

Accumulation pattern of oleoresin and related chemical constituents in black pepper (*Piper nigrum*) berries during growth and development

03-20 MAY 1981

C. E. T. R. I., Mys

C.K. MATHAI

Central Plantation Crops Research Institute, Regional Station, Vittal 574 243, Karnataka, India

(Received 7 December 1979; in revised form 5 February 1981)

Keywords: oil, oleoresin, *Piper nigrum* L., piperine, starch

Abstract. The accumulation pattern of various chemical constituents of commercial importance in black pepper berries of two cultivars has been studied. Oleoresin, piperine, essential oil and starch show a manifold increase, one to two months before complete maturity of the berries. The possibility of its commercial exploitation is discussed.

Introduction

Piper nigrum L. is a major spice crop of the orient. Black pepper of commerce, the well-known spice, is the matured, dried berry of the above climbing vine of the Piperaceae family. This is a plant of the humid tropics. Though a number of cultivars exist, the commercial pepper is a mixture of these varieties.

Black pepper is enjoyed for its biting pungency and spicy aroma. It is used in the manufacture of 'prepared oleoresins', whose use in place of whole spice is becoming more and more popular in the food industry due to many major advantages. The essential oil of this spice is an important ingredient in food flavourings and perfumery. The starch content of black pepper, although not contributing towards the flavour of this spice, is quite important in the manufacture of powdered spice.

Oleoresin is a natural plant product consisting of a resin dispersed in an essential oil. Spice oleoresin is an extremely concentrated produce that is obtained by solvent extraction and should contain all the flavouring ingredients (related to taste and smell) soluble in that particular solvent. Essential oil is a volatile substance contained in the special cells, glands or ducts, in one or several parts of certain aromatic plants, that imparts distinctive odour. In spices, oleoresins represent the complete spice flavour whereas essential oils only the aroma.

Besides the organoleptical aspect of this spice [9, 19], research has also been done on the various chemical aspects of piperine and related pungent alkaloids [4, 5, 13, 14, 16, 17, 19]. Berries, stalks and husks of cultivated varieties of black pepper as well as the commercial grades of this spice have also been examined for their chemical constituents [6, 7]. The accumulation

pattern of oleoresin and other chemical components of commercial importance during growth and development in various spices is an interesting topic of study, which was carried out in important ginger cultivars (*Zingiber officinale* Roscoe) [12]. The present study is of a similar nature in black pepper.

Materials and Methods

Two healthy, normal black pepper vines of eight years' growth, one a hybrid variety Panniyoor-1 and the other an unnamed local variety grown under normal cultivation practices and climbing on the trunks of mango trees in the farm of the Central Plantation Crops Research Institute, Vittal, were selected for this study. Collection of berries was started 3.5 months after flowering, at regular 30-day intervals.

The cross-flow-air oven-dried berries (at $55^{\circ} \pm 2^{\circ}\text{C}$) were ground in a Multiplex grinding mill and stored in glass jars for immediate chemical analysis.

Acetone being the common laboratory solvent for oleoresin extraction, these samples were extracted in 100% acetone, by the cold percolation method, using 10 g well-mixed, ground sample for each determination. The solvent was allowed to evaporate in vacuum. Piperine was estimated spectrophotometrically, after extracting into and further dilution in chloroform, at 345μ [8]. Starch and essential oil contents were determined by using the American Spice Trade Association (ASTA) methods [1, 2]. Crude fibre was estimated from the defatted samples by using the Association of Official Analytical Chemists (AOAC) methods [3].

Results and Discussion

Oleoresin

The black pepper flavour is represented by a combination of volatile and non-volatile constituents. The commercial spice flavour representative of black pepper is known as Oleoresin Black Pepper. Oleoresin, present in the oleoresin cells in the outer part of the fruit wall [10], is extracted after rupturing the above cells along with the principal pungent component piperine present in the cell vacuole by using chlorinated organic solvents, since piperine is most soluble in such solvents [15].

Studies similar to the present one conducted in ginger show an almost linear fall in oleoresin percentages towards maturity [12], whereas in this spice, it shows a steep rise towards the middle and a sudden fall thereafter of the above constituent (Fig. 1). It was further observed that the hybrid is rich in oleoresin almost throughout the berry development.

Though the oleoresin manufacturers prefer commercial grades of berries having a higher content of this constituent, such high yielders of oleoresin.

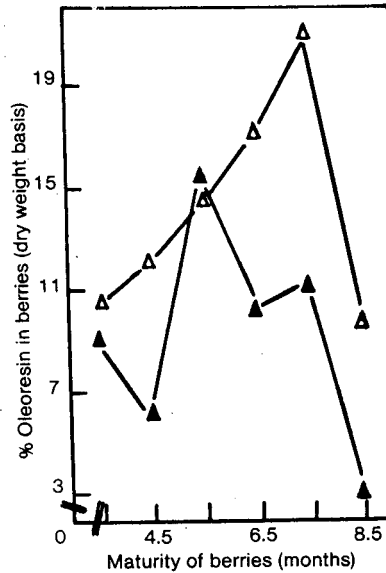


Figure 1. Accumulation pattern of oleoresin during the development of black pepper berries. Varieties: Δ Panniyoor-1 (hybrid); \blacktriangle local.

need not necessarily be rich in pungent constituents. Various types of black pepper berries collected from the Western Ghats forests showed piperine and oleoresin contents to be independent of each other [12a].

Starch

Starch constitutes about one-third of the weight of a mature berry. A sudden rise of this constituent towards maturity may well be connected with the almost proportionate fall in oleoresin percentage during the same stage of development of the berry. Figures 1 and 2 show that an early fourfold increase in starch does not cause a fall in oleoresin content; in fact the resin content rises. The late fall in oleoresin content at 7.5–8 months in the unnamed local variety is associated with a relatively small starch change. These observations further suggest an early harvest of black pepper for a doubly increased oleoresin yield, though it will be of disadvantage to the powdered-spice manufacturers.

Crude fibre

Early work in ginger cultivars has shown the crude fibre percentage to fall with maturity. This character was also found to be positively correlated with the oleoresin content in ginger [12]. In black pepper, this does not seem to

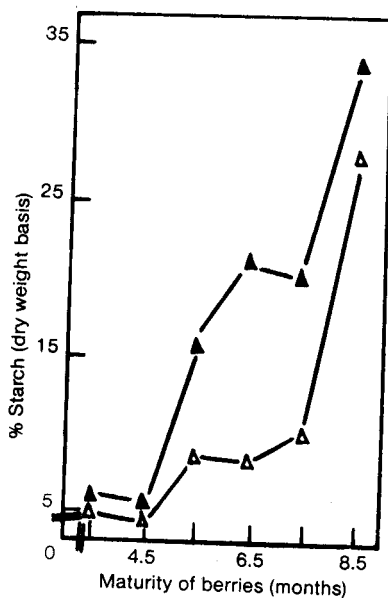


Figure 2. Seasonal accumulation of starch in black pepper berries.

be true throughout, except in the latter half when both the constituents show a similar rate of fall in their concentrations. During the former half of berry development, a steep fall in the concentration of crude fibre corresponds to a similar rise in starch content (Figs. 2 and 5). This to some extent may be due to the interconversion of these two constituents. It is also quite interesting to note the sudden fall in crude fibre percentage during the first half related to an almost similar rise in oleoresin and piperine content in both oleoresin and berries (Figs. 1 and 3–5).

Piperine

Pungency in black pepper is known as 'bite'. This is attributed to a group of alkaloids belonging to the piperidine group. Piperine – $(C_{17}H_{19}NO_3)$ -trans-5-(3,4-methylenedioxyphenyl)-2,4-pentadienoic acid piperidide – is the predominant alkaloid among them. *Piper nigrum* is the known rich source of this alkaloid. This yellow crystalline material is present in about the 5% level in cultivars. Pyrroperine ($C_{16}H_{17}NO_3$), piperanine ($C_{16}H_{21}NO_3$) and piperattine ($C_{19}H_{21}NO_3$) are the other related minor alkaloids of this group present in negligible proportions. The present part of the study is concentrated on the main pungency donor, piperine.

In berries

The general pattern of accumulation in berries of the two varieties studied during development appears to be very much similar to that of oleoresin

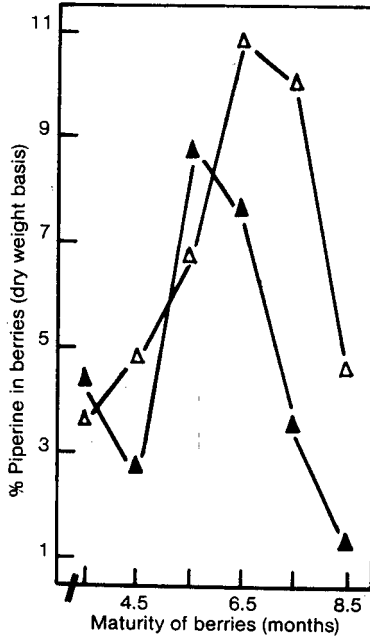


Figure 3. Piperine accumulation in black pepper berries during development.

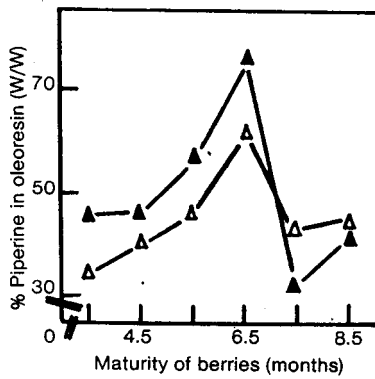


Figure 4. Piperine content in the oleoresin samples extracted at various stages of berry development in black pepper.

(Figs. 1 and 3). Here again the starch accumulation seems to have greatly affected the piperine percentages towards maturity. From the commercial point of view, harvesting about a month earlier could be recommended for

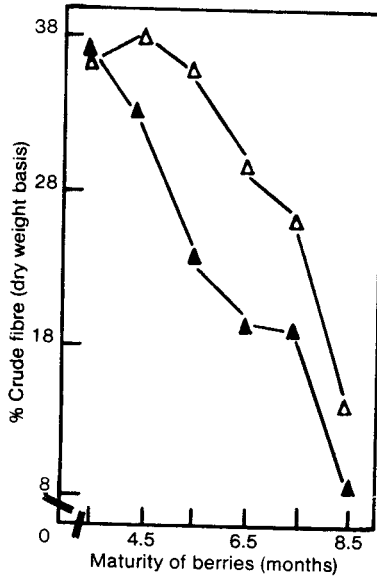


Figure 5. Accumulation pattern of crude fibre in the developing berries of black pepper.

an eight- to tenfold increase in piperine content. The optimum time of harvest will vary according to the physical factors prevailing in the pepper-growing areas, which is to be determined in various cultivars for the maximum return.

In oleoresin

Piperine content in oleoresin is the most important factor from the aspect of commercial utilisation. The oleoresin samples extracted from 6.5-month-old berries are doubly pungent (Fig. 4). This tendency seems to be true in both varieties under study. The local variety is much superior in piperine content of oleoresin almost throughout the course of berry development.

Essential oil

This valuable constituent is found in general at about 1.5%–3.5% levels in the common cultivars. The oil cells are found in the inner part of the fruit wall [10]. An increase in the essential oil content up to 7.5 months of development may be due to the proportionate increase in the area of oil-bearing cells in the inner part of the fruit wall. Like other constituents mentioned above, this also shows a falling tendency towards maturity (Fig. 6).

The importance in selecting the proper variety of a spice for oil and oleoresin extraction has been discussed [11]. From the flavour point of view, starch and crude fibre contents are of least importance. Hence, while selecting a proper variety, determining the optimum harvesting time to obtain a

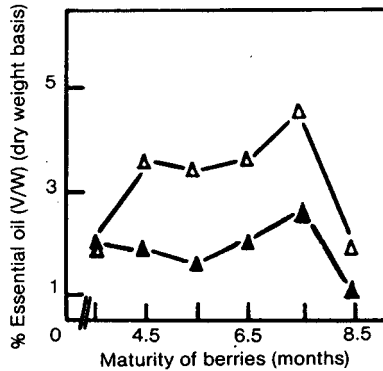


Figure 6. Essential oil accumulation pattern in black pepper berries during development.

manifold increase in the above constituents of commercial importance should be given priority by the oleoresin manufacturers.

References

1. Anonymous (1968) Steam volatile oil (modified Clevenger method). In: Official analytical methods of the American Spice Trade Association, 2nd edn. Englewood Cliffs NJ: American Spice Trade Association, Inc, p 8
2. Anonymous (1968) Starch (direct acid hydrolysis). In: Official analytical methods of the American Spice Trade Association, 2nd edn. Englewood Cliffs NJ: American Spice Trade Association, Inc, p 18
3. Anonymous (1970) Crude fibre. In: Official methods of analysis, 11th edn. Washington DC: Association of Official Analytical Chemists, p 513
4. Cleyn R de, Verzele M (1972) Constituents of peppers. I. Qualitative analysis of piperine isomers. *Chromatographia* 5:346-350
5. Cleyn R de, Verzele M (1972) Constituents of peppers. II. Piperinic acid and its isomers. *Bull Soc Chim Belg* 81:529-531
6. Dwarkanath CT, Ramachandra Rao TN, Johar DS (1961) Chemical analysis of some varieties of Indian pepper (*Piper nigrum* L.), II. *Food Sci* 10:1-2
7. Dwarkanath CT, Ramachandra Rao TN, Johar DS (1963) Chemical analysis of pepper varieties, stalks, and husks. *Spices Bull* (Annu no.) 21-26
8. Fagan HJ, Kolen EP, Hussong RV (1955) Spectrophotometric method for determining piperine in oleoresins of black pepper. *J Agric Food Chem* 3:860-862
9. Govindarajan VS, Dhanaraj S, Shanthi N (1973) Evaluation of spices and oleoresins. III. Evaluation of some horticultural varieties and trade types of pepper. *J Plantation Crops* 1:8-16
10. Hardman R (1972) Spices and herbs; their families, secretory tissues and pharmaceutical aspects. In: Nabney and Mathews (eds) *Spices*. Proceedings of the conference on spices, 1972. London: Tropical Products Institute, pp 23-33
11. Lewis YS (1972) The importance of selecting the proper variety of a spice for oil and oleoresin extraction. In: Nabney and Mathews (eds) *Spices*. Proceedings of the conference on spices, 1972. London: Tropical Products Institute, pp 183-185
12. Mathai CK (1975) Seasonal accumulation of chemical constituents in ginger varieties (*Zingiber officinale* Roscoe). *J Plantation Crops* 3:61-64
- 12a. Mathai CK, Kumaran PM, Chandy KC (1980) Chemical evaluation of wild black pepper types. *Qual Plant Plant Foods Hum Nutr* 30:199-202

13. Oerstedt (1820) Über des piperin, ein neues Pflanzenalkaloid. Schweigers J Chem Physics 29:80 [Quoted from Rogers JA, 1966]
14. Ott E, Eichler F (1922) Natürliche und künstliche Pfefferstoffe. II. Über des chavicin des Pfefferharzes den vorzugsweisen Bestandteil des schwarzen Pfeffers. Berichte Dtsch Chem Gesellschaft 55:2653-2663 [Quoted from Fagen et al., 1955]
15. Rogers JA (1966) Advances in spice flavour and oleoresin chemistry. In: Gould (ed) Flavour chemistry. Proceedings of the symposium sponsored by the Division of Agricultural and Food Chemistry at the 149th meeting of the American Chemical Society, Detroit, 1965. Washington DC: American Chemical Society, pp 203-224
16. Spring FS, Stark J (1950) Piperettine from *Piper nigrum*: its isolation, identification and synthesis. J Chem Soc (April): 1177-1180 (paper no. 241)
17. Traxler JT (1971) Piperanine, a pungent component of black pepper. J Agric Food Chem 19:1135-1138
18. Yamamoto Y (1974) Studies on the pungent constituents in black pepper (*Piper nigrum* L.). IV. Pungency of piperine. J Food Sci Technol (Tokyo) 21:579-584
19. Yamamoto Y, Torari, Mori K (1974) Studies on the pungent constituents in black pepper (*Piper nigrum* L.). III. Piperine isomers. J Food Sci Technol (Tokyo) 476-482