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# **Original Article**

# Geographical discrimination of *Cyclocarya paliurus* tea for origin traceability based on multielement analysis by ICP-OES and chemometrics multivariate

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#### ABSTRACT

*Objective:* This paper focused on the geographical discrimination of *Cyclocarya paliurus* tea for origin traceability based on multielement analysis by ICP-OES and chemometrics multivariate. *Methods:* In this study, eleven trace element concentrations were determined by ICP-OES and processed

*Methods*: In this study, eleven trace element concentrations were determined by ICP-OES and processed by multivariate statistical analysis.

*Results:* Based on ANOVA, the mean concentrations of 10 elements except Co differed significantly among six origins. Pearson's correlation analysis showed that 11 pairs of elements have a positive significant correlation and 12 pairs have a negative significant correlation. The geographical origins were effectively differentiated using the eleven elements combined with PCA. And the S-LDA model offered a 100% differentiation rate.

*Conclusion:* The overall results suggested that the combination of multielement analysis by ICP-OES and chemometrics multivariate could trace the geographical origins of tea. And the paper can provide reference for quality control and quality evaluation of *C. paliurus* in the future.

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# 1. Introduction

Cyclocarya paliurus (Batal.) Iljinskaja, commonly known as sweet tea tree, is an herbal tea used widely in China, grown in Southern China, such as Jiangxi, Hunan, and Zhejiang Provinces. With high nutritional values and health functions, the leaves of C. paliurus have been widely used in China both as an ingredient in health foods or dietary supplements for trace elements and as drug formulations in traditional Chinese medicine (TCM) (Xie et al., 2020; Xie, Li, Nie, Wang, & Lee, 2006). Significant attention has recently been drawn to the use of C. paliurus for developing functional food, as it has been reported to have many biological activities, including enhanced antihypertensive activity, hypoglycemic activity, hypolipidemic activity, improved mental efficiency, anticancer, antibacterial and antioxidant activity (Xie et al., 2006; Cao et al., 2017). It is believed that the therapeutic properties of *C. paliurus* are related to the enriched concentrations of several trace elements in leaves, such as Cr, Cu, Mn, and Se are cofactors for some enzymes which have crucial roles in the human body (Xie et al., 2006; Saribal, 2020). Therefore, determination of composition and concentration of trace elements in foods and related products is essential for understanding their nutritional importance. Also, mineral elements are a better choice for geographical origin traceability, which is more stable and closely related to the local environment, soil, and cultivation management conditions. It is not only used in tea geographical origin traceability, but also widely used in other agricultural products, such as wine, plant oil, rice and wheat, milk and dairy products (Zhang et al., 2020). Meanwhile, the accumulation of many beneficial and harmful mineral elements varies from different geographical environment. The content of elements are important evaluation criteria for the quality of tea. Thus, further research of the contents of the trace elements is being considered more and more important for the development of *C. paliurus* tea, especially the quality of the tea.

For multielement determination, several spectrometric techniques of atomic absorption and emission are available. Among these, inductively coupled plasma–optical emission spectrometry (ICP-OES) is used for the determination of multielement in leaves, due to high sensitivity, multielement capability, lower limits of detection and quantifications, ruggedness, and speed of analysis (de Aragão et al., 2021). Meanwhile, multielement analysis is considered to be one of the most reliable technical methods for food

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origin tracing, and it is well established. The composition of elements in organisms is directly affected by regional climatic conditions, biological environmental interactions, and biological metabolism.

In the present work, C. paliurus as a model and a total of 36 samples from six original regions were collected. Then 11 elements were analyzed by ICP-OES, combining with multivariate analysis, namely Analysis of Variance (ANOVA), principal component analysis (PCA), stepwise linear discriminant analysis (S-LDA), Duncan's multiple comparative analysis and Pearson's correlation coefficients analysis. The paper is expected to provide a reference for quality control and quality evaluation of C. paliurus tea. On the one hand, our study can provide a basis for the development of health care products of C. paliurus, such as the C. paliurus zinc supplement oral solution and C. paliurus unilateral beverage being developed by our team. On the other hand, at present, some researchers studied the immunoregulatory, hypoglycemic and antioxidative functions of selenium-enriched compound C. paliurus tea, our research can provide help for the selection of seleniumenriched C. paliurus origin.

### 2. Materials and methods

# 2.1. Chemicals and reagents

Analytical grade reagents and superior grade chemicals were used. Aron gas, with a minimum purity of 99.999%, was used to purge the optical system and generate plasma. All glasswares used were previously soaked in 20%  $\rm HNO_3$  for 24 h, cleaned with ultrapure water to remove any sour taste, then dried before use.

#### 2.2. Plant materials and sample treatment

*C. paliurus* tea-leaf samples were obtained from six regions of China: Xiushui S1 (Jiujiang, Jiangxi), Jinggangshan S2 (Jiangxi), Wannian S3 (Jiangxi), Leishan S4 (Guizhou), Zhangjiajie S5 (Hunan), and Wencheng S6 (Wenzhou, Zhejiang). Then, six samples were collected from each place of origin with a total of 36 samples. These samples were dried in an oven (Boxun Medical Biological Instrument Co., Itd., Shanghai, China) at 65 °C until they maintained constant weight. Then, they were ground using a ceramic mortar, and sived through 20 mesh sieves. All pretreated samples were stored in plastic bags at room temperature.

# 2.3. Apparatus

The elements were determined by an ICP-OES (725-ES, Varian, USA). The instrumental conditions were as follows: approximate RF power (radiofrequency) of 1.0 kW, gas flow (plasma flow, auxiliary flow) of 15.0 and 1.5 L/min respectively, nebulize gas pressure of 200 kPa, injection pump speed of 15 rpm, and stabilization time of 15 s. ICP-OES can select multiple characteristic wavelengths for each element at the same time, and the spectrometer has the function of synchronous automatic background correction. In our study, we chose the wavelengths (nm) with less interference, good precision and high signal-to-noise ratio. The wavelengths (nm) for the analyzed elements were 178.215 (I), 257.610 (Mn), 167.019 (Al), 213.857 (Zn), 249.772 (B), 327.395 (Cu), 407.771 (Sr), 196.026 (Se), 231.604 (Ni), 202.032 (Mo) and 238.892 (Co).

## 2.4. Graphite digestion

Approximately 0.5 g of each sample and 10 mL of mixed acid (nitric acid: perchloric acid, volume percentage, 4:1) were poured

into a graphite digestion vessel. Heat digestion was in a graphite digestion apparatus (SH 220F, Hanon Scientific Instruments Co., Itd., Dezhou, China). For the graphite digestion of the leaves, a graphite digestion apparatus (SH 220F, Hanon Scientific Instruments Co., Itd., Dezhou, China) was used, and the digestion procedure was conducted in two steps (1. 150 °C/ 30 min, 2. 200 °C/ 90 min). After the digestion procedure and subsequent cooling to room temperature, the resulting clear solution (about 1 mL) was dissolved in ultrapure water to a final volume of 50 mL. Blank was in the same way. All experiments were performed in triplicate.

#### 2.5. Calibration procedure

Monoelement stock solutions of 1000 mg/L I, Mn, Al, Zn, B, Sr, Se, Cu, Ni, Mo and Co were used to prepare multielement analytical calibration solutions. The calibration curves were prepared using 5% nitric acid (HNO<sub>3</sub>). Blank solutions were prepared in the same media.

### 2.6. Analytical validation parameters

The precision of the method was evaluated using the relative standard deviation, RSD%, of six replicates of each sample. The precision was obtained through the relative standard deviation of six replicates of each sample. The accuracy of the proposed method was estimated by determining the recoveries of the analytes by spiking experiments. Spiking experiment was carried out by addition of a certain amount of multielement standard solutions to 1.0 g sample. The spiked sample was prepared and measured by ICP-OES. The limits of detection (LOD) were determined by measuring an appropriate reagent blank solution 11 times. All standard deviations are based on measurements in triplicate.

#### 2.7. Statistical analysis

Statistical analysis was performed using the statistical package IBM Statistics SPSS 25.0 (IBM Company, NY, USA). Analysis of variance (ANOVA), PCA, S-LDA, Duncan's multiple comparative analysis and Pearson's correlation coefficients analysis were conducted to determine the different performances of the element data in tea from different geographic origins. To remove systematic bias from the datasets, ANOVA was applied as a non-parametric comparison for the significance analysis of all the parameters. Duncan's multiple range test (P < 0.05) was used to measure mean separation where the effect of location was significant. Pearson correlation analysis was used to test the correlations between each element in C. paliurus leaves (P = 0.05/0.01/0.001). PCA was used for dimensionality reduction, and could select the most significant variables, then, the six origins were ranked according to the Fvalue (Principal component comprehensive scores) using PCA. S-LDA was performed by a stepwise method based on the element content with significant differences (P < 0.05) presented in the ANOVA testing. The predictive power of the S-LDA model was evaluated by cross-validation method.

# 3. Results and discussion

# 3.1. Method validation

In the precision test, RSD values ranged from 3.2% to 7.1%, indicated a good precision of this method. The recoveries obtained for all elements after digestion ranged from 86.75% to 117.09%. The sensitivity of the method with respect to each element was evaluated using the resulted slope of the calibration curves. The correlation coefficients for all calibration curves were beyond 0.9991. The regression equations, correlation coefficients, linear ranges and the recoveries for all elements investigated were shown in Table S1 (see Supplementary material). The LOD in mg/L for each of the analyzed elements was as follows: I (0.0051), Mn (0.0012), Al (0.0020), Zn (0.0011), B (0.0583), Cu (0.0036), Sr (0.0106), Se (0.0114), Ni (0.0093), Mo (0.0100) and Co (0.0049).

#### 3.2. Differences in element concentrations

Table 1 showed the mean concentrations  $(\mu g/g)$  and standard deviations (SD) of the elements in C. paliurus tea. The results of ANOVA test showed that the mean concentrations of Co were not significantly different among the six regions (P > 0.05), whereas the mean concentrations of 10 elements (I, Mn, Al, Zn, B, Sr, Se, Cu, Ni and Mo) differed significantly (P < 0.05) among the six origins. Duncan's multiple comparison analysis was performed to discover the sources of the differences by comparing the averages of elements in tea from different regions. The results showed that characteristic element profiles existed for tea leaves from different origins (Fig. 1). Specifically, the tea leaves from S1 were characterized by the greatest mean concentrations of I, Se, Cu, Ni and Mo and the lowest mean concentrations of B. It is very noteworthy that the concentrations of Se from S1 were much higher than other regional tea, this could be due to the specific geological background in Huangao township, Xiushui county, S1. According to the sampling test by Jiangxi Food Fermentation Research Institute, the soil and water in Huangao township contain Se, and it is the only township in northern Jiangxi Province that contains Se in soil and water. Selenium is an essential mineral in human nutrition closely associated with the population health (Navarro-Alarcon, & Cabrera-Vique, 2008). A low Se status is associated with poor immunity, which can increase risks of mortality and cancer, and several chronic diseases. However, approximately 0.5-1 billion people throughout the world have inadequate Se intake levels, which is a problem that urgently needs to be addressed (Zhang et al., 2020). Therefore, C. paliurus tea from S1 can be made into some preparations or tea directly, and Se can be supplemented with appropriate use. The content of I in the tea from S2 and S3 was significantly lower than other regional tea, and the content of Mn was higher. Specifically, the content of Al in S2 was the lowest, while the highest in S3. However, the content of Co in S2 and S3 was similar and all higher than the other origins. Compared to other regional tea, S4 tea were characterized by the highest content of Sr. The contents of Mn, Zn and Sr in S5 tea were low. S6 tea was unique with the lowest contents of Co and Cu and the highest contents of Zn and B. In addition, Zn is essential for humans since it is a co-factor in enzymes, some of them being involved in protection against oxidative processes (Cindric et al., 2012). Therefore, *C. paliurus* tea can be a complementary source with several essential elements useful to the human organism.

#### 3.3. Pearson's correlation analysis

The Pearson's correlation coefficients of the elements in the *C. paliurus* tea were presented in Table 2. Statistically significant positive correlation coefficients were in the range of 0.717 to 0.850 and coefficient values between I-Se, I-Cu, I-Ni, I-Mo, Zn-Sr, Se-Cu, Se-Ni, Se-Mo, Cu-Ni, Cu-Mo, Ni-Mo were increased (P < 0.01 or P < 0.001). It showed that these 11 pairs elements had a synergistic effect. For example, I can promote the absorption and enrichment of Se, Cu, Ni, and Mo by plants, and Se can promote the absorption and enrichment of Cu, Ni and Mo. And there are 12 pairs of elements showing a negative significant correlation (P < 0.01 or P < 0.001): I-Mn, I-B, Mn-Se, Mn-B, Mn-Cu, Mn-Ni, Mn-Mo, Zn-Co, B-Sn, B-Cu, B-Ni, B-Mo, the *r*-values ranged from - 0.886 to - 0.425 was found between them, which indicating that these 12 pairs of elements have antagonistic effects.

#### 3.4. Principal component analysis (PCA)

Through the function of dimensionality reduction of PCA, all the information can be described by a few comprehensive variables, and the differences of feature elements among regions can be more intuitive and simpler to understand. The data was auto-scaled as a form of pre-processing. The results showed that three principal components (PCs) were generated, accounting for 74.71% of the overall variance. The concentrations of I, Mn, B, Se, Cu, Ni and Mo showed the highest loadings on the first PC, based on the absolute values of loadings, which accounted for 45.83% of the total variance. The second PC explained 19.78% of the variability, and included the concentrations of Al, Zn Sr and Co. And B and Al also showed the strong reverse loadings on the third PC (Table 3).

According to the Fig. 2A, the *C. paliurus* tea in S1 showed positive scores for PC1 and a combination of positive and negative scores for PC2. The leaves in S2 and S3 exhibited negative scores for PC1 and PC2. The tea in S4 and S5 exhibited a combination of positive and negative scores for PC1, but the PC1 scores was positive in S4, whereas negative in S5. The tea leaves in S6 showed negative scores for PC1 and positive scores for PC2. According to Fig. 2, most *C. paliurus* tea in the different origins occupy different spaces, indicating that it could be easily authenticated and differentiated, but some overlaps of the tea leaves in S2 and S3. The classification results of PCA cannot provide a satisfactory model to distinguish the six different origins of the tea.

Using the ratio of the eigenvalue corresponding to each principal component to the sum of the total eigenvalue of the extracted principal components as the coefficient (Eigenvalues: PC1 = 5.041,

Mean cor	centrations	and	standard	deviations	in	samples	from	six	regions	(S1	– S6)	(n	= 6	).
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Elements	Mean concentrations $(\mu g/g)$ from six regions						
	S1	S2	S3	S4	S5	S6	
Ι	2022.68 ± 198.25	723.70 ± 65.62	711.88 ± 59.67	1312.27 ± 91.56	1433.69 ± 109.56	839.49 ± 26.02	
Mn	746.36 ± 16.88	2415.80 ± 37.29	2444.84 ± 50.23	1354.84 ± 9.64	753.32 ± 53.14	1751.70 ± 12.94	
Al	114.69 ± 7.86	88.12 ± 6.83	132.37 ± 5.23	101.32 ± 6.17	108.54 ± 12.47	96.34 ± 3.49	
Zn	73.32 ± 4.59	57.72 ± 1.12	49.82 ± 1.34	80.13 ± 1.07	46.35 ± 3.17	140.13 ± 0.77	
В	34.86 ± 7.43	47.78 ± 13.39	59.07 ± 15.30	42.33 ± 5.33	57.47 ± 5.66	59.90 ± 6.67	
Sr	29.77 ± 4.61	16.32 ± 0.16	22.38 ± 0.42	50.28 ± 0.53	14.32 ± 0.87	42.83 ± 0.42	
Se	41.36 ± 7.43	10.00 ± 2.52	13.73 ± 1.95	10.17 ± 3.67	$12.34 \pm 4.04$	11.24 ± 2.21	
Cu	23.23 ± 4.44	13.04 ± 0.12	10.72 ± 0.22	13.84 ± 0.52	$12.14 \pm 0.98$	7.98 ± 0.06	
Ni	11.84 ± 2.17	7.05 ± 0.69	4.78 ± 0.46	7.15 ± 0.60	6.45 ± 0.64	4.99 ± 0.28	
Mo	5.11 ± 1.10	1.78 ± 0.16	1.83 ± 0.23	2.05 ± 0.33	1.79 ± 0.20	1.91 ± 0.24	
Со	$1.02 \pm 0.24$	1.09 ± 0.13	1.12 ± 0.15	$1.00 \pm 0.24$	$1.02 \pm 0.10$	0.86 ± 0.10	



Fig. 1. Profile of characteristic element content (Z-score standardization) of each region. The column labeled by the same lowercase letters represents a subset with no significant difference (*P* > 0.05) based on Duncan's multiple comparative analysis.

# Table 2 Correlation coefficients (r) of element values in C. paliurus leaves samples.

Elements	Correlation coefficients (r)										
	I	Mn	Al	Zn	В	Sr	Se	Cu	Ni	Мо	Со
I Mn Al Zn B Sr Se Cu Ni Mo Co	1.000 -0.886*** 0.132 -0.116 -0.474** 0.092 0.750*** 0.750*** 0.750*** 0.733*** -0.067	$\begin{array}{c} 1.000 \\ -0.026 \\ -0.006 \\ 0.28 \\ -0.127 \\ -0.503^{**} \\ -0.552^{***} \\ -0.555^{***} \\ 0.165 \end{array}$	$\begin{array}{c} 1.000 \\ -0.350^* \\ 0.042 \\ -0.143 \\ 0.307 \\ 0.201 \\ 0.036 \\ 0.171 \\ 0.209 \end{array}$	1.000 0.073 0.717*** -0.058 -0.247 -0.137 0.01 -0.425**	1.000 -0.196 -0.436 <sup>***</sup> -0.668 <sup>****</sup> -0.628 <sup>***</sup> -0.506 <sup>**</sup> -0.049	1.000 -0.037 0.001 0.001 0.066 -0.288	1.000 0.771*** 0.791*** 0.834*** -0.048	1.000 0.850*** 0.776*** 0.128	1.000 0.739*** -0.063	1.000 0.160	1.000

Note: \**P* < 0.05, \*\**P* < 0.01, \*\*\**P* < 0.001.

#### Table 3

Loadings of principal components (PC) for 11 elements in tea.

Elements		Loadings	
	PC1	PC2	PC3
Ι	0.917	0.093	-0.242
Mn	-0.708	-0.219	0.419
Al	0.197	-0.492	-0.337
Zn	-0.146	0.882	0.059
В	-0.657	-0.1	-0.56
Sr	0.047	0.806	0.203
Se	0.879	-0.033	-0.135
Cu	0.915	-0.121	0.177
Ni	0.913	0.034	0.071
Мо	0.873	0.008	0.11
Со	0.025	-0.649	0.478

PC2 = 2.174, PC3 = 1.002), the comprehensive principal component expression is obtained:  $F = 0.613 F_1 + 0.265 F_2 + 0.123 F_3$ .

And the six origins were ranked according to the mean of the *F*-value. As shown in Table 4, the comprehensive scores of samples from S1, S4, and S6 rank the top 3. The overall ranking of S1 was

the highest, indicating that the quality of sample S1 was superior compared to other tea samples.

#### 3.5. Stepwise linear discriminant analysis (S-LDA)

The S-LDA is an explicit statistical method to model the difference between classes. To acquire a more predictable classification model of new samples from the six regions, S-LDA was conducted based on the content of 10 significant elements (P < 0.05). During the S-LDA analysis, a stepwise discriminant method was applied to select the optimal variable for separating each region. As a result, 10 elements were selected and four discriminant functions were constructed on the basis of Wilks' lambda values. These five functions explained the 100% of the total variance (discriminant function 1 explained 77.1% of the total variance, discriminant function 2 accounted for 15.4%, discriminant function 3 accounted for 6.6%, discriminant function 4 accounted for 0.9% and discriminant function 5 accounted for 0.1%). The constricted discriminant functions based on 10 selected elements were shown as follows:

 $F_1 = 0.002 \ I + 0.038 \ Mn + 0.050 \ Al - 1.081 \ Zn - 0.014B - 2.700$ Sr + 0.021 Se + 3.672 Cu - 0.344 Ni - 0.455 Mo + 45.991.



Fig. 2. PCA score plots of PC1, PC2 (A) and PC1, PC2, PC3 (B).

**Table 4** Mean of the principal component scores  $(F_1, F_2, F_3)$ , comprehensive scores (F) and ranking.

Origins	$F_1$	$F_2$	$F_3$	F	Ranking
S1	2.059	0.024	0.013	1.270	1
S2	-0.541	-0.558	1.190	-0.333	4
S3	-0.725	-1.208	-0.223	-0.792	6
S4	0.049	0.821	0.589	0.320	2
S5	-0.024	-0.655	-1.307	-0.349	5
S6	-0.819	1.576	-0.261	-0.116	3

$$\begin{split} F_2 &= -\ 0.004\ I + 0.039\ Mn - 0.042\ Al - 0.495\ Zn + 0.040B + 1.774\\ Sr + 0.054\ Se - 1.407\ Cu + 0.363\ Ni + 0.469\ Mo - 54.305.\\ F_3 &= 0.006\ I - 0.005\ Mn + 0.007\ Al - 0.879\ Zn - 0.037B + 1.927\\ Sr - 0.076\ Se - 0.841\ Cu + 0.489\ Ni + 0.637\ Mo + 18.489.\\ F_4 &= 0.002\ I + 0.009\ Mn - 0.065\ Al + 0.022\ Zn + 0.015B + 0.125\\ Sr + 0.242\ Se + 0.412\ Cu + 0.684\ Ni + 2.509\ Mo - 36.145.\\ F_5 &= 0.002\ I + 0.001Mn + 0.134\ Al + 0.020\ Zn + 0.015B - 0.012\\ Sr + 0.060\ Se - 0.159\ Cu - 0.444\ Ni + 0.403\ Mo - 16.114. \end{split}$$

The discrimination of tea leaves from six different regions was validated by the bidimensional and three-dimension scatter plot

of scores based on the five discriminate functions' scores (Fig. 3). It is clearly shown that tea leaves samples from six different regions were well distinguished from each other. The results confirmed that the S-LDA method based on the trace element contents provided useful information for the geographical origins discrimination of the tea leaves. Furthermore, the leave-one-out cross-validation was conducted to obtain the predictability of the S-LDA model. The result indicated that the overall accuracy of the S-LDA model was 100%, indicating a good performance for the classification of tea samples from different regions, and 100% of the original tea samples were predicted correctly, showing an extre-



Fig. 3. S-LDA scatter plots of C. paliurus tea with different geographical origin from first two (A) and first three discriminant functions (B).

mely satisfactory prediction capacity, without any mistakes. Tea from each origin were congregated together, which indicated that their elemental composition was similar and the geographical origin played a vital role in determining the multielemental composition of tea leaves.

## 4. Conclusion

A total of 11 elements (I, Mn, Al, Zn, B, Sr, Se, Cu, Ni, Mo and Co) were determined in C. paliurus tea using ICP-OES, after a rapid and efficient graphite digestion procedure with adequate values of detection and quantification limits, precision, and accuracy. The 11 elements were selected for analysis, and statistical analysis (ANOVA, PCA, Duncan's multiple comparative analysis, Pearson's correlation analysis and S-LDA) confirmed that each region had characteristic element contents profile. The mean concentrations of 10 elements except Co in C. paliurus tea differed significantly (P < 0.05) among the six origins. Pearson's correlation analysis showed 11 pairs of elements have a positive significant correlation and 12 pairs have a negative significant correlation (P < 0.01). The tea leaves samples from the six regions can be well discriminated from each other based on these elements by PCA and S-LDA model. And the principal component comprehensive scores showed that the quality of sample S1 was superior compared to other tea samples. Tea from these six geographical origins can be authenticated robustly with 100% recognition capacity based on the 10 correlated mineral elements in the S-LDA model. The overall results suggested that the combination of inorganic element and chemometrics multivariate statistical analysis could be used as a rapid andcethod for geographical origin identification of tea. At the same time, it can provide reference for quality control and quality evaluation of C. paliurus in the future.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chmed.2022.05.005.

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