and $J_{5,6\beta}$ are approximately 10.5 and 8 Hz, respectively. In the absence of the ketone group, the J values are 12.2 and 3.4 Hz. Thus, the presence of a 7-ketone group is manifest in two ways: (1) it deshields H-5 by about 0.4 ppm by a field effect or by potentiating the local field already produced by the epoxide function; (2) the introduction of an sp^2-hybridized carbon atom into ring B alters the conformation such that changes in vicinal coupling constants are induced.

To determine whether the paramagnetic shift of H-5 was entirely due to the α-epoxide ring, compounds **18c** and **19c** were synthesized and examined. Table I demonstrates that neither substance exhibited the doublet of doublets; hence the downfield shift of the H-5 resonance is the result of cooperative deshielding effects on H-5 by the α-epoxide ring and the equatorial carbomethoxy group. Although the magnitude of the two components of the shift is difficult to estimate with any degree of precision, comparison of **18a** and **18c** indicates that the carboxyl group contributes at least 0.5 ppm, since the most deshielded line in the H-5 signal moved from above 2.1 (in **18c**) to 2.6 ppm (in **18a**).

Registry No. **1a**, 3582-25-0; **5a**, 7643-40-5; **6a**, 42855-23-2; **6c**, 42855-24-3; **7a**, 33952-78-2; **7b**, 33892-15-8; **8**, 42855-28-7; **9**, 42855-29-8; **10**, 42855-30-1; **12a**, 42855-31-2; **12b**, 42855-27-6; **13a**, 42855-32-3; **13b**, 42855-33-4; **13c**, 42855-34-5; **16a**, 42855-35-6; **17a** 2-amino-2-methyl-1-propanol salt, 42855-36-7; **17b**, 42855-37-8; **18a**, 42855-38-9; **18c**, 42855-39-0; **19a**, 42855-40-3; **19c**, 42855-41-4; **20a**, 42855-42-5; **20b**, 42855-43-6.

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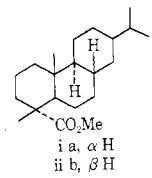
References and Notes

(1) Supported in part by a grant from the National Science Foundation (GP-12582). Previous paper: W. Herz and D. H. White, *J. Org. Chem.*, **39**, 1 (1974).
(2) W. Herz, A. R. Pinder, and R. N. Mirrington, *J. Org. Chem.*, **31**, 2257 (1966).
(3) W. Herz and J. J. Schmid, *J. Org. Chem.*, **34**, 3464 (1969).
(4) Peracid oxidation is not nearly as selective (*vide infra*), presumably because of the higher steric requirements of the osmate ester.
(5) P. S. Wharton and D. H. Bohlen, *J. Org. Chem.*, **26**, 3615 (1961).
(6) W. Herz and H. J. Wahlborg, *J. Org. Chem.*, **30**, 1881 (1965).
(7) Our argument for assuming a conformational change in **15** was based on a comparison of the observed $\delta_{C\text{-}10Me}$ (0.92 ppm) with that calculated on the assumption that $\Delta\delta_{C\text{-}10Me}$ (18a − i) = 1.17 − 0.85 ppm or 0.32 ppm was the incremental value for an 8α,9α-epoxide. A more nearly correct standard for calculating the effect of an α-8,9-epoxide is ii ($\delta_{C\text{-}10Me}$ 1.08), thus $\Delta\delta_{C\text{-}10Me}$ (18a − ii) =



i a, α H
ii b, β H

1.17 − 1.08 = 0.09 ppm; *i.e.*, an 8α,9α-epoxide produces an apparent shift of less than 0.1 ppm in the methyl signal. Even on this basis, however, $\delta_{C\text{-}10Me}$ of **15** seems anomalously small compared with that of the epoxy ketones **6a**, **6b**, and **6c** (Table I).

Resin Acids. XXVI. Biogenetic-Type Rearrangements of the Homoallylic Cation from Methyl 15(*R*)-Hydroxypimar-8(14)-en-18-oate[1]

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A modification of the solvomercuration–demercuration reaction is described which prevents the formation of cyclic ethers from dienes. Application of the procedure to methyl pimarate permitted the stereospecific synthesis of the title compound (**5a**) and a study of the homoallylic cation derived from it. Treatment of **5a** with toluenesulfonyl chloride–pyridine resulted in rearrangement to a new cyclopropane resin acid derivative **10** and a strobane derivative **11**. Similar treatment of methyl 15(*R*)- and 15(*S*)-hydroxy-$\Delta^{8(14)}$isopimarate (**18a** and **19b**) did not result in rearrangement. The results are ascribed to differences in the geometries of the homoallylic cations produced from **5a**, **18a**, and **19a**. Generation of the homoallylic cation from **5a** and the amine analog **6a** under different conditions resulted in conversion to methyl dehydroabietate. The rearrangements can be viewed as *in vitro* analogs of biological processes.

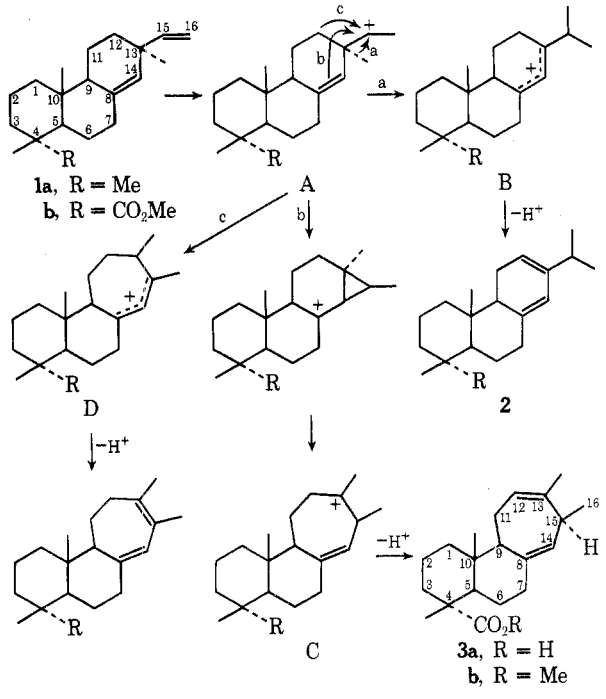
Methyl migration in cation A derived from a pimaradiene (**1a**, Scheme I, stereochemistry at C-13 as pictured) or isopimaradiene (stereochemistry at C-13 inverted) has been postulated as the crucial step (path a, Scheme I) in the biogenesis of the abietane (**2**) skeleton.[2] Our interest in the *in vitro* genesis of cation A under mild conditions was whetted by the recent discovery[4] of yet another resin acid type, exemplified by strobic acid (**3a**)[5] and its congeners, which is formally derivable from A by an alternate cationic rearrangement (path b, Scheme I). The realization of both rearrangement paths from suitable progenitors of cation A is reported herewith.[8]

Our approach was based on the introduction of a functional group at C-15 of the pimarane skeleton which could be subjected to methods customarily employed for generating transitory carbonium ions. Unfortunately, application of the original solvomercuration–demercuration procedure to methyl primarate (**1b**) had, in the hands of previous workers,[10] furnished ether **4**[11] rather than the hoped-for alcohol **5a** owing to participation by the 8(14) double bond; our use of modified procedures[9,12] applicable to dienes did not alter this result. Consequently, our initial efforts were directed toward the synthesis of the amine **6a**.

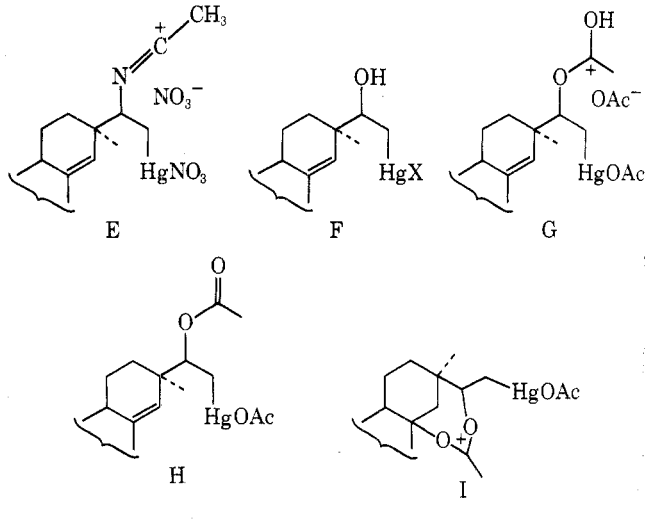
Solvomercuration–demercuration of **1b** in the presence of acetonitrile[13] afforded in nearly quantitative yield an amide **6b**.[14] Conversion of **6b** to the imino ether **7** by treatment with triethyloxonium fluoroborate[15] followed by hydrolysis with dilute acetic acid furnished **6a** in high yield.

The mechanism[13] by which **6b** is produced involves an intermediate such as E where, in contrast to the situation

Scheme I

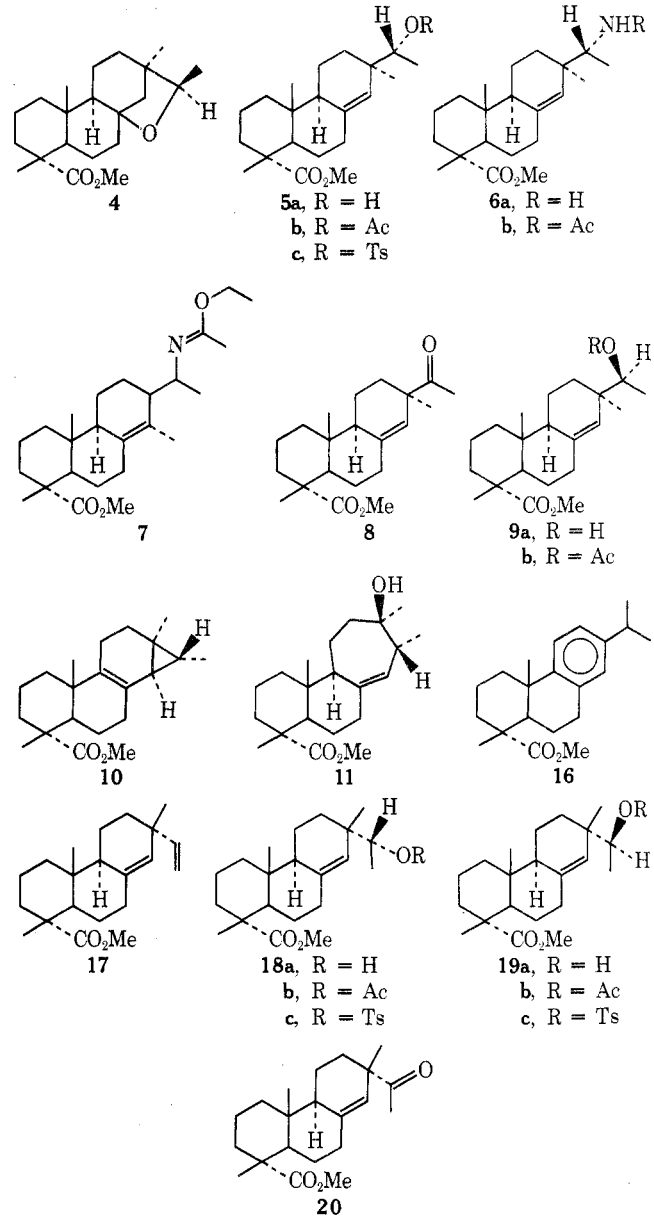


prevailing in intermediate F of the oxymercuration reaction, the nitrogen is not sufficiently nucleophilic to add to the 8,14 double bond. Accordingly, substitution of acetic acid for acetonitrile in the oxymercuration step should, it was reasoned, lead to an intermediate G which by proton transfer would furnish H. Subsequent intramolecular cyclization of H to I would not be expected to occur, since the oxygen is now deactivated. However, since the envisioned use of acetic acid as a solvent for the initial step would interfere with the second, reductive demercuration step, it would be necessary to remove it completely and conveniently. The solution to the second problem was azeotropic distillation with benzene at reduced pressure.



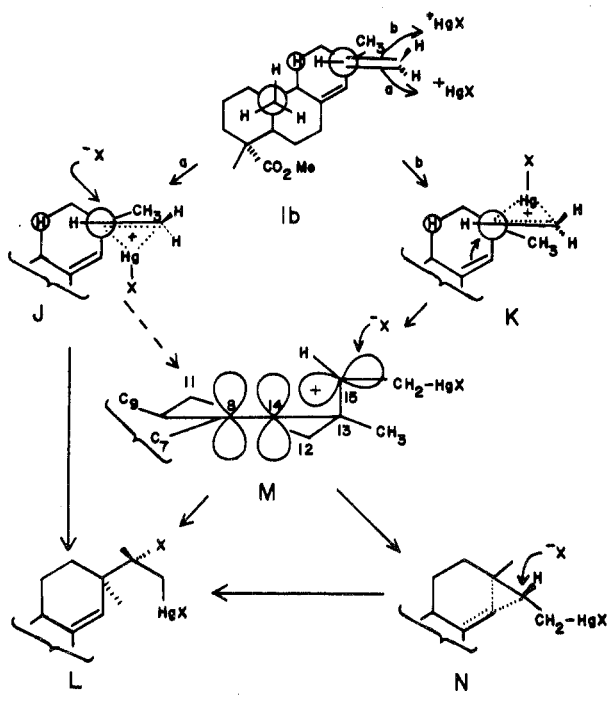
In the event, addition of 1 equiv of anhydrous $Hg(NO_3)_2$ to **1b** in acetic acid followed by addition of benzene, evaporation at reduced pressure and temperatures below 50°, and reduction with $NaBH_4$ furnished the crystalline acetate **5b** in 90% yield. This modification of the solvomercuration–demercuration reaction for the preparation of esters which can be hydrolyzed subsequently should therefore be useful whenever ether formation is a problem.

Hydrolysis of **5b** furnished crystalline **5a.** Oxidation of the latter gave **8**; $NaBH_4$ reduction of 8 produced a mixture of **5a** and the C-15 epimer **9a** which resisted separation attempts, as did the mixture of acetates **5b** and **9b.** The absolute configuration of **5a** at the new asymmetric center C-15 was determined as *R* by application of Horeau's method[16] (24% optical yield). Further solvomercuration–demercuration of **5a** gave ether **4,** thus establishing the stereochemistry of the latter.



That only one acetate **5b** (and only one amide **6b**) was formed in the solvomercuration reaction is of considerable interest. Models show that mercuration of the 15,16 double bond is most probable in that conformation of **1b** in which the vinyl group is oriented away from ring C (Scheme II) if steric interactions are to be minimized. If the mercuric reagent approaches **1b** from a direction syn to the 8,14 double bond (Scheme II, path a), subsequent attack by nucleophile on the mercurium ion J should give rise to L with C-15 stereochemistry corresponding to that of **5b.** If, on the other hand, the mercuric ion approaches **1b** from a direction anti to the 8,14 double bond (path b), a stabilized ion, either a homoallylic or a cyclopropyl carbinyl ion, could be formed. Since the developing p orbital on C-15 lies parallel to the plane of ring C (as in M), $2p\sigma$ overlap of one lobe with the upper portion of the π-electron system of C-8 and C-14 is almost inevitable owing to the close approach of C-14 and C-15. M might be a step-

Scheme II



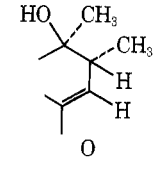
ping stone to the symmetrical homoallylic (cyclopropylcarbinyl) ion N, although intermediacy of N is doubtful since products derived from attack on C-8 or C-13 of N were not found.

In either M or N rotation about the 15,16 bond is possible such that the mercury atom is prevented from interfering sterically with approach of the nucleophile from the direction of original mercuric ion attack. This rotation, followed by subsequent nucleophilic attack, results in the same C-15 stereochemistry as that produced by path a.[17]

Attention could now be turned to preparation of a derivative of **5a** suitable for solvolysis studies. Prolonged treatment of **5a** with mesyl or tosyl chloride under carefully defined conditions (see Experimental Section) did not, however, result in the formation of the desired esters. Instead, two rearrangement products were isolated in 22 and 20% yield.

The nmr spectrum of the less polar substance, $C_{21}H_{32}O_2$, indicated the presence of the usual carbomethoxy group and the absence of vinyl protons, and exhibited four methyl singlets and a one-proton doublet at 0.30 ppm (J = 3.6 Hz). Three of the methyl singlets were easily accounted for by the C-4, C-10, and C-13 methyl groups; the remaining two signals of interest were interpretable in terms of formula **10** where the doublet at 0.30 ppm represents H-14. The fourth methyl resonance is that of C-16 whose appearance as a singlet instead of a doublet is due to a second-order nmr phenomenon; *i.e.*, the difference in chemical shift between the methyl signal and that of the proton to which it is coupled is of the same order as J. As regards stereochemistry, participation by the double bond in the loss of the oxygen function requires α orientation of the C-16 methyl group, a conclusion which is supported by the observed splitting (3.6 Hz, typical of trans coupling[18]) of H-14 which must be α.

The second substance, $C_{21}H_{34}O_3$, was a tertiary alcohol whose nmr spectrum exhibited three methyl singlets, one methyl doublet, and a vinyl resonance whose chemical shift and appearance (broadened doublet at 4.89 ppm) differed from that of H-14 in 8(14)-pimarenes. Double resonance experiments showed that the vinyl proton was spin coupled, hence adjacent, to the same (allylic) proton at 2.78 ppm which caused the methyl resonance at 0.98 ppm to appear as a doublet. Furthermore, irradiation at the frequency of the vinyl proton collapsed the complex multiplet of the allylic proton to a slightly broadened quartet, the broadening being presumably due to some homoallylic coupling to H-7α, H-7β, or H-9. It was therefore reasonable to assume that the proton at 2.78 ppm was adjacent to a quaternary center and that its chemical shift (in the low-field range for tertiary allylic protons) was due to deshielding by the hydroxyl group. Hence the two methyl groups should be cis and, on the basis of mechanistic considerations, α. Partial structure O indicated by the nmr spectrum could therefore be expanded to **11**, which possesses all the features of the strobane skeleton. Further support for this formulation was found in the observation of a mass spectrometric peak at m/e 221 ($C_{14}H_{21}O_2$ from the high-resolution mass spectrum) which appears to be characteristic of the methyl strobate system.[4-6,19,20]



O

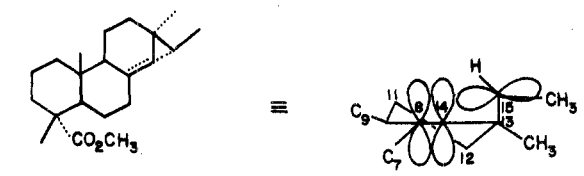
Thus, exposure of **5a** to toluenesulfonyl chloride–pyridine *resulted in operation of rearrangement path b of Scheme I*, although the enforced choice of starting material **5a** imposed a C-15 stereochemistry on the ring-expanded product **11** which is opposite to that of the strobanes so far found in nature. Moreover, *in vitro* realization of the rearrangement does not, of course, exclude the possibility that the strobanes are formed *in vivo* by direct cyclization of a labdane derivative rather than through the intermediacy of a pimarane.

Pertinent to the mechanistic aspects of the rearrangement are the following observations. Unbuffered acetolysis of **5a**, **10**, or **11** produced in each instance acetate **5b** in 95% yield. Treatment of **5b** and **10** with aqueous acid yielded only **5a**. Hence the homoallylic isomer **5** appears to represent the thermodynamically favored component of the homoallylic–cyclopropylcarbinyl–homoallylic system **5**, **10**, and **11** while **10** and **11** are products of kinetically controlled processes. Conversion of **5a** (and **10** or **11**) to **5b** with 100% retention of configuration at C-15 and genesis of **5b** by diazotization of **6a** with $NaNO_2$–acetic acid seems to implicate the unsymmetrical homoallylic ion **12** (analogous to ion M of Scheme II) as the result of 2pσ overlap between one lobe of the empty p orbital of cation A and the β face of the π-electron system at C-8 and C-14. Cyclopropyl derivative **10** could then be formed by kinetically controlled proton abstraction from the α face of **12**, a process which discharges the carbonium ion and renders the product immune to further reaction under the conditions of attempted tosylation.

Conversely, protonation of **10** in the usual manner from the α side leads to cation **13**, whose geometry resembles that of the skewed bisected cyclopropylcarbinyl ion P rather than that of the perpendicular bisected cyclopropylcarbinyl ion Q. As illustrated, such skewing favors overlap between the β lobe of the C-8 p orbital and the 14,15 bond rather than overlap between the α lobe and the 13,14 bond. Hence orbital control disposes ion **13** toward preferential cleavage of the 14,15 bond (*i.e.*, toward its representation as **12**), thus leading by subsequent reaction with an appropriate nucleophile to a product with the C-15 stereochemistry of **5**, as actually observed in the acetolysis of **10**.

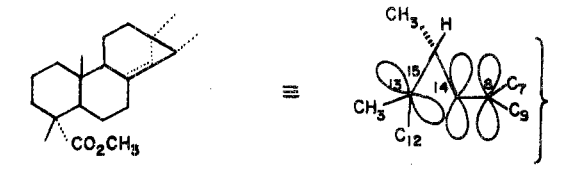
One representation of the initial cationic species from the acetolysis of **11** is the second asymmetrical homoallylic ion **14**, which is the result of 2pσ overlap between one

lobe of the empty p orbital of cation C (Scheme I) and the α face of the π-electron system at C-8 and C-14 and could also be described as stemming from preferential weakening of the 13,14 bond of P. It is interesting that the tertiary carbonium ion (or **14**) is completely converted to A, which must have substantial localization of charge at the secondary carbon atom C-15. In the absence of further information we would prefer not to speculate at this time on detailed aspects of the conversion of **5a** to **11**,[21] on the possible intermediacy of the symmetrical homoallylic (nonclassical cyclopropylcarbinyl) ion **15**,[22] and on the relative importance of **12**, **14**, and **15**[23] in the transformations we have observed. In any event, the required inversion at C-13 *en route* to the ring-expanded product, whether in **12** or **15**, leads to the stereochemistry (hydroxyl group β) depicted in formula **11**.

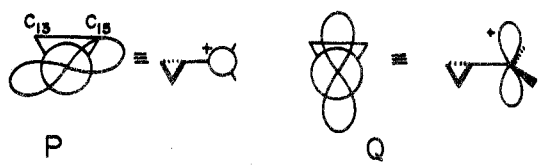


12

13 15



14

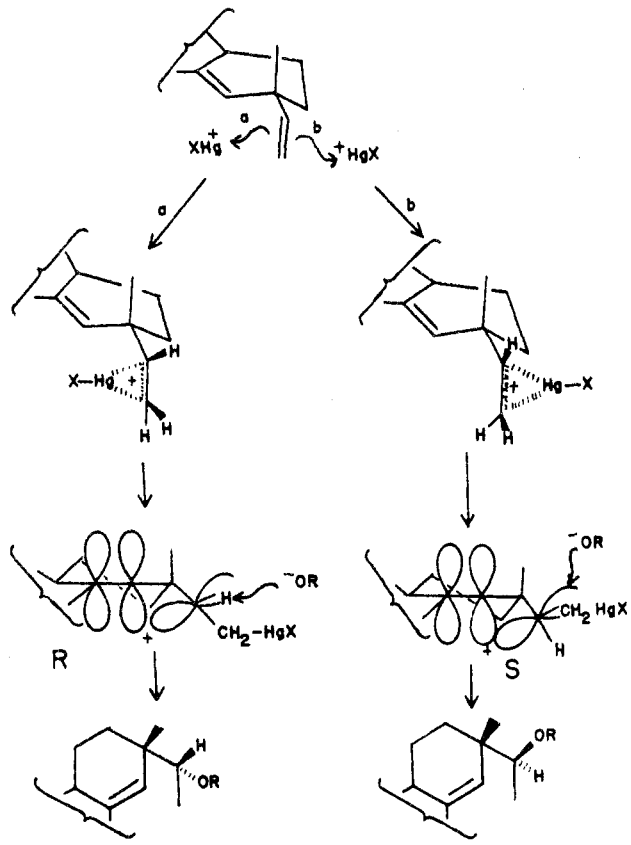


P Q

An additional series of experiments shed further light on the possible fate of cation A. Treatment of **5b** and **10** with anhydrous perchloric acid (0.12 *N*) in dioxane–acetic acid produced methyl dehydroabietate (**16**) in 58 and 28% yield, respectively, *thus resulting in realization of path a of Scheme I*.[24] Similarly, diazotization of **6a** in a nonnucleophilic solvent gave low yields of **1b** and **16**. Hence under more strongly acid conditions, irreversible rearrangement of homoallylic cation A, whatever its detailed aspect, to the allylic ion B takes place.

The observations recorded so far, which depend on the steric relationship of an axially oriented C-15 cation to the 8,14 double bond in the pimaric acid series, made it of interest to extend the study to sandaracopimaric acid. ApSimon and Krehm[10] had previously carried out the oxymercuration–demercuration of methyl sandaracopimarate (**17**) and obtained an inseparable 1:1 mixture of epimeric C-15 alcohols **18a** and **19a**. In the present work separation into a crystalline alcohol **18a** and a noncrystalline epimer **9a** could be achieved by combination of thin layer chromatography and fractional crystallization. Absolute configurations were again determined by the Horeau method.

Scheme III



The formation of two epimeric alcohols in the solvomercuration–demercuration of methyl sandaracopimarate contrasts with our observations in the pimarate series but is easily rationalized as follows. The spatial disposition of the vinyl group of **17** permits attack of mercuric ion from either side (Scheme III). Two different mercurium ions may therefore be formed, each of which gives rise by trans addition of the nucleophile water to a distinctive epimer. If, however, the mercurium ions are not immediately attacked by a nucleophile, but if the 8,14 double bond participates, a pair of homoallylic ions is produced as shown in Scheme III. This set of ions R and S is quite different from ion M of the pimarate series (Scheme II), since overlap between the C-15 carbonium ion and the 8,14 double bond will have to occur on the α face of the molecule. While ions R and S are more symmetrical about the nodal plane (*i.e.*, there is a greater amount of $2p\pi$ overlap than in M) nucleophilic attack would still be expected to proceed stereoselectively. Inclusion of further ions in the reaction scheme is not necessary since the yields of **18a** and **19a** were very high and no products corresponding to attack on C-8 and C-13 were found.

Treatment of **18a** and **19a** with toluenesulfonyl chloride under conditions identical with those of the attempted tosylation of **5a** gave excellent yields of the noncrystalline tosylates **18c** and **19c** in further evidence for the much poorer overlap between an equatorially oriented ion at C-15 and the 8,14 double bond than in the pimarate series. Preliminary attempts to investigate the solvolysis of **18c** and **19c** led to complex mixtures whose nmr spectra indicated the absence of ring-expanded substances corresponding to **11**. However, acetolysis of **18a** and **19a** occurred with retention of configuration; each alcohol gave in excellent yield a single but different acetate identical with the acetates **18b** or **19b** prepared from the respective alcohols by treatment with acetic anhydride–pyridine. This indicates that solvolysis leads to a pair of asymmetrical homoallylic ion

Experimental Section[25]

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(25) For experimental details, see W. Herz and J. J. Schmid, J. Org. Chem., 34, 3464 (1969).

Methyl 15(R)-Acetamino-8(14)-pimaren-18-oate (6b).--To a mixture of 10 g of dry mercuric nitrate and 22 ml of acetonitrile was added 10 g of methyl pimarate 1b in small portions with stirring during 15 min. Stirring was continued for 2.5 hr; this was followed by addition of 30 ml of 3N NaOH solution and, 5 min subsequently, by addition of 0.35 g of $NaBH_4$ in 30 ml of 3N NaOH solution followed by 1.5 hr of stirring. A chloroform-ether mixture was added followed by solid sodium chloride and 10 ml of 10% HCl solution. The organic layer was separated; the aqueous layer was acidified and again

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extracted with chloroform-ether. The combined organic layers were washed, dried and evaporated. Extraction of the residue with ether-hexane (1:1) furnished 3.42 g of methyl pimarate. Recrystallization of the remaining material from chloroform-hexane afforded two crops (7.13 g) of amide 6b. Column chromatography of the mother liquors resulted in recovery of an additional 0.45 g of 1b (hexane-ether 9:1) and isolation of an additional 0.67 g of 6b (hexane-ether 1:1). The product had mp 229.5-231°; $[\alpha]_D^{25}$-16 (c 1.10, $CHCl_3$); ir bands at 3270, 3080 (-NH), 1728 (ester) and 1643 cm^{-1} (amide), nmr signals at 0.85 (6p, C-10 and C-13 methyls), 1.08d (J = 7, C-16 methyl), 1.20 (C-4 methyl), 1.98 (acetyl), 3.67 (methoxyl), 4.1 m (H-15), 5.18 br (H-14).

Anal. Calcd for $C_{23}H_{37}NO_3$: C, 73.56; H, 9.93; N, 3.73; O, 12.78. Found: C, 73.60; H, 9.79; N, 3.83; O, 12.78.

An attempt to effect hydrolysis of the amide with 20% methanolic potassium hydroxide resulted only in partial hydrolysis of the ester function. Remethylation with diazomethane resulted in recovery of starting material. Treatment of 0.21 g of 6b with 7 ml of 50% H_2SO_4 for 30 min at 150° resulted in recovery of 0.097 g of starting material and a mixture of several unidentified products whose spectral properties indicated partial ester hydrolysis, but no amide hydrolysis.

Methyl 15(R)-Amino-8(14)-pimaren-18-oate (6a).--A mixture of 2 g of 6b in 50 ml of dry CH_2Cl_2 and 2.5 g of freshly prepared triethyloxonium tetrafluoroborate was stirred for 2 hr (nitrogen atmosphere), mixed with an additional 0.5 g of Meerwein's reagent, stirred overnight, mixed with one more g of the reagent, stirred

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the basicity of the medium. Recrystallization from methanol yielded pure 5b which melted at 109.5-110.5°, $[\alpha]_D^{25}$ +7 (c 1.42, $CHCl_3$); ir bands at 1725 cm^{-1} (double intensity); nmr signals at 0.80, and 0.89 (C-10 and C-13 methyls), 1.16 (C-4 methyl), 1.12d (J = 8.3 Hz, C-15 methyl), 2.02 (acetate), 3.63 (methoxyl), 4.84 g (J = 8.3 Hz, H-15), and 5.12 br (H-14).

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.37; H, 9.64; O, 17.00. Found: C, 73.22; H, 9.86; O, 16.97.

Perchloric Acid Treatment of 5b.--A) A solution of 0.265 g of 5b in 4 ml of dioxane and 1 ml of 0.13 N aqueous perchloric acid was refluxed for 12 hr, cooled and extracted with ether. Preparative tlc of the crude product gave a small amount of methyl pimarate, 0.1 g of starting material and 0.12 g of 5a (vide infra).

B) A solution of 0.275 g of 5b, 4 ml of dry dioxane and 1 ml of 0.6 N perchloric acid in acetic acid containing sufficient acetic anhydride to remove all water was refluxed for 28 hr (nitrogen atmosphere), cooled and stirred for 2 days at room temperature. The dark brown solution was poured on ice and extracted with ether. The material from the washed and dried ether layer was subjected to preparative tlc; this resulted in isolation of 52 mg of somewhat impure methyl dehydroabietate and 87 mg of a complex mixture. Acidification of the base washings of the ether extract followed by the usual work-up and methylation with diazomethane furnished an additional 98 mg of crude methyl dehydroabietate, total yield 150 mg (>80% pure) = 58%. When refluxing was continued for only 2.75 hr, the yield of methyl dehydroabietate was 34%.

TABLE 1

Mass Spectra of Resin Acid Derivatives

Compd	M⁺(%)	Major Ions(%)						Base Peak (100%)
1b	316(12)	257(10)	181(16)	180(22)	148(11)	133(10)		121
5a	334(2)	289(55)	229(32)	181(21)	107(30)			121
5b	376(1)	289(83)	229(35)	181(25)	107(28)	95(26)		121
6b	376(1)	289(63)	288(56)	229(42)	181(26)			121
8	332(1)	289(64)	229(33)	181(27)	107(24)			121
10*	316(95)	288(30)	159(31)	149(43)	135(66)	121(92)	119(48)	241
11	334(7)	316(18)	276(26)	181(25)	135(27)	109(25)	107(23)	121
12	316(13)	301(12)	257(13)	181(11)	180(10)	133(12)	107(14)	121
18a	334(1)	290(31)	289(58)	229(34)	181(23)	95(29)		121
19a	334(1)	290(25)	289(44)	229(31)	181(21)	95(25)		121
20	332(1)	289(34)	229(23)	181(12)	107(18)			121

*Run with probe temperature at 100° rather than usual 200°

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for 2 hr, concentrated at reduced pressure, and taken up in $CHCl_3$. The washed and dried extract was evaporated and the remaining gum extracted with ether-hexane. From the residue was recovered approx. 0.2 g of 6b. The ether-hexane extract furnished 1.68 g of gummy imino ether 7 which was homogeneous on tlc and had nmr signals at 0.83 (C-10 methyl), 0.93 (C-13 methyl), 0.94d (J = 7 Hz, C-16 methyl), 1.22 (C-4 methyl), 1.83 (imino methyl), 3.68 (methoxyl), 3.23q (J = 7 Hz, H-15), 4.08 q (2p, J = 7.5 Hz, ether methylene), and 5.31 br (H-14).

A mixture of 0.5 g of 7, 11 ml of acetic acid, 300 ml of water and 300 ml of $CHCl_3$ was refluxed for 2 days, made basic and separated. The amine was separated from neutral material by the usual methods; this furnished 3.87 g of non-crystalline 6a which was homogeneous on tlc and nmr signals at 0.82 (C-10 and C-13 methyl), 1.21 (C-4 methyl), 1.03d (J = 6.6 Hz, C-16 methyl), 3.74 (methoxyl) and 5.31 br (H-14). The substance was characterized by reacetylation to 6b.

Diazotization of 6a.--A) A mixture of 0.84 g of 6a, 15 ml of dry diglyme and 1 ml of isoamyl nitrite was refluxed for 4 hr (nitrogen atmosphere), an additional 1 g of nitrite being added after the first hour. The mixture was cooled, diluted with ether and extracted thoroughly with water. The washed and dried organic layer was evaporated and the residue separated by preparative tlc (developed with ether-hexane 3:2). This gave three bands. The top band (wt. 0.11 g) consisted of methyl pimarate (50%) and methyl dehydroabietate (20%), the other two bands were multicomponent mixtures. B) A solution of 0.127 g of 6a, 10 ml of

JOC-12-6

Methyl 15(R)-Hydroxy-8(14)-pimaren-18-oate (5a).--A solution of 6.13 g of 5b in 150 ml of methanol containing 15 g of KOH was refluxed until starting material had been consumed (monitoring by tlc), diluted with ether, brought to pH 1 with 10% hydrochloric acid and separated. Evaporation of the washed and dried ether layer and trituration with hexane furnished 2.35 g of crystalline material which was a mixture of 5a and the corresponding acid. The solid and the material from the hexane mother liquor was therefore taken up in ether and methylated with diazomethane, yield of crude methyl ester 5.1 g. Recrystallization from methanol-water afforded 5a which melted at 194-196°, $[\alpha]_D^{25}$ -1.6° (c 1.23, $CHCl_3$); ir bands 3440 and 1700 cm^{-1}; nmr signals at 0.80 and 0.85 (C-10 and C-13 methyls), 1.13d (J = 7 Hz, C-15 methyl), 1.18 (C-4 methyl), 3.64 (methoxyl), 3.66 q (J = 7 Hz, H-15) and 5.13 br (H-14).

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.41; H, 10.25; O, 14.35; mol. wt.: 334.2508. Found: C, 75.25; H, 10.39; O, 14.21; mol. wt. (MS): 334.2533.

5b (73 mg, 2.18 x 10^{-4} mol) was esterified with 346 mg (1.11 x 10^{-3} mol) of (±) α-phenylbutyric anhydride in 3 ml of pyridine for 3 days. The usual work-up[26] produced a quantitative

(26) W. Herz and H. B. Kagan, J. Org. Chem., 32, 216 (1967).

yield of ester (purity checked by nmr spectroscopy) and 306 mg of α-phenylbutyric acid (purity checked by nmr spectroscopy) which had $[\alpha]_D^{25}$ +2.45 (c 6.12, benzene). A fully stereospecific esterification should have given $[\alpha]_D^{25}$ +10.4°. Therefore the optical

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acetic acid and 0.75 g of sodium nitrite was heated on the steam bath. Addition of portions of 0.25 g and then 0.2 g of $NaNO_2$ were added at half-hour intervals. After two hours, the reaction was stopped; the usual work up yielded 0.118 g of product mixture which was subjected to tlc (development with ether-hexane 1:1). The only substance which could be identified was the acetate 5b (vide infra).

Methyl 15(R)-Acetoxy-8(14)-pimaren-18-oate (5b).--To a solution of 5g of 1b in 13 ml of acetic acid was added 6 g of dry mercuric acetate in small portions during 10 min. Vigorous stirring was continued for 2.5 hr. The mixture was diluted with 200 ml of dry benzene and concentrated at reduced pressure (temperature <50°); this process was repeated twice more to remove all of the acetic acid. The residue was taken up in 70 ml of dry ether, placed in a 3 neck flask, and mixed with 10 ml of 10% NaOH solution which caused the mixture to turn orange. This was followed by addition with stirring of 10 ml of 10% NaOH solution containing 0.7 g of $NaBH_4$ which caused separation of elemental mercury and liberation of considerable heat. Stirring was continued for 1 hr, the two phases were separated, the aqueous layer was extracted with ether, the combined ether extract were washed, dried and evaporated and the residue was taken up in hot methanol. Cooling and addition of small amounts of water furnished two crops, 4.24 and 0.67 g, of crystalline 5b; the mother liquors, wt. 0.5 g, were at least 80% pure 5b (nmr analysis), hence the total yield was above 90%. The yields were quite variable until it was discovered that the efficiency of the reductive step depended on

JOC-12-7

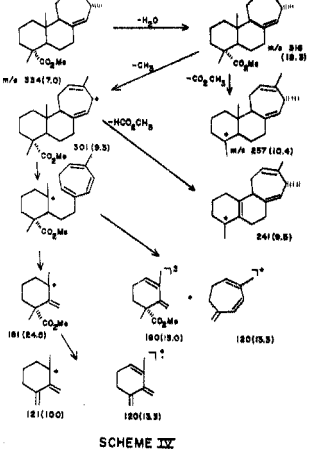
yield was 24%.

Perchloric Acid Treatment of 5a.--A solution of 0.115 g of 5b, 4 ml of dioxane and 1 ml of 0.13 N perchloric acid was stirred overnight and worked up in the usual fashion. Starting material was recovered in nearly quantitative yield.

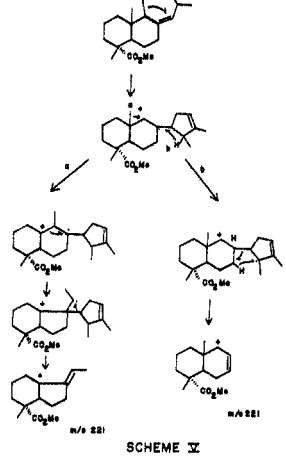
Acetolysis of 5b.--A solution of 0.1 g of 5b in 10 ml of acetic acid was refluxed (nitrogen atmosphere) for 3 days. Removal of solvent at reduced pressure resulted in isolation of crystalline 5a in quantitative yield.

Conversion of 5a to Ether 4.--A solution of 0.5 g of 5a in 15 ml of THF was gradually added with stirring to 0.6 g of mercuric nitrate in 10 ml of anhydrous THF. Addition of 10 ml of 10% NaOH solution after 35 min and subsequent addition of 0.13 g of $NaBH_4$ in 10 ml of 10% NaOH solution was followed by the usual work-up. This resulted in 0.5 g of 4, mp 129-131° (lit.[10] mp 130-132°), nmr signals at 0.84 (C-10 methyl), 1.01 (C-13 methyl), 1.16d (J = 6.3 Hz, C-15 methyl), 1.21 (C-4 methyl), 3.63 (methoxyl), and 3.74 q (J = 6.3 Hz, H-15).

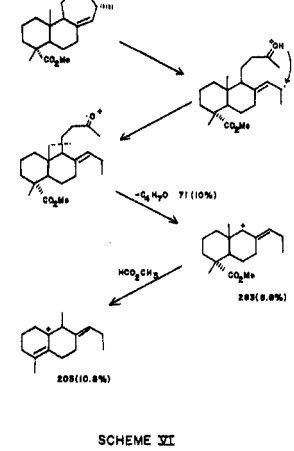
Methyl 15-Oxo-8(14)-pimaren-18-oate (8).--Oxidation of 0.5 g of 5a in 20 ml of acetone at ice bath temperature with Jones reagent, decomposition of excess reagent with methanol, dilution with water, extraction with ether and evaporation of the washed and dried ether extract furnished 0.5 g of ketone 8 which solidified on standing, was recrystallized from methanol and had mp 69.5-70°, $[\alpha]_D^{25}$ -32° (c 0.62, $CHCl_3$); ir bands 1724 and 1711 cm^{-1}; nmr signals at 0.67 (C-10 methyl), 1.09 (C-13 methyl), 1.18 (C-4 methyl), 2.12 (acetyl), 3.67 (methoxyl) and 5.45 br (H-14).



SCHEME IV



SCHEME V



SCHEME VI

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Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70; O, 14.44. Found: C, 75.49; H, 9.93; O, 14.73.

$NaBH_4$ reduction of 0.419 g of 8 in the usual manner yielded 0.406 g of a gummy mixture of alcohol 9a and its 15-epimer 9a (6:11 ratio based on integration of the H-14 signals) which could not be separated. Subtraction of the nmr spectrum of 9a from the spectrum of the mixture gave the following signals for the epimer: 0.83 and 0.88 (C-10 and C-13 methyls), 1.11d (J = 6.8 Hz, C-15 methyl), 1.20 (C-4 methyl), 3.67 (methoxyl), 3.69 q (J = 6.8 Hz, H-15) and 5.33 br (H-14). Acetylation of the alcohol mixture (acetic anhydride-pyridine) gave a mixture of acetates.

Rearrangement of 5a to 10 and 11.--A solution of 0.996 g of 5a in 10 ml of pyridine containing 0.898 g of p-toluenesulfonyl chloride was kept in a freezer at -15° with occasional swirling for 28 days[27]. The formation of crystals was noted after 5 days. Work-up

(27) Under the conditions of the standard method for tosylation[28] the desired tosylate was apparently unstable; as a result a complex mixture containing considerable amounts of starting material was produced. Temperature and reaction time used in the present work were chosen to optimize the yield of 10 and 11, two components of the mixture.

(28) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1., John Wiley and Sons, Inc., New York, N.Y., 1967, p. 1179.

in the usual way by pouring over ice, extraction with ether, washing, drying and evaporation of the extract yielded 0.64 g of gum which was subjected to preparative tlc. Development with ether-hexane

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(7:13) produced seven bands containing 16, 384, 79, 57, 22, 17 and 16 mg of material, respectively. Nmr analysis indicated that bands 1, 3, 5, 6 and 7 were complex mixtures, that band 2 contained 10 and 11 in the ratio 64/36 together with 10% of an impurity and that band 4 was pure 11. Further chromatography separated the components of band 2, total yield of 10, 0.210 g (22%), total yield of 11, 0.195 g (20%). Extraction of the aqueous layers gave a mixture of p-toluene sulfonic acid and starting material.

Recrystallization of 10 from methanol raised the mp to 76°, $[\alpha]_D^{25}$ -13° (c 1.50, $CHCl_3$), ir bands 1717 cm^{-1}, nmr signals at 0.81d (J = 3.8 Hz, H-14), 0.92, 1.08 (C-13 and C-10 methyl), 1.01 (C-15 methyl), 1.17 (C-4 methyl), and 3.65 ppm (methoxyl).

Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.90; H, 10.19; O, 10.11. Found: C, 79.64; H, 10.27; O, 10.40.

Alcohol 11 was recrystallized from ether-hexane and had mp 114-115°, $[\alpha]_D^{25}$ -29° (c 1.02, $CHCl_3$); ir bands at 3450 and 1727 cm^{-1}; nmr signals at 0.96, 1.06 (C-10 and C-13 methyls), 0.98d (J = 7 Hz, C-15 methyl), 1.17 (C-4 methyl), 2.78 m (H-15), 3.64 (methoxyl), and 4.89 dbr (J = 5 Hz, H-4).

Anal. Calcd for $C_{21}H_{34}O_3$: mol. wt.: 334.2507. Found (MS): 334.2509.

Reactions of 10.--A) A sample of 10 was kept at steam bath temperature for 3 hr and allowed to cool. Tlc and nmr analysis of the product indicated that 10 had undergone no change.

B) The cyclopropyl derivative was recovered unchanged after stirring overnight with silica gel in ether, and with silica gel,

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ether and a solution of 0.5 ml of 10% HCl in 5 ml of pyridine. Stirring of 10 overnight with silica gel and 5 drops of 10% hydrochloric acid resulted in quantitative transformation to 5a.

C) Acetolysis of 0.05 g of the cyclopropyl derivative by refluxing with 3 ml of acetic acid for 3 hr resulted in quantitative transformation to 5b.

D) A solution of 0.083 g of 10 in 4 ml of dioxane and 1 ml of 0.6 N perchloric acid in acetic acid containing sufficient acetic anhydride to remove all water was refluxed for 2.75 hr (nitrogen atmosphere), poured onto ice and worked up in the usual way. Preparative tlc resulted in isolation of 23 mg (28%) of pure methyl dehydroabietate.

Reactions of 11.--A) Acetolysis of 0.034 g of the tertiary alcohol by refluxing with 1 ml of acetic acid overnight (nitrogen atmosphere), cooling, dilution with toluene and removal of the solvents in vacuo resulted in isolation of 0.030 g of pure 5b.

B) An attempt to dehydrate 0.046 g of 11 with $POCl_3$-pyridine, work-up in the usual manner and preparative tlc of the gummy product resulted in isolation of 5 mg of starting material; transformation products could not be isolated.

Oxymercuration-Demercuration of Methyl Sandaracopimarate.--The sandaracopimaric acid utilized in this experiment was isolated from gum sandarac resin by the procedure of Edwards and coworkers[29]

(29) O. E. Edwards, A. Nicolson, and M.N. Rodgers, Can. J. Chem., 38, 663 (1960).

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and methylated with diazomethane. To a solution of 1 g of methyl ester 17 in 20 ml of THF-water (1:1) was added 1.0 g of mercuric acetate. After 10 min, 20 ml of 10% NaOH solution was added followed by an additional 10 ml of 10% NaOH solution containing 0.1 g of $NaBH_4$. This phase of the reaction was ended after 15 min and was followed by the usual work-up. The alcohol mixture, wt. 0.9 g, was separated partially by careful column chromatography. Starting material and traces of methyl callitrisate were eluted with ether-hexane (1:9). Ether-hexane (1:5) produced crystalline alcohol 18a at the leading edge of the band containing the epimeric mixture and gummy alcohol 18a at the trailing edge. Slow crystallization of the fractions rich in crystalline isomer yielded additional quantities of 18a. Recombination of mother liquors and rechromatography eventually permitted nearly complete separation of the mixture; the two isomers were obtained in pure form, as judged by nmr and tlc criteria.

Solid isomer 18a (methyl 15(R)-hydroxy-8(14)-isopimaren-18-oate), was recrystallized from methanol and had mp 125-127°, $[\alpha]_D^{25}$ +28° (c 1.16, $CHCl_3$); ir bands at 3240 and 1725 cm^{-1}; nmr signals at 0.83 (C-10 methyl), 0.97 (C-13 methyl), 1.14 d (J = 7.1 Hz, C-15 methyl), 1.23 (C-4 methyl), 3.44 q (J = 7 Hz), 3.74 (methoxyl), and 5.48 br (H-14).

Anal. Calcd for $C_{21}H_{34}O_3$: 334.2507. Found (MS): 334.2498.

A solution of 0.092 mg of 18a and 0.643 g of α-phenylbutyric anhydride in 5 ml of pyridine yielded 0.139 g of pure ester and 0.572 g of α-phenylbutyric acid (purity checked by nmr spectrometry), $[\alpha]_D^{25}$ +0.52° (c 28.6, benzene); theoretical [α] for fully stereospecific

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esterification 6.9°. Hence the optical yield was 7.5 %.

Acetylation of 0.025 g of 18a with pyridine-acetic anhydride in the usual fashion gave a quantitative yield of non-crystalline 18b which exhibited nmr signals at 0.81, 0.96 (C-10 and C-13 methyls), 1.08 d (J = 6.5 Hz, C-15 methyl), 1.20 (C-4 methyl), 2.03 (acetate), 3.65 (methoxyl), 4.62 q (J = 6.5 Hz, H-15), and 5.18 br (H-14). Tosylation of 0.969 g of 18b gave 1.360 g of non-crystalline tosylate 18c which was pure by tlc standards and exhibited nmr signals at 0.75, 0.91 (C-10 and C-13 methyls), 1.19 (C-4 methyl), 1.22 d (J = 6.5 Hz, C-15 methyl), 2.43 (aromatic methyl), 3.67 (methoxyl), 4.33 q (J = 6.5 Hz, H-15), 5.02 br (H-14), 7.30 d and 7.78 d (2p each, J = 8 Hz, aromatic hydrogens).

Non-crystalline alcohol 18a had ir bands at 3470 and 1727 cm^{-1}; nmr signals at 0.83 (C-10 methyl), 0.94 (C-13 methyl), 1.12 d (J = 6.6 Hz, C-15 methyl), 1.23 (C-4 methyl), 3.48 q (J = 6.6 Hz, H-15), 3.74 (methoxyl) and 5.53 br (H-14).

Anal. Calcd for $C_{21}H_{34}O_3$: mol. wt. 334.2507. Found (MS): 334.2508.

A solution of 0.089 g of 18a and 0.440 g of α-phenylbutyric anhydride in 5 ml of pyridine yielded 0.125 g of pure ester and 0.466 g of α-phenylbutyric anhydride (purity checked by nmr spectroscopy), $[\alpha]_D^{25}$ -0.60°, (c 23.3, benzene), theoretical $[\alpha]_D$ for fully stereospecific reaction -10.0°; optical yield 6%.

The gummy acetate 18b was prepared from 18a in quantitative yield and had nmr signals at 0.80, 0.94 (C-10 and C-13 methyls), 1.11 d (J = 6.5 Hz, C-15 methyl), 1.20 (C-4 methyl), 1.99 (acetate), 3.65 (methoxyl), 4.90 q (J = 6.5 Hz, H-15) and 5.22 br (H-14).

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The non-crystalline tosylate 18c (1.30 g from 1.015 g of 19a) had nmr signals at 0.78, 0.90 (C-10 and C-13 methyls), 1.12 d (J = 7.2 Hz, C-15 methyl), 1.19 (C-4 methyl), 2.43 (aromatic methyl), 3.67 (methoxyl), 4.36 q (J = 7.2 Hz, H-15), 5.00 br (H-14), 7.35 dbr and 7.78 d (2 p each, aromatic hydrogens).

Acetolysis of 18a and 19a.--A) A solution of 0.115 g of 18a in 5 ml of acetic acid was refluxed overnight (nitrogen atmosphere). Removal of acetic acid by codistillation with toluene gave 0.138 g of gummy acetate identical in all respects with 18b produced by pyridine-acetic anhydride treatment of 18a.

B) Repetition of this experiment with 0.107 g of 19a yielded 0.119 g of 19b identical in all respects with the acetate produced by pyridine-acetic anhydride treatment of 19a.

Methyl 15-Oxo-8(14)-isopimaren-18-oate (20).--Oxidation of 0.3 g of the mixture of crude 18a and 19a from the oxymercuration reaction in 10 ml of acetone at ice bath temperature with Jones reagent and standard work-up gave 0.295 g of crude product which was recrystallized from methanol and then melted at 72-74° (lit[14] mp, 73-75°]; nmr signals at 0.84 (C-10 methyl), 1.17 (C-13 methyl), 1.23 (C-4 methyl), 2.15 (acetyl), 3.74 (methoxyl) and 5.61 br (H-14).

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Appendix

Mass Spectral Studies Related to Substance 12.--Mass spectra of strobic acid derivatives have been reported[4,6,19]. These spectra and the spectra obtained in the course of the present work (Table I) contain most of the patterns found in the mass spectra of other tricyclic resin acids[19,30-34], particularly those which are minimally influenced by changes in the C-ring. Presumably

(30) H. E. Audier, S. Bory, M. Petizon, and N. T. Anh., Bull. Soc. Chim. France, 4002 (1966).

(31) H. H. Bruun, R. Ryhage, and E. Stenhagen, Acta Chem. Scand., 12, 789 (1958).

(32) L. A. Genge, Anal. Chem., 31, 1750 (1959).

(33) C. R. Enzell, R. A. Appleton, and I. Wahlberg in "Biochemical Applications of Mass Spectrometry", G. R. Waller, ed., John Wiley and Sons, Inc., New York, N.Y., 1972, Chapt. 13.

(34) T. L. Chang, T. E. Mead, and D. F. Zinkel, J. Amer. Oil Chem. Soc., 48, 455 (1971).

fragments such as m/e 301, 257, 241, 181, and 121 in the mass spectra of methyl strobate and its derivatives arise by the same or similar pathways (Scheme IV) suggested earlier for other tricyclic resin acids.

Examination of the various spectra disclosed, however, that a peak at m/e 221, previously reported for methyl strobate and methyl dihydrostrobate (21) was also characteristic of 10 and 11.

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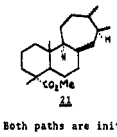
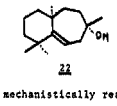
High resolution mass spectrometry revealed that this fragment had the elemental composition $C_{14}H_{21}O_2$; inclusion of the oxygen atoms requires that it be derived from rings A and B with loss of most of the ring C carbon atoms. Two possible paths leading to this fragment are detailed in Scheme V.



21



22

Both paths are initiated by a mechanistically reasonable cleavage of the allylic 9,11-bond which would be expected to occur in any 8(14)-unsaturated resin acid. The observation of a unique pattern in resin acid derivatives of the methyl strobate type is rationalized by invoking a rearrangement-cum-cyclization step to form a five-membered ring. The same pathway, if followed by $\Delta^{8,14}$-resin acids with the "normal" six carbon C-ring, would generate an energetically unfavorable four-membered ring. The mass spectrum of methyl levopimarate (2, R = CO_2Me), the closest possible analog to 3b, gives no indication that this pathway is operational.

Evidence for the mechanism postulated to account for the appearance of the m/e 221 fragment is the difference in relative intensities for 3b (25%), 21 (2%), and 12 (5%). In 3b, the 9,11-double bond is doubly allylic; cleavage of this bond produces a structure in which both electron-deficient carbon atoms are

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allylically stabilized. In substances 12 and 21 which contain only the 8,14-double bond, only an electron deficiency at C-9 can be stabilized. Therefore reduced intensity of m/e 221 is to be expected. Appearance of the m/e 221 fragment in the mass spectrum of 10 (relative intensity 3%) may be due to thermolysis or fragmentation to a structure closely related to 3b or 11.

Burlingame and coworkers[35] have described the fragmentation

(35) A. L. Burlingame, C. Fenselau and W. J. Richter, J. Am. Chem. Soc., 88, 3232 (1967).

of widdrol (22) which bears a strong structural resemblance to rings B and C of 11. When the scheme postulated by them to account for the base peak in the widdrol system is applied to 11, the fragmentation shown in Scheme VI results which can account for several observed peaks.

Most significantly, however, the mass spectrum of widdrol exhibits an ion equivalent to m/e 221 at m/e 123 (~25%). Since in widdrol the position equivalent to C-7 of 3b is blocked by two methyl groups, the last proton abstraction step, comparable to path b of Scheme V for 3b, is not possible in the widdrol case. Therefore path a of Scheme V is preferred as an explanation for the formation of the ion m/e 221.

R′ and S′ similar to R and S of Scheme III (with CH_3 replacing CH_2HgX) and that crossover between them must be small.

Failure of **18a** and **19a** to yield ring-expanded products from substitution at C-13 is not surprising. When the charge of homoallylic ions R′ and S′ is localized at C-8 by conversion to a cyclopropylcarbinyl cation, the vacant p orbital at C-8 is aligned almost exactly with the 14,15 bond of the cyclopropane ring, while the 13,14 bond is very close to the nodal plane of the carbonium ion, making overlap most difficult. This means that conversion of homoallylic ions R′ and S′ to homoallylic ions analogous to **14** is an extremely unfavorable process, more so than in the pimarate series (see ion Q).

Registry No. 1b, 3582-26-1; **4,** 24267-82-1; **5a,** 42401-43-4; **5b,** 42401-44-5; **6a,** 42401-45-6; **6b,** 42401-46-7; **7,** 42401-47-8; **8,** 42401-48-9; **9a,** 42401-49-0; **10,** 42401-50-3; **11,** 42401-51-4; **17,** 19907-21-2; **18a,** 42401-52-5; **18b,** 42401-53-6; **18c,** 43025-21-4; **19a,** 42401-55-8; **19b,** 42401-56-9; **19c,** 42573-18-2; **20,** 24267-84-3.

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References and Notes

(1) Supported in part by a grant from the National Science Foundation (GP-12582). Previous paper: W. Herz and A. L. Hall, *J. Org. Chem.*, **39**, 11 (1974).

(2) The plausibility of the hypothesis has been successfully demonstrated,[3] but the conditions, which involved exposure of pimaric (**1**, R = CO_2H) and isopimaric acids to concentrated sulfuric acid can scarcely be classified as closely approximating those prevailing *in vivo*.

(3) E. Wenkert and J. W. Chamberlin, *J. Amer. Chem. Soc.*, **81**, 688 (1959).

(4) (a) D. F. Zinkel and B. F. Spalding, *Tetrahedron Lett.*, 2459 (1971); (b) D. F. Zinkel and B. P. Spalding, *Tetrahedron*, **29**, 1441 (1973); (c) D. F. Zinkel and B. B. Evans, *Phytochemistry*, **11**, 3387 (1972).

(5) In the original report[4a] the stereochemistry of strobic acid at C-15 was unspecified. More recent results[4b] which appeared after the work described in the present communication was completed led to the assignment detailed in formula **3a**.[6]

(6) Numbering in formula **3a** is based on the systematic name abeopimaradienoic acid[7] originally used by the discoverers for strobic acid. In their recent paper[4b] Zinkel and Spalding have corrected the systematic name of strobic acid to that of a cyclolabdane[7] [(14S)-17-cyclolabda-8(17),12-dien-18-oic acid]. Thus; carbon atoms 14, 15, and 16 of formula **3a** become carbon atoms 17, 14, and 15, respectively.

(7) Numbering and nomenclature used in this paper follow the proposals of a committee chaired by J. W. Rowe, "The Common and Systematic Nomenclature of Cyclic Diterpenes," Forest Products Laboratory, U. S. Department of Agriculture, Madison, Wis., 1968 (with Addenda and Corrigenda 1969).

(8) Scheme I illustrates a third possible rearrangement route (path c) of the homoallylic ion A. Paths a and c involve simple alkyl migrations leading to allylic ions, one of which (D) could generate double-bond isomers of strobic acid; path b involves a homoallylic–cyclopropylcarbinyl–homoallylic rearrangement.

(9) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(10) J. W. ApSimon and H. Krehm, *Can. J. Chem.*, **47**, 2865 (1969).

(11) The Canadian workers did not specify the stereochemistry at C-15. As well will be evident from the sequel, the methyl group is β as shown in the formula.

(12) H. C. Brown, P. J. Geoghegan, Jr., G. J. Lynch, and J. T. Kurek, *J. Org. Chem.*, **37**, 1941 (1972).

(13) H. C. Brown and J. T. Kurek, *J. Amer. Chem. Soc.*, **91**, 5647 (1969).

(14) The assignment of stereochemistry to C-15 is based on the stereochemistry subsequently established for the acetate **5b**, which was prepared by an analogous procedure (*vide infra*).

(15) S. Hanessian, *Tetrahedron Lett.*, 1549 (1967).

(16) A. Horeau, *Tetrahedron Lett.*, 506 (1961); 965 (1962).

(17) It is also possible that π complex J rearranges to the same ions M or N as are necessarily produced by path b. This would eliminate the need to propose nucleophilic attack on two separate ions, J and M or N.

(18) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 286.

(19) D. F. Zinkel, L. C. Zank, and M. W. Wesolowski, "Diterpene Resin Acids, a Compilation of Infrared, Mass, Nuclear Magnetic Resonance, Ultraviolet Spectra and Gas Chromatographic Retention Data," U. S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wis., 1971.

(20) The significance of this peak and other pertinent mass spectrometric information is discussed in an appendix following the Experimental Section.

(21) A possible candidate is an intimate ion pair corresponding to **13**, with the tosylate situated on the β face of the molecule.

(22) For definition, see K. Wiberg, B. Andes Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., p 1297. It appears to us that the discussion of relative degree of overlap in P implies that **15** is either unsymmetrical (*i.e.*, that the partial bonds to C-13 and C-15 are of unequal strength) or possesses a geometry which rules out a role in the acetolysis of **10**.

(23) For leading references, see P. R. Story and B. C. Clark, Jr., in ref 22, p 1007.

(24) Aromatization of the expected methyl levopimarate (**2**, R = CO_2Me) to **16** is probably the result of disproportionation, a phenomenon frequently observed in resin acid chemistry. The lower yield of **16** from **10** may be due to partial protonation at C-9, which would be expected to lead to backbone rearrangements.