A similar experiment where the initial heating with dilute bicarbonate was for 1 hr. and the solution was allowed to stand with periodate for 38 hr. indicated a periodate uptake of 3.70 ± 0.02 equivalents.

Dihydroapopicrotoxininic Dilactone. (A) By Hydrogenation of Apopicrotoxininic Dilactone.—One gram of apopicrotoxininic dilactone was hydrogenated in the presence of platinum oxide (50 mg.) at atmospheric pressure. Hydrogen absorption slowed down rapidly, because of the separation of solid product upon the catalyst, but began again when the solution was heated to near the b.p.; absorption stopped after the uptake of 80.7 ml. (at 28°). The calculated volume for one equivalent is 79.6 ml. Enough hot acetone to dissolve the dihydrodilactone was added, the catalyst was removed by filtration, and the solvent was evaporated. The residue was recrystallized from acetone–ether; the first crop yield was 0.750 g. (75%). For analysis a sample was recrystallized from acetone–water and again from methanol–water. It formed short needles, m.p. 325°.

Anal. Calcd. for $C_{15}H_{20}O_7$: C, 57.68; H, 6.46. Found: C, 57.41; H, 6.11.

Infrared spectrum (Nujol mull): 3450(s), 3350(s), 2900(vs), 1780(s), 1727(s), 1450(vs), 1372(s), 1326(w), 1304(w), 1295(w), 1277(m), 1258(m), 1242(m), 1212(w), 1179(sh), 1164(s), 1142(w), 1124(w), 1097(m), 1066(m), 1045(s), 1032(w), 1017(s), 998(w), 979(w), 964(m), 939(w), 914(m), 898(m), 870(w), 846(w), 827(w), 794(w), 752(w), 734(w), 721(w).

The acetate was prepared with excess acetic anhydride and pyridine, as given in the other examples. It was recrystallized from ethanol and formed leaflets, m.p. 330–331° dec. Because the calculated figures are so close, it is unfortunately not possible to distinguish between a mono- or diacetate from the analysis.

Anal. Calcd. for $C_{17}H_{22}O_8$ (monoacetate): C, 57.62; H, 6.26. Calcd. for $C_{19}H_{24}O_9$ (diacetate): C, 57.57; H, 6.10. Found: C, 57.33; H, 6.18.

Infrared spectrum: 3412(m), 2967(w), 1795(vs), 1748(vs), 1723(vs), 1468(w), 1431(w), 1377(m), 1368(m), 1314(w), 1261(vs), 1235(vs), 1220(sh), 1185(w), 1152(w), 1142(m), 1106(w), 1098(m), 1062(m), 1031(s), 1007(w), 921(m), 867(w), 852(w), 826(w).

Dihydroapopicrotoxininic Dilactone. (B) Isolation from Dihydro-α-picrotoxininic Acid Mother Liquor.—α-Picrotoxininic acid (10.3 g.) dissolved in 350 ml. of acetic acid containing 1.0 ml. of concentrated hydrochloric acid was hydrogenated in the presence of platinum oxide at atmospheric pressure. The required volume (800 ml.) of hydrogen was absorbed in about 2 hr. The solution was heated until clear, the catalyst was removed by filtration and the filtrate evaporated under reduced pressure. The residue was recrystallized from aqueous acetic acid; the yield of crystalline dihydro-α-picrotoxininic acid was highly variable but was usually in the neighborhood of 3 to 5 g., even though upon occasion none at all could be isolated. The mother liquor, from which it was usually not possible to recover additional dihydro-α-picrotoxininic acid, a sirup being obtained, was set aside. In one run, when the sirup had aged nearly four months, long needles of a sparingly soluble neutral compound separated, which upon recrystallization from ethanol and comparison with mixed m.p. and infrared spectra was found to be identical with the dihydroapopicrotoxininic dilactone prepared by method A.

Bromoapopicrotoxininic Dilactone.—A solution (8.17 ml.) of bromine in acetic acid containing 30.0 mg. of bromine per ml. was added to 475 mg. of apopicrotoxininic dilactone. The suspension was stirred and heated rapidly to 100°; the bromine was decolorized in several minutes. The suspension was cooled and centrifuged immediately. The solid obtained was washed three times with 4-ml. portions of petroleum ether. It weighed 144 mg. (24%) after it was dried *in vacuo* at 25°. The solid was recrystallized for analysis from acetone–petroleum ether; it gave dec. 228–230°.

Anal. Calcd. for $C_{15}H_{17}O_7Br$: C, 46.29; H, 4.41; Br, 20.53. Found: C, 46.06; H, 4.59; Br, 21.67.

Infrared spectrum: 3448(s), 3356(s), 3257(s), 2976(w), 2933(w), 1792(vs), 1739(vs), 1647(vw), 1453(m), 1414(m), 1377(w), 1355(m), 1316(sh), 1304(w), 1280(m), 1267(m), 1241(m), 1222(sh), 1212(m), 1189(m), 1161(s), 1117(m), 1100(m), 1085(m), 1071(m), 1056(w), 1043(m), 1017(s), 1000(m), 986(w), 968(w), 943(w), 928(sh), 923(m), 913(w), 895(w), 856(w), 797(w), 713(w), 705(w), 675(w).

WALTHAM, MASS.

[CONTRIBUTION NO. 1390 FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Chromate Esters. III. Mechanism of Oxidation of 2-Methylfenchol and 1-Methyl-α-fenchene[1]

BY HAROLD H. ZEISS[2] AND FRANCES R. ZWANZIG

RECEIVED AUGUST 24, 1956

Kinetic and ultraviolet evidence are combined with product analysis to show that chromic anhydride oxidation of 2-methylfenchol in acetic acid involves the formation of chromate ester and that the oxidation of the dehydration products of 2-methylfenchyl alcohol, 1-methylcamphene and 1-methyl-α-fenchene, does not, although both reactions lead to the same products. Oxidation of hitherto unknown pure 1-methyl-α-fenchene, obtained by pyrolysis of camphane-2-carbinyl acetate, gives camphor containing little of the rearranged ketonic product, α-fenchone. It is proposed that the oxidation of 2-methylfenchol and 1-methyl-α-fenchene by hexavalent chromium proceeds through a tetravalent chromium intermediate.

In the preceding papers of this series[3] the preparation and reactions of tertiary chromate esters have been discussed, and the proposal of a common oxidation intermediate in the chromic acid oxidation of a tertiary alcohol and its corresponding olefin was made. This hypothesis was based on the experimental fact that 2-methylfenchol and the mixture of its dehydration products, 1-methylcamphene and 1-methyl-α-fenchene, were oxidized in acetic acid to the same products, *i.e.*, camphor, fenchone and a mixture of C_{12}-acids. We wish now to present further evidence for this postulate and for the identity of the oxidation intermediate.

The rate of decomposition of di-2-methylfenchyl chromate (II) was measured in absolute methanol at 25 and at 50° and in 80% aqueous methanol, anhydrous acetic acid and 90% acetic acid at 25°. In all cases first-order kinetic results were obtained (Table I). Regardless of solvent the ultraviolet spectrum of the ester exhibited two distinct maxima, one at 287 mμ and the other at 393 mμ; and strictly comparable rate constants were obtained from data (decrease in optical density) taken at

[1] This work was supported in part by Contract No. DA-19-059-ORD-1494 between the Office of Ordnance Research, U. S. Army, and Yale University. Taken from the doctoral dissertation of F. R. Zwanzig, Yale University, 1955, and published in part as a Communication, *Chemistry & Industry*, 545 (1956).

[2] Monsanto Chemical Co., Dayton 7, Ohio.

[3] (a) Paper I, THIS JOURNAL, **78**, 1694 (1956); (b) paper II, **78**, 3182 (1956).

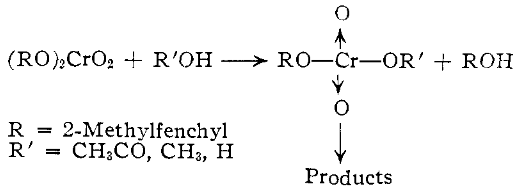
either wave length. The first-order decomposition of the chromate in methanol ($\Delta H^{\neq}$ 23 kcal./mole) gives unrearranged 2-methylfenchol (I) a mixture of 1-methylcamphene (III) and 1-methyl-α-fenchene (IV) and formaldehyde.[3b] The addition of water to solvent methanol increases the rate of decomposition of II by a factor of 5. In acetic acid II decomposes to a mixture of camphor, fenchone, the C_{12}-acids and an unidentified carbonyl substance. The rate of this oxidation, not significantly changed either by the addition of water or by the presence of small amounts of I, is 5×10^3 times faster than that of the reaction in methanol.

TABLE I

RATE OF DECOMPOSITION OF DI-2-METHYLFENCHYL CHROMATE (II)

Solvent	T, °C.	k_1, sec.$^{-1}$
CH_3OH	25.00 ± 0.01	7.54×10^{-7}
CH_3OH	$50.00 \pm .10$	1.29×10^{-5}
80% CH_3OH-H_2O	$25.00 \pm .01$	4.14×10^{-6}
CH_3COOH	$24.95 \pm .04$	3.63×10^{-3}
CH_3COOH + I	$25.10 \pm .10$	3.39×10^{-3}
90% CH_3COOH-H_2O	$24.98 \pm .03$	3.88×10^{-3}

The first-order decomposition of II in acetic acid or methanol reveals that the only other species participating in the rate-determining step is solvent. Since the ultraviolet data do not permit differentiation between chromate mono- or diesters, for it is probable that the two substances have similar or indistinguishable spectra, the hexavalent chromium absorption measured here may be the sum of that contained in the two types of esters. However, the high heat of activation (23 kcal.) would indicate that hydrolysis or transesterification is not the rate-determining step, since ΔH values of 14–18 kcal./mole are obtained for acid-catalyzed hydrolyses, the lower values being those for esters of strong acids.[4] This reasoning is further supported by the fact that the rate of decomposition of II is unchanged by the addition of I, which should cause it to be slower if the rate-determining step involved an esterification equilibrium. It is concluded, therefore, that the rate step in the decomposition of chromate ester is its reduction.



$$(RO)_2CrO_2 + R'OH \longrightarrow RO\text{—}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{Cr}}\text{—}OR' + ROH \downarrow \text{Products}$$

R = 2-Methylfenchyl
R′ = CH_3CO, CH_3, H

Transesterification to give a mixed ester in methanol and transacetylation to ester anhydride in acetic acid is shown indirectly by the isolation of unrearranged 2-methylfenchol I from the decomposition of II in both of these solvents. The existence of mixed and anhydride esters as actual, reactive intermediates is supported too by the kinetic data. On the basis of the dependence of rate of acid-catalyzed solvolyses on the acidity of the solvent, the magnitude of the rates of formation and decomposition of the intermediates in the present examples should be in the order of $CH_3OH <$ aq. $CH_3OH << CH_3COOH <$ aq. CH_3COOH. In Table I the order is $CH_3OH <$ 80% aq. $CH_3OH << CH_3COOH =$ 90% CH_3COOH.

In summation, the first step in the decomposition of II is a non-rate-determining solvolysis of II with the formation of mixed ester or ester anhydride, these intermediates being analytically indistinguishable from the diester. The nature of the solvent fixes the concentration of the active intermediate which is reduced in the rate-determining step. These data, however, yield no information about the mechanism of the latter step.

The rate of oxidation of 2-methylfenchol (I) by chromic anhydride in acetic acid was measured next. The ultraviolet spectrum of I in the presence of chromic anhydride was the *same* as that of II in acetic acid, although the intensity of its equimolar solutions was less. During this reaction the concentration of the ester, the only substance observable spectrophotometrically, first increased by a small increment and then decreased by an apparent first-order reaction. The rate of this reaction, for which a first-order rate constant, $k_1^{25} = 2.06 \times 10^{-4}$, could be calculated over intervals of about 1000 seconds, increased over long periods of time (1.5 hr.) from one-tenth to one-half the rate obtained from the decomposition of II. Thus, the formation of a chromate ester, consisting possibly of little or no diester, during the oxidation of I is verified by the ultraviolet spectrum of the reaction mixture which exhibits the qualitative features of the ester (393 mμ) rather than those of chromic anhydride in acetic acid (270, 322, 347 mμ). These results are interpreted to mean that the esterification process is not complete and that a significant quantity of I remains; hence the concentration of active intermediate is lower than in the solution of II in acetic acid. Incomplete esterification is also demonstrated by the consistently low yields of II (50%) obtained during its synthesis, even in the presence of excess I with chromic anhydride and also by observations made during the course of the kinetic runs. An increase in the concentration of ester occurred during the first 400 seconds of reaction, showing that establishment of equilibrium is by no means instantaneous. Measurement of the rate of the decomposition reaction was complicated by the continuing production of ester in this instance. If it be assumed that esterification of I, occurring concurrently with the decomposition of ester as it is formed, is slower than the more rapid formation of ester anhydride from II and acetic acid, then the slower rate of oxidation of alcohol I as compared to the decomposition of II can be understood. However, this information, while establishing the presence of chromate ester during the oxidation of I, does not contribute to an understanding of the mechanism of its decomposition.

A mixture of the exocyclic olefins 1-methylcamphene (III) and 1-methyl-α-fenchene (IV) obtained from the dehydration of 2-methylfenchol (I), and similar to the mixture produced in the solvolysis of II in methanol, acetic acid, acetonitrile or carbon tetrachloride,[3b] was oxidized in acetic acid with chromic anhydride to the same products iso-

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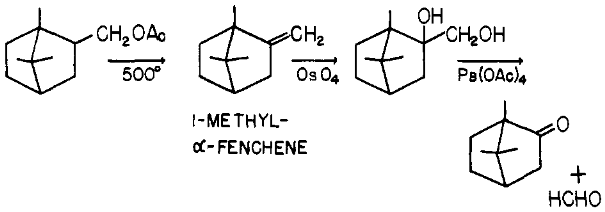
[4] E. W. Timm and C. N. Hinshelwood, *J. Chem. Soc.*, 862 (1938).

lated either from the oxidation of I or the decomposition of II. Therefore, while I and olefin may pass through a common intermediate in the course of reaction with chromic anhydride, this intermediate is not olefin or the diester.

Returning to the consideration of monochromate ester as the intermediate in the oxidation of olefins III–IV, it is apparent that, if this ester is formed in the rate-determining process, an electron deficiency would develop at the tertiary C-2 atom during this step and would create a favorable condition for rearrangement of the bicyclic structure. Although rearrangement has been shown to occur in the course of the oxidation of I and the decomposition of II,[3b] it is not known with certainty whether it occurs before, during or after the oxidation step. In order to cast new light on this point, the synthesis of pure 1-methyl-α-fenchene was undertaken. It seemed desirable not only to examine the products arising from the oxidation of IV for rearrangement but also to obtain kinetic data on the olefin itself.

Attempts to prepare 1-methyl-α-fenchene (IV) either by a Hofmann elimination of the quaternary iodide of N-dimethylcamphane-2-carbinylamine, pyrolysis of camphane-2-carbinyl xanthate, dehydrohalogenation of camphane-2-carbinyl chloride or by decomposition of camphane-2-carbinyl-N-nitrosoacetamide failed. Success came only by way of the vapor phase pyrolysis of camphane-2-carbinyl acetate (V) after the procedure of Bailey and Rosenberg.[5] The structure of IV was established by oxidation of IV with osmium tetroxide to the glycol VI which, on lead tetraacetate cleavage, yielded only camphor and formaldehyde.

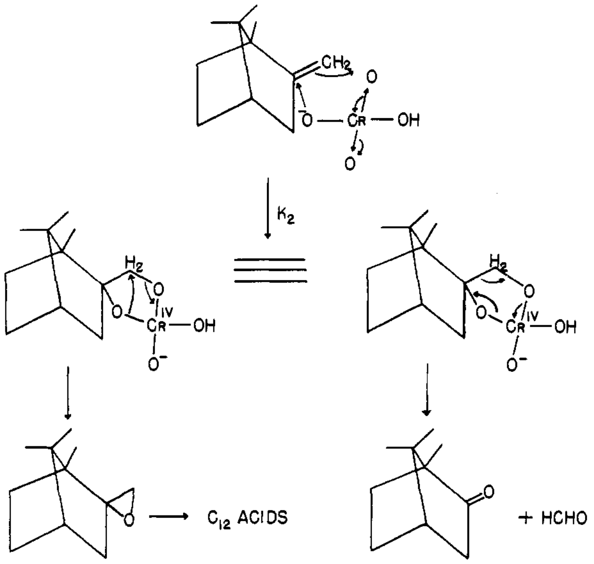


V IV VI

The oxidation of IV was found to proceed as expected by second-order kinetics, the rate, $k_2^{25} = 5.68 \times 10^{-5}$ l./mole-sec., being one-half that of the mixture III–IV. An examination of the products revealed that camphor was the major ketonic product containing about 6% fenchone (infrared spectral comparison with synthetic mixtures) and another unidentified carbonyl fraction. This result is consistent with the isolation of α-fenchocamphorone by Treibs and Schmidt[6] as the ketonic product from the chromic acid oxidation of α-fenchene in acetic anhydride. The acidic fraction from the present oxidation resembled camphane-2-carboxylic acid. However, comparison of their spectra allowed the presumption that the former consisted of a mixture of diastereoisomers. The fact that so little rearrangement occurred in the formation of the ketonic product is considered to render a monochromate ester an unlikely oxidation intermediate. Furthermore, there is no *a priori* reason to believe that monochromate esters decompose so fast as to be unobservable spectrophotometrically.

A mechanism for the oxidation of 1-methyl-α-fenchene (IV) which is consistent with the kinetic, product and spectral data is one which involves *oxidative addition* of chromate ion to the double bond in the rate-determining step. The tetravalent chromium ester,[7] being the true oxidation intermediate, may cleave in one direction to give camphor or in the other to give the epoxide, a further intermediate isolated by Hickinbottom, *et al.*,[8] from the chromic acid oxidation of camphene and other olefins and shown to give product mixtures. The mechanism also permits the formation of glycol by hydrolysis of the tetravalent chromium intermediate without rearrangement in agreement with Hickinbottom's experimental results and conclusions.

The oxidation of 2-methylfenchol (I) and the decomposition of II can proceed through the same tetravalent chromium intermediate preceded by rearrangement. While aliphatic tertiary chromate esters are solvolyzed by almost exclusive chromium–oxygen bond cleavage,[3a] II, in which the chromium atom is buried in its surrounding structural cage gives some methyl ether in the same solvent by carbon–oxygen bond fission.[3b] This is considered to signify that the ester anhydride formed from chromate ester and acetic acid may also rearrange to the bornyl structure prior to closure to the cyclic ester and chromium reduction. These tetravalent chromium esters may then decompose to a mixture of fenchone and camphor and to a mixture of epoxides which in turn lead to the acid mixtures obtained.



Our proposal of tetravalent chromium ester in the oxidation of olefins is analogous to that sug-

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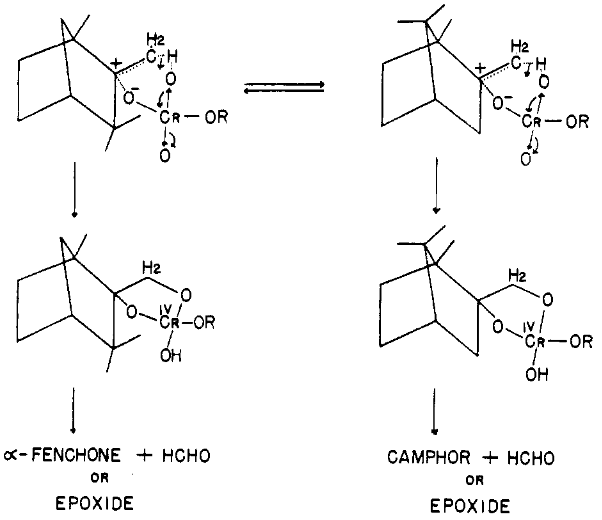
(5) W. J. Bailey and J. Rosenberg, THIS JOURNAL, **77**, 73 (1955).

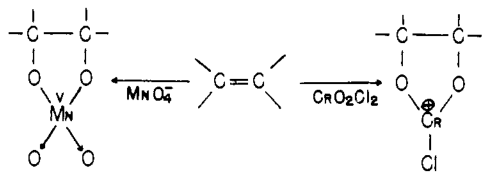
(6) W. Treibs and H. Schmidt, *Ber.*, **61**, 459 (1928).

(7) This intermediate was suggested by Professor F. H. Westheimer of Harvard University as a likely possibility during a discussion prior to a knowledge of the results now reported.

(8) A. Byers and W. J. Hickenbottom, *J. Chem. Soc.*, 1334 (1948); W. J. Hickinbottom and D. G. M. Wood, *ibid.*, 1600 (1951); 1906 (1953); W. J. Hickinbottom, D. Peters and D. G. M. Wood, *ibid.*, 1360 (1955).

gested by Böeseken[9] and by Drummond and Waters[10] for the oxidation of olefins by permanganate in which the oxidative addition of permanganate ion to the double bond results in a Mn^V cyclic ester. Similarly, Cristol and Eilar[11] have also written such a "complex" as one of the possibilities for the addition of chromyl chloride to olefins.





Experimental[12]

Reagents.—**Di-2-methylfenchyl chromate** was prepared according to the procedure described earlier.[3b] Samples of the ester were recrystallized from acetone prior to use, m.p. 108–109°. **2-Methylfenchol** was obtained from the reduction of the chromate diester by lithium aluminum hydride,[3b] m.p. 59–60°. The mixture of **1-methyl-α-fenchene and 1-methylcamphene** was isolated from the dehydration of 2-methylfenchol with fused potassium hydrogen sulfate.[3b] Absolute **acetic acid** (% H_2O, 0.875) was prepared from glacial acetic acid by adding the stoichiometric quantity of acetic anhydride.[13] This was refluxed for 10 hr. and then distilled between 119–120° into an addition funnel, m.p. 16.33° (% H_2O, 0.135). This acid did not reduce chromic anhydride over a period of 3 days. Absolute **methanol** was prepared over magnesium.[14] **Chromic anhydride** was twice recrystallized from water.

1-Methyl-α-fenchene.—α-Pinene (Matheson, Coleman and Bell), 94 g., redistilled, b.p. 153–154°, n^{25}_D 1.4630, $[\alpha]^{25}_D$ +19.15° (neat, α 16.35°), infrared spectrum superimposable on that of an authentic sample[15] was treated with 25 g. of dry hydrogen chloride at 0° in 100 ml. of chloroform.[16] After neutralization with potassium carbonate and steam distillation, the 700 ml. of distillate was extracted with chloroform. **Bornyl chloride** remaining after removal of solvent was crystallized from ethanol: 48.6 g. (41%), m.p. 125–126°, $[\alpha]_D$ +12.3° (α 1.28°, *c* 10.41).

To methylmagnesium iodide prepared from 14 ml. of methyl iodide and 11.2 g. of magnesium in 200 ml. of ether under nitrogen was added 40.2 g. of bornyl chloride.[17] This bornylmagnesium iodide was then carbonated at −15° until Gilman's Grignard test was negative. After hydrolysis with 500 ml. of cold 25% sulfuric acid, the ether layer was washed with 10% sodium bisulfite and extracted with 10% sodium hydroxide. **Camphane-2-carboxylic acid** was precipitated with concentrated hydrochloric acid, collected on a filter and dried over phosphorus pentoxide at 1 mm.: 15 g. (35%), m.p. 67.5–70°, infrared spectrum superimposable on the acid obtained by permanganate oxidation of camphane-2-carbinol.[18]

Camphane-2-carboxylic acid, 25.2 g., in 300 ml. of ether was added to 15.0 g. of lithium aluminum hydride in 500 ml. of the same solvent, and the mixed solution was refluxed for 3.5 days. After treatment with several ml. of water, the ether solution was filtered and dried over magnesium sulfate. Removal of ether at the steam-bath left camphane-2-carbinol which sublimed at 50° (1 mm.): 19.7 g. (85%), m.p. 77.5–79°, infrared spectrum superimposable on that of carbinol prepared by reaction between bornylmagnesium chloride and formaldehyde.[19]

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.12; H, 11.66.

Camphane-2-carbinol, 19.1 g., was acetylated by reaction with 100 ml. of acetic anhydride and 1 drop of pyridine at 60° for 10 hr. and 80–90° for 5 hr. Water was added to the refluxing solution and the acetate was then extracted with pentane, chromatographed on a column of alumina and developed with 10% benzene–pentane. Pure **camphane-2-carbinyl acetate** was distilled between 90–92° (1.5 mm.): 16.7 g. (68%), n^{26}_D 1.4672, infrared spectrum exhibited ester and acetate absorption at 5.79 and 8.03 μ, respectively. Saponification of the ester in 4% methanolic potassium hydroxide regenerated the original carbinol.

Pyrolysis of camphane-2-carbinyl acetate was carried out in a 13 mm. i.d. Vycor tube mounted in a 6″ Sargent electric furnace. The tube was connected at one end through two Dry Ice–acetone traps to a vacuum pump and at the other through a right-angle bend and a $^{14}/_{35}$ quartz joint to a distillation flask in an oil-bath. In a typical run 5.6 g. of the acetate was distilled through the pyrolysis tube, maintained at 560°, from a bath at 100 ± 10° (0.2–0.8 mm.) in the course of one day. The contents of the traps were washed out with pentane and water and the acetic acid present was titrated with base (25%). The layers were separated and the pentane solution was chromatographed on alumina. All fractions giving positive tetranitromethane tests were combined, the solvent removed and the olefin sublimed at room temperature at 1 mm.: 780 mg. (77% based on the acetic acid titer). Of this, 180 mg. of **1-methyl-α-fenchene** was isolated as a white solid, m.p. 62.5–64°, whose infrared spectrum showed olefinic absorption at 6.01 μ, vinyl olefin at 3.26 μ and exocyclic methylene at 11.40 μ (very strong). Spectra of all samples, solid or liquid (traces of pentane), were superimposable.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.96; H, 11.64.

1-Methyl-2-hydroxy-2-camphanylcarbinol.—Osmium tetroxide (1.0 g.) was added to 615 mg. of 1-methyl-α-fenchene in 20 ml. of ether. After 4 days at room temperature the solution was evaporated to dryness and the black residue, after dissolution in 25 ml. of ethanol, was treated with 7 ml. of 2 *N* sodium hydroxide and 5 ml. of 37% formaldehyde. Most of the osmium which had precipitated overnight was removed by centrifugation. This solution was then diluted with water and extracted with ether. After drying, the solvent was removed and the glycol (350 mg.) was sublimed from the black residue at 70–90° (1 mm.). Pure 1-methyl-2-hydroxy-2-camphanylcarbinol was obtained after 3 resublimations: 76–77° (1 mm.), m.p. 155–165°; 70–75° (1 mm.), m.p. 158–165°; 100–105° (760 mm.), m.p. 175–178°.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.76; H, 10.89.

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(9) J. Böeseken, *Rec. trav. chim.*, **41**, 199 (1922).

(10) A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 435 (1953).

(11) S. J. Cristol and K. R. Eilar, THIS JOURNAL, **72**, 4355 (1950).

(12) All melting points are corrected and boiling points are uncorrected. Infrared measurements were made in one molar solutions in chloroform. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(13) S. Winstein, C. Hanson and E. Grunwald, THIS JOURNAL, **70**, 815 (1948).

(14) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 360.

(15) American Petroleum Institute Project No. 44, p. 566.

(16) O. Wallach, *Ann.*, **258**, 344 (1890).

(17) G. Vavon and C. Riviere, *Bull. soc. chim.*, (v) **10**, 460 (1943).

(18) R. Bousset and M. Vaugin, *ibid.*, (iv) **47**, 986 (1930).

(19) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 188.

The glycol (247 mg.) in 5 ml. of acetic acid was cleaved with 659 mg. of lead tetraacetate in small portions over a 30-minute period. After stirring for 13 hr. and then hydrolyzing by the addition of 15 g. of ice, the aqueous solution was extracted with pentane, and this latter solution was washed with 5% sodium carbonate and dried over magnesium sulfate. Removal of solvent left a solid residue (no trace of the liquid α-fenchone) which was sublimed at room temperature (1 mm.), 93 mg. This was resublimed at 35° (1 mm.), m.p. 174–176°, and its infrared spectrum was superimposable on that of authentic *dl*-camphor.

Formaldehyde was isolated from the aqueous layer above with dimedone, m.p. 193–194°.

Ultraviolet Spectra of Hexavalent Chromium Solutions.—The ultraviolet spectra of solutions of chromic anhydride, potassium chromate and potassium dichromate in acetic acid were determined using the Cary recording spectrophotometer. The results of these measurements carried out on 1.00×10^{-3} *M* solutions of these compounds are summarized in Table II.

TABLE II

ULTRAVIOLET SPECTRA OF HEXAVALENT CHROMIUM IN ACETIC ACID

λmax, mμ	*D*	λmax mμ	*D*	λmax mμ	*D*
CrO_3		K_2CrO_4		$K_2Cr_2O_7$	
270	2.276	271	1.372	270	2.456
322	0.888	320	0.393	320	0.743
347	0.937	347	.688	348	1.253
		403	.136	403	0.199
		450	.183	448	0.282

The spectrum of di-2-methylfenchyl chromate in both absolute methanol and acetic acid exhibited common maxima at 393 and 287 mμ. A mixture of 2-methylfenchol and chromic anhydride in acetic acid likewise gave the 393 mμ absorption maximum, whereas 1-methyl-α-fenchene (or a mixture of 1-methyl-α-fenchene and 1-methylcamphene) and chromic anhydride in acetic acid showed a maximum at 347 mμ.

Rate of Decomposition of Di-2-methylfenchyl Chromate in Methanol.—Absolute methanol, b.p. 65.9°, was distilled into an addition funnel, the first 20 ml. of distillate being used to rinse the distillation apparatus. This methanol was placed in 100-ml. volumetric flasks containing previously weighed samples of di-2-methylfenchyl chromate which had been dried at 25° (1 mm.). The flasks were stoppered with self-sealing rubber stoppers, and the joints were then sealed with paraffin. From these thermostated flasks 5-ml. aliquots were removed at intervals by means of a hypodermic needle inserted through the stoppers. The aliquots were immediately packed in Dry Ice–acetone to halt reaction until the analyses could be made. The stability of these reaction mixtures at −80° was demonstrated by storing aliquots of a solution at this temperature and observing their optical densities to be unchanged after 19 hr.

The course of the reaction was followed spectrophotometrically using the chromate ester maximum at 393 mμ. Analyses were made by scanning the spectra slowly on a Cary recording spectrophotometer from 350–400 mμ. The optical density measured was used directly in the calculations, and the rates were determined graphically (Table III).

For aqueous methanol measurements weighed samples of the chromate diester were dissolved in *ca.* 75 ml. of absolute methanol, 20.00 ml. of water was added and the solution was then made up to 100-ml. volume with methanol. As before, 5-ml. aliquots were withdrawn at intervals and the reactions stopped at −80° before analyzing spectrophotometrically at 393 mμ.

Rate of Decomposition of Di-2-methylfenchyl Chromate in Acetic Acid.—Absolute acetic acid was distilled from acetic anhydride into an addition funnel and then transferred under dry nitrogen into a self-sealing stoppered flask. This was allowed to equilibrate in a thermostat at 24.95 ± 0.04° for at least 30 minutes before use. The solutions were prepared using weighed samples of chromate ester which had been dried over phosphorus pentoxide *in vacuo* for 1–2 hr., transferred to the cell of the Cary spectrophotometer and allowed to come to thermal equilibrium for 45 seconds. A continuous record at 393 mμ (or alternatively at 287 mμ) was made, and the optical density curve thus obtained was used directly in the calculations. The rate (Table III) was determined both graphically and by the method of least squares using the first 8 points taken at 10 second intervals. The two methods gave results agreeing within 1%.

In order to show that the rate of the reaction, within reasonable limits, was independent of the time required to dissolve the sample and to allow it to come to thermal equilibrium in the spectrophotometer, four runs were carried out with all factors constant except this time which was 120, 135, 150 and 165 seconds. The rate consistency obtained indicates that within the experimental variation in the time required to prepare the solutions for measurement, the rates are independent of this time. However, in another experiment in which the preparation time was much longer (3.5 minutes) the rate obtained was significantly lower.

For the aqueous runs chromate diester was dissolved in *ca.* 8 ml. of absolute acetic acid, 1.00 ml. of water was added and the solution was made up to 10 ml. with acetic acid. After this solution had been in the spectrophotometer for 30 seconds, a continuous record was made at 393 mμ. Rate constants were calculated by the method of least squares using data taken during the first 200 seconds of the reaction.

Weighed samples of the chromate diester were dissolved in solutions of 2-methylfenchol in acetic acid which were then allowed to stand in the spectrophotometer for 20 seconds before commencing the record at 393 mμ. First-order rate constants were determined graphically from the optical density data (Table III).

TABLE III

RATES OF DECOMPOSITION OF DI-2-METHYLFENCHYL CHROMATE (II) AT 25° (c_I/c_{II} 2:1)

Solvent	No. of runs	$c_{II} \times 10^4$ *M*	k_1, sec.$^{-1}$
CH_3OH	5	4.0–4.9	$7.54 \pm 0.4 \times 10^{-7}$
CH_3OH (50°)	2	4.0	$129 \pm 1.4 \times 10^{-7}$
80% CH_3OH–H_2O	2	4.0	$4.14 \pm 0.2 \times 10^{-6}$
CH_3COOH	16	4.8–8.67	$3.63 \pm .2 \times 10^{-3}$
90% CH_3COOH–H_2O	2	4.8	$3.88 \pm .1 \times 10^{-3}$
CH_3COOH–I	4	4.8–5.5	$3.39 \pm .3 \times 10^{-3}$

Rate of Oxidation of 2-Methylfenchol by Chromic Anhydride in Acetic Acid.—A standard solution of chromic anhydride in acetic acid, freshly distilled from chromic anhydride, was prepared, and this solution was allowed to thermally equilibrate at 25°. Solutions for rate measurement were prepared immediately prior to use by adding a weighed sample of 2-methylfenchol to an aliquot of the chromic anhydride solution. This solution was transferred to the spectrophotometer cell and allowed to stand at 25° for at least 30 seconds, after which a continuous record to 393 mμ was made. First-order rates were calculated graphic-

TABLE IV

RATE OF OXIDATION OF 2-METHYLFENCHOL (I) BY CHROMIC ANHYDRIDE IN ACETIC ACID AT 25°

Run	$c_I \times 10^3$ *M*	c_I/c_{CrO_3}	$k_1 \times 10^4$, sec.$^{-1}$	$k_2 \times 10^4$, l. mole^{-1} sec.$^{-1}$
7	1.57	2:1	2.20	1.14
9	3.42	4:1	2.11	0.289
13	1.61	2:1	1.82	.936
14	1.58	2:1	1.66	.717
16	33.8	44:1	0.965[a]	.0104
17	7.7	1:1	1.89	
18	1.56	2:1	2.68,[b] 5.26[c]	
19	3.04	4:1	2.19,[b] 5.26,[c] 6.70[d]	
19	1.57–33.8	1:1–44:1	$1.95 \pm 0.1 \times 10^{-4}$ sec.$^{-1}$	

[a] Omitted from average. [b] Calcd. at t = 1000–2000 sec. [c] Calcd. at t = 3000–4000 sec. [d] Calcd. at t = 5000–8000 sec.

ally, but it was found that different rates could be obtained using different portions of the same data. However, the rate was not second order, since it was independent of the concentrations of the reactants except at very high concentrations of chromic anhydride relative to 2-methylfenchol, when it was somewhat lower (see Table IV). In most of the runs the concentration of the intermediate having λ_{max} 393 mμ was recorded early enough to observe the density curve passing through a maximum. In these runs the rate was determined from data taken beyond the maximum point.

Rate of Oxidation of 1-Methyl-α-fenchene by Chromic Anhydride in Acetic Acid.—Standard solutions of chromic anhydride and 1-methyl-α-fenchene, m.p. 62.5–64°, in acetic acid were prepared and thermostated at 25°. Aliquots were mixed just prior to making a run, transferred to the Cary cell and allowed to stand for 30 seconds before following the reaction at 347 mμ. At no time during these oxidations was there an indication of a maximum at 393 mμ. The second-order rate constants were calculated directly and graphically from the optical density data (Table V). Similar measurements were performed on mixed olefin.

TABLE V

RATE OF OXIDATION OF 1-METHYL-α-FENCHENE (IV) AND MIXED OLEFIN BY CHROMIC ANHYDRIDE IN ACETIC ACID AT 25°

No. of runs	(Olefin) $\times 10^{-3}$	(CrO_3) $\times 10^{-3}$	k_2, mole^{-1} sec.$^{-1}$
6 (IV)	0.960–1.92	1.03–2.06	$5.68 \pm 0.1 \times 10^{-5}$
14 (III–IV)	0.963–6.0	0.965–1.6	$1.03 \pm 0.04 \times 10^{-4}$

Chromic Anhydride Oxidation of 1-Methyl-α-fenchene.—1-Methyl-α-fenchene (0.50 g.) was dissolved in 6 ml. of acetic acid, and a solution of 0.87 g. of chromic anhydride in 13 ml. of acetic acid and 0.5 ml. of water was added dropwise during 15 min., the temperature never exceeding 25°. This mixture was then heated to *ca.* 90° for 3.5 hr., after which it was poured into 30 g. of ice-water and extracted first with five 10-ml. portions of pentane and then with four 10-ml. portions of ether. Each of these was then extracted with three 10-ml. portions of 5% sodium carbonate.

The pentane solution was dried over magnesium sulfate, the solvent was evaporated on the steam-bath and the residue was distilled at room temperature (1 mm.): 105 mg. The infrared spectrum of this product had peaks at 5.75, 5.85 and 6.00 μ, showing the presence of camphor (fenchone), another carbonyl substance and olefin. Comparison of the absorption peaks at 9.55 and 9.77 μ with those of authentic mixtures of camphor and fenchone indicated the identity of the mixture to be chiefly camphor containing not more than 6% fenchone. The ether layer, when worked up in the same manner, gave a very small amount of additional product of similar composition.

The combined carbonate extracts were acidified with concentrated hydrochloric acid and extracted with ether. After drying over magnesium sulfate, the solvent was evaporated and the residue was sublimed at 40° (1 mm.), 93 mg. The infrared spectrum, although similar to that of camphane-2-carboxylic acid, indicated a mixture of acids of almost the same composition as that obtained from the chromic acid oxidation of the mixed olefins, 1-methyl-α-fenchene and 1-methylcamphene.

In order to show that the pure olefin was not significantly rearranged by acetic acid under the conditions of the oxidation just described, 364 mg. of 1-methyl-α-fenchene in 10 ml. of acetic acid was held at 33° for 2 hr. and then at 80–90° for 2.5 hr. The olefin was then recovered by the method of workup described above for the oxidation, from which 146 mg. of starting substance was recovered having an infrared spectrum indistinguishable from that of the pure olefin.

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[CONTRIBUTION FROM THE GOVERNMENT FOREST EXPERIMENT STATION, JAPAN]

Flavonoids of Various *Prunus* Species. VI. The Flavonoids in the Wood of *Prunus aequinoctialis*, *P. nipponica*, *P. Maximowiczii* and *P. avium*

BY MASAO HASEGAWA

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From the wood of *Prunus aequinoctialis*, naringenin, aromadendrin, sakuranetin, eriodictyol, genistein, prunetin, verecundin, prunin, genistin and chrysin-7-glucoside were obtained. The name aequinoctin is proposed for the chrysin-7-glucoside, new to the natural product literature. The wood of *P. nipponica* contains *d*-catechin, naringenin, sakuranetin, eriodictyol, taxifolin, genistein, prunetin, aequinoctin (a little), chrysin (trace) and genistin (a little); and that of *P. Maximowiczii*, *d*-catechin (a little), naringenin, sakuranetin, eriodictyol, taxifolin (a little), aromadendrin (trace), chrysin (trace), prunetin and genistein. The wood of *P. avium* contains *d*-catechin, naringenin, prunin, aromadendrin (trace), eriodictyol, taxifolin, chrysin, aequinoctin, genistein, prunetin and genistein.

This report deals with the flavonoids obtained from the wood of *Prunus aequinoctialis* Miyoshi, which is distributed in the mountainous region of Japan. The flavonoid compounds which were isolated are naringenin, aromadendrin, sakuranetin, eriodictyol, genistein, prunetin, verecundin,[1] prunin,[2] genistin[3] and chrysin-7-glucoside.

Chrysin-7-glucoside is hydrolyzed by acids into one mole each of chrysin and glucose, and, since it shows a violet-brown coloration with ferric chloride, only one possibility remains for the glycosidic bond in it. Since it is hitherto not described as having been isolated from a natural product, I propose the name "aequinoctin" for it.

In 1944, Zemplén, Bognár and Mechner[4] reported the synthesis of chrysin-7-glucoside and gave 242 and 196° as the melting points of it and its pentaacetate, respectively. These coincide well with those of aequinoctin (m.p. 245°) and its pentaacetate (m.p. 197°). Zemplén, *et al.*, considered that the glycoside toringin has the constitution chrysin-7-glucoside, as revealed in the title of their article "Synthesis of the glucoside toringin." Toringin, however, is chrysin-5-glucoside as was elucidated by Hirose[5] and synthesized by Hattori and Shimokoriyama.[6] It does not give any coloration with ferric chloride.

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