ments indicate that m/e 191 decomposes further by successive losses of carbon monoxide and ethylene to m/e 163 (45% of $C_{11}H_{15}O^+$) and 135 (100% of $C_9H_{11}O^+$ and the base peak of the spectrum). Both of these ions must be skeletal rearrangement fragments,[8] most plausibly arising as indicated in Scheme III, although either ethyl group could in principle be eliminated in passing from e′ to f′. The usual sequence of loss of an ester group (with hydrogen rearrangement), ethylene, and then water is operative and terminates in the formation of a $C_{10}H_{10}O^+$ fragment (m/e 146, represented as g′).

Finally, it should be noted that both XVII and diethyl phenylmalonate (X) lose carbon dioxide (hr) from their molecular ions to form m/e 220 and 192 (8 and 17% or the base peaks, respectively), thus necessitating ethyl migrations in both cases.[8]

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[8] For numerous examples of skeletal rearrangement processes occurring in ketones and esters upon electron impact, see J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson and G. Schroll, *Chem. Commun.*, (London), 403 (1965); W. H. McFadden, K. L. Stevens, S. Meyerson, G. J. Karabatsos, and C. E. Orzech, *J. Phys. Chem.*, **69**, 1742 (1965); P. Natalis and J. L. Franklin, *ibid.*, **69**, 2943 (1965).

Experimental Section

This investigation was carried out using an A.E.I. MS9 double-focussing mass spectrometer. Spectra were obtained with an ionizing energy of 70 ev at a source pressure between 0.1 $\times 10^{-6}$ and 1.0 $\times 10^{-6}$ mm. Samples were introduced into the ionization chamber *via* a heated inlet system operating at a temperature of approximately 150°.

Structure of Two Solanone Precursors from Tobacco[1]

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Two acyclic diterpenoid precursors of solanone have been isolated from tobacco and identified as diastereoisomers of 6,8-dihydroxy-11-isopropyl-4,8-dimethyl-14-oxo-4,9-pentadecadienoic acid.

The genesis of the tobacco terpenoid solanone[2] (III) is of interest because of the apparent violation of the isoprene rule. Almost all of the available III in tobacco is presumed to be in the form of thermally unstable precursors, and the isolation of a carboxylic acid precursor preparation from Burley tobacco has been described.[3] In this report, we wish to describe the isolation and identification of two diastereoisomeric solanone precursors, Ia and b, from tobacco.

A mixture containing Ia and b (Scheme I), which occur in the acid form in tobacco, was obtained by a modification of the published solvent-extraction procedure.[3] The mixed acids were not readily separated by adsorption chromatography, but their methyl esters (IIa and b) were easily separated from one another by thin layer chromatography (tlc) on silica gel G using diethyl ether as the developing solvent. Both Ia and b, obtained by saponification of IIa and b, thermally decompose in the injector block of a gas chromatograph at 250° to yield III in 15.9 and 13.5 wt %, respectively. It is assumed that the thermal decomposition is almost instantaneous since there is no broadening of the gas–liquid partition chromatography (glpc) peak of III. Mass spectral examination of IIa and b showed that both gave cracking patterns characteristic of III, and the III molecular ion was one of the most intense mass fragments in both spectra. The yields of Ia and b from Burley tobacco amounted to 0.04 and 0.03%, respectively, on a dry tobacco weight basis.

The acidic precursors and their methyl esters were slightly unstable in storage even at 0° and slowly decomposed in acidic media. The methyl esters, which were the more stable form, were used in the identification studies, and spectral data were obtained on samples immediately after isolation. Both IIa and b were indicated to be pure by tlc on four different adsorbants.

Infrared spectra of both IIa and b show strong hydroxyl bands at 3410 cm^{-1}, two carbonyl functions at 1740 and 1720 cm^{-1}, and a *trans* double bond band at 970 cm^{-1}. The only differences in these spectra occur in the 1100–1000- and 930-cm^{-1} regions. Both compounds gave mass spectra with small parent peaks at m/e 368 and intense peaks at 350 and 332 which correspond, respectively, to the loss of one and two molecules of water from the parent ion.

Nuclear magnetic resonance (nmr) data and assignments obtained on deuteriochloroform solutions of IIa and b are presented in Table I. In each case, the resonances were consistent with the presence of five oxygen atoms: two in hydroxyl functions, one in a methyl ketone carbonyl, and two in the carboxylate group. Thus, the mass spectral parent peaks of 368 for IIa and b must correspond to the empirical formula $C_{21}H_{36}O_5$. The three olefinic protons apparent in the nmr spectra must be due to the *trans* double bond indicated by infrared evidence and a trisubstituted double bond. These double bonds are not conjugated since IIa and b do not absorb above 220 mμ in the ultraviolet spectrum. Lack of reaction of IIa and b with sodium metaperiodate indicates that the hydroxyl groups in each compound are not vicinal.

Nmr data obtained on IIa and b in dry pyridine provided further structural information. In this solvent, the δ 1.40 methyl resonance and the δ 4.77 multiplet of IIa are shifted about 0.30 ppm to lower field which confirms their assignments, respectively, to that of a methyl group and a single proton attached to hydroxyl-bearing

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[1] Presented at the Nineteenth Tobacco Chemists' Research Conference, Lexington, Ky., Oct 26–28, 1965.

[2] R. R. Johnson and J. A. Nicholson, *J. Org. Chem.*, **30**, 2918 (1965).

[3] R. B. Griffith, R. R. Johnson, and A. D. Quinn, U. S. Patent 3,174,485 (1965).

SCHEME I

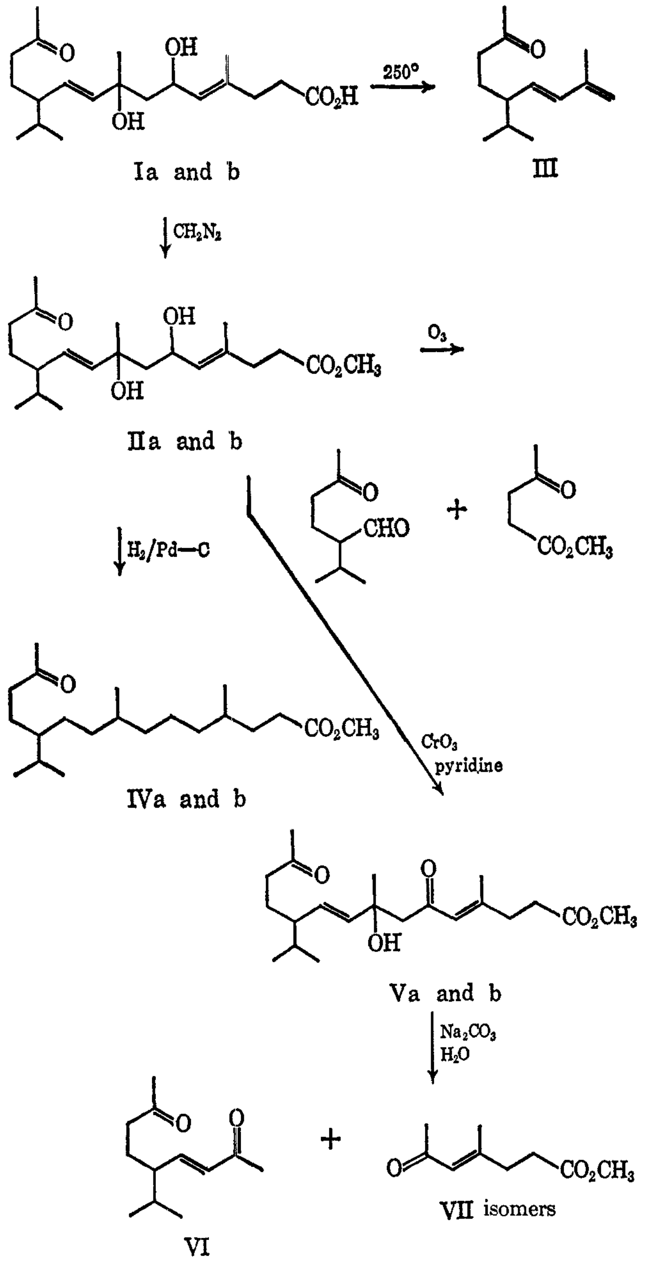

TABLE I

NMR DATA FOR IIa AND b IN DEUTERIOCHLOROFORM

Chemical shift, δ, from $Si(CH_3)_4$, ppm IIa	IIb	Assignment	Relative area[a]
0.85	0.90	$(CH_3)_2CH$–	6
1.40	1.27	$CH_3\overset{\vert}{\underset{\vert}{C}}OH$	3
1.00–2.40	1.00–2.80	–CH_2– and >CH–	6–8[b]
1.70	1.63	$CH_3\overset{\vert}{C}=\overset{\vert}{C}$–	3
2.12	2.12	$CH_3\overset{\vert}{C}=O$	3
2.38	2.37	–$CH_2C=X$[c] and >$CHC=X$[c]	6
3.22	3.28	–OH	2
3.65	3.67	$CH_3O\overset{\vert}{C}=O$	3
4.77	4.63	–$CH_2CH(OH)\overset{\vert}{C}=\overset{\vert}{C}$–	1
5.25	5.25	$\overset{H}{-C}=\overset{\vert}{C}-$	3
5.45	5.48	$\overset{H}{-C}=\underset{H}{C}-$	
		Total	36–38

[a] Based on three methoxyl protons. [b] Area obtained by difference (accounting for 9 methyl protons for the $CH_3\overset{\vert}{\underset{\vert}{C}}OH$, $CH_3\overset{\vert}{C}=\overset{\vert}{C}$–, and $CH_3\overset{\vert}{C}=O$ resonances and the 6α protons for the –$CH_2C=X$ and >$CHC=X$ resonances). [c] X = C or O.

carbons.[4] It was also noted that the olefinic proton resonances shifted about 0.30 ppm to lower field which suggested that both hydroxyl groups were allylic.[5] These observations were supported by the finding that on oxidation of IIa and b with chromic oxide in pyridine, each gave a product containing an α,β-unsaturated ketone and a hydroxyl group resistant to oxidation.

On reductive hydrogenolysis of IIa and b in ethanol with palladium, both gave saturated keto esters IV which were demonstrated to be identical by their mass, nmr, and infrared spectra, and by glc of a mixture on an SE-30 capillary column. The spectral data indicated that methyl ketone and methyl ester were the only functionalities remaining. The mass spectra showed small parent peaks at *m/e* 340 which correspond to $C_{21}H_{40}O_3$ and are attributed to reductive replacement of two hydroxyl groups and saturation of two double bonds in the hydrogenation. Thus, IIa and b must have the same carbon skeleton and must also be acyclic.

Both IIa and b gave methyl levulinate and 2-isopropyl-5-oxohexanal on ozonolysis at −70° in ethyl acetate solution containing tetracyanoethylene.[6] The keto aldehyde was oxidized to the corresponding acid and then converted to the methyl ester which was identified by comparison with an authentic sample.[7] Since methyl levulinate was isolated directly from the reaction mixtures without esterification, the carboxyl function must be that of IIa and b. These products must then represent both ends of the IIa and b molecules.[8]

Oxidation of the allylic secondary hydroxyl function in IIa and b with chromic oxide in pyridine gave α,β-unsaturated ketones [Va and b, λ_{max}^{EtOH} 239 mμ (ε >12,000)] which had identical infrared spectra. Their nmr spectra were essentially identical with the exception that the $CH_3\overset{\vert}{C}=\overset{\vert}{C}$– resonance in Vb occurred about 0.02 ppm farther upfield than in Va. In aqueous sodium carbonate solution, Va and b undergo reverse aldolization to give norsolanadione[2] VI and the two geometrical isomers of methyl 4-methyl-6-oxo-4-heptenoate (VII). VI was identified by comparison with an authentic sample, while the structures of VII were deduced from spectral data which allow only the VII isomers as possible products. In addition to the infrared, ultraviolet, and nmr spectra, which agreed with the proposed structure, the mass spectrum showed peaks at *m/e* 170, 138, 127, 111, and 97 corresponding to the expected fragmentation pattern for VII.

Together, VI and VII contain all of the carbon atoms in IIa and b. Hence, the Ia and b isomers must then

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[4] These chemical shifts are in agreement with those observed for the $CH_3\overset{\vert}{\underset{\vert}{C}}O$– and $H\overset{\vert}{\underset{\vert}{C}}O$– resonances for 1,3-butanediol on going from deuteriochloroform to pyridine.

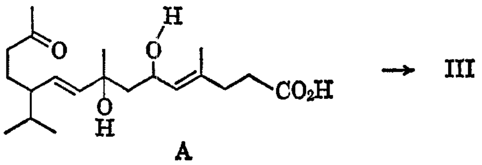
[5] The olefin protons of 2-butene-1,4-diol are shifted 0.26 ppm to lower field in pyridine than in deuteriochloroform while compounds like octene-1 have almost the same chemical shifts in these solvents.

[6] R. Criegee and P. Gunther, *Ber.*, **96**, 1964 (1963).

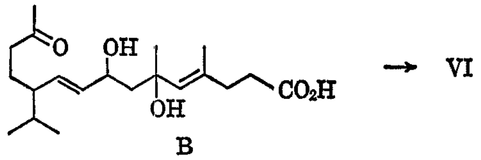
[7] J. C. Bardahn, N. C. De, and B. B. Datta, *J. Chem. Soc.*, 3195 (1951).

[8] Oxidation of IIa with potassium permanganate–sodium periodate gave methyl levulinate and 2-isopropyl-5-oxohexanoic acid.

be represented by A or B. Thermal decomposition of A to give III by the well-known 1,3-glycol cleavage[9] provides compelling evidence for Ia and b being diasterioisomers with the structure A. A similar cleavage of B would yield VI, but no III. Some further evidence supporting structure A for both Ia and b is the nmr of the olefinic hydrogen at C-5 which appears as a doublet at δ 5.25 (J = 9.6 cps) in IIa and at δ 6.0 in Va. A similar shift in the C-4 methyl resonance from δ 1.70 in IIa to δ 2.09 in Va is found. These shifts can readily be interpreted on the basis of formation of the ketone function at C-6 in A. Formation of a ketone function at C-8 in B would not be expected to lead to shifts of this magnitude. A further argument in favor of A as the structure of the I diastereoisomers resides in the better adherence of this structure to the isoprene rule.

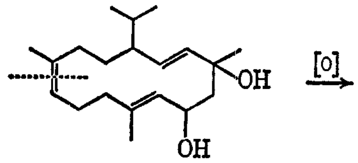


A

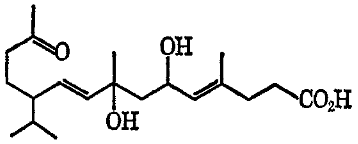


B

A striking similarity was noted between the chemistry and structure of the solanone precursors Ia and b and α- and β-4,8,13-duvatriene-1,3-diols (VIII) reported by Roberts and Rowland.[10] Indeed, oxidative cleavage of the double bond between C-8 and C-9 in VIII would give the general structure I proposed for the solanone precursors. If this is indeed the case, it would finally reconcile solanone with the isoprene rule.



VIII



I

Experimental Section[11]

Isolation of Solanone Precursors Ia and b from Tobacco.—The acids fraction from a chloroform extract of Burley tobacco (Type 31) was prepared as previously described[8] except that citric acid was used in place of HCl to acidify the $NaHCO_3$ solutions. The crude mixture of acids was esterified by treatment with ethereal diazomethane, and, after concentration, the precursor methyl esters were partially purified by elution chromatography on Davidson silica gel G which had been washed with water and then air dried. Methyl esters, IIa and b, of solanone precursors were eluted with 5 and 10% (v/v) diethyl ether in methylene chloride. The methyl esters of the mixed precursors were separated by preparative tlc on E. Merck silica gel GF_{254} (a fluorescent adsorbent) with diethyl ether used as developing solvent. Bands were located by observing the quenching of fluorescence under an ultraviolet lamp. The plates were dried 30 min at 110° prior to use. The R_f values of IIa and b in this tlc system were 0.33 and 0.45, respectively. The two isomeric methyl ester precursors were further purified by tlc on this same adsorbent by use of a 15% (v/v) acetone–chloroform mixture as developing solvent. The R_f values of IIa and b in this system were, respectively, 0.34 and 0.40. Each compound appeared as a single spot in the tlc systems of Table II. The yields of Ia and b, based on the recovery of their methyl esters, were about 0.04 and 0.03%, respectively, based on the dry weight of the tobacco.

TABLE II

		—R_f values—	
Adsorbent	Solvent	IIa	IIb
Silica gel G	Chloroform–ethyl acetate (1:1)	0.25	0.37
Alumina oxide G (neutral)	Ethyl acetate–diethyl ether (5:95)	0.40	0.53
Silica gel G–silver nitrate (5:2)	Diethyl ether	0.38	0.51
Kieselguhr G	*n*-Butyl ether	0.70	0.75

The acid precursors Ia and b, which were not readily separated by adsorption chromatography, were obtained by saponification of IIa and b, respectively. The free acids were assayed for solanone by glpc using methyl myristate as an internal standard and an injector block temperature of 250°. The conversion of Ia and b to solanone must be almost instantaneous, since there is no apparent broadening of the solanone peak. In these assays, a peak corresponding in retention time to norsolanadione VI was also observed. The peak area represented about 1 wt % yield.

Physical Data on Solanone Precursors, Methyl Esters IIa and b. Isomer IIa was an oil: $[\alpha]^{25}_D$ +14.0°; infrared spectrum (film), 3410, 1735, 1715, 975 cm^{-1}.

Anal. Calcd for $C_{21}H_{36}O_5$: C, 68.48; H, 9.78; mol wt, 368. Found: C, 67.7; H, 9.6; mass, 368.

Isomer IIb was an oil, $[\alpha]^{25}_D$ −36.7°. The infrared spectrum of IIb was similar to that of IIa with the exception of some minor differences in the 900–1100-cm^{-1} region.

Anal. Calcd for $C_{21}H_{36}O_5$: C, 68.48; H, 9.78; mol wt, 368. Found: C, 67.6; H, 9.6; mass, 368.

Reductions of IIa and b to IVa and b.—A solution of 353 mg of IIa in 10 ml of ethanol was shaken with 100 mg of 10% Palladium on charcoal under 60 psi g of H_2 at room temperature for 72 hr. The saturated keto ester obtained, methyl 11-isopropyl-4,8-dimethyl-14-oxopentadecanoate (IVa), was purified by tlc on Silica gel G using chloroform as the developing solvent (R_f 0.50); infrared spectrum (film), 1735, 1715 cm^{-1}; nmr spectrum, $(CH_3)_2C<$, δ 0.85; $>CH-$ and $-CH_2-$, δ 1.20–2.15; $CH_3-\overset{|}{C}{=}O$, δ 2.13; $-CH_2-\overset{|}{C}{=}O$, δ 2.36; $CH_3O-\overset{|}{C}{=}O$, δ 3.66.

Anal. Calcd for $C_{21}H_{40}O_3$: C, 74.12; H, 11.76, mol wt, 340. Found: C, 74.25; H, 12.1; mass, 340.

Reduction of IIb under the same conditions gave IVb which gave nmr, infrared, and mass spectra identical with those from IVa. Moreover, both had identical retention times on a 200 ft × 0.02 in. stainless steel SE-30 capillary column at 240°, and a mixture gave a single peak with no peak broadening on this column.

Ozonolysis of IIa and b.—A mixture of 130 mg of IIa and 216 mg of tetracyanoethylene in 6 ml of ethyl acetate was cooled to

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[9] J. English, Jr., and F. W. Brutcher, Jr., *J. Am. Chem. Soc.*, **74**, 4279 (1952); H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949); H. E. Zimmerman and J. English, Jr., *ibid.*, **76**, 2285, 2291, 2294 (1954). The mechanism of this reaction would also predict direct formation of norsolanadione as a minor product from Ia and b, and this was observed in some cases.

[10] D. L. Roberts and R. L. Rowland, *J. Org. Chem.*, **27**, 3989 (1962).

[11] Nmr spectra were obtained on a Varian Associates HR-60 spectrometer in deuteriochloroform or pyridine solutions. Chemical shifts (δ values) are reported in parts per million downfield from an internal tetramethylsilane standard. Infrared spectra were obtained on a Perkin-Elmer 521 spectrometer and ultraviolet spectra were obtained on a Cary Model 14 spectrometer. Molecular weights were determined on an AEI MS-9 high-resolution mass spectrometer. Column chromatographic separations were made using Davidson silica gel G which had been washed with water and then air dried. Tlc separations were made on E. Merck silica gel G or GF_{254}.

−70° and treated with 1 mmole of ozone. The reaction mixture was analyzed by glpc on an EGS column at 125° using methyl myristate as an internal standard. The chromatogram showed two products, A and B, present in amounts, respectively, of 8.2 and 3.9%. The two products were separated by tlc on silica gel GF_{254} with 15% (v/v) diethyl ether in chloroform. Component A (R_f 0.65) was identified as methyl levulinate by its glpc retention time, and infrared spectrum which were identical with those of an authentic sample. The glpc indicated yield was 23% of theory. Component B (R_f 0.76) was shown to be 2-isopropyl-5-oxohexanal by oxidation to the corresponding acid and subsequent esterification with ethereal diazomethane. The infrared spectrum and glpc retention time of the ester thus obtained were identical with those of an authentic sample of methyl 2-isopropyl-5-oxohexanoate. The glpc indicated yield of this keto aldehyde was 9% of theory. Similarly, ozonolysis of IIb (164 mg) and isolation of products gave methyl levulinate (34% yield) and 2-isopropyl-5-oxohexanal (16% yield).

Oxidation of IIa and b with Chromic Oxide in Pyridine[12] to Form Va and b.—A slurry of 120 mg of CrO_3 in 3 ml of pyridine was added to a solution of 121 mg of IIa in 3 ml of pyridine. Tlc examination of the reaction mixture showed that oxidation of IIa was virtually complete after 24 hr at room temperature. After removing the pyridine under vacuum, the residue was extracted twice with diethyl ether to give 85 mg of crude product. Preparative tlc of the product on silica gel G with diethyl ether (R_f 0.70) gave 41 mg of methyl 8-hydroxy-11-isopropyl-4,8-dimethyl-6,14-dioxo-4,9-pentadecadienoate (Va). The purified product was an oil: λ_{max}^{EtOH} 239 mμ (ε 12,600); infrared spectrum (film), 3470, 1738, 1711, 1673, 1610, 977 cm^{-1}; nmr spectrum, $(CH_3)_2\overset{|}{C}-$, δ 0.82; $CH_3-\overset{|}{C}-O$, δ 1.26; $CH_3-\overset{|}{C}=O$, δ 2.07; $CH_3-\overset{|}{C}=\overset{|}{C}-$, δ 2.11; $=C-CH_2-CH_2-(O=)C-O-$, δ 2.46; $-O-\underset{|}{C}-CH_2-\overset{|}{C}=O$, δ 2.65; $CH_3O-\overset{|}{C}=O$, δ 3.66; −OH, δ 4.32; $-CH=CH-$, δ 5.4; $-\overset{|}{C}=CH-$, δ 6.0.

Similarly, oxidation of 126 mg of IIb and isolation of product gave 45 mg of Vb. This product had λ_{max}^{EtOH} 239 mμ (ε 12,890). The R_f values and infrared spectra of Va and b were identical. The only difference in the nmr spectra was that the $CH_3\overset{|}{C}=\overset{|}{C}-$ resonance occurred at about 0.02 ppm farther upfield in Vb than in Va.

Reverse Aldolization of Va and b.—A solution of 41 mg of Va in 5 ml of ethanol was stirred overnight with 5 ml of 5% Na_2CO_3. Extraction of the reaction mixture with diethyl ether and subsequent fractionation of the extract by tlc on silica gel G using diethyl ether as solvent gave 12 mg of norsolanadione (VI, R_f 0.76) which was identified by comparison of its nmr and infrared spectra with those of an authentic sample.[2]

The aqueous phase was acidified with dilute H_2SO_4 to pH 2 and extracted with diethyl ether. The extracted material (12 mg) was treated with ethereal diazomethane and the methyl esters formed were fractionated by tlc on silica gel G using diethyl ether as solvent. The infrared, nmr, and mass spectra of the major product (7 mg, R_f 0.88) allow only methyl 4-methyl-6-oxo-4-heptenoate (VII) as a possible structure. Doublets at δ 1.89 and 2.13 indicated that the VII obtained was probably a mixture of the two geometrical isomers of this structure.

Reverse aldolization of 140 mg of Vb with 5% Na_2CO_3 and the same isolation of products gave 34 mg of VI and 17 mg of VII. Preparative glpc of VII on an Apiezon L column at 100° allowed collection of two components, VII-A and VII-B, in their order of elution. Both components had the same mass, 170, and the same mass fragmentation pattern as the product from Va.

VII-A.—Infrared spectrum (film), 1739, 1689, and 1816 cm^{-1}; nmr spectrum, $CH_3-\overset{|}{C}=\overset{|}{C}-$, δ 1.85; $CH_3-(O=)C-$, δ 2.14; $=C-CH_2-CH_2-(O=)C-O-$ (multiplet), *ca.* δ 2.61; $CH_3-O-(O=)C-$, δ 3.63; $-\overset{|}{C}=\overset{|}{C}H$, δ 6.09; λ_{max}^{EtOH} 237 mμ (ε *ca.* 9300).

Anal. Calcd for $C_9H_{14}O_3$: mol wt, 170. Found: mol wt, 170.

VII-B.—The infrared spectrum (film) was similar to that of VII-A except that weak absorption occurred at 965 cm^{-1}. The nmr spectrum was similar to that of VII-A except that the doublet at δ 1.85 was shifted downfield to δ 2.13 and the complex A_2B_2 multiplet at δ 2.61 was collapsed to an apparent singlet at δ 2.45. The ultraviolet spectrum showed λ_{max}^{EtOH} 235 mμ (ε *ca.* 11,600).

Component VII-A is assigned the configuration in which the 4-methyl group, δ 1.85, is *trans* to the acetyl group and VII-B, δ 2.13, the configuration in which it is *cis*. These chemical shifts are in good agreement with those for the 3-methyl group in the geometrically isomeric phytenoates[13,14] which are reported to be δ 1.80 when the methyl group is *trans* to the ester carbonyl and δ 2.15 when *cis*.

Acknowledgment.—The authors are indebted to E. Jack Kahler and R. H. Poirier (Battelle Memorial Institute) for their many helpful suggestions.

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[12] G. L. Poos, G. E. Arth, R. E. Bezler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[13] L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp 119–125.

[14] J. W. K. Burrell, L. M. Jackman, and B. C. L. Weedon, *Proc. Chem. Soc.*, 263 (1959).

Resin Acids. VIII. Reaction of Levopimaric Acid with Acetylenic Dienophiles[1,2]

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The diene synthesis of levopimaric acid (1) with acetylenic dienophiles has been investigated. Condensation of 1 with diethyl acetylenedicarboxylate and benzyne at moderate temperatures results in the expected adducts which undergo thermal rearrangement at 200°. At the temperatures necessary to effect condensation of 1 with ethyl propiolate and ethyl phenylpropiolate, thermal isomerization proceeds spontaneously. Structures of the products have been established.

In the course of a program aimed at the utilization of Diels–Alder adducts of levopimaric acid (**1**) for complex syntheses we had occasion to study the reaction of **1** with acetylenic dienophiles and hereby report our results.

The only previous reference to this matter is that of Sandermann[4] who claimed the successful condensation of pine gum or abietic acid with acetylenedicarboxylic ester. The product, presumed to be **2a**, was not isolated, but crude material obtained by condensation of the reactants at 190° was converted, by hydrolysis, to a substance, mp 169–170°, which was assigned formula **2b**. Application of the Alder and Rickert

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[1] Previous paper: W. Herz and R. N. Mirrington, *J. Org. Chem.*, **30**, 4338 (1965).

[2] Supported in part by a grant from the National Science Foundation (GP-1962).

[3] U. S. Public Health Service Fellow, 1962–1964; Ethyl Corporation Fellow, 1964–1965.

[4] W. Sandermann, *Ber.*, **74**, 155 (1941); W. Sandermann and R. Höhn, *ibid.*, **76**, 1257 (1943).