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Extraction of apricot kernel skin oil and analysis of its nutritional composition

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Abstract

Apricot kernel skin (AKS) is not fully utilised, except for some that are used as feed. In the present work, the effect of extrusion pre-treatment on the extraction yield, acid value, and peroxide value of AKS oil (AKSO) was investigated. In addition, the physicochemical properties, fatty acid and triglyceride compositions, Sn-2 fatty acid distribution, and content of various active ingredients in AKSO were further analysed. The results showed that AKS contained 12.1% crude oil. Furthermore, AKSO contained approximately 90.0% unsaturated fatty acids, and was high in tocopherols, phytosterols, squalene, and polyphenols. After AKS was extruded, granulated, and extracted with hexane as a solvent, the quality and extraction yield of AKSO were significantly improved, confirming its feasibility for AKSO extraction. From the perspective of nutrition and cost-efficiency, AKS could be a promising new oil-bearing resource, and AKSO could be used as a nutritional oil in food, medicine, and cosmetics.

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Introduction

Apricot (*Prunus armeniaca* L.) belongs to the Rosaceae family, and is cultivated worldwide. According to FAO, global apricot production in 2022 was more than 3.9 million tonnes (FAO, 2022). Currently, large quantities of apricots are consumed, resulting in the production of significant amounts of apricot stone by-products. The seeds of apricot stones, also known as apricot kernels (AK), are rich in protein, oil, and other nutrients (Akhone *et al*., 2022). During AK processing, it is usually necessary to remove the apricot kernel skin (AKS) using blanching. AKS, a by-product of the AK processing industry, accounts for 5 - 7% of the total AK weight. Currently, research on AKS is mainly focused on its active ingredients. Researchers have investigated the extraction of polyphenols from AKS, analysed their composition, and evaluated their antioxidant, antimicrobial, and anticancer activities (Han *et al*., 2013; Qin *et al*., 2019). Although AKS is rich in antioxidant components, it has mostly been abandoned, except for small portions that are used as animal feed.

In recent years, extrusion technology has been widely used in the food and feed industries. Owing to the destruction of the cell wall, accumulation of oil, and formation of a large number of capillary channels during extrusion, the oil extraction yield can be significantly improved (Liu *et al*., 2020). Therefore, it has been applied in the pre-treatment of oil-bearing materials worldwide (Li *et al*., 2015; 2020; Yin *et al*., 2015; Offiah *et al*., 2019; Ribeiro *et al*., 2024). Based on our previous work, AKS contained approximately 12% crude oil on a dry matter basis. So, the total amount of AKS oil (AKSO) in the world will reach 1,000 tonnes. Therefore, whether this technology is beneficial for AKSO extraction is worth exploring.

Vegetable oils with nutritional and health benefits are increasingly welcomed by consumers. To evaluate whether AKSO could be used as a nutritional oil, a comprehensive investigation of its physicochemical properties and chemical composition is essential. Unfortunately, systematic reports on AKSO remain unavailable to date. This situation prompted us to conduct relevant research on this novel oil-bearing source, rather than directly discarding valuable raw materials.

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In the present work, the main chemical composition of AKS was determined, the effects of extrusion on the extraction yield, acid value, and peroxide value of AKSO were assessed, and the physicochemical properties and chemical composition of AKSO were analysed. The present work provided basic yet important information regarding AKSO, which will be useful for further exploration of its application as a high-quality edible oil.

Materials and methods

Materials

AKS, which was obtained by soaking apricot kernel in water bath at 80°C for 30 min, and peeled in a peeler, was kindly provided by the Zhuolu Nuts Co. Ltd. in August 2017. AKS was washed with a 10-fold volume of deionised water for 10 min at ambient temperature. The washed AKS was dried for 5 h at 50°C in an oven to a moisture content of approximately 4%. AKS was then smashed with a grinder, and passed through sieves of different meshes to obtain AKS powder with different sizes, which were finally packed in polyethylene bags, and stored at -18°C until further treatment. Standards for fatty acid methyl esters, tocopherol (α-, β-, γ-, and δ-isomers), and 5α-cholestane, as well as pancreatic lipase were obtained from Sigma-Aldrich Chemical Co., Ltd. (Shanghai, China). Silica G was purchased from Qingdao Haiyang Chemical Co., Ltd. (Qingdao, China). All other reagents were of analytical grade, and used without further purification.

Extrusion of AKS

AKS (40 mesh) and deionised water were mixed in a blender at a ratio of 10:1 (g/mL), and maintained for 30 min. The obtained AKS was then added to a flat-die granulator (Zhengzhou, China) for extrusion into rod-shaped extrudates with a length of approximately 15 mm, a diameter of approximately 3 mm, and a moisture content of approximately 8%. The preparation process for the rod-shaped AKS is shown in Figure 1.

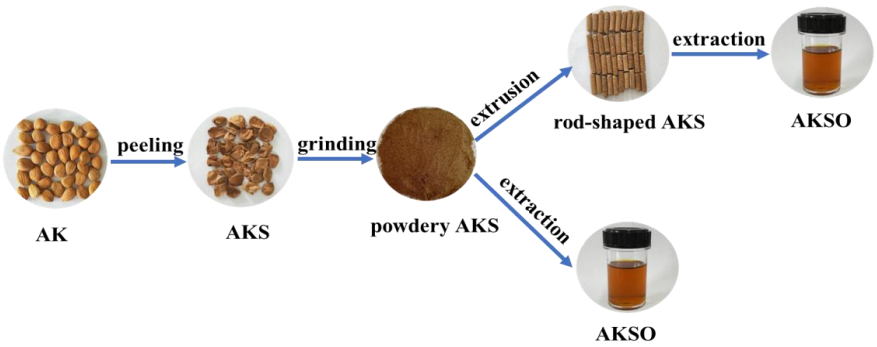

Figure 1. Schematic diagram of preparation process of powdery and rod-shaped AKS, and the corresponding obtained AKSO. AK: apricot kernel; AKS: apricot kernel skin; and AKSO: apricot kernel skin oil.

Extraction of AKSO by hexane

A total of 10.0 g powdered AKS or rod-shaped AKS was added into 100 mL hexane, and extraction was carried out for 60 min at 60°C. AKSO was obtained after filtering through a filter paper, and removing the solvent using a rotary evaporator. The AKSO extraction process is also shown in Figure 1.

Calculation of AKSO extraction yield

The extraction yield of AKSO was calculated using Eq. 1:

$$Y = (m / M) \times 100\% \quad \text{(Eq. 1)}$$

where, Y = extraction yield of AKSO (%), m = mass of AKSO (g), and M = mass of AKS (g).

Determination of AKS main components, and AKSO physicochemical properties

The moisture, ash, crude protein, crude oil, and crude fibre contents of AKS were analysed following the AOAC official methods 934.01, 942.05, 968.06, 920.39, and 962.09, respectively (AOAC, 2016). The important physicochemical properties of AKSO, including relative density, refractive index, saponification value, and unsaponifiable matter content, were determined following the official

AOAC methods 920.213, 921.08, 920.160, and 933.08, respectively (AOAC, 2016). The colour, acid value, peroxide value, and iodine value of AKSO were characterised following the official AOCS methods Cc 13e-92, Cd 3d-63, Cd 8b-90, and Cd 1c-85, respectively (AOCS, 2017).

Analysis of fatty acids

The fatty acid composition was determined after methyl esterification of AKSO as described by Ivanova-Petropulos *et al.* (2015). The fatty acid methyl esters were analysed by gas chromatograph (GC) (Agilent 6890N, USA) combined with an autoinjector, a flame-ionisation detector, and a BPX-70 capillary column (30 m × 250 µm × 0.25 µm). The column, injector, and detector temperatures were set at 180, 230, and 300°C, respectively. The oven temperature was programmed from 180°C for 5 min, increased to 230°C at a rate of 1.5°C/min, and held for 20 min. The flow rates of nitrogen, hydrogen, and air were 1.5, 30, and 400 mL/min. The fatty acids present in the samples were identified based on the retention time of the standard fatty acids. The area normalisation method was used to determine the relative fatty acid content.

Analysis of tocopherols

Quantitative analysis of tocopherols in the AKSO was performed by HPLC (Shimadzu, Japan) equipped with an Agilent SIO column (250 × 4.6 mm, 5 µm) as described by Oomah *et al*. (2000). The temperature of column was kept at 40°C. The AKSO was eluted with isopropyl ether:*n*-hexane (10:90, v/v) at 1.5 mL/min. The excitation and emission wavelengths of the fluorescence detector (Shimadzu, Kyoto, Japan) were 298 and 325 nm, respectively. The absolute tocopherol content was measured based on standard curves.

Analysis of phytosterols and squalene

Quantitative analysis of phytosterols and squalene in AKSO was performed as described by Li *et al.* (2011). Briefly, 100 mg of AKSO was mixed with 5α-cholestan (2 mg as internal standard), and saponified by adding 3 mL of 2 M ethanolic potassium hydroxide solution, and then heating at 80°C for 20 min. After cooling, 4 mL of deionised water was added, and the unsaponifiable fraction was extracted by mixing with 4 mL of hexane. The hexane phase was washed with deionised water until it became neutral. After the removal of hexane, the residue was mixed with 0.4 mL of bis(trimethylsilyl)-trifluoroacetamide.

Analysis of phytosterols and squalene from AKSO was carried out using a GC-MS (Shimadzu, Japan), equipped with a TRACE TR-5MS column (30 m × 0.25 mm × 0.25 µm). Helium was used as a carrier gas at a flow rate of 1.2 mL/min. Column temperature was initially 200°C, which was gradually increased to 250°C at a rate of 25°C/min, and then finally increased to 280°C at a rate of 5°C/min. The mass range was 50 - 550 amu.

Analysis of Sn-2 fatty acids distribution in triglycerides

The Sn-2 fatty acid composition of the AKSO triglycerides was analysed using a 1,3-specific pancreatic lipase as described by Bi *et al.* (2006). In brief, 100 mg of AKSO, 20 mg of 1,3-specific pancreatic lipase, and 2 mL of Tris buffer solution (1 M, pH 8.0) were thoroughly mixed in a centrifuge tube, followed by the addition of 0.5 mL of sodium cholate solution (0.1%, w/v) and 0.2 mL of calcium chloride (20%, w/v). The tube was then stood in a water bath at 40°C for 10 min. Afterwards, it was taken out and cooled in a water bath at 4°C. After adding 1 mL of hexane and 1 mL of hydrochloric acid (6 M), the mixture was shaken for 2 min, and centrifuged (4,000 rpm for 5 min). The obtained AKSO enzymatic hydrolysate was separated using thin layer chromatography. The silica gel containing the monoglyceride was removed and extracted with hexane. Finally, the monoglyceride was methylated, and the resultant fatty acid methyl ester was analysed using GC.

Analysis of total polyphenols

The total polyphenol content of AKSO was determined by the Folin-Ciocalteau colorimetric method, as described by Lachman *et al.* (2010). In brief, polyphenols in the AKSO were extracted by dissolving 1 g of AKSO in a 20 mL of mixture of isopropanol and methanol (1:3, v/v) at 60°C for 20 min, followed by centrifugation (10,000 rpm, 5 min), with the extraction process repeated thrice. The supernatants were combined and dried under nitrogen atmosphere. The volume was fixed at 10 mL using anhydrous methanol. Next, 1 mL of the methanolic extract was mixed with 1 mL of Folin-Ciocalteau reagent and 3 mL of sodium carbonate solution (7.5%, w/v). After 90 min, the absorbance was measured at 765 nm using a spectrophotometer. Each

sample was measured in triplicate, and quantification was performed based on the standard curve of gallic acid.

Statistical analysis

Statistical analyses were performed using the SPSS software package (SPSS21.0, SPSS Inc., Chicago, IL, USA). Means comparison was performed using the least significant difference test at the level of significance of $p < 0.05$. The data were represented as mean ± standard deviation.

Results and discussion

Chemical compositions of AKS

The main chemical components of AKS are crude oil, crude protein, and crude fibre, which were 12.1, 11.9, and 54.0%, respectively. Currently, oil extracted from grape seeds, a by-product of food processing, is produced on a large scale. The oil content of AKS is higher than that of grape seeds, therefore, AKS can also be considered a potential oil-bearing source (Passos *et al*., 2009). In addition, the abundant dietary fibre and protein make AKS a valuable food source. From the point of view of biorefinery, the recycling of abandoned AKS can not only turn waste into valuable source, but also make a significant contribution to the sustainable development of the food industry.

Effect of pre-treatment on AKSO extraction yield

Figure 2 shows that the extraction yields of AKSO from un-smashed AKS, AKS with different particle sizes, and rod-shaped AKS were significantly different. After smashing, the extraction yield of AKSO was significantly improved, owing to the destruction of the cell wall, a decrease in the diffusion resistance between the solvent and oil, and an increase in the interfacial area. When the AKS particle size was reduced from 20 to 80 mesh, the extraction yield of AKSO first increased, and then decreased; the highest extraction yield (8.9%) was achieved when the AKS particle size was 60 mesh. This can be easily interpreted as follows: the finer the raw material, the smaller the oil globules. However, when they were adsorbed onto powder materials, a stable emulsion system was formed, which eventually led to a decrease in the oil diffusion rate. A similar result for a smaller particle size effect was observed by Ishak *et al.* (2021). Therefore, when the AKS particle size was 80 mesh, the extraction yield of AKSO slightly decreased.

After extrusion, the cell walls were further splintered, and a large number of capillary channels were formed in the rod-shaped AKS, which was very conducive to diffusion between the solvent and oil; thus, the extraction yield of AKSO was 12.0%, which was 35.8% higher than that of AKS of 60 mesh.

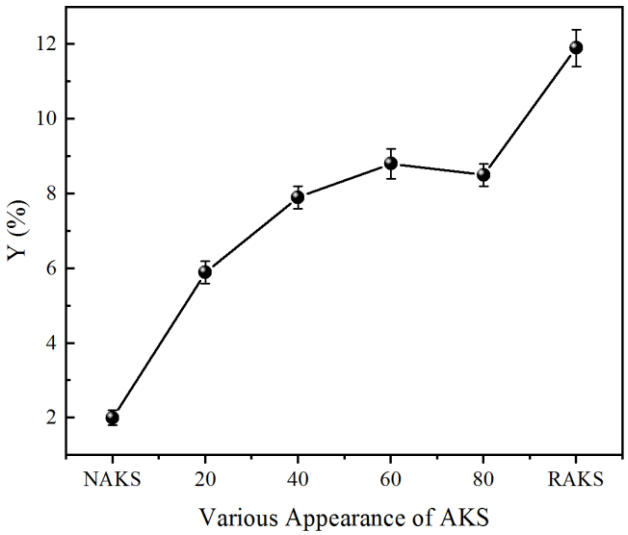

Figure 2. Effect of AKS with various appearances on extraction yield of AKSO (20, 40, 60, and 80 correspond to the mesh size of AKS, respectively; NAKS and RAKS represent non-smashed AKS and rod-shaped AKS, respectively).

Physicochemical properties of AKSO

The physicochemical properties of AKSO are summarised in Table 1. AKSO was orange in colour because the pigments from AKS were transformed into oil during the extraction. The refractive index was positively correlated with the degree of oil unsaturation owing to the presence of specific functional group, such as hydroxyl groups (Diwakar *et al*., 2009). The specific gravity was 0.9206 at 20°C. It should be emphasised that compared with untreated AKSO, the acid value of AKSO decreased from 10.2 to 2.4, and the peroxide value decreased from 2.8 to 2.7 after extrusion, suggesting that extrusion pre-treatment had a positive effect on the quality of AKSO. The iodine value is an important characteristic of the oil. The higher the iodine value, the higher the unsaturated fatty acid content. The degree of unsaturation and the properties of the oil can be identified based on the iodine value. AKSO had a high iodine value, and belonged to the dry oil. The saponification value indirectly reflects the fatty

Table 1. Physicochemical properties and fatty acid composition of AKSO.

Parameter	Value	Fatty acid	Content (%)
Colour (Lovibond, 25.4 mm)	Y: 30.0, R: 6.4	C16:0	8.24 ± 0.06
Specific gravity (20°C)	0.9206 ± 0.21	C16:1	0.91 ± 0.03
Refractive index (20°C)	1.4735 ± 0.01	C18:0	1.94 ± 0.08
Acid value (mg KOH/g)	2.35 ± 0.13	C18:1	34.20 ± 0.15
Peroxide value (mmol/kg)	2.76 ± 0.01	C18:2	51.77 ± 0.06
Iodine value (mg/g)	130.15 ± 3.46	C18:3	2.94 ± 0.06
Saponification value (mg KOH/g)	154.31 ± 4.13	SFAs	10.18
Unsaponifiable matter (%)	3.24 ± 0.12	UFAs	89.82

Values are mean ± SD; C16:0: palmitic acid; C16:1: palmitoleic acid; C18:0: stearic acid; C18:1: oleic acid; C18:2: linoleic acid; C18:3: linolenic acid; SFAs: saturated fatty acids; and UFAs: unsaturated fatty acids.

acid composition of the oil. Generally, the smaller the relative molecular weight of the triglycerides, the higher the saponification value. Unsaponifiable matter from oils usually contains sterols, squalene, tocopherols, pigments, and phenolic compounds, which typically exhibit antioxidant activities (Dhavamani *et al*., 2014). The unsaponifiable matter content of AKSO (3.2%) was between that of grape seed oil (2.3%) and rice bran oil (4.2%), and was much higher than that of soybean oil (0.6%), peanut oil (0.4%), and rapeseed oil (1.0%) (Rukmini and Raghuram, 1991; Anwar *et al*., 2016; Konuskan *et al*., 2018).

Analysis of fatty acids

The fatty acid profile of AKSO is presented in Table 1. Linoleic acid (C18:2; 51.8%) was the most abundant fatty acid in AKSO, followed by oleic acid (C18:1; 34.20%), palmitic acid (C16:0; 8.2%), linolenic acid (C18:3; 2.94%), stearic acid (C18:0; 1.9%), palmitoleic acid (C16:1; 0.9%), heptadecanoic acid (C17:0; 0.06%), and heptadecenoic acid (C17:1, 0.04%). Unsaturated fatty acids accounted for approximately 90% of the total fatty acid content. As linoleic and linolenic acids are essential fatty acids for human health, AKSO can be used as a dietary supplement to provide essential fatty acids for humans. Therefore, from the perspective of view of cost-efficiency and nutritional value, AKS could be a valuable oil-bearing source that warrants further development and utilisation.

Analysis of tocopherols, polyphenols, phytosterols, and squalene

Tocopherols (α-, β-, γ-, and δ-) are well recognised for their antioxidant and biological activities (Barouh *et al*., 2022). However, only α-tocopherol, also known as vitamin E, satisfies the criteria of being a vitamin (Azzi, 2018). Additionally, polyphenols are capable of scavenging free radicals, and considered natural antioxidants in food and biological systems (Zhang and Tsao, 2016).

Table 2 shows that the most abundant tocopherols in AKSO were γ-tocopherols (200.0 μg/g), followed by δ-tocopherols (69.0 μg/g) and α-tocopherols (68.3 μg/g), and that the total tocopherol content was 337.4 μg/g. In addition, AKSO was rich in polyphenols (15.3 μg/g). Therefore, AKSO could be a good source of tocopherols and polyphenols, which can be used as natural antioxidants in the food industry.

Table 2. Composition of tocopherols, polyphenols, phytosterols, and squalene in AKSO.

Species	Content (μg/g)
α-tocopherol	68.31 ± 8.73
γ-tocopherol	200 ± 17.84
δ-tocopherol	69.04 ± 9.15
Polyphenols	15.33 ± 0.92
β-sitosterol	793.22 ± 3.54
Ethyl linoleate	125.79 ± 2.16
Campesterol	50.47 ± 1.35
Stigmasterol	31.54 ± 1.04
Cycloartenol acetate	16.79 ± 0.97
Pentacosanoic acid	3.44 ± 0.15
Ethyl palmitate	3.22 ± 0.11
Palmitic acid	1.86 ± 0.08
Lupeol	1.16 ± 0.13
Squalene	22.47 ± 1.35

Phytosterols and squalene belong to unsaponifiable matter, which are widely found in various vegetable oils, nuts, and plant seeds. They have been found to have cholesterol-lowering, anti-cancer, and other health advantages (Shen *et al*., 2024).

As shown in Table 2, the major phytosterols in AKSO were β-sitosterol (793.2 μg/g) and ethyl linoleate (125.8 μg/g), followed by campesterol (50.5 μg/g), stigmasterol (31.5 μg/g), and cycloartenol acetate (16.8 μg/g). In addition, there were trace amounts of other compounds whose contents were less than 5 μg/g. The contents of total phytosterols and squalene were 1,027.5 and 22.5 μg/g, respectively. As AKSO contained abundant active ingredients, such as phytosterols and squalene, it could be used as a daily nutritional supplement in the development of health food.

Analysis of AKSO triglycerides' composition

The stereospecific structure of triglycerides is determined by the fatty acids and their distribution on the triglyceride backbone. This structure is controlled by genes; therefore, each oil has a unique triglycerides' composition (Barreira *et al*., 2009). As a result, triglycerides can be used for oil identification (Christopoulou *et al*., 2004).

Table 3 shows the composition and contents of triglycerides in AKSO. The level of triglycerides was estimated based on the 1,3-random-2-random hypothesis, which was compared with the values determined using HPLC (Bi *et al*., 2006). The dominant triglyceride in AKSO was LLO (21.8%), followed by LLL (13.4%), OOL (9.5%), OLO (8.9%), PLL (6.1%), and LOL (5.9%). In addition, other important minor triglycerides in AKSO were PLO (5.0%), OOO (3.9%), POO (2.2%), LnLL (1.9%), LnLO (1.6%), LPO (1.3%), and SLL (1.0%). These unique characteristics of AKSO provided a basis for its identification and assessment in the quality control.

Analysis of Sn-2 fatty acids distribution in AKSO triglycerides

The physical, chemical, and physiological characteristics of lipids are highly dependent on their fatty acid composition, and distribution on the glycerol backbone (Hunter, 2001). Therefore, the stereospecific analysis of fatty acids in triglycerides is of great significance for the absorption, metabolism, and application of lipids.

Table 3. Composition and Sn-2 fatty acid distribution of main triglycerides in AKSO.

Species	Content (%)
LLO	21.83 ± 0.05
LLL	13.39 ± 0.03
OOL	9.53 ± 0.02
OLO	8.90 ± 0.04
PLL	6.12± 0.03
LOL	5.85 ± 0.01
PLO	4.99 ± 0.06
OOO	3.87 ± 0.03
POO	2.18 ± 0.03
LnLL	1.92 ± 0.01
LnLO	1.56 ± 0.07
LPO	1.28 ± 0.04
SLL	1.01± 0.02
P	3.72 ± 0.15
S	0.35 ± 0.20
O	27.71 ± 0.86
L	63.43 ± 1.24
Ln	1.93 ± 0.14

Values are mean ± SD; P: palmitic acid; S: stearic acid; O: oleic acid; L: linoleic acid; and Ln: linolenic acid.

As shown in Table 3, the fatty acids at the Sn-2 position in the triglycerides of AKSO were mainly unsaturated fatty acids such as linoleic acid (63.4%) and oleic acid (27.7%), followed by palmitic acid (3.7%), stearic acid (2.4%), and linolenic acid (1.9%). Unsaturated fatty acids accounted for 93.0% of the total fatty acids.

From a nutritional perspective, fatty acids at the Sn-2 position are more easily absorbed by the human body than those at the Sn-1,3 positions (Qi *et al*., 2018). As the Sn-2 position in the triglycerides of AKSO was mainly occupied by unsaturated fatty acids, AKSO could be an excellent nutrient oil that can be easily digested and absorbed in the human body.

Conclusion

The present work demonstrated the feasibility of AKS as a new oil-bearing source, developed a suitable AKSO extraction process, and systematically analysed its physicochemical properties, fatty acid composition, and the active ingredients. The

extraction yield of AKSO using extrusion-assisted hexane extraction was 12.0%, confirming the suitability and excellence of the developed extraction method. AKSO contained abundant unsaturated fatty acids located at the Sn-2 position of triglycerides, and was rich in many bioactive components, including tocopherols, phytosterols, squalene, and polyphenols. These characteristics of AKSO indicated that it could be used as a high-quality substitute for vegetable oil or as a valuable supplement to functional foods and diets. In summary, from economic and nutritional perspectives, AKS could be a potential high-quality oil-bearing source, and the corresponding AKSO should be properly explored in the near future.

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