Mass Spectra of Diterpene Resin Acid Methyl Esters[1]

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ABSTRACT

The mass spectra of 35 tricyclic, diterpene resin acid methyl esters were examined. It was found that unsaturation substantially influenced the initial fragmentation. The carbomethoxy group is readily eliminated, with the positive charge usually being retained in the cyclic fragment. No significant differences were noticed among stereoisomers.

INTRODUCTION

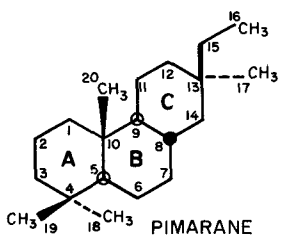
Rosin and rosin products contain a large number of component resin acids. As most of these resin acids are not readily available, we have completed a program in obtaining reference IR, UV, NMR and mass spectra (MS) of high purity resin acids, as the methyl esters. A compilation of the spectra will be published as a Forest Service paper and, in addition, the spectra will be deposited with the Thermodynamics Research Center, College Station, Texas.

In this work, we have studied the high and low resolution MS for 35 resin acid methyl esters having the parent abietane, pimarane and isopimarane skeletons (Fig. 1). [The numbering and systematic nomenclature in this paper follow the recent proposals of a group chaired by J.W. Rowe (1).] The MS for a few of the more common of these resin acid esters have been published (2-4) and Genge (5) has used a mass spectrometer with heated inlet system for the quantitative analysis of rosin constituents. The study of fragmentation mechanisms for the resin acid esters, however, has been limited to the work of Biemann (3) on pimarate, isopimarate and sandaracopimarate, and the work of Audier et al. (4) on several additional dienic, diterpene hydrocarbons, acids and esters. The MS work described herein is a comprehensive investigation of all the known resin acid esters having the above three skeletons. MS for resin acid esters having the parent labdane skeleton have been investigated by Enzell and Ryhage (6). Enzell and Wahlberg (7) and Audier et al. (8) have studied the related spectra of aromatic tricyclic diterpenes having the podocarpane, totarane and abietane skeletons.

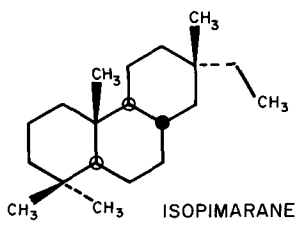
EXPERIMENTAL PROCEDURES

Resin acids were methylated with diazomethane. Gas liquid or silver nitrate column chromatography, or both, were used to prepare the esters in 99+% purity; purity was ascertained by gas liquid chromatography (GLC)on DEGS and SE-30/EGiP columns (20), and by NMR, UV and MS, where appropriate.

MS were obtained with a CEC 21-110B mass spectrometer operating at an ionization voltage of 70 eV. Compounds were introduced by direct insertion probe (except methyl palustrate and XXIX) at source temperature of 100-110 C. Methyl palustrate and XXIX were introduced through a tandem GLC-MS unit after gas chromatographic purification. This unit included a Perkin Elmer 881 gas chromatograph, a Biemann-Watson molecular separator and CEC 21-110B mass spectrometer. The recorded high resolution spectra on photoplates were measured and processed using a comparator-densitometer on-line with a XDS 930 computer as was previously reported (20). The contrast function (=0.7), as shown in the same paper, was used to calculate relative intensity of peaks. The elemental compositions given in the text were used to study the fragmentation pattern and also to observe metastable peaks.

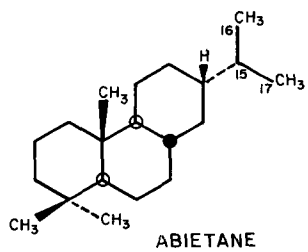


PIMARANE



ISOPIMARANE

I. 18-pimaranoate (9,10; also D.F. Zinkel and A.W. Burgstahler, in preparation
II. 8α-pimaran-18-oate (10; D.F. Zinkel and A.W. Burgstahler, in preparation)
III. 8-pimaren-18-oate (11)
IV. 8(14)-pimaren-18-oate (10)
V. 8,15-pimaradien-18-oate (11)
VI. 8(14),15-pimaradien-18-oate (12) (pimarate)
VII. 18-isopimaranoate (D.F. Zinkel and A.W. Burgstahler, in preparation)
VIII. 8α-isopimaran-18-oate (D.F. Zinkel and A.W. Burgstahler, in preparation)
IX. 7-isopimaren-18-oate (10)
X. 8-isopimaren-18-oate (11)
XI. 8(14)-isopimaren-18-oate (10)
XII. 7,15-isopimaradien-18-oate (12) (isopimarate)
XIII. 8,15-isopimaradien-18-oate (11)
XIV. 8(14),15-isopimaradien-18-oate (12) (sandaracopimarate)



ABIETANE

XV. 18-abietanoate (13)
XVI. 13β-abietan-18-oate (13)
XVII. 8α,13β-abietan-18-oate (13)
XVIII. 9β-abietan-18-oate (14)
XIX. 7-abieten-18-oate (13)
XX. 13β-abiet-7-en-18-oate (13)
XXI. 8-abieten-18-oate (13)
XXII. 13β-abiet-8-en-18-oate (13)
XXIII. 8(14)-abieten-18-oate (13)
XXIV. 13β-abiet-8(14)-en-18-oate (13)
XXV. 13-abieten-18-oate (13)
XXVI. 13(15)-abieten-18-oate (13)
XXVII. 7,13-abietadien-18-oate (abietate)
XXVIII. 8,13-abietadien-18-oate (15) (palustrate)
XXIX. 8,12-abietadien-18-oate (16)
XXX. 8,13(15)-abietadien-18-oate (13)
XXXI. 8(14),13(15)-abietadien-18-oate (neoabietate)
XXXII. 13β-abieta-7,9(11)-dien-18-oate (17)
XXXIII. 8(14),12-abietadien-18-oate (levopimarate)
XXXIV. 8,11,13-abietatrien-18-oate (dehydroabietate)
XXXV. 6,8,11,13-abietatetraen-18-oate (18)

FIG. 1. Resin acid methyl esters in the pimarane, isopimarane and abietane series.

[1]Presented in part at the Meeting of the American Chemical Society, Chicago, September 1970.

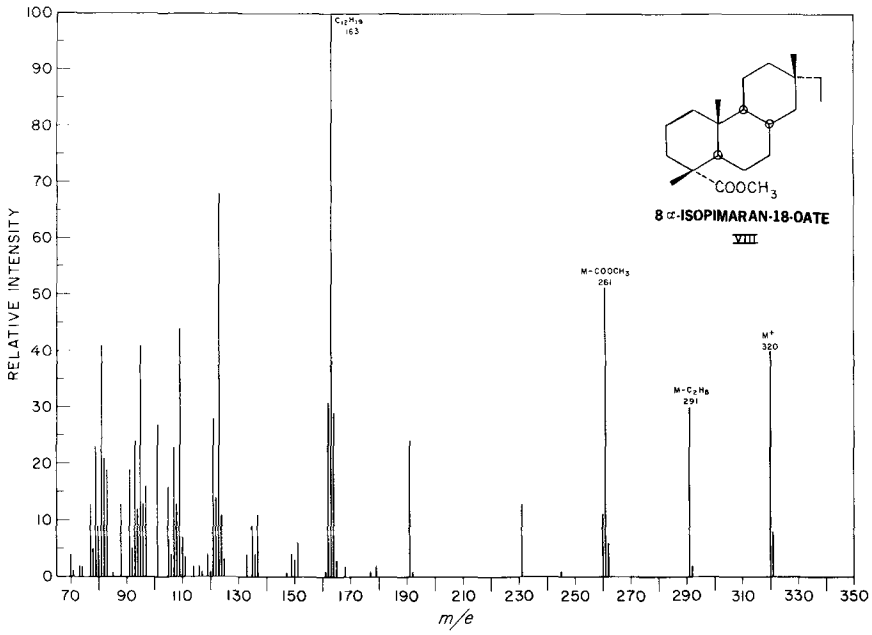


FIG. 2. Mass spectrum of methyl 8α-isopimaran-18-oate.

RESULTS AND DISCUSSION

The resin acid esters considered in this study have certain similarities in that all skeletons have 4β- and 10β-methyl and 4α-carboxymethyl substitution. In addition, the abietane series has a 13-isopropyl substituent whereas the pimarane and isopimarane series have epimeric ethyl and methyl substituents at this position. Further differences lie in degree and position of unsaturation and in stereochemistry.

The MS of a resin acid ester consists of a molecular ion, several high mass peaks (m/e over 200), and abundant low mass peaks (m/e below 150). The intensity of the molecular ion for the resin acid esters is very strong, 40-100% of the base peak, compared with that of an *n*-alkanoate ester of similar molecular weight. The cyclic structure obviously stabilizes the molecular ion (21). The location of double bonds is important in inducing fragmentation, as will be discussed later.

Most of the high mass peaks arise from the loss of substituent groups from the molecular ion. Cleavage of the ring structure usually is not involved in these high mass peaks. When two substituents are eliminated either simultaneously or consecutively, one of them always is the carbomethyoxy group. Thus, spectral patterns for these diterpene resin acid esters are significantly different from that of the diterpene hydrocarbons (4), an observation noted with the podocarpanes and dehydroabietanes (7).

Very few oxygen-containing peaks were observed in the MS of the resin acid esters. This may be partly attributed to the facile elimination of the carbomethyoxy group. One of the few exceptions is m/e 101 ($C_5H_9O_2$). This peak is probably formed by the following mechanism—[Cf. methyl 2α-[2'-(*m*-isopropylphenyl)ethyl]-1β,3α-dimethylcyclohexanecarboxylate (secodehydroabietate) (22)]:

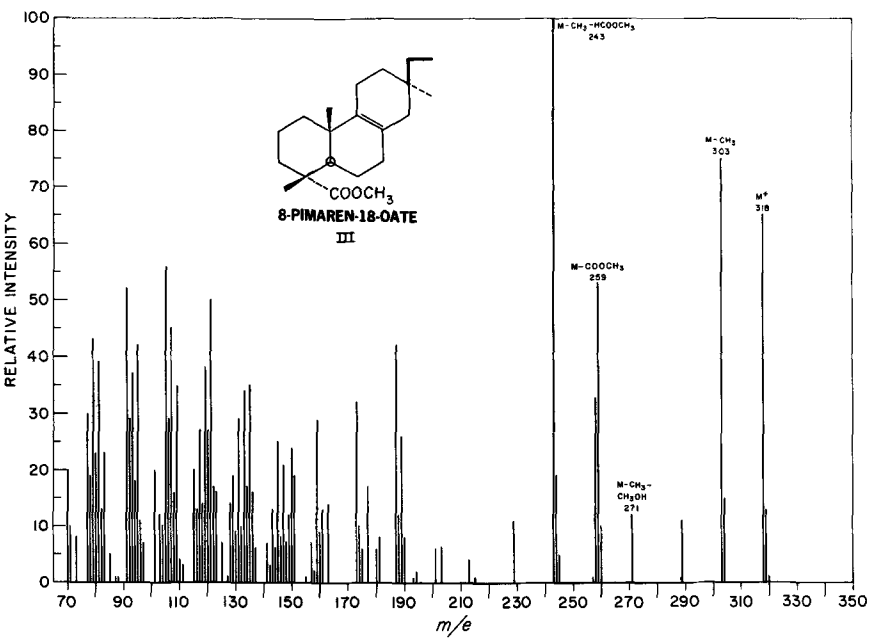


FIG. 3. Mass spectrum of an 8-ene; methyl 8-pimaren-18-oate.

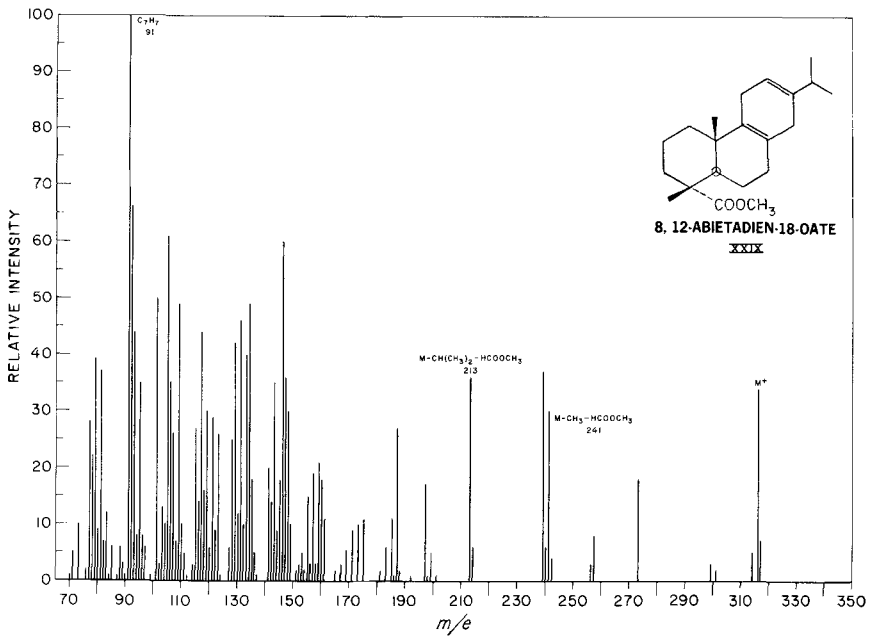
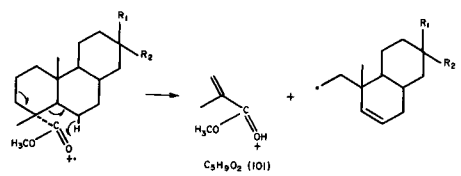


FIG. 4. Mass spectrum of methyl 8,12-abietadien-18-oate.



Although metastable ions were observed for most of the high mass peaks, their intensities were all very weak. Only a few metastable ions were observed for formation of low mass peaks. This may be partially due to the Mattauch-Herzog geometry of our instrument which is not particularly suitable for the observation of metastable ions (23). The fragmentation pathways proposed here are based on careful cross examination and comparison of the MS.

Saturated Resin Acid Esters

The abietanoates (XV-XVIII, Fig. 1), pimaranoates (I,II) and isopimaranoates (VII,VIII) have almost identical MS with the difference that the MS for the abietanoates have weak M^+-C_3H_7 peaks and the MS of the pimaranoates and isopimaranoates have weak M^+-C_2H_5 peaks. The base peak of these compounds is m/e 163 ($C_{12}H_{19}$). The only significant high mass fragment ion is m/e 261 ($C_{19}H_{33}$), which is M^+-$COOCH_3$. The relatively low intensity of other high mass peaks indicates that the loss of carbomethoxy radical is the dominant direct loss from the molecular ion. This loss of carbomethoxy radical appears to induce the cleavage of ring C to give the base peak m/e 163 ($C_{12}H_{19}$). This base peak probably is stabilized by resonance:

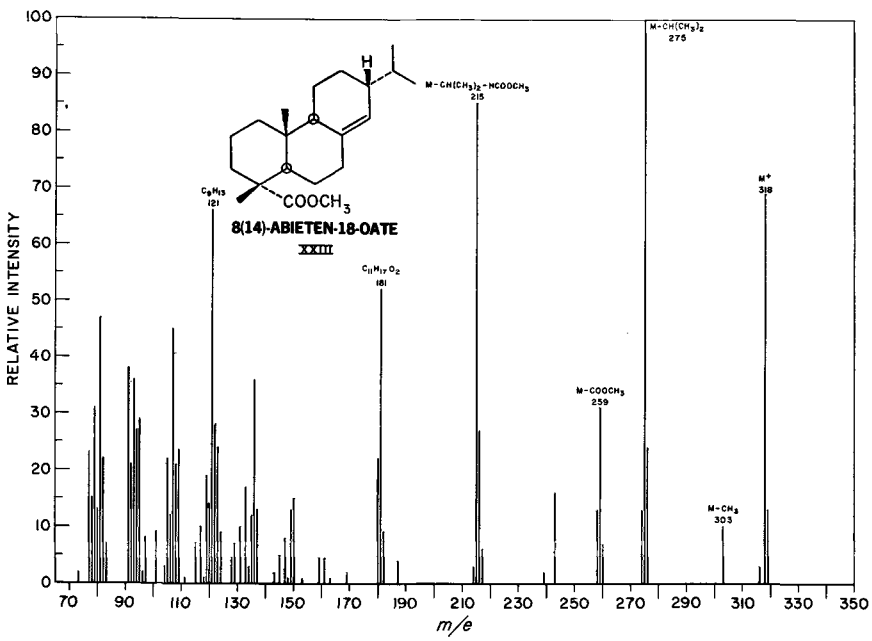


FIG. 5. Mass spectrum of an 8(14)-ene; methyl 8(14)-abieten-18-oate.

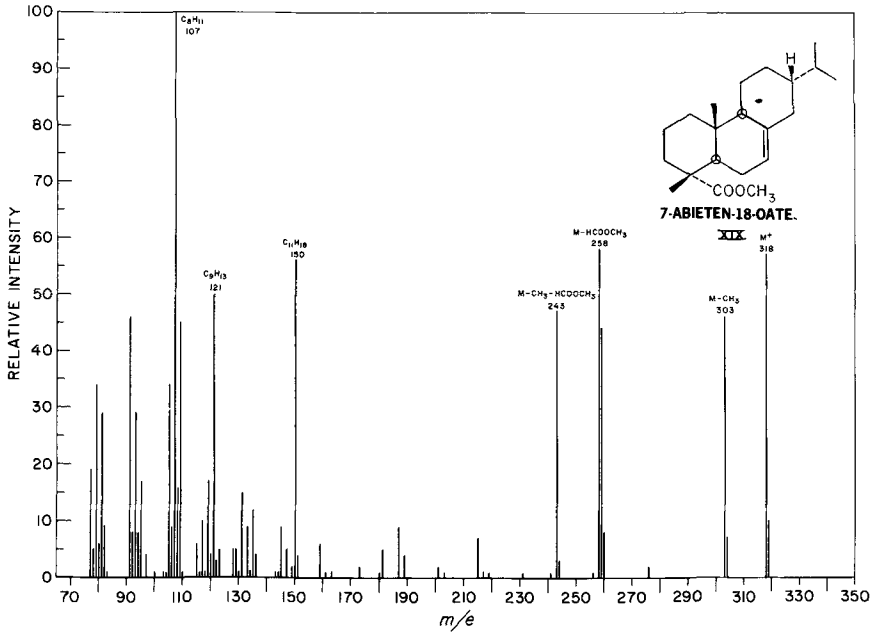
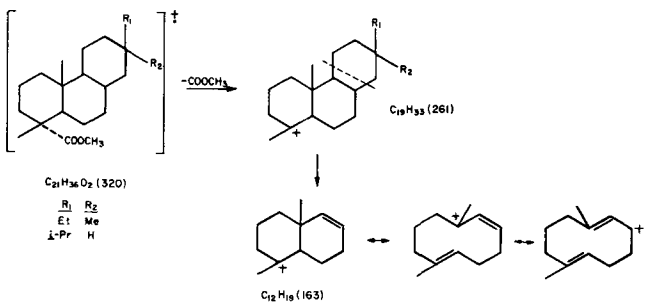


FIG. 6. Mass spectrum of a 7-ene; methyl 7-abieten-18-oate.



No significant differences were observed among the abietanoate, pimaranoate or isopimaranoate stereoisomers except that the 8α-isopimaran-18-oate (VIII, Fig. 2) has a M^+-C_2H_5 peak of 30% relative intensity compared with 5% or less for the other isopimaranoate and pimaranoates.

Unsaturated Resin Acid Esters

8-Enes. Unsaturated resin acid esters have more abundant high mass peaks than have the saturated resin acid esters. The relative intensities of these peaks vary significantly from one compound to another. As the position of double bond is the major difference in these compounds, it indicates that the double bond not only induces but also directs the fragmentation. A primary fragmentation of the 8-enes (III,X,XXI,XXII,e.g.,Fig.3) is M^+-CH_3 and has a relative intensity of 60-80% (5% or less occurs with the saturated resin acid esters). The relative intensity of this peak drops to about 20% for most of the 7-enes (IX,XIX, XX) and further decreases to less than 10% for the 8(14)-enes (IV,XI,XXIII,XXIV). It is presumed that the C-20 methyl, allylic in the 8-enes, is eliminated (4,24). Loss of this methyl radical results in an unsaturated ion which is resonance stabilized:

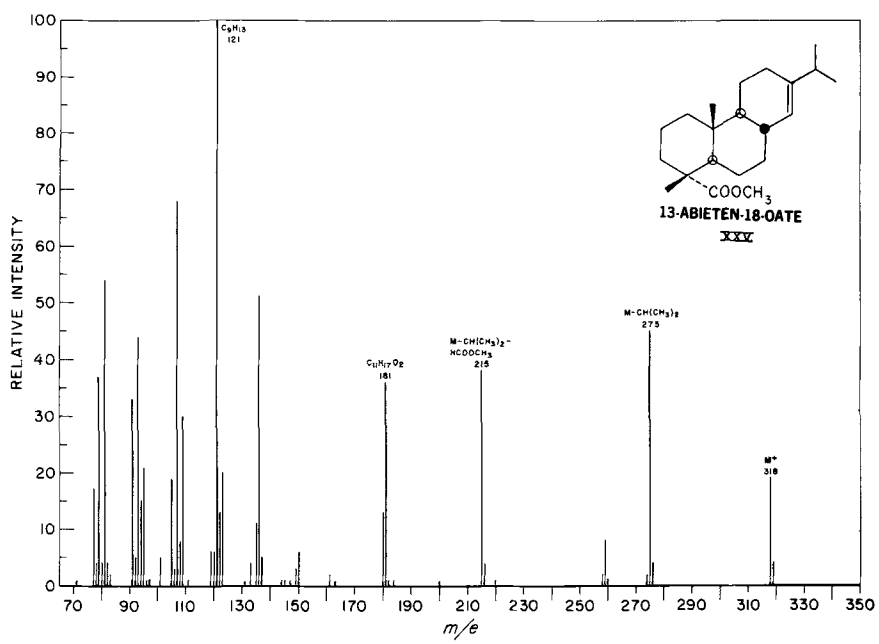


FIG. 7. Mass spectrum of methyl 13-abieten-18-oate.

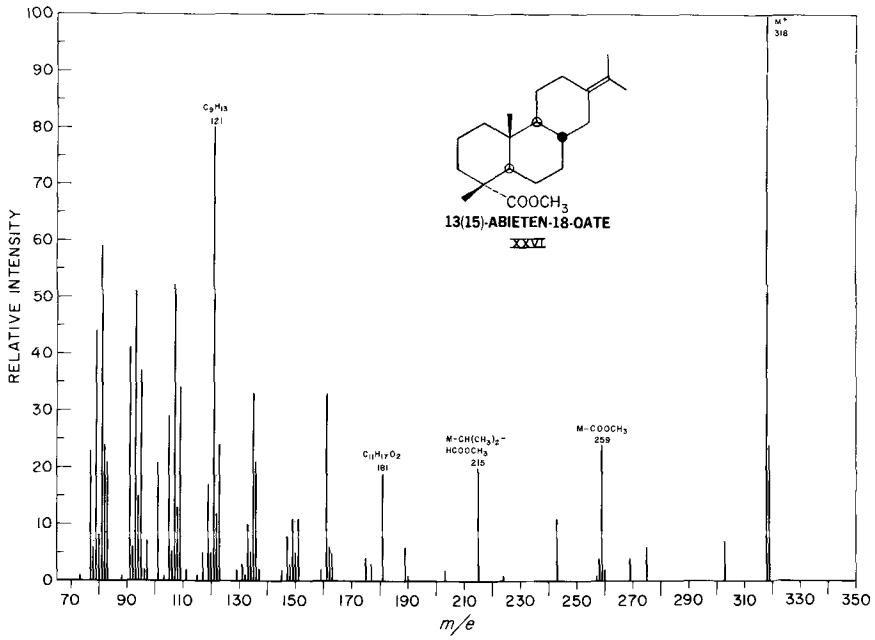
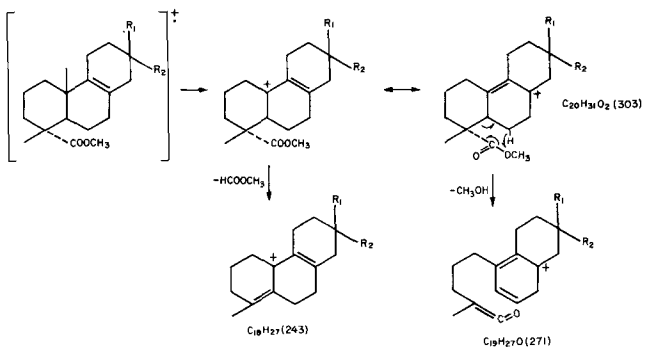


FIG. 8. Mass spectrum of methyl 13(15)-abieten-18-oate.



The contribution to the M^+-CH_3 peak through elimination of the C-19 methyl group is probably not significant. The C-18 carbomethoxy group is larger than the methyl and appears to be the favored loss from this (C-4) site. The same argument can be also applied to the substituents located on the C-13 position of the pimarenoates in that the bulkier ethyl group is lost in preference to the methyl group. For resin acid esters having the abietane skeleton, a possible methyl loss (C-16 or C-17) can occur from the isopropyl substituent. However, only a very weak M^+-CH_3 peak was observed in the spectrum of 13-abieten-18-oate (XXV) and the nonconjugated 8,12-abietadien-18-oate (XXIX) even though the C-16 and C-17 isopropyl methyl groups are allylic to the double bonds.

The carbomethoxy group is lost only as a carbomethoxy radical or methyl formate. The relative intensity of the M^+-$COOCH_3$ peak is about 30-60% for most resin acid esters. This relatively constant value indicates that unsaturation in rings B or C usually does not effect the expulsion of the ionized carbomethoxy group from the molecular ion. Significant exceptions are dehydroabietate (XXXIV), 13-abieten-18-oate (XXV), and abietadienoates having both double bonds in or exocyclic to ring C, i.e., 8,12-abietadien-18-oate (XXIX, Fig.4), 8,13(15)-abietadien-18-oate (XXX), 8(14),12-abietadien-18-oate (levopimarate, XXXIII) and 8(14),13(15)-abietadien-18-oate (neoabietate, XXXI). The M^+-$HCOOCH_3$ peak on the other hand is somewhat affected by the position of a double bond. The intensity of this peak is about half of the M^+COOH_3 peak for the 8-enes (III,X,XXI,XXII), about one third and one fifth for 8(14)-enes (IV,XI and XXIII,XXIV, respectively), and is slightly greater for the 7-enes (IX,XIX,XX). The position of the hydrogen involved is not known as isotope experiments were not run.

Loss of methoxy radical from the molecular ion was not observed from any of the resin acid esters investigated. [Direct loss of methanol from the molecular ion only was observed in the spectrum of a secodehydroabietate (22).] Only the 8-ene resin acid esters gave the M^+-CH_3-CH_3OH [m/e 271 ($C_{19}H_{27}O$)] peak, and only with a 10% intensity. Consecutive elimination of a methyl radical and a neutral methyl formate molecule produces m/e 243 ($C_{18}H_{27}$) as the base peak for all the 8-enes (III,X,XXI, XXII) and m/e 241 ($C_{18}H_{25}$) for 8.15-pimaradien-18-oate (V) and 8,15-isopimaradien-18-oate (XIII). This reflects the summing of the facile M^+-CH_3 and M^+-$COOCH_3$ fragmentations for these 8-enes as discussed above and for these 8,X-dienes as discussed below.

8,X-Dienes. The pimaradienoates and isopimaradienoates are similar in having the 15-ene double bond but differ in that this C-13 vinyl substituent is epimeric. The influence of this double bond does not appear to extend beyond ring C, as the fragmentation patterns of the MS of these dienes are very similar to that of the monoenes. The fragmentation pattern and the relative intensity of the peaks in the MS of the abietane resin acid esters are significantly affected by the addition of a second double bond. The relative intensity of the M^+-CH_3 peak for 8,13-abietadien-18-oate (XXVIII, palustrate), which has a second double bond and conjugated double bond at the 13-ene position, decreases from that for the 8-abietenoates (XXI,XXII). When the second double bond is present as the 12-ene, the relative intensity of this peak becomes insignificant. The presence of a second double bond may stabilize the molecular ion against the loss of methyl radical and accentuates another fragmentation pathway, and thereby minimizing the effect of the first 8-ene double bond.

8(14)-Enes. Loss of an allylic alkyl substituent from the C-13 position is the favored fragmentation for the 8(14)-ene resin acid esters (Fig. 5), as shown below. Ethyl radical is lost from 8(14)-pimaren-18-oate (IV) and 8(14)-isopimaren-18-oate (XI) to give the m/e 289 ($C_{19}H_{29}O_2$) peak whereas the m/e 275 ($C_{18}H_{27}O_2$) peak is the result of a loss of isopropyl radical from the 8(14)-abietenoates (XXIII,XXIV).

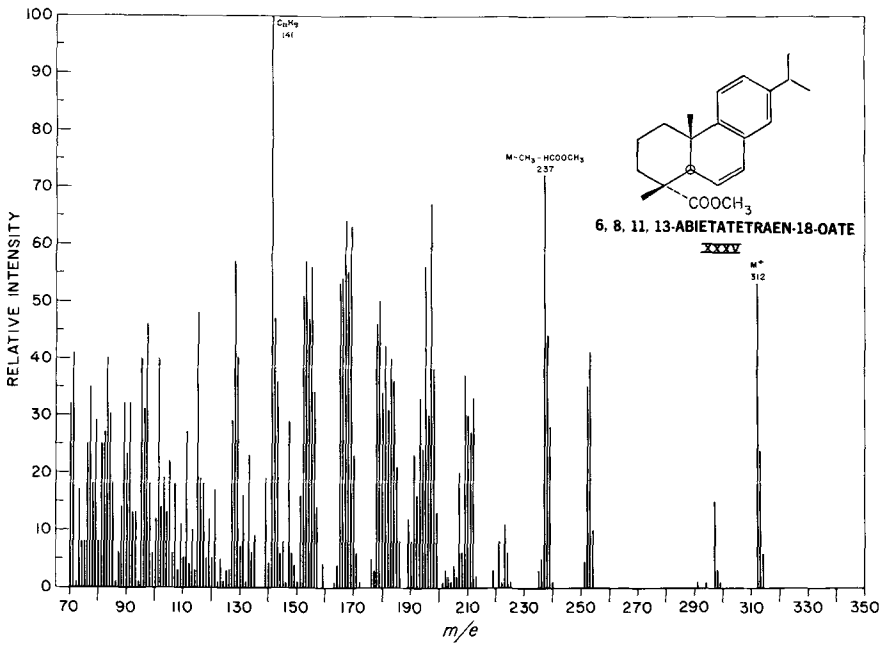
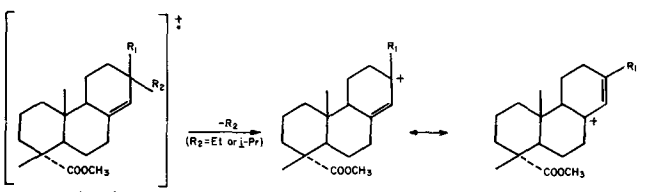
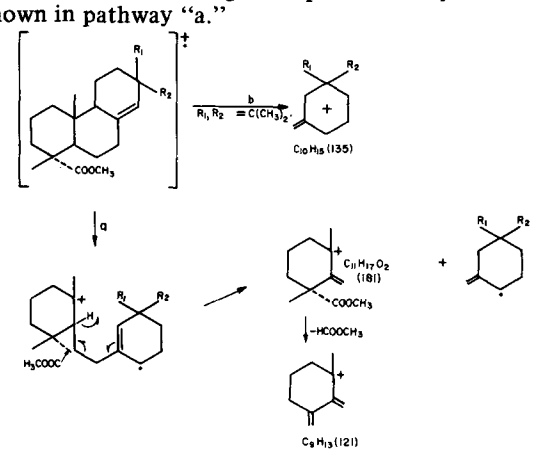


FIG. 9. Mass spectrum of methyl 6,8,11,13-abietatetraen-18-oate.



Both the C6-C7 and C9-C10 allylic bonds are possible sites of additional C-C bond cleavage; the rupture of the bond between the more highly substituted C9 and C10 carbon atoms is expected to be favored. This is seen in the formation of the m/e 181 ($C_{11}H_{17}O_2$) ion via rupture of this bond and McLafferty rearrangement of γ-hydrogen. Consecutive loss of methyl formate leads to its resonance stabilized base peak, m/e 121 (C_9H_{13}). The fragmentation mechanism of this cleavage was postulated by Biemann (3) as shown in pathway "a."



This fragmentation mechanism is observed for the nonconjugated 8(14),15-pimaradienoate (VI) and 8(14),15-isopimaradienoate (XIV) as well as the 8(14)-monoenoates (IV,XI,XXIII,XXIV).

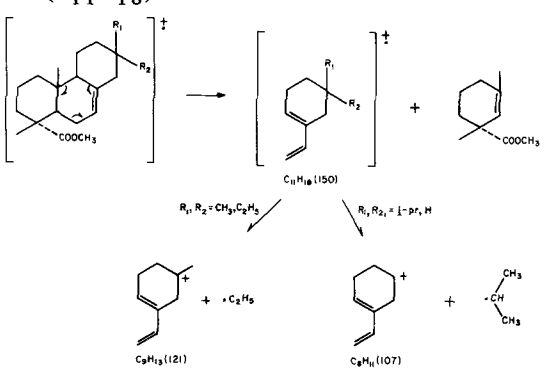
8(14),X-Dienes. The fragmentation patterns of 8(14),15-pimaradien-18-oate (VI, pimarate) and 8(14),15-isopimaradien-18-oate (XIV, sandaracopimarate) are very similar to the corresponding 8(14)-monoenoates (IV and XI, respectively). The second (15-ene) double bond affects fragmentation in an expected way in that these dienoates show loss of methyl radical with formation of the resonance stabilized C-13 (m/e 301)ion.

The second double bond of 8(14),13(15)-abietadien-18-oate (neoabietate, XXXI) is at the C13-C15 position in conjugation with the C8-C14 double bond. The favored fragmentation pathway of this compound is again the cleavage of the C9-C10 and C6-C7 bonds accompanied by a hydrogen transfer. However, the positive charge is mainly retained in ring C (see second fragmentation mechanism, 8(14)-Enes). Thus, instead of forming the m/e 181 ($C_{11}H_{17}O_2$), fragmentation results in the m/e 135 ($C_{10}H_{15}$) ion, which is the base peak. This indicates that the π bonding system of the conjugated double bond is also a favorable site of initial electron loss.

In addition to 8(14),12-abietadien-18-oate (levopimarate, XXXIII), both 8,12-abietadien-18-oate (XXIX) and 8,13-abietadien-18-oate (palustrate, XXVIII) have both double bonds in ring C. The MS of the 8,12-dienoate (XXIX) consistently showed evidence of dehydroabietate (8,11,13-abietatrien-18-oate, XXXIV) even when a tandem GLC-MS technique was used to obtain the MS of freshly prepared material. Methyl levopimarate, palustrate and XXIX undergo an indefined transformation into dehydroabietate in hydrocarbon solvent (19; also, D.F. Zinkel, unpublished data). Palustrate and XXIX undergo this transformation as pure liquids even when stored under N_2 at -10C, but crystalline levopimarate has limited stability.

7-Enes. The favored fragmentation pathway for the 7-ene resin acid esters is the simultaneous rupture of the C5-C6 and C9-C10 bonds in a retro Diels-Alder reaction (4) (Fig. 6).

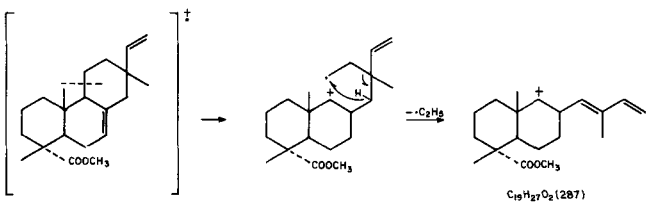
The positive charge is retained in ring C resulting in the m/e 150 ($C_{11}H_{18}$) ion:



For 7-isopimaren-18-oate (IX), consecutive loss of an ethyl radical leads to m/e 121 (C_9H_{13}), which is the base peak. For the 7-abietenoates, consecutive loss of isopropyl radical leads to the m/e 107 (C_8H_{11}) base peak.

It should be noted that although the 8(14)-pimaren-18-oate (IV), the 8(14)-isopimaren-18-oate (XI) and the 7-isopimaren-18-oate (IX) all have base peak intensities at m/e 121 (C_9H_{13}), the base peak of the latter consists of ring C and arises from the pathway described above, whereas the base peak for these 8(14)-enes is derived from ring A [see 8(14)-Enes]. The m/e 181 peak is almost absent in the MS of IX.

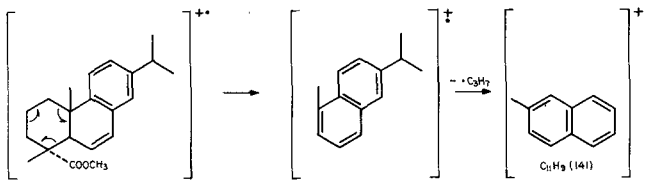
7,X-Dienes. The presence of a $M^+-C_2H_5$ (20% intensity) in the spectrum of 7,15-isopimaradien-18-oate(isopimarate, XII) is unexpected in that the compound does not have an ethyl substituent. [This peak is seen in the spectra published by other workers (2,3).] Formation of this m/e 287 ($C_{19}H_{27}O_2$) peak can be visualized as occurring via cleavage of the C9-C11 bond, which is β to the 7-ene position, followed by hydrogen transfer from C14 to C11 and cleavage of the C12-C13 bond:



The base peak of the two 7,X-abietadienoates, 13β-abieta-7,9(11)-dien-18-oate (XXXII) and 7,13-abietadien-18-oate (abietate, XXVII), is the molecular ion, m/e 316 ($C_{21}H_{32}O_2$). The 7,13-dienoate has significantly less intense M^+-CH_3 and $M^+-CH(CH_3)_2$ ions than the 7,9(11)-dienoate. This difference in loss of methyl radical is expected (see earlier discussion, 8-Enes).

13- and 13(15)-Enes. Of the monoenoic resin acid esters, only 13-abieten-18-oate (XXV) and 13(15)-abieten-18-oate (XXVI) do not have the C-8 position involved in unsaturation. The base peak for the 13(15)-enoate is the molecular ion, m/e 318 ($C_{21}H_{34}O_2$)(Fig. 7). The MS for the 13-enoate (Fig.8) has features that are quite similar to the spectra of the 8(14)-abietenoates (XXIII,XXIV). Particularly interesting is the presence of the m/e 121 (C_9H_{13}) ion as the base peak and the m/e 181 ($C_{11}H_{17}O_2$) ion of 36% relative intensity. The mechanism for formation of these ions is not clear.

Aromatic Esters. Dehydroabietate, the 8,11,13-abietatrien-18-oate (XXXIV) has a spectrum in which the M^+-CH_3 peak, the molecular ion and the m/e 239 ($C_{18}H_{23}$) base peak predominate. The fragmentation mechanism for dehydroabietate and its C-4 epimer, callitrisate, has been studied in detail by Enzell and Wahlberg (7). The base peak for 6,8,11,13-abietatetraen-18-oate (XXXV) is m/e 141 ($C_{11}H_9$) (Fig. 9). Formation of this peak can be envisioned as rupture of the C1-C10 and C4-C5 bonds which yields a very stable naphthyl ion, and consecutive loss of isopropyl radical:



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REFERENCES

1. Rowe, J.W. et al., "The Common and Systematic Nomenclature of Cyclic Diterpenes," Forest Products Laboratory, USDA, Madison, Wisconsin, 1969, 57 p.
2. Bruun, H.H., and S. Gasland, Acta Acad. Aboensis Math Phys. 22:24 (1960).
3. Biemann, K., "Mass Spectrometry," McGraw Hill, New York, 1962, p. 336.
4. Audier, H.E., S. Bory, M. Fetizon and N.T. Anh, Bull. Soc. Chim. France 1966:4002.
5. Genge, C.A., Anal. Chem. 31:1750 (1959).
6. Enzell, C.R., and R. Ryhage, Arkiv Kemi 23:367 (1965).
7. Enzell, C.R., and I. Wahlberg, Acta Chem. Scand. 23:871 (1969) and *loc. cit.*
8. Audier, H.E., S. Bory, G. Defaye, M. Fetizon and G. Moreau, Bull. Soc. Chim. France 1966:3181.
9. Herz, W., and R.H. Mirrington, J. Org. Chem. 30:3198 (1965).
10. ApSimon, J.W., P.V. Demarco and J. Lemke, Can. J. Chem. 43:2793 (1965).
11. Edwards, O.E., and R. Howe, Ibid. 37:760 (1959).
12. Church, R.F., and R.E. Ireland, J. Org. Chem. 28:17 (1963) and *loc. cit.*
13. Burgstahler, A.W., J.N. Marx and D.F. Zinkel, Ibid. 34:1550, 3716 (1969).
14. Herz, W., and J.J. Schmid, Ibid. 34:3473 (1969).
15. Schuller, W.H., R.N. Moore and R.V. Lawrence, J. Amer. Chem. Soc. 82:1734 (1960).
16. Burgstahler, A.W., and L.R. Worden, Ibid. 86:96 (1964).
17. Herz, W., and H.J. Wahlborg, J. Org. Chem. 30:1881 (1965).
18. Dupont, G., R. Dulou, G. Ourisson and C. Thibault, Bull. Soc. Chim. France 1955:708.
19. Nestler, F.H.M., and D.F. Zinkel, Anal. Chem. 39:1118 (1967).
20. Desiderio, Jr., D.M., and T.E. Mead, Ibid. 40:2090 (1968).
21. McLafferty, F.W., "Interpretation of Mass Spectra," W.A. Benjamin Inc., New York, 1966, p. 41.
22. Zinkel, D.F., J.W. Rowe, L.C. Zank, D.W. Gaddie and E.R. Ruckel, JAOCS 46:633 (1969).
23. Barber, M., and R.M. Elliott, "Proceedings of the 12th Annual Conference of Mass Spectrometry and Allied Topics," Montreal, 1964, p. 150.
24. Enzell, C.R. and R. Ryhage, Arkiv Kemi 27:213 (1967).

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