Communications TO THE EDITOR

The Presence of C_{20} Unsaturated Fatty Acids in Tall Oil

Sir:

There have been many investigations of the fatty acid constituents of tall oil, a mixture of resin acids, fatty acids, and neutral material, which is obtained by acidifying the black liquor skimmings of the sulfate process for the manufacture of pulp. Pine wood is used almost exclusively.

It is well known that the fatty acids of tall oil consist largely of oleic and linoleic acids although small amounts of stearic, palmitic, and conjugated linoleic acids are also present. A trace of linolenic acid is present in crude tall oil. Traces of myristic[1] and lignoceric[2] acids have been reported as being present in European oil. Palmitic and myristic acids could possibly be formed from oleic acid during the pulping.[3]

Most of the tall oil being produced in the South is by distillation fractionated to produce rosin and fatty acids. While working with the methyl esters of one type of distillate we observed that a small amount of a higher boiling fraction was obtained when the esters were fractionated through a laboratory column.

Vapor phase chromatography confirmed the presence of a fraction boiling higher than the known C_{18} acids. The methyl esters, free of rosin acids, occurring in about 12% concentration in the particular fraction we were examining, had a 20 min. retention time as compared to 13.5 min. for the C_{18} acids and 7.5 min. for palmitic acid. Helium was used as the carrier gas—30 ml./min. at 116.6 cm. absolute pressure at the column inlet and 76 cm. at the outlet. The column was 1/4 in. o.d. and 6 ft. long, packed with Dow-Corning high vacuum silicone grease supported on 60–100 mesh white Celite and maintained at 248°.

In order to study this fraction we esterified a large batch of distilled tall oil with methanol–sulfuric acid and removed the unesterified rosin acids by extracting with 1% sodium hydroxide. The recovered methyl esters of the fatty acids were fractionated at 1–2 mm. through a 2 × 48 in. vacuum jacketed column packed with protruded stainless steel packing. The first fractions were rich (37–61%) in conjugated acids, probably linoleic. As fractionation progressed the conjugated acids were slowly removed and they amounted to only 1% in the higher boiling fractions. A center cut of the higher boiling fraction had an iodine number of 213 and n_D^{30} 1.4677. The free acids recovered from a saponified sample had a neutralization equivalent of 307.5, n_D^{30} 1.4750 and an iodine number of 212. The methyl esters (18.8 g.) were hydrogenated in acetic acid at 60 lb. pressure using platinum oxide as the catalyst. Hydrogenation was rapid and complete, about 2.5 moles of hydrogen was absorbed. After filtering hot, the acetic acid was allowed to cool, thus recovering 10.8 g. of white crystals. One crystallization from ethanol in 95% yield yielded a product that melted at 46.5–47.5° (corr.). A reference sample of methyl arachidate melting at 46.6° did not lower the melting point of our sample. The remainder of the ester was removed from the acetic acid solution by adding water. This product was also nearly pure methyl arachidate as evidenced by the melting point and vapor phase chromatography data.

The saturated methyl esters were saponified and crystallized once from ethanol in 95% yield. The recovered acid had a melting point of 76° (corr.). A reference sample of arachidic acid did not lower the melting point. The neutralization equivalent was 312.9; calculated 312.5. From the iodine number, the amount of hydrogen absorbed, the refractive index, the boiling point of the methyl esters and the inability to obtain any crystallization of either the free acids or the methyl esters it appears that this higher boiling fraction is composed of approximately equal amounts of dienoic and trienoic nonconjugated C_{20} acids. From our fractionation data and vapor phase chromatography analysis we estimate there is approximately 1.4–1.7% unsaturated C_{20} acids in crude tall oil based on our analyses of the amounts present in the volatile fractions we have studied.

We believe this observation to be of special interest as, to the best of our knowledge, C_{20} unsaturated fatty acids of vegetable origin are not known to occur in such widely used and common source as the southern pine.[4,5]

THE GLIDDEN CO.
ORGANIC CHEMICAL DIVISION
PORT ST. JOE, FLA.

BURT L. HAMPTON
DWIGHT LEAVENS

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(1) H. Bergstrom and K. G. Trobeck, *Svensk Papperstidning 48*, 551–552 (1945).

(2) H. Sandquist, J. Gorton, and E. Bergtsson, *Ber.*, **64**, 2172–2174 (1931).

(3) T. Hasselstrom, *Paper Trade J.*, *85*, No. 1, 49–53 (1927).

(4) T. P. Hilditch, "The Chemical Constitution of Natural Fats," John Wiley and Sons, New York, N. Y., 1956, pp. 511–550.

(5) We wish to express our appreciation to Dr. H. G. Hunt for the chromatography data.