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PERMANGANATE–PERIODATE OXIDATION

PART VII. THE OXIDATION OF SOME ACYCLIC MONOTERPENES[1]

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ABSTRACT

The reaction of permanganate–periodate with 1-decene and 1-octadecene in aqueous suspension or media containing *tert*-butanol has been studied. C_{10}-compounds are oxidized almost quantitatively with the aqueous reagent. Myrcene, *cis*-ocimene, citronellol, citronellal, citronellic acid, geraniol, nerol, linalool, and linalyl acetate are all oxidized in high yield to the predicted products. These can serve conveniently for chemical identification of the aliphatic terpenes when isolated from mixtures by gas–liquid chromatography. The reaction may also be useful in locating the ^{14}C-label in tracer studies.

INTRODUCTION

Rapid progress in the analysis of essential oils and other complex mixtures of mono- and sesquiterpenes has been made with the advent of gas–liquid chromatography (g.l.c.). However, the chemical identification of such terpenes in milligram amounts has remained very difficult and usually physical data alone must be relied upon for characterization. Also, even the more efficient liquid phases developed (1–6) do not give complete resolution of all terpenes, and therefore a chemical means of identification for overlapping components is very desirable. Thus, the detection of small amounts of β-pinene in oils containing much sabinene was found to be impossible by physical data (7, 8), and many other such overlaps have been encountered by the author in the analysis of conifer leaf oils and other essential oils.

Since many terpenes have olefinic double bonds it was of interest to determine if these could be oxidized to predictable end products by means of the permanganate–periodate reagent. Earlier, we established that this reagent cleaves olefinic double bonds giving characteristic end products in almost quantitative yields (9–11) and this observation, together with the known behavior of oxygenated functional groups in a wide variety of aliphatic compounds towards the reagent (12), permits a reasonable prediction to be made of the mode of reaction of such groups in terpenes. This communication deals with the oxidation of the common aliphatic monoterpenes.

The permanganate–periodate reagent oxidizes isopropylidene groups almost quantitatively to acetone (11) and isopropenyl groups to varying amounts of formaldehyde (10). When commercial samples of citronellol, citronellal, and geraniol were analyzed by this technique it was confirmed that these exist essentially in the isopropylidene form. Chemical evidence for the predominance of this group in the aliphatic terpenes has been obtained by Caldwell and Jones (13, cf. also 14); Barnes *et al.* (15) have shown by means of infrared spectroscopy that in purified acyclic terpenes the isopropenyl form does not exceed 3%. In the present study the formation of acetone was confirmed by the iodoform reaction and that of formaldehyde by reaction with chromotropic acid.

Souček and Dolejš (16) have oxidized (−)-dihydrolavandulol to L(−)-isopropyl succinic acid by means of the permanganate–periodate reagent which is in full agreement with prediction. The isolation of this acid was useful in establishing the absolute configuration of (−)-lavandulol.

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Since most terpenes are only very slightly soluble in water, the reaction of permanganate–periodate was first studied with 1-decene and 1-octadecene in the presence of 10 to 50% *tert*-butanol. This solvent was found to give good results in the oxidation of water-insoluble lipids (17). In subsequent experiments with terpenes it was found that the presence of *tert*-butanol is detrimental to the recovery and analysis of neutral oxidation products. Hence, particular attention has been paid to the reaction of 1-decene and 1-octadecene in aqueous suspension. Since this reaction is heterogeneous (at least in the early stages) two procedures were used. In procedure A aliquots of the olefin were shaken with the reagent in separate flasks. This procedure was also used when 30% or more *tert*-butanol was added since it had been found previously (17) that an insoluble periodate salt may be formed. In procedure B the olefin and oxidant were shaken vigorously until solution appeared to be complete and aliquots were withdrawn after various intervals for back-titration of unconsumed oxidant.

EXPERIMENTAL

Melting points were recorded on a Leitz hotstage microscope. Infrared spectra were recorded either as films between sodium chloride plates or as potassium bromide disks, using a Perkin–Elmer model 21 double-beam spectrophotometer. Analytical g.l.c. runs were carried out with an F & M model 500 (F & M Scientific Corp.) chromatograph having a thermal conductivity detector. The purity of starting materials and the composition of oxidation products were determined on 180 × 0.45 cm o.d. polyethylene glycol (Carbowax 20 M, 15% on Gaschrom P, 60–80 mesh) or Apiezon N (10%) columns. In standard runs temperature-programming from 55° to 210° at 4° per min was employed and the helium flow rate was 103–105 ml per min. The percentage composition was determined by measurement of the area under the peaks (triangulation methods) and no correction factor was employed for compounds of different molecular weight. Relative retention times (r.r.t.) were measured with respect to methyl octanoate. Preparative g.l.c. runs were carried out with an Aerograph model A700 instrument (Wilkins Instrument and Research Inc.). Optical rotations were measured either neat or in chloroform solution (3–5%) at room temperature (23–26 °C).

Purification of Starting Materials

All terpenes except linalool contained more than 1% impurities, most of which were removed by preparative g.l.c. on 2.5 to 5 m × 9 mm o.d. polyethylene glycol columns. In a typical experiment citronellol (73.5%) was injected repeatedly in 50 μl aliquots in 24 min cycles, using temperature-programming (non-linear, voltage regulator setting at 50) from 120° to 180°. The trip switch on the recorder was set to collect the upper two-thirds of the recorded citronellol peak. The purity of the collected material was found to be 98.5% and the identity with citronellol was confirmed by comparison of the infrared spectra and physical constants, including relative retention times (r.r.t.).

Several compounds could not be purified to better than 92–95% by preparative g.l.c. Purification by silver nitrate – silicic acid column chromatography (18) was tried, but only citronellol was purified satisfactorily by this method.

Oxidation Procedure

A. Water-Insoluble Compounds

1-Decene (3.55 mg, 0.025 mmoles) was weighed into a glass-stoppered Erlenmeyer flask (50 ml) and to this was added water and *tert*-butanol (8.0 ml), potassium carbonate (6.7 mg), and stock oxidant solution (2.0 ml). The latter consisted of an aqueous solution of sodium metaperiodate (97.5 mmoles/l) and potassium permanganate (2.5 mmoles/l) (12). The mixture was shaken for the required length of time; unconsumed oxidant was determined by addition of excess 0.1 *N* sodium arsenite solution (10.0 ml) and sodium bicarbonate (1 g) followed by back-titration (after 15 min) with standard iodine solution, using starch indicator (2%) for the end point. The values obtained were calculated as atoms of oxygen per mole of olefin (9, 12) (see Tables I and II).

When 30% or more *tert* butanol was used, an insoluble precipitate formed which reacted with arsenite only on heating (17). When more than the above amount of potassium carbonate was added, this precipitate formed more readily. Additional potassium carbonate is required when more than 1 equiv of acid is formed in the reaction.

B-1. Slightly Water-Soluble Compounds

Citronellol (39.06 mg, 0.25 mmole) was weighed into a 100 ml volumetric flask. Water (60–70 ml), potassium carbonate (67 mg), and stock oxidant solution (20.0 ml) were added and the mixture was shaken vigorously until the initial turbidity had disappeared. The solution was made up to volume and aliquots (10.0 ml) were withdrawn at the desired intervals. The amount of residual oxidant was determined as above.

B-2. Water-Soluble or Highly Reactive Compounds

Highly reactive compounds tend to reduce permanganate faster than the latter is reoxidized by periodate. To prevent this extensive reduction of permanganate, the compound to be oxidized was added to the oxidant (same proportions as above) (12). After mixing, the procedure in B-1 was followed.

Preparative Scale Oxidations

The olefin (1–2 mmoles) was added to the required amounts of water, potassium carbonate, and oxidant, and the mixture was shaken for the optimum length of time. The excess oxidant was reduced with a minimum of sodium bisulfite, and the weakly alkaline solution was extracted with ether to remove neutral products. If necessary, potassium carbonate was added to maintain a pH of 7 to 8. The ethereal solution was dried over anhydrous sodium sulfate and evaporated carefully to a small volume. The residue was analyzed by g.l.c. The aqueous portion was evaporated *in vacuo* (rotary evaporator) to a small volume. The aqueous distillate was used for qualitative acetone determination by the iodoform reaction (11) or for qualitative formaldehyde determination with chromotropic acid (10). The precipitated iodoform was filtered off, washed, and dried. The melting point (119–122°) was undepressed in admixture with authentic iodoform. The residue from the evaporation was completely reduced with bisulfite, acidified, and extracted continuously with ether. The ethereal solution was dried and evaporated to give the crude acidic oxidation products. An aliquot (5 to 10 mg) was methylated either with freshly prepared diazomethane or by the methanol – sulfuric acid method (19), and the derived methyl esters were analyzed by g.l.c. The balance of the acidic product was used for crystallization or preparation of crystalline derivatives.

TABLE I

Oxidant consumed (atoms oxygen per mole) by 1-decene and 1-octadecene at 0, 10, 20, 30, and 50% *tert*-butanol in the reaction mixture and using procedure A (continuous shaking) or procedure B-1 (1 h shaking)

	Time (h)	0%, proc. A	10%, proc. A	10%, proc. B-1	20%, proc. A	20%, proc. B-1	30%, proc. A	50%, proc. A
1-Decene	1	0.57	1.30	0.63	3.30	0.87	3.85	3.8
	3	1.42	2.20	1.25	3.65	1.85	3.90	3.85
	6	1.89	2.78	1.58	3.85	2.10	3.97	4.0
	24	3.65	3.35	1.78	3.90	2.38	4.02	4.1
	48	3.93	3.80	1.95	3.90	2.60	4.05	4.15
	72	3.95	3.90	2.25	3.95	3.05	4.10	4.15
	96	—	—	2.55	—	3.43	—	—
	144	—	—	—	—	4.10	4.10	4.15
1-Octadecene	3	—	0.20		0.15		3.90	4.0
	6	—	0.30		0.45		4.00	4.0
	24	0.30	0.80		2.20		4.00	3.95
	48	0.60	0.80		3.90		4.05	4.05
	72	0.88	0.85		4.10		—	—

1-Decene

The single impurity (5%; possibly 2-decene) could not be removed by preparative g.l.c. or by silver nitrate – silicic acid column chromatography. The rate of oxidation in aqueous suspension and in the presence of 10, 20, 30, and 50% *tert*-butanol was determined by procedure A (see Table I). An aliquot (300 mg) was oxidized in aqueous suspension for 24 h. No neutral product was recovered but the aqueous distillate gave a positive formaldehyde test. The acidic product (328 mg; 96%) showed three peaks on g.l.c. analysis (as methyl esters) with r.r.t. 0.70, 0.99, and 1.69 in 1.5, 5.0, and 93.5% amounts respectively; r.r.t. of methyl heptanoate = 0.71, methyl octanoate = 1.00, and methyl nonoate = 1.69. The derived hydrazide (19) was recrystallized twice from aqueous ethanol; m.p. 92.5–93.5° (undepressed by admixture of authentic *n*-nonanoic hydrazide, m.p. 94–95°).

Anal. Calcd. for $C_9H_{20}N_2O$: C, 62.74; H, 11.70; N, 16.26. Found: C, 62.48; H, 11.51; N, 16.08.

The oxidation was repeated using 20% *tert*-butanol solution. No neutral extract was obtained and the acidic product (96%) contained *n*-heptanoic (2%), *n*-octanoic (8.5%), and *n*-nonanoic (85%) acids as well as several unidentified minor components (g.l.c. analysis of methyl esters).

1-Octadecene

The single impurity (8%, possibly 2-octadecene) could not be removed by g.l.c. or column chromatography. The olefin was oxidized by procedure A and the rate of oxidation in aqueous suspension and media containing *tert*-butanol is shown in Table I. Because of the low solubility, duplicate runs gave values which differed by as much as 0.2 atoms oxygen per mole.

Preparative oxidation (24 h) of 1-octadecene (126.5 mg) in 30% *tert*-butanol gave a neutral extract

(2.8 mg) and a solid acidic fraction (133 mg, 98.5%); m.p. 54–58°. Recrystallization raised the m.p. to 59.7–61.3°; mixed m.p. with *n*-heptadecanoic acid undepressed.

Anal. Calcd. for $C_{17}H_{34}O_2$: C, 75.50; H, 12.67. Found: C, 75.42; H, 12.34.

Analysis by g.l.c. of the methyl esters derived from the total acidic fraction showed 4 peaks with r.r.t. (methyl octanoate = 1.00) 4.72, 5.10, 5.48, and 5.84 in 0.5, 2, 11.5, and 86% amount respectively. The r.r.t. values corresponded to those of the *n*-C_{14}, C_{15}, C_{16}, and C_{17} methyl esters.

TABLE II

Oxidant consumed (atoms oxygen per mole) by aliphatic monoterpenes

Compound	Time, hours								
	1	2	3	6	24	48	72	96	144
Myrcene	7.02	7.47	7.60	8.02	9.30	9.70	10.15	—	—
cis-Ocimene	8.31	8.85	9.57	9.67	10.90	11.15	11.50	—	—
cis-Ocimene*	9.26	9.78	10.18	10.73	11.27	11.55	11.60	—	—
Citronellal	2.74	2.89	2.95	3.02	3.40	3.64	3.70	—	—
Citronellal*	3.42	3.48	3.52	3.54	3.70	3.70	—	—	—
Citronellic acid	2.60	2.78	2.85	2.92	3.04	3.04	—	—	—
Citronellol	3.84	—	3.93	—	3.96	4.00	4.15	4.20	4.30
Geraniol	5.42	5.82	6.07	6.27	6.65	—	—	7.20	—
Nerol	5.67	5.96	6.22	6.44	6.83	7.11	7.29	—	7.53
Linalool	5.88	6.21	6.39	6.62	7.12	—	—	7.83	—
Linalyl acetate	5.52	—	5.78	6.07	6.32	6.44	6.59	—	—

*Mixture containing 10% *tert*-butanol.

Myrcene

Technical grade myrcene was purified by g.l.c. to give a product of 97% purity; n_D^{24} 1.4688, $[\alpha]_D$ +0.25°. The rate of oxidation with the aqueous reagent (procedure B-2) is shown in Table II. Preparative oxidation (150 mg; 48 h) gave acetone (as iodoform), formaldehyde (chromotropic acid color test) and succinic acid (91 mg, 72%); m.p. 185–188.5°. Recrystallization from acetone–chloroform raised the m.p. to 187–189° (undepressed by admixture of authentic succinic acid). Analysis by g.l.c. of the derived methyl esters gave only a single peak with r.r.t. (1.44) of methyl succinate.

cis-Ocimene

The sample, kindly donated by Messrs. International Flavors and Fragrances Inc., Union Beach, N.J., U.S.A., showed four minor impurities (2%) on g.l.c. analysis. The rate of oxidation in water and 10% *tert*-butanol (procedure B-2) is shown in Table II. Preparative oxidation gave acetone and formaldehyde. No ether-soluble acidic product was obtained.

Citronellol

The g.l.c. purified material (see above) had n_D^{23} 1.4552; $[\alpha]_D$ +4.18° (neat) and that obtained by column chromatography n_D^{25} 1.4535; $[\alpha]_D$ +3.52°. The rate of oxidation with the aqueous reagent (procedure B-1) is shown in Table II. Preparative oxidation (156 mg; 6 h) gave a neutral fraction (12 mg), acetone and an acidic extract (142.5 mg, 92.5%), which contained mainly an hydroxy acid (infrared spectrum). Analysis by g.l.c. of the derived methyl esters showed two peaks with r.r.t. 2.03 (4%) (3-methyl adipate = 2.04) and 2.52 (96%). Attempts to purify the expected 6-hydroxy-4-methyl hexanoic acid by distillation or column chromatography failed because of lactone formation and polymerization. The acid was characterized via the methyl ester, $[\alpha]_D$ +4.67° (*c*, 5.0); 3,5-dinitrobenzoate m.p. 145–147°.

Anal. Calcd. for $C_{15}H_{18}N_2O_8$: C, 50.85; H, 5.12; N, 7.91. Found: C, 50.78; H, 5.05; N, 7.75.

When the oxidation was allowed to continue for 4 d the amount of 6-hydroxy-4-methyl hexanoic acid dropped to about 58% and that of 3-methyl adipic acid increased to 28%. In addition at least 9 other acidic oxidation products were recorded in 0.5 to 3% amounts.

Geraniol

The g.l.c. purified material (98%) had n_D^{23} 1.4745 $[\alpha]_D$ −0.20° (neat). The rate of oxidation with the aqueous reagent (procedure B-1) is shown in Table II. Preparative oxidation (160 mg, 24 h) gave no neutral product, acetone and an acidic fraction (106 mg, 88%), n_D^{23} 1.4460, which consisted mainly of levulinic acid (g.l.c. methyl ester r.r.t. = 1.41); phenylhydrazone, m.p. 106.5–108° from benzene and aqueous ethanol (lit. 108° (20)); mixed m.p. undepressed. It is noteworthy that this phenylhydrazone (prepared in ethanolic solution) is in the form of the ethyl ester.

Anal. Calcd. for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.60; H, 7.76; N, 11.94.

Nerol

The g.l.c. purified material (97%) had n_D^{23} 1.4737, $[\alpha]_D$ −0.1°. The rate of oxidation with the aqueous reagent (procedure B-1) is shown in Table II. Preparative oxidation (152 mg, 24 h) gave acetone and levulinic acid (90%); phenylhydrazone m.p. 105–107°.

Linalool

The commercial sample (99%), n_D^{24} 1.4620, $[\alpha]_D$ +0.03° was oxidized as above (see Table II) and acetone and levulinic acid (88%) were identified as the major oxidation products.

Citronellal

The g.l.c. purified compound (96%) n_D^{25} 1.4572 $[\alpha]_D$ +9.39° was oxidized as above (see Table II). Preparative oxidation (308 mg, 48 h) gave acetone and an acidic fraction (270 mg, 90%), but no neutral extract. 3-Methyl adipic acid, m.p. 78–85°, $[\alpha]_D$ +0.1° crystallized from ether–hexane mixture (lit. m.p. 84.5–85° (21)). Purification via the methyl ester did not give a sharp melting compound. Analysis by g.l.c. of the crude methyl esters showed one major peak (95%) with r.r.t. 2.04.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.72; H, 7.74.

Citronellic Acid

The commercial sample was purified via the methyl ester; n_D^{25} 1.4561, $[\alpha]_D$ +3.86°. The free acid was oxidized as above (see Table II). Preparative oxidation (212 mg, 6 h) gave acetone and an acidic fraction (184 mg, 93%) from which 3-methyl adipic acid, m.p. 79–85°, $[\alpha]_D$ +0.2°, was obtained; r.r.t. of derived methyl ester = 2.05.

Linalyl Acetate

The commercial sample (95%) could not be purified further owing to decomposition. The compound was oxidized as above (see Table II). Preparative oxidation (392 mg, 18 h) was carried out with the pH not exceeding 7.5 and yielded a neutral extract (7 mg), acetone, formaldehyde, and an acidic fraction (303.4 mg, 79%). The infrared spectrum of the latter showed it to be an acid containing an acetoxy group (1 250 cm^{-1}, strong).

RESULTS AND DISCUSSION

The rate of reaction of the permanganate–periodate reagent with 1-decene and 1-octadecene in aqueous suspension and media containing 10 to 50% *tert*-butanol is shown in Table I. The oxidation of 1-decene proceeded entirely satisfactorily in aqueous suspension (procedure A) and the assumed product, *n*-nonanoic acid, was isolated in 95% yield.[2] Although the rate of reaction was markedly increased by the addition of *tert*-butanol, no advantage was gained since the yield of *n*-nonanoic acid dropped and measurable amounts of the next lower homologue were formed. With 1-octadecene, at least 20% *tert*-butanol had to be added for a satisfactory rate of oxidation. Under these conditions the yield of the expected acidic oxidation product, *n*-heptadecanoic acid, was 92%.[2] Hence is was concluded that monoterpenes are best oxidized in aqueous suspension but that sesquiterpenes would in all probability require the presence of solvent.

The polyunsaturated monoterpene hydrocarbons myrcene (I) and *cis*-ocimene (IV) were oxidized very rapidly in aqueous suspension (see Table II). Both olefins gave acetone and formaldehyde as neutral products, but only myrcene was oxidized to an isolable acidic product.

Figure 1 shows the various steps of the permanganate–periodate oxidation of myrcene in detail. At pH 7.5 each double bond is hydroxylated by permanganate to a mixture of polyol (II) and isomeric acyloins (e.g. III) (9). These are cleaved by periodate to acetone, succinic semialdehyde, succinic acid, formaldehyde, and formic acid. Acetone and succinic acid are relatively stable towards the reagent (at pH 7.5), but succinic semialdehyde would be oxidized fairly rapidly to succinic acid, formic acid to carbon dioxide, and formaldehyde slowly to formic acid and carbon dioxide (10, 11, 12). Hence the expected products from myrcene would be acetone, formaldehyde, carbon dioxide, and succinic acid, which is in agreement with the experimental results. *cis*-Ocimene (IV) would be expected to yield acetone, formaldehyde, carbon dioxide, and acetic acid, the central fragment (malonic semi- and dialdehyde) being cleaved further (12, 16).

In g.l.c. analysis myrcene overlaps with camphene, sabinene, or β-pinene on non-polar columns, and with 3-carene or α-phellandrene on polar columns (3, 5, 7, 8). Hence the

[2]*Allowing for the impurity being the 2-isomer.*

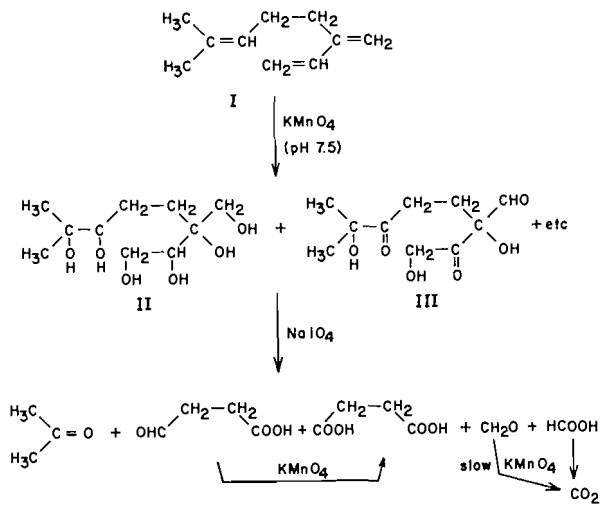
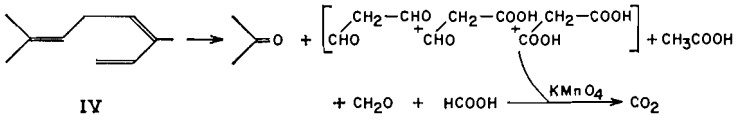
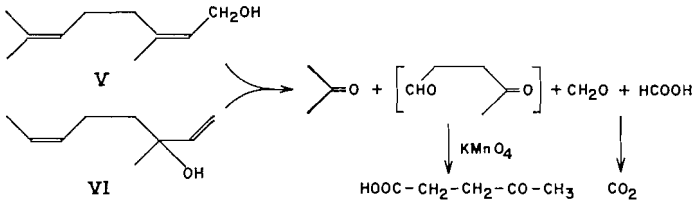


FIG. 1. Permanganate–periodate oxidation of myrcene.

formation of acetone and succinic acid by permanganate–periodate oxidation would confirm the presence of myrcene. Formaldehyde would also be expected from camphene, sabinene, and β-pinene and would have little diagnostic value. *cis*-Ocimene may overlap with limonene, *p*-cymene, 1,8-cineole, and α-terpinene, none of which would be expected to yield acetone in the oxidation. Thus, even qualitative detection of acetone in the oxidation product would have diagnostic value.



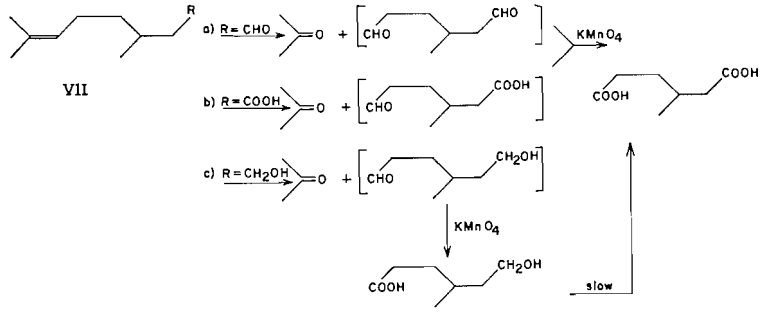
The oxygenated aliphatic monoterpenes citronellol, geraniol, nerol, linalool, citronellal, citronellic acid, and linalyl acetate all reacted at a satisfactory rate with the aqueous reagent (see Table II). The rate of reaction of the dienoid compounds was very rapid and precautions against too rapid reduction of permanganate (procedure B-2) was advisable. The amount of oxidant consumed by each of these compounds was in agreement with expected values and in each instance the presumed products were isolated in good yield. Thus geraniol (V*a*), nerol (V*b*) and linalool (VI) gave acetone and levulinic acid as



characteristic products. Since methyl ketones are relatively stable towards the oxidant (12), levulinic acid may be presumed to be fairly stable too and the duration of oxidation is not critical. It is noteworthy that the rates of oxidation of geraniol and nerol did not differ significantly. Hence it appears that the reagent does not differentiate between *cis*- and *trans*-isomers, unless steric hindrance is involved (12). In g.l.c. analysis geraniol

may overlap with bornyl and sabinyl acetate (non-polar columns), neither of which would be expected to yield acetone or an acidic product. Linalool has much lower retention characteristics and tends to overlap with either fenchone or camphor, neither of which is expected to react with the oxidant.

Citronellal (VII*a*) and citronellic acid (VII*b*) were oxidized smoothly to acetone and 3-methyl adipic acid in 6 to 48 h. When citronellol (VII*c*) was oxidized for 4 d, 3-methyl



adipic acid was also obtained, but side reactions became apparent which may detract from the analytical value. Since it was shown previously (12) that primary alcohols reacted only very slowly with the reagent, citronellol was oxidized only for 6 h when 6-hydroxy-4-methyl hexanoic acid and acetone were obtained in excellent yield. 3-Methyl adipic acid was formed only in amounts of 3–5%. 6-Hydroxy-4-methyl hexanoic acid was not obtained previously from citronellol (22), nor does the acid seem to have been prepared by other means. This acid, together with acetone, could serve conveniently for differentiation from borneol, *p*-methan-8-ol, thujyl alcohol, and myrtenol, with which citronellol may overlap.

Finally, linalyl acetate was oxidized to determine if an allylic acetoxy group would be stable. It was already demonstrated that saturated esters were not attacked by the reagent provided the pH was kept at 7.5 or lower (12). The products after 24 h reaction were acetone, formaldehyde, and 2-acetoxy-2-methyl glutaric acid. Hence, this acetoxy group is unaffected by the reagent.

The above results demonstrate clearly that aliphatic terpenes are oxidized by the permanganate–periodate reagent in high yield to predictable end products. These may serve conveniently in the differentiation from the cyclic monoterpenes which may be present in fractions isolated by g.l.c. In this study millimole amounts of the terpenes were oxidized to permit isolation of crystalline derivatives of the characteristic oxidation products. However, the acidic products were also characterized readily by g.l.c. analysis of the methyl esters and acetone and formaldehyde may be detected colorimetrically in very small amounts. Hence for routine analysis of these terpenes milligram amounts will suffice for characterization by permanganate–periodate oxidation. Because of the high yield of characteristic fission products and little, if any, side reaction the method may also be of considerable value in locating the position of ^{14}C-labelled carbon atoms in studies with radioactive compounds. The study is being continued with cyclic terpenes to determine whether equally satisfactory results can be obtained with this group of compounds.

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