

Differential Analysis of Camphor Wood Products by Desorption Atmospheric Pressure Chemical Ionization Mass Spectrometry

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ABSTRACT: In the course of this study, desorption atmospheric pressure chemical ionization mass spectrometry (DAPCI-MS) was applied to readily acquire the mass spectral fingerprints of camphor wood and other wood samples under ambient conditions. Characteristic natural analytes, such as camphor and geraniol, were successfully detected in their protonated form and then identified by tandem mass spectrometry (MSⁿ). Further principal component analysis (PCA) and cluster analysis (CA) of the mass spectrometric results allow a confident discrimination of camphor wood products from inferior/fake ones. These experimental findings demonstrate that DAPCI-MS is a valuable tool for differential analysis of untreated camphor wood products with sufficient sensitivity and high throughput.

KEYWORDS: desorption atmospheric pressure chemical ionization, mass spectrometry, principal component analysis, camphor, cluster analysis

■ INTRODUCTION

Cinnamomum camphora (L.) Presl (usually known as camphor tree) is widely planted in southern China, Vietnam, and Japan. *C. camphora* trees contain a large amount of valuable volatile chemical compounds such as camphor, 1,8-cineole, nerolidol, campherenol, and campherenone, among which camphor plays a significant role in the celluloid and pharmaceutical industry. Camphor wood itself has long been taken as a kind of rigid and insect-resistant structural material for luxury architecture and furniture, and its anthropogenic consumption dates back centuries in China and many other countries in the world.

As the total supply of the camphor wood is heavily deficient judged on commercial scale of modern society and industry, the price of genuine camphor materials has been dramatically inflated in recent decades. Artificial camphor wood and inferior camphor wood products have been commonly found on the camphor wood market. Meanwhile, camphor wood and other precious wood species are illicitly imported/exported as common wood logs, posing great challenges to uncover such smuggling activities with proper analytical techniques. Certainly, authentication of the wood species, from raw materials to finished products, is of primary importance against illegal logging and counterfeit products.

Traditionally, sensory methods are commonly employed to distinguish camphor wood species due to its simple implementation and easy operation, despite it being widely known that the sensory methods are short of precision and accuracy even executed by experienced specialists. Some advanced techniques, e.g., wood retrieval table¹ and wood computer recognition,^{2–4} are useful to discriminate the wood species. However, these methods often fail in cases where the final products are lacking the bark or other surface features.

Currently, optical spectroscopy,⁵ gas chromatography (GC),⁶ and gas chromatography–mass spectrometry (GC-MS)^{6,7} are the major instrumental methodologies employed for identifying wood products. Together with proper extraction techniques, liquid chromatography–mass spectrometry (LC-MS) has been also applied to screen potential aroma contributor in oak wood.⁸ The aforementioned methods unavoidably require laboriously tedious, time-consuming, and destructive sample preparations prior to practical sample interrogation. Therefore, it is highly desirable to develop methods for authentication of camphor wood samples with high sensitivity, good accuracy, and high throughput.

Among the many techniques^{9–15} available for high-throughput mass spectrometric analysis, surface desorption atmospheric pressure chemical ionization mass spectrometry (DAPCI-MS)^{16–18} is of particular interest for the purpose of fast camphor wood analysis. DAPCI-MS has been well demonstrated as a noninvasive analytical method of high sensitivity, good chemical selectivity, and fast analysis speed. To date, DAPCI-MS has been successfully applied for trace analysis in food safety,^{17,19} forensic science,^{20–23} environmental science,²² pharmaceutical analysis,^{24,25} and plant science.²⁶ Herein, application of DAPCI-MS has been extended to fast discrimination of camphor wood products, obviating general sample preparations. Together with further principal component analysis (PCA) and cluster analysis (CA), DAPCI-MS was applied for better differentiation of camphor wood products

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from other wood samples. The method developed here is a particularly powerful tool for rapid verification of camphor wood chemotype at molecular levels, and it opens a window to rapidly differentiate rare wood materials from ordinary wood samples.

MATERIALS AND METHODS

Camphor Wood Samples and Chemicals. All camphor wood samples were obtained from diverse origins. In particular, 6 different brands of paperweights and 10 camphorwood sticks were purchased from local exclusive agencies, and 10 untreated camphorwood combs were bought from one local scenic spot (Jiangxi, China). Each camphor wood product was carefully wrapped with wax paper to avoid mutual contaminating and labeled with a number. No further sample pretreatments except cleaning with water, if necessary, were performed before being subjected to mass spectrometric analysis, though most of the camphor wood samples were vanished on the surface for beauty (see below for explanations). As a reference, a piece of common wood was obtained from a shipping package (Thermal Co., Alabama).

Methanol (HPLC grade) was purchased from Sigma-Aldrich Co. Ltd. (USA). Deionized water was provided by the chemistry facilities in the East China Institute of Technology.

Instruments and Working Conditions. Experiments were performed using a commercial LTQ-XL linear ion trap mass spectrometer (Thermo Fisher Scientific, San Jose, CA) coupled with a homemade DAPCI source for ion generation and Xcalibur software for instrument control and data processing, as described elsewhere.^{16,27} Briefly, as shown in Figure 1, a stainless steel (SS)

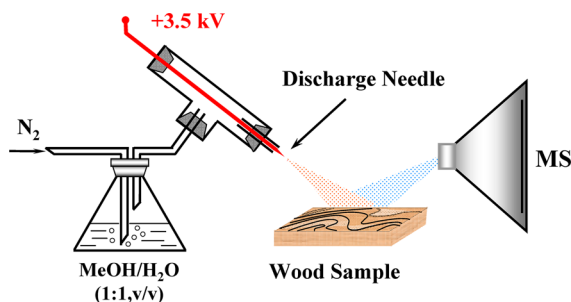


Figure 1. Schematic illustration of DAPCI for wood material analysis.

needle—with an insulator on the back end—was inserted coaxially into a fused silica capillary (0.5 mm i.d.). Geometry was carefully arranged so that the sharp SS needle was protruding ~ 5 mm out of the capillary orifice. The capillary and sharp needle were secured coaxially with a union tee and silica ferrule. The unoccupied end of the tee piece was connected with a gas line, being fed with a high-pressure nitrogen gas (~ 0.5 MPa), bubbled through a 1:1 (v:v) methanol/ H_2O solution, carrying the methanol/ H_2O mixture vapor as the reactive reagent. After a high voltage (3.5 kV, with a discharge current of ~ 0.1 mA) was applied to the SS needle, a corona discharge was lit to produce primary radical cations and the secondary cluster ions of the reactive reagents subsequently via gas-phase ion–molecule reactions in ambient air. The ion source was carefully aligned with respect to the LTQ mass spectrometer, and the electrode tip was placed ~ 5 mm away from the inlet orifice. The height between the needle tip and the sample surface was 1–3 mm, and the angle of incident charging ions against MS inlet is adjustable and set in the range between 30° and 40° . Generated ionic species were accelerated by the highly localized electric field and the nebulizing flow and subsequently bombarded on the sample surface to produce ions of analytes from the sample surface at ambient surroundings.

The DAPCI source and LTQ mass spectrometer were both set to run in positive modes. The temperature of the heated capillary was set to 180°C . Other parameters were default values recommended by the instrument manufacturer. All mass spectra were collected and averaged over a period of 1.6 min, followed by background subtraction.

Collision-induced dissociation (CID) experiments, up to MS^3 , with a collision energy (CE) of 10–30% and a mass-to-charge window width of 1.5 units, were performed on the characteristic ions for the sake of molecular structure identification.

Data Analysis. PCA and CA were used to recognize the pattern based on the mass spectral raw data by virtue of Matlab software (version 7.0, Mathworks, Inc., Natick, MA) and MVSP software (version 3.0, Kovach Computing Services, Wales, U.K.), respectively. Single, full-scan mass spectrum data was exported to Microsoft Excel as a one-to-one function. The file used the m/z values as independent variables and the relative intensities of the full-scan mass spectra (MS^1) as dependent variables. To ensure the quality of the statistical analysis, 15 pieces for each camphorwood comb sample and 20 pieces for every other sample were obtained. Hence, there were a total of 490 mass spectra which were again assembled into a $N \times 490$ matrix, where N represents the total number of m/z values collected in the mass spectrum. This matrix was readily loaded from the Excel file into the Matlab or MVSP software for PCA or CA analysis, respectively. The principle components for output were automatically determined by the Matlab software with the “princomp” function, and the accuracy for PCA was set at a high level (1×10^{-8}). The scores and loadings of the first three principle components (PCs) were 3D plotted in Matlab. In the MVSP software, CA was done with the arithmetic mean (UPGMA) algorithm, which employs a sequential clustering algorithm to identify the similarity with the local topological relationships. The output for UPGMA is a rooted tree in sequence of similarity of different wood samples.

RESULTS AND DISCUSSION

Representative DAPCI Mass Spectra. As previously reported, hundreds of chemical compounds, such as ester, hydrocarbon, ether, terpene, and so on, are found in camphor tree oil,^{28–30} making the camphor wood a complex sample for mass spectrometric analysis. Under optimized experimental conditions, the DAPCI mass spectra for all camphor wood products were recorded without sample pretreatment. Note that measurements of blank wood samples were performed prior to each sample analysis in order to exclude the interference of possible carry-over effects. Typical DAPCI-MS spectra of five kinds of camphor wood as well as the common wood are illustrated in Figure 2. The most abundant peak at m/z 97 dominated on the background mass spectrum (Figure 2A and 2Ba) is assigned to the protonated methanol clusters $[(CH_3OH)_3H]^+$, due to the dominance of methanol as the extractive/reactive solvent and proton donor in the experiments.³¹ Presumably, most compounds contained in common wood could not be effectively desorbed and then ready for chemical ionization in the DAPCI process. Thus, only a few peaks (for example m/z 195, 212) were detected with relatively high intensities from normal wood samples. It could also be simply attributed to the lack of endogenously volatile/semivolatile compounds in common woods. On the contrary, mass spectra from camphor wood samples are rich of peaks spanning from m/z 130 to m/z 300 due to plenty of volatile/semivolatile phytochemicals available in camphor wood (Figure 2Ba–Bf). Generally, for noncamphor or fake-camphor sample (i.e., common wood in Figure 2B), the signals representing low-concentration camphor and other characteristic chemicals are so weak that the signals at 97 and 279 appeared stronger. For all wood samples tested, no signal was notably detected in the mass range beyond m/z 300, suggesting that no molecules of high molecular weight were efficiently desorbed/ionized from the wood surface. Note that few signals were detected below m/z 100, due to the fact that the LTQ instrument was not specially tuned for detecting chemicals of low molecular weight.

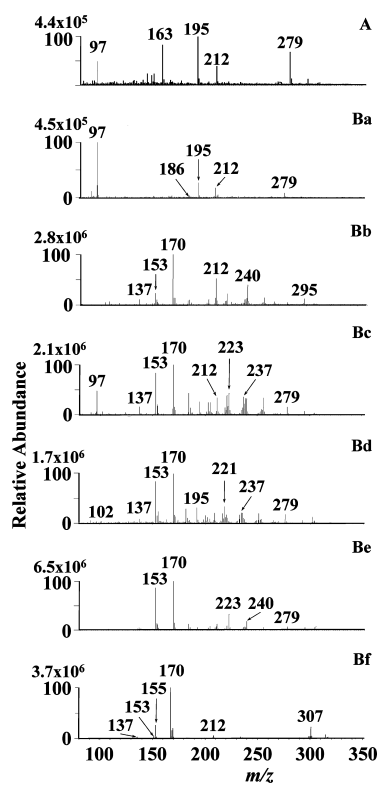


Figure 2. DAPCI mass spectra of six kinds of wood samples: (A) blank DAPCI mass spectrum; (Ba) common wood; (Bb) paperweight 1; (Bc) paperweight 2; (Bd) paperweight 3; (Be) camphor comb; (Bf) camphor wood stick.

Nevertheless, the compounds detected in mass range m/z 130–300 yield abundantly characteristic information about camphor wood, making subsequent differentiation of wood samples feasible.

Camphor (MW 152), a typical marker of genuine camphor wood, was commonly detected from all the camphor wood samples at m/z 153 (Figure 2Bb–Bf) as the protonated molecules but not from other noncamphor wood samples (Figure 2Ba). Upon CID, the protonated camphor (m/z 153) produced major fragment ions of m/z 135, 109, and 95 by loss of H_2O , C_2H_4O , and C_3H_6O (Figure 3a), respectively. The fragmentation pattern is very consistent with results using electron impact (EI) ionization.^{32–34} However, in comparison with the EI technique, a relatively clear fragmentation pattern was obtained in the DAPCI mass spectrum of camphor, facilitating easier confirmation of the camphor signal out of the complex matrix. More interestingly, the abundant peak at m/z 170 present from all camphor wood samples was identified as the water adduct with camphor radical cations $[M + H_2O]^{*+}$. During the CID process, the precursor ions (m/z 170) preferably yielded a fragment at m/z 153 (Figure 3b), which produced the same fragmentation pattern (the inset of Figure 3b) as that of protonated camphor (Figure 3a). Water adducts to other analytes were well observed under comparably ambient conditions.³⁵ Formation of such radical cations of water adduct $[M + H_2O]^{*+}$ presumably were attributed to the ion–molecule reactions in the ambient ionization region, suggesting a blend of different charging species available for ionizing a sort of compounds of various chemical properties.³⁵ In the current scenario, a 50/50 water/methanol solution was being used; thus, the role of environmental humidity is highly limited.

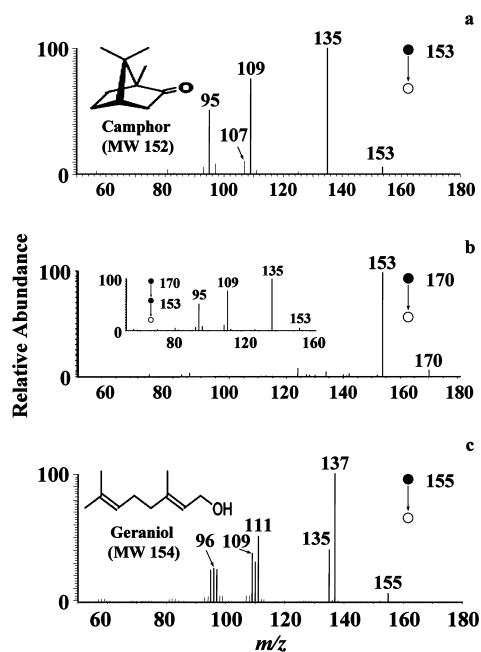


Figure 3. MS^n spectra of precursor ions of m/z 153, 170, and 155: (a) DAPCI- MS^2 spectrum of camphor in paperweight 1 (precursor ion m/z 153); (b) DAPCI- MS^2 spectrum of camphor (m/z 170) in one camphor wood; (inset) MS^3 spectrum of m/z 170 (CID performed on m/z 153); (c) DAPCI- MS^2 spectrum of geraniol (m/z 155) in camphor wood.

Moreover, the highly intensive camphor peak at m/z 170 ($[M + H_2O]^{*+}$), against its protonated one at m/z 153, implies that stabilization of the molecular radical cations might be assisted by the water molecule. The abundant peak at m/z 155 detected from the camphor stick sample (Figure 2Bf) was assigned to protonated geraniol, which gave characteristic fragments of m/z 137, 109, and 95 by loss of H_2O , CH_3CH_2OH , and $CH_3CH_2CH_2O$, respectively. This fragment pattern is in a good agreement with the CID results of geraniol.³⁵ Peaks at m/z 223 and 221 were tentatively identified as protonated campherenol and campherenone molecules, respectively. It can be concluded that a variety of characteristic volatile/semi-volatile chemicals, originated from camphor wood sample, can be clearly recorded and identified without chemically removing the thin vanish layer on the sample surface prior to sample analysis. It is also possible that some of the chemicals would not penetrate the vanish layer, being available for ionization and subsequent analysis; however, in the context of nondestructive, quick fingerprinting, and differentiation of valuable camphor woods, minimum/no sample preparation was applied in the current study.

Principal Component Analysis. As previously discussed, detection of authentic camphor signal provides a molecular indicator of genuine camphor wood sample. Generally, this requires expensive MS instruments with advance tandem MS capabilities. High-performance miniature mass spectrometers can be a solution for online and in situ applications. Alternatively, a cheap MS sensor with a narrow mass range (m/z 130–260) and no CID performance might be useful once pattern recognition methods are combined for data processing.

Principal component analysis (PCA), a powerful tool for data compression and information extraction,^{36,37} was employed to process the DAPCI-MS data for differentiation of common wood (Figure 4Aa), three types of paperweights (Figure 4Ab–

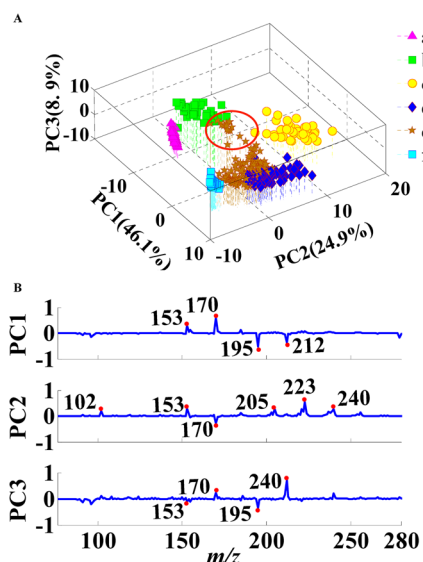


Figure 4. PCA results of DPACI-MS data of six kinds of wood sample. (A) 3D score plots: (a) Common wood; (b) paperweight 1; (c) paperweight 2; (d) paperweight 3; (e) camphor combs; (f) camphor wood stick. (B) Corresponding PCA loading plots.

d), and a collection of camphor wood combs (Figure 4Ae), camphor wood stick (Figure 4Af), after excluding the possible cluster/background ions from the mass spectra, i.e., m/z 97 and m/z 279. As a result, the score and loading plots of PCA of six types of wood products are shown Figure 4A and 4B, respectively. There was 79.9% of the total variations represented, and the percentages of variance explained by PC1, PC2, and PC3 were 46.1%, 24.9%, and 8.9%, respectively. Along the PC1 direction, common wood (Figure 4Aa), paperweight 3 (Figure 4Ad), and camphor stick (Figure 4Af) can be fully separated. Note that the predominant ions in the loading plot of PC1 (Figure 4B) are m/z 153 and 170 (in the positive direction), which are the fingerprints for the camphor molecules. Therefore, PC1 mainly reflects the camphor content difference in these wood product samples. Camphor stick (Figure 4Af) and paperweight 3 (Figure 4Ad) are mutually close in PC1 direction, indicating that these samples were similar in chemical contents but with a small difference. In fact, the camphor stick (Figure 4Af) was also made from genuine camphor wood, which possesses a different content of the phytochemical such as camphor, geraniol (m/z 155), and campherenol (m/z 223). In addition, the paperweight 1 (Figure 4Ab) signals partially mixed with those of the common wood (Figure 4Aa), which indicates that some of the paperweight 1 (Figure 4Ab) products might be only rubbed with camphor odor but not fully made from genuine camphor wood materials. The data points of camphor combs (Figure 4Ae) partially overlapped with the ones of the common wood, as emphasized in the red circle in Figure 4A, suggesting that some of the combs might not be a real camphor product, most likely made of fake camphor woods.

Similarly, paperweight 2 (Figure 4Ac), camphor combs (Figure 4Ae), and camphor stick (Figure 4Af) can be separated in the PC2 direction. On the basis of the loading plots of PC2, separation was mainly contributed by the ions of m/z values higher than 200, suggesting more characteristic ions alongside camphor available as potential molecular indicators for recognition of genuine camphor wood. The paperweight 2

(Figure 4Ac) samples are isolated in the 3D PCA scheme (Figure 4A), suggesting that the camphor paperweight 2 (Figure 4Ac) samples are of unique feature which differentiates itself from other camphor products. This is also consistent with the fact that the camphor paperweight 2 (Figure 4Ac) was made from the most expensive camphor wood materials.

Cluster Analysis. Although PCA was proven successful for discrimination of the camphor wood products, a cross-validation was desired using another statistics method. Cluster analysis (CA), a multiple-classes process which classifies the abstract objects based on their similarities, has been used for classification of unknown samples.^{27,38} Thus, CA has been adapted to cross-check the PCA results obtained based on the DAPCI-MS fingerprints. As a demonstration, a total of 150 DAPCI mass spectra recorded from 10 camphor wood combs were processed by CA using the UPGMA method of MVSP software. The CA results show that the similarity of all samples was higher than 80% except for the camphor comb 4, which was only 35% (Figure 5A). It indicates that the camphor comb

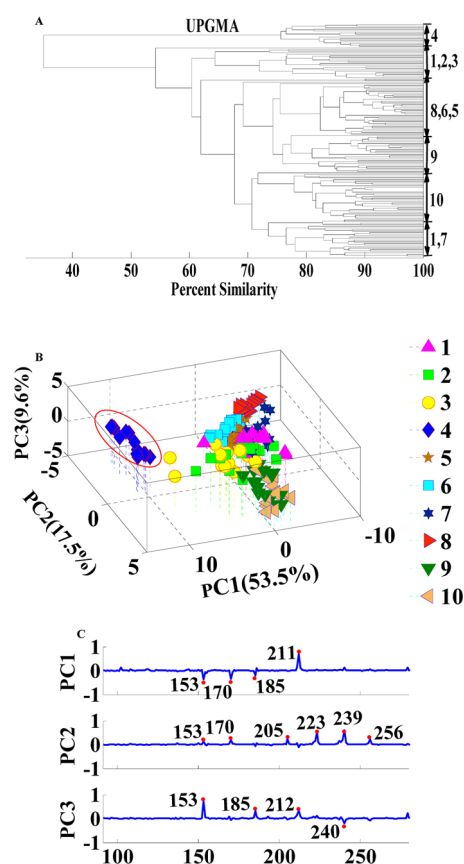


Figure 5. Cross-check analysis of DAPCI-MS for fast differentiation of camphor wood comb samples using both UPGMA and PCA. (A) Similarity plots obtained using UPGMA. (B) Score plots obtained in PCA. (C) Corresponding loading plots in PCA. Note that the red circle is only to guide readers' eyes.

4 samples were counterfeits. The genuine samples were further classified by the CA results into four subgroups, i.e., (1) combs 5, 6, and 8; (2) combs 1, 2, 3, and 7; and (3) comb 9; and (4) comb 10. Within these four groups, the similarity is at least 80%, except that comb 2 and 3's similarity with comb 7 is only 70%. As shown in Figure 5B, these samples were also clustered in a very similar way in the PCA score plots, although the

digitalized similarity of the groups was not obviously available in the PCA score plots. The existence of the 4 subgroups illustrates the camphor combs were made from camphor wood materials but with slight differences. Many environmental factors including the growth regional, growth era, soil, and water content, etc., may cause the differences.

In comparison with PCA, another advantage of CA is to display the deviation of each measurement, which generates a signal MS spectrum (i.e., a data point in the PCA score plot). Ideally, the similarity between individual data points should be 100% for the same sample, but the similarity percentage is actually less because of nonuniformity in sampling. As shown in Figure 5A, the deviation was about 15% for most measurements, and high deviation of 25% was also possible for some cases. However, the similarity is still high enough to ensure a clear separation, showing that a relatively high deviation of the measurement will not affect the qualitative results obtained using either PCA or CA methods.

All experimental data showed that surface desorption atmospheric pressure chemical ionization mass spectrometry (DAPCI-MS) was able to visualize the differences between the genuine and the inferior camphor wood products without any sample pretreatment. With the help of tandem mass spectrometry, characteristic chemicals such as camphor and geraniol were identified, providing molecular indicators to discriminate camphor wood materials from the fake ones. On the basis of pattern recognition methods such as principal component analysis (PCA) and cluster analysis (CA), camphor wood products were easily grouped using mass spectral fingerprints obtained in a narrow mass range (e.g., 130–260 Da), allowing a confident differentiation of camphor wood products from other wood samples within 3 min, requiring no expensive MS instruments coupled with advance tandem MS capability. Therefore, the proposed DAPCI method has great potential in applications of screening other kinds of wood sample and thus benefits wood engineering and the wood industry.

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Notes

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ABBREVIATIONS USED

DAPCI-MS, desorption atmospheric pressure chemical ionization mass spectrometry; PCA, principal component analysis; CA, cluster analysis; MS, mass spectrometry; RSD, relative standard deviation; LTQ, linear ion trap

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