New Sources of Natural Safrole

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Safrole is a phenylether (Figure 1) which occurs as a component of the volatile oil in many plant species. In its pure form, it is a mobile liquid with a camphoraceous aroma at ambient temperature.

The earliest extensive use of natural safrole was as a flavoring for root beer and sasparilla beverages in the United States,[1] but this was dicscontinued in 1958. Another early application was as a fragrancing agent in a range of products which include floor waxes, soaps, glues and disinfectants.

Today, the two major outlets for natural safrole lie in its chemical conversion to heliotropine, a fragrance compound, and piperonyl butoxide (PBO). The latter plays a critical role as a synergist for natural pyrethrum-based insecticides which alone are much less effective. In several countries, natural pyrethrum/PBO mixtures are the only formulations permitted for use in food stores and food processing industries. Demand is growing also in the retail insecticide market owing to the 'soft' (biodegradable) characteristics and 'green' image of these mixtures.

Demand

Recent worldwide consumption of natural safrole is estimated at 2,000 tons per annum. The PBO and heliotropine outlets appear about equal and jointly account for 75% of total consumption.

Heliotropine, from natural safrole, is manufactured principally in Japan and China while smaller scale operations exist in Spain, the USA and Brazil.

Italy is the largest PBO producer and is followed in importance by Japan. There is a smaller scale production in Brazil.

The United States is the largest market for other uses of natural safrole.

Supply

Natural safrole is a 'non-timber forest product' which is obtained by the destructive harvesting and steam distillation of the wood of wild growing species of *Lauraceae*. The product, containing in excess of 84% safrole, is traded as 'sassafras' oil. This name originates from the earliest source, the roots of *Sassafras albidum* (Nutt) Nees, a tree which is indigenous to the Appalachian Mountains of the United States.[1,2]

The sassafras oil industry in the United States steadily declined after the entrance of Japan to the market in the early part of the 20th century. The Japanese oil was derived from varieties of the camphor tree (*Cinnamomum camphora*), harvested principally on the then province of Formosa. Comminuted stem, branches and roots were steam distilled to obtain a crude oil (yield 2%) from which camphor was first isolated and then other fractions, including a 'sassafras' oil with a safrole content of 90%.

The cessation of trade with the Far East during World War II stimulated production in the state of Santa Caterina in southern Brazil, based on the trunk wood of wild growing trees of *Ocotea pretiosa* (Nees) Mez, syn. *O. cymbarum*. The Brazilian product is obtained in a yield of about 1% and contains a minimum of 84% safrole. Annual production peaked at 2,500 tons in 1970. Thereafter, renewed competition from the Far East, together with fewer and more remote large trees, led to a reduction in output to between 1,000 and 1,500 tons of oil annually. Nevertheless, Brazil remained the main sassafras oil exporter until 1991.

China is the major Far East producer of sassafras oil today. The industry is based on destructive harvesting of *C. camphora* varieties in Jiangxi and other southern provinces. The annual production was around 1,000 tons in the late 1980s. A significant proportion of the output is consumed by the domestic chemical industry[3] while Japan has been the major export market.

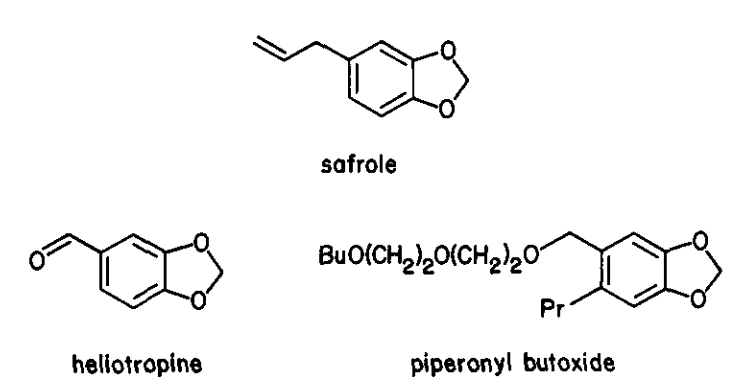

Figure 1. Safrole and its derivatives

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Vietnam entered into production around 1990, using stumps of *C. camphora* trees killed by Agent Orange during the war in the 1960s. Output is expected to peak at around 200 tons per annum within a few years and then to rapidly decline as the resource is expended.

In 1990, total world production of sassafras oil was perhaps 2,000 tons and roughly in balance with demand. Prices (FOB) had in fact remained fairly stable at around US$4/kg for a decade.[4,5]

The supply situation changed dramatically during 1991. A Brazilian Presidential Decree banned the felling of *Ocotea* sp. in the primary forest of the Mata Atlantica, while in China restrictions were imposed on *Cinnamomum* harvesting at the same time that domestic production of heliotropine increased. Toward the end of 1991, supplies to the international market virtually dried up and spot prices were approaching US$13/kg.

In early 1992, supplies improved when Brazil eased its felling controls and China redirected its production to the export market in order to acquire foreign exchange. However, the events of 1991 had confirmed the worst fears of industries based on sassafras oil over their strategic dependence on raw material resource that could not be managed sustainably.

An increased market penetration by heliotropine derived from the totally synthetic route is expected in future. In the case of PBO, however, the economics of total synthesis remains questionable and sustained shortages of sassafras oil could have a severe impact on natural pyrethrum-based insecticides and, by implication, pyrethrum producers such as Kenya.

Alternative Sources of Natural Safrole

This topic has been the subject of investigations in a number of countries for many years but the options appear relatively limited.

Considerable screening work has been devoted to the *Cinnamomum* family. For example, *C. iners* and *C. parthenoxylon* in Malaysia[6] and *C. rigidissum* on China's Hainan island[7] contain significant safrole contents in their wood oil but exploitation would be dependent either on destructive harvesting or the questionable economics of coppicing. A more promising alternative has been reported in China with *C. petrophilum,* whose leaves furnish a 97% safrole content oil in a yield of 3-4%.[8]

In South America, the natural range of *Ocotea pretiosa* extends from southern Brazil, through Paraguay to Colombia. It is unlikely, however, that non-Brazilian sources will be exploited because of either conservation legislation or the unsuitability of the chemotypes.[9]

Among the flora of Latin America, certain forest shrubs of the Piperaceae family offer better prospects as new sources of safrole. *Piper auritum* HBK, which occurs from Mexico to Panama, contains around 70% safrole in its leaf oil.[10-13] Pilot-scale cultivation and distillation trials were conducted on this species in the mid 1980s at the Regional National Resources Institute (INIREB) at Xalapa, Veracruz State in Mexico. The work ceased on the closure of INIREB.

Several *Piper* species indigenous to the Brazilian Amazon possess a safrole content of 70% or more in their leaf oil.[14-16] The remainder of this paper is devoted to a progress report on their development.

Trials with *Piper* Species in Brazil

The current trials in Brazil involve two previously unexploited species, *P. hispidinervium* and *P. callosum.* This work is a component of a larger project which has as its objective the evaluation of essential oil crops for new sustainable agro-forestry systems in the Brazilian Amazon.[17] The project was initiated in late 1990 and is funded by the United Kingdom's Overseas Development Administration (ODA) under its Amazon Forestry Initiative. Supplementary funding for the *Piper* species sub-project has been provided by three private-sector companies: Endura Spa (Italy), Takasago International Corporation (Japan) and Roussel Uclaf Environmental Health Ltd (United Kingdom). These companies have a strategic interest in the long-term supply of natural safrole.

The *Piper* species project is led by the Museu Paraense Emilio Goeldi in Belem, State of Para, and involves the collaboration of EMBRAPA-CPAF, a unit of the national agricultural research organization, based in Rio Branco, State of Acre. Technical cooperation inputs are being made by several scientific organizations in the United Kingdom under the leadership of the Natural Resources Institute (NRI), the Executive Agency of the ODA.

The work with both of the *Piper* species encompasses: studies of biology and provenance characteristics in their natural habitats; propagation methodology research; and field management trials on two research stations with differing climates and soils in the Belem area. The yield and quality of the oil obtainable from leaf and stem harvested from the research plots is being determined by distillation of 10-30 kg loads on pilot-scale equipment, manufactured locally from designs provided by E.F.K. Denny.[18]

The following paragraphs summarize the information acquired for both *Piper* species by mid 1992.

P. hispidinervium: This is a large (3 meter high), woody-stemmed shrub which occurs on the forest margins in the vicinity of the town of Rio Branco, State of Acre in the southeast of the Brazilian Amazon. Leaf harvested from wild, mature plants possesses 3-4% of volatile oil (calculated on a moisture-free basis) with a safrole content of 81-88%. It is not yet known whether these variations represent provenance differences or arise from the season of harvesting.

Plants, raised from rooted cuttings, have been established on unshaded research plots. By eight months, growth to a height of 1 meter is achieved and the first cropping of leaf and stem is practiced. Subsequent observation of plant regeneration suggests that sequential harvesting might be possible at six-month intervals.

On the first harvesting trials with cutting at 20 cm above ground level, the fresh biomass yield (leaf plus stem) averaged 0.5 kg per plant and the oil content was 4.7 ml.

The safrole content of the distilled oil was 81%.

Extrapolation of these preliminary yield results suggests that a 1 hectare area with 28,000 plants would furnish on the first cut 100 kg of oil at a distillation efficiency of 80%. Such a yield would compare favorably with certain species of 'medicinal-type' eucalyptus whose essential oil has a similar unit value to sassafras oil.[19]

The distillation characteristics of *P. hispidinervium* have been found similar to that of the mint (*Mentha*) family; cut leaf and stem must be wilted to below 30% moisture content to achieve high oil recoveries. However, the safrole content of the oil is virtually constant during the course of distillation and this implies that no great skill is demanded of the processor in achieving product of a marketable quality. Quality will be dependent instead upon the germplasm characteristics and any field management factors.

Piper callosum: This species is indigenous to the State of Para, northeast Amazon region. It is a small (1 meter high), self-layering shrub with glossy leaves. It grows under the shade of forest trees. Only one provenance has been examined as yet and its leaf contains about 3% volatile oil (calculated on a moisture-free basis) with a safrole content of 70%. Chemotypes with a superior, more marketable safrole content are being sought from other areas of occurrence in Para.

Field management trials with *P. callosum* are less advanced than for *P. hispidinervium*. Poor growth is displayed in open field situations and trials are now concentrating on interplanting among trees. In its natural habitat, *P. callosum* appears capable of sustaining cropping of leaf and stem at about six-month intervals.

Developmental application: *P. hispidinervium* shows particular promise as a first crop in rehabilitating degraded forest land for sustainable agroforestry developments. It tolerates open situations and poor soils and should provide a cash income within one year of planting. This early cash flow would allow farmers to await the returns from intercropped trees.

The probable application for *P. callosum* lies as a lowerstory crop under the shade of established trees. In plantations of cash crop trees, it could provide an additional source of income and, possibly, facilitate weed control. Alternatively, it could be cultivated within the undeveloped secondary forest which many farmers have on their land, particularly in the State of Para.

As noted earlier, processing skills are not beyond the capabilities of farmers. Also, investment in distillation equipment should be within the resources of some individual farmers or of cooperatives. Models for this form of production exist with mint oil (*Mentha arvensis*) in the Parana areas of Brazil and Paraguay and with petitgrain oil in Paraguay.[20,21] Marketing systems in Para and Amazonas states could be developed, perhaps, to interlock with the existing trade structures for rosewood and copaiba balsam oils.

These developmental facets will be examined more closely during 1993, subject to a positive techno-economic appraisal of the *Piper* field trials.

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