International Journal of Agricultural Technology 2017 Vol. 13(6): 869-881
Available online http://www.ijat-aatsea.com
ISSN 1686-9141

Some Chemical and Functional Properties of Dry Pulp from Riang (*Parkia timoriana* (DC.) Merr.)

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Apirattananusorn, S. (2017). Some chemical and functional properties of dry pulp from Riang (*Parkia timoriana* (DC.) Merr.). International Journal of Agricultural Technology 13(6): 869-881.

The aim of this research was to evaluate some chemical and functional properties of natural dry pulp of Riang (*Parkia timoriana* (DC.) Merr.), a native tree in the south of Thailand, in order to promote its utilization. The total phenolic content in Riang pulp powder (RPP) was higher than carboxymethyl cellulose (CMC), carrageenan (CG) and low methoxyl pectin (LMP). When RPP was heated by oven, the phenolics decreased from 16.75 to 14.93 mg GAE/g, but the DPPH radical scavenging activity increased from 32.94% to 75.02%. RPP contained 15.85% galacturonic acid and 45.66% total sugar, and it presented a water and oil holding capacity of 5.44 and 3.56 g/g, respectively. Solubility, analyzed between 30-90ºC, ranged from 43.17-46.67%. RPP (1%) was prone to stabilize the emulsion when salt and sugar were added. The addition of RPP at the concentration of 0.5 and 1.0% resulted in gel formation of tapioca flour paste (8%, w/v). Comparison to 0.5% of RPP, syneresis of tapioca flour gel with 1.0% of RPP significantly (p<0.05) decreased after kept at 4 and 25ºC for 7 days. These results suggest that RPP may be added to food for emulsifying and stabilizing reasons.

Keywords: Riang pulp, *Parkia timoriana* (DC.) Merr., water and oil holding capacity, emulsion, syneresis

Introduction

Riang (*Parkia timoriana* (DC.) Merr.) is a native tree legume and commonly known as a tree bean belonging to the Leguminosae family (Suwannarat and Nualsri, 2008). It is a big tree (Figure 1) which grows in the south of Thailand, and flowers from November to December and produces pods (fruits) from December to April. The ripe dry pods, generally falling down from its tree, are collected to obtain seeds for food. The natural dry pulp of Riang is usually discarded, but in some local areas it has been used to make a jelly-like dissert. The odor of dry Riang pulp is like tamarind and it is light yellowish-brown in color that may act of interfering if used in some prospective food

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products. However, a previous study showed that an estimated 10% of Riang pulp (in dry pods) was composed of 10.71% moisture, 5.49% ash, 5.04% protein, 0.77% fat and 27.86% total dietary fibers, and it could promote gel formation with limewater, so that it might be a good source of pectic polysaccharides to produce flavored jellies (Apirattananusorn, 2013). Hydrocolloids, often called gums, such as pectic polysaccharides, are widely used to improve quality attributes of food due to their functional properties such as viscosity, gelling and stabilizing (Saha and Bhattacharya, 2010; Li and Nie, 2016). They are also applied as emulsifier and thickener in food systems (Huang *et al*., 2001; Phillips and Williams, 2009). In addition, the antioxidant activity of some gums, such as, carrageenan has been established, depending on the treatment used (Dashipour *et al*., 2014; Rafiquzzaman *et al*., 2016). Natural dry Riang pulp shows viscosity when crushed with water, which could thicken and stabilize food texture. Up to date, there has been very limited information about chemical and functional properties of non-chemical dry Riang pulp. Therefore, the objective of this research was to investigate its properties to enhance utilization in food products or cosmetics.

In the presented work, some chemical and functional properties of dry Riang pulp were studied in comparison with those of commercial gum. The ability of dry Riang pulp to prevent emulsion separation and syneresis of flour gel was also determined.

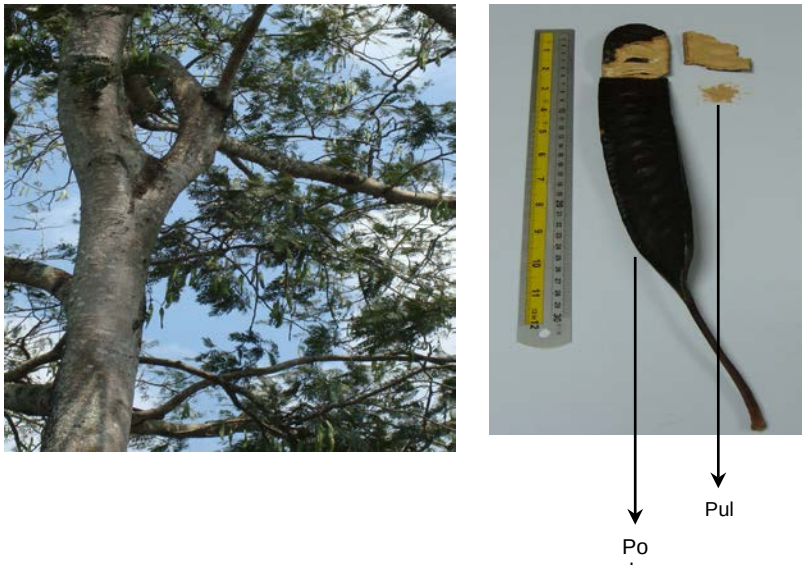

Figure 1. Riang (*Parkia timoriana* (DC.) Merr.)

Materials and methods

Materials and chemicals

The ripe dry blackish pods of Riang falling from its tree in May were collected from Suratthani Province, Thailand. They were rubbed and washed with running water to remove the surface dust, and dried with a clean cloth. The pods were manually cut and grounded to obtain dry pulp powder (mesocarp) while the husk (exocarp), endocarp and seeds were discarded. The dry Riang pulp powder (RPP) (~10% moisture) was passed through a 35-mesh sieve and kept at 4ºC until used. Low methoxyl pectin was kindly donated from Burapacheep Ltd., Thailand. Carrageenan, carboxymethyl cellulose and xanthan gum were purchased from Bronson and Jacobs International Co. Ltd., Thailand. Agar was purchase from SengHuad Part., Ltd., Thailand and tapioca flour was purchased from Kriangkrai, Co. Ltd., Thaliland. All chemicals used were of analytical grade unless otherwise specified.

Phenolic content and antioxidant activity

Each sample of 10 g was extracted with 80% ethanol at 70ºC for 60 min. The mixture was filtered through a filter paper (Whatman No. 1) and the filtrate was finally evaporated by vacuum rotary evaporator at 40ºC until dried. The residue was kept in the dessicator until analysis. The total phenolic content, determined by means of the Folin-Ciocalteu reagent and expressed as gallic acid equivalents (GAE), followed the method of Singleton and Rossi (1965). The antioxidant activity was determined by the method of DPPH radical scavenging activity as described by Hatano *et al*. (1988). Briefly, the extract was prepared to the sample concentration of 10 mg/ml. The sample of 0.1 ml was added to the test tube and mixed with 3.9 ml of DPPH solution (2,3-diphenyl-1-picrylhydrazyl concentration of 6×10^{-5} M in methanol). The mixture was kept in the dark for 30 min. The absorbance at 517 nm was recorded and calculated using the following equation.

$$\text{DPPH radical scavenging activity (\%)} = [(Abs_{control} - Abs_{sample})]/(Abs_{control})]\times100$$

$Abs_{control}$ = the absorbance of DPPH radicals + distilled water
Abs_{sample} = the absorbance of DPPH radicals + sample extract/standard

Galacturonic acid and total sugar

The galacturonic acid content was determined by the *m*-hydroxydiphenyl method as described by Blumenkrantz and Asboe-Hansen (1973). The sample of 5 mg/ml was heated in a water bath at 50ºC for 3 hr, and then 0.5 ml was taken and mixed with 3 ml of 1.25×10^{-2} M $Na_2B_4O_7$ in 18 M H_2SO_4 and heated at 100ºC for 5 min. After cooling, the *m*-hydroxydiphenyl reagent of 50 µL was added to form colour. The standard galacturonic acid solutions were used to construct the standard curve at the absorbance of 520 nm, measured by UV-visible spectrophotometer (T60 PG Instrument, England). Total sugar was determined by the phenol-sulphuric acid method (Dubois *et al*., 1956). A calibration curve was prepared using glucose as standard solution and measured at 490 nm. The 10 mg sample was hydrolyzed with 1 ml of 12 M H_2SO_4 solution for 30 min and subsequently diluted to fit into a range of standard curve.

Water and oil holding capacity

The water holding capacity (WHC) of the samples was determined according to the method described by Sciarini *et al*. (2009) with slight modification. The sample of 0.5 g was weighed in a centrifuged tube with distilled water (20 ml), vortexed for 5 min until the sample was totally wet and left for 30 min. The mixture was centrifuged at 3,000 rpm for 15 min. The supernatant was decanted, and the wet sample was weighed. The WHC was calculated and expressed as g of water held per g of the sample (g/g). Oil holding capacity (OHC) of the samples was also determined in the same manner as previously described for WHC, using commercial palm oil instead of distilled water.

Solubility

Solubility was determined according to the method described by Betancur-Ancona *et al*. (2002) with minor modification. The sample of 1% (w/v) with distilled water (40 ml) was placed in a shaking water bath at 30, 40, 60, 80 and 90ºC for 30 min and constantly shaken to evaluate the effect of temperature on the solubility of the sample. The mixture was centrifuged at 3,000 rpm for 15 min. The supernatant (10 ml) was then dried in a hot air oven at 105ºC, until the constant weight was obtained. Solubility was calculated according to the following equation.

Solubility (%) = [(Wd×40)/(Ws×10)]×100
Wd = Dry weight at 105 °C
Ws = Sample weight

Emulsion capacity

Emulsion capacity was measured by the method that modified from Sciarini *et al*. (2009). The RPP samples at a concentration of 0.25, 0.5 and 1.0% (w/v) were dispersed and stirred in distilled water (200 ml) for 30 min at room temperature (25ºC). The 20 ml of commercial palm oil was added and homogenized (15,000 rpm) for 2 min using homogenizer (OV5 VELP scientific, Italy). Various amounts of NaCl (0, 0.5 and 1.0 wt%) and commercial sugar (0, 5 and 10 wt%) were added and stirred thoroughly for 5 min to completely dissolve. The mixtures were then left in cylinders for 30 min prior to observe layer separation. The emulsion capacity was calculated as follows.
Emulsion capacity (%) = [Ve/Vt]×100
Ve = Emulsion volume
Vt = Total volume

Effect of heat on phenolic content and antioxidant activity

The sample of RPP was heated in a hot air oven at 60ºC for 2.30 hr. Phenolic content and antioxidant activity was then determined as described above.

Effect of RPP on syneresis of tapioca flour gel

The samples of 8% (w/v) commercial tapioca flour with distilled water (100 ml) containing different RPP (0, 0.5 and 1.0%) and 0.02% sodium azide were prepared. The mixture was gelatinized by heating in a boiling water bath with continuous stirring for 10 min, transferred to a container and left to cool at room temperature. All samples were kept at 4 and 25ºC for 7 days before analysis. After storage, the samples of flour gel were taken to measure syneresis of flour gel by centrifugation-filtration method as described by Charoenrein *et al*. (2008) with modification. A syringe (20 ml) with a piece of filter paper (Whatman No. 1) on slim cotton at the bottom was filled with distilled water, placed in a centrifuge tube and centrifuged at 3,000 rpm for 10 min to remove the excess water. The flour gel samples were cut into a piece of 1×1×2 cm^3 and put in the syringe. The tube was then centrifuged again at 3,000 rpm for 10 min.

The centrifuged sample was weighed and the separated liquid at the bottom was calculated as percentage of syneresis. All samples were analyzed in triplicate.

Statistical analysis

A completely randomized design at differences between means was analyzed using the Duncan's New Multiple Range Test at a 95% confidence level. For a Paired Samples T-Test, the mean difference (95% confidence level) was used. All data were calculated using SPSS version 21 for Windows.

Results and Discussion

Chemical properties and characterization

Total phenolic content and antioxidant activity

Table 1 shows the content of phenolic compounds and the DPPH radical scavenging activity of Riang pulp powder (RPP) compared to three commercial gums; carboxymethyl cellulose (CMC), carrageenan (CG) and low methyl pectin (LMP). The results revealed that the content of phenolics in RPP and RPP (Heated), 16.75 and 14.93 mg GAE/g respectively, were significantly higher than in the commercial gums, because they were unpurified compounds generally found in many fruits and vegetables and usually coincided with antioxidant activity (Tomas-Barberan *et al*., 2000; McDonald *et al*., 2001; Liu *et al*., 2007; Vasco *et al*., 2008). However, CMC and CG with lower amount of phenolics possessed higher DPPH activity than RPP, probably due to their polymer structures such as degree of sulfate group on CG which indicated functionality of antioxidant activity (Rocha de Souza *et al*., 2007; Barahona *et al*., 2011; Zhou *et al*., 2014). CG displayed higher (74.59%) DPPH scavenging activity than the finding (45.09%) reported by Rafiquzzaman *et al*. (2016), which may be related to the different sources and treatment process. Phenolics in RPP were affected by heating, and reduced to 14.93 mg GAE/g similar to the findings of Lemos *et al*. (2012) and Guiné *et al*. (2015) explaining that phenolic compounds and antioxidant activity were reduced according to temperature and time period of treatment. However, the reduction of phenolics in this report was not associated with a higher antioxidant activity, measured by DPPH. The DPPH radical scavenging in heated RPP was increased to 75.02%, representing an overall significant increase of about 50% (p<0.05). As the results obtained by Žilić*et al*. (2013), heating condition caused the reduction of phenolic compounds while the new certain maillard reaction products was increased, inducing the antioxidant activity to some extent. The results suggest that the

heat treatment causes chemical changes in RPP and may promote protein denaturation to form new chemicals, supporting antioxidation ability**.** However, an interaction of other compounds is also a complex phenomenon and should be further investigated for antioxidant activity.

Table 1. Total phenolic content and antioxidant activity (DPPH)

Samples	Total phenolic content (mg GAE/g sample)	DPPH radical scavenging (%)[1]
CMC	1.11±0.09a	56.08±0.00c
CG	1.44±0.04b	74.59±0.16d
LMP	4.55±0.82c	29.17±0.30a
RPP	16.75±0.88e	32.94±0.30b
RPP (Heated)[2]	14.93±0.92d	75.02±0.76d

Means (n=2) with different letters in each column are significantly different (p<0.05)
[1]Concentration of 10 mg/ml
[2]The sample was in an oven heated to 60°C for 2.30 hr
CMC = Carboxylmethyl cellulose, CG = Carrageenan, LMP = Low methoxylpectin, RPP = Riang pulp powder

Galacturonic acid and total sugar

The composition showed that RPP registered a high content of 45.66±0.84% total sugar. The value of galacturonic acid found in RPP was 15.85±0.11%, higher than that in Ambarella peels (10.8%) but lower than in lime peels (19.2%) reported by Koubala *et al*. (2008). The galacturonic content revealed that RPP might be a potential source of pectin.

Functional properties

Water and oil holding capacity

Table 2 shows the water and oil holding capacity of RPP compared to five commercial gums; agar, LMP, CMC, CG and Xanthan gum (XG). The water holding capacity (WHC) value of RPP was 5.44 g/g, not significantly different from agar (5.63 g/g), but less than that of CG and close to gum extracted from tarmarillo (5.82 g/g) reported by Gannasin *et al*. (2012). LMP, CMC and XG could not be measured for WHC by this method because they seemed to totally hold water and lead to high viscosity, so that water could not be separated by centrifugation similar to the findings by Thanatcha and Pranee (2011). For the oil holding capacity (OHC), RPP had the value of 3.56 g/g, significantly higher than agar, LMP, CMC, CG and XG and similar to what was reported in mucilage extraction from *Ocimum canum* Sims. seeds (3.83 g/g) (Ruangchakrpet and Anprung, 2002). These properties have been attributed to the physical entrapment of molecules such as nonpolar side chains of protein

molecules (Zayas, 1997) and structural characterization of gum as well as particle size. The other components such as ash, soluble and insoluble fiber, containing in RPP were also implicated (Elleuch *et al.*, 2008). The results indicate that RPP could be used in some food emulsions such as sausages and meat balls to stabilize or replace some fat in low-fat food products.

Table 2. Water and oil holding capacity

Samples	WHC (g/g)[1]	OHC (g/g)
RPP	5.44±0.08a	3.56±0.14c
Agar	5.63±0.08a	2.62±0.12b
LMP	ND[2]	2.44±0.27b
CMC	ND	2.46±0.41b
CG	7.59±0.56b	1.84±0.17a
XG	ND	2.45±0.05b

Means (n=3) with different letters in each column are significantly different ($p<0.05$)
[1]The amount (g) of water or oil per g dry sample
[2]Not detectable
WHC = Water holding capacity, OHC = Oil holding capacity, RPP = Riang pulp powder, LMP = Low methoxyl pectin, CMC = Carboxylmethyl cellulose, CG = Carrageenan, XG = Xanthan gum

Solubility and emulsion capacity

Likewise, LMP, CMC and XG were not determined for solubility due to their high viscosities and totally water absorption. In this study, CG presented the highest solubility of 56.83% at low temperature (30°C) while agar and RPP exhibited the lowest (2.29%) and intermediate values (43.17%), respectively. An increase in RPP solubility was observed when the temperature rose up to 40°C, but it was not significantly affected by temperature during 40-90ºC (46.17-47.67% solubility). RPP was likely to be sufficient to stable oil-in-water emulsions, different from what the author mentioned elsewhere with response to the application method. The emulsion could be expected to be stable at high sample concentrations (0.5 and 1.0%) while the separate layer was observed at low level (0.25%) due to very limited concentration. Gums or polysaccharides could prevent the emulsion from coalescence of oil droplets due to concentration, nature and chemical composition of gums. It was demonstrated that sufficient hydrocolloid, such as crude fenugreek gum (13.9% protein), produced a very stable oil-in-water emulsion. However, fenugreek gum with low residual protein (0.8%) could also exhibit surface activity and form stable emulsions (Garti *et al*., 1997; Huang *et al*., 2001; Vilela and Cunha, 2016). The ionic strength of NaCl (0.5 and 1.0% added) significantly promoted the oil droplet flocculation, approximately a half of the original volume, and then reducing the emulsion capacity (0.5% RPP) as shown in Figure 2. The results

explained that NaCl probably decreased electrostatic repulsion of the hydrocolloids in emulsions, and hence oil droplets came closer and aggregated, which was in accord with reported accelerated coalescence as a result of electrolytes in emulsion system (Ogawa *et al*., 2004; Baloch and Hameed, 2005). The addition of sugar to the emulsion did not affect or encourage emulsion separation in this study. It was stated that sugar increased the viscosity of the aqueous phase and might retard the rate of oil droplet accumulations (McClements, 2004). Similarly, Maskan and Göğüş (2000) observed that sunflower oil-water emulsions were stabilized by sugar, depending on various concentrations (0-8%). On the other hand, the addition of NaCl (0.5 and 1.0%) and sugar (5 and 10%) in the higher RPP content (1.0%) did not show a reduction in capacity of emulsion. It was assumed that the surface charge density remained relatively stable at a high RPP concentration. The results showed the possibility of using an adequate amount of RPP in an emulsion system in the presence of added NaCl and sugar.

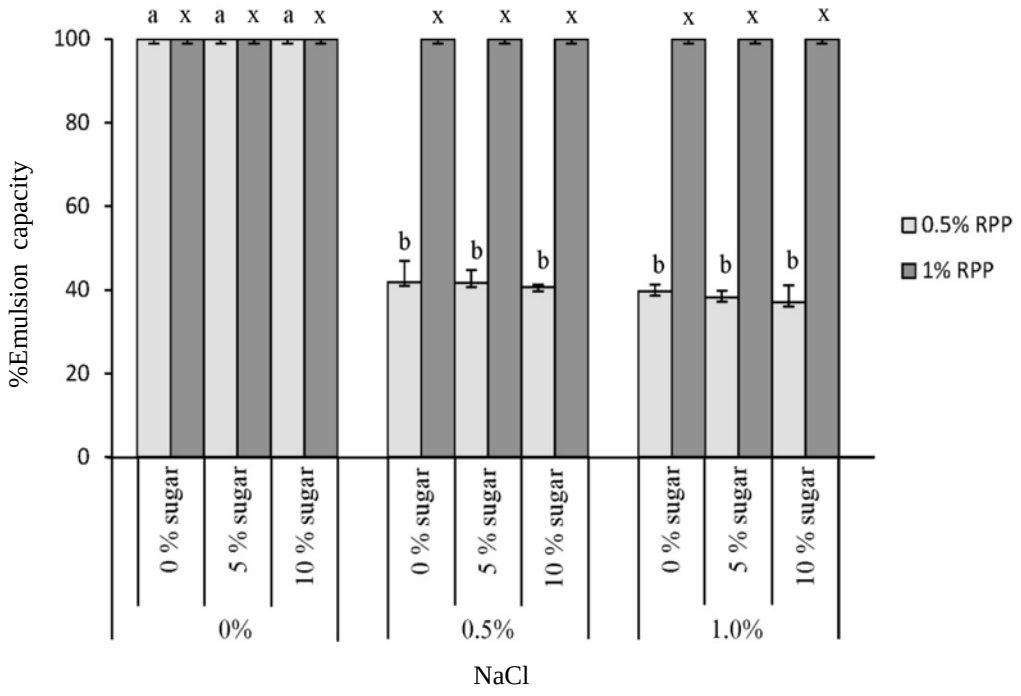

Figure 2. Emulsion capacity of RPP at several concentrations of NaCl and sugar
RPP = Riang pulp powder
Means (n=3) with different letters on each concentration bar are significantly different (p<0.05)

Syneresis of tapioca flour gel

Gelatinized tapioca flour with distilled water (8%, w/v) was converted to flour paste rather than flour gel, but when mixed with RPP (0.5 and 1.0%), it led to gel formation. The results indicated that RPP could promote tapioca flour gel formation. All samples (tapioca flour with RPP) stored at 4 and 25ºC for 7 days, showed the retrogradation of starch implied by syneresis of the gels (Table 3). After storage at both temperatures, significant reduction of syneresis was found in tapioca flour gel with addition of 1.0% RPP when compared to that of 0.5%. The results explained that RPP, which may contain pectic polysaccharides (15.85% galacturonic acid in RPP), could induce gelation by cross-linking with starch molecules and inhibit the crystalline structure of starch retrogadation, so that the syneresis reduced when higher amount of gums were used (Khondkar *et al*., 2007; Funami *et al*., 2008; Leite *et al*., 2012). The effect of storage temperature (4 and 25ºC) on syneresis was not obviously different in flour gels with 0.5% RPP. In contrast, the sample of 1% RPP stored at 25ºC had a significant lower syneresis (3.36%) than the one stored at 4ºC (4.15%). It is likely that the retrogradation occurred during storage at low temperature, similar to tapioca starch gels, with and without hydrocolloids, stored at 4°C for 7 days, which showed a higher percentage of retrogradation than those stored at 25°C for the same period (Babić *et al*., 2006). It is indicated that a low temperature generally accelerates retrogradation of starch when kept for a time long enough, since the linear molecules of amylose and some linear parts of amylopectin recrystalline themselves and squeeze some water out (Hoover, 1995; Li *et al*., 2014).

Table 3. Syneresis of tapioca flour gel (%) with addition of RPP

Content of RPP (%)	**Storage temperature**	
	4°C	**25°C**
0.5	4.92±0.48a,x	4.92±0.42a,x
1.0	4.15±0.36b,x	3.36±0.30b,y

Means (n=3) with different letters (a, b) in each column are significantly different (p<0.05)
Means (n=3) with different letters (x, y) in each row are significantly different (p<0.05)
RPP = Riang pulp powder

Conclusion

The phenolic content and DPPH radical scavenging in RPP were affected by thermal treatment. RPP contained 15.85% galacturonic acid and 45.66% total sugar. Moreover, RPP presented good OHC (3.56 g/g) and WHC (5.44 g/g) and it could be dissolved 43.17-46.67% between 30-90ºC. NaCl and sugar did not influence the phase separation of emulsion when using RPP at the

concentration of 1.0% (w/v). RPP at the level of 1% in tapioca flour gel reduced syneresis at both investigated temperatures of 4 and 25ºC after 7 day-storage. Further study is required to investigate characteristics of pectic polysaccharides in RPP which may influence functionality in this experiment.

Acknowledgement

The author would like to express sincere gratitude to Professor Dr. Katsuyoshi Nishinari and Dr.Thavorn Juntachote for their kind opinions. I am also grateful to Burapacheep Ltd., Thailand for providing me with low methoxyl pectin. This research was funded by a grant from Suratthani Rajabhat University.

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(Received 4 August 2017, accepted 30 October 2017)