Minor Carboxylic Acids in Finnish Tall Oil Fatty Acids: Aromatic, Alicyclic, and Branched Chain Aliphatic Constituents

A. HASE, T. HASE, Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo 15, Finland; and B. HOLMBOM, Institute of Wood Chemistry and Cellulose Technology, Åbo Akademi, SF-20500 Turku 50, Finland

ABSTRACT

Thirteen aromatic carboxylic acids in Finnish tall oil fatty acids were identified and quantified by gas chromatography-mass spectrometry. Their sum content was 1.08%. Main aromatic acids were two stereoisomeric secodehydroabietic acids and dehydroabietic acid. The other aromatic acids were various secoditerpene and *o*-alkylphenylalkanoic acids. A number of minor nonaromatic acids with mono- and bicyclic, and branched chain structures were also identified and quantified.

INTRODUCTION

It is known that distilled tall oil contains cyclic carboxylic acids other than pimaric and abietic type resin acids (1-4). Their amount depends on the origin of the crude tall oil and on the conditions of the distillation process (1,3). About 80% of these cyclic acids are nonaromatic cyclic C_{18} acids consisting mainly of two stereoisomers of 4-(5-pentyl-3a,4,5,7a-tetrahydro-4-indanyl)butanoic acids (compounds *18* and *22*).

Cyclic components in tall oil are of particular interest owing to the potential nutritional value of tall oil fatty acids. The purpose of this work was to isolate and analyze primarily the aromatic carboxylic acids in tall oil fatty acids.

EXPERIMENTAL PROCEDURES

A tall oil fatty acid distillate (Enso-Gutzeit Oy, Finland) having an acid value of 193.4 and containing ca. 2% of resin acids and ca. 2% of neutral material was studied. Straight chain fatty acids were removed through urea adduct formation as described earlier (1). The acids were separated from neutral constituents by extraction with aqueous KOH solution. Methylation was carried out by methanol under acidic conditions. The methyl esters were distilled in vacuo. Unmethylated acids, primarily resin acids, were left in the residue, which also contained certain aromatic carboxylic acids, i.e., the two stereoisomeric secodehydroabietic acids *11* and *15* and dehydroabietic acid (*1*) that were determined directly from the tall oil fatty acid sample. The distillate represents a concentrate of cyclic methyl esters of the tall oil fatty acids, totaling about 6% of the original sample, and containing about 45% of cyclic methyl esters, the major linear fatty acid methyl esters being methyl 5,9,12-octadecatrienoate (36%) and methyl linoleate (4%).

This concentrate of cyclic acid was analyzed qualitatively and quantitatively for aromatic carboxylic acid methyl esters. The qualitative method was as follows. To prevent interference by the linear fatty acid methyl esters, the sample was fractionated using countercurrent argentation distribution as described earlier (1). It was found that the aromatic carboxylic acid methyl esters were not present quantitatively in any of the 12 fractions obtained, but enriched slightly in the first hexane phase, their content decreasing in later fractions. The first hexane phase was examined by high pressure liquid chromatography (HPLC) using a 30-cm fatty acid column (Waters Associates, MA) and a Waters M6000 liquid chromatograph equipped with a refractometer and UV detector. A THF:CH_3CN:H_2O (25:45:50) mixture was used as the eluent with a flow rate of 1.5 ml/min. The distribution of the cyclic methyl esters is shown in Figure 1. From the eluent, eight fractions were collected as shown in Figure 1, and the fractions were examined by gas chromatography-mass spectrometry (GC-MS) on a LKB 900 instrument using a glass capillary column coated with 1,4-butanediol succinate (BDS). The column was 35 m long with an internal diameter of 0.31 mm and had a liquid phase film thickness of 0.23 μm. Equivalent chain length (ECL) values were determined from isothermal analyses at 190 C.

The aromatic methyl esters eluted in HPLC fractions II and III. Gas chromatograms of the fractions are shown in Figure 2. After identification of the aromatic carboxylic methyl esters, their content was determined quantitatively by GC from the original cyclic concentrate obtained from urea fractionation. These results are summarized in Table I.

Alicyclic methyl carboxylates were eluted in HPLC fractions IV-VI, and unsaturated branched chain methyl esters in fractions VI-VIII. Saturated branched chain fatty acids were removed in urea adduction and were analyzed directly from tall oil fatty acid samples. The alicyclic and branched chain fatty acids in tall oil fatty acids are summarized in Table II.

RESULTS AND DISCUSSION

Previously, certain aromatic carboxylic acids in tall oil fatty acids have been quantified (3,4), and include the two stereoisomeric secodehydroabietic acids *11* and *15*, dehydroabietic acid (*1*), and methyl dehydroabietate. The present sample contained 0.35% and 0.21% of *11* and *15*, respectively, and 0.07% of *1*, as determined by GC of the original sample. The sum content of the other aromatic acids identified in this work was 0.45% (Table I). Thus the

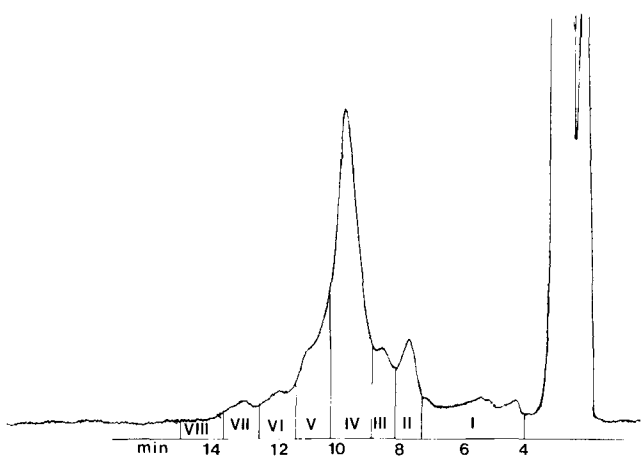

FIG. 1. HPLC chromatogram (differential RI detector) of cyclic acid methyl ester concentrate with collected fractions marked. Column: 30 cm fatty acid column (Waters Associates), eluent: THF/CH_3CN/H_2O, 25:45:50, 1.5 ml/min.

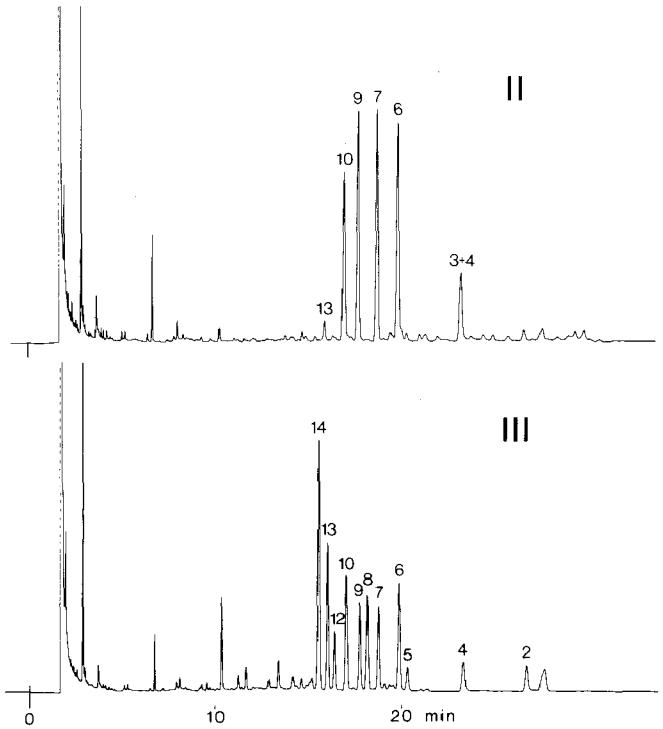

FIG. 2. Gas chromatograms of HPLC fractions II and III. Column: BDS 35 m x 0.31 mm ID. Column temperature: 190 C. Peaks numbered as in Table I.

total content of aromatic carboxylic acids was 1.08%.

The majority of the carboxylic acid methyl esters were identified by comparing their mass spectra with published spectra. Compounds *8*, *11*, *14*, and *15*, which are the main aromatic acids in tall oil fatty acids, are identical with those formed via ring opening and aromatization of levopimaric acid on alkaline thermal treatment (8,9). This was confirmed by GC-MS analysis of the original reaction product mixture of Takeda et al. (8,9). Compounds *11* and *15* have been shown to be formed in the alkaline kraft pulping process (3) and are present in distilled tall oil (4). Compounds *8* and *14* have also been identified in tall oil fatty acids (1). Thus it is apparent that levopimaric acid reacts in the same way in the kraft pulping process and under the alkaline thermal conditions used by Takeda et al. (8,9).

Two other diterpenoid acids *5* and *12* (MW 316, Me ester), which apparently have not been observed before, were also found and appear among the other ring cleaved aromatized diterpenoid compounds *8*, *11*, *14*, and *15*. The new acids (mass spectral data given below) are of the doubly ring cleaved type, similar to *8* and *14*, as is shown by (a) the appearance of the ester McLafferty cleavage ion (m/e 88), shown only by ring A cleaved diterpene esters; (b) the absence of a m/e 101 ion, observed (2,8,9) in the MS of the (ring A cyclohexanoid) secodehydroabietic acids *11* and *15*; and (c) the near absence of a m/e 284 ion, again shown (2,8,9) only by *11* and *15*. Further key information is provided by the peaks at m/e 187 and 133 which establish (9) the location of the double bond at C-6. Thus, *5* and *12* must differ from *8* and *14* at ring C which in the last-mentioned is present as a 3-isopropylphenyl group. We suggest tentatively that *5* and *12* have ring C in 5-methyl-5-vinyl-1,3-cyclohexadien-3-yl form as shown, and would thus originate from the pimaric type acids. In the MS of *8* and *14*, the ratio of peaks at m/e 133 and 146 (benzylic cleavage and C-7/C-8 cleavage with H^+ migration, respectively) is ca. 0.8, whereas in the MS of *5* and *12*, that ratio is ca. 0.3. This would indicate that in *5* and *12*, the cleavage leading to the m/e 133 ion is less favored owing to the absence of aromatic character at ring C. Alternatively, one might invoke a 4-methyl migration and a double bond shift in the pimaric type acids, which should provide good

Mass spectrum of *5*, m/e (% rel. int.): 55 (23), 67 (14), 81 (14), 88 (60), 91 (36), 92 (22), 95 (15), 105 (23), 109 (9), 115 (8), 117 (25), 119 (12), 123 (8), 131 (77), 132 (12), 133 (43), 134 (13), 146 (100), 151 (14), 159 (7), 187 (57), 188 (10), 219 (6), 241 (1), 281 (1), 284 (1), 285 (1), 316 (5).

Mass spectrum of *12*, m/e (% rel. int.): 67 (8), 69 (8), 79 (8), 81 (11), 88 (36), 91 (20), 92 (11), 93 (6), 95 (10), 105 (10), 109 (7), 117 (13), 123 (6), 131 (29), 132 (4), 133 (19), 134 (4), 144 (4), 145 (4), 146 (100), 147 (15), 151 (8), 173 (2), 183 (3), 187 (14), 188 (3), 316 (1).

TABLE I

Aromatic Carboxylic Acids Present in Tall Oil Fatty Acids

Compound no.	MW (methyl ester)	HPLC fraction	ECL value[a]	Content, wt %[b]	Literature
1	314		24.25	0.07	
2	290	III	22.72	0.01	5
3	288	II	22.17	0.015	1
4	290	II, III	22.17		6
5[c]	316	III	21.62	0.005	
6	290	II, III	21.63	0.03	7
7	290	II, III	21.44	0.03	7
8	316	III	21.29	0.09	8
9	290	II, III	21.25	0.03	7
10	290	II, III	21.10	0.03	6
11	316		20.96	0.35	2,3,8,9
12[c]	316	III	20.94	0.03	
13	290	III	20.89	0.03	6
14	316	III	20.76	0.18	8
15	316		20.30	0.21	3,8,9

[a]BDS, 190 C.

[b]Wt % of tall oil fatty acids.

[c]Non-aromatic, appearing among aromatic acids.

TABLE II

Nonaromatic Carboxylic Acids of Cyclic or Branched Chain Structure Present in Tall Oil Fatty Acids

Compound no.	MW (methyl ester)	HPLC fraction	ECL value[a]	Content, wt %[b]	Literature
16	320	VI	20.75	0.03	1
17	340		20.73	0.05	3
18	292	IV, V	19.83	2.3	1
19	308	VI	19.50	0.17	12
20	308	VI	19.22	0.33	12
21	310	VIII	18.97	0.67	3
22	292	IV, V	18.96	0.9	1
23	312		18.72	0.24	1
24	294	VI	18.30	0.05	
25	310	VIII	18.17	0.06	
26	294	VI	17.97	0.05	
27	298		17.72	0.05	3
28	282	V	17.06	0.06	13
29	284		16.72	1.03	3
30	270		15.71	0.05	3

[a]BDS, 190 C.
[b]Wt % of tall oil fatty acids.

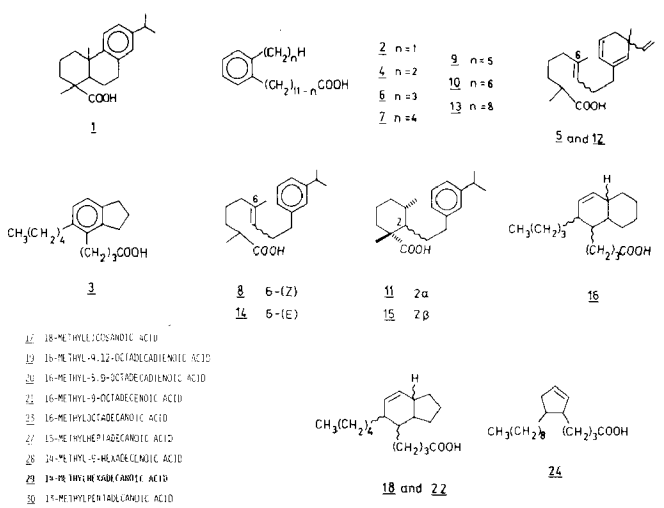

FIG. 3. Structures of aromatic, cyclic, and branched chain carboxylic acids in tall oil fatty acids. Compounds *1-24* and *27-30*.

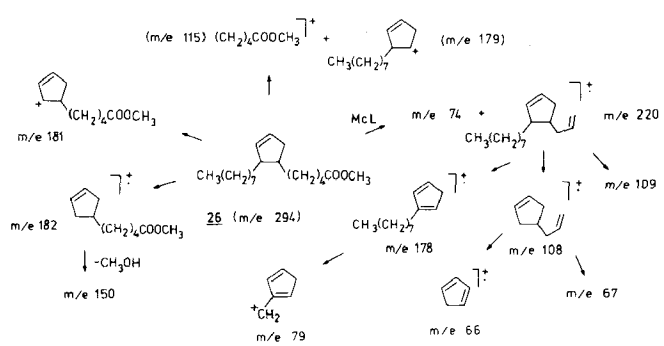

FIG. 4. Proposed structure and fragmentation scheme for compound *26*.

driving force for a subsequent thermal ring B cleavage as ring C would then be able to aromatize. Further studies are now underway to establish the identity of *5* and *12*.

The ring formation and aromatization of linoleic and pinolenic (all *cis* 5,9,12-octadecatrienoic) acids during tall oil distillation produces the *o*-alkylphenylalkanoic acids *2, 4, 6, 7, 9, 10,* and *13* (*o*-heptylphenylbutanoic acid was conspicuously absent). The composition of aromatic isomers is more similar to that formed from eleostearic acid (9,11,13-18:3) than that from linoleic acid (9,12,15-18:3) (10). Michael (11) found that methyl linoleate gave 0.6% of a mixture of 7 and *9* when heated at 200 C for 200 hr. Also, Hutchison et al. (5) have isolated the *o*-methyl isomer *2* from heated linseed oil.

A number of nonaromatic carboxylic acids with a cylic or nonlinear carbon chain structure were also found (Table II), consisting mainly of acids known before. It is well known that linoleic and linolenic acids readily form cyclic carboxylic acids with cyclohexene or cyclohexadiene structures (14,15). Many of these are present in tall oil fatty acids in small amounts, eluting in HPLC fraction V and having ECL values on BDS column between 18.5 and 19.6. These compounds show up in about 20 peaks, each representing less than 0.01% of the original tall oil fatty acids. Separate from these are elute compounds *24* and *26* (ECL values 18.30 adn 17.97, respectively) which probably are formed via the ene reaction (16) from the 5,9-octadecadienoic acid present in tall oil. The tentative structures and fragmentation of the methyl esters are shown in Figures 3 and 4 (mass spectrum for *26* is given below).

In addition to the above-mentioned artifact acids, tall oil fatty acids also contain a number of fatty acids with a branched carbon chain. These acids originate, in contrast to the previous group, from the wood material used for pulping. The most prominent group of these naturally occurring acids consists of the saturated anteiso fatty acids *17, 23, 27, 29,* and *30* (3) (Table II). The unsaturated branched fatty acids present in the sample are listed in Figure 3 and in Table II and are known to occur in spruce and pine wood extractives and in tall oil (12, and unpublished results of R. Ekman, B. Holmbom, and H. Yildirim). Compound *25* is evidently a doubly branched, possibly 11,15-dimethylheptadecenoic acid, and previously has not been detected. The mass spectrum (see listing on next page) does not reveal the position of the double bond.

Mass spectrum of *25*, m/e (% rel. int.): 55 (81), 56 (38), 57 (29), 67 (20), 68 (11), 69 (100), 70 (15), 71 (14), 74 (14), 81 (19), 82 (8), 83 (45), 84 (16), 85 (6), 87 (8), 95 (13), 96 (11), 97 (24), 98 (10), 109 (8), 110 (4), 111 (11), 112 (5), 123 (6), 124 (5), 125 (16), 126 (5), 138 (9), 139 (18), 140 (22), 141 (6), 151 (5), 171 (18), 179 (9), 180 (3), 181 (3), 194 (14), 195 (2), 207 (5), 211 (6), 236 (1), 278 (4), 279 (17), 280 (3), 281 (2), 310 (5).

Mass spectrum of *26*, m/e (% rel. int.): 53 (14), 54 (38), 55 (77), 56 (13), 57 (15), 59 (14), 65 (9), 66 (9), 67 (99), 68 (27), 69 (32), 74 (17), 77 (14), 78 (6), 79 (38), 80 (32), 81 (90), 82 (56), 83 (26), 84 (10), 85 (6), 87 (14), 91 (17), 93 (24), 94 (18), 95 (65), 96 (31), 97 (20), 101 (13), 106 (11), 107 (20), 108 (55), 109 (3), 110 (13), 111 (8), 115 (11), 119 (7), 121 (30), 122 (14), 123 (20), 124 (7), 133 (8), 135 (14), 136 (11), 137 (12), 145 (5), 149 (33), 150 (100), 151 (31), 152 (6), 163 (12), 164 (15), 178 (14), 179 (23), 180 (15), 181 (15), 182 (18), 193 (5), 194 (4), 195 (10), 196 (7), 197 (4), 220 (6), 240 (4), 244 (5), 262 (4), 263 (10), 294 (26).

ACKNOWLEDGMENTS

Mass spectra were recorded by M. Reunanen. A sample of the original reaction product mixture of Takeda et al. from alkaline treatment of levopimaric acid was provided by D.F. Zinkel, USDA, Forest Products Laboratory, Madison, WI. One of the authors (A.H.) has been financially supported by the Finnish Academy.

REFERENCES

1. Hase, A., T. Hase, and R. Anderegg, JAOCS 55:407 (1978).
2. Zinkel, D.F., J.W. Rowe, and LC. Zank, Ibid. 46:633 (1969).
3. Holmblom, B., "Constituents of Tall Oil," Ph.D. thesis, Åbo Akademi, Turku, Finland, 1978.
4. Holmbom, B., JAOCS 55:876 (1978).
5. Hutchinson, R.B., and J.C. Alexander, J. Org. Chem. 28:2522 (1963).
6. Zeman, A., H. Scharmann, and W.R. Eckert, Fette Seifen Anstrichm. 71:283 (1969).
7. Scharmann, H., W.R. Eckert, and A. Zeman, Ibid. 71:118 (1969).
8. Takeda, H., W.H. Schuller, and R.V. Lawrence, J. Org. Chem. 34:1459 (1969).
9. Takeda, H., W.H. Schuller, and R.V. Lawrence, Ibid. 33:3718 (1968).
10. Mikusch, J.D., and A.N. Sagredos, Fette Seifen Anstrichm. 73:8 (1971).
11. Michael, W.R., Lipids 1:359 (1966).
12. Ekman, R., Phytochemistry (In press).
13. Boon, J.J., Lipids 12:712 (1977).
14. Perkins, E.G., and W.T. Iwaoka, JAOCS 50:44 (1973).
15. Artman, N.R., in "Advances in Lipid Research," Vol. 7, Edited by R. Paoletti and D. Kritchevsky, Academic Press, New York, NY, 1969, p. 245.
16. Hoffmann, H.M.R., Angew. Chem. Int. Ed. 8:556 (1969).

[Received June 28, 1979]