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Raman Spectroscopy for Non-Destructive Detection of Pesticide on Guava Peel

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Abstract: Pesticides are one of the substances that are widely used to protect plants from pests and plant diseases, and their use must be controlled for the public health. Currently, the pesticide contamination is determined by chromatographic, but this technique is destructive and not easy to implement. Therefore, this research is proposed to overcome these problems. Raman scattering technique as a non-destructive testing technique and easy to implement is used in this research. This technique utilizes Raman scattering resulting from laser excitation in a sample. Pesticide detection was carried out by observing the difference in Raman shift wavelength between samples containing pesticides and samples that did not contain pesticides. The experiments were done on guava peels with coated pesticide delthametrin 25 g/l. By excitation with laser wavelengths 532 nm and 785 nm, the differences in Raman shifts at wavelengths 1,225 nm and 1,480 for samples coated pesticide, and Raman shifts at wavelengths 1,008 nm and 1,480 nm for samples which is treated are obtained, respectively. From this research, it can be concluded that Raman scattering technique can be used as non-destructive and easy technique for detection pesticide contamination.

Keywords: Guava; Laser; Pesticide; Raman; Spectroscopy

Introduction

Pesticide ingredients in plants seem to be familiar in the agriculture which pesticides contain of harmful ingredients that are used to maintain the quality of fruits and vegetables from pests and plant diseases (Zhang, et al., 2022; Rajak, 2023). Exposure to these harmful chemicals is pesticide residues that found on fruits (Osaili, et al.,2022; Umayah, et al, 2021), vegetables (Amilia, et al., 2016; Hendriadi, et al., 2021), animals that consume plants containing pesticide residues (Kurnia, et al, 2023; Nurhalisa, et al., 2023), and also environment (Badrudin, et al., 2022). Without realizing it, pesticide residues will enter the human body through the food consumed, which the higher the pesticide residue, the more dangerous it is for health (Vutrianingsih, 2020; Versari et al., 2021).

Currently, Chromatographic techniques are widely used to determine pesticide contamination. Gas Chromatography (Kurnia, 2018), Gas Chromatography Mass Spectrophotonetry (GC-MS) (Duniaji & Suter, 2021), High Performance Liquid Chromatography (HPLC) (Hasibuan, 2018; Buwono, et al., 2019), Liquid Chromatography Mass Spectrometry (LC-MS) (Septaningsih, 2018; Cortese, et al., 2020) are accurate techniques for detection pesticide contamination and other harmful ingredients. The working principle of chromatography is that the gas in a high-pressure steel cylinder is flowed through a column containing the stationary phase. A sample of the mixture to be separated, usually in the form of a solution, is injected into the gas stream. Then the sample is carried by the carrier gas into the column and in the column a separation process occurs. A detector is placed at the end of the column to detect the type and amount of each component of the mixture. (Cortese, et al., 2020).

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However, the chromatographic method requires difficult sample preparation and the testing has to be donein laboratory (Tankiewicz, & Berg, 2022).

Characterization techniques using lasers with low power and large wavelengths are widely used as characterization techniques that are non-destructive and easy to apply. This technique utilizes the scattering of light when the object is excited by laser beam, which the substances or element contained in it will have different characteristics of the light scattering (Yulianto E., et.al, 2019). The important characteristic of light scattering is wavelength, by knowing the wavelength, a substance can be identified (Yulianto E., et.al, 2019).

One of the technique uses of laser excitation techniques is the Raman scattering technique, by knowing the Raman shift of a substance, the substance can be defined. But this technique is still under research and development to be used as a non-destructive characterization technique and can be applied easily (Tegegne, 2020; Hassan, 2019; Nurhalisa, 2022).

Guava fruit is one of fruits that is widely cultivated and consumed by many people. And in consuming guava fruit, mostly eaten with the skin as well. In fact, to prevent pests and diseases in guava fruit, fruit farmers use pesticides, so that the pesticides in guava fruit will also be consumed by humans. So it is important to do research on the pesticide content in guava fruit.

Thus, this research is proposed in order to obtain a non-destructive and easy-to-apply with Raman scattering method by modifying the sample in the form of guava peel. The proposed method is to perform heat treatment on the samples prior to characterization using the Raman scattering technique. It is hoped that from this research a sample preparation method for characterization with Raman scattering can be found which is non-destructive and easy to perform.

Method

This study uses the HORIBA RAMAN iHR320 Spectroscopy equipment which has a resolution of 0.06 nm, a step size of 0.02 nm, with an x100 objective lens. Raman peak data taken is from 1000 nm – 1500 nm and using 532 nm and 785 nm in wavelength for excitation. The pesticide used has the active ingredient Deltamethrin 25 g/l. The pesticide deltamethrin (has a molecular formula: C22H19Br2NO3) which has chemical bonds C-Br, C=C, C=N, C=O, C-H, benzene ring and N-H (Dong, T., et, 2018). The research mechanism is described as in Figure 1. Three types of samples are used in this research, namely guava peel, guava peel coated with pesticides, and guava peel coated with pesticides which was given heat treatment, all samples are pieces of the same guava. Heat teatment was done by heating the guava skin at $40^{o}C$ for about 30 seconds. The three samples will be tested by Raman spectroscopy to produce spectral Raman.

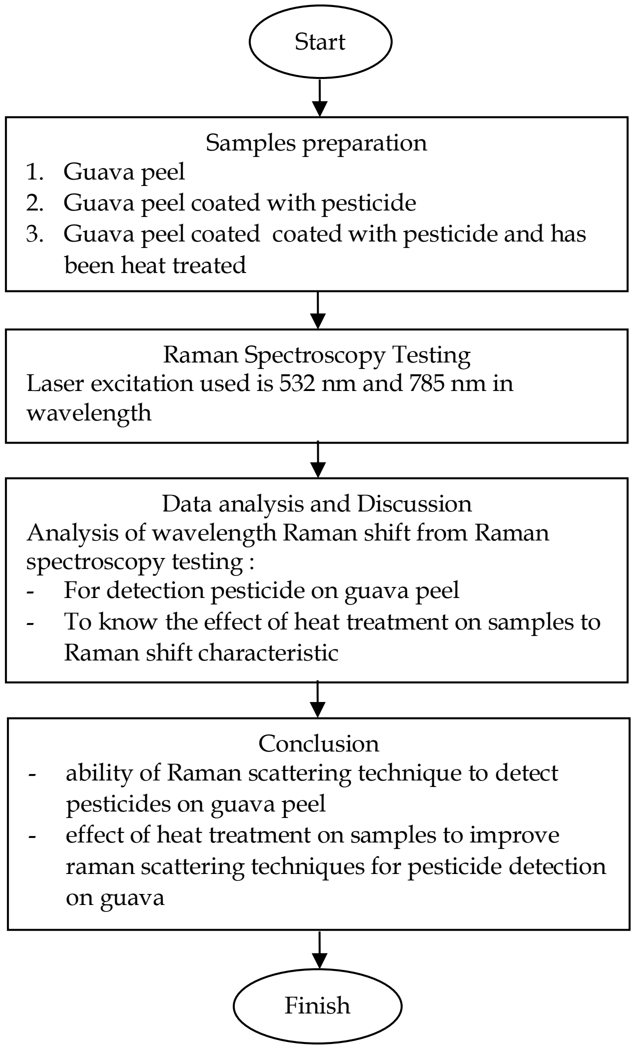

Figure 1. Flow chart of research of raman scattering research for pesticide detection on guava peel

Figure 2 describes the flow diagram of this research, methodology of this research. the research began with the preparation of three types of test samples, followed by Raman spectroscopy tests to obtain Raman scattering data. Sample 1 is the guava peel, sample 2 is guava peel coated with pesticide, and sample 3 is guava peel coated with pesticide which has been treated. Raman spectroscopy testing was carried out three times for each sample and the average results were taken from the Raman shift obtained, so that the result will be valid.

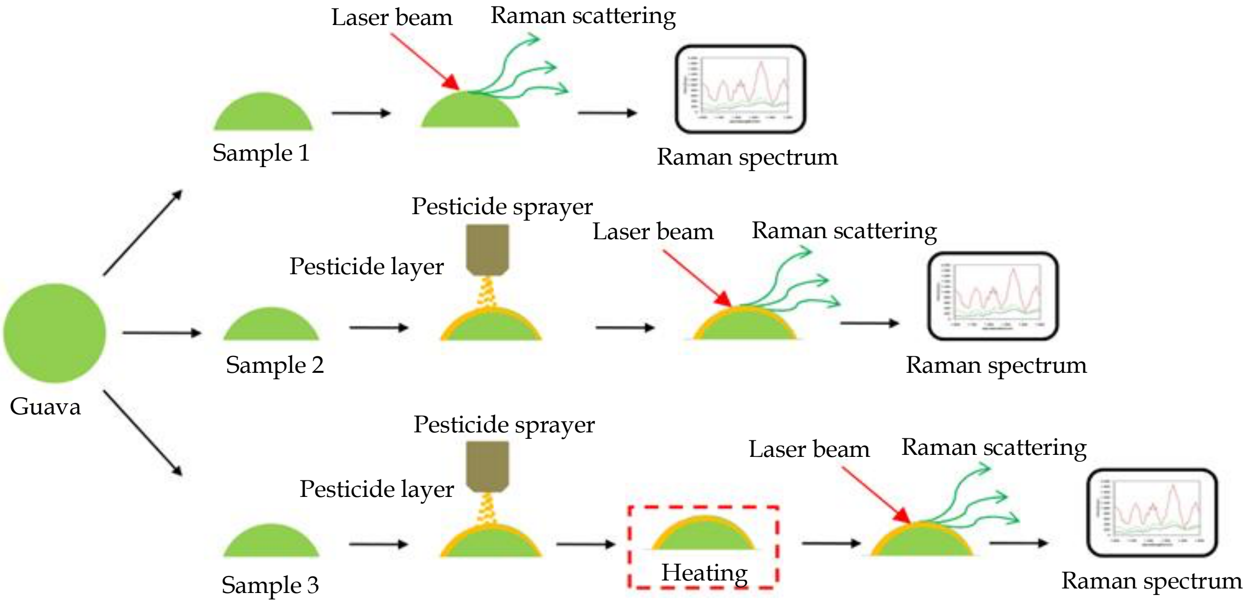

Figure 2. Mechanism of detecting pesticides on guava peel using Raman spectroscopy

Table 1. Raman shift of the samples

Sample	Wavelength of Raman Shift (nm)	
	Laser Excitation 532 nm	Laser Excitation 785 nm
Sample 1	1,120; 1,215; 1,350.	1,060; 1,200; 1300; 1440.
Sample 2	1,120; 1,215; 1,225; 1,350; 1,480.	1,008; `,060; 1,200; 1,300; 1,440; 1,480.
Sample 3	1,120; 1,215; 1,225; 1,350; 1,480.	1,008; `,060; 1,200; 1,300; 1,440; 1,480.

Result and Discussion

Figure 3 shows the images from Raman Spectroscopy's camera of three samples; guava peel, guava peel coated with pesticide, and guava peel coated with pesticide which has been heat treated. This images show the differences between guava peel, guava peel coated with pesticide, and guava peel coated with pesticide and has been treated. On guava peel without pesticide, it only looks black, in contrast to guava peel that has been coated with pesticide, there are white splashes indicating of pesticide. The experiments for detecting pesticide on guava peel using Raman Spectroscopy with laser wavelength of 532 nm and 785 nm . Tabel 1 shows some differences in the Raman shift between pure guava peel, guava peel coated with pesticide, and guava peel coated with pesticide has been heat treated. On excitation with 532 nm and 785 nm laser wavelength, there were some changes in the Raman shift between the guava peel and the guava peel coated with pesticides.

Fig. 4a. shows the differences of Raman shift from Raman spectroscopy with 532 nm of laser excitation on the guava peel which was coated with pesticides and guava peel which is treated compared to the guava peel without coated with pesticide at the wavelength of 1,225 nm and 1,480 nm. And in Fig. 4b, it is shown that the difference of the Raman Shift from Raman Spectroscopy with 785 nm laser excitation on the guava peel coated with pesticide are at the wavelength 1,008 nm and 1,480 nm. From Fig. 4a and Fig. 4b, they can be seen that the guava peel coated with pesticides and heat treated guava peel shows the same Raman shift trend.

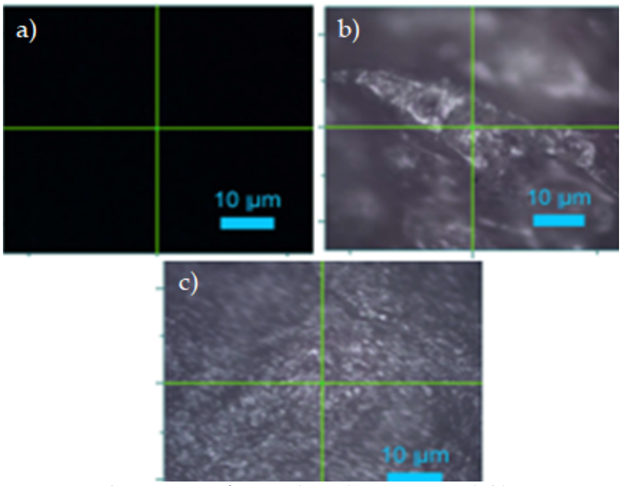

Figure 3. The image of samples a) guava peel; b) guava peel coated with pesticide, and c) guava peel coated with pesticide which has been treated.

From Fig. 4a, the intensity of the Raman shift resulting from Raman Spectroscopy using 532 nm wavelength excitation is different and there is a proportional increase in the intensity of the Raman shift from the guava peel, the guava peel coated with pesticide, and the guava peel coated with pesticide which has been heat treated. Meanwhile, the Raman Shift intensity from Raman Spectroscopy using laser excitation with a wavelength of 785 nm is similar between guava peel, guava peel coated with pesticides, and guava peel coated with pesticides which has been heat treated (Fig.4b).

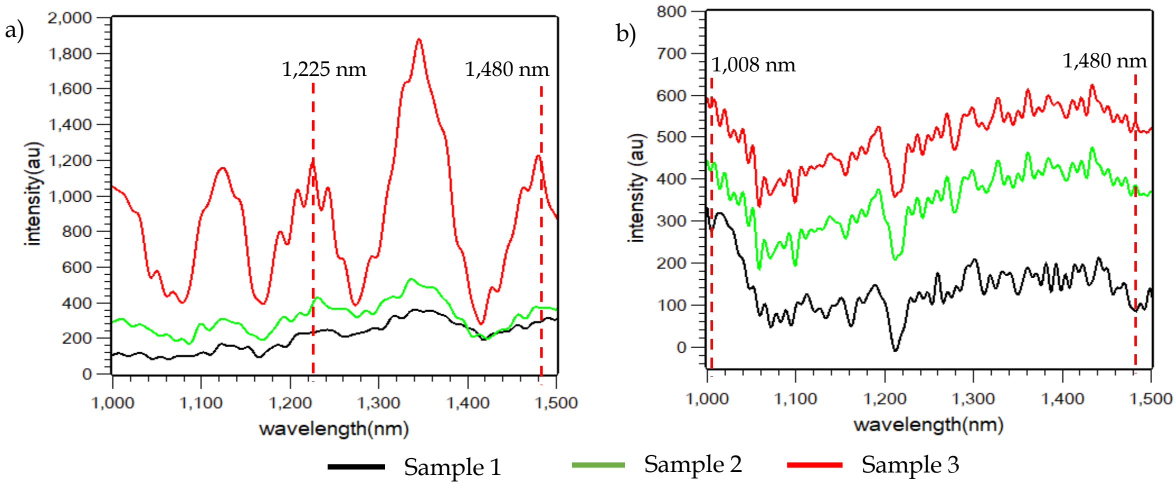

Figure 4. Raman Shift from Raman Spectroscopy with laser excitation (a) 532 nm; (b) 785 nm in wavelength

The increase in intensity of guava peels coated with pesticides and given heat treatment experienced an increase in intensity of about five times compared to those without heat treatment, in laser excitation with a wavelength of 532 nm. Observation of the results of Raman spectroscopy was carried out at a wavelength of 1,000-1,500 nm, this is because the Raman shift for pesticides with C-C, C=C, and C-H was detected at that wavelength. The Raman Shift that occurs is the result of a reaction between laser energy that excites bonds in the pesticide molecule. As in Fig. 4a, for 532 nm laser excitation on guava peel coated withpesticides has been heat treatedproduces higher intensity than in guava peel coated withpesticide it can be concluded that the molecular bonds in guava peel coated withpesticides has been heat treateds are easier to excite by laser than other conditions.

Differences in the Raman shift that occur in guava peel and guava peel coated by pesticides as in Fig. 4a and Fig.4b, can be used as reference to determine the presence of pesticide layer on guava peels

Conclusion

Raman scattering technique is proven to be used as pesticide detection technique on guava peel. Pesticide detection is done by analyzing the Raman shift resulting from laser excitation, which guava peel without pesticide coating and guava peel with pesticide coating, there are differences in Raman shift, which guava peel with pesticide coating obtained Raman shift at wavelengths of 1,225 nm and 1,480 at excitation laser wavelengths of 532 nm, and 1,008 nm and 1,480 nm at laser excitation wavelengths of 785 nm, and for guava peel without pesticide coating there are no Raman shift at these wavelengths. Heat treatment method on guava peel samples has been shown to increase the Raman shift intensity by about five times compared to guava peel samples without heat treatment. So, heat treatment makes the Raman scattering technique as a non-destructive technique with easy sample preparation and is very suitable for detecting pesticides on guava peel

References

Badrudin, U., Jazilah, S., & Prakoso, B. (2022). The effect of soil submersion and conditioner materials on residual organophosphate pesticides in soil and shallot bulbs. *Agrivita*, 44(1), 1. http://doi.org/10.17503/agrivita.v41i0.1291

Buwono, N. R., Gultom, T., Ayuning, S. W., & Supriatna, S. (2019). Bioakumulasi residu pestisida pada komunitas gastropoda di perairan Sungai Kalisat, Kabupaten Malang. *Depik*, 8(3), 167-175. https://doi.org/10.13170/depik.8.3.14368

Cortese, M., Gigliobianco, M. R., Magnoni, F., Censi, R., & Di Martino, P. (2020). Compensate for or minimize matrix effects? Strategies for overcoming matrix effects in liquid chromatography-mass spectrometry technique: a tutorial review. *Molecules*, *25*(13), 3047. https://doi.org/10.3390/molecules25133047

Dong, T., Lin, L., He, Y., Nie, P., Qu, F. and Xiao, S. (2018). Density Functional Theory Analysis of Deltamethrin and Its Application in Strawberry by Surface-Enhanced Raman Spectroscopy. *Molecules*, (23), 1458. https://doi.org/10.3390/molecules23061458

Duniaji, A., & Suter, I. (2021). Pengujian Kandungan Residu Pestisida Pada Tanaman Sayuran Di Kabupaten Badung Dengan Kartu Pendeteksi Pestisida (Pesticide Detection Cards) Dan Gas Chromatography Mass Spectrophotometry. *Jurnal Ilmu Dan Teknologi Pangan (ITEPA), 10*(4), 746-752. https://doi.org/10.24843/itepa.2021.v10.i04.p19

Hassan, M. M., Li, H., Ahmad, W., Zareef, M., Wang, J., Xie, S., ... & Chen, Q. (2019). Au@ Ag nanostructure based SERS substrate for simultaneous determination of pesticides residue in tea via solid phase extraction coupled multivariate calibration. *Lwt,* 105, 290-297. https://doi.org/10.1016/j.lwt.2019.02.016

Hendriadi, A., Sulistiyorini, & Devilana, M. R. (2021). Pesticides residues in fresh food of plant origin:Study case in Indonesia. *AGRIVITA Journal of Agricultural Science*, 43(2), 285–299. https://doi.org/10.17503/agrivita.v43i2.2570

Hidayah, A. N., Herbani, Y., Triyono, D., & Saleh, R. (2022). Effect of Yield Silver Nanoparticles in Enhancing Raman Signal of SERS Substrate Fabricated on Whatman Filter Paper. *Journal of Physics and Its Applications,* 4(2), 47-50. https://doi.org/10.14710/jpa.v4i2.13226

Kurnia, A. (2018). Analisis Residu Klorpirifos pada Tanah dan Validasinya. *Agrikultura*, 29(2), 61-65. https://doi.org/10.24198/agrikultura.v29i2.19247

Kurnia, N., Kholik, K., & Khaeruman, K. (2023). Mapping Chemical Hazards in Animal Food Origin Product for Food Safety Teaching Materials. *Jurnal Penelitian Pendidikan IPA*, 9(1), 455-461.. https:// doi.org/10.29303/jppipa.v9i1.2534

Malan, D., Van Der Walt, S. J., & Rohwer, E. R. (2020). A high-repetition-rate, fast temperature-programmed gas chromatograph and its online coupling to a supercritical fluid chromatograph (SFC× GC). *Review of Scientific Instruments*, *91*(3), 034101. https://doi.org/10.1063/1.5125060

Nurhalisa, N., Arfiati, D., Andayani, S., Osa, A., & Nadiro, V. N. (2023). Insecticide with the active ingredient methomyl interferes with the growth and survival of the jatiumbulan tilapia strain (Oreochromis niloticus). *Jurnal Penelitian Pendidikan IPA,* 9(2), 485-490. https:// doi.org/ 10.29303/jppipa.v9i2.2928

Osaili, T. M., Al Sallagi, M. S., Dhanasekaran, D. K., Odeh, W. A. B., Al Ali, H. J., Al Ali, A. A., ... & Obaid, R. S. (2022). Pesticide residues in fresh fruits imported into the United Arab Emirates. *Heliyon, 8*(12), e11946. https://doi.org/10.1016/j.heliyon.2022.e11946

Septaningsih, D. A., Darusman, L. K., Afendi, F. M., & Heryanto, R. (2018). Liquid chromatography mass spectrometry (LC-MS) fingerprint combined with chemometrics for identification of metabolites content and biological activities of curcuma aeruginosa. *Indonesian Journal of Chemistry*, *18*(1), 43-52. https://doi.org/10.22146/ijc.25456

Tankiewicz, M., & Berg, A. (2022). Improvement of the QuEChERS method coupled with GC–MS/MS for the determination of pesticide residues in fresh fruit and vegetables. *Microchemical Journal, 181*, 107794. https://doi.org/10.1016/j.microc.2022.107794

Tegegne, W. A., Su, W. N., Tsai, M. C., Beyene, A. B., & Hwang, B. J. (2020). Ag nanocubes decorated 1T-MoS2 nanosheets SERS substrate for reliable and ultrasensitive detection of pesticides. *Applied Materials Today, 21*, 100871. https://doi.org/10.1016/j.apmt.2020.100871

Umayah, A., & Wagiyanti, W. (2021). Cara Penggunaan Pestisida dan Analisis Residu pada Cabai Merah (Capsicum annuum L.)(Studi Kasus: Desa Saleh Mukti, Kecamatan Air Salek, Kabupaten Banyuasin). *Agrikultura, 32*(1), 57-62. https://doi.org/10.24198/agrikultura.v32i1.32566

Versari, A., Sukendra, D. M., & Wulandhari, S. A. (2021). Overview of Domestic and Agricultural Pesticides Use Contributing to Aedes aegypti Resistence in Ambarawa Subdistrict, Indonesia. *Unnes Journal of Public Health, 10*(1), 100-109. https://doi.org/10.15294/ujph.v10i1.39923

Vutrianingsih, N. E., Zulfa, I., & Mukono, J. (2020). Risk Factors Related To Carbamate And Organophosphate Pesticide Poisoning In Rice Farmers In Masangan Kulon Village, Sidoarjo District. *The Indonesian Journal of Public Health,* 191-200, http://dx.doi.org/10.20473/ijph.v15i2.2020.190-200

Yulianto, E., Chatterjee, S., & Mizeikis, V. (2019). Characterization of Latent 3D Laser Photoexposure Patterns in Photoresist Created by Direct Laser Writing. *Materials Today: Proceedings*, *13*, 149-153. https://doi.org/10.1016/j.matpr.2019.03.205

Yulianto, E., Chatterjee, S., Purlys, V., & Mizeikis, V. (2019). Imaging of latent three-dimensional exposure patterns created by direct laser writing in photoresists. *Applied Surface Science, 479*, 822-827. https://doi.org/10.1016/j.apsusc.2019.02.033

Zhang, A. A., Sutar, P. P., Bian, Q., Fang, X. M., Ni, J. B., & Xiao, H. W. (2022). Pesticide residue elimination for fruits and vegetables: the mechanisms, applications, and future trends of thermal and non-thermal technologies. *Journal of Future Foods, 2*(3), 223-240. https://doi.org/10.1016/j.jfutfo.2022.06.004