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NOTES ON TWO MENTHA HYBRIDS GROWN IN THE PHILIPPINES

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ABSTRACT

Two hybrid mint plants are included in this report: a hairy strain of *Mentha cordifolia* Opiz (*M. rotundifolia* x *spicata*) and a strain of *M. piperita* L. (*M. aquatica* x *spicata*).

The first plant, collected in Surigao, closely resembles the plant previously identified by the author as *M. cordifolia* Opiz and is reported to have been introduced by the Japanese. The volatile oil of the plant is of the type containing chiefly 2-oxygenated cyclic monoterpenes.

M. piperita is a native of temperate regions and it has been continuously growing in the pharmacognosy garden in the UP Diliman campus for the last twenty-one years but it has never flowered under Philippine daylengths. The volatile oil is of the type containing chiefly 3-oxygenated cyclic monoterpenes. The composition of the oil of the flowering plant supports the previously postulated biosynthetic pathway in *M. piperita*.

Introduction

The genus *Mentha* includes perennial herbs with creeping underground stems and characteristically aromatic foliage (Clapham, *et al.*, 1962). It belongs to the family Labiatae (or Lamiaceae) which includes herbs, less often shrubs, distinguished by quadrangular stems, opposite leaves, and fruit of four nutlets. It is a very natural family, usually recognizable at sight. The Labiatae are frequently aromatic and have a characteristic odor.

The flowers of *Mentha* species are aggregated into whorls which are borne on the axils of leaves or which form a terminal spike-like or head-like inflorescence. The species are very variable and hybridize freely. Propagation is largely vegetative and even sterile hybrids can persist and be dispersed so that hybrids may be found away from their parents and the parentage of many of them is in doubt (Clapham, *et al.*, 1962). Some cultivated mints easily become naturalized or can cross with wild species to produce a series of spontaneous hybrids which blur the distinction between what is native or introduced (Harley, 1973).

In the genus *Mentha*, almost 2,300 names have been published for essentially 20 species; possibly 50% of these are synonyms, the remaining, legitimate infraspecific names (Tucker, *et al.,* 1980). *M. x cordifolia* Opiz and *M. x piperita* L. are natural hybrids, in contrast to artificial hybrids which were created to select hardy individual strains which combine a useful fragrance with a high yield of volatile oil, to determine the parentage of cultivated hybrids, and to assist in understanding the biosynthesis of the volatile oil constituents. Peppermint (*M. x piperita*) is the most widely cultivated of all the mints. As a consequence, it is very widespread around the world as a garden escape (Lawrence, 1978).

More than any other genus of comparable size, *Mentha* poses problems of identification and classification (Harley, 1973). The use of modern methods such as feeding with labeled precursors and gas chromatography to analyze the aromatic mint oils has provided new characters to assist the taxonomist in his classification. Chromosome counts, as well as data from breeding experiments, used in conjunction with orthodox taxonomic procedures, have been available in elucidating the taxonomy of *Mentha* (Harley and Brighton, 1977). As a result, changes from the traditional classification have been adopted and nomenclatural changes have become necessary.

I. Surigao Mint [*Mentha x cordifolia* Opiz (?)]

Characteristics of the Plant

A strain of mint was found being cultivated in home gardens in Surigao which is called "yerba buena" by the natives. The plant resembles yerba buena, previously identified as *M. x cordifolia* Opiz (Cantoria, 1980). The Surigao strain is distinguished from yerba buena by its hairy leaves (Fig. 1) and spearmint odor. Under long-day conditions, simulated by two hours of light in the middle of the night, the plant flowers, producing a terminal spike (Fig. 2). Surigao mint appears to be a hairy strain of *M. x cordifolia.*

Dry Weight Production, Oil Yield, and Moisture Content

The plant is being grown in 6 x 1.5 m plots, fertilized with complete fertilizer once a month, and watered and cultivated regularly. Tops are collected weekly and sorted into tops with the first to the sixth pairs of leaves intact (younger tops) and parts with the seventh to the tenth pairs of leaves intact (older tops). The youngest pair of visible leaves is counted as the first pair. The plant materials are spread on table tops to dry for four days then weighed and distilled with water to obtain the volatile oil. Moisture determinations are also done except when there is not enough sample, which is quite often in the case of the older tops.

Dry weight production varied from 5.44 g in May 1985 to 16.20 g in September 1984 per 100 tops with the first six pairs of leaves intact (Table 1). Based on the moisture-free weight, the oil yield of younger tops varied from 1.87% in February 1985 to 3.65% in April 1985. The oil yield from older tops was less, ranging from 1.20% to 2.18% in September 1984, based on the moisture-free weight.

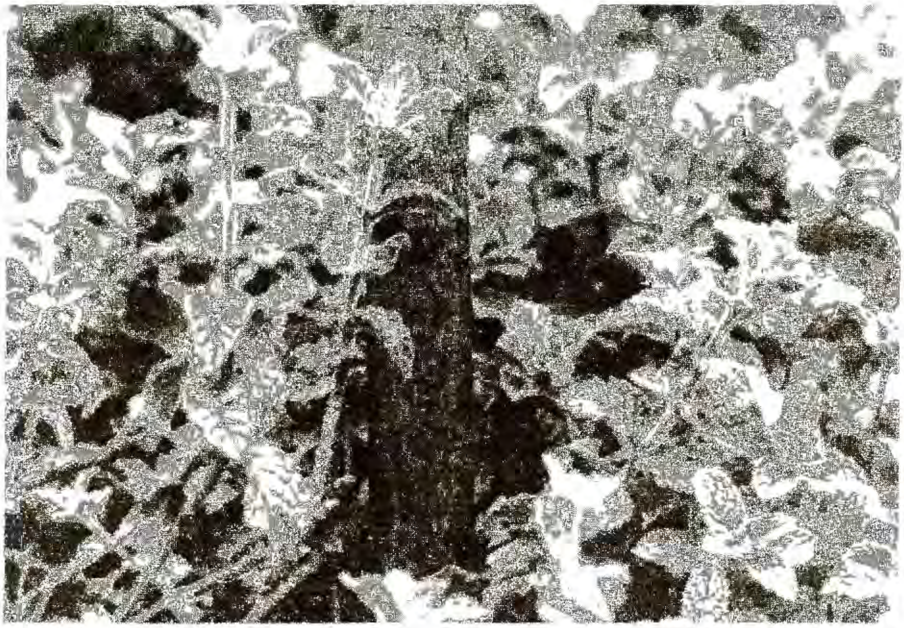


Figure 1. Field-grown Surigao mint plants.

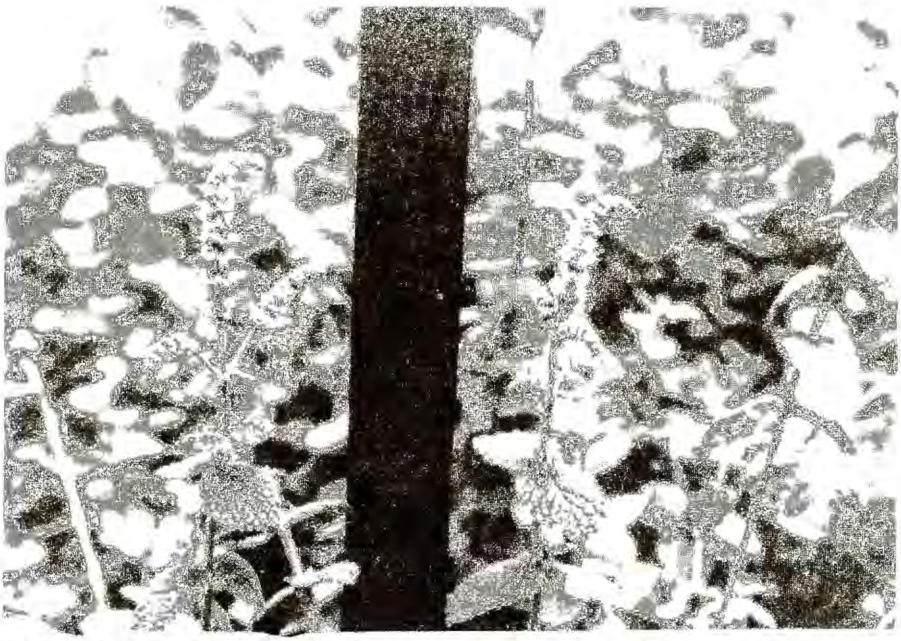


Figure 2. Flowering Surigao mint plants growing under long-day conditions.

Table 1. Dry weight production, oil yield, and moisture content of Surigao mint, September 1984 to May 1985

	Dry Weight Production (g/100 Tops with 1st to 6th pairs of leaves)[1]	Oil Yield (% Moisture-free weight)[2]		Moisture Content (% Air-dry weight)[3]	
		Younger Tops (Tops with the 1st to 6th pairs of leaves)	*Older Tops (Tops with the 7th to 10th pairs of leaves)*	*Younger Tops (Tops with the 1st to 6th pairs of leaves)*	*Older Tops (Tops with the 7th to 10th pairs of leaves)*
1984					
September	9.31-16.20	2.16-3.40	1.20-2.18	13.05-40.66	15.64-38.40
October	6.80-10.10	2.26-2.86	1.36*-1.79	10.54-23.88	14.50-24.83
November	6.22-7.85	2.16-2.64	1.32*-1.81*	11.86-22.92	--
December	6.11-6.40	1.55*-2.45	1.76	11.29	--
1985					
January	8.33	2.02*-2.52*	--	10.43-16.94	--
February	6.23-9.02	1.87-2.83	1.51-1.64*	9.52-12.32	10.80
March	7.01-9.30	2.43-3.30	1.32*-1.95	9.52-12.37	9.97-11.80
April	7.24-8.75	3.32-3.65	1.83*	10.14-13.65	11.28
May	5.44-7.75	2.46-2.84	1.54*	7.42-13.73	--

*Based on air-dry weight.
[1]Based on 1 to 2 counts a week.
[2]Based on 1 to 5 distillations a week.
[3]Based on 1 determination a week.

Gas chromatography of the oil collected in September and October 1984 was done at the Takasago Corporation using a Hewlett Packard HR-5880 instrument (Fig. 3). The oil contains carvone (70.537-71.777% in younger tops and 71.839-75.626% in older tops) and limonene (19.386-21.098% in younger tops and 15.554-18.569% in older tops) as the chief constituents (Table 2). The structures of the terpenes identified in the oil are shown in Fig. 4.

Figure 3. Gas chromatography analysis of the oil of Surigao mint and of the oil of flowering tops of peppermint, Michigan strain.

Sample: 0.1 ul injection (Split 1:100)
Column: PEG 20M, Fused silica capillary
Carrier gas: He, 0.6 ml/min
Column temperature: 55-210°C (Prog. rate 4°C/min)
Detector: FID
Instrument: Hewlett Packard HP-5880
Analyst: Dr. Shigeru Muraki, through the kindness of Dr. Akira Komatsu, Executive Vice-President, Takasago Corporation, Tokyo.

Table 2. Analysis of Surigao mint

Peak No.		*Younger Tops*		*Older Tops*	
		September	*October*	*September*	*October*
1	*alpha*-Pinene	0.854	0.782	0.891	0.467
2	*beta*-Pinene	0.941	0.910	0.918	0.678
3	Sabinene	0.493	0.449	0.456	0.337
4	Myrcene	1.029	0.918	0.945	0.715
5	Limonene	21.098	19.386	18.569	15.554
6	1,8-Cineole	0.760	0.767	0.720	0.597
7	*cis-beta*-Ocimene	0.353	0.324	0.362	0.270
8	*trans-beta*-Ocimene	0.160	0.185	0.182	?
10	1-Octen-3-ol + Limonene-1,2-oxide	?	?	?	?
13	*beta*-Bourbonene	0.574	0.685	0.632	0.841
14	Linalool	0.201	0.210	0.202	0.206
15	Dihydrocarvone	0.467	1.004	0.874	1.605
16	Caryophyllene	0.482	0.492	0.367	0.402
17	Humulene	0.241	0.169	?	0.172
18	*alpha*-Terpineol + *beta*-Farnesene	0.413	0.349	0.351	0.353
19	Carvone	70.537	71.777	71.839	75.626
21	Dihydrocarveol	?	0.226	?	?
24	Calamenene	?	0.184	0.194	0.231
25	Carveol (1)	0.901	0.731	1.443	1.090
26	Carveol (2)	0.164	0.169	0.298	0.260
27	Piperitenone	0.332	0.301	0.510	0.422
30	*alpha*-Cadinol	?	?	?	?
31	Phytol	?	?	0.165	0.172

Biogenetic Relationships

M. x cordifolia Opiz has been known as a cross between *M. rotundifolia* (L.) Huds. *x M. spicata* L. (Clapham, *et al.,* 1962). The principal component of the oil of *M. rotundifolia* (apple-scented mint) is piperitenone oxide and that of *M. spicata* (spearmint) is carvone. It is to be expected that hybrids will yield oils which may vary in composition but still resemble either parent. The Philippine and American hybrids previously studied (Cantoria, 1980) contain piperitenone oxide and carvone as the chief constituent, respectively. Surigao mint is of the latter type. The Philippine and American hybrids are similar in appearance and it is hard to distinguish one plant from the other (Cantoria, 1980). Surigao mint looks like the other two but is characteristically more hairy, resembling *M. rotundifolia* in this respect. The leaves of Surigao mint are ovate or oblong in shape while those of *M. rotundifolia* are ovate-oblong to suborbicular and densely tomentose. It is possible that the

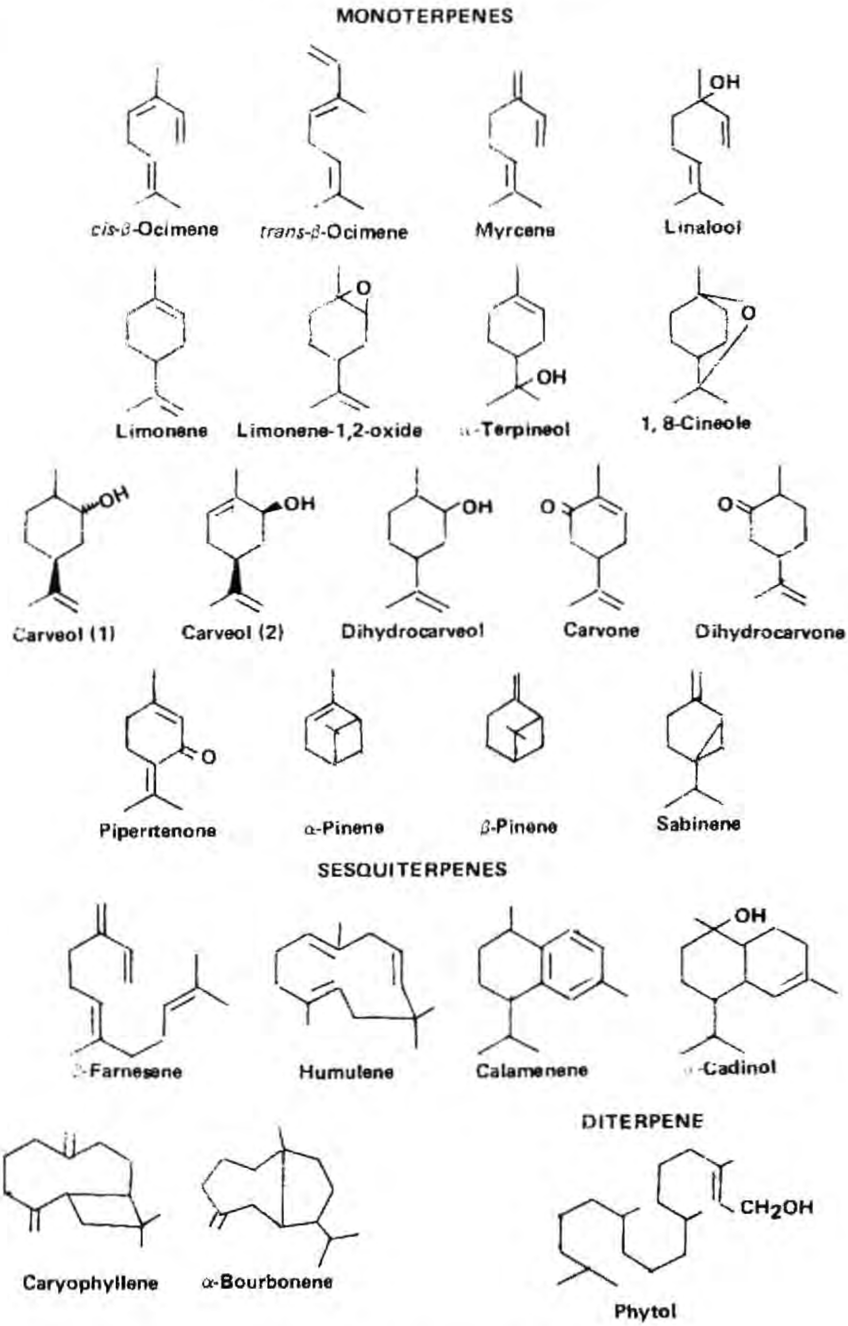


Figure 4. Terpenes in the oil of Surigao mint.

parentage of Surigao mint may be traced to plants growing wild or cultivated in Japan because it is reported that the plant was introduced in Surigao by the Japanese.

Dai (1981) reports that the *M. x cordifolia* plants growing in the botanical gardens of Beijing and Hangchow were misidentified as *M. citrata* Ehrh. The plant has glabrous leaves and the oil contains carvone and linalool but has no lemon smell.

A chemical analysis of eleven populations of *M. x cordifolia* by Lawrence (1978) shows the existence of two chemotypes (Fig. 5):

Figure 5. Chemotypes in *M. x cordifolia* Opiz based on eleven populations (Lawrence, 1978).

Chemotype 1. Oils rich in carvone and limonene with lower quantities of other reduced 2-substituted compounds

Chemotype 2. Oils containing piperitenone and *cis-* and *trans*-piperitone oxide

Surigao mint belongs to the first chemotype, while yerba buena belongs to the second.

For a long time, *M. suaveolens* Ehrh. was incorrectly known as *M. rotundifolia* (Lawrence, 1978). However, studies on morphological structures and chromosome numbers showed that the correct name of the species is *M. suaveolens* Ehrh. (Harley, 1963). A summary of reported studies on the oil of *M. suaveolens* (*M. rotundifolia* auct., non (L.) Huds.) shows that six chemotypes can be realized (Fig. 6) (Lawrence, 1978):

Figure 6. Chemotypes in *Mentha suaveolens* Ehrh. (*M. rotundifolia* auct., non (L.) Huds.) (Lawrence, 1978)

1. Oils rich in pulegone
2. Oils rich in carvone
3. Oils rich in neoiso (iso) pulegol
4. Oils rich in piperitenone oxide
5. Oils rich in piperitone oxide
6. Oils rich in dihydrocarvone, dihydrocarveols, and acetates

The 1,2-epoxidized, 3-substituted compounds (piperitenone oxide/piperitone oxide type) and the 2-substituted compounds (carvone/dihydrocarvone type) are found in the oil of *M. suaveolens* (apple mint).

Although *M. x cordifolia* (2n = 36, 48) has been regarded as a hybrid between *M. spicata x M. rotundifolia* (Clapham, *et al.*, 1962), Harley (1963) considered it to be a hybrid of *M. longifolia* (2n = 24, 48) and *M. suaveolens* (2n = 24). He also considered *M. x cordifolia* to be a synonym of *M. x villosa*. According to Clapham, *et al.*, (1981), *M. x villosa* Huds. (large apple mint) is a highly variable plant which is always sterile. On the other hand, Philippine yerba buena, a strain of *M. x cordifolia*, which was previously worked on, is fertile. Studies on chromosome numbers and chemical analysis of the oil confirm Harley's view that *M. x cordifolia* could be a hybrid between *M. longifolia x M. suaveolens* of the piperitenone oxide and carvone chemotypes (Lawrence, 1978).

In the British Isles, hairy forms of *M. spicata* have been mistaken for *M. longifolia* (L.) Huds. which is not a British plant (Clapham, *et al.*, 1981). Harley (1972) showed by means of breeding experiments, that in *M. spicata* hairiness is a recessive character controlled by a single gene, the glabrous condition being dominant. Cytological studies indicated the presence of diploids and tetraploids. Ecological differences were also noted. The diploids are hairy plants especially characteristic of montane areas. These are referable to *M. longifolia* (horse-mint). The tetraploids may be either hairy or glabrous and are typically associated with cultivation by which they may have originated. These are referred to *M. spicata.* Hairiness alone has been demonstrated to be no longer a valid means to separate species nor to separate their hybrids. While a glabrous hybrid indicates that *M. spicata* is one of the parents involved, a hairy hybrid may involve *M. spicata* or *M. longifolia.* While cytological differences can be found, further studies are needed to find good morphological characters between the various hybrid "pairs". Genuine hybrids between *M. spicata* and *M. suaveolens* or *M. longifolia* frequently occur and are often cultivated (Harley, 1973). The complex as a whole cannot be satisfactorily treated taxonomically, and identification may be very difficult, though certain clones (or cultivars) are often easy to recognize.

Although much work has been done on the nomenclature of *M. longifolia* (L.) Huds. (*M. spicata* L. var. *longifolia* L., *M. sylvestria* L.) and a number of subspecies have been recognized, it may suffice to state that taxonomic nomenclature within *M. longifolia* is very complex (Lawrence, 1978). He analyzed fifteen populations of *M. longifolia* and recognized three chemotypes (Fig. 7):

Figure 7. Chemotypes in *M. longifolia* (L.) Muds. based on fifteen populations (Lawrence, 1978)

Chemotype 1. Oils rich in *cis-* and *trans*-piperitone oxide and piperitenone

Chemotype 2. Oils rich in carvone/carvyl acetate and limonene

Chemotype 3. Oils rich in linalool

II. Peppermint [*Mentha x piperita* L. (Michigan Strain)]

Photoperiodic Nature

M. x piperita, Michigan strain, obtained from Dr. Merritt J. Murray, geneticist of the A. M. Todd Company in Kalamazoo, Michigan, has been growing in the pharmacognosy garden at the U.P. Diliman campus. The plant is a very low-growing herb which does not flower under natural Philippine environmental conditions (Fig. 8). One of the plants used in early studies on photoperiodism by Garner and

Allard in 1920 was peppermint, which they demonstrated to require long days in order to flower. Cuttings of the Philippine-grown peppermint were propagated in pots and subjected to long-day conditions. The plants grew taller and produced longer and larger internodes and larger leaves (Fig. 9a). The field-grown plants grow up to 7 cm high while the plants grow up to 60 cm high under long-day conditions (757% taller). The latter eventually produced flowers borne in clusters in terminal spikes (Fig. 9b).

Volatile Oil Yield

When sufficient samples of the plants grown under long days were available, the oil was distilled. The vegetative tops yielded 1.17% of oil, based on air-dry weight, in March 1984. Seven determinations of the oil yield from flowering tops during the period May to September 1984 ranged from 1.40% to 2.17% of the air-dry weight. GC analysis of the oil from the flowering tops revealed the presence of menthofuran (27.661%), pulegone (18.373%), menthol (12.580%), menthyl acetate (11.376%), and menthone (7.533%) as the principal constitutents (Table 3). The presence of mintlactone, *p*-menth-1(7)-en-8-ol, thymol, and spathulenol has not been previously reported in the oil of *M. x piperita*. The structural formulas of the identified terpenes are shown in Fig. 10. Thirteen wild populations of *M. x piperita* were studied by Lawrence (1978) and the results are also shown in Table 3. Two compounds hitherto unidentified in cultivated plants were lavandulyl acetate and

Figure 8. Field-grown peppermint plants, Michigan strain.

Figure 9. Flowering peppermint plants, Michigan strain, growing under long-day conditions.

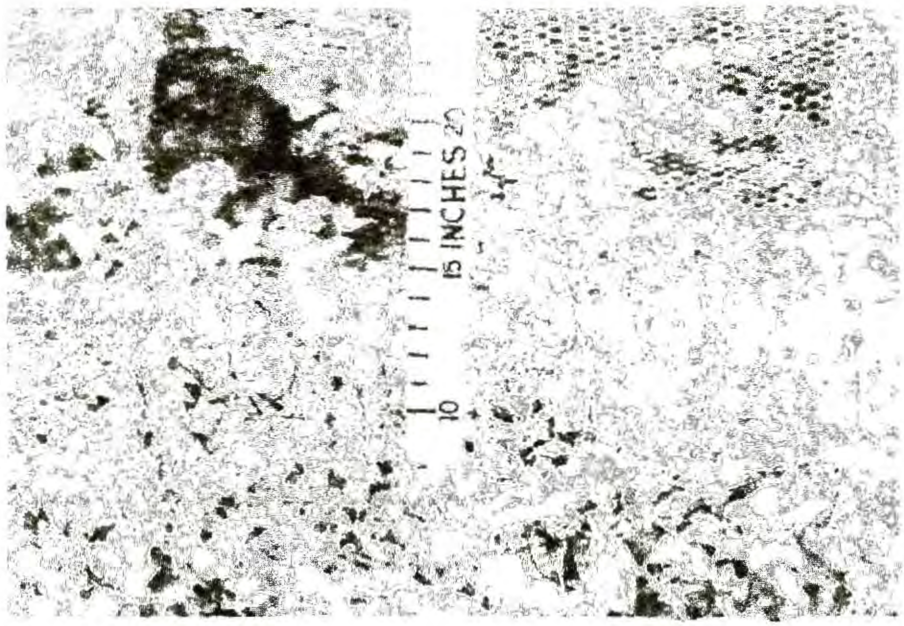
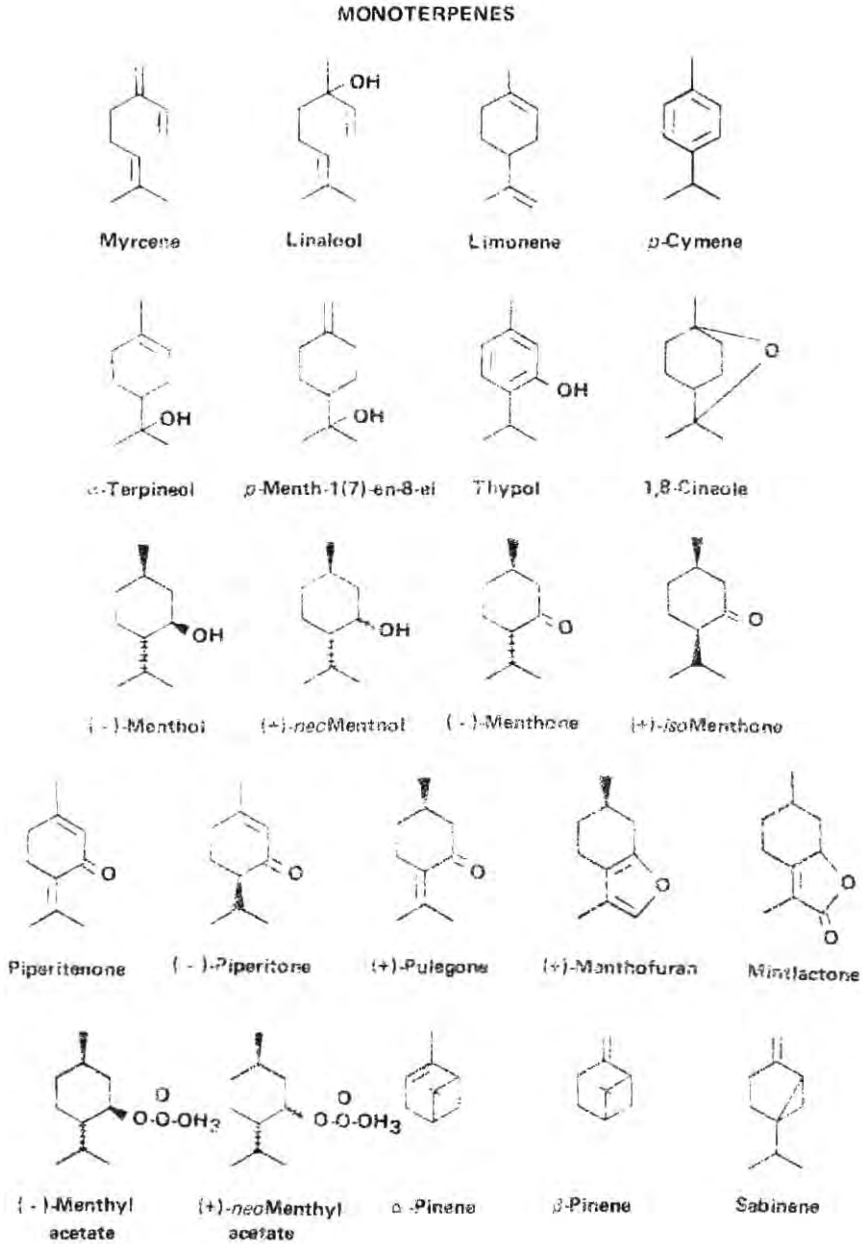
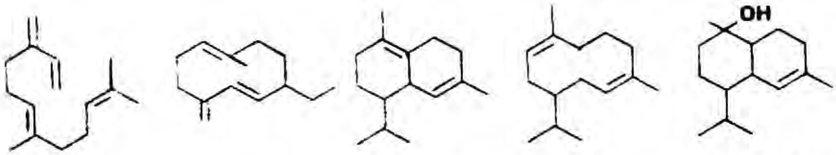


Figure 9a. Peppermint (long days).

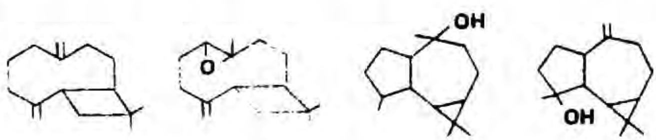
Figure 10. Terpenes in the oil of flowering Philippine-growth peppermint, Michigan strain.



SESQUITERPENES

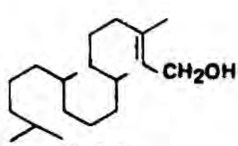


β-Parnesone | Germacrene D | δ-Cadinene | Muurolene | α-Cadinol



Caryophyllene | Caryophyllene oxide | Viridiflorol | Spathulonol

DITERPENE



Phytol

trans-piperitone oxide. The chemical composition was found to be fairly consistent as can be seen from the percentage range of compounds given in Table 3. An analysis by Lawrence (1978) of the oil from cultivated *M. x piperita* showed that menthol, menthone, and menthofuran are the main constitutents. The oil from vegetative parts contained 90% more menthol, 33% more menthone, but 94% less menthofuran than the oil from the flowers (Table 4). Only the oil from the flowers of cultivated plants contains carvone, although *alpha*-terpineol and limonene which are precursors of carvone, are found in small quantities in all the peppermint oils analyzed (Tables 3 and 4). Piperitone and pulegone, precursors of the 3-oxygenated constituents, are also found in all the oils.

Peppermint oil is required by the United States NF XVI (1984) to yield not less than 5.0% of esters, calculated as menthyl acetate ($C_{12}H_{22}O_2$), and not less than 50.0% of total menthol ($C_{10}H_{20}O$), free and as esters. A test for the presence of menthofuran is given as a test for identification and chemical assay methods for total esters and free menthol are included.

Biogenetic Relationships

M. x piperita L. is a cross between *M. aquatica* L. (2n = 96) and *M. x spicata* L. (2n = 48) (Murray, *et al.*, 1972). Cytological examination of *M. x piperita* has resulted in a wide range of chromosome numbers recorded in literature and it may be reasonably assumed that all counts above 2n = 48 are valid (Lawrence, 1978). *M. aquatica* (water mint) has flowers aggregated into terminal globose or subglobose spikes with axillary clusters below and the leaves are hairy. The volatile oil is characterized by the presence of menthofuran as the principal constituent. *M. spicata* has flowers in terminal interrupted, slender spikes and the leaves are glabrous. Hairy plants, often with a weaker smell, are likely to be spontaneous hybrids (Clapham, *et al.*, 1981). Carvone is the principal constituent of the oil. Varying amounts of menthofuran, pulegone, menthone, menthol, and menthyl acetate are found in the oils of Philippine-grown Michigan strain of peppermint, wild populations, and cultivated plants, but carvone is reported only in the flowers of cultivated plants (Tables 3 and 4).

Table 3. Analysis of peppermint oils.

	Philippine Sample			*Thirteen Wild Populations (Lawrence, 1978)*	
Peak No.	*Compound*	*Percent*	*Peak No.*	*Compound*	*Percent Range*
1	*alpha*-Pinene		1	*alpha*-Pinene	0.2-0.9
2	*beta*-Pinene	1.154	2	*beta*-Pinene	0.3-1.1
3	Sabinene	0.509	3	Sabinene	0.3-0.8
4	Myrcene	0.465	4	Myrcene	1.0-3.1
			5	*alpha*-Terpinene	t.-0.2
5	Limonene	2.913	6	Limonene	1.8-6.3
6	1,8-Cineole	3.188	7	1,8-Cineole	2.0-6.7
			8	*cis*-Ocimene	t.-1.4
			9	*trans*-Ocimene)	
				)	t.-1.7
			10	*gamma*-Terpinene)	
9	*p*-Cymene	0.265	11	*p*-Cymene	t.-0.5
			12	Terpinolene	t.-0.2
			13	3-Octanol	t.-0.3
			14	*trans*-Sabinene hydrate	0.2-1.4
12	Menthone	7.533	15	Menthone	4.2-11.6
13	Menthofuran	27.661	16	Menthofuran	4.4-8.7
14	*iso*-Menthone	0.651	17	*iso*-Menthone	0.9-1.9
16	*neo*-Menthyl acetate	0.631	18	*beta*-Bourbonene)	
				)	0.2-1.4
17	Linalool	0.214	19	Linalool)	
			20	*cis*-Sabinene hydrate	t.-0.8

Table 3 (Continued)

	Philippine Sample			*Thirteen Wild Population (Lawrence, 1978)*	
Peak No.	*Compound*	*Percent*	*Peak No.*	*Compound*	*Percent Range*
19	Menthyl acetate	11.376	21	Menthyl acetate	10.6-20.1
	?	0.207			
21	*neo*-Menthol	2.142	22	*neo*-Menthol	2.1-2.9
			23	Lavandulyl acetate)	
				)	t.-2.3
			24	Terpinen-4-ol)	
22/23	Caryophyllene	2.778	25	Caryophyllene	2.0-5.0
24	Pulegone	16.373	26	Menthol	28.0-35.6
25	Menthol	12.580	27	Pulegone	1.6-6.7
26	*p*-Menth-1(7)-en-8-ol	?			
28	*beta*-Farnesene	0.294	28	*trans-beta*-Farnesene	t.-0.5
29	*alpha*-Terpineol	0.233	29	*alpha*-Terpineol	0.1-1.9
			30	*alpha*-Muurolene	t.-0.5
30	Germacrene D +				
	Piperitone	0.988	31	Germacrene D	2.1-3.7
31	Muurolene	?	32	*trans*-Piperitone	
				oxide	0.5-3.1
			33	Piperitone	0.5-1.3
32	*delta*-Cardinene	0.197	34	*gamma*-Cadinene	t.-0.7
34	Piperitenone + ?	1.462	35	Piperitenone	t.-0.7
36	Carophyllene		36	Caryophyllene	
	oxide	0.417		oxide	t.-0.5
37	Viridiflorol	0.392	37	Viridiflorol	0.5-1.3
38	?	0.209			
39	Spathulenol	0.209			
40	Thymol	0.184			
42	*alpha*-Cadinol	0.195	38	*alpha*-Cadinol	t.-0.3
43	?	0.206			
44	Mintlactone	1.081			
46	Phytol	?			
47	?	0.439			

Table 4. Composition of the oil from cultivated *Mentha x piperita* L.* (Lawrence, 1978)

Peak No.		Herb	Flowers
20	Limonene	1.2	2.6
27	Terpinolene	0.1	0.1
37	Menthone	24.2	18.2
38	Menthofuran	1.2	21.5
39	*iso*-Menthone	3.5	6.8
47	*alpha*-Gurjunene)		
	)	3.7	
48	Menthyl acetate)		0.2
51	*neo*-Menthol)		
	)		
52	*neo-iso*-Menthyl acetate)		
	)	4.9	
54	*beta*-Copaene)		
	)		
54A	*trans-iso*-Pulegone)		0.2
60	Menthol	45.8	24.1
61	Pulegone	1.0	13.9
63	*alpha*-Terpineol	0.1	t.
73A	Carvone	–	0.2
74	Piperitone)		
	)	0.5	–
75	Citronellol)		

*Only compounds involved in Figs. 11 and 12 are included in this table.

The pathway for the metabolic interconversions of the 3-oxygenated monocyclic monoterpenes in peppermint is shown in Fig. 11 (Burbott and Loomis, 1967). Each of the reactions shown by solid arrows has been demonstrated in cell-free systems from peppermint and several of the enzymes have been partially purified (Loomis and Croteau, 1980). Analyses of the monoterpenes of individual leaf pairs from plants grown in the greenhouse showed a consistent trend from unsaturated ketones and menthofuran in the upper (young) leaves to menthol and menthyl esters in the lower (old leaves). However, there was considerable variation from one shoot to the other. Studies confirm the fact that the metabolism of monoterpenes in peppermint is strongly influenced environmental conditions (Battaile and Loomis, 1961).

In peppermint, monoterpene catabolism is greatly accelerated at the onset of flowering (Loomis and Croteau, 1980) coincident with the conversion of menthone to menthol and to lesser quantities of menthyl acetate and neomenthol, most of the latter being converted to the corresponding *beta*-D-glucoside. Thus, during the turnover of menthone in peppermint, this ketone is reduced to roughly similar quantities of menthol and neomenthol and, while the menthol and menthyl acetate accumulate in the oil, the neomenthol is specifically converted to the water-soluble glucoside.

Figure 11. Metabolic interconversions of the 3-oxygenated monocyclic monoterpenes in peppermint (Burbott and Loomis, 1967). Each of the reactions shown by the solid arrows has been demonstrated in cell-free systems from peppermint and several of the enzymes have been partially purified (Loomis and Croteau, 1980).

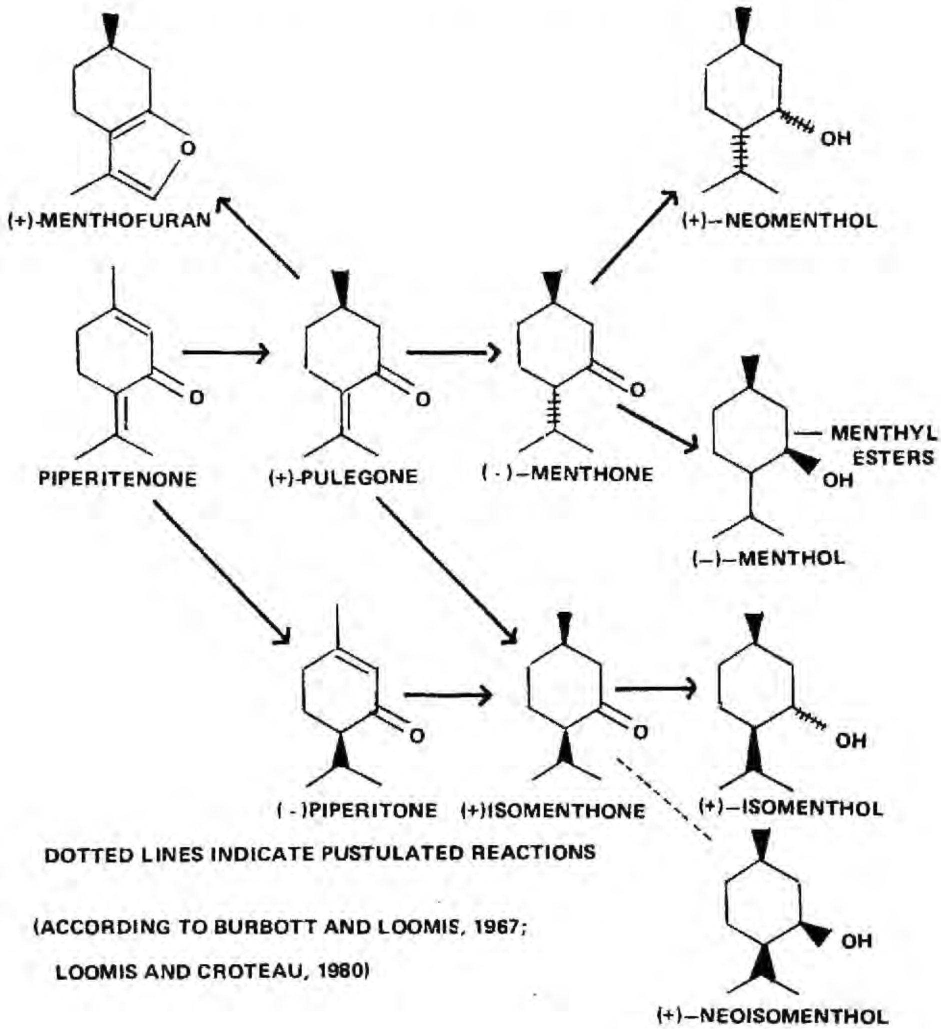
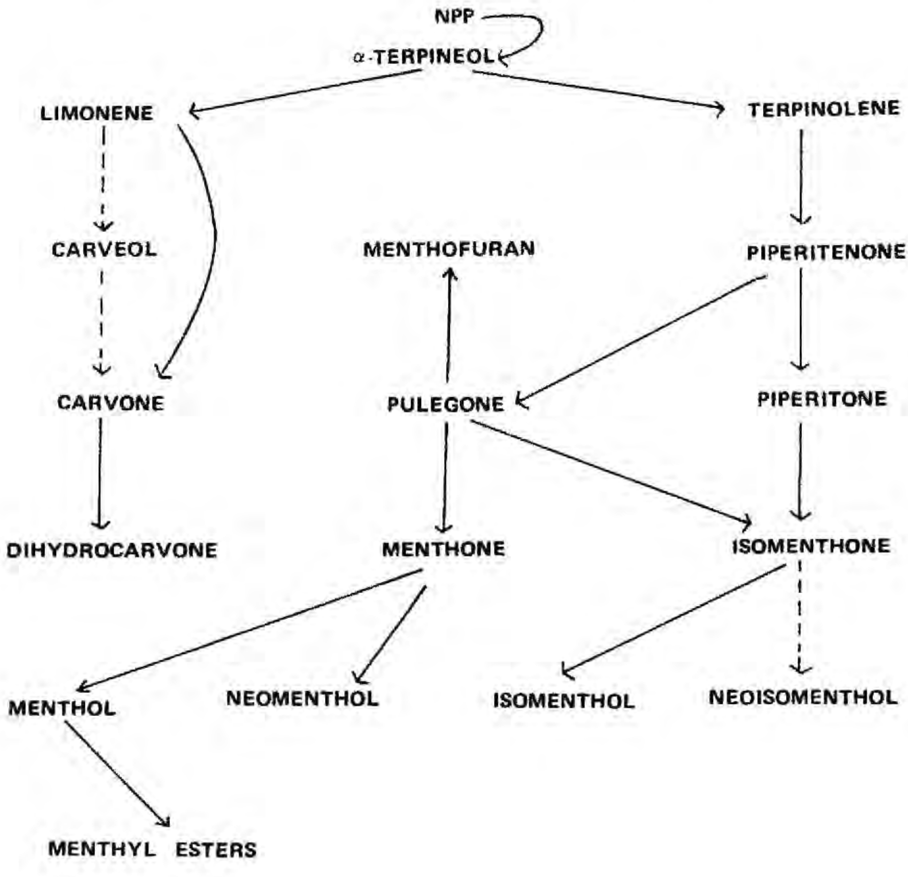


Figure 12. Biosynthesis of two series of oxygenated compunds in *Mentha* species (Loomis, 1967). Reactions starting from limonene yield the 2-oxygenated (carvone) series. The terpinolene-piperitenone transformation leads to the 3-oxygenated (pulegone) series.



On the basis of both stereochemical and genetic evidence, terpinolene and limonene are considered precursors of two series of oxygenated compounds in *Mentha* species (Fig. 12) (Loomis, 1967). Reactions starting from limonene yield the 2-oxygenated (carvone) series. This is thought to be operative in *M. spicata* L. The mechanism of the postulated oxygenation of terpinolene to piperitone and of limonene to carvone has not yet been determined (Loomis and Croteau, 1980).

The other pathway leads to the 3-oxygenated (pulegone) series (Fig. 12). Formation of a second double bond in *alpha*-terpineol produces either limonene or terpinolene depending on which hydrogen atom is lost (Loomis and Croteau, 1980). The addition of an oxygen atom is directed by the position of the double bonds. In the terpinolene-piperitenone transformation, the two double bonds act together in directing the position of the oxygen atom while in the limonene-carvone series, the two double bonds are too far apart to interact and the double bond in the ring would act alone. Limonene is a very widespread compound while terpinolene is less common. It is also common to find compounds of the pulegone series extensively reduced, even as far as the saturated alcohols (menthols). In the carvone series, the process tends to stop at carvone or dihydrocarvone.

The monoterpenes identified and the amounts present in the oils of Surigao mint and of peppermint, Michigan strain, appear to support the pathways indicated in Figs. 11 and 12.

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Domingo A. Madulid, Discussant

Dr. Cantoria's work may be regarded as one of the pioneering works in chemical systematics or chemotaxonomy in our country and her contribution to the advancement of this field is acknowledged by the Philippine systematics community. Chemotaxonomy is a relatively modern method in plant taxonomy, the field having originated and popularized in Europe and the United States. In the Philippines, I know of only very few scientists doing this kind of study. As many plant taxonomists know, the genus *Mentha* (Labiatae) possess problems of identification and classification "more than any other genus of comparable size". Recent survey shows that almost 2,300 names have been published for this genus and possibly 50% of these are synonyms, and the rest legitimate infraspecific names. According to Dr. Harley, taxonomist in Kew, England working on the Labiatae family, "it would be more than a life's work to reduce these names (*Mentha*) to order". Dr. Cantoria's work, surely is an important contribution towards untangling the taxonomic mesh of *Mentha*. She showed us that through gas chromatography of the aromatic mint oil it is possible to recognize several chemotypes of *Mentha x cordifolia* i.e. the strain grown in Surigao and the common mint locally called "yerba buena". It was also possible to reflect the possible biogenetic relationships of the plants and the possible origin of the hybrid. Such distinctness will not be so evident if one will rely mainly on morphological evidences. For example, the garden forms of *Mentha spicata* have been observed to be most often glabrous, but hairy forms also occur and are frequently present among the progeny grown from seed.

This work of Dr. Cantoria in the two *Mentha* hybrids is only part of her research output on the pharmacognosy and chemotaxonomy of certain Philippine plants. As a follow up to this study, she has to decide now whether to formally create infraspecific categories for the chemically distinct "strains" of *Mentha x cordifolia*. What infraspecific category will she employ - subspecies, variety, forma or perhaps nothomorph? Aside from gas chromatography of the mint oil, it is perhaps worth comparing the flavonoid patterns of the leaves of *Mentha x cordifolia* and correlate the results with those obtained from the study on mint oils. This is, I think, important because flavonoids is recognized today as being one of the most valuable of all classes of secondary chemical constituents as systematic markers in angiosperms. Many chemotaxonomists prefer to use flavonoids because it is found widespread in plants, it is stable and easy to detect. The result of the flavonoid study in *Mentha* would be very interesting in the systematic point of view.

I congratulate Dr. Cantoria for her most interesting and valuable research work. I hope this will serve as a catalyzer for more chemotaxonomic investigations on Philippine plants.

Mildred B. Oliveros, Discussant

Dr. Cantoria's report on the Surigao mint further confirms the complex nature of the mint species. Other researchers like Laurence, Harley, Chopra & Murray have shown the complex relationship between mint species in their effort to thresh out taxonomic problems within this large group of plants. Cytological, morphological, and chemical studies have helped solve some of these problems. A number of significant relationships have been discovered leading to the reclassification of some and renaming of others. However, the taxonomic problems within this group are far from over. From some 2,300 names of species, about 50% are reported to be synonyms.

The misnomer of some mint species has long been a problem. Some insist on using the incorrect names even after these have been found to be wrong. In 1978, Laurence, through morphological and cytological studies showed that *Mentha rotundifolia* is rightfully *Mentha suaveolens*. More recently, Dr. Cantoria showed that yerba buena, long erroneously referred to as *Mentha arvensis*, is a *Mentha cordifolia* hybrid. It is sad to note, however, that new books and pamphlets authored by fellow Filipinos still carry the incorrect name for yerba buena.

Distinguishing hybrids of mint species from each other is another problem that has been very difficult to tackle. Chemical studies conducted by Laurence on the volatile oils of *Mentha cordifolia*, *Mentha longifolia* and *Mentha suaveolens* hybrids have helped group these hybrids into chemotypes. The *Mentha cordifolia* hybrids were grouped into 2 chemotypes, *Mentha longifolia* into 3 chemotypes, and *Mentha suaveolens* into 6 chemotypes. These show the existence of chemical relationships between closely related species in the genus *Mentha*. It is highly possible therefore to group mint species on the basis of their oil composition. Their chemical differences and similarities, as well as their morphological characters, which are supported by cytological characters, may help taxonomists restore order to this complex group of plants. In using chemical differences as a criterion, however, utmost care and sound judgement must be exercised since environmental conditions greatly affect monoterpene metabolism.

I wish to congratulate Dr. Cantoria for her valuable contribution to the study of mint species. More power to you.