Volatile Components of *Meratia praecox*

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The major volatile constituents present in different parts of a deciduous tree, *Meratia praecox*, have been identified by combination of GC-MS and spectral analysis of the isolated compounds. From the results, some biogenetic implications were discussed.

The family Calycanthaceae consists of two genera, *Meratia* (Chinese origin) and *Calycanthus* (American origin). *Meratia praecox* Rehd. et Wils. (*Chimonanthus praecox*) is a small deciduous tree producing fragrant flowers during a period of two months in midwinter. Early works on the essential oils of Chimonanthus fragrance were reviewed by Louveau.[1] Among the compounds reported were benzyl alcohol, linalool, terpineol, farnesol, and indole. By means of recent techniques, we have made an exhaustive study of the oils isolated from the different parts of *M. praecox*, and determined the relative amounts of various components as a function of growing season. This paper presents the results of investigation and a discussion on biogenetic implications.

Experimental

Of many samples collected, the results for six characteristic specimens will be described. Samples were flower bud bursting flower, fresh flower, faded flower, leaf and fresh branch (Table 1). All the specimens were collected from the same tree. Each specimen was steam-distilled under atmospheric pressure. The distillates were saturated with sodium chloride and extracted with ether; the ether extract was dried over anhydrous sodium sulfate, and the ether was removed to give the essential oil. The yields of essential oils are also given in Table 1. Characterization of the components was carried out by a combination of GC-MS and spectral analysis after their isolation by adsorption chromatography (silica gel or silver nitrate-impregnated silica gel) and preparative gas chromatography (Carbowax-20M). The identity of the major constituents was confirmed by a comparison of their IR and NMR spectra with those of authentic samples.

TABLE 1. ANALYTICAL SAMPLES FROM THE DIFFERENT PARTS OF *M. praecox* AND THE CONTENTS OF VOLATILE COMPOUNDS

Sample No.	Plant part	Harvested date (1977)	Yield (%)
I	Flower bud	17/Jan.	0.082
II	Bursting flower	5/Feb.	0.087
III	Fresh flower	10/Feb.	0.19
IV	Faded flower	1/March	0.012
V	Leaf	7/June	0.04
VI	Fresh branch	1/March	0.02

Apparatus and Operating Conditions. Preparative GLC was carried out with a Varian Aerograph 920 fitted with a thermal conductivity detector, using a 10 ft. × 3/8 in. aluminum column containing 20% Carbowax-20M on 60—80 mesh Diasolid-L. Helium was used as a carrier gas, the column temperature being set at 100—200 °C.

For quantitative analytical GLC, a Hitachi K-53 apparatus equipped with a flame ionization detector and a computer system was used. The capillary column used for the analysis was 45 m × 0.25 mm, made of stainless steel and coated with HB 2000; the column temperature was 150 °C, isothermal. The inlet pressure for nitrogen carrier gas was set at 1.5 kg/cm^2.

The GC-MS spectra were measured by combination of GLC fitted with a Golay column (45 m × 0.25 mm, HB 2000) and mass spectrometry using a Hitachi RMU-6 mass spectrometer with operating conditions: ionization energy, 70 eV; acceleration voltage, 2000 V. The column temperature was programmed non-linearly at 100—150 °C with a gas inlet pressure of 0.6 kg/cm^2.

The IR spectra were measured with a Hitachi EPI-G2 spectrometer. The PMR spectra were taken with a Hitachi R-20B spectrometer at 60 MHz in CCl_4 with TMS as internal standard.

Results and Discussion

The components identified in six specimens, together with their contents as determined with the GC/computer system are given in Table 2. The major compound common to the oils of the flower bud and the bursting flower was found to be elemol, corresponding to more than 80% of the volatile oils. However, hedycaryol, instead of elemol, was isolated from ether extracts obtained without steam distillation by preparative TLC on silica gel. Hedycaryol, identified by its NMR spectrum, was converted into elemol on being injected into a gas chromatograph. Elemol is known to be an artifact caused by thermal isomerization. Thus, its biosynthetic equivalent, hedycaryol, appears to be one of the basic products of sesquiterpene biosynthesis. The data for bursting flower oil indicate that benzyl alcohol is produced at an early stage in the flowering. In the fresh flower oil, bicyclogermacrene and related compounds, δ-, β-, γ-elemenes, and germacrene-B, were found to be the major components. Considerable amounts of benzyl alcohol, its acetate, and linalool (possibly responsible for the flowery odor) were detected. Because of the marked increase of volatiles in the fresh flower, the detection of elomol or its equivalent would be masked by the post-products. In the faded flower oil, elemol was found to be the main compound, the level of components predominant when the flower was in full bloom decreasing. The characteristic compounds of the flower odor might have evaporated into the air, only sesquiterpens remaining. The leaf oil was similar to the faded flower oil, but not to the woody branch oil. In the woody branch oil, major components were humulene, caryoph-

TABLE 2. IDENTIFIED COMPONENTS AND THEIR CONTENTS (%) IN SIX SPECIMENS

Compound	I	II	III	IV	V	VI
1-Pentanol					+	
cis-3-Hexen-1-ol					0.45	
trans-3-Hexen-1-ol						
Heptanal			0.38	0.31		
Nonanal	0.31		2.37	4.40		0.15
Furfural				+		+
Octane				+		
Tridecane			0.07	0.08		
Heptadecane			0.17	0.13		0.07
Nonadecane			0.50	0.39		
α-Pinene						4.17
Camphene						0.18
β-Pinene						7.10
Myrcene						0.44
α-Phellandrene						1.02
α-Terpinene						0.44
Limonene						1.22
β-Phellandrene						1.24
cis-β-Ocimene			0.27	0.23		
trans-β-Ocimene	4.83		0.87	8.44	0.17	
p-Cymene						2.58
Terpinolene						0.13
1,8-Cineol					+	+
trans-Linalool oxide (THF)			0.19			
cis-Linalool oxide (THF)			0.54			0.05
Linalool			6.92		0.66	0.44
Terpinen-4-ol						2.01
α-Terpineol						0.77
Borneol						0.61
trans-Linalool oxide (THP)			0.64			
Thymol						0.12
Benzaldehyde				0.04		
Benzyl acetate		0.93	2.39	0.48		
Benzyl alcohol		4.86	15.9	5.52		
Cinnamaldehyde				0.06		
Cinnamyl alcohol			+			
Cinnamic acid			+			
Indole			1.07			

Compound	I	II	III	IV	V	VI
α-Cubebene			0.43	+		0.02
δ-Elemene			1.79	0.47		
α-Copaene			0.76	0.10	0.11	1.02
β-Cubebene	+		0.59	0.10	0.37	0.54
α-Gurjunene						0.23
β-Elemene	0.69	1.38	8.87	0.78	3.60	2.14
Caryophyllene			2.17	1.26	4.30	18.6
γ-Elemene			2.72	1.85	4.60	0.06
β-Farnesene			0.32	0.16		0.11
α-Humulene	0.77		0.87	0.39	1.20	4.60
γ-Muurolene	+		0.30		0.28	0.49
Germacrene-D	1.01		4.56	0.26	0.54	0.30
Zingiberene			3.09	1.38	1.40	
α-Muurolene			+	0.12	1.30	0.94
Bicyclogermacrene	1.01		18.1	5.52	6.90	2.07
trans-α-Farnesene			2.16	0.45	0.50	0.19
δ-Cadinene	1.01	0.92	2.77		2.40	6.94
γ-Cadinene			+			1.98
1,4-Cadinadiene	+		0.16	0.07	0.60	0.34
α-Cadinene			0.10	0.08		0.09
Calamenene			+	+		0.29
Germacrene-B	1.01		1.93	2.90	4.00	0.51
α-Calacorene			0.13			0.28
Cadalene			+		0.40	0.25
Caryophyllene oxide			0.77	2.10	0.12	5.20
Humulene epoxide-II						0.67
Caryophyllene alcohol						0.01
Nerolidol	+		1.19	0.56	0.81	2.97
Elemol (hedycaryol)	81.0	84.9	1.84	45.5	43.3	1.14
epi-Cubenol			0.75	+	2.30	2.49
Spatulenol (tentative)			0.70	1.51	1.70	0.24
γ-Eudesmol	1.20	0.48	+	0.97	3.80	
T-Cadinol	+	0.31	1.66	0.69	0.90	9.52
δ-Cadinol						0.63
α-Eudesmol	3.00	1.52		2.38	1.90	
β-Eudesmol					1.60	
α-Cadinol			0.74	0.47	0.60	3.97
Total	95.84	95.30	91.62	90.15	90.81	91.57

Contents were calculated by means of the GC/computer system (HB 2000, 0.25 mm×45 m).

TABLE 3. CONTENTS (%) OF SOME DISTINCTIVE COMPONENTS FROM SIX SPECIMENS

Group of component	I	II	III	IV	V	VI
Linalools (linalool, its oxides)			**8.29**		0.66	0.49
Other monoterpenes	4.83		1.14	**8.67**	0.17	**22.03**
Aromatic comps.		5.79	**19.36**	6.10		
Germacrene-B type	**87.91**	**88.28**	**35.25**	**60.37**	**69.70**	5.92
(germacrene-B, elemenes)	1.70	1.38	**15.31**	6.00	**12.20**	2.71
(bicyclogermacrene)	1.01		**18.10**	5.52	6.90	2.07
(elemol, hedycaryol)	**81.0**	**84.9**	1.84	**45.5**	**43.3**	1.14
(eudesmols)	4.20	2.00		3.35	7.30	
Germacrene-D type	2.02	1.23	10.29	1.69	6.62	**25.20**
(germacrene-D, cadinenes, muurolenes)	2.02	0.92	7.89	0.53	5.12	**11.08**
(cadinols)		0.31	2.40	1.16	1.50	**14.12**
Humulene, caryophyllene type	0.77		3.81	3.75	5.62	**29.08**

yllene and its oxides (*t,t*-farnesyl-pp type), together with considerable amounts of compounds of *c,t*-farnesyl-pp type such as germacrene-D, cadinenes, and cadinols.

The contents (%) of some distinctive components are given in Table 3. Linalool, its oxides and aromatic compounds such as benzyl alcohol, its acetate and indole are distinctive components of the fresh flower oil, appearing to have been translocated or partly lost by evaporation in the faded flower. These compounds were formed before the leaf emerged, thus before the start of vigorous assimilation. Sesquiterpenes of the germacrene-B type, such as hedycaryol and related hydrocarbons, amounted to 35—88% of the flower oils (I—IV) and the leaf oil (V). The branch oils did not contain nearly as much, while germacrene-D and related hydrocarbons and oxygenated compounds, in addition to humulene and caryophyllene, were major components of the woody branch oils. All these components were absent or present in only small quantities in the oils of flowers and the leaf. The difference in biosynthetic pathways is thus distinct.

References

1) G. Louveau, *Rev. Marques Parfum. Savonn.*, **9**, 531, 573, 622 (1931); *cf. Chem. Abstr.*, **27**, 3776 (1933).