-glucuronide concentrations are expressed in nM. Values represent the mean ± SEM. The metabolic ratio for each species was calculated as the ratio of glucuronide *versus* unconjugated precursor. Statistically significant differences between pre- and post-stenting

samples were determined by the Wilcoxon matched-pairs signed-ranks test: \*:  $p < 0.05$ ; \*\*:  $p < 0.01$ . CA: cholic acid; CDCA: chenodeoxycholic acid; DCA: deoxycholic acid; HCA: hyocholic acid; HDCA: hyodeoxycholic acid; LCA: lithocholic acid; G: glucuronide. NA: Not applicable due to the previously reported absence of unconjugated LCA in these urine samples [24].