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Screening of some vegetables for the biotransformation of bicyclo[3.3.1]nonane-2,6-diol diacetate

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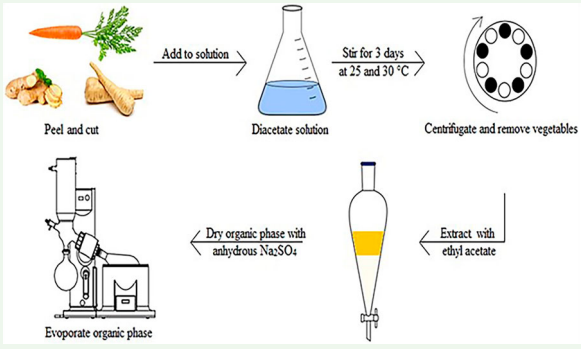
ABSTRACT

Vegetables as biocatalysts were screened for the stereoselective biotransformation of racemic bicyclo[3.3.1]nonane-2,6-diol diacetate. The best results were obtained using the roots of carrot (*Daucus carota)* and parsnip (*Pastinaca sativa*) and the rootstocks of ginger (*Zingiber officinale*). During the biotransformation of racemic bicyclo[3.3.1]nonane-2,6-diol diacetate the enzymatic hydrolysis took place. Under different reaction conditions, i.e. the reaction temperature and time, and using different plant material as biocatalyst, (*1R*,*2R*,*5R*,*6R*)-(+)-bicyclo[3.3.1]nonane-2,6-diol monoacetate or (*1S*,*2S*,*5S*,*6S*)-(-)-bicyclo[3.3.1]nonane-2,6-diol monoacetate were obtained as reaction products. (–)- Enantiomer with the optical purity of 29.3% was obtained at 25°C using parsnip as biocatalyst for 2 days and (+)- enantiomer with the optical purity of 44.1% was obtained at 30°C using carrot for 3 days.



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1. Introduction

Biocatalysis is a powerful tool in organic synthesis. Enzymes are widely applied in the production of pharmaceuticals and fine chemicals. Biocatalytic processes satisfy the requirements of green and sustainable chemistry. Biocatalysts are renewable and highly selective; most reactions occur in water, fewer reaction steps are required to produce the final product. Moreover, protein engineering enables the improvement of existing biocatalysts (*1*,*2*).

Intact plant materials as biocatalysts have also received great attention in organic chemistry. Reactions catalyzed by whole plant cells are carried out under mild conditions, and the process is simple and ecofriendly. Moreover, the process saves time and resources as it does not require purified enzymes (*3*). Fruits and vegetables find their application in the catalysis of various types of reactions, especially in the preparation of enantiomerically pure compounds. The enantioselective reduction of acetophenones (*4*,*5*) as well as other various ketones (*6*–*8*) and the hydrolysis of racemic acetates (*9*) was previously described using carrot roots as a chemical reagent. The stereoselective reduction of acetophenone and its derivatives and the preparation of optically active phenylethanols with high enantioselectivity was also performed using various weeds (*10*), ginger roots, mandarin (*11*), yellow mustard seeds (*12*) and the seeds of the plant 'cow hoof' (*Bauhinia variegata* L.) (*13*). Bordon et al. demonstrated that the seeds of glossy privet (*Ligustrum lucidum*) were efficient not

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only in reducing ketones to chiral alcohols, but also in the biotransformation of aldehydes to alcohols (*14*). To obtain indanol isomers with a high enantiomeric excess, various plants as biocatalysts were also tested (*15*). Orange peels act as biocatalysts for the hydrolysis of aromatic esters and the resolution of racemates (*16*). Moreover, fresh peels of orange *Citrus sinensis* (L.) containing acetylesterase were an efficient green biocatalyst for the production of geraniol from geranyl acetate, mono- and diacetins from triacetin and 1-acetoxy-4-hydroxy-2-methylnaphthalene as a key intermediate in the synthesis of vitamin K_1 from 1,4-diacetyl-2-methylnaphtalene (*17*). As recently exemplified, the reactions catalyzed by plant material can be performed in organic (*18*) and natural deep eutectic solvents (*19*).

Bicyclo[3.3.1]nonane skeleton is the common motif of many chiral natural compounds such as huperzine A, garsubellin A or lycopodine (*20*). Therefore, there are a lot of works devoted to the synthesis of bicyclo[3.3.1]nonane derivatives (*21*,*22*) and the investigation of their biological activity (*23–26*). In this context, the preparation of enantiomerically pure bicyclo[3.3.1]nonane derivatives is a topic of special importance. Previously, we applied various vegetables as biocatalysts for the stereoselective bioreduction and resolution of racemic bicyclo[3.3.1]nonane-2,6-dione. As a result, (+)-enantiomer of bicyclo[3.3.1]nonane-2,6-dione was obtained using the roots of parsnip, celery, parsley and carrot (*27*).

Here, we present the screening of some vegetables for the enzymatic hydrolysis of racemic bicyclo[3.3.1]nonane-2,6-diol diacetate and the preparation of (+)- and (-)- bicyclo[3.3.1]nonane-2,6-diol monoacetate. We demonstrate the principal possibility to use intact plant materials for the enantioselective hydrolysis of more complex molecules and broaden the circle of possible substrates.

2. Results and discussion

The possible scheme of (±)-bicyclo[3.3.1]nonane-2,6-diol diacetate biotransformation based on our previous work (*27*) was proposed (Figure 1). According to this scheme, (±)-bicyclo[3.3.1]nonane-2,6-diol diacetate (**1**) biotransformation could be carried out by the hydrolysis of one or two acetyl groups. Resulting products bicyclo[3.3.1]nonane-2,6-diol monoacetate (**2**) or bicyclo[3.3.1]nonane-2,6-diol (**3**) could be further oxidized to 6-acetoxybicyclo[3.3.1]nonane-2-one (**4**) or 6-hydroxybicyclo[3.3.1]nonane-2-one (**5**) and bicyclo[3.3.1]nonane-2,6-dione (**6**), respectively. During the reaction both (+)-enantiomer and/or (-)-enantiomer could be obtained.

For the preliminary screening, the experiments were performed at 25°C and 30°C for three days using the rootstocks of ginger and the roots of carrot, parsnip, celery, parsley and black radish as biocatalysts. NMR analysis and the measurement of specific rotation showed that (*1R*,*2R*,*5R*,*6R*)-(+)-bicyclo[3.3.1]nonane-2,6-diol monoacetate and (*1S*,*2S*,*5S*,*6S*)-(-)-bicyclo[3.3.1]nonane-2,6-diol monoacetate are the main products of the biotransformation. Some traces of (*1R*,*2R*,*5R*,*6R*)-(+)-bicyclo[3.3.1]nonane-2,6-diol were also identified as a reaction product. Overall, the biotransformation of racemic bicyclo[3.3.1]nonane-2,6-diol diacetate proceeds similarly to our proposed reaction scheme. However, the further oxidation process of bicyclo[3.3.1]nonane-2,6-diol monoacetate and bicyclo[3.3.1]nonane-2,6-diol in our experiment was not observed.

For further experiments, both enantiomers of bicyclo[3.3.1]nonane-2,6-diol monoacetate were chosen as end-products. The roots of carrot and parsnip and the rootstocks of ginger were used as biocatalysts. The roots of celery, parsley and black radish were not effective for (**1**) biotransformation, and the obtained values of specific rotation of reaction products were insignificant. The results of (±)-bicyclo[3.3.1]nonane-2,6-diol diacetate biotransformation reaction are presented in Table 1. Using the roots of carrots and the rootstocks of ginger, the enantiomeric excess of (+)-**2** was obtained independent on the reaction temperature and duration. Using the roots of carrot, the highest optical purity of (+)-**2** was found at 30°C after 3 days. The optical purity of (+)-**2** at 25°C using carrots as biocatalyst as well as ginger at both 25°C and 30°C temperature was practically independent on the reaction duration. It seems that in mentioned plants there is a hydrolase enantioselective for (+)-**1.** Another hydrolase enantioselective for (-)-**1** is absent or its catalytic constant for (-)-**1** hydrolysis is very low compared with (+)-**1** hydrolysis. Slight changes of optical purity depending on the reaction duration and temperature suggest the sensitivity of enzyme to temperature or the possibility of the reverse reaction. The roots of parsnip obviously contain both hydrolases, i.e. enantioselective for (+)-**1** and for (-)-**1**. (*1S*,*2S*,*5S*,*6S*)-(-)-bicyclo[3.3.1]nonane-2,6-diol monoacetate was obtained at 25°C after 2 days with the optical purity of 29.3%. However, the enzyme enantioselective for (-)-**1** is less stable than the one enantioselective for (+)-**1**. The optical purity of (-)-**2** decreased after 3 days, and at 30°C the enantiomeric excess of (+)-**2** was obtained. Similar variations of optical purity were observed previously in the stereoselective bioreduction process of bicyclo[3.3.1]-nonane-2,6-dione (*27*).

As mentioned above, the formation of products **4, 5** and **6** was not observed (Figure 1). Our previous

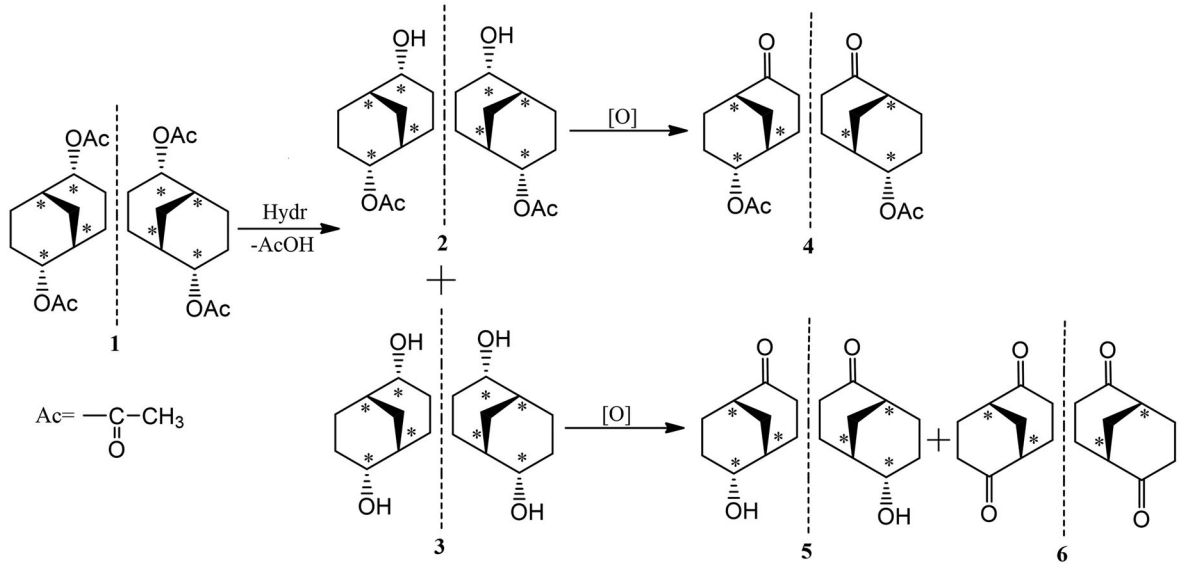

Figure 1. The possible scheme of (±)-bicyclo[3.3.1]nonane-2,6-diol diacetate biotransformation by intact plant material.

experience shows that roots of carrot and parsnip as well rootstocks of ginger are good biocatalysts for bicyclo [3.3.1]nonane-2,6-dione bioselective reduction (*27*). It is plausible that the reverse reaction of oxidation is slow or the concentration of bicyclo[3.3.1]nonane-2,6-diol monoacetate and bicyclo[3.3.1]nonane-2,6-diol are too low to obtain detectable amount of mono- or diketone by the enzymatic system of vegetables cells.

Here, we demonstrated the possibility to obtain bicyclo[3.3.1]nonane derivatives using parts of fresh plants. The enzymes of hydrolase class, i.e. esterases were exploited as biocatalysts for the synthesis of both enantiomers of bicyclo[3.3.1]nonane-2,6-diol monoacetate. Usually, the application of plant material in organic chemistry is focused on the enantioselective reduction of ketones and the exploitation of plant oxidoreductase system (*3*,*28*). It is understandable because chiral alcohols are important building blocks for the synthesis of pharmaceuticals as well as flavors, pesticides and fragrances. Moreover, the application of whole plant tissue eliminates the additional reactions for cofactors regeneration (*29*). The reactions of hydrolysis using intact plant material have been studied to lesser extent when compared with oxidation – reduction reactions. There are some papers dealing with the enantioselective hydrolysis of aryl ethyl acetates (*9*,*16*,*30*–*32*). We exemplified that plant parts could be used for the enantioselective hydrolysis of other more complex molecules. In fact, the optical purity of obtained products was not high. On the other hand, limited number of plants was tested. Having in mind that a large number of taxonomically different plants is available all over the world, the results are encouraging. Nowadays, even a new term 'Botanochemistry' has been introduced for the description of the methodology of plant material used in organic chemistry (*30*).

Overall, the synthesis of organic compounds by intact plant materials are very attractive for mild and environmentally friendly conditions. However, our experiments and the papers of many others authors suggest that comprehensive screening of various plants should be performed to find the best biocatalyst for particular compound and type of reaction (*30*,*33*–*35*). For today, it seems that carrots are the most useful source and the most frequently used as an effective biocatalyst (*36*,*37*).

3. Materials and methods

3.1. Materials

Racemic bicyclo[3.3.1]nonane-2,6-dione (97%) was purchased from Sigma-Aldrich. Ethyl acetate, anhydrous sodium sulfate, chloroform and acetone of analytical grade were purchased from UAB Eurochemicals (Lithuania). Silica gel 60 (0.063–0.200 mm) and diatomaceous earth powder (Celite® 545) for column chromatography and aluminum thin layer chromatography plates (TLC Silica gel 60 F_{254}) were purchased from Merck. Ethanol was received from UAB Stumbras (Lithuania)

3.2. Synthesis of racemic bicyclo[3.3.1]nonane-2,6-diol diacetate

Racemic bicyclo[3.3.1]nonane-2,6-diol diacetate (**III**) was synthesized from bicyclo[3.3.1]nonane-2,6-dione (**I**) by the reduction with $NaBH_4$ in absolute methanol and

Table 1. Results obtained after (±)-bicyclo[3.3.1]nonane-2,6-diol diacetate biotransformation at 25°C and 30°C temperature using vegetables as biocatalysts.[a]

		$[\alpha]^{25}_{546}$, °		Overall yield of monoacetate, %		Optical purity, %	
		Reaction temperature, °C					
Vegetables	Reaction time, days	25	30	25	30	25	30
Carrot (*Daucus carota*)	1	+(10.1 ± 1.8)	+(7.27 ± 2.01)	46.8 ± 10.5	44.5 ± 3.9	15.9 ± 2.9	11.4 ± 3.2
	2	+(7.4 ± 1.8)	+(10.9 ± 3.7)	36.0 ± 4.6	49.7 ± 12.3	11.7 ± 2.8	17.2 ± 5.8
	3	+(11.6 ± 0.9)	+(28.2 ± 3.0)	49.3 ± 1.7	41.5 ± 7.8	18.1 ± 1.4	44.1 ± 4.8
Ginger (*Zingiber officinale*)	1	+(6.2 ± 1.7)	+(8.7 ± 1.7)	54.2 ± 18.5	41.3 ± 5.9	9.7 ± 2.6	13.6 ± 2.6
	2	+(7.4 ± 3.4)	+(6.9 ± 1.4)	45.7 ± 3.3	48.7 ± 3.1	11.7 ± 5.3	10.9 ± 2.2
	3	+(5.6 ± 2.9)	+(9.9 ± 2.1)	43.3 ± 10.3	53.2 ± 5.9	8.8 ± 4.6	15.5 ± 3.4
Parsnip (*Pastinaca sativa*)	1	+(3.4 ± 0.6)	+(4.4 ± 0.9)	44.0 ± 3.9	37.3 ± 6.7	5.3 ± 0.9	6.9 ± 1.4
	2	−(18.7 ± 2.3)	+(3.7 ± 0.9)	44.0 ± 4.3	45.2 ± 2.9	29.3 ± 3.6	5.9 ± 1.3
	3	−(7.1 ± 1.5)	+(6.5 ± 0.5)	44.3 ± 4.3	51.2 ± 9.2	11.1 ± 2.4	10.2 ± 0.8

[a]The experimental data are presented as mean values ± standard deviations of 3 parallel experiments.

the following reaction of obtained racemic bicyclo [3.3.1]nonane-2,6-diol (**II**) with acetyl chloride (Figure 2).

Racemic bicyclo[3.3.1]nonane-2,6-diol (**II**) was obtained as previously described (*38*). Briefly, 1.52 g (1 mmol) of racemic diketone **I** were put into a round-bottomed flask (100 mL) and 50 mL of absolute methanol was added. The mixture was stirred and cooled to 0°C in an ice-bath and 1.0 g (3 mmol) of $NaBH_4$ was added in portions. Then, the reaction mixture was stirred for one hour at 0°C. Methanol was evaporated and the product was extracted with ethyl acetate using a Soxhlet extraction apparatus. Finally, diol **II** was purified by flash chromatography (silica gel, ethyl acetate). After evaporation of ethyl acetate, 1.4 g of product **II** was recovered with the yield of 90%. Melting point determined with a Gallencamp melting point apparatus was 77°C.

Racemic bicyclo[3.3.1]nonane-2,6-diol diacetate (**III**) was obtained as previously described (*39*). Briefly, 1.56 g (1 mmol) of racemic diol **II** were refluxed with 4.1 mL acetyl chloride for 2 h. Then, 20 mL of benzene was added to the reaction mixture and solvents were evaporated under vacuum. The procedure was repeated once again and then, the liquid residue was distilled at 140°C (5 mm Hg) as a colorless viscous material with the low melting point (31–34°C). The yield of the reaction was 82.5%.

3.3. Biotransformation of bicyclo[3.3.1]nonane-2,6-diol diacetate

All vegetables were purchased in the local market. To increase the contact of substrate with biocatalyst, vegetables were peeled and cut into small thin pieces (approximately 1 cm long). An amount of 200 mg of racemic bicyclo[3.3.1]nonan-2,6-diol diacetate was diluted in 5 mL of ethanol and 100 mL distilled water. Then, 20 g of vegetables were added to the suspension. The mixture was stirring for 24–72 h at 25 and 30°C temperature. After the reaction time, the suspension was centrifuged to remove vegetables. Then, 15 mL of distilled water was added, and the centrifugation was repeated. Finally, both aqueous solutions were combined, and the products of the reaction were extracted with ethyl acetate (4 × 40 mL). The organic phase was dried with anhydrous Na_2SO_4 and evaporated using rotary vacuum evaporator.

To purify the products of (±)-bicyclo[3.3.1]nonane-2,6-diol diacetate biotransformation, column chromatography was performed on a silica gel 60 using ethyl acetate as an eluent. Compounds in the fractions were analyzed by thin layer chromatography (TLC) using silica gel covered aluminum plates and ethyl acetate as a mobile phase. Spots of compounds were developed by spraying $KMnO_4$ solution in water (3 g $KMnO_4$, 20 g

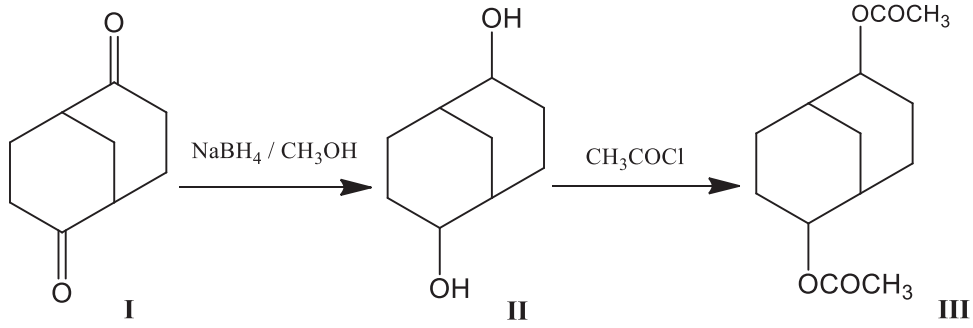

Figure 2. The scheme of (±)-bicyclo[3.3.1]nonane-2,6-diol diacetate synthesis.

K_2CO_3, 5 mL 5% NaOH and 300 mL of distilled water). *Rf* values of bicyclo[3.3.1]nonane-2,6-diol diacetate and bicyclo[3.3.1]nonane-2,6-diol monoacetate were 0.71 and 0.33, respectively.

The optical activity of the final product dissolved in chloroform was recorded in a 5 cm path length cuvette using polarimeter Polamat A (Carl Zeiss/Jena). The specific rotation was calculated as followed: $[\alpha]^{25}_{546} = \frac{\alpha}{c \cdot l}$, where l was a path length in dm and c was the concentration of final product in g/mL. The optical purity was equal to ($\alpha_{observed}/\alpha_{pure\ enantiomer}$) × 100%. For pure (*1R,2R,5R,6R*)-(+)-bicyclo[3.3.1]nonane-2,6-diol monoacetate, $[\alpha]^{25}_{546} = +63,8^{\circ}$ and for (-)-enantiomer, $[\alpha]^{25}_{546} = -63.8^{\circ}$ were used (*40*).

3.4. Spectral data for the compounds

^{1}H NMR (400 MHZ, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compounds were recorded on a nuclear magnetic resonance spectrometer Bruker Ascend™ 400 and presented in Supplemental Material (Figures 1S–6S).

^{1}H NMR of (±)-bicyclo[3.3.1]nonane-2,6-diol diacetate: δ, ppm ($CDCl_3$); 1.53–1.64 (m, 2H at C4 and C8); 1.71-1.80 (m, 2H at C4 and C8, 2H at C3 and C7); 1.89-2.05 (m, 2H at C9, 2H at C3 and C7); 2.06 (s, 6H, $2CH_3$); 4.93-5.10 (m, 2H at C2 and C6).

^{1}H NMR of (+)-bicyclo[3.3.1]nonane-2,6-diol: δ, ppm ($CDCl_3$); 1.38–1.49 (m, 2H at C1 and C5), 1.58–1.63 (m, 4H at C3 and C7), 1.76-1.79 (m, 4H at C4 and C8), 2.06-2.07 (m, 2H at C9), 2.93-2.95 (d, J = 5 Hz, 2H, 2OH), 3.77-3.82 (m, 2H at C2 and C6).

^{1}H NMR of (+)-bicyclo[3.3.1]nonane-2,6-diol monoacetate: δ, ppm ($CDCl_3$); 1.50-2.17 (m, 12H, bicyclic protons and 1H, OH); 2.08 (s, 3H, CH_3); 3.87-3.92 (m, 1H at C2); 4.93-4.99 (1H at C6).

^{1}H NMR of (-)-bicyclo[3.3.1]nonane-2,6-diol monoacetate: δ, ppm, ($CDCl_3$); 1.49-2.15 (m, 12H, bicyclic protons); 2.09 (s, 3H, CH_3), 2.68 (s, broad, 1H, OH); 3.87-3.96 (m, 1H at C2); 4.94-4.99 (m, 1H at C6).

^{13}C NMR of (±)-bicyclo[3.3.1]nonane-2,6-diol diacetate: δ, ppm, ($CDCl_3$); 21.42 (2 CH_3); 23.37 (C3 and C7); 27.50 (C4 and C8); 30.42 (C9); 32.11 (C1 and C5); 75.10 (C2 and C6); 170.60 (2 CO).

^{13}C NMR of (+)-bicyclo[3.3.1]nonane-2,6-diol monoacetate: δ, ppm, ($CDCl_3$); 21.41 (CH_3), 22.43 (C8), 23.53 (C4), 27.66 (C3), 30.61 (C7), 31.16 (C9), 32.33 (C5), 33.66 (C1), 72.79 (C2), 75.35 (C6), 170.65 (CO).

4. Conclusion

We exemplified that optically active derivatives of bicyclo[3.3.1]nonane-2,6-dione can be synthesized using vegetables as biocatalysts. Under different reaction conditions, i.e. the reaction temperature and time, and using different plant material as biocatalyst, (*1R,2R,5R,6R*)-(+)-bicyclo[3.3.1]nonane-2,6-diol monoacetate or (*1S,2S,5S,6S*)-(-)-bicyclo[3.3.1]nonane-2,6-diol monoacetate could be obtained.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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