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NITROGEN-DOPED CARBON DOTS FROM BILIMBI JUICE (*Averrhoa Bilimbi L.)* VIA HYDROTHERMAL METHOD FOR IRON AND MERCURY SENSING

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Abstract: Carbon dots (CDs) have been widely used in various applications, one of them being metal ion sensing. Synthesizing CDs with sensing characteristics is influenced by two factors, i.e., precursor and dopant agent. This study aims to use bilimbi (*Averrhoa bilimbi*) with N, N-dimethylformamide (DMF) as a nitrogen source to synthesize CDs via the hydrothermal method. The result of hydrothermal showed significant colors of CDs with and without the presence of nitrogen, and these behaviors were also confirmed by the differential absorption of the CDs, with λ_{max} of absorption at 291 nm. FTIR spectra confirmed the presence of functional groups related to CDs, such as C-H, C=H, C=N, C=O, C-O-C, and NH_2. Meanwhile, emission spectra displayed fluorescent emission at λ_{max} 495 nm (DMF 2%) and 491 nm (DMF 4%). The ion metal sensing test showed that these two samples with 2% and 4% of DMF were sensitive to Fe^{3+} and Hg^{2+} sensing. These characteristics concluded that NCDs from bilimbi juice via hydrothermal method were able in sensing metal ions, such as Fe^{3+} and Hg^{2+}.

Keywords: Carbon dots; bilimbi; nitrogen doping; metal ion sensing

Abstrak: Karbon dots (CDs) telah banyak diterapkan pada berbagai penggunaan, salah satunya adalah sebagai alat pendeteksi ion logam. Sintesis Cds dengan kemampuan mendeteksi dipengaruhi oleh dua faktor, yaitu prekursor dan agen dopant. Penelitian ini bertujuan untuk menggunakan asam belimbing wuluh (*Averrhoa bilimbi*) dengan penambahan N, N dimetilformamida (DMF) sebagai sumber nitrogen sebagai bahan sintesis CDs melalui metode hidrotermal. Hasil hidrotermal menunjukkan perbedaan emisi warna dari CDs dengan dan tanpa penambahan DMF, dan karakteristik ini juga ditunjukkan dengan adanya perbedaan penyerapan panjang gelombang maksimum (λ_{max}) di 291 nm. Spektra FTIR juga mengkonfirmasi adanya gugus fungsi terkait dengan CDs, seperti C-H, C=H, C=N, C=O, C-O-C, dan NH_2. Sementara itu, emisi spekra menunjukkan emisi fluorosensi pada λ_{max} sebesar 495 nm (DMF 2%0, dan 491 nm (DMF 4%). Pendeteksian ion logam pada kedua sampel sensitif pada ion Fe^{3+} dan Hg^{2+}. Karakteristik ini menyimpulkan bahwa NCDs dari jus asam belimbing dapat digunakan sebagai alat pendeteksi ion logam dalam air, khususnya pada ion logam besi dan merkuri.

Kata Kunci: Karbon dots; Bilimbi; doping nitrogen; deteksi ion logam

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Introduction

Carbon Dots (CDs) have been widely interested scientists with their fluorescent behaviors, which are owing to surface passivation and doping agents, such as oxygen (H. Wang et al., 2017), nitrogen (Li et al., 2018), and sulfur (Rai et al., 2017; Sun et al., 2013) in the graphitic structures. Differences in emission produced by CDs varied between dopants and precursors used. Therefore, CDs can be specifically synthesized by selectively choosing the precursors and doping agents. By tuning the presence of the nitrogen dopant, a certain application of CDs particularly in sensing water contaminants could be achieved, such as metals sensing of iron (Shen et al., 2017), mercury (Yahyazadeh & Shemirani, 2019), and cobalt (J. Shi et al., 2013). With its high biocompatibility and nano-size characteristics, the use of nitrogen-doped CDs opens the potential application as most metals are commonly found in water pollution. However, most precursors that are commonly used are chemical substance, which generates high expenses during large-scale synthesis.

The use of biomass is economically affordable due to its environmentally friendly and its availability features. The reason behind its affordability lies in the renewable resources as well as the chemical constituents. Moreover, the original constituents from the biomass itself already have dopant resources. For instance, the use of lignin and fruits as precursors has successfully synthesized CDs with blue fluorescence (Y. Shi et al., 2019). Although precursors contribute importantly to the CDs yield, emission colors such as green and red could be obtained by modifying the dopants in the surfaces or structures (Bhatt et al., 2018; Kumari et al., 2019). The fluorescent behaviors can be obtained via the methods of synthesizing, for instance; the hydrothermal method is relatively affordable and environmentally friendly even though it requires a longer reaction of time than the other methods. Moreover, compared to microwave or pyrolysis methods which take a high energy, the hydrothermal allows the doping reaction to be easily controllable due to the use of protected reactors (Marpongahtun et al., 2018; W. Wang et al., 2015). Although the reaction time takes place for a longer time, the possibility of dopant agents in the structure increases. Thus, reducing the reaction time by slightly increasing the reaction temperature could be a promising strategy.

One of the promising fruit precursors is bilimbi which is a native fruit from Southeast Asia. This contains various chemical compounds, such as hexadecenoic, erucic, oleic, and boronic acid as well as methyl pyroglutamate, which are carbon-based materials (Suluvoy & Berlin Grace, 2017). These extracts indicate the potential use of bilimbi as green precursors in synthesizing CDs. The

use of the juice of fruit-based precursors has shown features in low-cost, affordability, and green synthesis (Hoan et al., 2019; Zulfajri et al., 2019), and on the other hand the liquid phase allows the synthesis to be easily done via hydrothermal reaction due to the free-movements of atoms. To the best of our knowledge, the use of bilimbi has not been utilized yet. In this present work, bilimbi juice was introduced as a precursor to synthesize nitrogen-doped CDs (NCDs) with N, N dimethylformamide (DMF) as the doping agent for ion sensing application.

Methods

Materials

Bilimbi fruits (*Averrhoa bilimbi*) were the biomass precursor to synthesize CDs. The fruits were collected from the trees found locally in Medan, Indonesia. Chemical reagents such as distilled water, ion standard solutions such as iron ($Fe(NO_3)_3$), mercury ($Hg(NO_3)_2$), and zinc ($Zn(NO_3)_2$), as well as DMF, were supplied by Sigma-Aldrich.

Preparation of Bilimbi Juice

The collection of fruit samples was done without any treatments. Fruits collected were washed using water, while the stems were removed. Then, they were randomly cut and crushed in a household blender. The crushed fruits were squeezed to get the juice. Next, bilimbi juice was centrifugated for five minutes at 5000 rpm (523 rad/s) to remove macro-size particles and stored at 4°C.

Synthesis N-doped CDs

CDs (Sample A) were synthesized hydrothermally by following the previous studies with slight modifications (Zulfajri et al., 2019). In brief, approximately 40 ml of bilimbi juice was poured into a 50-ml PTFE autoclave. This reactor was placed in an oil bath and heated at 220°C for 4 hours. Next, the reactor was directly placed into cold water to reach room temperature. The resulting sample was poured with 20 ml of distilled water and filtered with Whatman no. 40 filter paper. The filtrate was then collected, and placed into a rotary evaporator to remove the water content at 100°C. The remaining liquid after being evaporated was stored in a container at 4°C and labeled as sample A.

The same procedure above was carried out to get N-doped CDs. The DMF was added to the bilimbi juice in the PTFE autoclave. The steps were carried out at a volume ratio of 2%, 4%, and6% of the total volume of bilimbi juice (40 ml) and labeled as Sample B, C, or D respectively.

Characterizations CDs

CDs and NCDs (NCDs) produced were characterized. Functional groups were analyzed by FT-IR (Agilent/ FTIR Cary 630) measurements, absorption characteristics were determined by Spectrophotometer UV-Vis (Jenway 7315), fluorescent emission was determined by Spectrophotometer Photoluminescence

(PL) (Fiber Optic Spectrometer Ocean Optics) at 375 nm. The fluorescent characteristics were observed under UV light irradiation (λ = 365 nm).

Metal Ion Sensing Procedures

Metal ion sensing characteristics were carried out by Spectrophotometer Photoluminescence (PL) and observation under UV and daylight radiations. First, 10µL of CDs samples (samples A, B, C, and D) were prepared Standard metal ion solutions (Zn^{2+}, Fe^{3+}, Hg^{2+}) were each diluted to 100µM. Then, from these concentrations, 10 mL of diluted ion solutions were taken, and then the 10µL CDs samples were dripped into the 10 mL wisely. The mixture solutions were shaken to ensure the mixing steps. Then, these samples were characterized via spectrophotometer PL.

Results and Analysis

FTIR Analysis

In this study, functional groups were analyzed to determine whether CDs synthesis was successful. With different DMF concentrations used, nitrogen was expected to be doped in graphitic structures and CDs surfaces. The following Fig. 1 shows the FTIR spectra of samples.

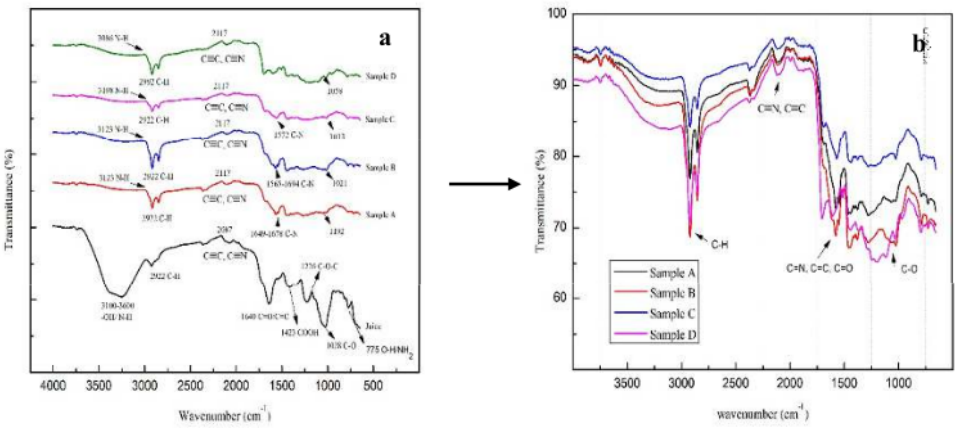


Figure 1. (a) The Comparison of FTIR spectra of Juice and NCDs, and NCDs (b) Peaks comparison of CDs based on the Functional Groups

Based on Fig. 1 (a), there were significant changes in several wavenumbers. The hydrothermal method in this study (at 220°C) allowed the reduction of -OH/N-H indicated by the stretching at 3100-3200 cm^{-1}. Several studies have reported that at 180°C, -OH groups in hydrothermally-reacted juices were removed due to most of the water evaporating, allowing the insertion of doping

agents (Liu et al., 2016; Zulfajri et al., 2019). The FTIR results also confirmed the formation of C-N from C=O/C=C, indicated by the shifting wavenumber between 1600-1700 cm^{-1}. In the juice sample, the presence of nitrogen was confirmed from the stretching vibration, which is the vibration of C=N and C-O, and the vibrations in the juice sample and sample A-D were at 2087 cm^{-1} and 2117 cm^{-1} respectively. In summary, the nitrogen allowed the shifting of wavenumbers of COOH, C-O-C, and O-H/NH_2, implying the decomposition of functional groups from the juice samples after the hydrothermal method.

In Fig. 1 (b), the highest peak of C-H was indicated in samples B (2% DMF) and D (6% DMF). Although sample D had the highest peak, the optimum samples must have the presence of C=N, C=C, and C=O which implied the successful formation of carbon clusters. Studies have suggested that the formation of nitrogen-doped CDs can be considered to be successful with the presence of C=N within the graphitic structure as well as C=C and C=O (Jia et al., 2012a). Thus, in Fig. 1 (a) all the samples with the presence of DMF show the functional groups associated with CDs, whereas Fig. 1 (b) indicated the highest peaks of C-H, C=N, C=C, and C=O in sample B.

UV-Vis Analysis

The absorption properties of NCDs were determined to confirm the sample's ability to emit fluorescence. A previous study suggested that the π-π^* transition of carbon double bond (C=C) was between 230 -270 nm (Sharma et al., 2017), which was also described by Gayen et al., (Gayen et al., 2019). Fig. 2 below shows UV-Vis spectra of all CDs samples, such as samples A-D.

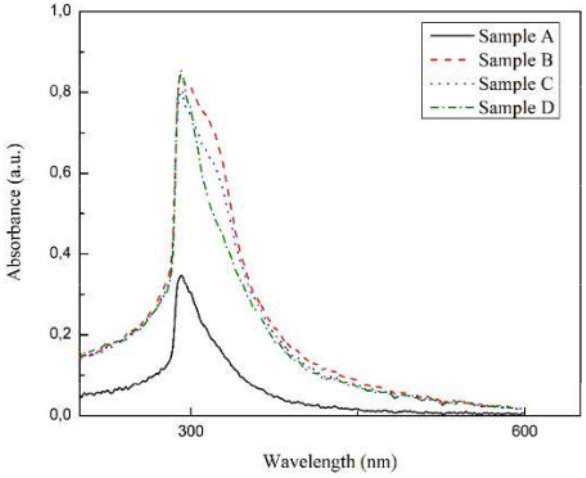


Figure 2. UV-Vis spectra of CDs samples

The highest peak (λ_{max}) was observed at 291 nm for samples A-D. The most significant difference was observed in the absorbance, where samples B, C, and D had high absorbance with UV light irradiation. By referring to FTIR results, samples B and C showed similar absorption behavior that contributed to the highest intensities of C=C bonds. Unlike sample D, both samples B and C showed a wider emission, and despite this, samples with the addition of DMF as the source of nitrogen showed higher intensities of absorption compared to the sample without the presence of DMF. Presumably, the difference in absorption intensities occurs due to the presence of nitrogen that contributes to the HOMO-LUMO mechanisms. A study by Jia et al. suggested that the absorption characteristics of CDs were contributed by the presence of double bonds within C=C and C=O with sigma and phi transition (Jia et al., 2012a), while a study by Hu et al., reported blue-emission of CDs derived from the presence of N atom. Furthermore, the π-π^* transition is displayed at λ_{max} at 291 nm, indicating the electron transition in the C=C bond.

UV-Vis spectra also indicated emission energy in certain wavelengths. Emission is known to occur due to electron transfer following HOMO-LUMO mechanisms. The presence of nitrogen in samples B and C confirmed that photons excited electrons from the nitrogen in amine (NH_2) and graphitic nitrogen (C=N). The maximum absorption and wider area of absorption could be contributed by the presence of DMF, and several studies have reported that the C=N (graphitic nitrogen) is responsible for different emissions (Holá et al., 2017; Jia et al., 2012b). Also, different absorption peaks of CDs vary due to the precursor and doping agents, such as 340 nm (Holá et al., 2017), 300 nm, and 407 nm (R. Wang et al., 2017). The variations occur due to the different atoms within the graphitic structure or on the surface passivation of the CDs. Based on Woodward-Fieser rules the C=C bond generally occurs between 230-270 nm (π-π^* transition), while the addition of atoms differently contributes to other groups. Therefore, our UV-Vis spectra have also confirmed the successful synthesis of CDs with the presence of nitrogen from DMF at 220°C for all samples with λ_{max} of 291 nm, with the highest intensities and optimum width of absorption in samples B and C.

PL Measurements

As samples B and C demonstrated optimum absorption behavior with wider wavelengths based on Fig. 2, the samples that were selected for PL measurements were these two samples. The irradiation of 375 nm was carried out to determine their fluorescent properties. The following Fig. 3 shows the results of PL measurements.

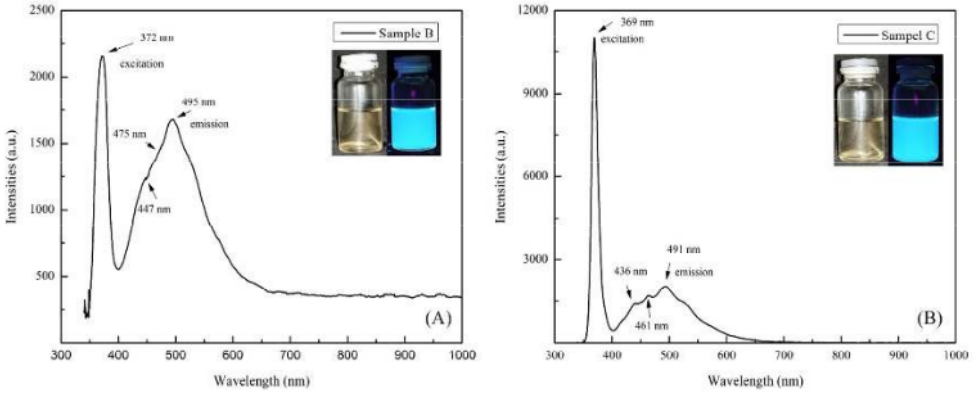


Figure 3. Photoluminescence behaviors of (A) sample B and (B) sample C, with photographic inset of samples under daylight radiation (left) and 365 nm (right)

Based on Fig. 3, radiation at 375 nm was maximally absorbed in 372 nm and 369 nm in samples B and C respectively. The maximum fluorescent emissions for both samples were at 495 nm and 491 nm, respectively, which indicated the presence of radiative emission in cyan color. As both samples consisted of C=N and NH_2, there were transitions of aromatic sp^2 from n-π^* to π - π^* (Chen et al., 2016). Fluorescence excited electrons from LUMO to HOMO band, in which radiative emission spectra were emitted when electrons return to the ground state.

Meanwhile, the presence of the hydroxyl groups contributed to a water-soluble characteristic that enables its application to detect metal ions in water (Cai et al., 2019; D'Angelis Do E. S. Barbosa et al., 2015). The presence of solvent and its relationship to fluorescent mechanisms appeared to be significantly crucial, such as the fluorophore. To understand the relationship between fluorophore emissions in solutions, the following equation (1) was used.

$$\phi_u = \phi_s\,(Y_u/Y_s)(A_s/A_u)(\eta_s/\eta_u)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

The determination of quantum yield (QY) was based on the QY ratio that was relative to the Quinine Sulphate (QS). In Eq. 1, ϕ_u is the $QY_{relative}$ of NCDs, while the ϕ_s is the QY of quinine which is 0.54% in 0.01 M. Y_u and Y_s are the emission fluorescent of NCDs and QS respectively. A_s and A_u are the absorption behavior of NCDs and QS, whereas η_s and η_u are the refractive indexes of water and sulfate respectively. By calculating these parameters, the relationship between fluorophore emissions in solutions of both samples B and C was calculated and shown in Table 1.

Table 1. Quantum yield ($QY_{relative}$) of NCDs in samples B and C

Samples	Ratio of NCDs/H_2O (v/v)	$QY_{relative}$
Sample B	10µL/ 10 mL	10.3%
Sample C	10µL/ 10 mL	12.6%

The addition of DMF as the source of nitrogen increased $QY_{relative}$ behavior. These results are in accordance with a study that used β-alanine as the source of nitrogen with citric acid as the precursors, where QY was 21% (Jung et al., 2016). On the other hand, by using the watermelon peel with nitrogen dopant, 7.1% of QY was obtained (Zhou et al., 2012). Both these two studies have suggested that the presence of nitrogen both in graphitic structure and functional groups increase the QY behavior. Via hydrothermal method, the reaction rearranged carbon cluster, which in the end allowed nitrogen to dope into carbon structure as graphitic nitrogen or in the surface as the functional groups (The FTIR results in Fig 1 confirmed the presence of these two groups in both samples B and C). Hola et al have reported that different amounts of nitrogen dopants in the graphitic structure displayed different emission wavelengths. Moreover, a higher amount of graphitic nitrogen allowed higher emission wavelength to be near-infrared (Holá et al., 2017). Nevertheless, in this study, the NCDs from bilimbi juice emitted cyan blue colors with 491-495 nm with an increase of QY with the presence of DMF.

Ion Sensing Analysis

Due to their fluorescent behaviors, NCDs have been extensively utilized to detect metal ions. The following Fig. 4 shows PL behaviors of NCDs after being mixed with 10 ml of metal ions solution.

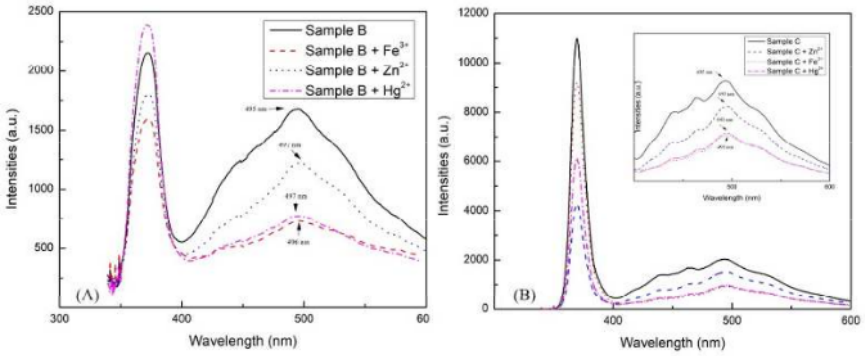


Figure 4. NCDs fluorescent behavior as metal ion sensing in (A) sample B and (B) sample C with inset of emission spectra

Both samples B and C showed decreases in intensities after being tested with metal ions. A significant decrease was seen in iron (Fe^{3+}) and mercury (Hg^{2+}) which indicated fluorescence quenching. PL spectra results indicated the sensitivity of NCDs to detect metal ions (10µL if NCDs were dissolved in 10 mL of distilled water). The sensitivity of NCDs in detecting metal ions was owing to the nitrogen in the amine groups, in which electron transfer occurred from metal ions, such as Hg^{2+} (Chen et al., 2016). On the other hand, the amount of nitrogen affinity on the surface of NCDs could also increase fluorescent behavior (Muthurasu & Ganesh, 2021). All of these implied that the functional groups interact with metal ions which are called the quenching mechanisms (Chen et al., 2016). A decrease in fluorescent intensities before and after mixing with metal ions solutions is displayed in the following Fig. 5.

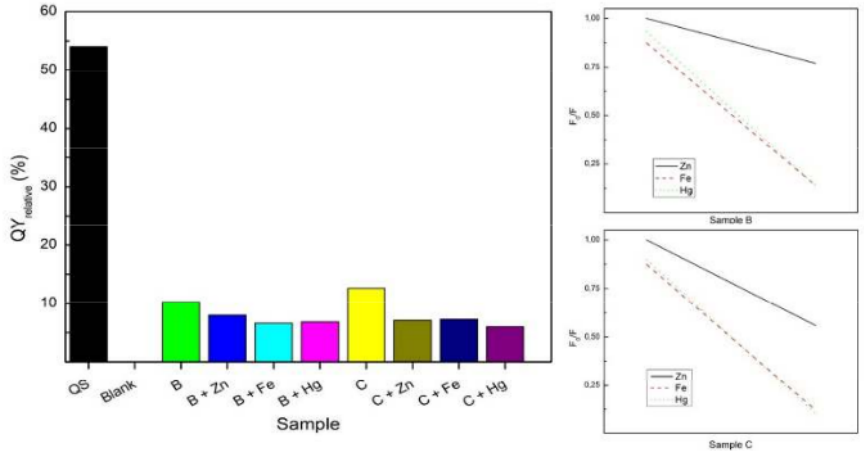


Figure 5. Decreases in $QY_{relative}$ to sensitivities in sensing metal ions in samples B and C

The comparison of $QY_{relative}$ in both samples B and C before and after the presence of metal ions. Several studies have reported that the decrease in QY was due to the pH. In base conditions, the carboxyl groups in CDs would experience deprotonation in regards to electron transfer, and the presence of hydroxyl allowed the hydrogen bonds to form agglomeration (Muthurasu & Ganesh, 2021). In the FTIR spectra, the presence of amine may be assumed to form van der Waals interaction due to the ionic behavior of metal ions.

Conclusion

The use of bilimbi juice has shown a successful source of CDs. The presence of nitrogen in samples B and C emitted cyan fluorescent at 491 nm and 495 nm respectively in form of amine. A noticeable difference showed in the absorption characteristic, in which a higher percentage of DMF increased

absorption peaks. The $QY_{relative}$ calculation of 2% and 4% DMF were accounted for 10.3% and 12.6% with sensitivities to iron (Fe^{3+}) and mercury (Hg^{2+}), with a decrease of QY to 6.6% (Fe^{3+}) and 6.8% (Hg^{2+}) for NCDs with 2% DMF (Sample B), and 7.3% (Fe^{3+}) and 6% (Hg^{2+}) for NCDs with 4% DMF (Sample C).

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