

山核桃与大别山山核桃种仁营养成分比较分析

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摘要:【目的】比较山核桃与大别山山核桃种仁一般营养成分、功能性成分、氨基酸、脂肪酸以及矿质元素含量的差异。【方法】对两种坚果种仁51种营养成分进行测定分析。【结果】山核桃与大别山山核桃种仁 γ 维生素E、单宁、角鲨烯、棕榈酸、Na和Zn含量存在极显著差异($p < 0.01$); 脂肪、天冬氨酸、苏氨酸、甘氨酸、胱氨酸、缬氨酸、异亮氨酸、亮氨酸、赖氨酸、硬脂酸、亚麻酸、K、Ca和Mg含量存在显著差异($p < 0.05$); 其余营养成分无显著差异。【结论】山核桃种仁蛋白质、淀粉、 α 维生素E、氨基酸、多不饱和脂肪酸和矿质元素含量较高, 单宁含量低; 大别山山核桃种仁脂肪、可溶性糖、 γ 维生素E、总酚、角鲨烯和单不饱和脂肪酸含量较高, 且变异丰富。

关键词: 山核桃; 大别山山核桃; 种仁; 营养成分

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Comparative analysis of kernel nutrients between *Carya cathayensis* and *Carya dabieshanensis*

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Abstract: 【Objective】 *Carya cathayensis* is an important economic and oil crop. Its kernel is rich in protein, fat, fatty acid, minerals and other nutrients, and thus has a high nutritional value. The kernel of *C. dabieshanensis* has high oleic acid and linoleic acid and low palmitic acid. At present, there is no systematic analysis of nutritional components in the two species. This study aims to provide the basic information about the nutritional components in the kernels of the two species, which is important for cross breeding and nutritional quality evaluation. 【Methods】 In Hangzhou city, Zhejiang province and Lu'an city, Anhui province, the main producing areas of *C. cathayensis* and *C. dabieshanensis*, respectively, 40 plants with strong growth were selected, and 5.0 kg fruit from each tree were sampled. The nut were dried and the shell was removed. The contents of general nutrients, functional components, amino acids, fatty acids and mineral elements in the kernels were determined and analyzed. Protein content was determined by spectrophotometry. Amino acid was determined with an amino acid analyzer. The contents of K, Ca, Na, Mg, Fe, Zn, Cu, Mn and B were determined with atomic absorption spectrophotometry. The content of fat was determined with the Soxhlet extractor method and fatty acids using the internal standard method. Tannin was quantified with spectrophotometry method. Starch and soluble sugars were determined by anthranone colorimetry. Squalene was determined with gas chromatography and vitamin E with high performance liquid chromatography. Data were expressed as $X \pm SE$ (mean \pm standard

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error), and MS Excel 2016 software was used to draw the tables. Data analysis were performed using SPSS 25.0.【Results】(1) Fat content in *C. dabieshanensis* was significantly higher than in *C. cathayensis* ($p < 0.05$), and there was no significant difference in the contents of protein, starch and soluble sugars. (2) The contents of γ vitamin E, tannin and squalene in *C. dabieshanensis* were extremely significantly higher than in *C. cathayensis* ($p < 0.01$), and there was no significant difference in the contents of α vitamin E and total phenols. (3) The contents of total amino acids, essential amino acids and delicious amino acids in *C. cathayensis* were extremely significant higher than those in *C. dabieshanensis* ($p < 0.01$). Aspartic acid, threonine, glycine, cystine, valine, isoleucine, leucine and lysine were all significantly higher in *C. cathayensis* than in *C. dabieshanensis* ($p < 0.05$), and there was no significant difference in serine, glutamic alanine, methionine, tyrosine, phenylalanine, histidine, arginine and proline. (4) Monounsaturated fatty acids in *C. dabieshanensis* were significantly higher than in *C. cathayensis* ($p < 0.05$), while polyunsaturated fatty acids were the opposite, and there was no significant difference in total amount of unsaturated fatty acids and saturated fatty acids. Palmitic acid content in *C. dabieshanensis* was extremely significant higher than in *C. cathayensis* ($p < 0.01$); the stearic acid and linolenic acid in *C. cathayensis* were significantly higher than in *C. dabieshanensis* ($p < 0.05$), and there was no significant difference in arachidonic acid, palmitoleic acid, methyl *cis*-11-eicosenoate, oleic acid and linoleic acid. (5) The content of Zn in *C. dabieshanensis* was extremely significantly higher than in *C. cathayensis* ($p < 0.01$), and the content of Na in *C. cathayensis* was significantly higher than in *C. dabieshanensis* ($p < 0.05$). The contents of K, Ca and Mg were significantly higher in *C. cathayensis* ($p < 0.05$), and there was no significant difference in Fe, Cu, Mn, P and B.【Conclusion】The contents of protein, starch, α vitamin E, amino acid, polyunsaturated fatty acid and mineral element were higher but the content of tannin was lower in *C. cathayensis*; the contents of fat, soluble sugars, γ vitamin E, total phenol, squalene and monounsaturated fatty acid in *C. dabieshanensis* were higher with great variation. Therefore, *C. dabieshanensis* has a greater potential for breeding.

Key words: *Carya cathayensis*; *Carya dabieshanensis*; Kernel; Nutrients

山核桃(*Carya cathayensis*)和大别山山核桃(*C. dabieshanensis*)属胡桃科(Juglandaceae)山核桃属(*Carya* Nutt.)。山核桃主要分布在浙皖交界天目山区,包括临安、淳安、安吉、宁国、绩溪、歙县等县。种仁富含蛋白质、矿质元素、可溶性糖、脂肪及脂肪酸等营养成分^[1-3],其中的不饱和脂肪酸质量分数比被称为“液体黄金”的食用橄榄油还要高^[4],此外还含有多种对人体有益的必需氨基酸等,具有较好的营养、保健和药用价值^[5]。大别山山核桃主要分布在皖湘豫三省交界的大别山山区,包括金寨、罗田、商城等县。种仁具有高油酸、高亚油酸、低棕榈酸的特点^[6]。

目前对山核桃和大别山山核桃品质的研究集中在坚果表型、氨基酸成分和脂肪酸成分等方面^[7-10]。张鹏等^[11]对4种山核桃种仁的含油率、脂肪酸组成及含量进行了比较分析,但未研究种仁的其他营养成分。周红等^[12]研究了新疆野核桃内10种不同果

实类型的营养成分。刘力等^[13]研究了山核桃种仁蛋白质及氨基酸含量,李财运等^[14]用不同浓度的硒处理薄壳山核桃果实,测定其对果实品质的影响,但在营养成分对比分析方面两者没有进行系统性的研究。笔者对山核桃和大别山山核桃种仁一般营养成分、功能性成分、氨基酸、脂肪酸以及矿质元素含量等51种营养成分进行了测定和比较研究,旨在为两种山核桃种仁营养成分提供基本资料,同时为山核桃杂交育种、亲本选择和营养品质评价等提供科学依据。

1 材料和方法

1.1 材料

山核桃的取样地位于浙江省杭州市临安区(30°20'N, 119°70'E)、淳安县(29°11'N, 119°20'E)和安吉县(30°38'N, 119°34'E)。大别山山核桃的取样地位于安徽省六安市金寨县(31°10'N, 115°30'E)。在山

核桃和大别山山核桃的取样地内分别挑选40株树龄50 a(年)、生长健壮、无病虫害、光照充足的优良实生母树。在9月上旬采集充分成熟的果实,每株采集果实约为5.0 kg,用塑料网兜包装,在运输过程中随时通风、翻动,防止堆积发热霉变。带回实验室后风干并脱去果皮,取出种仁用于营养成分测定。

1.2 测定方法

试验按照国家标准方法进行测定:蛋白质含量测定参照GB 5009.5-2016《食品中蛋白质的测定》;氨基酸含量测定参照GB 5009.124-2016《食品中氨基酸的测定》^[15];钙、钾、镁、锰、硼、铁、铜、锌、磷和钠含量测定参照GB 5009.268-2016《食品中多元素的测定》^[16];脂肪含量测定参照GB 5009.6-2016《食品中脂肪的测定》^[17];脂肪酸含量测定参照GB 5009.168-2016《食品中脂肪酸的测定》^[18];单宁含量测定参照NY/T 1600-2008《水果、蔬菜及其制品中单宁含量的测定分光光度法》;总酚含量测定采用张春江等^[19]的方法;淀粉和可溶性糖含量采用蒽酮比色法测定;角鲨烯含量测定参照LS/T 6120-2017《粮油检验植物油中角鲨烯的测定气相色谱法》;维生素E含量测定参照GB 5009.82-2016《食品中维生素A、D、E的测定》。

1.3 数据处理方法

数据采用Excel 2016软件进行计算和分析,百分比经反正弦平方根转化后用SPSS 25.0软件进行 t 检验。

2 结果与分析

2.1 山核桃与大别山山核桃种仁一般营养成分含量比较分析

两种山核桃种仁一般营养成分中(表1),山核

表1 山核桃与大别山山核桃种仁一般营养成分含量

Table 1 General nutrient contents in *C. cathayensis* and *C. dabieshanensis* %

| 指标 Index | 山核桃 <i>C. cathayensis</i> | 大别山山核桃 <i>C. dabieshanensis</i> |
|--------------------|------------------------------|------------------------------------|
| 蛋白质 Protein | 9.14±0.85 | 7.85±1.13 |
| 脂肪 Fat | 64.54±2.03 | 67.07±2.80* |
| 淀粉 Starch | 4.11±2.17 | 3.01±0.84 |
| 可溶性糖 Soluble sugar | 5.68±0.99 | 5.98±0.93 |

注:*和**分别表示差异显著($p < 0.05$)和差异极显著($p < 0.01$)。下同。

Note: * and ** mean significant difference at $p < 0.05$ and $p < 0.01$, respectively. The same below.

桃变异较丰富,变异系数以淀粉最高($CV=52.80\%$),可溶性糖次之($CV=17.43\%$),脂肪含量变异系数最低($CV < 5\%$)。两种种仁的脂肪含量达到显著性差异($p < 0.05$),其余成分无显著性差异。大别山山核桃种仁脂肪含量为67.07%,比山核桃高3.92%。

2.2 山核桃与大别山山核桃种仁功能性成分含量比较分析

两种山核桃种仁功能性成分中(表2),大别山山核桃变异较丰富,变异系数以角鲨烯最高($CV=28.99\%$), α 维生素E次之($CV=27.08\%$)。两种种仁的 γ 维生素E、单宁和角鲨烯含量达到极显著性差异($p < 0.01$),其余无显著性差异。大别山山核桃种仁 γ 维生素E、单宁和角鲨烯含量分别为267.60 mg·kg⁻¹、37 403.78 mg·kg⁻¹和312.63 mg·kg⁻¹,比山核桃分别高10.81%、35.42%和95.06%。

表2 山核桃与大别山山核桃种仁功能性成分含量

Table 2 Functional components in *C. cathayensis* and *C. dabieshanensis* (mg·kg⁻¹)

| 指标 Index | 山核桃 <i>C. cathayensis</i> | 大别山山核桃 <i>C. dabieshanensis</i> |
|----------------------------------|------------------------------|------------------------------------|
| α 维生素E α vitamin E | 13.50±1.90 | 9.60±2.60 |
| γ 维生素E γ vitamin E | 241.50±20.20 | 267.60±48.70** |
| 总酚 Total phenol | 53 647.98±12 171.75 | 58 665.75±11 250.70 |
| 单宁 Tannin | 27 620.73±4 450.34 | 37 403.78±7 200.88** |
| 角鲨烯 Squalene | 160.27±19.99 | 312.63±90.66** |

2.3 山核桃与大别山山核桃种仁氨基酸含量比较分析

两种山核桃种仁氨基酸含量中(表3),大别山山核桃变异较丰富,变异系数以蛋氨酸最高($CV=28.57\%$),胱氨酸次之($CV=26.32\%$)。氨基酸总量(TAA)、必需氨基酸含量(EAA)和呈味氨基酸(DAA)达到极显著性差异($p < 0.01$);天冬氨酸、苏氨酸、甘氨酸、胱氨酸、缬氨酸、异亮氨酸、亮氨酸和赖氨酸含量达到显著性差异($p < 0.05$),其余均无显著性差异。山核桃种仁中TAA、EAA和DAA含量分别为9.35%、2.84%和3.69%,比大别山山核桃分别高27.21%、28.51%和26.80%。山核桃种仁中天冬氨酸、苏氨酸、甘氨酸、胱氨酸含量分别为0.87%、0.32%、0.45%和0.21%,比大别山山核桃分别高27.28%、23.07%、24.32%和10.52%;缬氨酸、异亮氨酸、亮氨酸和赖氨酸含量分别为0.44%、0.37%、0.64%和0.44%,比大别山山核桃分别高25.71%、

表 3 山核桃与大别山山核桃种仁氨基酸含量

Table 3 Amino acids in *C. cathayensis* and *C. dabieshanensis* %

| 指标 Index | 山核桃 <i>C. cathayensis</i> | 大别山山核桃 <i>C. dabieshanensis</i> |
|------------------------|------------------------------|------------------------------------|
| 天冬氨酸 Asp | 0.87±0.08* | 0.70±0.13 |
| [△] 苏氨酸 Thr | 0.32±0.03* | 0.26±0.05 |
| 丝氨酸 Ser | 0.47±0.04 | 0.38±0.07 |
| 谷氨酸 Glu | 1.92±0.21 | 1.48±0.32 |
| 甘氨酸 Gly | 0.46±0.04* | 0.37±0.07 |
| 丙氨酸 Ala | 0.44±0.04 | 0.36±0.07 |
| 胱氨酸 Cys | 0.21±0.04* | 0.19±0.05 |
| [△] 缬氨酸 Val | 0.44±0.04* | 0.35±0.07 |
| [△] 蛋氨酸 Met | 0.11±0.02 | 0.07±0.02 |
| [△] 异亮氨酸 Ile | 0.37±0.03* | 0.28±0.06 |
| [△] 亮氨酸 Leu | 0.64±0.06* | 0.51±0.10 |
| 酪氨酸 Tyr | 0.30±0.04 | 0.23±0.05 |
| [△] 苯基丙氨酸 Phe | 0.52±0.05 | 0.40±0.07 |
| [△] 赖氨酸 Lys | 0.44±0.03* | 0.34±0.05 |
| 组氨酸 His | 0.24±0.02 | 0.18±0.03 |
| 精氨酸 Arg | 1.19±0.14 | 0.95±0.21 |
| 脯氨酸 Pro | 0.41±0.04 | 0.30±0.05 |
| 呈味氨基酸 DAA | 3.69±0.37** | 2.91±0.59 |
| 必需氨基酸 EAA | 2.84±0.26** | 2.21±0.42 |
| 氨基酸总量 TAA | 9.35±0.95** | 7.35±1.47 |

注: [△]为人体必需氨基酸。Note: [△] is the essential amino acid for human body.

32.14%、25.49%和 29.41%。

2.4 山核桃与大别山山核桃种仁脂肪酸含量比较分析

两种山核桃种仁脂肪酸含量中(表 4),大别山山核桃以亚油酸含量变异系数最高($CV=27.06\%$),山核桃以硬脂酸含量最高($CV=25.00\%$),棕榈酸含量最为稳定($CV=2.85\%$)。棕榈酸含量达到极显著性差异($p < 0.01$);多不饱和脂肪酸(PUFA)、单不饱和脂肪酸(MUFA)、硬脂酸和亚麻酸含量达到显著性差异($p < 0.05$),其余无显著性差异。大别山山核桃种仁棕榈酸含量为 5.86%,比山核桃高出 19.35%。大别山山核桃种仁单不饱和脂肪酸为 76.57%,比山核桃分别高出 17.17%。山核桃种仁多不饱和脂肪酸含量为 27.06%,比大别山山核桃高 76.40%。山核桃种仁硬脂酸、和亚麻酸含量分别为 2.32%和 1.91%,比大别山山核桃分别高 26.09%和 60.50%。

表 4 山核桃与大别山山核桃种仁脂肪酸含量

Table 4 Fatty acids in *C. cathayensis* and *C. dabieshanensis* %

| 指标 Index | 山核桃 <i>C. cathayensis</i> | 大别山山核桃 <i>C. dabieshanensis</i> |
|--|------------------------------|------------------------------------|
| 棕榈酸 C16:0 | 4.91±0.14 | 5.86±0.33** |
| 硬脂酸 C18:0 | 2.32±0.58* | 1.84±0.11 |
| 花生酸 C20:0 | 0.14±0.02 | 0.16±0.01 |
| 棕榈烯酸 C16:1 | 0.18±0.04 | 0.18±0.03 |
| 油酸 C18:1 | 65.17±4.34 | 76.39±4.21 |
| 亚油酸 C18:2 | 25.15±4.32 | 14.15±3.83 |
| 亚麻酸 C18:3 | 1.91±0.21* | 1.19±0.24 |
| 顺-11-二十碳烯酸 C20:1 | 0.22±0.02 | 0.23±0.02 |
| 单不饱和脂肪酸 Monounsaturated fatty acids | 65.35±4.38 | 76.57±4.24* |
| 多不饱和脂肪酸 Polyunsaturated fatty acids | 27.06±4.53* | 15.34±4.07 |
| 饱和脂肪酸 Saturated fatty acids | 7.37±0.93 | 7.86±0.45 |
| 不饱和脂肪酸 Unsaturated fatty acids | 92.63±8.93 | 92.14±8.33 |

2.5 山核桃与大别山山核桃种仁矿质元素含量比较分析

两种山核桃种仁矿质元素含量中(表 5),山核桃以 Mn 含量变异系数最高($CV=35.51\%$),大别山山核桃以 Na 含量最高($CV=35.04$)。Na 和 Zn 含量达到极显著性差异($p < 0.01$),K、Ca 和 Mg 含量达到显著性差异($p < 0.05$),其余无显著性差异。山核桃种仁 Na 含量为 7.11 $\text{mg} \cdot \text{kg}^{-1}$,比大别山山核桃高 14.30%。大别山山核桃种仁 Zn 含量为 52.52 $\text{mg} \cdot \text{kg}^{-1}$,比山核桃高 1.41%。山核桃种仁 K、Ca 和 Mg 含量分别为 3 235.48 $\text{mg} \cdot \text{kg}^{-1}$ 、1 804.60 $\text{mg} \cdot \text{kg}^{-1}$ 和 1 405.03 $\text{mg} \cdot \text{kg}^{-1}$,比大别山山核桃分别高 11.00%、51.55%和 6.10%。

表 5 山核桃与大别山山核桃种仁矿质元素含量

Table 5 Mineral contents in *C. cathayensis* and *C. dabieshanensis* ($\text{mg} \cdot \text{kg}^{-1}$)

| 指标 Index | 山核桃 <i>C. cathayensis</i> | 大别山山核桃 <i>C. dabieshanensis</i> |
|----------|------------------------------|------------------------------------|
| 钾 K | 3 235.48±421.80* | 2 914.80±661.99 |
| 钙 Ca | 1 804.60±234.04* | 1 190.78±159.61 |
| 钠 Na | 7.11±1.02** | 6.22±2.18 |
| 镁 Mg | 1 405.03±167.56* | 1 324.30±223.58 |
| 铁 Fe | 37.54±4.77 | 22.45±5.41 |
| 锌 Zn | 51.79±6.66 | 52.52±11.98** |
| 铜 Cu | 10.49±1.98 | 11.68±1.89 |
| 锰 Mn | 94.98±33.73 | 113.53±31.81 |
| 磷 P | 2 814.18±264.49 | 2 393.80±247.40 |
| 硼 B | 14.46±3.25 | 11.84±2.55 |

3 讨 论

坚果种仁内一般营养成分主要为蛋白质、脂肪、淀粉及可溶性糖。本研究发现,山核桃和大别山山核桃种仁中一般营养成分含量较高的是脂肪,其次是蛋白质和可溶性糖,淀粉含量相对较低,这与榛子^[20]、杏仁^[21]、腰果^[22]等的营养成分类似。其中大别山山核桃种仁脂肪含量(67.07%)高于山核桃(64.54%),两者虽然相差较小(3.92%),但由于脂肪含量在山核桃和大别山山核桃种仁中非常稳定,变异系数分别为3.14%和4.17%,统计学上达到显著性水平。这与何国庆等^[23]对山核桃的研究结果类似。而山核桃与大别山山核桃种仁蛋白质、淀粉和可溶性糖含量变异系数较大,所以差异不显著。由于山核桃和大别山山核桃都是天然实生繁殖群体,不同的单株间具有不同的基因型,受这些基因型差异的制约,不能够真实反映出两个群体间的差异。但是这些变异性较大的性状的存在,从另一方面说明大别山山核桃群体在选择育种方面具有较大的潜力。

种仁功能性成分包括维生素E、酚类化合物、单宁等^[24]。单宁是导致种仁涩口的主要物质,其含量的高低直接影响着山核桃仁的风味,在食品工业有很高的应用价值^[25]。目前已有学者对单宁和果实涩味关系进行了系统性的研究^[26],为今后的果实脱涩技术提供了理论支撑。本研究发现,山核桃和大别山山核桃种仁中功能性成分主要为维生素E、总酚、单宁和角鲨烯,大别山山核桃种仁 γ 维生素E、单宁和角鲨烯含量极显著高于山核桃, α 维生素E和总酚含量无显著性差异。角鲨烯具有广泛的生物活性,对心血管具有保护作用,因此被广泛利用于医药领域^[27]。以往角鲨烯的提取来源主要为深海鲨鱼,因野生鲨鱼来源有限,研究者逐渐将研究重点转向植物。研究发现大别山山核桃角鲨烯含量较高($312.63 \text{ mg} \cdot \text{kg}^{-1}$),远高于南瓜籽($30.00 \text{ mg} \cdot \text{kg}^{-1}$)^[28]等种子,这为角鲨烯的提取提供了重要的种质资源。

本研究发现两种山核桃种仁中含量最多的矿质元素是K,含量最低的元素是Na,测定结果与李新委等^[29]的研究结果基本一致。山核桃仁属于高钾低钠型食品。除此之外,含量较多的元素还有Ca和Mg,Ca是构成人体骨骼的主要元素,可以促进身体的新陈代谢;Mg负责调节神经系统,对于维持正常

肌肉收缩有着重要作用。可见山核桃是人体必需矿物质元素的来源食品。

山核桃种仁中含17种氨基酸,包含人体8种必需氨基酸中的7种。山核桃和大别山山核桃种仁的EAA/TAA的值分别为30.37%、30.07%,这与WHO/FAO规定的标准(40.00%)^[30]差距较小。呈味氨基酸是评价植物味道的重要指标,主要包括天冬氨酸、谷氨酸、甘氨酸和丙氨酸。山核桃和大别山山核桃种仁DAA/TAA的值分别为39.47%和39.59%,其中谷氨酸所占含量最高,分别占52.03%和50.86%。在人体所必需的氨基酸中,山核桃种仁亮氨酸含量最高,苯基丙氨酸次之,分别为0.64%和0.52%,比大别山山核桃分别高出25.49%和30.00%。必需氨基酸中的赖氨酸是肝和胆的组成成分,能够促进脂肪代谢,防止细胞退化等;蛋氨酸具有促进脾脏、胰脏及淋巴的作用;异亮氨酸参与胸腺、脾脏及脑下腺的调节与代谢;天冬氨酸具有抗疲劳、降血压等作用;精氨酸具有促进生长发育和增强细胞免疫力等作用^[31-33],因此青少年食用适量的山核桃仁有利于生长发育。

山核桃种仁中具有丰富的饱和脂肪酸和不饱和脂肪酸。不饱和脂肪酸是大脑组织细胞的主要结构脂肪,具有预防心血管疾病和改善内分泌等作用^[34]。山核桃种仁中的脂肪酸营养价值主要取决于单不饱和脂肪酸(油酸)的含量,山核桃与大别山山核桃的不饱和脂肪酸含量平均值为92.63%和92.14%,高于南疆杏仁85.50%的平均脂肪酸含量^[35]。根据本试验对山核桃和大别山山核桃种仁脂肪酸组成结构分析认为,两种坚果种仁的脂肪酸组成成分及含量与当前国际公认的高档植物油相当,因此,山核桃和大别山山核桃均可作为优质食用植物油资源予以开发。

4 结 论

山核桃种仁蛋白质、淀粉、氨基酸、多不饱和脂肪酸和矿质元素含量较高,单宁含量低;大别山山核桃种仁脂肪、可溶性糖、 γ 维生素E、总酚、角鲨烯和单不饱和脂肪酸含量较高并且变异丰富,良种选育的潜力更大。

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