

what soluble in saturated bicarbonate solutions. The BIIAG will, however, be free from GSA₂ in all cases. BIIAG and BSIAG fractions corresponding to nearly pure GS₂A and GSA₂ (S content within 0.5% to 1.0% of that theoretically required for specific values of S and A) have been isolated in nearly theoretical (within $\pm 1.0\%$ on fat basis) yields [as computed from analyses of the IAG (4)] from IAG specimens of the following seed fats in this laboratory (Kartha and Ali, unpublished observations): *Garcinia indica*, Sm 66; *Vateria indica*, Sm 59; *Garcinia cambogia*, Sm 55; *Sarcestigma kleinii*, Sm 43; *Madhuca latifolia*, Sm 47; *Azadirachta indica*, Sm 33 to 40; and *Erythrina indica*, Sm 30 to 34.

In the case of fats containing GS₃, the BIIAG will be a mixture of GS₂A with all the GS₃ present in the fat and the proportions of GS₃ can be calculated from the theoretical S contents of GS₃ and GS₂A and the corrected S content of the fraction determined according to procedures described earlier (4).

The quantitative separation of GSA₂ from IAG serves two important purposes: (a) A large majority of vegetable and animal fats do not contain any GS₃, and in these cases complete separation of individual glyceride types as type derivatives is now possible. (b) So far it has not been possible to

estimate the proportions of GS₃ present in oxidation products from fats except in the case of lower saturated acid fats (6,7) and even this is on a provisional basis. The present procedure makes possible a reasonably accurate oxidative estimation of GS₃ for any fat regardless of saturated acid composition or saturated acid content. The procedure will be particularly useful for analysis of fats which do contain appreciable amounts of GS₃ as it is more convenient than crystallization or chromatographic procedures and further, is not liable to error caused by autoxidative deterioration of unsaturated glycerides to iodine value free products.

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Unusual Resin Acids in Tall Oil¹

Abstract

Combinations of silver nitrate column, gel permeation and gas liquid chromatography were used to isolate 8,15-pimaradien-18-oic, 8,15-isopimaradien-18-oic and the secodehydroabietic, 2 α -[2'(*m*-isopropylphenyl)ethyl]1 β ,3 α -dimethylcyclohexanecarboxylic acids as their methyl esters from a fraction of distilled tall oil.

Gas chromatographic examination of an intermediate fraction from the distillation of tall oil revealed that the fraction contained resin acids other than the standard abietic and pimaric type acids usually found in rosin. Although the constituents are minor components of tall oil itself, their enrichment in certain tall oil products can have an important effect on the end uses of these products.

In our work on the separation and purification of rosin acids for use as primary standards for GLC and spectral use, a combination of silver nitrate column chromatographic (as used to purify the abietenoates) (1) and preparative GLC methods has been useful. Multibore columns (15 \times 1.2, 15 \times 1.9, 19 \times 2.6 and 15 \times 3.5 cm stages) containing 200 g of silver nitrate-Woelm neutral alumina (4:10) were used in all column chromatographic separations. Petroleum ether with ethyl ether in increasing steps was used as the eluting solvent.

A 20 g fraction of methyl esters of an intermediate fraction from a tall oil distillation (the bulk of the fatty acids had been removed by preferential esterification) was placed on the column in an equal volume of petroleum ether. The eluate was monitored

by GLC and appropriately combined as follows in order of increasing amount of ethyl ether in the eluant: Fraction I, 6.3 g; Fraction II, 1.8 g; Fraction III, 5.2 g; Fraction IV, 0.3 g; Fraction V, 2.1 g; Fraction VI, 1.8 g; and Fraction VII, 0.6 g. Fractions II, IV and VI were similar to the neighboring fraction, but were not as enriched in components of current interest; they were not investigated further. Fraction VII was shown by GLC (2) to contain methyl *cis*-5, *cis*-11, *cis*-14-eicosatrienoate as its major component, a common constituent in tall oil (3).

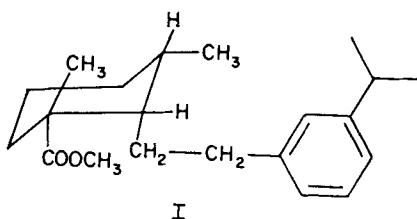
On the basis of the relative retention on DEGS and SE-30 columns, (2), the major constituent of the intermediate tall oil fraction was suspected to be methyl Δ^8 -isopimarate [methyl 8,15-isopimaradien-18-oate. The numbering and systematic nomenclature follow the recent proposals by J. W. Rowe et al. (4)]. Fraction V was recrystallized from methanol and was indeed shown to be nearly pure methyl Δ^8 -isopimarate by comparison of the NMR, IR and GLC spectra with those for authentic material. Δ^8 -Isopimaric acid has been identified as a minor constituent of pine oleoresin (5,6) and tall oil rosin (6).

Rechromatography of a 2.5 g portion of Fraction III on a new silver nitrate-alumina column yielded more Δ^8 -isopimarate and about 500 mg of a second major component in high purity. Recrystallization from methanol gave pure material (GLC) (2) of mp 37.5–38 C, cor. The postulated identity of this second component as methyl Δ^8 -pimarate [methyl 8,15-pimaradien-18-oate] (4) based on comparative GLC retention data (2), was confirmed by comparison of the NMR with the data reported by ApSimon (6). The presence of Δ^8 -pimaric acid in naval stores products has not been reported, although Genge (7) postulated its presence on mass spectral evidence.

Rechromatography of Fraction I on silver nitrate-

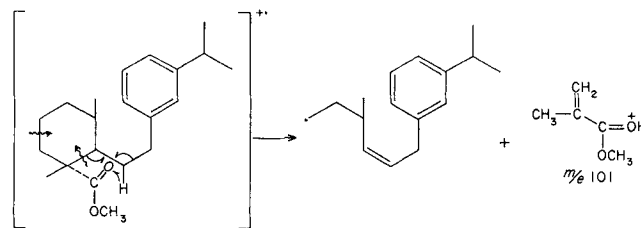
¹ Presented before the Division of Cellulose, Wood and Fiber Chemistry at the 155th National Meeting of the American Chemical Society, San Francisco, April 1968.

alumina and preparative GLC yielded a major component whose purity was improved from 80% to 98% by three passes through a Styragel gel permeation column; GPC retention volume, 107 ml (9) (a K of 0.65 with the system of Chang) (9). Final purification to 99+% was accomplished by GLC on DEGS (homogeneous by GLC on DEGS and SE-30/EGiP columns, $r_{pim} = 0.80$ and 0.77 , respectively), to give an oil; $n_D^{22} = 1.5072$; $[\alpha]_D^{20} = -25^\circ$ (c 1.0, methanol), uv_{max} (isooctane), 271 nm ($\epsilon = 240$), 267 nm ($\epsilon = 205$), 263.5 nm ($\epsilon = 282$), 262 nm(sh) ($\epsilon = 280$), 257 nm(sh) ($\epsilon = 225$) and 251 nm(sh) ($\epsilon = 165$). The material was originally assigned the 9-secodehydroabietate structure.¹ Materials very similar to this secodehydroabietate were later and independently reported as products of the base catalyzed thermal rearrangement of methyl levopimarate (11) and sodium levopimarate (12). Comparison of spectral data of our compound with that corresponding to compound 2 of the former paper suggested that the compounds were identical (see footnote 9 of Ref. 11), although there were minor discrepancies in the 60 MHz NMR spectra. However, further studies on the products from the rearrangement of sodium levopimarate (12) led to the isolation of an isomeric substance. A detailed comparison of the 100 MHz NMR data for our compound and this latter isomeric substance shows that our compound is identical to the isomeric substance rather than with 2 (also see Ref. 12 for a revision in the structure of 2). GLC on DEGS, SE-30/EGiP and Versamide 900 further substantiated this correlation (sample of Takeda's isomeric substance was obtained by GPC and preparative GLC on the mixture from treatment of methyl levopimarate with base; the mixture was furnished by W. H. Schuller, Naval Stores Laboratory, Agricultural Research Service, USDA, Olustee, Fla.). Takeda et al. have assigned the methyl 2 α -[2'-(*m*-isopropylphenyl)ethyl]-1 β ,3 α -dimethylcyclohexanecarboxylate, I, structure with which we concur and thus revise our previous isomeric 9-secodehydroabietate assignment.¹



Our mass spectrum of this compound I is essentially the same as reported by Takeda et al. (12). Of

particular note is the presence of the m/e 101 ion, identified by element mapping to be $C_5H_9O_2$, as a major fragment in a relative abundance of 49% [Takeda et al. (12) report 45.6%, but only 18% for compound 2 (11)]. Thus, although the expected elimination of methanol is shown by a weak m/e 284 peak, the major fragmentation involving the ester group is to form the stable m/e 101 allylic ion as shown.



This is analogous to that found in the fragmentation of 2-ethylheptanoate and dimethyl-di-*n*-propyl malonate (13).

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