

不同干燥方式对龙眼多酚及抗氧化活性的影响

谭 颺¹, 彭思维¹, 李玮轩¹, 任 珊¹, 王金霞¹, 张应玲¹, 石胜友^{1,2*}

(¹长江师范学院现代农业与生物工程学院, 重庆涪陵 408100; ²中国热带农业科学院亚热带作物研究所, 广东湛江 524091)

摘 要:【目的】探讨真空干燥、冷冻干燥和热风干燥对龙眼酚类成分及其体外抗氧化活性的影响, 为高品质龙眼干的生产提供依据。【方法】龙眼果肉经过3种不同干燥处理, 龙眼果壳和果核只经过热风干燥处理, 利用福林-酚比色法和液质联用技术(UPLC-QqQ-MS/MS)分别检测龙眼总酚含量和各酚类物质的组分, 同时利用DPPH、ABTS和FRAP法检测多酚抗氧化活性。【结果】真空干燥、冷冻干燥和热风干燥后龙眼果肉总酚含量(w)分别是2.934/5.288和2.855 mg·g⁻¹, 对DPPH自由基清除能力分别是2.537、5.478、1.501 mg·100 g⁻¹, 对ABTS自由基清除能力分别是0.919、1.216、0.870 mg·100 g⁻¹, 以及还原力(FRAP)分别是5.810、6.634、5.538 mg·100 g⁻¹。液质分析结果表明龙眼不同部位酚类组成差别较大, 龙眼果皮中多酚种类和含量均高于龙眼果肉和果核。与新鲜果肉相比, 3种干燥方式均降低了龙眼果肉中大部分酚类成分含量。其中, 真空干燥、冷冻干燥和热风干燥后主要酚酸阿魏酸分别降低了74.05%、63.67%和73.16%, 主要类黄酮芦丁分别降低了51.58%、52.80%和46.50%。【结论】3种干燥方式对龙眼果肉酚类成分及抗氧化活性影响有显著差异, 与真空干燥、热风干燥相比, 冷冻干燥能够减少龙眼果肉在干燥过程中酚类成分及其抗氧化活性的损失。

关键词: 龙眼; 真空干燥; 冷冻干燥; 热风干燥; 酚类成分; 抗氧化活性

中图分类号: S667.2

文献标志码: A

文章编号: 1009-9980(2021)03-0411-10

Effects of different drying methods on polyphenol profile and antioxidant activities in longan (*Ficus carica* Linn.)

TAN Si¹, PENG Siwei¹, LI Weixuan¹, REN Shan¹, WANG Jinxia¹, ZHANG Yingling¹, SHI Shengyou^{1,2*}

(¹School of Advanced Agriculture and Bioengineering, Yangtze Normal University, Fuling 408100, Chongqing, China; ²South Subtropical Crops Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524091, Guangdong, China)

Abstract: 【Objective】 Longan is widely distributed in subtropical zones and usually used to treat chronic diseases in Traditional Chinese Medicine. Longan can be eaten fresh or processed as dried fruit, juice, wine and so on. During processing, drying is the most commonly used method. Since the variation of nutrients and bioactive compounds of different fruits subjected to different drying methods is distinct, in order to process high-quality dried longan fruits, the effects of vacuum drying (VD), freeze drying (FD) and hot air drying (OD) on total polyphenols, phenolic profile and antioxidant activities of longan were studied. 【Methods】 Fresh longan fruits at commercial maturity stage were collected from the garden in the Institute of China Southern Subtropical Crop Research (Zhanjiang, Guangdong). Longan fruits were manually peeled and enucleated. Then, the longan pulps were dehydrated by VD, FD and OD. The longan pericarps and kernels were dehydrated only by OD. For VD, longan pulps were dried in the vacuum chamber at 70 °C for 48 h. For FD, before vacuum freeze drying, the pulps were frozen at -60 °C for 12 h. Then, the frozen pulps were dried in an experimental vacuum lyophilizer for 48 h. For OD, longan fruits were placed in a forced air circulation oven at 70 °C for 48 h. The dried fruits

收稿日期: 2020-11-06

接受日期: 2020-12-28

基金项目: 重庆市科委项目(cstc2018jcyjAX0687); 广东省重点领域研发计划项目“现代种业”(2020B020220006); 广东省自然科学基金(2020A1515011365); 国家现代农业产业技术体系建设专项(CARS-32-02); 中国热带农业科学院基本科研业务费(1630062020003)

作者简介: 谭颺, 女, 讲师, 博士, 研究方向为果品营养与安全。Tel: 18323078246, E-mail: tsok1990715@163.com

*通信作者 Author for correspondence. Tel: 13763046918, E-mail: syy7299@163.com

were grinded rapidly and sieved thorough a 60-mesh screen. Moisture content was measured according to the national standard method. Fresh pulps and dried powder were ultrasonic extracted three times at 40 °C for 30 min using 80% aqueous methanol. Folin-Ciocalteu colorimetric method was used to measure the total polyphenols. Ultra high pressure liquid chromatography and triple quadruple mass spectrometry (6460QQQ-MS, Agilent, California, USA) equipped with an electrospray ionization source (UPLC-QQQ-MS/MS) was used to analyze the polyphenol profile of longan. ZORBAX Eclipse Plus C18 column (100 mm × 2.1 mm i.d., 1.8 μm, Agilent, Waldbronn, Germany) was used. In addition, the antioxidant activities of longan polyphenols were determined with DPPH (2, 2-diphenyl-1-picrylhydrazyl), ABTS (2, 2'-azino-bis (3-ethylbenzothiazoline-6-sulfonate) and FRAP (ferric ion reducing antioxidant power) methods. At last, the Sparse Partial Least Squares regression (sPLS) was used to analyze the correlation between polyphenols and antioxidant activities. All the values were presented as means ± SD ($n=3$). Nonlinear regression and multivariate linear regression analysis were performed by using the IBM SPSS statistics (version 20.0). Statistically significant differences among the treatments were analyzed by one-way analysis of variance (ANOVA), followed by Tukey test. Principle component analysis was performed in R (×64, 3.4.3) using the mixOmics package. **【Results】** The contents of total polyphenols and antioxidant activity in longan pericarp were significantly higher than those in longan pulp and kernel. The total phenolic contents of longan pulp dried by VD, FD and OD were 2.934, 5.288 and 2.855 mg · g⁻¹, respectively. The DPPH radical scavenging ability was 2.537, 5.478 and 1.501 mg · 100 g⁻¹, respectively. The ABTS radical scavenging ability was 0.919, 1.216 and 0.870 mg · 100 g⁻¹, respectively, and the FRAP was 5.810, 6.634 and 5.538 mg · 100 g⁻¹, respectively. In this study, 17 polyphenols including gallic acid, chlorogenic acid, 4-hydroxycinnamic acid, ferulic acid, cinnamic acid, naringin, rutin, quercetin-7-*O*-β-*D*-glucopyranoside, isoquercitrin, hesperidin, phloridzin, rhoifolin, methyl hesperidin, quercetin, naringenin, luteolin and phloretin were identified and quantified by UPLC-QQQ-MS/MS, among which hesperidin, phloridzin, methyl hesperidin, naringin, luteolin and phloretin were firstly reported in longan fruits. The results also showed that phenolic profile in different parts of longan was distinctly different. The variety and content of polyphenols in pericarp were higher than those in pulp and kernel. Except for gallic acid, longan pericarp contained all the other 16 polyphenols. Quercetin-7-*O*-β-*D*-glucoside was detected only in the pericarp, while gallic acid was detected only in the kernel. Isoquercetin, quercetin and luteolin were mainly found in the pericarp and kernel, but not detected in the pulp. 4-Hydroxycinnamic acid, ferulic acid, rutin and hesperidin were the main phenolic compounds in fresh longan pulps. Compared with fresh fruits, contents of most of phenolic components in dried longan pulps were significantly reduced by all the drying methods. Expectedly, contents of most of the polyphenols in FD pulps were higher than those in VD and OD pulps. There was no significant difference in polyphenol profile between hot air dried and vacuum dried longan pulps. At last, correlation analysis indicated that all the phenolic compounds except for 4-hydroxycinnamic acid and methyl hesperidin were positively correlated with total polyphenols content and antioxidant activity. However, cinnamic acid contributed little to the antioxidant activity of longan polyphenols. **【Conclusion】** These information indicated that longan pericarp and kernel also contained abundant phenolic compounds and possessed high antioxidant activities, which had potential utilization value. Different drying methods showed different effects on the phenolic components and the antioxidant activity of longan pulps. Compared with VD and OD, FD can reduce the loss of phenolic components and antioxidant activity in longan.

Key words: Longan; Vacuum drying; Freeze drying; Oven drying; Phenolic profile; Antioxidant activity

龙眼(*Dimocarpus longan* Lour.)俗称桂圆,是无患子科龙眼属常绿果树,原产于我国,主要分布于福建、广东等亚热带地区,因其具有开胃健脾、补虚益智的作用,是药食两用的滋补佳品,享有“南方人参”的美称^[1]。龙眼果肉中含有丰富的维生素、碳水化合物等营养成分和多酚类生物活性物质,此外,龙眼果皮和果核也含有丰富的黄酮类化合物^[2]。多酚作为天然抗氧化剂,具有清除自由基、抗炎、抗癌、抗衰老、抗辐射、预防心脑血管疾病等作用^[3]。

龙眼鲜果水分、糖分多,采后易受到微生物的侵染,导致腐烂变质,这不利于龙眼的长期贮藏和远距离销售,制约了其经济价值。因此,龙眼除少量鲜食外(20%),大部分被干燥加工成龙眼干^[4]。干燥能够有效去除水分,降低酶活性,抑制微生物繁殖,进而延长货架期^[5]。目前果蔬加工的干制技术主要有热风干燥、冷冻干燥、真空干燥、热泵干燥、微波干燥等。其中,热风干燥因其具有操作简单、适应性强、不受气候条件限制等特点成为目前应用最广泛的一种干燥技术。冷冻干燥能较好地维持果蔬原有风味形态,对果蔬营养物质有较高的保持率,其冻干产品具有良好的速溶性和快速复水性,在果蔬粉的生产上得到广泛应用。真空干燥能较好地保持物料原有特征,对物料中挥发性物质的破坏程度较小,减小传统干燥时发生的热变性,干燥品质较好^[6]。研究发现不同干燥方式对不同果蔬生物活性成分特别是多酚类物质的影响不同^[7]。例如,与冷冻干燥相比,热风干燥处理后的柠檬果实中总酚含量下降,但是游离态酚酸和结合态总类黄酮含量显著增加^[8]。而真空干燥后香蕉片中的总酚含量和自由基清除能力均显著高于热风干燥处理的样品^[9]。但是,与真空干燥相比,冷冻干燥处理能减少蓝莓酚类物质的损失^[10]。由此可见,为了减少果蔬中营养成分的损失,不同果蔬应根据自身特性选择合适的干燥方式。

不同干燥方式对龙眼总酚含量及抗氧化活性影响还有待于分析,并且龙眼酚类成分在热风干燥、真空干燥和冷冻干燥3种加工方式下的变化情况缺少质谱的系统研究。本研究对比分析热风干燥、真空干燥和冷冻干燥对龙眼总酚含量及酚类物质组分的影响,同时评价不同干燥方式对其抗氧化活性的影响,最后利用偏最小二乘分析法探究多酚组分与抗氧化活性之间的关系,旨在为我国龙眼的加工利用提供一定的参考依据。

1 材料和方法

1.1 材料与试剂

材料:新鲜龙眼,采于中国热带农业科学院亚热带作物研究所,品种名为‘蜀冠’。

试剂:抗坏血酸标准品(色谱纯)、芦丁标准品(色谱纯)、没食子酸标准品(色谱纯)、本研究所用17个多酚标准品(色谱纯)、福林酚、2,2-联氮-二(3-乙基-苯并噻唑-6-磺酸)二铵盐(ABTS)、1,1-二苯基-2-三硝基苯肼(DPPH)和2,3,5-氯化三苯基四氮唑(TPTZ)由上海源叶生物科技有限公司提供;其他试剂均为分析纯。

1.2 仪器与设备

JA50型电子分析天平:常州市幸运电子设备有限公司;SB-5200BD7D型超声波清洗仪:宁波新芒生物科技有限公司;TDL-80-2B型离心机:上海安亭科学仪器厂;FW-100型电热热风干燥箱、FW-100型高速万能粉碎机:上海浦东荣丰科学仪器有限公司;LGJ-10型冷冻干燥机:盛超科创(北京)生物科技有限公司;DZF-1B型电热恒温真空干燥箱:上海跃进医疗器械有限公司;PT-3502C型全波长酶标分析仪:北京普天新桥技术有限公司;超高效液相色谱-三重四级杆质谱(6460QqQ-MS/MS):Agilent。

1.3 方法

1.3.1 干燥处理 新鲜龙眼洗净沥干后将果皮、肉、核分离,果肉分别进行热风干燥(OD)、真空干燥(VD)和冷冻干燥(FD)处理,果皮、核进行热风干燥处理。在热风干燥过程中,烘干温度为70℃,干燥48h;在真空干燥过程中,设置温度为70℃,真空度为50Pa,干燥48h。在冷冻干燥前,先将新鲜果肉置于-60℃下预冻12h,然后转移到冷冻干燥机中干燥48h,冷阱温度为-60℃,真空度为20Pa。干果经粉碎后过60目(0.25mm)筛网,粉末收集于自封袋中储存在-20℃备用。

1.3.2 水分测定 参考GB 5009.3—2016采用直接干燥法测定^[11]。

1.3.3 龙眼酚类物质的提取及其含量测定 (1)提取。采用超声波辅助法提取,步骤为:准确称取1g待测样品,加入10mL 80%甲醇溶液,用超声波提取30min(25℃)后进行离心(1700r·min⁻¹,10min),取上清液,重复上述操作3次,合并上清液,最后用80%甲醇溶液定容至30mL。此溶液即为龙眼多酚

提取液,用于总多酚含量、酚类物质组分及抗氧化活性的测定。每个样品平行重复提取3次。

(2)总酚含量测定。总酚含量的测定参考谭颍等^[12]的方法,取不同浓度梯度的没食子酸标准溶液和样液 50 μL 于 96 孔酶标板中,分别加入福林酚试剂 10 μL 与样品充分混合后避光反应 6 min,加入 7% (ρ) Na_2CO_3 溶液 100 μL 、去离子水 80 μL ,混匀,后避光反应 90 min,于 760 nm 处测定吸光值。所有样品均平行测定 3 次。以没食子酸的质量浓度为横坐标,吸光值为纵坐标,绘制标准曲线,结果以没食子酸质量分数表示 ($\text{mg} \cdot \text{g}^{-1}$)。

(3)酚类物质组分的测定。采用液质分析法检测龙眼的酚类成分^[13]。液质分析检测系统(6460QqQ-MS/MS, Agilent)配备有电喷雾离子源和 ZORBAX Eclipse Plus C_{18} 柱(100 mm \times 2.1 mm i.d., 1.8 μm , Agilent, Waldbronn, Germany)。流动相 A 为 0.1% 甲酸水溶液,流动相 B 为乙腈溶液。进样体积为 5 μL ,柱温为 30 $^{\circ}\text{C}$ 。线性梯度洗脱程序为:80%~10% A 0~11.5 min, 10% A 11.5~12.5 min, 10% A~

80% A 12.5~15 min。通过与标准品比对 MRM 信息(包括保留时间,母离子,碎片离子等)对龙眼多酚进行定性分析,通过标准品建立的标准曲线对龙眼多酚进行定量分析。

(4)抗氧化活性测定。用 DPPH 法、ABTS 法和 FRAP 法测定龙眼体外抗氧化活性^[12-13]。所有样品平行测定 3 次,样品结果以抗坏血酸质量分数表示 ($\text{mg} \cdot \text{g}^{-1}$)。

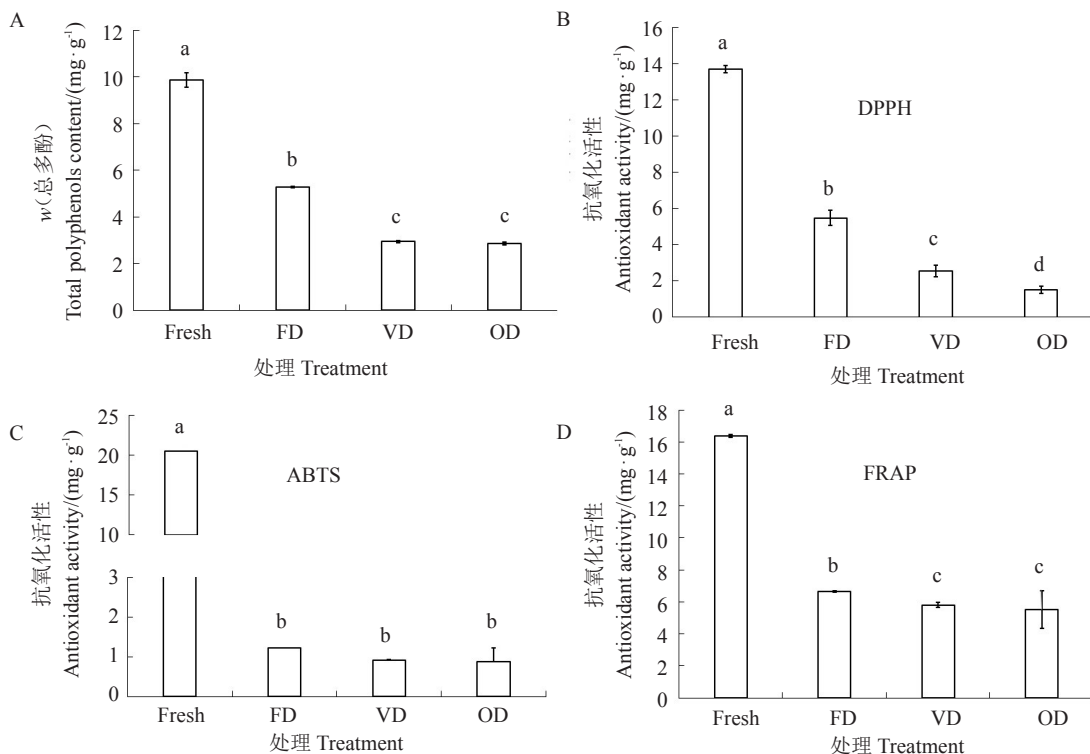
1.4 数据分析

所有实验均 3 次重复,数据结果以平均值 \pm 标准差表示,采用 SPSS 单因素方差分析(ANOVA)和 Duncan's 多重比较进行差异显著性分析 ($p < 0.05$)。用 R 语言 mixOmics 中 Pearson 相关性系数进行多酚和抗氧化活性的相关性分析。

2 结果与分析

2.1 不同干燥方式对龙眼果肉总酚含量的影响

由图 1 可知,新鲜龙眼、冷冻干燥、真空干燥和热风干燥后龙眼果肉中总多酚质量分数分别为



A. 总多酚含量; B. DPPH; C. ABTS; D. FRAP; FD. 冷冻干燥; VD. 真空干燥; OD. 热风干燥。不同小写字母表示差异显著,采用图基(Tukey)事后比较法($p < 0.05$)。

A. Total polyphenols; B. DPPH radical scavenging capacity; C. ABTS radical scavenging capacity. D. Ferric ion reducing antioxidant power. Different small letters mean significant difference as determined by Tukey's post hoc test ($p < 0.05$).

图 1 不同干燥方式对龙眼果肉中总多酚含量和抗氧化活性的影响

Fig. 1 Effects of different drying methods on the content of total polyphenols and antioxidant activities of longan

9.860、5.288、2.934和2.855 $\text{mg} \cdot \text{g}^{-1}$ 。3种干燥方式均在不同程度上减少了龙眼总酚含量,与真空干燥、热风干燥相比,冷冻干燥能减少龙眼中总酚的损失。真空干燥和热风干燥的龙眼果肉中总多酚含量无显著性差异(图1-A)。

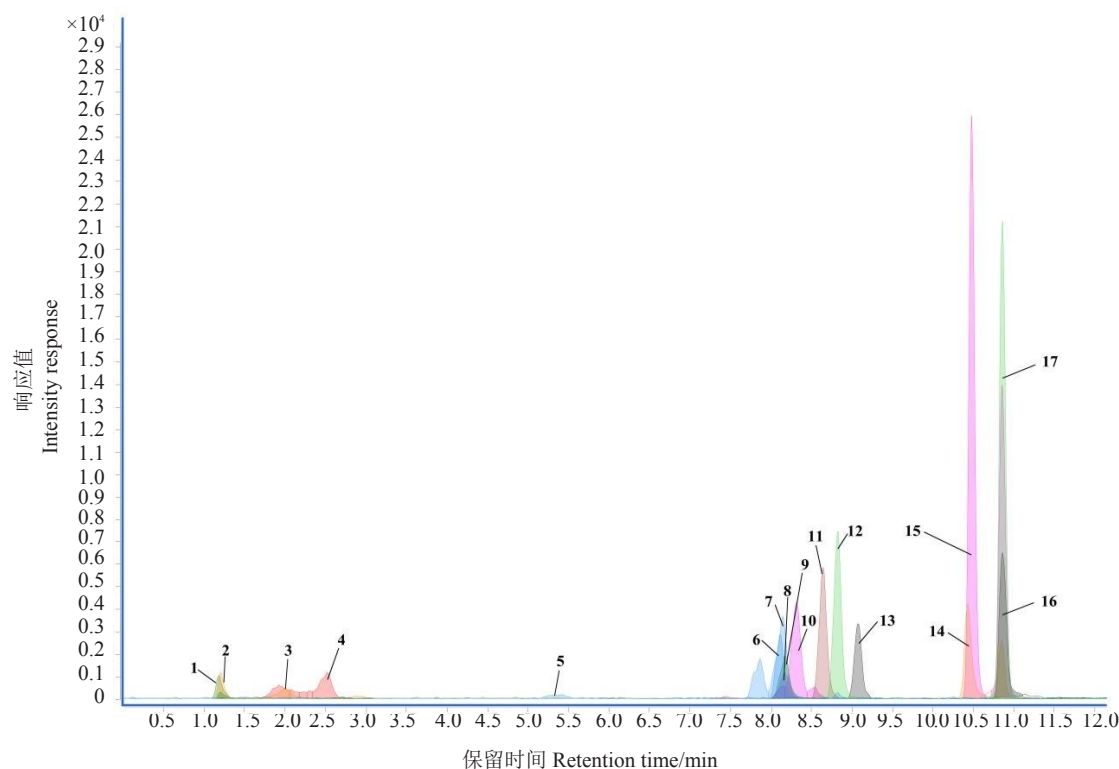
2.2 不同干燥方式对龙眼果肉抗氧化活性的影响

由图1-B~D得知,新鲜龙眼、冷冻干燥、真空干燥和热风干燥后龙眼多酚对DPPH自由基清除能力分别是13.678、5.478、2.537和1.501 $\text{mg} \cdot 100 \text{g}^{-1}$,对ABTS自由基清除能力分别是20.512、1.216、0.919和0.870 $\text{mg} \cdot 100 \text{g}^{-1}$,同时还原能力分别是16.390、6.634、5.810和5.538 $\text{mg} \cdot 100 \text{g}^{-1}$ 。3种干燥方式均显著降低了龙眼多酚抗氧化活性。冷冻干燥处理后龙眼多酚清除DPPH自由基能力(图1-B)以及还原能力(FRAP)(图1-D)显著高于真空干燥处理和热风干燥处理样品。然而,3种干燥方式对龙眼多酚清除ABTS自由基能力无显著差别(图1-C)。

2.3 不同干燥方式对龙眼酚类成分的影响

由于福林酚法测定的总酚含量不能准确地表明每一种酚类物质的变化情况,因此本研究还利用液质联用技术对龙眼果实包括果皮和果核中17种酚类物质进行了准确的定性和定量分析,其色谱图和具体信息见图2和表1、2。定量分析结果(表2)表明,龙眼不同部位含有的多酚种类和含量具有显著差异,果皮中多酚的种类和含量均高于果肉和果核。果皮中含有除没食子酸以外的16种多酚物质。槲皮素-7-*O*- β -D-葡萄糖苷只在果皮中检测到,而没食子酸只在果核中检测到。异槲皮素、槲皮素和木犀草素主要存在于果皮和果核,而在果肉中未检测到。果皮中含量较高的多酚是芦丁、橙皮苷和根皮苷,而果核中含量最显著的多酚是没食子酸,其余多酚在果核中含量较少。这些信息表明龙眼果核和果皮也含有丰富的酚类物质,具有潜在的利用价值。

在龙眼果肉中,与新鲜果肉相比,3种干燥方式



1. 没食子酸;2. 绿原酸;3. 4-羟基肉桂酸;4. 阿魏酸;5. 肉桂酸;6. 柚皮苷;7. 芦丁;8. 槲皮素-7-*O*- β -D-葡萄糖苷;9. 异槲皮素;10. 橙皮苷;11. 根皮苷;12. 野漆树苷;13. 甲基橙皮苷;14. 槲皮素;15. 柚皮素;16. 木犀草素;17. 根皮素。

1. Gallic acid; 2. Chlorogenic acid; 3. 4-hydroxycinnamic acid; 4. Ferulic acid; 5. Cinnamic acid; 6. Naringin; 7. Rutin; 8. Quercetin-7-*O*- β -D-glucopyranoside; 9. Isoquercitrin; 10. Hesperidin; 11. Phloridzin; 12. Rhoifolin; 13. Methyl hesperidin; 14. Quercetin; 15. Naringenin; 16. Luteolin; 17. Phloretin.

图2 龙眼酚类化合物代表性色谱图

Fig. 2 Representative chromatograms of the identified phenolic compounds in longan

表 1 龙眼多酚标准品 UPLC-QqQ-MS 测定信息

Table 1 Detail information for polyphenol standards using UPLC-QqQ-MS

No.	化合物 Compounds	保留时间 Retention time/min	MS[M-H] ⁻	MS/MS/ (m/z)	碎裂电压 Fragmentor/V
1	没食子酸 Gallic acid	1.181	168.9	125, 106.8	100
2	绿原酸 Chlorogenic acid	1.210	353.0	190.9	90
3	4-羟基肉桂酸 4-hydroxycinnamic acid	2.134	163.0	119	70
4	阿魏酸 Ferulic acid	2.527	192.9	134, 147	90
5	肉桂酸 Cinnamic acid	5.421	147.0	103	80
6	柚皮苷 Naringin	8.117	304.9	271, 151	150
7	芦丁 Rutin	8.149	609.0	299.9	160
8	槲皮素-7-O-β-D-葡萄糖苷 Quercetin-7-O-β-D-glucopyranoside	8.175	462.9	300.8, 342.9	150
9	异槲皮素 Isoquercitrin	8.175	462.9	300, 270.9	160
10	橙皮苷 Hesperidin	8.313	609.0	301, 324.9	160
11	根皮苷 Phloridzin	8.646	434.9	272.9, 167	150
12	野漆树苷 Rhoifolin	8.829	577.0	268.9	100
13	甲基橙皮苷 Methyl hesperidin	9.080	623.0	315.0	100
14	槲皮素 Quercetin	10.422	300.9	150.9, 107	130
15	柚皮素 Naringenin	10.446	271.0	119, 150.8	100
16	木犀草素 Luteolin	10.860	284.9	132.9	150
17	根皮素 Phloretin	10.861	273.0	167, 123	120

表 2 新鲜及干燥后龙眼果实中多酚含量

Table 2 Contents of polyphenols in fresh and dried longan

(mg · 100 g⁻¹)

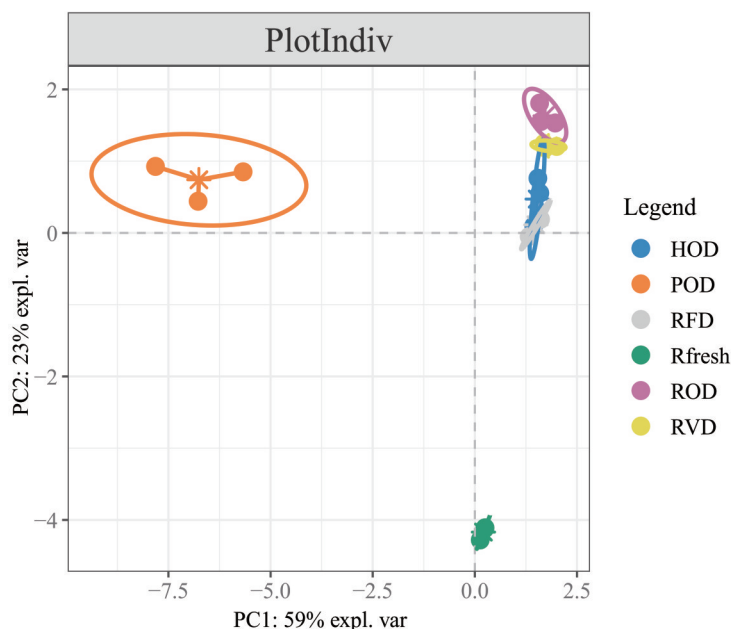
No.	化合物 Compounds	新鲜果肉 Fresh pulps	冷冻果肉 Freeze dried pulps	真空果肉 Vacuum dried pulps	热风果肉 Hot air dried pulps	热风果皮 Hot air dried peels	热风果核 Hot air dried kernels
1	没食子酸 Gallic acid	ND	ND	ND	ND	ND	97.68±182.7
2	绿原酸 Chlorogenic acid	2.525±0.070 b	0.901±0.107 d	0.803±0.107 d	0.648±0.022 e	10.47±2.294 a	1.292±0.499 c
3	4-羟基肉桂酸 4-hydroxycinnamic acid	16.68±3.154 b	15.60±3.389 b	11.210±1.857 d	10.51±1.808 c	18.24±1.568 a	8.164±0.271 e
4	阿魏酸 Ferulic acid	23.25±0.183 a	8.445±0.193 c	6.033±0.111 d	6.240±0.711 d	13.088±1.012 b	7.345±1.877 c
5	肉桂酸 Cinnamic acid	ND	ND	21.13±7.795 b	47.45±14.85 a	28.76±1.733 b	ND
6	柚皮苷 Naringin	0.603±0.004 b	0.241±0.035 c	0.138±0.004 d	0.141±0.008 d	10.30±0.453 a	0.373±0.036 c
7	芦丁 Rutin	4.180±0.425 b	1.972±0.202 c	2.024±1.271 c	2.236±0.756 c	280.1±64.81 a	3.283±0.659 b
8	槲皮素-7-O-β-D-葡萄糖苷 Quercetin-7-O-β-D-glucopyranoside	ND	ND	ND	ND	46.13±5.277	ND
9	异槲皮素 Isoquercitrin	ND	ND	ND	ND	28.62±4.133 a	0.34±0.111 b
10	橙皮苷 Hesperidin	4.615±3.589 b	ND	1.251±0.149 c	ND	47.003±10.85 a	ND
11	根皮苷 Phloridzin	0.615 2±0.014 c	0.223±0.007 d	0.162±0.007 e	0.165±0.012 e	36.310±5.871 a	1.678±0.222 b
12	野漆树苷 Rhoifolin	0.861 5±0.019 a	0.306±0.002 c	0.213±0.002 d	0.217±0.003 d	0.333±0.021 c	0.449±0.112 b
13	甲基橙皮苷 Methyl hesperidin	2.356±0.177 b	2.392±0.621 b	1.595±0.450 c	2.316±0.816 b	12.541±1.697 a	ND
14	槲皮素 Quercetin	ND	ND	ND	ND	7.424±2.267 a	1.782±0.484 b
15	柚皮素 Naringenin	3.458±0.013 a	1.207±0.013 c	0.866±0.003d	0.836±0.007 d	2.211±0.114 b	1.688±0.192 c
16	木犀草素 Luteolin	ND	ND	ND	ND	6.09±1.801 a	5.202±1.547 a
17	根皮素 Phloretin	0.944±0.044 a	0.298±0.141 c	0.241±0.014 c	0.254±0.006 c	0.667±0.091 b	0.239±0.011 c

注: ND. 未检测到。结果表示为平均值±标准差, 同一行不同小写字母表示差异显著($p < 0.05$)。Note: ND. Not detected. Results are presented as the means±SD of three replicates. Different small letters in the same row indicate significantly difference as determined by ANOVA and Tukey's post hoc test ($p < 0.05$).

均显著减低了龙眼多酚含量。特别地,新鲜果肉中未检测到肉桂酸含量,而真空干燥和热风干燥显著性地增加了肉桂酸含量。在3种干燥方式中,与冷冻干燥相比,真空干燥和热风干燥显著增加了龙眼中大部分酚类化合物的损失,该结果与上面总酚测定结果一致,均说明冷冻干燥能减少龙眼多酚的损失。然而,真空干燥和热风干燥对龙眼果肉中黄酮类化合物的影响无显著差别。

在本研究中,对测得的多酚化合物进行主成分

分析。如图3所示,第一主成分(PC1)明显地将果皮与其他样品分离开,第二主成分(PC2)将新鲜样品与其他样品分离开,这个结果与上面表2的结果均说明果皮和果核中龙眼多酚显著区别于(高于)果肉样品。3种干燥方式处理后样品与新鲜样品被PC2分离开,而且真空干燥和热风干燥处理样品的空间距离非常靠近,这都说明干燥显著地影响了龙眼多酚类化合物含量,然而,真空干燥和热风干燥处理对果肉中多酚含量的影响差别不明显。



HOD. 热风干燥龙眼果核;POD. 热风干燥龙眼果皮;RFD. 冷冻干燥龙眼果肉;ROD. 热风干燥龙眼果肉;Rfresh. 新鲜龙眼果肉;RVD. 真空干燥龙眼果肉。

HOD. Hot air dried longan kernels; POD. Hot air dried longan peels; RFD. Freeze dried longan pulps; ROD. Hot air dried longan pulps; Rfresh. Fresh longan pulps; RVD. Vacuum dried longan pulps.

图3 主成分分析新鲜龙眼、热风干燥、真空干燥和冷冻干燥龙眼样品中多酚情况

Fig. 3 Principal component analysis for phenolic compounds in the fresh and dried longan by freeze drying (FD), vacuum drying (VD) and oven drying (OD)

2.4 相关性分析

本研究利用偏最小二乘分析法(sPLS)探究龙眼酚类成分与总酚含量和抗氧化活性之间的关系,结果如图4所示。从图中可以看出大部分的酚类化合物与总酚含量以及抗氧化活性呈正相关,只有少部分酚类物质甲基橙皮苷以及4-羟基肉桂酸与多酚抗氧化活性相关性较低。特别地,本研究结果表明肉桂酸几乎不贡献多酚抗氧化活性。

3 讨论

3种干燥方式均显著性降低龙眼总多酚含量,

其中真空干燥和热风干燥处理后龙眼总多酚含量显著低于冷冻干燥处理后样品,这有可能是因为在高温条件下,龙眼酚类物质易被氧化分解,使得其含量降低。本研究与前人研究结果一致^[14],冷冻干燥方式处理的杨梅中总多酚含量最高,其次是真空干燥,最低是热风干燥。Winny等^[15]研究也表明冷冻干燥对草莓叶多酚的损失率最小。然而,Tan等^[16]研究表明与冷冻干燥和热风干燥相比,真空干燥能增加红心番石榴总酚含量,这有可能是在加热条件下结合型多酚释放游离,同时在较高温度下多酚氧化酶的活性被破坏,进而减少了多酚氧化损失。秦丹丹

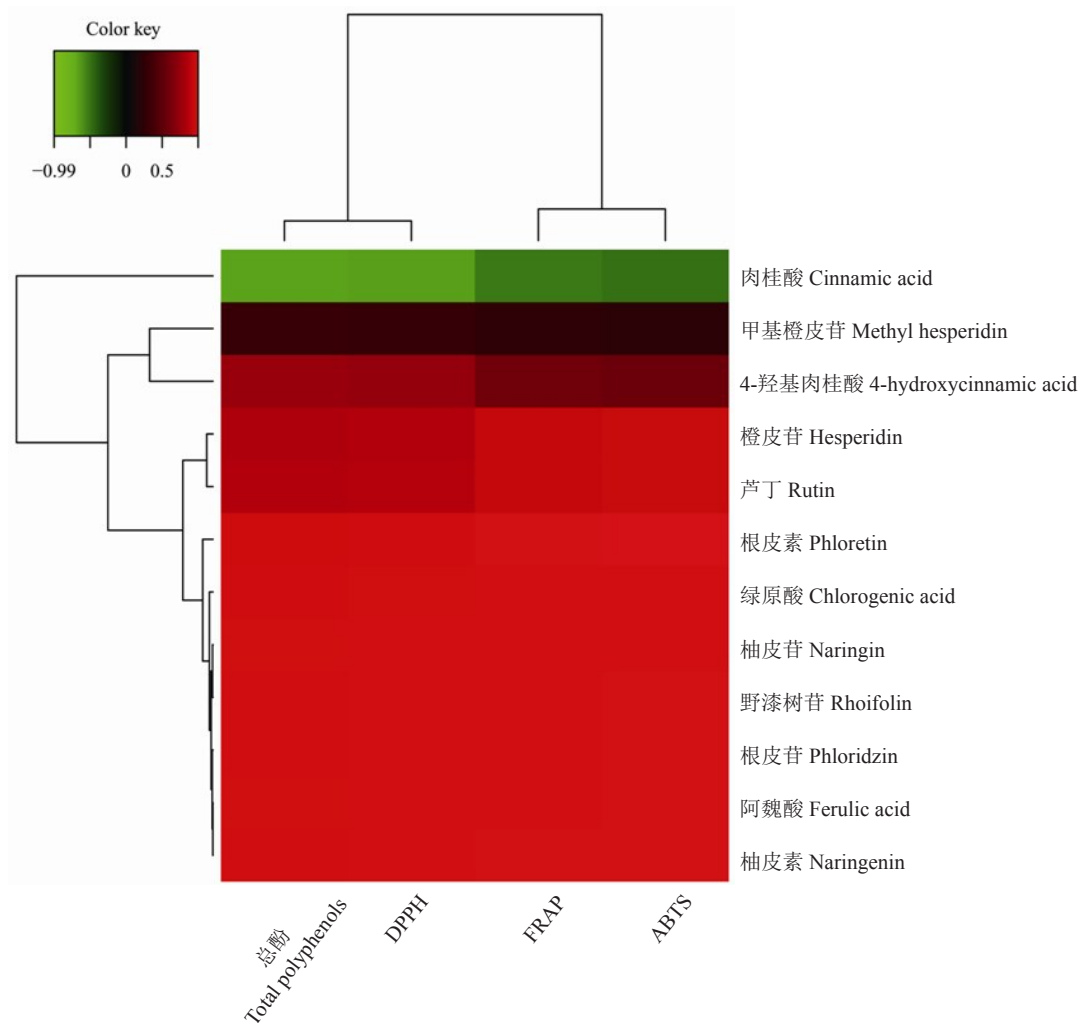


图 4 多酚组分与抗氧化活性相关性分析

Fig. 4 Heat-map for correlation between chemical compounds and total polyphenols or antioxidant activity

等^[17]研究也表明真空干燥的无花果总多酚含量高于晒干、热风干燥、冷冻干燥和远红外干燥方式处理的样品。这些研究结果表明不同干燥方式对不同果蔬总多酚含量影响不同。

干燥后果蔬抗氧化活性也会受到影响。有研究表明,与其他干燥方式相比,冷冻干燥后蓝莓叶样品表现出较高的DPPH自由基清除能力^[10]。同样,香蕉冷冻干燥后清除DPPH自由基能力高于真空干燥处理后样品^[9],这很有可能与冷冻干燥后样品多酚含量更高直接相关。秦丹丹等^[17]研究表明真空干燥的无花果对DPPH,ABTS自由基清除能力和总还原力均高于热风干燥、冷冻干燥等方式处理的样品,相关性分析也表明无花果抗氧化活性与其含有的主要多酚类物质呈显著相关。本研究中,干燥对龙眼总多酚含量和几种抗氧化活性影响趋势也相同。

本研究基于常见的几十种多酚标准品数据信息建立了多酚靶向代谢组数据库,对龙眼中多酚类化合物进行了全面系统的定性和定量分析。文献报道^[18-19],龙眼中含有的酚类物质主要有绿原酸、阿魏酸、丁香酸、没食子酸、4-甲基邻苯二酚、对香豆酸、原儿茶酸、异槲皮苷、槲皮素、鞣花单宁和鞣花酸等。本研究发现龙眼中还含有橙皮苷、根皮苷、甲基橙皮苷、柚皮素、木犀草素和根皮素。之前大部分研究都集中于龙眼果肉,少部分研究关注龙眼果核中生物活性成分,而很少有关于龙眼壳中多酚类物质的分析研究。本研究表明龙眼果皮中含有的多酚种类和含量显著高于果核和果肉,果肉中多酚种类和含量最低,由此说明龙眼果渣具有潜在的利用价值。为了充分利用这一富含多酚的资源,同时减少龙眼果渣对环境的影响,龙眼果渣多酚类化合物的提取和

深加工利用值得进一步探索。此外,与真空干燥和热风干燥相比,冷冻干燥能减少龙眼果肉总酚的损失,同时也能减少大部分酚类成分的损失。然而真空干燥和热风干燥后肉桂酸含量显著增加,这可能是在加热条件下由高分子物质分裂形成或者是细胞基质中结合态的多酚变成了游离态的多酚^[20]。

果蔬中酚类化合物是贡献抗氧化活性的主要成分^[21]。本研究结果也表明大部分酚类化合物与抗氧化活性呈正相关,特别地,本研究结果表明肉桂酸几乎不贡献多酚抗氧化活性,这与前人研究结果一致。Luo等^[22]报道油柑子(*emblica*)中没食子酸、鞣花酸等都具有很强的清除DPPH和ABTS自由基能力,然而肉桂酸几乎没有任何抗氧化活性。此外赵春贵等^[23]研究也表明,肉桂酸没有清除超氧阴离子自由基($\cdot\text{O}_2^-$)能力。相关性分析结果对于明确龙眼中的多酚活性,进而指导对龙眼多酚类物质的进一步加工利用具有重要意义。

4 结 论

龙眼果皮和果核中多酚种类和含量显著高于龙眼果肉,具有潜在利用价值。不同干燥方法对龙眼多酚类物质含量和抗氧化能力均有显著性影响。与真空干燥、热风干燥相比,冷冻干燥能够降低龙眼中酚类物质及其抗氧化活性的损失,对于龙眼的干制加工更具优势。

参考文献 References:

- [1] 郑少泉,曾黎辉,张积森,林河通,邓朝军,庄伊美. 新中国果树科学研究 70 年: 龙眼[J]. 果树学报, 2019, 36(10): 1414-1420.
ZHENG Shaoquan, ZENG Lihui, ZHANG Jisen, LIN Hetong, DENG Chaojun, ZHUANG Yimei. Fruit scientific research in New China in the past 70 years: Longan[J]. Journal of Fruit Science, 2019, 36(10): 1414-1420.
- [2] 张晓卫,曹蔚,王玉琨,王四旺. 龙眼的化学成分及药理作用研究进展[J]. 西北药学杂志, 2012, 27(5): 493-496.
ZHANG Xiaowei, CAO Wei, WANG Yukun, WANG Siwang. Study of the progress on chemical constituents and pharmacological activities of longan[J]. Northwest Pharmaceutical Journal, 2012, 27(5): 493-496.
- [3] 董科,冷云,何方婷,徐佳伊,李杨,裴晓方. 植物多酚及其提取方法的研究进展[J]. 食品工业科技, 2019, 40(2): 326-330.
DONG Ke, LENG Yun, HE Fangting, XU Jiayi, LI Yang, PEI Xiaofang. Research progress of polyphenol and extraction in plants[J]. Science and Technology of Food Industry, 2019, 40(2): 326-330.
- [4] 张宏康,李嵩琪,林小可,黄育杭,郑雪宜. 龙眼加工研究现状及展望[J]. 轻工科技, 2017, 33(1): 1-4.
ZHANG Hongkang, LI Aiqi, LIN Xiaoke, HUANG Yuhang, ZHENG Xueyi. Research status and prospect of longan processing[J]. Light Industry Science and Technology, 2017, 33(1): 1-4.
- [5] 王宸之,邓自高,李琳,毛世林,李伯康,刘路,钟意,张清,秦文. 热风 and 微波干燥对龙眼品质的影响[J]. 食品与生物技术学报, 2018, 37(4): 429-436.
WANG Chenzhi, DENG Zigao, LI Lin, MAO Shilin, LI Bokang, LIU Lu, ZHONG Yi, ZHANG Qing, QIN Wen. Changes in the quality of *Dimocarpus longan* during the hot-air drying and microwave drying progress[J]. Food Science and Biotechnology, 2018, 37(4): 429-436.
- [6] 丁俊雄,吴小华,王鹏,杨绪飞. 干燥技术在果蔬中的应用综述[J]. 制冷与空调, 2019, 19(8): 23-27.
DING Junxiong, WU Xiaohua, WANG Peng, YANG Xufei. Overview of the application of drying technology in fruits and vegetables[J]. Refrigeration and Air-conditioning, 2019, 19(8): 23-27.
- [7] SENEM K, GAMZE T, DILEK B, JULES B, ROBERT D, ESRA C. A review on the effect of drying on antioxidant potential of fruits and vegetables[J]. Critical Reviews in Food Science and Nutrition, 2016, 56(S.1): S110-S129.
- [8] 高炜,张群,王蓉蓉,李高阳,张菊华,单杨,丁胜华. 干燥方式对柠檬片中游离态、结合态多酚及抗氧化特性的影响[J]. 中国食品学报, 2019, 19(6): 106-115.
GAO Wei, ZHANG Qun, WANG Rongrong, LI Gaoyang, ZHANG Juhua, SHAN Yang, DING Shenghua. Impact of dehydration methods on the phenolic compounds and antioxidant activity of lemon slices[J]. Journal of Chinese Institute of Food Science and Technology, 2019, 19(6): 106-115.
- [9] 王玉婷,陈奕,李雨波. 干燥方式对香蕉片总多酚含量及其抗氧化活性的影响[J]. 食品科学, 2013, 34(23): 113-117.
WANG Yuting, CHEN Yi, LI Yubo. Effects of different drying methods on the content and antioxidant activity of total polyphenol from banana slices[J]. Food Science, 2013, 34(23): 113-117.
- [10] 李晓英,薛梅,樊汶樵,罗洁. 不同干燥方式对蓝莓叶中酚类物质及其抗氧化活性的影响[J]. 中国农业科学, 2018, 51(13): 2570-2578.
LI Xiaoying, XUE Mei, FAN Wenqiao, LUO Jie. Analysis of phenolic compounds and antioxidant activities of blueberry leaves from different drying methods[J]. Scientia Agricultura Sinica, 2018, 51(13): 2570-2578.
- [11] 中华人民共和国卫生和计划生育委员会. 食品安全国家标准 食品中水分的测定: GB 5009.3-2016[S]. 北京: 中国农业出版社, 2016.
National Health and Family Planning Commission of the People's Republic of China. National food safety standard: Determination of moisture in foods: GB 5009.3-2016 [S]. Beijing: China Agricultural Science and Technology Press, 2016.

- na Agriculture Press, 2016.
- [12] 谭颺, 夏国灯, 韩杨, 王小雪. 辣木籽多酚提取工艺优化及其抗氧化活性研究[J]. 食品科技, 2019, 44(1): 280-285.
TAN Si, XIA Guodeng, HAN Yang, WANG Xiaoxue. Optimization extracting process and antioxidant activity of polyphenol in moringa seed[J]. Food Science and Technology, 2019, 44(1): 280-285.
- [13] LI W, WANG X, ZHANG J, ZHAO X, WU Y, TAN S, ZHENG Q, GAO X. Multivariate analysis illuminates the effects of vacuum drying on the extractable and non-extractable polyphenols profile of loquat fruit[J]. Journal of Food Science, 2019, 84(4): 726-737.
- [14] 解红霞, 陈相艳, 王文亮, 曲静然, 程安玮, 弓志青. 不同干燥方式对杨梅中总多酚和花青素含量的影响[J]. 食品科技, 2014, 39(2): 96-98.
XIE Hongxia, CHEN Xiangyan, WANG Wenliang, QU Jingran, CHENG Anwei, GONG Zhiqing. Effect of drying methods on the content of polyphenols and anthocyanins in barberries[J]. Food Science and Technology, 2014, 39(2): 96-98.
- [15] WINNY R, VALERIE O, YVAN G. Effect of different drying methods on the microwave extraction of phenolic components and antioxidant activity of highbush blueberry leaves[J]. Biocontrol Science and Technology, 2014, 32(16): 1888-1904.
- [16] TAN S, WANG Z, XIANG Y, DENG T, ZHAO X, SHI S, ZHENG Q, GAO X, LI W. The effects of drying methods on chemical profiles and antioxidant activities of two cultivars of *Psidium guajava* fruits[J]. LWT-Food Science and Technology, 2020, 118: 108723.
- [17] 秦丹丹, 张生万, 郭萌, 郭彩霞, 李美萍. 干燥方式对无花果酚类物质及其抗氧化活性的影响[J]. 食品科学, 2018, 39(9): 102-107.
QIN Dandan, ZHANG Shengwan, GUO Meng, GUO Caixia, LI Meiping. Effect of drying methods on polyphenol composition and antioxidant activities of figs (*Ficus carica* L.)[J]. Food Science, 2018, 39(9): 102-107.
- [18] RANGKADILOK N, WORASUTTAYANGKURN L, BENNETT N, SATAYAVIVAD J. Identification and quantification of polyphenolic compounds in Longan (*Euphoria longana* Lam.) fruit[J]. Journal of Agricultural and Food Chemistry, 2005, 53(5): 1387-1392.
- [19] ZHANG R, KHAN S, LIN Y, GUO D, PAN X, LIU L, WEI Z, ZHANG Y, DENG Y, ZHANG M. Phenolic profiles and cellular antioxidant activity of longan pulp of 24 representative Chinese cultivars[J]. International Journal of Food Properties, 2018, 21(1): 746-759.
- [20] ANETA W, ADAM F, KRZYSZTOF L, PAULINA N, JAN O. Effect of convective and vacuum-microwave drying on the bioactive compounds, color, and antioxidant capacity of sour cherries[J]. Food and Bioprocess Technology, 2014, 7(3): 829-841.
- [21] 韩文凤, 郭红英, 贾娟, 谭兴和. 果蔬多酚及其抗氧化研究进展[J]. 保鲜与加工, 2019, 19(4): 191-194.
HAN Wenfeng, GUO Hongying, JIA Juan, TAN Xinghe. Research progress on polyphenols and antioxygenic property of fruits and vegetables[J]. Storage and Process, 2019, 19(4): 191-194.
- [22] LUO W, ZHAO M M, YANG B, SHEN G L, RAO G H. Identification of bioactive compounds in *Phyllanthus emblica* L. fruit and their free radical scavenging activities[J]. Food Chemistry, 2009, 114(2): 499-504.
- [23] 赵春贵, 张立伟, 王晖, 黄登宇. 肉桂酸及其衍生物抗氧化活性研究[J]. 食品科学, 2005, 26(1): 218-222.
ZHAO Chungui, ZHANG Liwei, WANG Hui, HUANG Dengyu. Study on anti-oxidation effects of cinnamic acid and its derivatives[J]. Food Science, 2005, 26(1): 218-222.