24° gave α_D + 0.42° (*l* 1), $[\alpha]^{24}D$ + 12.9°. The yield was 94%.

Anal. Calcd. for $C_{20}H_{25}NO_4S$: C, 63.97; H, 6.71; N, 3.73. Found: C, 63.64; H, 6.70; N, 3.74.

Resolution of N-Benzenesulfonyl-N-carboxymethyl-*t*-butylmesidine.—This resolution was carried out as previously described.[3] The less-soluble salt melted at 195–196° (lit.[3] m.p. 195–196°); rotation, 0.0176 g. made up to 2 ml. with absolute ethanol at 27° gave α_D −0.25° (*l* 1), $[\alpha]^{27}D$ −29° (lit.[3] $[\alpha]^{28}D$ −36.0°).

(+)-N-Benzenesulfonyl-N-carboxymethyl-*t*-butylmesidine.—The optically active acid was regenerated from the less-soluble salt by the usual procedure. The product, purified from benzene, had m.p. 170–171° (resolidified and melted again at 182.5–183.5°); rotation, 0.0644 g. made up to 2 ml. with dimethylformamide at 28° gave α_D +1.23° (*l* 1), $[\alpha]^{28}D$ +38.2°. The yield was 90%.

Anal. Calcd. for $C_{21}H_{27}NO_4S$: C, 64.75; H, 6.99; N, 3.60. Found: C, 64.71; H, 7.01; N, 3.55.

Racemization of N-Benzenesulfonyl-N-carboxymethylalkylmesidines.—The optically active acid was dissolved in purified dimethylformamide, and the solution was transferred to glass tubes (55 mm. long, 9 mm. internal diameter) in 6 to 10 equal portions. The tubes were sealed and immersed all at the same time (within 20 seconds) in boiling 1-butanol (118°). The first tube was withdrawn after 8–15 minutes, after which time the thermal equilibrium was assumed to be reached; this was considered as zero time. The remaining tubes were removed at successive time intervals, quenched in ice-water, then allowed to come to room temperature, and the rotation determined.

The following results were obtained.

N-Benzenesulfonyl-N-carboxymethylethylmesidine: 0.0 hr., $\alpha^{26}D$ −0.88°; 1.0 hr., $\alpha^{26}D$ −0.83°; 2.25 hr., $\alpha^{26}D$ −0.74°; 3.5 hr., $\alpha^{27}D$ −0.67°; 4.9 hr., $\alpha^{27}D$ −0.62°; 6.0 hr., $\alpha^{27}D$ −0.56°; 7.25 hr., $\alpha^{27}D$ −0.53°; 8.5 hr., $\alpha^{28}D$ − 0.47°; 9.8 hr., $\alpha^{28}D$ − 0.43°; 11.0 hr., $\alpha^{28}D$ −0.39°.

A plot of ln α *vs.* time afforded a straight line from whose slope was derived the rate constant, K = 7.26 × 10^{-2} hr.$^{-1}$ and the half-life, $t_{1/2}$ = 9.6 hr.

Two check racemizations were carried out in the same manner. The values of the rate constant and half-life were: K 7.10 × 10^{-2} hr.$^{-1}$, $t_{1/2}$ 9.8 hr. and K = 7.22 × 10^{-2} hr.$^{-1}$, $t_{1/2}$ = 9.6 hr.

N-Benzenesulfonyl-N-carboxymethyl-*n*-propylmesidine: 0.0 hr., $\alpha^{27}D$ −1.02°; 1.5 hr., $\alpha^{27}D$ −0.90°; 3.0 hr., $\alpha^{27}D$ −0.87°; 5.0 hr., $\alpha^{27}D$ −0.75°; 7.0 hr., $\alpha^{27}D$ −0.64°; 9.0 hr., $\alpha^{27}D$ −0.58°; 11.0 hr., $\alpha^{27}D$ −0.50°; 13.0 hr., $\alpha^{27}D$ −0.48°.

Rate constant derived is K = 6.14 × 10^{-2} hr.$^{-1}$, and half-life $t_{1/2}$ = 11.3 hr. Two check racemizations gave: K = 5.68 × 10^{-2} hr.$^{-1}$, $t_{1/2}$ = 12.2 hr., and K = 6.34 × 10^{-2} hr.$^{-1}$, $t_{1/2}$ = 10.9 hr.

N-Benzenesulfonyl-N-carboxymethylisopropylmesidine: 0.0 hr., $\alpha^{28}D$ +0.30°; 3.25 hr., $\alpha^{28}D$ +0.23°; 6.0 hr., $\alpha^{28}D$ +0.20°; 9.0 hr., $\alpha^{28}D$ +0.17°; 11.5 hr., $\alpha^{28}D$ +0.15°; 15.0 hr., $\alpha^{28}D$ +0.12°. Rate constant derived is K = 6.10 × 10^{-2} hr.$^{-1}$, and half-life $t_{1/2}$ = 11.3 hr. Two check racemizations gave: K = 6.70 × 10^{-2} hr.$^{-1}$, $t_{1/2}$ = 10.3 hr., and K = 6.74 × 10^{-2} hr.$^{-1}$, $t_{1/2}$ = 10.3 hr.

N-Benzenesulfonyl-N-carboxymethyl-*t*-butylmesidine: 0.0 hr., $\alpha^{28}D$ +1.35°; 0.5 hr., $\alpha^{28}D$ +1.10°; 1.25 hr., $\alpha^{28}D$ +0.76°; 2.25 hr., $\alpha^{28}D$ +0.52°; 3.5 hr., $\alpha^{28}D$ +0.29°; 5.0 hr., $\alpha^{28}D$ +0.17°. Rate constant derived is K +42.2 × 10^{-2} hr.$^{-1}$, $t_{1/2}$ = 1.6 hr.

The average rate constants, half-lives, melting points and specific rotations of the optically active acids are summarized in Table II.

TABLE II

RACEMIZATION OF N-BENZENESULFONYL-N-CARBOXYMETHYL-3-SUBSTITUTED MESIDINES

Substituent	Opt. active acid, m.p., °C.	Rotation in dimethylformamide: Wt., g.	Vol., ml.	$[\alpha]D(l1)$	t, °C.	K[b] av. × 10^3 hr.$^{-1}$	$t_{1/2}$
CH_3[a]	184–186	0.7670	10.0	+ 2.9	30	9.4	7.3
C_2H_5	155–157	1.2021	10.5	−12.5	26	7.18	9.6
n-C_3H_7	148–149	0.9713	15.0	−15.8	27	6.06	11.4
i-C_3H_7	149–150	.0648	2.0	+12.9	24	6.52	10.6
t-C_4H_9	170–171	.0644	2.0	+38.2	28	46.22	1.6[a]

[a] Lit.[3] m.p. 171.5–172.5° (cor.); K = 23.2 × 10^{-2} hr.$^{-1}$, $t_{1/2}$ = 1.49 hr. [b] In some of the previous papers, ref. 1 and 3, the rate constants have been given as k (invers. instead of k (rac.)

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION, OLUSTEE, FLA.[1]]

Air Oxidation of Resin Acids. III. The Photosensitized Oxidation of Neoabietic Acid and the Configurations of the Pine Gum Resin Acids

BY WALTER H. SCHULLER AND RAY V. LAWRENCE

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The photosensitized oxidation of the exo, endo transoid diene, neoabietic acid, was found to yield a crystalline diperoxide; analytical and chemical evidence indicate the structure to be 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid. Pimaric, isopimaric and dehydroabietic acids were found to be unreactive. A transition state is proposed which appears to accommodate many of the known facts regarding the photosensitized oxidation of olefins. Data are cited to suggest the configurations for all asymmetric centers in palustric acid and for the C-13-hydrogen atom in levopimaric acid. The conclusion is drawn that all seven of the major pine gum resin acids contain the same absolute configurations in the "asymmetric backbone chain" (positions 1, 11, 12 and 13) with the exception of the C-13-hydrogen atom in isopimaric acid.

The photosensitized oxidation of levopimaric and palustric acids, two of the seven major resin acids of known structure found in pine gum, has been investigated and the structure of the transannular peroxide obtained in each case has been established.[2–4] At about the same time, it was noted that neoabietic acid (I), a third major resin acid of pine gum, was oxidizable under the same conditions.[5] This reaction has now been investigated in some detail.

The absorption of oxygen on photosensitized oxidation was followed quantitatively and found to be linear with respect to time up to about 1.3 moles of oxygen/mole of neoabietic acid after which the rate progressively decreased to a final value of 1.78 moles of oxygen/mole of resin acid. The reaction was also followed by the change in optical rotation and ultraviolet absorption spectrum (Fig. 1). Suitable blank experiments were carried out which demonstrated that all three elements of air, light and dye were necessary for reac-

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) R. N. Moore and Ray V. Lawrence, *J. Am. Chem. Soc.*, **80**, 1438 (1958).

(3) R. N. Moore and Ray V. Lawrence, *ibid.*, **81**, 458 (1959).

(4) W. H. Schuller, R. N. Moore and Ray V. Lawrence, *ibid.*, **82**, 1734 (1960).

(5) Unpublished observation by Mr. R. N. Moore.

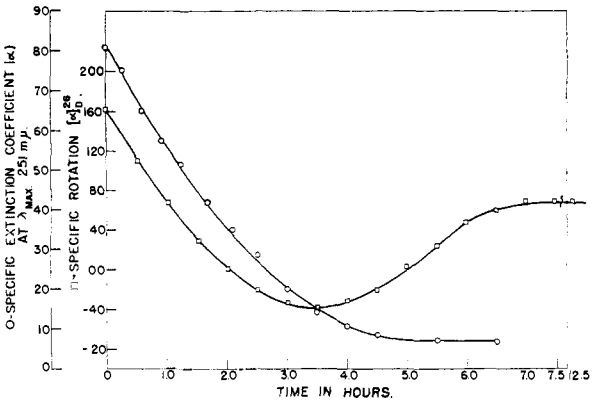
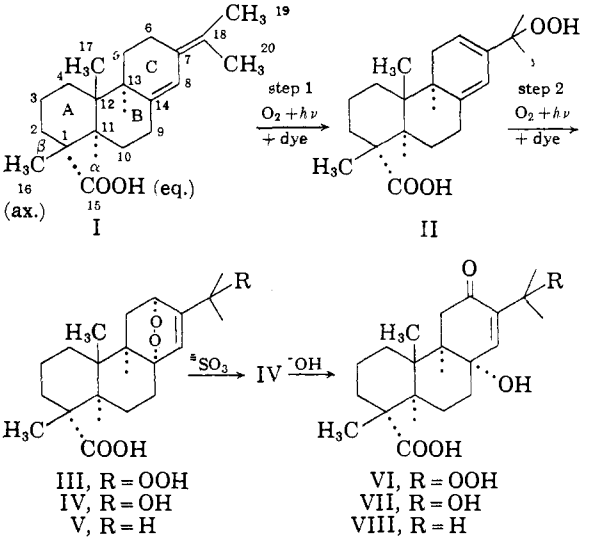


Fig. 1.—The photosensitized oxidation of neoabietic acid at 0.02 *M* resin acid and 50 mg./l. erythrosin B concentration in 95% ethanol.

tion throughout the entire course of the specific rotation change (Fig. 1).

The crystalline product of the oxidation was determined to be a diperoxide. Since this reaction apparently represents the first photosensitized oxidation of a transoid diene (see later), the distribution of the peroxide groups was problematical. The formation of a 14,18-peroxy-$\Delta^{7(8)}$-dihydroabietic acid[6] is impossible on spacial grounds. The reactivity of the olefinic groups in the manner of isolated double bonds was considered possible, although no previous report of this type of behavior could be found. It was then discovered that pimaric, isopimaric and dehydroabietic acids were inert toward photosensitized oxidation. The 18,19-double bond in the first two acids would be expected to be inert as double bond migration is prevented by tetrasubstitution at C-7. The unreactivity of the 8,14-double bond in pimaric and isopimaric acids is apparently not due to a conformational factor at C-13 as the two acids differ[7] only in that they are epimeric at C-13 and C-7. Thus, it would not seem inconsistent that the 8,14-double bond in neoabietic acid might also be unreactive. Attack by oxygen on the 7,18-double bond of neoabietic acid at C-7 would result in a $\Delta^{18(19)}$-peroxide; however, the absence in the diperoxide of infrared bands characteristic of a terminal methylene group disproves this possibility. Attack, however, of oxygen upon C-18 would be expected to yield 18-hydroperoxylevopimaric acid (II) which would be expected to react further in the previously demonstrated fashion of levopimaric acid itself.[2]

Substantiation for the above hypothesis is found in the following data which strongly indicate the diperoxide to be 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (III). (a) Elemental analyses, neutralization equivalent and peroxide analyses indicate the compound to be a diperoxide. (b) The molar rotations of the diperoxide (M_D +346) and of 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (V) (M_D +338) are very similar. The replacement of a hydrogen atom with a hydroperoxide group at C-18 would not be expected to result in a significant difference in rotation due to the non-asymmetry of the C-18 carbon atom in both cases. (c) The diperoxide exhibits no absorption in the 220–320 mμ region; while it, as well as the corresponding cyclohexylamine salt and methyl ester, exhibits a strong alcoholic O–H stretching band in the 3 μ region. (d) (by Dr. Wallace S. Brey, Jr., of the University of Florida). A comparison of the n.m.r. spectra of the methyl esters of 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid and of neoabietic acid diperoxide support the structural assignment of the latter compound as 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid. The presence of a hydroperoxide hydrogen in the diperoxide is confirmed by the presence of a broad low-field peak (which is absent in 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid) as well as the absence in the diperoxide of the resonance of the hydrogen attached to the middle carbon of the isopropyl group. In 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid this resonance appears as a septet (the upper



two components are obscured) because of coupling to the six nearly equivalent hydrogens in the two methyl groups. The resonance is at a lower field than the ring proton resonances because this proton is alpha to a double bond. The observed shift to lower field of the resonances of the methyl hydrogens in the isopropyl group in the diperoxide as compared to those in 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid is considered to be a result of the presence of the hydroperoxide group attached to the same carbon atom as are these methyl groups. The doublet structure of the resonances of the methyls in the isopropyl group in 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid is believed due to the coupling with the hydrogen on the middle carbon atom. This doubling does not appear in the diperoxide. (e) No reaction was observed on treatment of 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid with bisulfite while a similar treatment of the diperoxide resulted in the expected reduction of the hydroperoxide group. A monoperoxide was obtained which was crystallized and characterized as the expected 18-hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (IV) on the basis of elemental analyses;

(6) The ring numbering system used is that suggested by W. Klyne, *J. Chem. Soc.*, 3072 (1953).

(7) A. K. Bose and W. A. Struck, *Chemistry & Industry*, 1628 (1959).

neutralization equivalent; peroxide analysis; M_D +347: and in the corresponding methyl ester, a strong alcoholic O-H stretching band at 2.88 μ with no absorption from 220–320 mμ. (f) The treatment of the diperoxide with base and then with mineral acid results in a change of ultraviolet absorption spectrum at each step which parallels the changes observed on similar treatment of 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid.[3] The products from the diperoxide could not be crystallized; however, the peroxide content and the infrared spectrum of the amorphous product from the base rearrangement were in accord with the expected structure of the compound[3] VI. (g) The treatment of 18-hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid with base and then with a weak acid (acetic) and a strong acid (hydrochloric), respectively, resulted in changes in ultraviolet absorption spectrum at each step which were almost identical to those observed on similar treatment of 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid, presumably due to identical reactions.[3] In addition, the specific rotation of the solution after treatment with base and the complete absence of peroxide were in agreement with the presumed structure of the product[3] VII, although the amorphous solid could not be crystallized. (h) The treatment of the diperoxide with base and then with strong acid resulted in the liberation of acetone. This constitutes good evidence[8-10] for the location of the hydroperoxy group at C-18.

The data expressed in Fig. 1 and the initial linear consumption of oxygen in the photosensitized oxidation of neoabietic acid are consistent with the herein suggested two-step reaction (I → II → III). The shape of the time *vs.* specific rotation curve for the reaction is of interest. The final value of +76° is close to the value of the pure diperoxide ($[\alpha]_D$ +94.4°). The rotation of the proposed intermediate, 18-hydroperoxylevopimaric acid, would be expected to be only slightly less than that of levopimaric acid ($[\alpha]_D$ −278°). If the reaction of neoabietic acid to yield the diperoxide occurred in a single concerted step, one would expect a straight line plot passing from about +160° to +94°. If the reaction proceeded *via* an initial exclusive formation of 18-hydroperoxylevopimaric acid, one would expect two consecutive straight line plots, passing from about +160° to −278° and then from −278° to +94°. The almost bell-shaped nature of the curve actually obtained would suggest that as the intermediate, 18-hydroperoxylevopimaric acid, is formed, it reacts further at roughly the same rate as the starting neoabietic acid. The combination of neoabietic acid with almost two moles of oxygen requires almost twice as long for the reaction to reach completion (7.0 hr.: Fig. 1) as palustric[4] (3.7 hr.) and levopimaric[4] (3.2 hr.) acids under essentially identical conditions. The reaction of exactly 1.0 mole of oxygen with one mole of neoabietic acid was carried out and the specific rotation of the final solution found to be close to the minimum of the plot of time against specific rotation (Fig. 1).

Based on the oxygen uptake of 1.78 moles oxygen/mole neoabietic acid, the yield of 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid would seem to be 89%. It is noteworthy that the final reaction solutions exhibit λ_{max} 241 mμ (α 8.7). Assuming this absorption to be due to abietic acid formed as a side product in the reaction, its yield from the absorption data would be 11% and the calculated value for the specific rotation of the reaction mixture would be +73°, in good agreement with the observed value of +76°. An accumulation of abietic acid rather than its subsequent reaction would be expected.[11]

An examination of models indicates that a "backside or α-attack" of most reagents would seem generally preferred in the resin acid series, as it is in the sterol series,[12] due to the blocking action of the β-methyl groups. This should be especially true for the relatively bulky dye–oxygen intermediate suggested below. The data on photosensitized hydroperoxide formation in the sterol series[13-15] can be interpreted as a prohibited β-attack by the dye–oxygen intermediate as well as a preferential abstraction of axial hydrogen atoms (see below). An α-orientation is thus suggested for the transannular peroxide addend in 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (III) (M_D +346), 18-hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (IV) (M_D +347), 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid[2] (V) (M_D +338), and 7,13-peroxy-$\Delta^{8(14)}$-dihydroabietic acid.[4]

The importance of the photosensitized oxidation of homoannular conjugated dienes led[16] to the attempted application of this reaction to heteroannular conjugated dienes with potential cortisone synthesis as an objective. It was concluded that in the sterol series, a cisoid arrangement of the heteroannular diene system is necessary for reaction and in the single case in which a reaction was observed, a mixture of at least three non-peroxidic and one peroxidic compound was obtained.[16] The photosensitized oxidation of neoabietic acid as reported herein apparently represents the first case of the extension of this reaction to a transoid diene. It is believed that the reactivity is due to the exo, endo nature of the transoid diene system as compared to the endo, endo nature of transoid heteroannular dienes. Preliminary experiments[17] indicate that in the terpene series the exo, endo transoid diene, β-phellandrene, absorbs oxygen very rapidly on photosensitized oxidation to yield a peroxidic product. The independent reaction of one portion of a conjugated diene in a photosensitized oxida-

(8) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

(9) M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, *ibid.*, **17**, 207 (1952).

(10) P. F. Ritchie, T. F. Sanderson and L. F. McBurney, *J. Am. Chem. Soc.*, **75**, 2610 (1953); **76**, 723 (1954).

(11) The authors are currently investigating the photosensitized oxidation of abietic acid. Preliminary results indicate an extremely slow loss of abietic acid and the formation of a non-crystalline product from which insoluble crystalline amine salts are apparently not obtainable.

(12) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 14, 98.

(13) G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957).

(14) G. O. Schenck, K. Gollneck and O.-A. Neumuller, *Ann.*, **603**, 46 (1957); G. O. Schenck and O.-A. Neumuller, *ibid.*, **618**, 194 (1958).

(15) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **81**, 6330 (1959).

(16) D. H. R. Barton and G. F. Laws, *J. Chem. Soc.*, 52 (1954).

(17) J. C. Braun and G. S. Fisher, unpublished results.

tion would also appear to have been observed for the first time and is possibly due to the fact that no loss in conjugation is suffered in the double bond migration of step 1.

The parallelism between the Diels–Alder addition of maleic anhydride, and the photosensitized addition of oxygen to conjugated diene systems[4] would seem to fail in those cases in which the addition of maleic anhydride requires strong heating; *e.g.*, palustric acid[4] and neoabietic acid are inert toward maleic anhydride at room temperature while reacting at 150–200° to yield maleopimaric acid. However, the possibility is being explored (W.H.S. and R.V.L.) that maleic anhydride may add initially in the manner of oxygen on photosensitized oxidation, followed by secondary reactions under the influence of heat to give the stable 6,14-adduct as a final product.[18]

A number of dyes, quinones and diketones were tested for photosensitizing activity with the results as indicated in Table I.

The results suggest that under the conditions employed, the rate-determining step for the over-all transformation apparently does not involve the olefinic reactant for the three resin acids studied to date.

A consideration of the compounds in Groups A and B would seem to indicate that an effective photosensitizer fulfills the following conditions: (a) it contains a grouping which on irradiation is elevated to a diradical in which one or both of the terminal atoms are heteroatoms[4] such as O, N, S or halogen; (b) it contains at least two but preferably three or more unsaturated groupings, such as aromatic rings, positioned so as to stabilize the diradical by resonance; and (c) the geometry of the diradical is such that it can readily add a mole of oxygen to form a 6-membered, cyclic peroxide—which is suggested as being the very reactive, discrete intermediate in the reaction[4]. Such high energy peroxidic intermediates may also be important in systems of possible biological importance, *e.g.*, in the demonstrated catalytic effect of polynuclear orthoquinones and bis-(orthoquinones) on the uptake of oxygen by amino acids.[19]

A possible transition state[20] (IX) for the reaction of the cyclic peroxide intermediate with isolated olefinic groups or reactive transoid dienes such as neoabietic acid (to give the hydroperoxide intermediate) can thus be written, in accord with that postulated for homoannular dienes[4] (A = 1,4-naphthoquinone moiety and B = neoabietic acid moiety). The non-reactivity of heteroannular transoid dienes may thus be ascribed to the bridgehead position of the central or "pivot" carbon atom (C-7 in IX) which results in a prohibitive amount of strain as the transition state is approached. A similar rationale can be used to explain the non-reactivity of certain fused polycyclic non-conjugated olefins, *e.g.*, pimaric and isopimaric acids, and also helps predict the point of hydroperoxidation in a wide variety of reactive monoölefins.[13–15]

The geometry of the proposed transition state IX would require that the entering hydroperoxide group and the departing hydrogen atom must lie on the same side of the molecule and that in addition, an axial hydrogen will almost always involve less strain (will be preferred) in the complex than an equatorial hydrogen. Recent experimental results from these laboratories[21] in connection with the photosensitized oxidation of carvomenthene, and elsewhere in the sterol series,[13–15] are in full accord on these two points and thus support the concerted nature of the hydroperoxidation reaction and a cyclic transition state. The reported[22] formation of preponderantly (about 50%) *trans*-3-methylene-7-hydroperoxy-7-1,5-octadiene (plus 25–30% of the 6-hydroperoxy compound) upon the photo-

TABLE I

TESTING OF COMPOUNDS AS PHOTOSENSITIZERS FOR THE PHOTOSENSITIZED OXIDATION OF RESIN ACIDS

Group A: Compounds of relatively high activity

Compound	Color of the ethanol soln.	Percentage resin acid reacted in 1 hr.; resin acid concn. 0.01 *M*, dye concn. 50 mg./l. Neo[a]	Levo[b]	PA[b]
Rose bengal	Red	53	58	64
Erythrosin B	Red	41	50	54
Methylene blue	Blue	38	46	58
Chlorophyll[c]	Green	34	46	48
Eosin YS	Orange	25	26	26
9,10-Anthraquinone[d]	Essentially colorless	25[e]	..	..
Mercurochrome	Orange	19	..	..
1,4-Naphthoquinone[f]	Very pale yell.	10[g]	..	..
9,10-Phenanthrenequinone[h]	Yellow	6[i] (5)[j]	..	..
Benzil[k]	Colorless	4[l] (6)[j]	..	..

Group B: Compounds of borderline activity[m] (The percentage of neoabietic acid reacted is given in parentheses after the dye)[n] 1,2-naphthoquinone[n] (5); basic fuchsin (5); thymol blue (4); martius yellow (4); *p*-benzoquinone (3); acridine orange (3); fluorescein (2); biebrich scarlet (2); dimethylglyoxime (2); tartrazine (2); azorubin (1); brom phenol blue (1); benzopurpurin 4B (0); gallocyanin (0); crystal violet (0); acid rosolic (0); benzil monoxime (0); 1,2-naphthoquinone-4-sulfonic acid, sodium salt (0); diacetyl (0); brilliant yellow (0); congo red (0); and auramine hydrochloride (0).

[a] The data for neoabietic acid are based on the decrease in α at 251 mμ. [b] The data for levopimaric and palustric acids are calculated from the over-all reaction times reported in ref. 4. [c] A 4% solution in oil obtained from the Keystone Chemurgical Corp. [d] Eastman Kodak sublimed grade. [e] In 3 hr., 54% reacted. [f] Found m.p. 125–126°, lit. m.p. 125–126°. [g] In 2 hr., 20% reacted. [h] Found m.p. 207–208.5°, lit. m.p. 206–207.5°. [i] Solution bleached at 22 min., 0% reacted; 1.0 hr., 6% reacted; 2.0 hr., 11% reacted. [j] Repeat experiment. [k] Found m.p. 95.5°, lit. m.p. 95°. [l] At 22 min., 2% reacted; at 1.0 hr., 4% reacted; at 2.0 hr., 10% reacted. [m] The purity of the last three compounds in Group A would indicate that the relatively low order of activity exhibited can probably be ascribed to the compound in question, while the activity of the compounds at the top of the list in Group B might be due to the possible presence of active impurities. [n] Eastman Kodak, practical grade, lit. m.p. 115–120° dec.

(18) Presented at the Symposium on Diterpenic Resin Acids at the 138th National Meeting of the American Chemical Society, New York, N. Y., September 12–16, 1960.

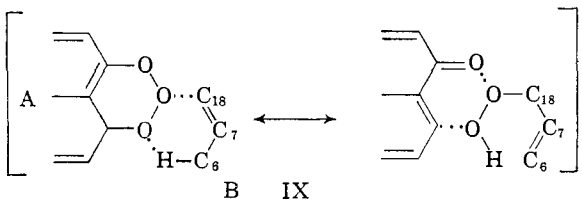
(19) B. Lukowczyk, *J. prakt. Chem.*, **8**, 372 (1959).

(20) W. H. Schuller and R. V. Lawrence, presented at the American Chemical Society, Southeastern Regional Meeting, Richmond, Va., Nov. 6, 1959.

(21) R. L. Kenney and G. S. Fisher, Abstr. of Papers, 138th Meeting Am. Chem. Soc., New York, N. Y., Sept. 11–16, 1960, p. 79-P.

(22) R. L. Kenney and G. S. Fisher, *J. Am. Chem. Soc.*, **81**, 4288 (1959).

sensitized oxidation of myrcene is in accord with the proposed cyclic transition state IX, the removal of a



B IX

hydrogen atom axial with respect to the plane of the 6,7-double bond, and the preferred conformation of myrcene about the 5,6-single bond, in which the conjugated diene system is located in the position furthest away from the dimethyl substituents on C-7.

The similarity of molar rotations[23] of 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (III, M_D +346) and 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (V, M_D +338) would suggest that the two peroxides are identical with respect to their relative configurations about all points of asymmetry. Since in both the photosensitized oxidation of levopimaric and neoabietic acids none of the asymmetric centers would appear to be involved, it would also seem that the relative configurations of these two resin acids are identical at all points. The absolute configurations at all asymmetric centers have been assigned for neoabietic acid by Djerassi.[24] The configurational assignments suggested by Klyne[6] for levopimaric acid are in agreement at all centers but C-13. In connection with the matter of configurational relationships, it is of interest to note that the acid-catalyzed isomerization of levopimaric acid,[25,26] neoabietic acid,[27] palustric acid[28] and abietic acid[25] all give mixtures containing no products other than these resin acids. Chromatographic analysis combined with optical and spectrographic measurements throughout the runs consistently accounted for 99–100% of all compounds present in these terms.[25–28] These results suggest that levopimaric and neoabietic, as well as abietic and palustric acids, are all four identical with respect to their configurations at C-1, C-11, C-12 and C-13. It is not considered feasible that changes in configuration have occurred at C-1 and C-12 during the isomerizations as carbon-to-carbon bond ruptures and resyntheses would necessarily be involved and in essentially quantitative yields. It is also considered unlikely that under the conditions employed,[25] carbonium ion inversions have occurred at C-11 and C-13 and to a quantitative extent at both centers. The formation of a carbonium ion at C-13 would be expected[29] to result in intramolecular, rapid, simultaneous lactone formation at C-13 and migration of the angular methyl group with lactone formation also at C-12. It might be considered as an additional possibility that the isomerization of levopimaric acid yields first palustric acid followed by proton attack at C-13. However, the recent work[28] on the isomerization of palustric acid clearly demonstrates that the isomerization rate of palustric acid is far too slow for this acid to function as the sole intermediate in the conversion of levopimaric acid to abietic and neoabietic acids. Similarly, inspection of the plots of the data from the isomerization of levopimaric acid[25] indicates a simultaneous reaction and not a consecutive one, which precludes palustric acid as the major intermediate. The absolute configurations assigned for abietic acid by Klyne[6] and Bose and Struck,[7] are in agreement with the prior discussion. The following conclusions would therefore appear justified: (a) the absolute configuration of the C-13-hydrogen in levopimaric acid is α(C-13-α-hydrogen) and not β as previously suggested by Klyne[6]; (b) palustric acid,[4] for the first time, can be assigned the absolute configurations C-1-β-methyl, C-11-α-hydrogen and C-12-β-methyl; and (c) the identity of absolute configurations at all asymmetric centers in these four resin acids would appear to be on a relatively firm footing.[30]

The average (M_D +202) molar rotation value for palustric (M_D +216) and dehydroabietic acid (M_D +187) would seem to represent the total contribution of the C-1, C-11 and C-12 centers.[4] Subtracting this value from the molar rotations of levopimaric (M_D − 740 − 202 = −1042) neoabietic (M_D + 480 − 202 = +278) and abietic acids (M_D − 317 − 202 = −519) yields a very large spread in values for the contribution of the optical center at C-13 in each acid. However, the molar rotations of the 7-*gem*-dimethyl C-13-epimeric degradation products[31] of pimaric acid (M_D +52) and isopimaric acid (M_D −20) would indicate that the contribution of the C-13 center is only around 36 units. It is thus suggested that the individual rotational contributions of the asymmetric centers in the "backbone chain" (C-1, C-11, C-12 and C-13) are very much influenced by the varying amounts of strain exerted at the ring juncture positions by the different arrangements of the unsaturation in ring C corresponding to the various resin acids. The acid isomerization of the 7-*gem*-dimethyl C-13-epimeric acids from pimaric and isopimaric acids is reported to yield the same $\Delta^{13(14)}$-acid[31] of M_D +200. This would suggest that pimaric and isopimaric acids have the same configuration about C-1, C-11 and C-12 as palustric and dehydroabietic acids. Ring C in the $\Delta^{13(14)}$-acid of M_D +200 and in palustric and dihydroabietic acids is devoid of asymmetric centers and the $\Delta^{13(14)}$-double bond in the first two cases and the aromatic ring in the last case would be expected to behave similarly with respect to the nature and amount of molecular strain imparted to the asymmetric backbone chain. The absolute configurations of the pertinent asymmetric centers in pimaric and

(23) All values of molar rotation cited in this paper are calculated from values of specific rotations in ethanol.

(24) C. Djerassi, R. Riniker and B. Riniker, *J. Am. Chem. Soc.*, **78**, 6365 (1956).

(25) D. E. Baldwin, V. M. Loeblich and Ray V. Lawrence, *ibid.*, **78**, 2015 (1956).

(26) V. M. Loeblich, D. E. Baldwin, R. T. O'Connor and Ray V. Lawrence, *ibid.*, **77**, 6311 (1955).

(27) V. M. Loeblich and Ray V. Lawrence, *ibid.*, **79**, 1497 (1957).

(28) N. M. Joye and Ray V. Lawrence, *J. Org. Chem.*, **26**, 1024 (1961).

(29) D. H. R. Barton, *Chemistry & Industry*, 638 (1948); E. E. Royals, W. C. Bailey and R. W. Kennedy, *J. Org. Chem.*, **23**, 151 (1958).

(30) M. Tsutsui and E. A. Tsutsui, *Chem. Revs.*, **59**, 1067 (1959).

(31) O. E. Edwards and R. Howe, *Chemistry & Industry*, 537 (1959).

isopimaric acids have been also recently established by Bose and Struck,[7] while Klyne[6] has suggested configurations for dehydroabietic acid. The above relationships confirm the herein suggested configurations for palustric acid, confirm the configurations suggested in the literature and discussed above for the other six resin acids at C-1, C-11 and C-12, and result in the following conclusion[18]: *all seven* resin acids of known structure found in pine gum apparently contain the *same absolute configurations* in the asymmetric backbone chain, *i.e.*, C-1-β-methyl, C-11-α-hydrogen, C-12-β-methyl and C-13-α-hydrogen with the exception of isopimaric acid in which the presence of a C-13-β-hydrogen has been established.[7]

This identity of configurations in the asymmetric backbone chain of all seven resin acids is of considerable biogenetic interest in that it suggests a common precursor in the formation of the pine gum resin acids by the pine tree.

Experimental[32]

Neoabietic Acid (I).—Neoabietic acid was isolated from pine gum[33]; $[\alpha]^{25}D$ +161.6° (*c* 2.5); λ_{max} 251 mμ, α 82.4; m.p. 173–173.5° (sealed capillary under nitrogen); (These physical constants are the highest reported in the literature to date for this resin acid and the high purity of this preparation is supported by the correspondingly high constants reported below for the cyclohexylamine salt of same); λ_{max} (CCl_4) 5.82(s) μ; λ_{max} (Nujol mull)[34] 3.10(s), 5.82(s), 5.93(s) μ.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.4; H, 10.0. Found: C, 79.7, 79.7; H, 10.0, 10.2.

Cyclohexylamine Salt of Neoabietic Acid.—To 3.02 g. of neoabietic acid in 50 ml. of acetone was added 1.27 ml. of cyclohexylamine and the salt collected by filtration; yield 3.93 g. (98%). One recrystallization from aqueous ethanol gave 2.88 g. of needles, $[\alpha]^{27}D$ +110.2° (*c* 0.295), rotation unchanged on further recrystallization; m.p. 211–214° with dec.; λ_{max} 251 mμ, α 62.8; λ_{max} (Nujol mull) 6.14(s) μ, no bands in 3 nor 5.8 μ regions.

Anal. Calcd. for $C_{26}H_{43}NO_2$: C, 77.8; H, 10.8; N, 3.5; neut. equiv., 402. Found: C, 77.5, 77.8; H, 10.7, 10.9; N, 3.5, 3.5; neut. equiv., 402.

Apparatus.—The apparatus used was the same as that described by Moore and Lawrence for the photosensitized oxidation of levopimaric acid.[2] Ordinary fluorescent 15-watt daylight bulbs were used. Test-tube reactors (100-ml. capacity) were used throughout unless stated to the contrary. Erythrosin B was used as the sensitizer at a concentration of 50 mg./l. in 95% ethanol as the solvent unless indicated otherwise. A neoabietic acid concentration of either 0.01 *M* or 0.02 *M* was used in all cases.

Oxygen Absorption.—A solution comprised of 0.242 g. of neoabietic acid and 2.0 mg. of erythrosin B dissolved in 40 ml. of 95% ethanol (0.02 *M* in resin acid and 50 mg./l. in dye) was charged to a 50-ml. erlenmeyer flask fitted to a gas buret. The flask was immersed in a constant temperature bath maintained at 26 ± 0.3°. The system was flushed and filled with oxygen in the dark. Magnetic stirring and irradiation were started simultaneously and the reaction followed by means of periodic readings of the volume of oxygen absorbed. Oxygen absorption was essentially complete in 3 hr. with no further oxygen take-up on 30 min. additional irradiation. The sample absorbed 34.8 ml. of oxygen at 26.0° and 760.8 mm. pressure which corresponds to 1.78 moles of oxygen per mole of neoabietic acid. The final solution exhibited $[\alpha]^{26}D$ +76°.

Effect of Solvent.—The photosensitized oxidation of neoabietic acid was carried out in the following alcohols of indicated dielectric constant. The amount of resin acid reacted after 70 min. was calculated from the decrease in α at 251 mμ and found to be essentially identical in all cases; methanol (33.6), ethanol (25.1) and 2-methylpropanol-2 (10.9).

Effect of Dye Concentration.—Photosensitized oxidations of neoabietic acid were carried out in which the erythrosin B concentration was varied. The reactions were followed by measuring α at 251 mμ periodically. The shape of the curve in all cases was found to be the same. The rate at 500 mg./l. was about 10% greater than at 50 mg./l. while the rate at 50 mg./l. was about 140% greater than at 5.0 mg./l.

Blank Experiments.—No change in α at λ_{max} 251 mμ nor of $[\alpha]D$ was observed after 6.0 hr. of each of the following treatments: aeration in the dark, irradiation with visible light, aeration plus irradiation, contact with erythrosin B in the dark, aeration plus erythrosin B in the dark, and irradiation plus erythrosin B. In the last experiment, the air was first swept out of the ethanol solution with nitrogen and the system sealed. Irradiation resulted only in the bleaching of the dye. Aeration of the bleached solution in the dark regenerated the colored form of the dye.

A second photosensitized oxidation was stopped at the point of minimum specific rotation (see Fig. 1). The tube was wrapped in black paper and aeration only continued for 2.5 hr. with no change in $[\alpha]^tD$ occurring. The reaction mixture was swept with nitrogen and sealed, and irradiation only carried out for 1.0 hr. The solution immediately turned colorless; however, essentially no change in $[\alpha]^tD$ occurred. Simultaneous aeration and irradiation were then continued. The first burst of air regenerated the colored form of the dye and the $[\alpha]^tD$ was observed to rise steadily, finally leveling off in the general range observed for the uninterrupted reaction.

Reaction with 1.0 Mole of Oxygen.—One mole of oxygen/mole of neoabietic acid was added in a photosensitized oxidation carried out in an erlenmeyer flask fitted to a gas buret. The final solution exhibited $[\alpha]^{26}D$ −42°. The residue obtained on evaporating could not be crystallized; λ_{max} (Numol mull) 2.94(s) μ.

18-Hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic Acid Cyclohexylamine Salt.—A solution of 8.16 g. of neoabietic acid and 0.135 g. of erythrosin B (0.01 *M* in resin acid and 50 mg./l. in dye) in 2700 ml. of 95% ethanol was charged to the 40-watt reactor. The reaction was followed by the change in $[\alpha]^tD$ and was well over in 2 hr.; final values $[\alpha]^{26}D$ +76°, λ_{max} 241 mμ (α 8.7). The solution was concd. under reduced pressure to about 100 ml., chilled in an ice-bath, and 3.35 ml. of freshly distilled cyclohexylamine added slowly with stirring and cooling; final *p*H 9. On standing, the crystalline salt slowly appeared. It was collected by filtration, washed thoroughly with pentane and dried over Drierite; yield 8.64 g. (69%), $[\alpha]^{25}D$ +58.8° (*c* 0.478). The salt was dissolved in 95% ethanol (containing a few drops of cyclohexylamine) at about 50 to 60° and on cooling a first crop, 2.83 g., and a second crop, 2.33 g., were obtained, both of the same rotation; $[\alpha]^{25}D$ +72.2° (*c* 0.476), rotation unchanged on further recrystallization. The pure salt exhibited m.p. 181–181.5° with dec. and evolution of gas; no characteristic absorption from 220–320 mμ; λ_{max} (Nujol mull) 2.95(s), 6.20(s), 8.78(s), no band in 5.8 μ region.

Anal. Calcd. for $C_{26}H_{43}NO_6$: C, 67.1; H, 9.3; N, 3.0; neut. equiv., 466. Found: C, 67.3, 67.3; H, 9.4, 9.4; N, 3.0, 3.0; neut. equiv., 467.

18-Hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic Acid (III).—The cyclohexylamine salt of 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (2.55 g.) was suspended in ether and shaken with dilute aqueous phosphoric acid (1 mole phosphoric acid/1 mole salt). The ether layer required only two water washings to be free of mineral acid. Evaporation of the ether gave 2.03 g. (80%) of the free acid which was crystallized from aqueous methanol, yield 1.77 g. of needles, $[\alpha]^{27}D$ +91.7° (*c* 1.0). Recrystallization from aqueous methanol gave star clusters; yield 0.67 g., $[\alpha]^{27}D$ +94.4° (*c* 1.08), rotation unchanged on further recrystallization; m.p. 176° with dec. and evolution of gas; no characteristic absorption from 220–320 mμ; λ_{max} (Nujol mull) 3.02(s), 5.97(s), 8.81(s), no bands in the 6.05 μ region and no strong bands in the 11 to 12 μ region; λ_{max} ($CHCl_3$) 2.85(s), 5.92(s) μ.

(32) All m.p.'s uncorrected. All specific rotations and ultraviolet absorption spectra in 95% ethanol unless otherwise designated.

(33) V. M. Loeblich and Ray V. Lawrence, *J. Org. Chem.*, **21**, 610 (1956).

(34) H. H. Bruun, *Acta Chem. Scand.*, **11**, 907 (1957).

TABLE II

PEROXIDE ANALYSES[a] OF RELATED COMPOUNDS FOR VARYING REACTION PERIODS WITH REAGENT

Reacn. period in dark, min.	Moles of titratable peroxide/mole of peroxidic cmpd. NeOP[b]	NeOP·CH[c]	LAP[d]	Difference[e] (NeOP - LAP)
5	1.13	1.05	0.43	0.73
10	1.31	1.25	.56	.78
30	1.50	1.44	.68	.82
60	1.49	1.39	.75	.78
240	1.58	1.54	.77	.81

[a] Peroxide analyses *via* the modified Wheeler method.[35] [b] 18-Hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid. [c] Cyclohexylamine salt of 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid. [d] 6,14-Peroxy-$\Delta^{7(8)}$-dihydroabietic acid. [e] The results for NeOP and LAP were plotted as a function of time and the values taken from the plots used in calculating the difference, NeOP-LAP.

Anal. Calcd. for $C_{20}H_{30}O_5$: C, 65.6; H, 8.3; neut. equiv., 366. Found: C, 65.6, 65.6; H, 8.5, 8.6; neut. equiv., 368.

Methyl 18-Hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietate.—The ester was prepared using diazomethane in ether solution. The residue, after solvent stripping, was crystallized from methanol–water; yield 0.48 g. (81%), $[\alpha]^{25}D$ +91.3° (*c* 0.489). Recrystallization from methanol–water gave long needles; yield 0.33 g., $[\alpha]^{29}D$ +91.3° (*c* 0.936), m.p. 147–147.5° with dec. and evolution of gas; no characteristic absorption from 220–320 mμ; peroxide analysis[36] 1.79 moles peroxide/mole of ester; λ_{max} (Nujol mull) 2.97(s), 5.81(s) μ; λ_{max} (CCl_4) 2.83(w), 2.93(m), 5.79(s) μ.

Anal. Calcd. for $C_{21}H_{32}O_6$: C, 66.3; H, 8.5. Found: C, 66.6, 66.6; H, 8.6, 8.5.

Treatment of 18-Hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic Acid with Base.—(a) To 0.50 g. of 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid was added 2.08 ml. of 0.916 *N* sodium hydroxide (1.4/1 base/diperoxide) and diluted to 25.0 ml. with water. The specific rotation dropped rapidly from +94° to +21° in 24 min. with little further change to 75 min., at which time 0.64 ml. of 0.52 *N* acetic acid was added; final *p*H 5. A precipitate formed; weight 0.25 g. (52%), $[\alpha]^{28}D$ +41.9° (*c* 0.989); λ_{max} 234 mμ, α 9.3; peroxide content[36] 0.54 mole peroxide/mole of presumed hydroxy-ketone; λ_{max} 2.95(s), 5.9(s), 6.04(s) μ. The compound could not be crystallized as the acid nor as the methyl ester from the wide variety of solvents tried. (b) To a solution of 0.0732 g. of 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid in 5 ml. of 95% ethanol was added 5 ml. of a 0.40 *M* solution of potassium hydroxide in 95% ethanol (10/1 molar ratio of hydroxide/diperoxide). After standing overnight, 2 ml. of water was added followed by concd. hydrochloric acid to *p*H 1. The solution was refluxed 1.25 hr.; λ_{max} 288 mμ, α 9; no essential change in ultraviolet spectrum on further refluxing for 0.75 hr. The reaction mixture was vacuum dried, the residue dissolved in water, extracted with ether, and the ether evaporated. The residue could not be crystallized.

18-Hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic Acid (IV).—To a solution of 1.13 g. of 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid in 20 ml. of chloroform was added 20 ml. of a 0.5 *M* aqueous sodium phosphate buffer of *p*H 6.0. Sodium metabisulfite (0.29 g.; 1/1 on a stoichiometric basis) was added with continuous stirring under a nitrogen sweep. After 27 min. all the bisulfite had reacted (aqueous layer did not bleach an iodine solution). Another 0.87 g. of sodium metabisulfite was added (400% excess). The next day, the aqueous layer rapidly bleached an iodine solution and the peroxide content[36] of the chloroform layer was 0.77 mole peroxide/mole of 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid charged. The aqueous layer was extracted with chloroform and with ether. The organic layers were concentrated to 5 ml. Ether (15 ml.) was added and cyclohexylamine (0.36 ml.; 1/1) added dropwise. The precipitate was ether washed; yield 1.05 g. (75%), $[\alpha]^{25}D$ +64.3° (*c* 0.552). The salt was recrystallized from 95% ethanol–ether; $[\alpha]^{27}D$ +67° (*c* 0.433); no characteristic absorption from 220–320 mμ; λ_{max} (Nujol mull) 2.87(s), 6.14(s), 8.93(m) μ.

18-Hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid was regenerated from the salt (0.98 g.) with phosphoric acid (see earlier experiment). The yield of crude acid was 0.522 g. (68% from salt), $[\alpha]^{25}D$ +82.3° (*c* 0.32); after several recrystallizations from aqueous methanol, 0.10 g., $[\alpha]^{25}D$ 98.9° (*c* 0.394); m.p. softened at 156° and melted at 161.5° with dec.; peroxide content[36] 0.89 mole peroxide/mole of 18-hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid; λ_{max} (Nujol mull) 2.90(s), 5.88(s), 8.82(s) μ; λ_{max} ($CHCl_3$) 2.75(w), 2.81(m), 2.87(m), 2.96(m), 5.92(s) μ.

Anal. Calcd. for $C_{20}H_{30}O_5$: C, 68.5; H, 8.6; neut. equiv., 350. Found: C, 68.0; H, 8.9; neut. equiv., 351.

Methyl 18-Hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietate. The ester was prepared employing diazomethane in ether. After solvent stripping, the residue was recrystallized from diethyl ether–diamyl ether; yield 0.16 g. (59%), $[\alpha]^{26}D$ +96.2° (*c* 0.266), no change in rotation on further recrystallization from diethyl ether–dibutyl ether. Additional crops of ester raised the total yield to 78%. The pure ester, after drying at 78° and 0.01 mm. pressure over Drierite for 2 hr., exhibited m.p. 169.5–171°, peroxide analysis[36] 0.66 mole peroxide/mole ester, no characteristic absorption from 220–320 mμ; λ_{max} (Nujol mull) 2.88(s), 5.82(s) μ.

Anal. Calcd. for $C_{21}H_{32}O_5$: C, 69.2; H, 8.9. Found: C, 69.3; H, 9.1.

The ester could be sublimed onto a cold finger at about 160–165° and 0.01 mm. without decomposition; sublimate exhibited m.p. 169.5–171°.

Anal. Found: C, 68.9; H, 8.8.

Treatment of 18-Hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic Acid with Base.—(1) Free acid form: To 0.00222 g. of 18-hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid was added 2.2 ml. of 0.0147 *N* sodium hydroxide in 95% ethanol (5/1 hydroxide/peroxide); after 89 hr. at room temperature, $[\alpha]^{26}D$ +27°; λ_{max} 230–231 mμ, α 18.5, essentially no further change on standing. The remainder of the reaction mixture was then analyzed and found to contain essentially no peroxide.[36] Two larger scale runs were made in an attempt to isolate and crystallize the product. Both times, a 75% yield of an amorphous solid was obtained which resisted all attempts at crystallization; $[\alpha]^{26}D$ +30.7° (*c* 0.521); λ_{max} (Nujol mull) 2.98(s), 5.9(s); 6.05 μ (shoulder). The methyl ester and the cyclohexylamine salt were also prepared, but neither could be crystallized.

(2) Methyl ester: (a) A solution of 0.00198 g. of methyl 18-hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietate in 1.27 ml. of freshly prepared 0.0171 *M* sodium hydroxide in 95% ethanol was prepared. After 24 hr. at room temperature λ_{max} 233 mμ, α 17.4, and after 44 hr. α 18.0 and $[\alpha]^{27}D$ +29°. One drop of concd. hydrochloric acid was added (*p*H <1) and the solution refluxed for 1.0 hr.; λ_{max} 287–288 mμ, α 14.8°; essentially no change on refluxing for an additional 1.0 hr. (b) A solution of 0.00236 of methyl 18-hydroxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietate in 1.86 ml. of 0.0140 *N* sodium hydroxide in 95% ethanol was allowed to stand at room temperature for 27 hr. at which time λ_{max} 233 mμ, α 17.6. The solvent was stripped and to the residue was added 1.5 ml. of glacial acetic acid. The resulting solution was refluxed for 10 min. after which λ_{max} 292–293 mμ, α 11.2; essentially no change on refluxing the solution for an additional 20 min.

6,14-Peroxy-$\Delta^{7(8)}$-dihydroabietic Acid (V)[2]: λ_{max} (Nujol mull) 5.93(s), no bands in 3 and 8.8 μ regions; cyclohexylamine salt: λ_{max} (Nujol mull) 6.16(s), no bands in 3, 5.8, nor 8.8 μ regions; methyl ester: λ_{max} (Nujol mull) 5.82(s), no bands in 3 μ region; λ_{max} (CCl_4) 5.8(s), no band in 3 region.

Attempted Sulfite Reduction of 6,14-Peroxy-$\Delta^{7(8)}$-dihydroabietic Acid.—To a solution of 0.201 g. of 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid was added 30 ml. of water and the mixture well stirred; *p*H 4; peroxide content[36] of chloroform layer 0.85 mole peroxide/mole of acid. An equimolar quantity (0.114 g.) of sodium bisulfite was added and the two-phase mixture stirred continuously. At intervals, the solution was analyzed for peroxide content and the *p*H determined. After 24 hr., essentially no change in *p*H nor

(35) G. S. Fisher, J. S. Stinson and L. A. Goldblatt, *J. Am. Chem. Soc.*, **75**, 3675 (1953).

(36) Peroxide analysis via the modified Wheeler method,[35] 1.0 hr. reaction period in the dark.

in peroxide content was found and the aqueous layer was observed to bleach rapidly an iodine solution.

Liberation of an Acetone Fragment from 18-Hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic Acid.—A solution of 0.3164 g. of 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid in 10 ml. of 95% ethanol was charged to a small flask equipped with a nitrogen inlet tube, a gas outlet tube leading to two traps containing a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid, and a side arm closed with a serum stopper. Sodium hydroxide aqueous solution (1.58 ml. of 0.96 *N*; 1.75 NaOH/1 photoperoxide) was injected into the reactor and nitrogen sweeping carried out at room temperature for 50 minutes with no appearance of precipitate in the traps. A solution of 0.493 g. of trichloroacetic acid in 1.0 ml. of water (3.5/1 molar ratio of acid/diperoxide) was injected and the reactor heated to 90° during slow nitrogen sweeping. A very slow distillation with gentle nitrogen sweeping was carried out for 40 minutes. The yellow flaky precipitate in the first trap was collected, washed with 2 *N* hydrochloric acid, and water; yield 0.0424 g. (21%), m.p. 118.5–120.5°.; after recrystallization from 95% ethanol, m.p. 124.5–125°, mixed m.p. with authentic sample 125–125.5°.

Attempted Photosensitized Oxidation of Pimaric, Isopimaric and Dehydroabietic Acids.—In each case, 100 ml. of a 0.02 *M* solution of the pure resin acid in 95% ethanol containing 50 mg./l. of erythrosin B was simultaneously aerated and irradiated for over 12 hr. in a test-tube reactor. No titratable peroxide[36] was found at the end of this time and no change in specific rotation nor in the absorption spectrum from 220–320 mμ was observed. The solutions were stripped to dryness under reduced pressure, the unchanged resin acids recovered in quantitative yields, and identified by m.p. and by the essential identity of their infrared spectra with the infrared spectra of the starting resin acids.

Nuclear Magnetic Resonance Spectra (by Wallace S. Brey, Jr., of the University of Florida).—Hydrogen nuclear magnetic resonance spectra were obtained with a Varian 4300-2 high-resolution spectrometer operating at 56.4 megacycles. Samples were contained in precision bore tubes and a quantity of benzene sufficient to give a peak height equivalent to that of a methyl group in the solute compound was added to the solution as an internal reference. Spectral grade carbon tetrachloride was used as a solvent, except that for the ester of neoabietic acid diperoxide, spectra were also run in which a drop of acetone was added to increase the solubility. This permitted a more accurate determination of the chemical shifts, and to the accuracy that shifts could be measured for the more dilute solution in carbon tetrachloride alone, there was no effect on the spectrum except that the resonance of the hydroperoxide hydrogen was shifted downfield by the presence of the acetone. Chemical shifts were obtained by applying side bonds from a calibrated audio oscillator; the averages of repeated sweeps through the spectrum and side bands were used in the computations. Chemical shifts are expressed as parts per million displacement upfield from the reference.

TABLE III

CHEMICAL SHIFTS

Hydrogen assignment	Me.V[a] (in CCl_4)	Me.III[b] (in CCl_4–acetone)
Hydroperoxide hydrogen	...	−1.7
Vinyl hydrogen	1.54[c]	1.29[d]
Hydrogen on carbon attached to transannular peroxide oxygen	2.86	2.46
Methyl ester hydrogen	3.68	3.67
Hydrogen on central carbon of isopropyl group	4.95 (center of septet)	..
Ring hydrogens, prominent peaks	5.36, 5.55 5.76, 6.02	5.74
Isopropyl methyl hydrogens	6.21, 6.25 (center of doublets)	5.91 5.98
Hydrogens on C-1 methyl	6.22	6.19
Hydrogens on C-17 (angular) methyl	6.76	6.71

[a] Methyl 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietate.[2] [b] Methyl 18-hydroperoxy-6,14-peroxy-$\Delta^{7(8)}$-dihydroabietate. [c] The values[37] for the chemical shifts due to the two vinyl hydrogens in levopimaric acid in saturated CCl_4 solution are 1.46 and 1.86, and are given here for comparison purposes. [d] The value[37] for the chemical shift due to the single vinyl hydrogen in neoabietic acid in saturated CCl_4 solution is 0.82.

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(37) W. S. Brey, Jr., W. H. Schuller and Ray V. Lawrence, unpublished results.

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The Isomerization and Dimerization of Aziridine Derivatives. IV

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The isomerization of 1-aroyl-2-alkylaziridines, 1-aziridinethiocarboxanilide, N,N-diphenyl-1-aziridinecarboxamide, 2,4,6-tris-(1-aziridinyl)-*s*-triazine and 1-aziridinecarboxanilide by nucleophiles such as iodide ion and thiocyanate ion in acetone into 4-alkyl-2-aroyl-2-oxazolines, 2-anilino-2-thiazoline, 2-diphenylamino-2-oxazoline, 2,3,6,7,10,11-hexahydrotrisimidazo-(1,2-a; 1′,2′-c; 1″,2″-e)-*s*-triazine and to 1-phenyl-2-imidazolidinone, respectively, are described. Nucleophiles also bring about dimerization of 1-arylsulfonylaziridines and 1-aziridinecarboxanilide to 1,4-bisarylsulfonylpiperazines and to N,N′-bisphenylcarbamylpiperazine. The isomerizations and dimerizations are of significance since they represent ring openings of aziridine derivatives without the need of the usual acid catalysts. The dimerization of 1-phenylaziridine and 1-*p*-tolylaziridine to the corresponding piperazines in aqueous ethanol containing iodide ion is noted.

Recent studies have shown that iodide ion and thiocyanate ion are effective catalysts for the isomerization of 1-aroylaziridines[2a] and 1-benzimidoylaziridines[2b] into 2-aryl-2-oxazolines and 2-aryl-2-imidazolines, respectively, in solvents such as acetone, 2-propanol or acetonitrile. The isomerizations are of interest since they represent examples of the opening of the aziridine ring by nucleophilic reagents without the need of the usual acid catalysts. Previously, acid catalysts were employed

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(2) (a) H. W. Heine, M. E. Fetter and E. M. Nicholson, *J. Am. Chem. Soc.*, **81**, 2202 (1959); (b) H. W. Heine and H. S. Bender, *J. Org. Chem.*, **25**, 461 (1960).