Figure S1

Instrument Device:

Instrument Categories	Instrument Model
Pump Model	Agilent 1260 G1312B Binary Pump
AutoSampler	Agilent 1260 G1367E HiP ALS Autosampler
Degasser	Agilent 1260 G1379B Degasser
Column	Phenomenex Kinetex-Phenyl-Hexyl-100A (100 mm x 2.1
	mm i.d., 2.6 um)
Mass Spectrometer	AB Sciex Instruments QTRAP 5500
Source type	Turbo V Ion Source

HPLC Method Properties:

Duration : 10 min Injection volume : 5 ul

Mobile Phase : A: 0.1% (v/v) Formic acid / Water ; B: 0.1% (v/v) Formic acid /

Acetonitrile

Step Table :

Step	Total Time(min)	Flow Rate(µl/min)	A (%)	B (%)
0	0.10	100	85.0	15.0
1	2.00	100	85.0	15.0
2	5.00	100	70.0	30.0
3	6.00	100	10.0	90.0
4	7.00	100	10.0	90.0
5	8.00	100	85.0	15.0
6	10.0	100	85.0	15.0

Sample Preparation:

A volume of 100 μ L of the sample was taken, followed by the addition of 200 μ L of methanol. The mixture was vortexed thoroughly to ensure complete dissolution and subsequently incubated at -20°C for 30 minutes. Centrifugation was performed at 15,000 × g for 10 minutes, and the supernatant was collected and diluted 10× with 50% methanol prior to analysis. (Total dilution factor: 30×)

Mass Spectrometer Information:

Scan Type : MRM (Multiple Reaction Monitor)

Polarity : Positive ion mode

Source temperature : 400 °C

Data acquisition : Analyst 1.5 software

Parameter Table:

CUR (curtain gas) : 20.00 psi Nebulizing gas (GS1) : 45.00 psi Collision-activated Dissociation (CAD) : High Heating gas (GS2) : 40.00 psi

Electrospray capillary voltage : 5500.00 V

Preparation of Calibrators

The powdered standard was dissolved in methanol to prepare stock solutions of each target compound. These stock solutions were then used to prepare mixed working solutions with concentrations around $\mu g/mL$, which were stored at -20°C for future use. Calibration solutions were freshly prepared and serially diluted with 50% methanol to achieve a concentration range of ng/mL.

Quantitation Method:

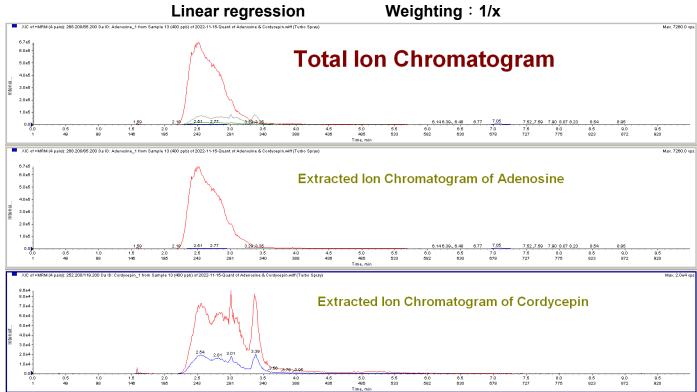
As the provided standards are not isotope-labeled, the Multiple Point External Standard method was employed for quantitation.

Selected Transitions and Parameter Settings

Analytes	Q1 mass	Q3 mass	DP (V)	EP (V)	CE (V)	CXP (V)
Adenosine	268.2	85.2	180	10	34	13
		136.2			24	10
Cordycepi	252.2	119.2	220	10	57	10
n		136.2			21	12

Note: Red indicates the ion pairs used for quantitation.

Calibration Curve of Standard

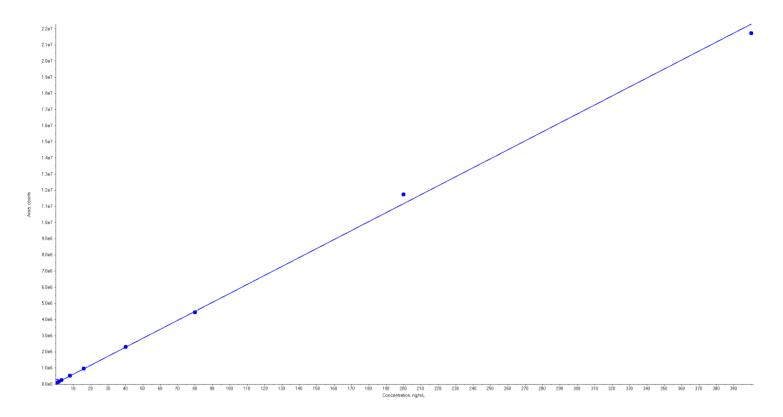


Note: Since cordycepin is a derivative of adenosine, their physicochemical properties are similar, making it difficult to completely separate them under HPLC conditions. However, the EIC chromatogram shows that the selected ion pairs produce distinct signals at their respective retention times, indicating specificity.

Analyte NameRegression Equation : Adenosine

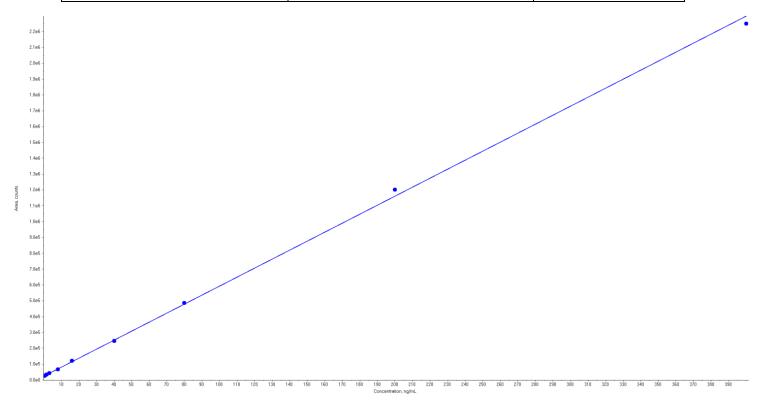
y = 5.56e + 004 x + 6.19e + 004 (r = 0.9994)

Expected Concentration (ng/ml)	Mean Calculated Concentration (ng/ml)	% Accuracy
0.32	0.27	84.9
1.6	1.69	105.5
3.2	3.29	102.7
8	8.28	103.5
16	16.19	101.2
40	40.36	100.9
80	78.98	98.7
200	210.15	105.1
400	389.90	97.5



Analyte Name: Cordycepin Regression Equation: y = 5.68e+003 x + 2.41e+004 (r = 0.9996)

Expected Concentration (ng/ml)	Mean Calculated Concentration (ng/ml)	% Accuracy
0.32	0.26	81.8
0.64	0.67	104.7
1.6	1.72	107.5
3.2	3.29	102.7
8	7.71	96.4
16	16.92	105.7
40	39.27	98.2
80	81.24	101.5
200	207.10	103.5
400	391.58	97.9



Results

Sample 1

Analyte Name	Spectrum	Calculated concentration (ng/ml)
Adenosine	2 flood	855.00
Cordycepin	000	1500.0

Sample 2

Analyte Name	Spectrum	Calculated concentration (ng/ml)
Adenosine	2 0x6 - 1 5x6	660.00
Cordycepin	3.0 ms 3.0 ms 4.0 ms 4.	1070.0

Sample 3

Analyte Name	Spectrum	Calculated concentration (ng/ml)
Adenosine	1 forth 1 fort	630.00
Cordycepin	3 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	1030.0

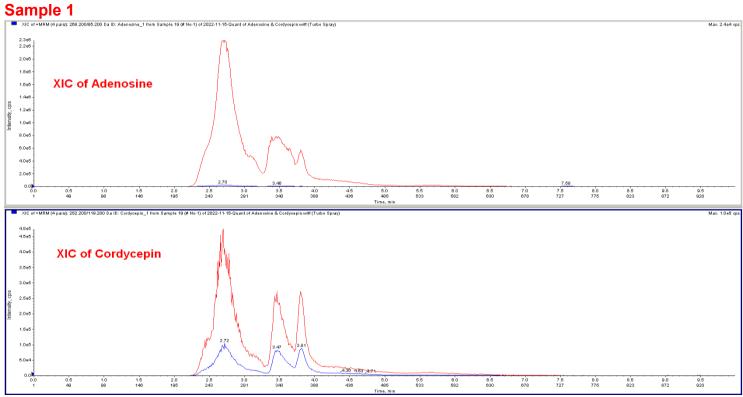
Summary (unit : ug/ml)

Calculation Formula: Analyte calculated concentration × 30 (dilution factor) / 1000

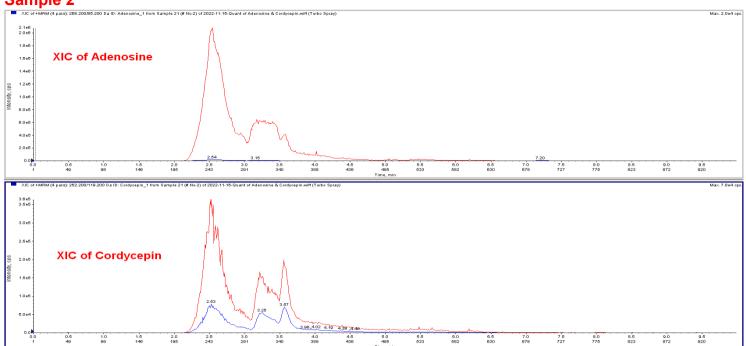
Analyte Name	Sample 1	Sample 2	Sample 3
Adenosine	25.65	19.80	18.90
Cordycepin	45.00	32.10	30.90

Sample Spectrum





Sample 2



Sample 3

