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Study the potential activity of some newly synthesized thiazolidine derivatives and its 10 % dustable powder formulation against pink bollworm *Pectinophora gossypiella* (Saunders) (Lepidoptera: Gelechiidae)

Saad ES Hamouda[1], Reda A El-Sharkawy[2], Hemat Z Moustafa[2]

[1] Department of Formulation Research, Central Agricultural Pesticides Lab (CAPL), Agriculture Research Center (ARC), Dokki, Giza, Egypt

[2] Department of Pesticides Evaluation Research, Plant Protection Research Institute, Agriculture Research Center (ARC), Dokki, Giza, Egypt

Abstract

2-Cyano-N-(2-hydroxyphenyl) acetamide was used as starting material to synthesize some new thiazoilidine and acrylamide compounds. Their structures were elucidated through the use of spectral analysis. The newly prepared compounds were tested against Pink Bollworm *Pectinophora Gossypiella* (Saunders) (Lepidoptera: Gelechiidae) under laboratory conditions. Thiazoilidine (2d) showed the most potent effect as its LC_{50} was 0.85 mg/ml compared to the other compounds that have been synthesized. It was then regarded as promising derivative and formulated as dustable powder (DP) 10 %. The prepared formulation was then also tested against Pink Bollworm *Pectinophora Gossypiella* under laboratory conditions; it showed LC_{50} 0.92 mg/ml.

Keywords: thiazoilidine, pink bollworm, formulation, dustable powder and biological efficiency

Introduction

Cotton, *Gossypium spp.* is known as one of the most significant commercial fuel, fiber, and edible oil crops (Prasad *et al.*, 2018) [22]. Cotton was described previously as, "white gold", In Egypt, it is one the most valuable economic agriculture products. In addition to exportation, a significant amount of the product is used in manufacturing of garments and fabrics by the local textile industry (Zaki, 2012) [30]. Compared to other crops, cotton is one of the crops that are very vulnerable to pest attack. (Umer and Ahmad, 2019) [27], during its different growth stages, it is vulnerable to infestation with a large number of insect pests, but the most harmful is the damage caused by cotton bollworms to green bolls. Pink bollworm, *pectinophora gossypiella* (Saunders), (Lepidoptera: Gelechiidae) (PBW) is the most powerful (Amin *et al.*, 2006) [3]. Squares and bolls are affected by pink bollworms, the damage to bolls being the most severe. Larvae burrow into bolls, to feed on seeds through the lint. As the larva burrows within a boll, it cuts and stains lint, resulting in severe loss of quality. In dry conditions, the percentage of bolls infested and the number of larvae per boll are directly related to yield and quality losses. With high humidity, the destruction of an entire boll needs only one or two larvae because damaged bolls are prone to infection by boll rot fungi. In open bolls, stained lint becomes noticeable and this is a distinct damage symptom. It takes place once the damage is done in the next stages of the growth of the crop (Sarwar, 2017) [25]. Pink bollworm, *Pectinophora gossypiella* (Saunders) has become the most damaging cotton pest economically and has been known to cause a loss of 2.8 - 61.9 % in seed cotton production, a loss of 2.1 - 47.10 % in oil content and a loss of 10.70 - 59.20 % in normal opening of bolls (Patil, 2003) [21]. The Total loss estimated for the first time in Egypt by Pink bollworm, *Pectinophora gossypiella* (Saunders) was more than one million (Menally and Mullins, 1996) [18].

The use of synthetic chemical pesticides is the most common approach used to control cotton pests, particularly bollworms (Mohamed *et al.*, 2010) [19].

Resistance to pesticides has been described as one of the most important challenges for sustainable integrated pesticide management practices (Labbe *et al.*, 2005) [16]. Resistance has emerged from the ongoing and intensive use of insecticides against this cotton pest, leading to the production of strains more tolerant and resistant to insecticides (Khurana & Verma 1990 and Kranthi *et al.*, 2002) [14, 15], and it became hard to control this insect.

In order to efficiently use an insecticide to control insects, pesticides cannot be used in their raw state; it must first be prepared into a form appropriate to a certain application method. This preparation is called a formulation and involves the addition of certain components including solvents or diluents to improve the physical properties of the insecticide which may be reflected in its efficacy (Carlisle, 1985) [5].

The objective of this study was a trial for gaining new effective active ingredient with a new completely prepared local formulation to use in the integrated pest management control programs of pink bollworm, *Pectinophora gossypiella* (Saunders) after completion of all required related research studies in the future.

Materials and Methods

Tested chemicals

a. **Fine chemicals:** Isothiocyanatobenzene (phenyl isothiocyanate, molar mass 135.19 $g.mol^{-1}$), ethyl bromoacetate (ethyl 2-bromoacetate, molar mass 167.002 $g.mol^{-1}$), chloroacetonitrile (molar mass 75.496 $g.mol^{-1}$), chloropropanone (chloroactone, molar mass 92.52 $g.mol^{-1}$), dimethyl sulfate (methyl sulfate, molar mass 126.13 $g.mol^{-1}$) and 2-Chloro-1-phenylethan-1-one (Phenacyl chloride, molar mass 154.59 $g.mol^{-1}$) were supplied by Sigma - Aldrich Co.
b. **Solvents:** Absolute ethanol, acetone, xylene, benzene and DMF were supplied by EL-Gomhoria Co., Cairo, Egypt.
c. **Diluent:** The diluent used was supplied by EL-Gomhoria Co., Cairo, Egypt.

The physico-chemical properties of the basic formulation components

Active ingredient

The physico-chemical properties of the newly synthesized (*E*)-2-cyano-N (2-hydroxypheny)-2-(4-oxo-3-phenylthiazolidin-2-ylidene) acetamide (2d) as an active ingredient were:

a. **Solubility:** It was determined by measuring the volume of different solvents (distilled water, acetone, DMF, ethanol and xylene) for complete solubility or miscibility of one gram of active ingredient at 20 ˚C (Nelson and Fiero, 1954) [20]. The % solubility was calculated according to the following equation:

$$\% \text{ solubility} = W/V \times 100$$

[Where; W= active ingredient weight, V= volume of solvent required for complete solubility].

b. **Free acidity or alkalinity:** It was determined according to the method described by WHO specification (1979) [29].
c. **Melting point:** It was determined on an electrical digital melting point (Gallenkamp) 9200 A apparatus.

The physico-chemical properties of diluent

a. **Surface activity:** Hammett indicators were used to estimate the surface activity of carriers or diluents (Malina *et al.*, 1956 and Anonymous, 1965) [4, 17]. Di phenyazodiphenylamine and di methyl aminazobenzene were used to determine PKa at different levels; for the former at 1.5 levels (yellow means safe and purple means unsafe or active), while the latter at 3.3 levels (yellow means safe, and red means unsafe or active).
b. **PH:** It was determined by using Cole-Parmer PH / conductivity meter 1484-44 according to Dobrat and Martijn (1995) [7].
c. **Free acidity or alkalinity:** It was determined as mentioned before.
d. **Bulk density:** This property was determined according to WHO specification (1975) [28].
e. **Screen analysis:** The Determination of particle size of the candidate diluents was carried out according to Zaazoua *et al.*, (1966) [30].

Preparation of thiazolidine derivative (2d) as dustable powder (DP)

The new formula was prepared as dustable powder (DP) formulation by dry mix method that involves mixing of the active ingredient with the most suitable chosen diluent (Furmidge, 1972) [11]. The newly prepared formulation contains 10 % (wt/wt) active ingredient.

Determination of the physico-chemical properties of the new local prepared 10 % dustable powder (DP) formulation

a. **Bulk density:** It was determined as mentioned before.
b. **Free acidity or alkalinity:** It was determined as mentioned before.
c. **Screen analysis:** It was determined by the same method reported before.

Bioassay

The newly hatched larvae of pink bollworm, used in this study, was obtained from a standard laboratory colony, reared at Bollworm Department, Plant Protection Research Institute; Agriculture Research Centre (ARC), Giza, Egypt on an artificial diet for several generations away from any insecticidal contamination under controlled conditions 26 ± 2 ºC and 70 - 85 % RH Abd El- Hafez *et al.* (1982) [2].

The toxicity of the prepared compounds and formulation was conducted against the newly hatched larvae of *P. gossypiella* by dissolving in ethanol to form a serial of concentrations (10, 8, 6, 4, 2, 1 and 0.5 mg/g artificial diet) for each compound, and then mixed with diet. Four replicates (each regarding 10 larvae) were transferred individually to the surface of the treated diet, after 48 hrs. live larvae were transferred on untreated diet and kept in glass tubes (2 x 7.5 cm). For the control test un untreated diet was used. All tubes were capped with cotton stopper and incubated at 26±2 ºC and 70-85 % RH and inspected daily until pupation. Mortality was recorded at intervals after 2, 5, 7 and 9 days after larval treatments.

Statistical analysis

The average regarding mortality portion had been determined by employing Abbott formula (1925) [1]. The actual remedied mortality portion of each compound had been statistically computed according to the method of Finney (1971) [10], Toxicity index was calculated by the following equation; Toxicity index = LC_{50} of the most powerful compound / LC_{50} of the screened compound × 100 according to (Sun, 1950) [26].

Chemistry Part

O-aminophenol on treatment with 3-(3,5-dimethyl-*1H*-pyrazol-1-yl)-3-oxopropanenitrile in benzene under reflux for 3 hrs. Afforded acetamide derivative (1) (El-Sharkawy *et al.*, 2020) [8]. Which on treatment with chloroacetonirile and α-halocarbonyl compounds (chloroacetone, ethyl bromoacetate and phenacyl chloride) cyclizes on thiazolidine derivatives (2a), (2b), (2d) and (2e) respectively, the reaction products that were characterized by the appearance of an amino group (NH_2) in IR spectrum at 3377 cm^{-1} of thiazolidine (2a) and the presence of two protons of the methylene group (CH_2) in ^{1}H-NMR spectra at δ/ppm 4.18 of thiazolidine derivative (2d). While dimethyl sulphate on reaction with acetamide (1) afforded acrylamide derivative (2c).All reaction products (2a - 2e) were formed through the formation of a non-isolable thiocarbamoyl salt resulted from the reaction of acetamide (1) and phenylisothiocynate in an alkaline medium.

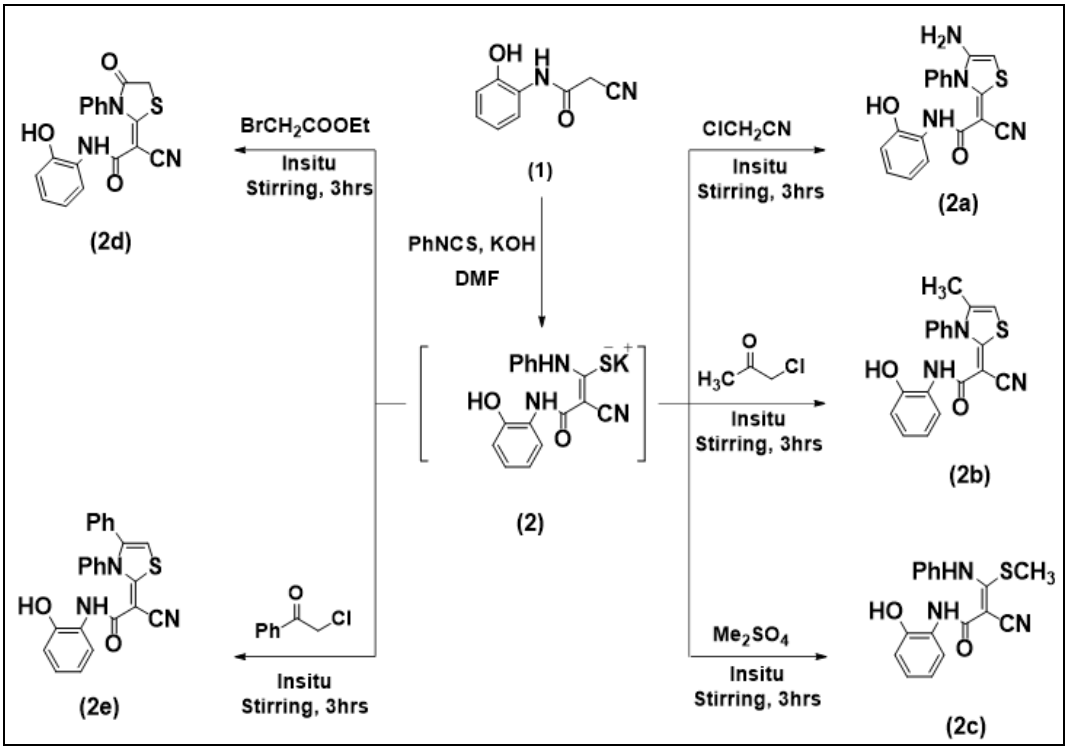

Fig 1: Synthesis of compounds (2a-e).

Experimental

All melting points were uncorrected and measured on an electric melting point (Gallenkamp) 9200 A apparatus. IR spectra (KBr) were recorded with a Perkin-Elmer model 157 infrared spectrophotometer. ^{1}H-NMR spectra were obtained from Varian Gemini 400 MHz spectrometer and chemical shifts are expressed in δ (ppm) using TMS as internal reference. Mass spectra were acquired with GCMS-QP1000 EX and Jeol JMS 600 spectrometers opening at 70 eV. Microanalytical data were obtained from the microanalytical data center of the Faculty of Science, Mansoura University.

Synthesis of 2-Cyano -N- (2-hydroxyphenyl) acetamide (1)

O-aminophenol (0.01 mole, 1.09 g), and 3-(3, 5-dimethyl-*1H*-pyrazol-1-yl)-3-oxopropanenitrile (0.01 mole, 0.16 g) were heated in benzene under reflux for 3 hrs. The obtained crystalline material was filtered off, washed with benzene to afford the corresponding acetamide derivative (1).

Silver crystals; yield 95 %; mp 280 °C; IR (KBr): *ν/cm^{-1}*: 3276 (NH), 3037 (CH-arom.), 2960 (CH-aliph.), 2271 (CN), 1672 (C=O) ^{1}H-NMR (400 MHz, DMSO-d6): δ/ppm 4.00 (s, 2H, CH_2), 6.77-7.84 (m, 4H, Ar-H), 9.57 (s, H, NH), 9.93 (s, H, OH), MS m/z (%): 176 (31.01), 136 (18.33), 109 (100.00), 107 (11.56), 77 (1.41).

Synthesis of thiazolidines derivatives (2a), (2b), (2d) and (2e)

A mixture of acetamide derivative (1) (0.01 mole, 1.76 g) and phenylisothiocynate (0.01 mole, 1.35 g) in DMF containing potassium hydroxide afforded the non-isolable thiocarbamoyl salt (2) which on treatment with equimolar amounts of chloroacetonirile and α-halocarbonyl compounds (chloroacetone, ethyl bromoacetate and phenacyl chloride) give thiazolidine derivatives (2a), (2b), (2d) and (2e) respectively.

(E)-2-(4-amino-3-phenylthiazol-2(3H)-ylidene)-2-cyano-N-(2-hydroxyphenyl) acetamide (2a)

Yellow crystals; yield 65 %; mp 240 °C; IR (KBr): *ν*/cm^{-1}: 3619 (OH), 3377 (NH_2), 3314 (NH), 2195(CN), 1655 (C=O). MS m/z (%): 350 (42.85), 335 (62.18), 305 (37.32), 297 (70.09), 235 (19.04), 223 (100), 195 (4.95), 181 (57.63) 77 (13.48).

(E)-2-cyano-N-(2-hydroxyphenyl)-2-(4-methyl-3-phenylthiazol-2(3H)-ylidene) acetamide (2b)

Yellow crystals; yield 80 %; mp 250 °C; IR (KBr): *ν*/cm^{-1}: 3566 (OH), 3357 (NH), 2162 (CN), 1647 (C=O). MS m/z (%): 349 (76.95), 270 (24.06), 257 (9.90), 213 (26.39), 163(100), 133 (24.76), 121 (19.77), 77 (24.79).

Synthesis of (E)-2-cyano-N-(2-hydroxyphenyl)-3-(methylthio)-3-(phenylamino) acrylamide (2c):

A mixture of acetamide derivative (**1**) (0.01 mole, 1.76 g) and dimethyl sulphate (0.01 mole, 1.29 g) in alkaline medium was heated in benzene under reflux for 3 hrs. The formed solid crystalline product was filtered off, washed with benzene to afford the corresponding acrylamide (2c).Orang crystals; yield 75 %; mp 170 °C; IR (KBr): ν/cm^{-1}: 3423 (OH), 3302, 3106 (2NH), 2219 (CN), 1649 (C=O). MS m/z (%): 325 (30.36), 297 (100), 251 (74.10), 151(81.04), 161 (41.69), 137 (31.12), 89 (83.57), 76 (31.24).

(E)-2-cyano-N-(2-hydroxyphenyl)-2-(4-oxo-3-phenylthiazolidin-2-ylidene) acetamide (2d)

Yellow crystals; yield 75 %; mp 250 °C; IR (KBr): *ν*/cm^{-1}: 3527 (OH), 3374 (NH), 2198 (CN), 1659, 1750 (2C=O). ^{1}H-NMR (400 MHz, DMSO-d6): δ/ppm = 4.18 (s, 2H, CH_2), 6.76–7.97 (m, 4H, Ar–H), 10.21 (s, H, NH), 10.61 (s, H, OH). MS m/z (%): 351 (46.47), 243 (76.50), 231 (6.66), 217 (39.69), 205 (9.34), 109 (100), 76 (31.63).

(E)-2-cyano-2-(3,4-diphenylthiazol-2(3H)-ylidene)-N-(2-hydroxyphenyl)acetamide (2e)

Yellow crystals; yield 60 %; mp 230 ˚C; IR (KBr): *v*/cm^{-1}: 3622 (OH), 3265 (NH), 2182(CN), 1639 (C=O). MS m/z (%): 411 (12.20), 303 (65.40), 277 (100), 248(36.18), 231 (3.54), 221 (9.08), 144 (15.06), 132 (17.96), 76 (15.62).

Results and Discussion

Biological activity

Mortality percentages of the newly hatched larvae of pink bollworm, treated with the newly synthesized compounds (2a-2e), are shown in Table (1). The LC_{50} values were 5.5, 4.6, 2.9, 0.85 and 7.6 mg/ml for (2a), (2b), (2c), (2d) and (2e) respectively. The most effective compound was thiazolidine (2d) as it showed the lowest LC_{50} value 0.85 mg/ml.

The efficacy of thiazolidine (2d) may be attributed to its chemical composition. Phenyl thiazolidines bonded to a double bond located between nitrile and carbonyl groups plays an important role in toxicity, in addition, to the presence of cyanoacetamide that showed biological efficiency on the cotton leafworm 2nd instar larvae, *S. littoralis* as reported by (Fadda *et al*., 2017) [9]. In addition compounds (1 and 2c) showed toxicity against the 3rd instar larvae of *S. littoralis* (Boisd.) and the adult stage of cotton mealybug *Phenacoccus solenopsis* under laboratory conditions (El-Sharkawy *et al*., 2020) [8].

Table 1: Efficacy of the synthesized compounds on the newly hatched larvae of Pink bollworm *Pectinophora gossypiella* under lab. Conditions

Compounds	LC_{50} (mg/ml) 95 % limit	LC_{90} (mg/ml) 95 % limit	Slope	Toxicity index percent
2a	5.52809 3.368024 12.91992	206.956 49.1471 12874.238	0.8146± 0.2053	15.42
2b	4.65243 2.92934 9.072	135.908 39.13875 3564.337	0.8745± 0.2055	18.32
2c	2.94388 1.98406 4.31108	39.95791 18.88174 183.17050	1.1315 ± 0.2089	28.95
2d	0.85238 0.58125 1.12690	5.33819 3.29365 14.40123	1.6085 ± 0.3105	100.00
2e	7.69219 4.99296 16.65233	136.04160 43.59386 2070.685	1.0272 ± 0.2211	11.08

Deepak *et al.*, (2014) [6] noted that substituted thiazolidine-4-ones showed antifeedant, acaricidal, contact toxicity, and stomach toxicity entomological activities on *S. littoralis* and *Tetranychus urticae* mites respectively. In addition, it's possible that it will react with the peptidoglycan in the bacterial cell wall causing harm by entering the cell in such a way that the phenyl ring is trapped inside and punctured, followed by the death of bacterial cells (Kant *et al*., 2008) [13]. Gaughan and Men (1974) [12] prepared and evaluated a series of compounds including thiazolidines for their biological activity. Many of these synthesized compounds revealed high level of biological efficiency, especially as systemic pesticides (insects and acari). Also, Rodriguez-Salus *et al.* (2016) [23] found that thiazolidine derivatives containing carboxylic acid that were used as bactericides and fungicides are commonly used in agriculture around the world to prevent or control plant diseases.

The toxicity of thiazolidine (2d) and its dustable powder 10 % formulation on *P.gossypiella* newly hatched larvae after 7 days from treatment are shown in Table (2). Their LC_{50} values were 0.85 and 0.92 mg/ml respectively. The Toxicity index (%) of the 10 % dustable powder formulation recorded 92.58 % compared with 100 % for its active ingredient.

Table 2: Synthesized thiazolidine (2d) and its dustable powder formulation 10 % efficacy against the larvae of the pink bollworm *Pectinophora gossypiella* under lab. conditions

Parameter Tested compound	LC_{50} 95 % limit	LC_{90} 95 % limit	Slope	Toxicity index percentage
Active ingredient	0.85238 0.58125 1.12690	5.338193.29365 14.40123	1.6085 ± 0.3105	100.00
10 % dustable powder (DP) Formulation	0.92067 0.58713 1.32796	8.10223 4.33608 30.05268	1.3569 ±0.2684	92.58

Formulation part

Physical properties of thiazolidine (2d) as active ingredient: Table (3) showed physical properties of the newly synthesized thiazolidine derivative (2d) as an active ingredient. It was insoluble in either aqueous or organic solvents, in addition it showed free acidity as percentage sulfuric acid (0.8), the acidic property determined the kind of additives to use in the formulation and the insolubility property directs the processes of formulation to one of the formulation kinds of insoluble active ingredients (flowable or suspension concentrate and dustable powder). Dustable powder was the most suitable type in this case.

Table 3: Physical properties of thiazolidine (2d) as active ingredient

% Solubility (W/V)					Free acidity as % H_2SO_4	Melting point ˚C
Water	Acetone	DMF	Ethanol	Xylene		
-*	-	-	-	-	0.8	250

-*: means insoluble.

Physical properties of the used diluents

Many trials were carried out to choose the most compatible diluent with the properties of active ingredient, Table (4) showed the physico-chemical properties of the used diluent. It showed small values of bulk density 0.36 and 0.41 before and after compaction respectively, these results were consistent with WHO specification (1979) [29] that stated that the packed bulk density of the powder after compaction (bulk density) must not exceed 60 percent of the value before compaction. The diluent also showed weak alkaline property appeared from free alkalinity as sodium hydroxide and alkaline PH value (8.33). PKa test must be carried out in combination with PH in determining the physical properties of diluents or carriers. Rosen Field, (1970) [24] stated that, the PH value determines the average acidic and alkaline sites, which do not neutralize each other in the solid state,

while PKa determines the acidic and alkali sites of the solid and the inert material and the interaction between them. In addition, the used diluent on screen analysis for their particle size, showed complete ability to pass from sieves ranging from 20-53 microns.

Table 4: Physico-chemical properties of the used diluent

PKa	PH	Free alkalinity as % NaOH	Bulk density		Screen analysis less than microns			
			Before compacting	After compacting	53	40	30	20
>1.5>3.3	8.33	0.0057	0.36	0.41	100	100	100	100

Physical properties of the prepared dustable powder formulation 10 %.

Table (5) showed that, the newly prepared dust formulation succeeded to pass the physico-chemical tests reported for dust formulations. The bulk density obtained before compacting and after compacting (packed) was consistent with the rule specified by WHO specification (1979) [29] that stated that the bulk density of the powder after compaction should not exceed the value obtained before compaction by more than 60 %. In addition, the dust showed an acidic property with particle size less than 74 microns as determined by WHO specification (1979) [29].

Table 5: Physical properties of the prepared dustable powder formulation 10 %

Bulk density		Free acidity as % H_2SO_4	Screen analysis less than 74 microns
Before compaction	After compaction		
0.4	0.6	0.04	84

Conclusion

Group of new thiazolidine and acrylamide derivatives were prepared, and tested against Pink Bollworm *Pectinophora Gossypiella* (Saunders) (Lepidoptera: Gelechiidae) under laboratory conditions. The most potent compound was (2d); it was formulated as 10 % dustable powder formulation and tested against Pink Bollworm under laboratory conditions. It showed good activity against the pest under study, and it could be used in the control of Pink Bollworm *Pectinophora Gossypiella* after finishing all required research studies.

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