Origin of Bicyclic Fatty Acids in Tall Oil

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ABSTRACT

It was shown that two bicyclic fatty acids present in Finnish tall oil were formed from (5Z,9Z,12Z)-5,9,12-octadecatrienoic acid, pinolenic acid (I). Under the alkaline conditions of sulfate pulping, pinolenic acid forms conjugated isomers which undergo Diels-Alder cyclization during the heating in the tall oil distillation. The cyclization products, here called cyclopinolenic acids, are bicyclic fatty acids and stereoisomers of 4-(5-pentyl-3a,4,5,7a-tetrahydro-4-indanyl) butanoic acid (IV and V).

INTRODUCTION

During the last decade, a number of new fatty acids have been isolated and identified from Finnish tall oil fatty acid distillates.

Quantitatively the most important (more than 10%) was the (5Z,9Z,12Z)-5,9,12-octadecatrienoic acid (1,2) later named pinolenic acid (I) (3), which also has been isolated from Finnish pine wood and pine seed oil (4). Pinolenic acid also is present in the fatty acid extract of New Zealand pine (5) and in North American tall oil (4). Also the benzene extract from lodge pole pine bark contains pinolenic acid (6).

A minor fatty acid (less than 5%) of Finnish tall oil is the (5Z,11Z,14Z)-5,11,14-eicosatrienoic acid (7). Finnish pine seed and tall oil fatty acids have been found to contain also small amounts of (5Z,9Z)-5,9-octadecadienoic acid (8,9) and (Z)-11-eicosaenoic acid (10). Also branched chain saturated fatty acids have been reported (1), the main component being 14-methylhexadecanoic acid (9).

The secondary tall oil fatty acids that arise during sulfate pulping and tall oil distillation processes are incompletely known. It has been proved that alkaline pulping causes double bond rearrangements with the formation of conjugated systems in di- and triunsaturated acids (11). Octadecadienoic acid with conjugated double bonds have been found (9,10). The conjugated trienoic fatty acids present (9) are probably conjugates of pinolenic acid (10). Recently, it was found in our laboratory that the Finnish tall oil fatty acid distillate contains two bicyclic fatty acids. The combined content of these two pentyl tetrahydroindanyl butanoic acids was 2.8-3.7% (12). It was assumed that those could have been formed from pinolenic acid analogously to the formation of bicyclic fatty acids from linolenic acid, as described by Eckert, et al. (13).

The purpose of this work was to elucidate the origin of the two bicyclic fatty acids in Finnish tall oil fatty acid distillate.

PROCEDURES

Materials and Methods

Crude tall oil and contemporary tall oil fatty acid distillate were obtained from Enso-Gutzeit O.Y., Finland. The distillate contained 2% rosin acids and 2% neutral material.

Pine wood fatty acids were isolated by extracting 15 kg of pine wood chips with 50 liter chloroform. Neutral material was removed from the extract (111 g) by extracting the alkaline soap solution with a mixture of benzene and ether. Rosin acids were removed from the remaining acid mixture (51 g) using the American Society for Testing and Materials 1585-63 method (14).

Pinolenic acid was isolated from tall oil fatty acid distillate (Yhtyneet Paperitehtaat, Valke O.Y., Finland) by urea fractionation. First a pinolenic acid concentrate was prepared in pilot plant scale (15) by adducting 97.5 kg starting material with 195 kg urea and 195 liter methanol (90%). The adduct was eluted in a column with methanol, of which 280 liter was collected. To this eluate, 71 kg urea was added; and the adduct which was formed was again eluted with methanol. From the second eluate, fatty acids were isolated with a yield of 14.5 kg. The content of pinolenic acid was 37%.

Part of the pinolenic acid concentrate was esterified in the laboratory with methanol using sulfuric acid catalyst, and the methyl esters were fractionated with urea using 4 ml methanol (90%) and 3 g urea/g fatty acid methyl ester. The methyl esters obtained from the adduct were refractionated with urea using 6 ml methanol (90%) and 1.8 g urea/g of methyl ester. Methyl esters of this filtrate were once more adducted with urea, and the methyl esters of this adduct containing 78% methyl pinolenate and 7% methyl linoleate were used as the source of pinolenic acid.

A small scale sulfate cellulose cooking experiment using pinolenic acid was conducted according to Kajanne (16).

The white lye had a sulfidity (Sulfidity $\% = \frac{100 \times Na_2S}{\text{total alkali}}$ calculated as N_2O) of 29% and was diluted to contain 32 g active Na_2O/liter. To 550 ml of this solution, 2.4 g

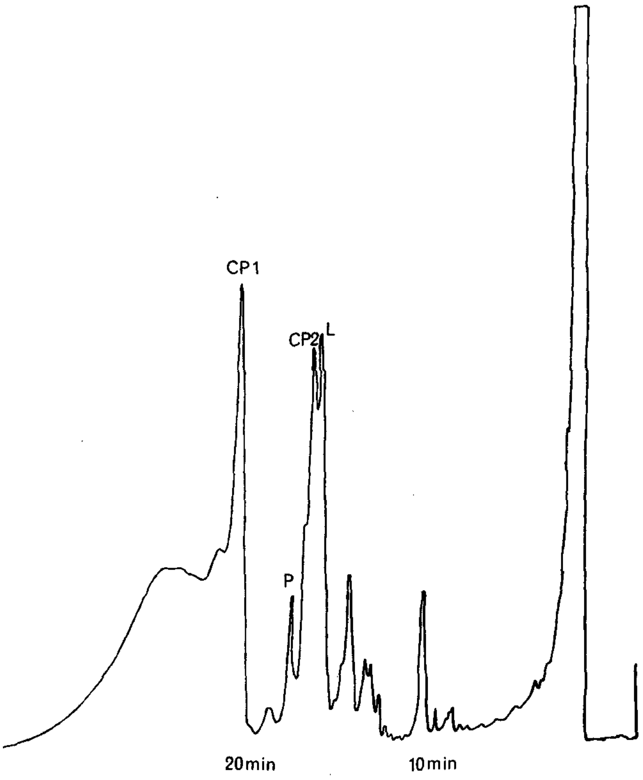


FIG. 1. Gas chromatogram of the methylated fatty acids formed in the heating of the isomerization products of pinolenic acid. Column 45 m x 0.25 mm butanediol succinate, temperature 190 C. L = linoleic acid methyl ester, P = pinolenic acid methyl ester, CP1 = methyl ester of cyclopinolenic acid (IV), CP2 = methyl ester of cyclopinolenic acid (V).

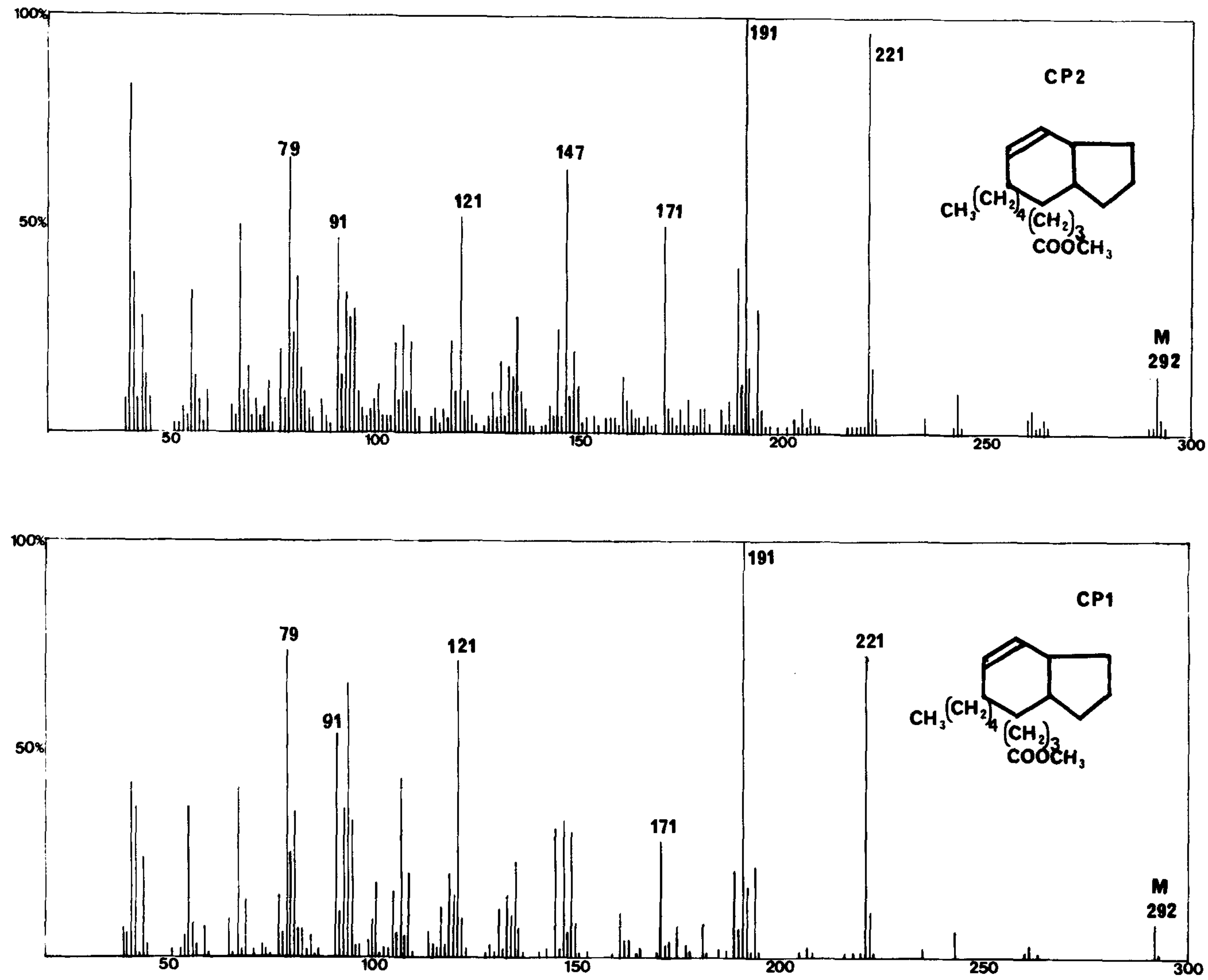


FIG. 2. Mass spectra of methyl esters of cyclopinolenic acids CP1 and CP2.

pinolenic acid was added. The experiment was carried out in a stainless steel bomb. Temperature was raised to 170 C in 2 hr and kept at 170 C 1 hr.

Instrumental Analysis

Quantitative and qualitative fatty acid analyses were made by gas liquid chromatography (GLC) using a Perkin-Elmer 900 instrument with a flame ionization detector. Operating conditions were: column 45 m x 0.25 mm, stationary phase butanediol succinate, temperature 190 C, and N_2 pressure 2 kg/cm^2. The methyl esters of the fatty acids were prepared using an etheral solution of diazomethane. Fatty acids were identified by comparing the retention times (Table I) and the mass spectra of the eluted methyl esters with reference compounds.

TABLE I

Relative Retention Times of Fatty Acid Methyl Esters on 45 m Butanediol Succinate Column at 190 C

Fatty acid	Symbol	Relative retention time
Stearic acid	S	1.00
Oleic acid	O	1.10
Linoleic acid	L	1.35
Bicyclic acid	CP1	1.40
Pinolenic acid	P	1.50
Bicyclic acid	CP2	1.70

In the quantitative analysis of the fatty acids, methyl heptadecanoate (Hormel Institute, Austin, Minn.) was used as internal standard; detector response factors were not determined for the individual fatty acid methyl esters.

The mass spectra were recorded on a Perkin-Elmer 270 GLC-mass spectrometer combination. The instrument was operated at an electron energy of 60 eV, and the ion source temperature was held at 270 C.

The IR spectra were recorded on a Perkin-Elmer 257 spectrometer using 0.1 mm cells of NaCl. The UV spectra were recorded on a Coleman Hitachi 124 spectrometer.

RESULTS AND DISCUSSION

Fatty acids extracted from pine wood chips did not contain bicyclic fatty acids IV and V, as was shown by GLC. Concentrating the sample used for GLC analysis by urea fractionation and argentation countercurrent distribution (12) confirmed the absence of bicyclic fatty acids in pine wood. The saponifiable part of the neutral material obtained in the pine chips extraction contained none of these acids either.

When neutral material and rosin acids were removed from the crude tall oil and the fatty acids were adducted with urea, it was found that the crude tall oil did not contain bicyclic fatty acids in more than trace amounts and less than 0.05%. The contemporary fatty acid distillate from the distillation plant contained ca. 2% of these bicyclic fatty acids.

These results show that the bicyclic fatty acids in tall oil distillates are not natural products but are formed in the tall oil distillation process. As linolenic acid has been shown to form bicyclic fatty acids (13,17), we assumed that pinolenic acid might have been responsible, in our case, for the formation of analogous reaction products.

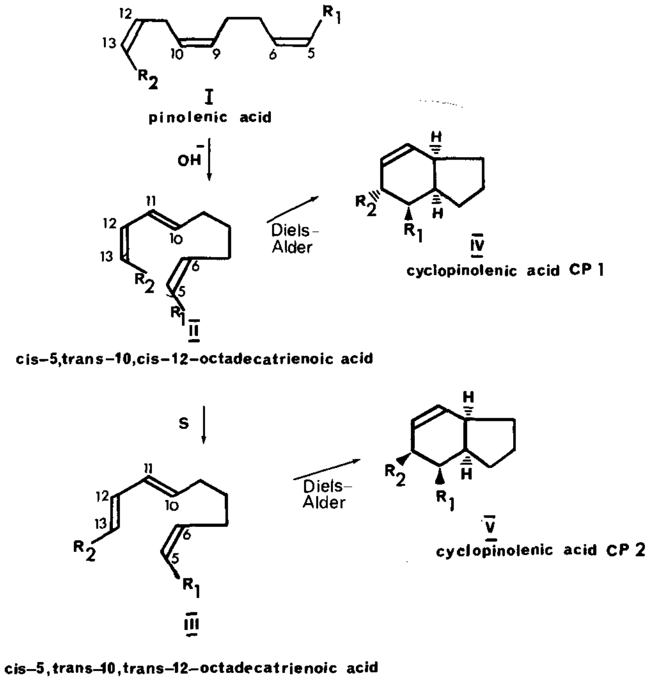
When pinolenic acid was processed by the sulfate pulping method, it was found that 90% pinolenic acid had reacted. Bicyclic fatty acids could not be detected in the reaction product. By means of UV spectrometry (18), it was found that the reaction products contained a conjugated diene structure. By means of IR spectrometry (19), it was established that the conjugated isomers from the pinolenic acid sulfate pulping contained equal amounts of conjugated *cis-trans-* and conjugated *trans-trans-*structures.

When the isomerized pinolenic acid from the sulfate pulping was distilled at a pressure of 4 mm Hg, the fatty acids started to boil at 225 C. The distillation was continued for 1.5 hr, and the temperature was 235 C at the end of the distillation. The distillate contained 30% bicyclic fatty acids. The heating of pinolenic acid at 236 C did not cause any formation of bicyclic acids. When the isomerized fatty acids obtained in the sulfate pulping were heated in a sealed glass tube at 236 C for 1 hr, the product was found to contain 19.6% bicyclic fatty acids. Figure 1 shows the gas chromatogram of this product. The mass spectra of the bicyclic fatty acids formed (Fig. 2) correspond to the mass spectra of the two 4-(5-pentyl-3a,4,5,7a tetrahydro-4-indanyl)butanoic acids (IV and V), which we earlier had isolated from the fatty acid distillate of Finnish tall oil (12). The ratio of the bicyclic fatty acids formed, CP2:CP1, was 2.2:1, which corresponds to their ratio in the Finnish tall oil fatty acid distillate. To indicate their origin, we now propose the name cyclopinolenic acid for these two bicyclic acids.

When pinolenic acid was alkali isomerized (18) no cyclopinolenic acids were found in the isomerate. According to GLC analysis, the same reaction products were formed here as in the sulfate pulping of pinolenic acid. Differences were seen only in the relative amounts of the isomerization products. According to IR spectrum, only the conjugated *cis-trans-*structure was formed, in contrast to the sulfate pulping where the ratio of the conjugated *cis-trans-* and conjugated *trans-trans-*forms was ca. 1:1. The total amount of conjugated dienes was 63% according to UV spectrum. This corresponds to the value 69% obtained by Hansen and Meiklen (20) in the alkali isomerization of pinolenic acid.

When the alkali-isomerized pinolenic acid was distilled at a pressure of 2 mm Hg and at 230 C, the distillate was found to contain 25% cyclopinolenic acids; and the ratio of the isomers formed was CP2:CP1 = 1:4.

We deduce that the bicyclic fatty acids present in Finnish tall oil fatty acid distillate are formed from pinolenic acid. Under the alkaline conditions of sulfate pulping, pinolenic acid (I) forms isomers containing a conjugated diene and an isolated double bond system (II and III) which undergo intramolecular Diels-Alder cyclization on heating in the tall oil distillation. This cyclization yields two bicyclic fatty acids with a tetrahydroindanyl structure (IV and V) (Fig. 3). These two acids which we name cyclopinolenic acids have almost identical NMR, UV, IR, and mass spectra. Thus, we assume that they are stereoisomers, their ratio depending upon the relative amounts of conjugated *cis-trans-* and *trans-trans-*isomers formed in the isomerization.



$R_1 = [CH_2]_3COOH$

$R_2 = [CH_2]_4CH_3$

FIG. 3. Tentative formation and stereochemistry of cyclopinolenic acids.

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