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Analysis and Comparison of Flavor Constituents in Aqueous Smoke Condensates from Various Woods†

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The nature of the commercial smoke condensates (wood vinegar liquors) obtained from six kinds of wood was studied in relation to their flavors.

Undistilled smoke condensates had an unpleasant resin-like odor, while distilled ones had a strong pungent smoky flavor mixed with cresolic and furfural-like doors. These differed slightly with various kinds of wood materials. Among the six kinds of wood materials, oak B* and bamboo gave organoleptically the most acceptable smoke flavors.

The amounts and compositions of flavor components in the carbonyl, non-carbonyl neutral, basic, acidic and phenolic fractions contributed to the differences in aroma. In particular, the composition of the phenolic fraction was thought to be important.

Smoking is a kind of food-processing method which has been used for preservation and/or improvement of flavors. However, since many methods for food preservation have now been developed, flavoring is regarded as the most important effect of smoking.

Though many studies have been made on smoke flavor, there are few studies on the smoke condensate obtained as a by-product in the manufacture of charcoal.

The aromatic character of smoke is influenced by the following factors; type of wood, method of generation and collection of smoke and conditions of combustion. Among the varieties of woods, broad-leaved trees are widely used for smoking and it is well-known that better smoke flavor is obtained from broad-leaved trees than needle-leaved ones. Tilgner[1] investigated the smoke flavor obtained from nine types of wood and found that beech, oak and plane-tree smokes scored about the same and were in the highest group; the second group, consisting of birch and common pine, scored a little lower, but both were about the same; alder, lime, aspen and fir produced smokes with relatively poor flavor. Ziember[2] reported that smoke from oak contained more organic acids than that from beech and was inferior to beech. Lustre and Issenberg[3] reported that only quantitative (not qualitative) differences were found in gas chromatograms of the phenolic fraction, between hickory and mixed hardwood sawdust. However, these differences were no greater than those observed in phenolic fractions isolated from different batches.

At present, commercial smoke condensate is produced from both broad- and needle-leaved trees and also from bamboo in Japan. In this paper, identification of smoke flavor components and the relationships between type of wood and smoke flavor are presented.

EXPERIMENTAL

Materials and preparation of smoke flavor concentrates

Wood chips of six kinds of woods (oak A,** oak B,* and cherry as broad-leaved trees, pine and Japanese cedar as needle-leaved trees and bamboo as a monocotyledonous plant) were heated in charcoal kilns, and the smoke generated was cooled and collected.

† Studies on Smoke Flavor. Part I. A part of this research was presented at the Annual Meeting of the Japanese Society of Food Science and Technology (Tokyo, April, 1971).

* *Quercus acuta.*

** *Quercus serrata.*

The smoke condensate was left to stand for a few days to separate to three layers; the upper layer consisted of wood oil, the middle layer of useful liquid smoke and the lowest layer of precipitated tars. The middle layer was collected (referred to as undistilled smoke condensate, UDSC) and distilled under atmospheric pressure. After the initial distillate (about 12%) was discarded to reduce pungent odors and obtain a clear solution, distilled smoke condensate was collected (DSC).

Flavor constituents were extracted with diethylether from DSC (450 g) or UDSC (250 g), and the ether extract was concentrated by evaporation.

Fractionation of the smoke flavor concentrates

The fractionation scheme for the smoke flavor concentrate is shown in Fig. 1. Carbonyl fraction was separated from the neutral fraction with Girard-T reagent by the method of Wheeler.[4] An ether solution of each fraction was dried with anhydrous sodium sulphate and then concentrated to a small volume.

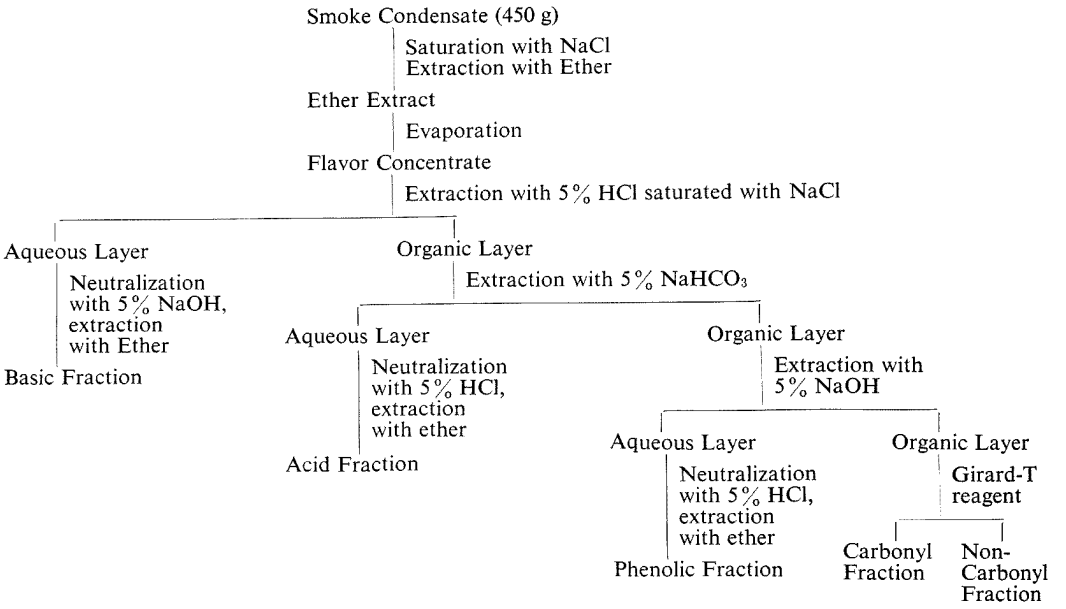

FIG. 1. Fractionation of Volatile Compounds from Smoke Condensate.

Gas chromatography (GC)

Each flavor concentrate was analysed with a Shimazu Model 4 AP dual-column gas chromatograph equipped with flame ionization detectors. A stainless steel column (3 mm × 3 m) packed with 20% Carbowax 20 M on Diasolid L (60~80 mesh) was used. The column oven temperature is shown in Fig. 2. The injection port and detector temperatures were ketp at 200°C. The carrier gas was nitrogen, with a flow rate of 30 ml per min.

Identification of flavor constituents

Flavor constituents were separated with a Hitachi Model K-23 gas chromatograph equipped with a thermal conductivity detector under the same conditions as described above, except that helium was used as the carrier gas. Constituents corresponding to peaks on the gas chromatograms were trapped in capillary glass tubes cooled in an acetone-dry ice bath for identification by infrared and NMR spectrometry.

IR spectra. IR spectra were taken as films with a Japan Spectroscopic Model IR-S infrared spectrometer.

NMR spectra. NMR spectra were recorded with a Model JNM-4H 100 in carbon tetrachloride with tetramethylsilane as an internal standard.

Gas chromatography-mass spectrometry (GC-MS). Mass spectra were measured with a Hitachi Model RMU-6L mass spectrometer connected with a Hitachi K-53 gas chromatograph. Gas chromatography was conducted under the same conditions described above except that the carrier gas was helium, with an inlet pressure of 1.0 kg per cm^2. The mass spectrometer was operated at *ca.* 70 eV ionization voltage, and the ion source and separator were heated at 200°C. Some MS data were obtained using a computer (GC-MS connected to a computer).

Organoleptic test

Simple organoleptic tests were carried out by five

trained members of our laboratory by means of the following procedure: Ether concentrates of each fraction were absorbed on filter papers in given quantities according to their yields. After the ether was removed, the paper filter was put in an Erlenmeyer flask (25 ml) and sealed with aluminium foil for a few min, and then subjected to the test.

RESULTS AND DISCUSSION

All UDSC's had a somewhat unpleasant resin-like odor, but DSC's had agreeable smoke flavors mixed with strong acidic, phenolic, cresolic and furfural-like aromas. There were some differences in flavor among the six kinds of smoke condensate. Oak A had a strong burnt odor with some sweetness. Pine and Japanese cedar had pungent phenolic and poor fragrant aromas, which might contribute to their monotonous flavors. On the other hand, oak B had a heavy, sweet smoke flavor and presented the most pleasant smoke flavor. Bamboo also presented a pleasant smoke flavor. Oak B and bamboo had stronger sweet and burnt aromas than pine, and had more pungent phenolic aromas than oak A. Good reproductivities of aroma were found in all kinds of wood except for cherry, which was said to give a most agreeable smoke flavor by Iwadare.[5] The smoke flavor obtained from cherry gave an oak-like smoke flavor in sample I, but a pine-like one in sample II.

We carried out organoleptic determinations in order to estimate the contribution of each fraction to the formation of the whole smoke flavor. The results of organoleptic tests on bamboo are shown in Table I, and similar results were obtained from the other woods. Following many authors' reports,[6~8] it was found that A (phenolic fraction) in Table I had a characteristic smoky aroma and might be the most important contributor to the smoke flavor. However, its aroma was monotonous. B (phenolic and carbonyl fractions) presented a fragrant smoke flavor and C (phenolic and neutral fraction) had a more complex smoke flavor with more fragrancy than B. Sample D (phenolic, neutral and basic fractions) gave the most pleasant complex smoke flavor, nearly reproducing the original smoke flavor but without acid odor. The results showed that not only the phenolic fraction but also the other fractions contributed to the pleasant smoke flavor. Although the smoke flavor might be affected by the acidic fraction, the authors did not investigate this due to poor reliability resulting from excessive stimulation of our olefactory organs.

Yields of the flavor compounds obtained from the smoke condensates and from each fraction are shown in Table II. As regards the whole and acidic fractions, broad-leaved trees gave higher yields than needle-leaved ones, and oak B showed an especially high yield of acid fraction. Yields of phenolic compounds were high in oak A, oak B, bamboo and pine. Flavor components in the carbonyl, non-carbonyl and basic fractions imparting a sweet aroma or burnt sweet aroma were included only to a small extent in pine. In oak A the ratio of the content of phenolic compounds to that of neutral ones was low. These factors might partially explain why pine and oak A had rather poor smoke flavors. Oak A and cherry showed high yields of basic fractions, with a strong burnt aroma.

Though differences in the smoke flavors

TABLE I. EFFECT OF EACH FRACTION ON THE WHOLE SMOKE FLAVOR

	Fraction			
	Phenolic	Phenolic and carbonyl	Phenolic, carbonyl and non-carbonyl	Phenolic, neutral and basic
Aroma	Monotonous smoky aroma	Smoky arona with fragrancy	Smoky aroma with fragrancy	Burnt smoky aroma
Quality[a]	+	++	+++	+++

[a] +, good; ++, better; +++, best.

TABLE II. YIELDS OF AROMA MATERIALS OBTAINED BY FRACTIONATION (mg %)[a)]

	Total	Basic	Carbonyl	Non-carbonyl	Phenolic	Acid
Oak A	1600	80	323	310	225	820
Oak B	1860	48	117	99	151	1140
Cherry	1490	108	111	60	101	660
Bamboo	1180	40	86	211	144	610
Pine	1180	33	53	24	166	640
Cedar	890	40	90	73	122	520

[a)] Entirely solvent-free.

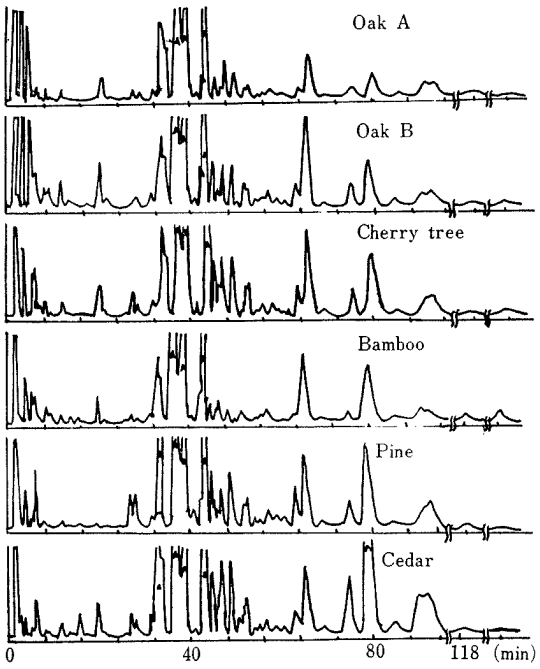

FIG. 2. Gas Chromatograms of Whole Flavor Concentrates Obtained from Distilled Smoke Condensates.

Column temp.: 70~180°C (2°C/min).

obtained from various kinds of wood were observed, differences in the flavor constituents were not apparent, as shown in their gas chromatograms (Fig. 2). Therefore, identification of the major constituents of each fraction and estimation of the approximate compositions were carried out. As an example, the gas chromatograms of each fraction from bamboo are shown in Fig. 3. For each fraction, there were differences in the peaks on the gas chromatograms among all six types of wood. Therefore the DSC's might consist of almost the same flavor constituent, but the compositions vary with the type of wood. Therefore, it was deduced that the differences in aroma were due to the compositions of flavor constituents rather than the presence of a specific compound with the characteristic aroma. The compositions of major compounds in the acidic, carbonyl and phenolic fractions and the methods of identifications are shown in Tables III to V. More detailed investigation of the basic fraction is in progress.

Acidic fraction

The acidic fraction consisted of acetic, propionic, *n*- and isobutyric acids and others in each case, as shown in Table III. Peak 43 was identified as *cis*-crotonic acid from its IR, MS and NMR data: IR (ν^{film} cm^{-1}: 1700, 1238, 1640 (*cis*), 1450, 1260, 940), MS (*m/e*: 86 (M^+), NMR ($\delta^{CCl_4}_{Me_4Si}$: 2.16 (3H, d, d, CH), 5.76 (1H, d, q. =CH), 6.37 (1H, m, =CH)).

Though good reproducibilities in alkaline titration values of the six kinds of smoke condensate were observed, oak A and pine showed different values between sample I and II. Very similar tendencies were found among all six kinds of woods. In spite of variations in sample I of oak A and pine, all samples contained *ca.* 40 to 70% of acetic and propionic acids in the acidic fractions. They have a stimulating odor and may mainly cause the stimulating odor of smoke flavor.

Phenolic fraction

Gas chromatograms of the phenolic fractions were similar to that of dried bonito, Katsuobushi.[9)] The DSC obtained from any of the woods mainly consisted of (unsubstitu-

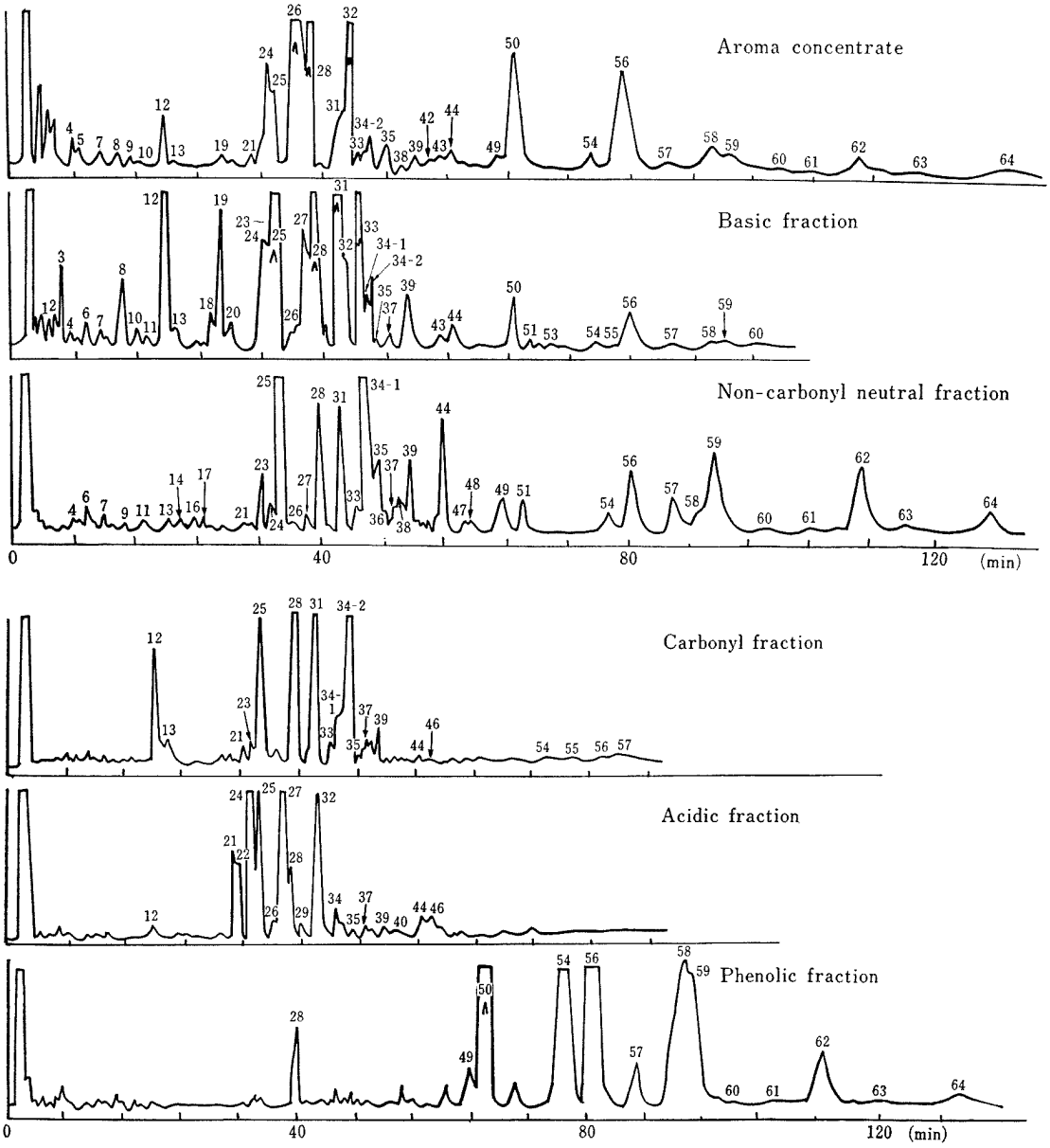

FIG. 3. Gas Chromatograms of Each Fraction Obtained from Bamboo.

ted, 4-methyl, 4-ethyl, 4-allyl) guaiacol, phenol, *o*, *m*- and *p*-cresols, 2,4- 2,6-, 3,4-, 3,5-xylenols with some 2,6-dimethoxyphenol (syringol) homologues *etc.* It is said that syringol has a characteristic smoky aroma and is one of the major components in broad-leaved woods.

A number of phenolic compounds appeared after syringol on the gas chromatogram, as found by Fiddler *et al.*[8] Therefore, phenolic fractions prepared from UDSC's of *Quercus acutissima*, bamboo and pine were analysed by GC, as shown in Fig. 4. It was found that unsubstituted, 4-methyl, ethyl and propylsyringols were contained in *Q. acutissima* and bamboo, whereas they were not present in needle-leaved trees. This result agrees with those of other authors.[10] In the DSC of pine

TABLE III. RELATIVE COMPOSITIONS OF AROMA CONSTITUENTS IN THE ACIDIC FRACTION

No.	Peak Compound	(% of Peak area on gas chromatograms) Oak A I	Oak A II[a]	Oak B I	Oak B II	Cherry I	Cherry II	Bamboo I	Bamboo II	Pine I	Pine II	Cedar I	Cedar II	Methods of identification
24	Acetic	56	13	28	20	9	14	17	13	74	6	10	5	IR, MS
27	Propionic	13	43	32	38	35	48	50	42	9	39	36	36	〃
29	Isobutyric	3	6	4	6	7	4	3	4	1	9	7	7	〃
32	*n*-Butyric	1	16	10	11	13	11	15	11	+	11	17	17	〃
34	Isovaleric	+[b]	3	1	1	2	2	1	2	+	3	3	3	〃
	cis-Crotonic	0.3	0.8	+		0.3		+		0.3	1.5	2.5	3	〃, NMR
35	*n*-Valeric	+	2	1	1	1	1	1	1		1	1	2	〃
37	*trans*-Crotonic	0.7	0.7	0.7	1	1.3	0.7	0.4	0.9	0.2	2	1.2	1	〃 〃, NMR
Total acidity[c] (ml of 0.05 N NaOH)		18.4	17.1	19.4	18.4	15.3	14.8	10.6	8.1	12.1	11.5	5.2	5.0	

[a] Sample II was mixed with *Quercus acutissima*.
[b] $+<0.1$
[c] 5 ml of a fivefold dilution of aqueous smoke condensate was titrated with 0.05 N NaOH.

TABLE IV. RELATIVE COMPOSITION OF FLAVOR CONSTITUENTS IN THE PHENOLIC FRACTION

No.	Peak Compound	Oak A I	Oak A II[a]	Oak A III[b]	Oak B I	Oak B II	Cherry I	Cherry II	Bamboo I	Bamboo II	Bamboo III[b]	Pine I	Pine II	Pine III[b]	Cedar I	Cedar II	Methods of identification
50	Guaiacol	45	34	15	40	39	30	11	36	20	40	26	21	16	24	22	IR, MS, NMR
54	4-Methyl guaiacol	12	9	6	12	13	9	1	7	5	13	10	11	12	11	12	〃 〃
57	4-Ethyl guaiacol	2	2	2	2	2	1	1	2	2	3	1	2	2	2	2	〃 〃
56	Phenol																
	o-Cresol	24	32	48	23	24	39	67	40	57	24	40	37	47	45	40	〃 〃
58	*m*-Cresol																
	p-Cresol	10	12	16	10	11	13	11	9	11	10	15	17	18	16	21	〃 〃
59	2,4-Xylenol																
62	3,5-Xylenol	4	1	2	4	1	4	3	3	3	1	1	2	1	2	2	〃 〃
63	3,4-Xylenol	+[c]	+	1	+	0	+	2	+	+	+	+	1	+	+	+	〃
64	Syringol	4	3	10	4	3	4	4	3	1	3	4	4	0	0	0	
65	4-Methyl syringol	2	0	2	1	0	1	0	+	0	1	1	0	0	0	0	〃 〃
66	4-Ethyl syringol	0	0	1	+	0	0	0	0	0	+	0	0	0	0	0	〃

[a] Sample II was mixed with *Quercus acutissima*.
[b] Sample III was undistilled smoke condensate, but sample III in oak A was *Quercus acutissima*.
[c] $0<+<0.5$.

TABLE V. RELATIVE COMPOSITION OF FLAVOR CONSTITUENTS IN THE CARBONYL FRACTION

No.	Peak Compound	Oak A	Oak B	Cherry	Bamboo	Pine	Cedar	Methods of identification
12	Cyclopentanone	3	4	3	11	1	3	IR, MS
25	2-Methyl-2-cyclopentenone	10	11	13	7	10	11	IR, MS, NMR
28	Furfural	38	38	37	41	49	27	IR, MS, NMR
31	2-Acetylfuran	8	11	9	11	6	9	IR, MS, NMR
33	3-Methyl-2-cyclopentenone	1	1	2	1	3	2	IR, MS, NMR
34–1	2,3-Dimethyl-2-cyclopentenone	2	2	4	2	2	2	IR, MS, NMR
34–2	5-Methylfurfural	24	22	22	12	17	31	IR, MS

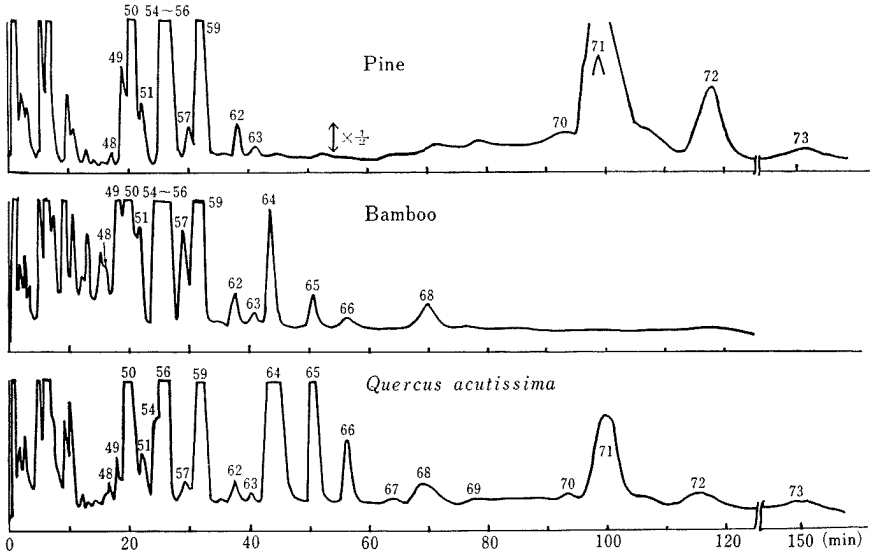

FIG. 4. Gas Chromatograms of the Phenolic Fractions from Undistilled Smoke Condensates.

Column temp.: 160~200°C (1°C/min).
49) 3-methylcyclopenta-1,2-dione, 50) guaiacol, 3,4-dimethylcyclopenta-1,2-dione 51) 3-ethylcyclopenta-1,2-dione, 54) 4-methylguaiacol, 56) phenol, *o*-cresol 57) 4-ethylguaiacol, 59) *m*- and *p*-cresol ,2,4-xylenol, 60) 4-propylguaiacol, 61) 2,3-xylenol, 62) 3,5-xylenol, eugenol, 63) 3,4-xylenol, 64) syringol (2,6-dimethoxyphenol) 65) 4-methylsyringol, 66) 4-ethylsyringol, 67) 4-propylsyringol, 68) 3-methoxycatechol, 69) 4-allylsyringol, 71) pyrocatechol, acetovanillone, 72) 4-methylpyrocatechol, 73) 4-ethylpyrocatechol.

(sample I and II), syringol homologues might be artifacts, because they were not detected in the UDSC (sample III).

Peak 60 was identified as 3-methylpyrocatechol by coincidence of the IR and MS spectra with those of an authentic sample, as well as the presence of each corresponding proton in the NMR data: MS (*m/e*: 124 (M^+)), IR (ν cm^{-1}: 3400, 1480, 1280, 1200, 760, 1245, 1335, 940, 720), NMR ($\delta^{CDCl_3+CCl_4}_{Me_4Si}$: 2.18 (3H, s, CH_3), 6.52 (3H, =CH), 3.44 (2H, OH)). The other peaks 61, 62 and 63 were confirmed to be pyrocatechol, 4-methylpyrocatechol and 4-ethylpyrocatechol, respectively. These compounds were also found in wood tar[11] and have a strong antioxidant effect. It was observed that they had heavy burnt and phenolic odors with some sweetness, and

that they were present in *Q. acutissima* and pine, but not in bamboo.

Some differences were found in compositions between broad- and needle-leaved trees. That is, guaiacol and alkyl-substituted guaiacol having a smoky sweet aroma were present to a greater extent than phenol and cresols with a harsh phenolic, medicine-like aroma in oak A and B. However, in needle-leaved trees, the latter were present to a greater extent than the former. It was thought that the relative ratio of the total content of guaiacol and its derivatives to that of phenol, cresols and xylenols had a considerable effect on the differences in aroma of the phenolic fractions from various kinds of woods. It has been claimed that syringol has the characteristic smoky aroma and that the differences in aroma between broad- and needle-leaved woods might be due to differences of the component units of their lignins. The latter have guaiacol-type units, while the former have both guaiacol and syringol types. However, syringol was not a major component in DSC's.

Carbonyl fraction

There were no very significant differences of aroma in the carbonyl fractions from the six kinds of woods, as with the phenolic or basic ones. Nearly similar aromatic compositions were found in the carbonyl fractions of oak A, B and cherry. 5-Methylfurfural was present to a greater extent in Japanese cedar than in bamboo and pine.

Since other carbonyl compounds were also found in the basic and non-carbonyl neutral fractions, however, further detailed investigations are needed to elucidate the precise relation between composition and flavor.

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