In the case of benzophenone, the mesomeric moment has been given[14] as 0.3×10^{-18}, while the molecular dipole moment is 2.97. As in the case of diphenyl ether, m_0 should be larger than the estimated mesomeric moment. Possibly 0.6 would be an upper limit. In view of the proportionality of the loss to the square of the moment involved, it is evident that the loss due to any orientation of mesomeric moment would be of the order of 0.04 of that associated with orientation of the molecular moment and would thus have escaped detection in the centimeter wave length measurements. The reason for the normal behavior of benzophenone in contrast to the abnormal behavior of diphenyl ether is thus evident.

Since Sutton[14] has obtained mesomeric moments of 1.02 for aniline and 1.66 for N,N-dimethylaniline, which have molecular moments of 1.52 and 1.61, respectively, abnormally low relaxation times found for diphenylamine[2] and triphenylamine[26] can be attributed to relaxation mechanisms involving ring rotation as proposed for diphenyl ether.

The molecule of diphenylmethane is very similar in size and shape to that of diphenyl ether, the respective molar volumes being 174 and 164 cc. at 60°. The reduced relaxation times at 60° are[5] 0.23×10^{-9} for diphenyl ether and 0.25×10^{-9} for diphenylmethane. The small dipole moment 0.26×10^{-18} found[5] for diphenylmethane is due to a small shift of electronic charge from the methylene group into the rings, similar to that occurring from the methyl group into the ring in toluene. This may be described[27,28] in terms of hyperconjugation or orbital overlap, which will vary as a ring rotates out of the plane of the two methylene-to-ring bonds. The variation should provide an intramolecular relaxation mechanism similar to that which has been shown to be plausible for diphenyl ether. The relaxation time should obviously be close to that of diphenyl ether, but the smaller charge shift involved should give rise to a smaller dielectric loss, as observed.

It would appear that change in the direction of a mesomeric moment accompanying rotation of a benzene ring in a molecule provides a quantitatively acceptable mechanism for the abnormally low relaxation times observed for several molecules containing two or three phenyl groups attached to a small central atom or group. The fact that molecules containing similar central groups with alkyl instead of aryl groups attached do not show the anomaly in relaxation time increases the probability of the correctness of the hypothesis. The intramolecular orientation process is facilitated by the steric repulsion which makes coplanarity of the rings highly improbable. Although, as has been shown, rotation of one ring can occur most readily when another ring rotates synchronously so as to maintain a 90° angle between the planes of the two rings, less favorable orientation of the ring planes relative to each other need not prevent the dipole orientation to which the loss is ascribed. Differences in dipole moment, in bond length, and in chemical reactivity often may be attributed to differences in orbital character or orbital overlap, perhaps described in terms of "mesomerism." The dynamic behavior of this phenomenon is evidenced or, perhaps, given a certain plausible reality by the apparent relaxation mechanisms of these molecules which have been discussed.

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[26] B. B. Howard, unpublished measurements carried out in this Laboratory.

[27] C. A. Coulson, "Valence," Oxford University Press, Oxford, 1952, Chap. XII.

[28] Ref. 22, p. 315.

[CONTRIBUTION FROM THE RESEARCH CENTER OF THE HERCULES POWDER COMPANY, WILMINGTON, DELAWARE]

Nuclear Magnetic Resonance Spectra of Resin Acids

BY JAMES C. W. CHIEN

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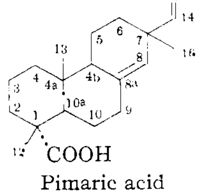
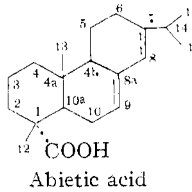
The nuclear magnetic resonance spectra of 17 resin acids were obtained. Most of the peaks were accounted for to give structural information. By consideration of the numbers of olefinic and allylic protons and of the shifts of various methyl groups, the positions of double bonds in several resin acids have been determined.

Introduction

The stereochemistry of pimaric and isopimaric acids has been the subject of many investigations.[1-3] Edwards and Howe[4] pointed out that while the pimaric and isopimaric acids are definitely epimeric at C_7,[5] the actual stereochemistry at this position as concluded by Wenkert and Chamberlin[2] has to be considered as not definitive in view of the very small observed percentages of the γ- and δ-lactones in the equilibrium mixtures derived from dihydropimaric and dihydroisopimaric acids.



Pimaric acid



Abietic acid

Subsequent to the completion of this work, Edwards and Howe[6] reported unequivocal proof

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[1] G. C. Harris and T. F. Sanderson, THIS JOURNAL, **70**, 334, 2079, 2081 (1948).

[2] W. Wenkert and J. W. Chamberlin, *ibid.*, **80**, 2912 (1958); **81**, 688 (1959).

[3] B. Green, A. Harris and W. B. Whalley, (a) *Chem. & Ind. (London)*, 1084 (1958); (b) *J. Chem. Soc.*, 4715 (1958).

[4] O. E. Edwards and R. Howe, *Can. J. Chem.*, **37**, 760 (1959).

[5] The numbering system used in this paper is that of G. C. Harris, "Rosin and Rosin Derivatives," *Encyclopedia Chem. Technol.*, Vol. XI, Interscience Publishing Co., New York, N. Y., 1953, p. 779.

that pimaric and isopimaric acids are epimeric at C_{4b}. These authors observed a faster rate of isomerization of the nuclear double bond in dihydroisopimaric acid than in dihydropimaric acid which suggests that the isopimaric acid has a C_{4b} β-proton. From infrared spectroscopic study, Bruun[7] also suggested that pimaric and isopimaric acids are epimeric at C_{4b}. In this paper, the observed differences in the nuclear magnetic resonance (n.m.r.) spectra of pimaric and isopimaric acids are described.

Another feature of n.m.r. is its ability to measure the number of protons on double-bonded carbon atoms. By means of this, the positions of double bonds in several resin acids have been determined.

Experimental

The resin acids[8] or their methyl esters were dissolved in CCl_4 at either 16.65 or 20% concentration. The physical constants of these compounds are listed in Table I. All spectra were obtained at 60 megacycles per second in a magnetic field of approximately 14,100 gauss. Both benzene and hexamethyldisiloxane were used as standards. The standard was introduced either in a capillary or in the outer tube of a coaxial cell manufactured by the Wilmad Glass Co., Landisville, New Jersey. All values of chemical shift in c.p.s. were referred to the resonance line position of pure benzene. Lines at the higher field side of benzene have positive shift values.

TABLE I

PHYSICAL PROPERTIES OF RESIN ACIDS

Compound	M.p., °C.	$[\alpha]^{24}$D, °	Ref.
Methyl dehydroabietate	62.5–63	+ 62[a]	
Abietic acid		−106	1
Dihydroabietic acid			[b]
Methyl tetrahydroabietate	96–98		
Levopimaric acid		−276	1
Dihydrolevopimaric acid			[b]
Neoabietic acid	167–169	+159	1
Dihydroneoabietic acid			[b]
Palustric acid		+ 69.5[c]	
Dihydropalustric acid	170–172.5		[b]
Methyl pimarate			[d]
Isopimaric acid	162–164	0	1
Methyl dihydropimarate			[e]
Dihydroisopimaric acid	173–175	0	1
Methyl tetrahydropimarate			[f]
Methyl tetrahydroisopimarate			[f]

[a] All rotations are of 1% in absolute ethanol unless otherwise noted. [b] C. A. Genge, unpublished. Prepared from corresponding acid by partial hydrogenation to calculated amount of hydrogen uptake using Pd on C catalyst. [c] Rotation measured at 2% in 95% ethanol. [d] Prepared from pimaric acid which has a rotation $[\alpha]^{24}$D + 75° and a melting point 217–219°. [e] Prepared from dihydropimaric acid which has a rotation $[\alpha]^{24}$D + 19° and a melting point 243–245°. [f] C. A. Genge, unpublished. Prepared by total hydrogenation of corresponding acid using Pd on C catalyst.

Levopimaric acid was studied at 20, 10 and 5% concentration in CCl_4. The position of all resonance lines was found to agree within ± 1 c.p.s. with the exception of the resonance of carboxyl protons where larger variations were observed. These results indicated that with the one exception of carboxyl proton resonance, the chemical shift of other protons obtained at 16.65 and 20% concentrations can be compared directly.

Results

The n.m.r. spectra of all resin acids contained lines ranging from − 349 to + 343 c.p.s. (Table II) and consisted of broad and narrow peaks. The broad peaks are due to protons attached directly to the perhydrophenanthrene ring carbon atoms. The reasons for broadening have been discussed by Shoolery and Rogers.[9] The narrow peaks are due to groups attached to the ring system by a single bond which possesses an additional degree of freedom.

The resonance line of the angular methyl group in resin acids was found between 322 and 343 c.p.s.

In the spectra of the methyl esters of the resin acids, there was a narrow peak representing three protons at 175.5 ± 1.5 c.p.s. Corresponding peaks were absent in the spectra of the resin acids. This resonance is definitely assigned to the protons of the carbomethoxyl group.

The peaks of the carboxyl protons were found from − 372 to − 270 c.p.s. Large variation in chemical shift usually is found for protons susceptible to hydrogen bonding. Concentration, temperature, small amounts of water and hydrogen ions present in the sample as impurities, and relative hydrogen bonding abilities could all contribute to the observed variation.

A methyl group peak at 318 ± 2 c.p.s., found in all the resin acid spectra, must be the resonance of C_{12}-protons. The large paramagnetic shift is due to the unshielding of the neighboring electron withdrawing carboxyl group.

Compounds with the abietic acid-type of skeleton structure usually have an isopropyl group on the C_7 atom. The proton resonance peaks of the two equivalent methyl groups, found between 321 and 339 c.p.s., are characterized by doublet structures with values of hyperfine coupling constants ranging from 6.5 to 7.5 c.p.s. The values of the chemical shift decrease with increasing number of double bonds in the molecule and with increasing proximity of these double bonds; methyl dehydroabietate has the lowest value of 321 c.p.s. The resonance of the two equivalent methyl groups in neoabietic acid was found to be a singlet. The chemical shift value was a very low 289 c.p.s. These observations are consistent with the known structure[1] of neoabietic acid which has an isopropenyl group on the C_7 atom.

The areas under the peaks in the region between − 28 to + 119 c.p.s. gave accurately the number of olefinic protons in resin acids. This region was devoid of absorption in the spectra of the tetrahydro derivatives of abietic, pimaric and isopimaric acids. In the case of dihydropalustric acid which is known to have one double bond, the n.m.r. spectrum showed no absorption for olefinic proton. The significance of this observation is discussed below.

It is consistent in all the cases studied that the broad resolvable peaks in the region 225 to 279 c.p.s. are due to allylic protons. In compounds

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(6) O. E. Edwards and R. Howe, *Chem. & Ind. (London)*, **537** (1959).

(7) H. H Bruun, *Acta Chem. Scand.*, **13**, 379 (1959).

(8) Most of the resin acids studied in this work were supplied by C. A. Genge and T. F. Sanderson, Hercules Powder Company. Samples of palustric and isopimaric acids were kindly furnished by R. V. Lawrence of the Naval Stores Station, U. S. Department of Agriculture, Olustee, Florida.

(9) J. N. Shoolery and M. T. Rogers, THIS JOURNAL, **80**, 5121 (1958).

TABLE II

PROTON MAGNETIC RESONANCE PEAKS[a] IN RESIN ACIDS

Compound	C_{13}	C_{12}	C_{15} and C_{16} in abietic-type acid	C_{16} in pimaric-type acid	Secondary allylic	Tertiary allylic	Protons allylic to conjugated double bonds	Olefinic	Carboxyl	Carbomethoxyl
Methyl dehydroabietate	322	318	321				266 (1), 225 (2)	−14, −22, −28 (3)		177
Abietic acid	343	318	333				271 (6)	74 (1), 48 (1)	−372	
Dihydroabietic acid	341	320	336		279 (2)[b]	260 (2)		49 (1)	−349	
Methyl tetrahydroabietate	341	319	336							174
Levopimaric acid	332	316	329				252 (6)	87 (1), 63.5 (1)	−332	
Dihydrolevopimaric acid	342	319	333		276 (2)	258 (2)		61 (1)	−337	
Neoabietic acid	343	319	289				276, 258[c]	34 (1)	−270	
Dihydroneoabietic acid	342	319	333		276 (2)	258 (2)		61 (1)	−337	
Palustric acid	327	319	331				272 (7)	74 (1)	−349	
Dihydropalustric acid	335	320	329		277 (6)				−345	
Methyl pimarate	343	320		329	278 (2)	259 (1)		107–42 (4)		177
Methyl isopimarate	343	320		341	277 (2)	277 (1)		109–25 (4)		177
Isopimaric acid	342	319		339	275 (2)	275 (1)		108–24 (4)	−340	
Methyl dihydropimarate	342	319		334	279 (2)	261 (1)		77 (1)		175
Dihydroisopimaric acid	341	319		337	274 (2)	274 (1)		69 (1)		
Methyl tetrahydropimarate	343	320		337						177
Methyl tetrahydroisopimarate	343	320		340						176

[a] In cycles per second from the resonance line position of pure benzene. [b] Numbers in parentheses represent number of protons represented by the peak. [c] Area cannot be determined.

where the phenanthrene ring is totally saturated as in the tetrahydro derivatives of abietic, pimaric and isopimaric acids, no absorption was found in this 225–279 c.p.s. region.

Compounds with one C—C bond were found to have two peaks at 275 ± 4 c.p.s. and 259 ± 2 c.p.s. which were attributed to the resonance of the secondary and the tertiary allylic protons, respectively. In the chart compiled by Chamberlain,[10] the average tertiary allylic proton shifts were about 18 c.p.s. lower than the secondary allylic proton shifts. The above assignment is found to agree with the known structures of resin acids. There was in the spectrum of dihydropalustric only one peak at 277 c.p.s. which represented six protons, the peak could be due only to the secondary allylic protons. The numbers of secondary and tertiary allylic protons found in other resin acids are listed in Table II. The peaks of secondary and tertiary protons allylic to conjugated double bonds were not resolved. In methyl dehydroabietate, multiple lines were obtained between 225 and 266 c.p.s. due to protons allylic to the aromatic system.

Discussion of Results

Angular Methyl Resonance.—Shoolery and Rogers[9] found that the chemical shifts of angular methyl groups were influenced by the structure of steroids. Similarly, correlation between the angular methyl resonance and the structure of resin acids was observed.

In one group of 13 resin acids, the resonance line of the angular methyl group was found at 342 ± 1 c.p.s. The members of this group differ structurally only on the part of the molecule distant from the angular methyl position; hence, the observed constant shift value of 342 ± 1 c.p.s. This shift value is the highest among all of the protons in resin acids.

In a second group of four resin acids, the angular methyl shifts were found between 322 and 335 c.p.s. The acids are dihydropalustric, levopimaric, palustric and dehydroabietic in the order of increasing paramagnetic shift. The paramagnetic shift must be attributed to the unshielding effects of nearby double bonds, conjugated double bonds and aromatic system. The C_{13}-proton shifts for dihydroabietic and dihydrolevopimaric acids, which have double bonds at Δ^8 and Δ^7, respectively, were found at the maximum value of 342 c.p.s. Therefore, a double bond situated at two or more carbon atoms away from the angular methyl group has no effect on the C_{13}-proton resonance frequency. The C_{13}-proton peak was found at 335 c.p.s. in dihydropalustric acid which has a $\Delta^{4b,8a}$ double bond. This is a shift of −7 c.p.s. Similarly, Shoolery and Rogers[9] observed that the C_{19}-proton shift was decreased by 9 c.p.s. and 7 c.p.s. in steroids with $\Delta^{9(11)}$ and Δ^5 double bonds, respectively.

The angular methyl group is further shifted to 327 c.p.s. in the presence of $\Delta^{4b(8a),7}$ conjugated double bonds in the case of palustric acid. When the conjugated double bonds are moved away from the angular methyl position, its unshielding effect is reduced. A shift value of 332 c.p.s. was obtained for levopimaric acid with $\Delta^{6,8}$ conjugated double bonds. It is interesting to note that the C_{13}-proton shift was 343 c.p.s. in neoabietic acid which has $\Delta^{7,8}$ conjugated double bonds.

The largest paramagnetic shift of the angular methyl group was found in methyl dehydroabietate. 322 c.p.s., which is clearly due to the magnetic moment caused by the aromatic ring current.[11]

Position of the Double Bonds in Some Resin Acids.—The position of double bonds in a resin acid was deduced from the number and the kinds of allylic protons, the number of olefinic protons and the shifts of the angular methyl group and of the two symmetrical methyl groups on the C_{14}-atom.

Levopimaric acid has two conjugated double bonds; their possible positions are $\Delta^{5,7(8)}$ and $\Delta^{6,8}$. Both structures are expected to give similar

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(10) N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).

(11) H. J. Bernstein, W. G. Schneider and J. A. Pople, *Proc. Roy. Soc.* (*London*), **A236**, 515 (1956).

shift values for the angular methyl group and the methyl groups on C_{14}. However, $\Delta^{5,7(8)}$ should have three olefinic protons and three protons allylic to the double bonds while $\Delta^{6,8}$ should have two olefinic protons and six allylic protons. The n.m.r. spectrum showed definitely that levopimaric acid has $\Delta^{6,8}$ double bonds.

The n.m.r. spectrum of neoabietic acid agrees with the known structure with double bonds at $\Delta^{7(14),8}$. The resonance of the two equivalent methyl groups was found to be a singlet, at 289 c.p.s. The large paramagnetic shift and the absence of hyperfine splitting unequivocally places one of the two double bonds at $\Delta^{7(14)}$. Furthermore, there was a peak at 34 c.p.s. representing one conjugated olefinic proton. Therefore, the second bond must be $\Delta^{8(8a)}$.

The spectra of dihydrolevopimaric and dihydroneoabietic acids were identical in every respect. 1,4-Hydrogenation of the levopimaric and neoabietic acids should yield the same product. The proton resonance of the methyl groups on C_{14} was decreased to 333 c.p.s. indicating that the double bond position is fairly close to these methyl groups. Therefore, dihydrolevopimaric and dihydroneoabietic acids are believed to be the same compound and with the double bond in position $\Delta^{7(8)}$. Dihydroabietic acid also has one double bond, but there was no paramagnetic shift of the proton resonance of the methyl groups on C_{14}. A Δ^{8} assignment for the double bond is favored.

The spectrum of palustric acid, which is known to have two double bonds, was characterized by the low angular methyl shift value of 327 c.p.s., the low C_{15}- and C_{16}-proton shift value of 331 c.p.s., and the presence of seven allylic protons. All these argue for the place of double bond at $\Delta^{4b(8a),7(8)}$. Dihydropalustric acid is known to have one double bond. The absence of olefinic proton resonance and the presence of six secondary allylic protons in the n.m.r. spectrum, and the angular methyl proton shift value of 335 c.p.s. all require the placement of the double bond at $\Delta^{4b(8a)}$.

Pimaric and Isopimaric Acids.—The n.m.r. spectra of pimaric and isopimaric acids and their hydrogenated derivatives differ in several aspects. The C_{16} methyl proton shifts were, methyl pimarate, 329 c.p.s.; methyl isopimarate, 340 c.p.s.; methyl dihydropimarate, 334 c.p.s.; dihydroisopimaric acid, 337 c.p.s.; methyl tetrahydropimarate, 337 c.p.s.; and methyl tetrahydroisopimarate, 340 c.p.s. These results indicate that the C_{16}-methyl groups in each pair of isomers have different structural environment. This is in agreement with the fact that C_7 is an epimeric position. Shoolery and Rogers[9] found that the magnetic anisotropy of the double bond produces a shift on its neighboring protons in a direction dependent on the orientation of the double bond. In pimaric and isopimaric acids, the relative orientation of the Δ^{8} and the Δ^{14} double bonds may be responsible for the observed up-field shift of the C_{16} methyl proton resonance in isopimaric acid.

The broad resonance peaks of the allylic protons in methyl pimarate and methyl dihydropimarate found at 260 c.p.s. and 277 c.p.s. are due to one tertiary and two secondary allylic protons, respectively. Only one peak was found at 276 c.p.s. in both methyl isopimarate and dihydropimaric acids representing three allylic protons. Edwards and Howe[6] have shown that pimaric and isopimaric acids are epimeric at C_{4b}. The observed up-field shift of the C_{4b} tertiary allylic proton to 276 c.p.s. in isopimaric acid indicates that the C_{4b}-protons in pimaric acid and isopimaric acids indeed have different environment.

The portions of the spectra due to the vinyl group protons were analyzed as ABX systems where X is the non-terminal proton and A and B are the terminal protons. The calculated spectra agreed well with the observed spectra. Values of the various spectra parameters are listed in Table III.

TABLE III

CHEMICAL SHIFTS AND SPIN-SPIN COUPLING CONSTANTS OF THE VINYL GROUP PROTONS IN METHYL PIMARATE AND METHYL ISOPIMARATE

Compound	Chemical shifts, c.p.s. δ_X	$\delta_A - \delta_B$	Coupling constants, c.p.s. J_{AX}	J_{BX}	J_{AB}
Methyl pimarate	37.8	5.5	13.4	11.2	2.2
Methyl isopimarate	48.7	3.1	18.2	11.9	1.5

It is interesting that in pimaric and isopimaric acids the spin-spin coupling constants of the vinyl group protons as well as the chemical shifts are different.

Acknowledgment.—The author is grateful to Dr. C. A. Genge and Mr. T. F. Sanderson for supplying most of the resin acids and for valuable discussions.