

枣果实风味研究进展

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摘要: 枣果实风味是枣果实品质的重要组成部分, 主要由枣果实中含有的糖、酸和挥发性芳香物质共同作用, 通过影响人们味觉和嗅觉形成的对枣果实品质的直接认知。目前对枣果实风味的研究, 主要关注于枣果实糖酸类物质的组成、含量及其动态变化, 并深入探讨其形成途径、影响因素和对品质形成的作用, 取得了显著成果, 而对于枣果实中挥发性芳香物质的研究略显不足, 主要针对部分枣品种开展了一些探索性研究。笔者就近年来与枣果实风味相关的有关文献进行了综述, 并提出了未来研究展望, 为从事相关领域工作的人员提供参考。

关键词: 枣; 风味; 糖; 酸; 香气

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Advances in research on jujube flavor

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Abstract: Jujube fruit flavor is an important component of fruit quality. It mainly consists of sugar, acid and volatile aromatic substances contained in the fruit, which directly affects the quality of jujube fruit formed by affecting human taste and smell. In recent years, with the rapid improvement of living standards, consumers have higher and higher requirements for the quality of jujube, and the most original flavor of jujube has become the first and most direct choice. Fruit flavor substances can be divided into taste and aroma substances, which are perceived by taste and smell, respectively. The research focus of the former is still sugar and acid substances, which determine the most important sweet and sour taste of fruits. Previous studies have been carried out on different fruits, varieties, treatment methods and fruits at different stages of maturity. Sugar is the basic material that constitutes the nutrition and flavor of the fruit, and it also has some important physiological functions. Jujube is mostly sucrose-accumulating fruit with the highest sucrose content, followed by fructose and glucose, in addition to sorbitol, lactose, etc.; organic acid is an important element in determining flavor, and most jujube varieties are malic acid dominant. The highest contents of succinic acid and tartaric acid are found, followed by oxalic acid, fumaric acid, betulinic acid, and behenic acid. The latter consists of a large number of volatile aromatic substances, and the different aroma components of different fruits are generally divided into fruity, fragrant, aldehyde, spicy and woody. At present, the research on fruit aroma has gradually become a hot spot in the world. In recent years, with the development and application of gas chromatography-mass spectrometry (GC-MS) analysis and testing technology, a great progress has been made in jujube aroma research, and there have been many reports on the formation of aroma, its production pathways, and species changes. However, there are few reports on key aroma factors in jujube fruit. The ju-

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jube planting industry has spread all over the country. Different environmental conditions lead to different flavors of jujube fruit. Soil type, fertilizer ratio, water irrigation and climatic conditions mainly affect the taste of jujube fruit by changing the content and proportion of sugar and acid in jujube fruit. In addition to the method and drying temperature, the content and proportion of sugar and acid in jujube fruit can be changed, and the flavor of the fruit can be changed by changing the aroma content and composition of the fruit. At present, the research on jujube flavor mainly focuses on the composition, content and dynamic changes of jujube fructose, and further explores its formation pathway, influencing factors and effects on quality formation, and has obtained remarkable achievement. However, the research on volatile aromatic substances is not enough, and some exploratory research is carried out mainly for some jujube varieties. If you have an in-depth understanding of the conversion conditions and mechanism of sugars, acids and aroma substances in jujube fruit, it will solve a series of problems such as the maintenance and improvement of jujube flavor and quality, and explore the key aroma components of jujube fruit. Volatile aromatic substances and their dynamic changes will make the evaluation of jujube flavor more comprehensive and accurate. Southern Xinjiang is the largest dried jujube cultivation area in the country. The quality of jujube fruit is deeply studied in the Mainland due to its flavor influence factor. The quality improvement of varieties and dates in the Mainland is of key significance. In this paper, the relevant literatures related to jujube flavor have been reviewed in recent years, and the future research prospects are put forward to provide reference for those engaged in related fields.

Key words: Jujube; Flavor; Sugar; Acid; Aroma

枣(*Ziziphus jujuba* Mill.)为鼠李科枣属植物,是原产于中国的传统名优特产树种^[1],枣的利用、驯化与栽植历史已有7 000多年^[2]。据中国林业统计年鉴(2017年)统计,全国枣树种植面积已达133.33多万hm²,产年(干枣)约562.5万t。全世界近99%的枣树面积、产量和全球近100%的枣产品国际贸易均集中在我国^[1]。

鲜枣维生素C含量在各种水果中名列前茅,素有维C之王的美称,广受消费者青睐。但是由于鲜枣供应期短,不耐贮运且成熟期容易裂果,导致鲜食枣的消费及其种植均受到一定的限制;而以生产制干枣为目的枣树种植面积高达117.33万hm²,占全国枣树面积的近75%,干枣依然是当前枣果实消费的主要形式^[2]。干枣可以入药,具有安神、补气、和胃、解毒的功效,从古至今在中药配方中被广泛应用^[3];干枣富含碳水化合物、盐类、矿物质、维生素、脂肪酸、氨基酸和蛋白质,这种高营养品质使其亦被应用于加工业,如枣醋、枣酒、枣饮料等^[4];但无论是入药还是深加工,在干枣的整体消费中还是很低,最为主流的消费依然是直接食用。

近年来随着生活水平的快速提高,消费者对枣内在品质的要求越来越高,而枣果实最原始的风味

成为最先和最直接的选择依据。梁乘榜等^[5]认为果实风味物质分为口味物质和香气物质。前者通过味觉感知,主要包括可溶性糖、呈味有机酸、核苷酸、有机酸、无机离子、维生素等物质,但一般来说口味物质的焦点还是果实中的糖酸类物质,其决定了果实最重要的两个口味甜和酸^[6];后者通过嗅觉感知,由果实中大量的挥发性芳香物质混合构成,主要通过气味影响人们对枣果实的风味评价。枣果实风味实际上主要是由枣果实中含有的糖、酸和挥发性芳香物质共同作用,通过影响人们味觉和嗅觉形成的对枣果实品质的直接认知,是枣果实品质的重要组成部分。笔者从影响味觉和嗅觉两个方面的物质阐述枣果实风味的研究进展,重点从影响味觉中的甜味和酸味物质、嗅觉中的香气物质进行综述,在此基础上探讨了影响风味物质的重要因子,并对进一步研究方向进行了展望。

1 风味物质

1.1 糖类

糖分是构成枣果实营养和风味物质的基础材料,也是维持植物生命活动和果实生长发育的基础物质,此外还具有一系列重要的生理功能^[6],如提高

机体免疫力、抗氧化、抗肿瘤、护肝和胃肠保护等^[3,7-8]。

1.1.1 种类及含量 一般成熟鲜枣含糖量达30%，干枣含糖量更高，为60%~70%，干枣降低了水分活度，增加了糖分浓度，使得干枣具有更好的口感和更长的保质期^[4]，这也是制干枣在市场中更受消费者青睐的关键因素。薛晓芳等^[9]利用超高效液相色谱法对枣果实中可溶性糖组分进行了测定，认为完熟期鲜枣中主要是蔗糖(最多)、果糖(其次)和葡萄糖(较少)，其中蔗糖含量显著高于果糖和葡萄糖，占总糖的52.77%。高京草等^[10]在枣干果实上验证了这一结果，蔗糖含量甚至占到总糖的56.12%，并指出干枣中还有含量很低的山梨醇及鼠李糖、木糖与半乳糖的混合物，未检测阿拉伯糖，但彭艳芳等^[11]曾在‘金丝小枣’和‘冬枣’的鲜果中检测到少量阿拉伯糖。此外，孙涛等^[12]表明鲜枣还含有少量麦芽糖(0.22%~1.85%)。无论是干枣还是鲜枣，蔗糖、果糖、葡萄糖皆为其关键糖类，其中蔗糖含量最高。

1.1.2 发育时期与动态变化 不同成熟期枣果实中的蔗糖、果糖和葡萄糖含量呈动态变化。发育前期(幼果期)枣果实以积累果糖、葡萄糖为主，此期间糖分以质外体途径卸载，蔗糖被细胞壁酸性转化酶^[13]分解为果糖和葡萄糖，蔗糖含量少；发育中期(膨大期)蔗糖通过共质体途径卸载，同化物经胞间连丝卸载而未被细胞壁酸性转化酶分解导致蔗糖含量缓慢增加；发育后期(白熟期)蔗糖迅速积累升高，同时果糖和葡萄糖含量也较之前有所提高^[9,14]。章英才等^[15]研究认为，灵武长枣发育前期果实内糖代谢相关酶的净活性为负值，葡萄糖和果糖含量较高，此时光合产物大部分被酶分解用于细胞分裂、细胞代谢和形态建成；成熟期时酶的净活力值为正，蔗糖含量迅速升高。幼果期至白熟期过程中，枣果实中不同糖分的合成、代谢和运输过程受到相关酶的影响，导致不同糖组分含量呈动态变化状态。

1.1.3 糖分积累类型 果实糖分积累类型分为淀粉转化型、糖直接积累型和中间类型。枣属于糖直接积累型。但不同果实、同种果实不同品种间各糖组分比例差异较大，后又将糖直接积累型划分为蔗糖积累型、还原糖积累型和中间类型^[16]。‘壶瓶枣’‘婆婆枣’为蔗糖积累型果实，且‘壶瓶枣’积累蔗糖早于‘婆婆枣’，‘婆枣’果实糖分积累最晚，为己糖积

累型^[17]。薛晓芳等^[9]对20个枣品种完熟期鲜果糖分含量分析得出，近90%的品种属于蔗糖积累型，其中滕州长红枣的蔗糖含量最高，达到62.02%，山东梨枣和北京鸡蛋枣中果糖含量高于蔗糖，尤其是北京鸡蛋枣，果糖含量高出蔗糖含量近21%，属于果糖积累型。绝大多数枣果实蔗糖含量最高，属于蔗糖积累型，少部分品种蔗糖含量低于其他糖分，属于还原糖积累型和中间类型。

1.2 酸类

有机酸是枣果实品质的重要组成部分，也是决定风味的重要元素。它还具有多重药用价值，如杀菌消炎、抗毒抗癌等^[18]。多数水果以苹果酸或柠檬酸为主。

1.2.1 种类与含量 鲜枣中含有丰富的有机酸，如苹果酸、柠檬酸、酒石酸、琥珀酸、奎宁酸、草酸、富马酸、山楂酸、桦木酸、齐墩果酸和熊果酸等^[9,19]。不同枣品种间有机酸含量(w, 以鲜质量计)存在差异，如‘骏枣’以苹果酸($2.97 \text{ mg} \cdot \text{g}^{-1}$)、柠檬酸($2.67 \text{ mg} \cdot \text{g}^{-1}$)为主^[20]；‘灰枣’主要以苹果酸($2.16 \text{ mg} \cdot \text{g}^{-1}$)、柠檬酸($0.94 \text{ mg} \cdot \text{g}^{-1}$)和酒石酸($0.95 \text{ mg} \cdot \text{g}^{-1}$)为主，此外还含有少量草酸、乙酸和乳酸^[21]；‘彬县晋枣’($9.43 \text{ mg} \cdot \text{g}^{-1}$)和‘临猗梨枣’($9.04 \text{ mg} \cdot \text{g}^{-1}$)总酸含量相近，都以苹果酸为主，但‘彬县晋枣’的苹果酸($6.73 \text{ mg} \cdot \text{g}^{-1}$)含量是‘临猗梨枣’的2.06倍，而‘临猗梨枣’的琥珀酸($2.90 \text{ mg} \cdot \text{g}^{-1}$)含量是前者的5.62倍^[9]。干枣也含有有机酸，但与鲜枣含量差异较大。侯丽娟等^[22]研究制干‘阜平大枣’‘沧州金丝小枣’‘赞皇大枣’和‘枣强大枣’中有机酸(以干质量计)发现，苹果酸、柠檬酸、富马酸和琥珀酸均能被检测出，但含量较低，如‘阜平大枣’的苹果酸含量仅为 $0.068 \text{ mg} \cdot \text{g}^{-1}$ 。宋锋惠等^[23]、张萍等^[24]分别对新疆‘骏枣’和‘灰枣’有机酸研究并表示干枣总酸含量不足1%。由于干枣中酸含量较低且有些酸组分间不易分离，因此对枣果实有机酸的研究多集中在鲜枣。

1.2.2 发育时期与动态变化 枣果实发育过程中，有机酸含量呈显著的动态变化，不同品种间含量变化也存在差异。‘骏枣’果实在发育前期有机酸含量升高，成熟过程中降低，呈高-低的变化趋势^[20,25]，而‘嘉平大枣’在发育前期有机酸含量升高，成熟过程中逐渐降低，成熟期又逐渐累积，果实中有机酸含量随着果实的不断成熟呈现高-低-高的变化趋势^[26]，薛晓芳等^[9]研究的20个枣品种除‘山东梨枣’

‘冷白玉’和‘太谷鸡心枣’这3个品种有机酸含量在完熟期略有下降外,其余17个品种有机酸含量随果实发育不断升高,完熟期达到顶峰,苹果酸、奎宁酸和酒石酸的含量变化与总酸一致,完熟期有机酸含量的上升主要由苹果酸引起。

1.2.3 有机酸优势类型 根据水果中的优势酸种类,一般将水果分为苹果酸优势型、柠檬酸优势型和酒石酸优势型等三类,如苹果、桃、杏、火龙果、荔枝等属于苹果酸优势型;柑橘、菠萝、杨梅属于柠檬酸优势型;葡萄属于酒石酸优势型^[27]。多数枣品种属于苹果酸优势型,如‘骏枣’,苹果酸含量占45%^[20];另外‘新郑灰枣’‘彬县晋枣’‘晋赞大枣’‘山东梨枣’‘赞皇大枣’等枣品种,苹果酸含量均高于其他有机酸,都为苹果酸优势型;而‘稷山板枣’所含奎宁酸、‘太谷鸡心枣’所含琥珀酸均高于苹果酸含量,则不属苹果酸优势型,但目前关于其划分类别尚未明确^[9]。

1.3 香气

在世界范围内果实香气的研究逐渐成为热点^[28]。果实中大量挥发性芳香物质混合构成果实香气,不同水果其香气组分不同,一般分为果香型、清香型、醛香型、辛香型、木香型等。果实香气的研究主要集中在对人的嗅觉器官起作用的物质^[29],这类化合物称为特征效应化合物(character impact compounds),人的嗅觉器官能感受到的这种化合物的最小浓度值称之为风味阈值(threshold)^[5]。目前针对枣果香气研究较少。

1.3.1 形成部位与产生途径 果实中挥发性物质的形成部位主要在果皮,果实内部也可形成一些挥发性芳香物质,前者通过果皮向果实内部和外部扩散,后者在缺氧或细胞间隙中CO₂浓度较高时产生^[30]。王淑贞等^[31]对‘金丝2号’枣果实芳香物质的研究发现,对枣果去皮处理检测到38种香气成分,而不去皮处理检测到44种,种类差异较大,因此枣果芳香物质的研究中选择不去枣皮处理。

枣香气产生途径主要有两种,一种是生长过程中在酶催化作用下通过自身的代谢反应进行的生物合成。糖不仅是香气合成的主要前体,而且是果实香气的主要来源,羧酸能以酯的形式与糖结合形成香气,在酶的作用下,糖(如葡萄糖)也可以通过生物合成形成酯类,此外糖还可以实现甜味和香味之间的感官互动^[32-33];枣香气中的呈香物质—酮类化

合物,其在合成时通过脂肪酸在脂氧化酶作用下降解,在亚油酸和亚麻油酸氧化过程中生成酸类、酮类和其他中间体,易被枣中的其他酶转变为醇类和酯类等香味挥发物^[34]。另一种是对红枣进行人为加热或烘烤过程中形成的非酶反应香味物质。枣在干燥过程中发生美拉德反应(Maillard Reaction),通过非挥发性糖类、氨基酸与还原糖或羰基化合物之间发生缩合、脱水、降解和氧化还原等一系列反应形成具有特殊香气的化合物,其中枣香气成分中的5-呋喃甲醛就是由糖类分解生成的。

1.3.2 香气种类及动态变化 近年来,随着气相色谱-质谱联用(GC-MS)分析测试技术的发展和应用,枣果实香气研究取得很大进展。张富县利用GC-MS分析法鉴定枣的香气组分得到,‘金丝小枣’含54种,‘骏枣’含36种,‘灰枣’含39种,共有挥发物27种^[35];赵进红等^[36]研究发现‘泰山圆红’‘泰山长红’枣分别含有37、25种香气成分,主要分为醇类、酮类、醛类、酯类和酸类化合物五类,其中醛类含量最高、种类最多;闫忠心等^[37]和穆启运等^[34]以‘陕北木枣’与‘团枣’为研究对象,分别采用主成分分析法和GC-MS鉴定法,确定酯类、醛类、酸类和酚类为‘木枣’与‘团枣’挥发性物质的主要成分,并认为其主要影响红枣香气;烷烃类物质也属于挥发成分,但并不是主要的香气成分,陈恺等^[38]研究表明,鲜枣中烃类物质的含量远高于干枣,但其对香气成分贡献不大,醛类、酯类、酸类和酮类物质才是影响枣果实香气成分的关键因素;乙酸辛酯、3-甲基丁酸乙酯和戊酸乙酯是越橘香气的主要作用成分^[39],*(Z)*-3-己烯醛、1,8-十六烷醚和芳樟醇是柠檬番石榴的重要香气物质^[40];关于枣果实,张娜等^[21]研究表明2-己烯醛、邻苯二甲酸二甲酯及邻苯二甲酸-2-2-乙基己酯对‘灰枣’香气贡献最大。综上,醇类、酮类、醛类、酚类及酸类是影响枣果实香味的主要成分,烷烃类物质虽然是挥发性物质,但对枣果实香味贡献较小。

枣果实不同的成熟期其挥发性成分和含量有差异,Song等^[33]用HS-SPME/GC-MS法研究发现,绿熟期、白熟期、半红期、全红期的香气物质种类分别为22、25、24、27种,醛类物质贡献最高,其中(E)-2-己烯醛含量最高,并且从绿熟期(169.2 μg·kg⁻¹)到全红期(733.4 μg·kg⁻¹)表现出显著的增长趋势,王淑贞等^[31]研究冬枣鉴定出49种挥发性物质,青白期、

半红期、全红期和浆果期分别含有 13、23、8、13 种，随着果实成熟，酯类物质含量不断下降，醇类、烷烃类等物质含量不断升高，最终导致果实品质下降。不同成熟期香气物质种类及含量的变化直接导致枣果香味受到影响，进而通过嗅觉影响消费者对枣果实风味的感官评价。

2 风味影响因子

2.1 土肥水

枣种植业遍布全国，以新疆和黄河中下游地区枣果实口感最为优良，除与品种有关外，土壤类型也对枣果实风味有重要意义。位杰等^[41]研究表明，适度的复合盐碱胁迫可增加枣果实可溶性糖含量，降低有机酸含量，糖酸比增大，枣果实风味提升。郑强卿等^[42]研究干旱沙漠区灌溉量对骏枣的影响表明，65%的灌溉量可有效提高枣果实中 5.52% 的可溶性糖含量。果实中含有丰富的矿质营养元素，与果实风味有着密切的关系，其主要依赖于根系、叶片从土壤或叶面对这些元素的吸收、运输及分配能力^[43]。钾肥素有“品质元素”之称，唐都等^[44]研究发现，速效钾与枣果实中的可溶性糖、可溶性蛋白和 Vc 含量呈显著正相关关系，土壤中速效钾的含量可作为预测枣果实品质的参考指标。杜振宇等^[45]研究钾肥对冬枣的影响中得到，施钾肥（每株 0.1 kg）可提高冬枣的可溶性糖、可溶性固形物含量及糖酸比，并且显著降低了可滴定酸含量，此外尹鸿飞等^[46]发现叶面喷施 SOD 也可提高冬枣可溶性糖含量，降低有机酸含量；氮素作为营养元素对植物的光合作用有重要作用，施加氮肥能够提高光合效率并促进光合产物的分配与运转，进而提高枣果实中糖含量，彭玲等^[47]研究发现，冬枣物候期进行四次分施氮肥能够延长肥效，提高枣树根系对氮素的利用效率，有利于果实风味的提高。氮磷钾作为枣树生长的三大关键营养元素，其含量水平能协同影响枣果实的风味。当磷、钾含量为中等水平时，高氮处理可使枣果实总糖含量提高 2.1%，但酸也会有所增加；当氮、磷为中等水平时，高、中钾处理可使总糖含量分别提高 2.4%、1.4%^[48]。因此，控制合适的施肥量和施肥比例对枣果实风味有重要的影响。

2.2 气象因素

气候因素对枣果实风味有重要影响，其影响程

度高于土壤因子^[49-50]。温度、湿度、光照、降雨量等气象因素对枣果实风味的影响程度不同^[51]。‘骏枣’受平均气温、平均最高温度、日照时数和降水量的影响较大，其中 Vc 受空气平均最低温度的影响较为明显，可溶性总糖与总酸含量与温度显著相关，随着温度的升高，糖酸比增大，枣果实口感提升。光照强度是影响枣果实口感的关键因素，光强和光质除对色泽和花青素苷有影响外，对枣果实酸甜度也有一定的促进作用^[50]。枣果实中的部分营养元素（如 Ca、Zn）通过根系从土壤中吸收，改善气候条件使温湿度产生变化可以调控矿质元素的含量进而影响枣果实风味，如阴面处理有利于土壤中氮素的富集，氮素又作为营养元素通过影响枣树的光合作用提高枣果实中的糖含量，提升果实口感^[51]。不同的地域特征导致环境条件存在差异，气候因子影响枣树的生长和枣果实的风味，为不同枣品种选择适宜的栽培区域对枣果实的风味提升具有重要的意义。

2.3 制干工艺

不同制干工艺对枣果实的品质有很大影响，制干过程中果实中的营养成分和风味成分因制干方法的不同具有差异性^[52]。丁胜华等^[53]研究不同干制方法对金丝小枣中糖类物质的影响发现，热风干燥处理后枣果实中果糖和葡萄糖含量显著升高，微波干燥后蔗糖和葡萄糖含量显著降低，经日晒处理后枣果实中山梨醇含量达到最低，此外，所有制干方法均导致果实内山梨醇和蔗糖含量的降低，尤其是蔗糖的含量。另外，冷冻干燥法、空气干燥法、日晒法、微波干燥法都会降低枣的抗氧化性、醛、酸和烷烃含量，提高酯类的含量^[54]。枣中含有大量糖类，干制过程中果糖、葡萄糖及还原糖含量呈上升趋势，蔗糖等非还原糖及可溶性总糖呈下降趋势，随着制干温度的升高，枣果实中还原糖及总糖的含量降低，为香气的形成提供了良好的物质基础^[55-56]。干制温度也会影响枣中酸的含量，鲜枣在干制过程中随着干制温度的升高苯甲酸和山梨酸含量升高^[57]。制干过程中枣果实香气成分也会发生变化，吕姗等^[56]研究发现，未烘干的大枣中酸类物质是其主要的挥发性物质，其种类和相对含量最高，高温烘干过程中，醛类、酮类及醇类物质含量升高，温度达到 140~160 °C 时酸类物质相对含量迅速下降，但种类变化不明显，此时醛类物质成为主要的挥发性物

质。综上,不同的制干方法、制干温度都会影响枣果实中糖、酸、香气物质的含量,进而影响枣果实风味,研究最适宜的制干工艺对干枣的品质改良、口感优化及鲜枣的深加工产业具有重要的指导作用。

3 研究展望

目前对枣果实风味的研究,主要关注于枣果实糖酸类物质的组成、含量及其动态变化,并深入探讨其形成途径、影响因素和对品质形成的作用,取得了显著的成果,而对于枣果实中挥发性芳香物质的研究略显不足,主要针对部分枣品种开展了初步研究。近年来,消费者对枣果实品质的要求不断提高,枣果实风味作为枣果实品质的重要组成部分会越来越受到重视。因此,在枣果实风味的研究中仍需在以下方面进一步深入:(1)对枣果实中糖、酸与香气物质的转换条件、转换关系、转化机制仍然较为模糊,若能深入研究,将会解决枣果实风味及品质的保持、提升等一系列问题。(2)加强枣果实中挥发性芳香物质及其变化研究,并探寻关键香气成分,将使得枣果实风味和品质的评价更为全面和准确,并带动枣果实香气成分的进一步利用研究。(3)新疆南疆作为全国最大的制干枣栽培区,其独特的自然条件造就了枣果实明显优于内地的风味,深入研究其风味差异及其影响关键因子,对于引种更多优良枣品种及内地枣的品质提升具有重要的意义。

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