657. *The Constitution and Stereochemistry of the Lactone* $C_{10}H_{16}O_4$ *Formed in the Oxidation of Camphor by Peracids.*[1]

By J. D. Connolly and K. H. Overton.

The minor product, $C_{10}H_{16}O_4$, of the Baeyer–Villiger oxidation of camphor is assigned the constitution and stereochemistry (II; R = R′ = OH) on degradative and spectroscopic evidence. The mechanism and stereochemistry of its formation are considered.

The oxidation of camphor by peracid was first recorded [2] by Baeyer and Villiger in a paper which discloses the oxidative procedure that has become associated with their names. The principal product, α-campholide, has a structure which appears anomalous when viewed in the light of the rules subsequently formulated [3] as governing bond migration during the Baeyer–Villiger oxidation. A number of recent publications have sought to rationalise this anomaly.[4] In addition to α-campholide, Baeyer and Villiger isolated a minor product, $C_{10}H_{16}O_4$, described as lactonic. This compound is the subject of the present paper; its acid-promoted degradation to a tetramethylcyclopentenone, allegedly (I), constitutes the sole published contribution [5] to its chemistry. We have investigated the properties of this lactone and deduce for it the constitution and stereochemistry (II; R = R′ = OH) from the evidence outlined in the sequel.

The lactone was obtained either with persulphuric [2] or, more conveniently, with peracetic acid. Analysis confirmed the molecular formula assigned by Baeyer and Villiger; Kuhn–Roth oxidation demonstrated the presence of two *C*-methyl groups. The lactone consumed one equivalent of base within two minutes at 95°. The infrared spectrum had bands (in Nujol) at 1393, 1379 (CMe_2) and (in chloroform) at 3628 (free OH), 3524 (bonded OH), and 1773 (γ-lactone) cm.$^{-1}$. Acetylation afforded either (pyridine–acetic anhydride) a monoacetate, $C_{12}H_{18}O_5$ (II; R = OAc, R′ = OH) or (refluxing acetyl chloride) a diacetate, $C_{14}H_{20}O_6$ (II; R = R′ = OAc). Oxidation with chromic acid in acetic acid smoothly furnished the cyclopentanone-lactone, $C_{10}H_{14}O_4$ (III; R = H) [$\nu_{max.}$ (in carbon tetrachloride) 1787 (γ-lactone) and 1747 (cyclopentanone) cm.$^{-1}$], which forms a monobenzylidene derivative. Thus, of the four oxygen atoms in the molecule of the original lactone, one is present as a secondary hydroxyl group, flanked by at least one methylene group and attached to a five-membered ring, the second probably as a tertiary hydroxyl, and the remaining pair in a γ-lactone system. The interrelation of these functions and definition of the framework to which they are attached followed in an unexpectedly simple manner. When the cyclopentanone (III; R = H) was refluxed with

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[1] Preliminary communication: Connolly and Overton, *Proc. Chem. Soc.*, 1959, 188.

[2] Baeyer and Villiger, *Ber.*, 1899, **32**, 3625.

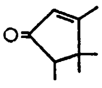
[3] Doering and Speers, *J. Amer. Chem. Soc.*, 1950, **72**, 5515.

[4] Murray, Johnson, Pederson, and Ott, *J. Amer. Chem. Soc.*, 1956, **78**, 981; Sauers, *ibid.*, 1959, **81**, 925; Rassat and Ourisson, *Bull. Soc. chim. France*, 1959, 1134; Meinwald and Frauenglass, *J. Amer. Chem. Soc.*, 1960, **82**, 5235.

[5] Locquin, *Compt. rend.*, 1911, **153**, 284.

0·1N-ethanolic potassium hydroxide, decarboxylation led to a hydroxycyclopentenone, $C_9H_{14}O_2$, whose spectroscopic properties indicated the structure (IV; R = OH) [$\lambda_{max.}$ 222 mμ (ε 12,000); $\nu_{max.}$ (in carbon tetrachloride) 3570 (free OH), 1710 (cyclopentenone), and 1620 (conjugated ethylenic linkage) cm.$^{-1}$]. This hydroxy-ketone (characterised as the semicarbazone) was reduced by zinc in refluxing acetic acid to the deoxy-ketone, $C_9H_{14}O$ (IV; R = H) (characterised as the 2,4-dinitrophenylhydrazone). These transformations demonstrate that the lactonic-carbonyl group is attached β (or vinylogously β) and the lactonic alkyl-oxygen atom α (or vinylogously α) with respect to the secondary hydroxyl group. Dehydration of the lactone (II; R = R′ = OH) with phosphorus oxychloride in pyridine gave the diene lactone, $C_{10}H_{12}O_2$ (V) [$\lambda_{max.}$ 262 mμ (ε 11,900); $\nu_{max.}$ (in carbon tetrachloride) 1769, 1749 (CO of lactone), and 1637 (conjugated ethylenic linkage) cm.$^{-1}$]. This, on hydrogenation over platinum, gave dihydro-β-campholenolactone[6] (VI), which was further reduced by lithium aluminium hydride to the crystalline diol[7] (VII), both of established structure. The constitution of the camphor oxidation product, $C_{10}H_{16}O_4$, as (II; R = R′ = OH) follows unambiguously from these experiments.

The tetramethylcyclopentenone obtained by the action of hot mineral acid on the dihydroxy-lactone was formulated by Locquin[5] as (I) on the basis of its degradation through a trimethyl-lævulic acid (there is no evidence for its structure) to trimethylsuccinic acid. This sequence of reactions, which we confirmed, does not, however, distinguish between the alternatives (I) and (IV; R = H) for the cyclopentenone. That the former (I) represents the correct structure follows from (*a*) non-identity with the cyclopentenone (IV; R = H) obtained as above, and (*b*) identity (established by direct comparison of the derived semicarbazones) with the compound of structure (I) obtained by an independent route.[8] *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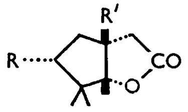

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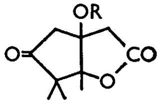

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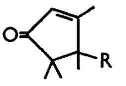

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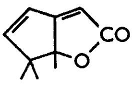

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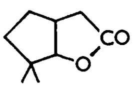
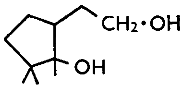
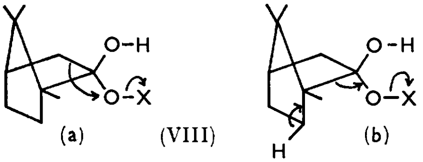


(VI)

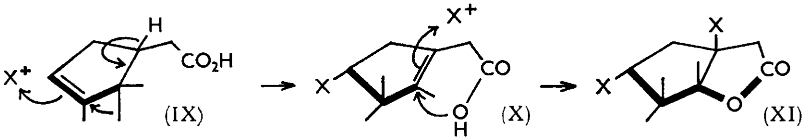


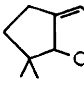
(VII)



(VIII)

X = OAc or HS_2O_7





(XII)

The formation of the dihydroxy-lactone has sound mechanistic analogy in the chemistry of camphor. Thus the transition state (VIII), instead of leading to α-campholide (*a*), can undergo the alternative collapse (*b*) to α-campholenic acid. This pathway is mechanistically akin to the Beckmann rearrangement of camphor oxime,[9] where α-campholenonitrile

* We record our gratitude to Dr. V. G. Kutcherov, Moscow, for providing an authentic specimen from the late Professor I. N. Nazarov's collection.

[6] Tiemann, *Ber.*, 1895, **28**, 2166; 1897, **30**, 405.

[7] Béhal, *Bull. Soc. chim. France*, 1904, **31**, 179.

[8] Nazarov and Bakhmutskaya, *Zhur. obshchei Khim.*, 1950, **20**, 1837.

[9] Simonsen and Owen, " The Terpenes," Cambridge Univ. Press, 1949, Vol. II, p. 437.

is the primary product (and ring expansion to the lactam does not apparently take place). The subsequent fate of the intermediate α-campholenic acid then parallels the well-established transformation to dihydro-β-campholenolactone, with the substitution in the presence of peracid of OH^+ instead of H^+ as the cationic species at the two points indicated [(IX) ⟶ (X) ⟶ (XI)].

Support for the intermediate rôle of α-campholenic acid was found in its oxidation to the dihydroxy-lactone in improved yield under Baeyer–Villiger conditions. Further support was oxidation of dihydro-β-campholenolactone (VI) [in equilibrium with β-campholenic acid (X; X = H)] to the monohydroxy-lactone, $C_{10}H_{16}O_3$ (II; R = H, R′ = OH without stereochemical commitment) as the major product.* It had in the infrared bands (in carbon tetrachloride) at 3618 (free OH) and 1778 (γ-lactone) $cm.^{-1}$ and resisted acetylation with acetic anhydride and pyridine. Dehydration with phosphorus oxychloride in pyridine gave the oily unsaturated lactone, $C_{10}H_{14}O_2$ (XII) [$\lambda_{max.}$ 219—220 mμ (ε 11,700)], which was converted by successive reductions into the compounds (VI) and (VII).

Formation of the dihydroxy-lactone is attended by partial racemisation; this is not surprising when the proposed pathway for its genesis is taken into account, and presumably proceeds by the partly indiscriminate attack of peracid on α-campholenic acid (IX) from either side. The extent of racemisation is about the same (around 50%) whether the substrate is (+)-camphor or (+)-α-campholenic acid, provided the oxidation is carried out in a homogeneous medium (peracetic acid), but it differs unpredictably between the two substrates when persulphuric acid in a two-phase system is used. The absolute stereochemistry of the enantiomer formed in excess is assigned tentatively on the assumption that the extended Hudson lactone rule[10] can be applied to systems with an angle-methyl group: on this assumption the large positive Δ value ($[M]_D$ lactone/ethanol — $[M]_D$ lactone/N-ethanolic KOH= + 124°; see p. 3369) supports the assignment as (II).

Finally we comment on the relative stereochemistries of the three asymmetric centres in the dihydroxy-lactone. The *cis*-nature of the ring fusion is assigned on stereomechanistic grounds. Thus we believe that, to account for the steric uniformity of the product (there is no evidence, in spite of careful scrutiny, for an epimeric lactone having a *trans*-ring-fusion) and therefore the implied stereospecificity of lactonisation, this is best visualised as being concerted with, and *trans* to, peracid attack on the double bond of the intermediate (X). Such concertion is sterically favoured and mechanistically unexceptionable[11] and would necessarily result in the proposed *cis*-fusion of the two five-membered rings. The rotatory dispersion curve of the ketone (III) (see p. 3370) is in harmony with such a proposal. The relative stereochemistry of the two hydroxyl groups—there was no evidence of the diastereomeric diol—is less easily predicted and its confirmation proved difficult.

We have become aware, since our preliminary communication,[1] that the infrared evidence on which we had previously based a *cis*-assignment, might be equivocal. For a diol studied recently[12] intermolecular hydrogen bonding was shown to persist at concentrations (0·002M) below those normally regarded[13] as limiting for such bonding. While the diol (II; R = R′ = OH) still showed bonded hydroxyl absorption in 0·0003M-solution in carbon tetrachloride, this eventually disappeared on further dilution and cannot therefore result from intramolecular bonding.† It would, however, be injudicious in our view

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* This compound was also obtained in minor amount when camphor or α-campholenic acid was oxidised with 5% peracetic acid.

† The absence of bonded hydroxyl absorption in the infrared solution spectrum of the monoacetate (II; R = OAc, R′ = OH) supports a *trans*-diol assignment.

[10] Klyne, *Chem. and Ind.*, 1954, 1198; Novotny, Herout, and Šorm, *Coll. Czech. Chem. Comm.*, 1960, **25**, 1500.

[11] Dauben, Hayes, Schwarz, and McFarland, *J. Amer. Chem. Soc.*, 1960, **82**, 2234 and references cited there; Woodward, Bader, Bickel, Frey, and Kierstead, *Tetrahedron*, 1958, **2**, 7.

[12] Burer and Gunthard, in " Hydrogen Bonding," Pergamon Press, London, 1959, p. 301.

[13] Cole and Jefferies, *J.*, 1956, 4391.

to infer the presence of a *trans*-diol from this observation, since the requisite data for *cis*-cyclopentane-1,3-diols are not available. It is evident that the geometry of the diol lactone is such as to favour molecular association by hydrogen bonding in very dilute solution.

Chemical evidence consistent with a *trans*-relation of the two hydroxyl groups is as follows. First, attempts to involve them in cyclic derivatives with acetone, benzaldehyde, diethyl carbonate, and oxalyl chloride under a variety of conditions (see Experimental section) were unsuccessful. Secondly, and perhaps more significantly, attempts to obtain the epimeric secondary alcohol by reducing the hydroxy-ketone (III) with sodium borohydride afforded only the known diol, apart from minor amounts of product resulting from reduction of the lactone. Such stereospecificity is explicable if reduction is supposed to occur by intramolecular hydride-transfer from an initial borate complex (as III; R = BH_3^-) of a kind discussed by Henbest and his colleagues [14] for the reduction of βγ-epoxycyclohexanols. If this were the case, the resulting diol would be *trans*-oriented.

EXPERIMENTAL

M. p.s were determined on the Kofler block. Infrared spectra were taken with Unicam S P. 100 and Perkin–Elmer 13 spectrometers by Dr. G. Eglinton and his staff. Microanalyses are by Mr. J. M. L. Cameron and his staff. Chromatographic alumina was prepared and standardised according to Brockmann.[15] Light petroleum was of b. p. 60—80° unless otherwise specified.

The Dihydroxylacetone (II; R = R′ = OH).—(a) *From* (+)-*camphor.* (i) (+)-Camphor, $[\alpha]_D$ +44° (in ethanol) (75 g.), in light petroleum (120 ml.) was added during 2 hr. to potassium persulphate (600 g.) suspended in water (360 ml.) and concentrated sulphuric acid (990 ml.); the camphor solution was dropped on the disc of a vibro-mixer, placed near the surface, and the temperature was kept at 20° by cooling. Agitation was continued for a further ½ hr., and the mixture poured into ice and neutralised (pH 5) with gaseous ammonia. The resulting brown gum containing ammonium sulphate and α-campholide was removed and the aqueous filtrate continuously extracted with ether for 16 hr. The yellow, semicrystalline residue obtained on removal of ether was purified by chromatography over alumina (grade V) in 1 : 1 benzene–ethyl acetate, furnishing the *lactone* (II; R = R′ = OH) (10·0 g.) as prisms (from acetone–benzene), m. p. 192—193°, $[\alpha]_D$ +8° (*c* 0·90 in acetone), the constants not being appreciably altered by successive crystallisations (Found: C, 59·85, 60·1; H, 7·95, 8·2; *C*-Me, 14·15. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0; 2*C*-Me, 15·0%).

Hydrolysis of the lactone (5·00 mg.) with 0·1N-sodium hydroxide (4 mol.) for 2 min. at 95° gave, on back-titration, an equivalent weight of 207 (Calc., 200).

(ii) (+)-Camphor (20 g.) in "AnalaR" acetic acid (100 ml.) was added dropwise to a stirred, cooled mixture of sulphuric acid (40 ml.) and 43% peracetic acid (40 ml.), then kept at 20° for 5 days, poured on ice, saturated with sodium chloride, and extracted with ether (3 × 150 ml.), and the combined extracts were washed with saturated sodium hydrogen carbonate and water. Chromatography of the product over alumina (grade III) afforded successively (benzene) α-campholide, (ethyl acetate–benzene; 1 : 2) non-crystalline hydroxy-lactonic material, and (ethyl acetate) dihydroxy-lactone (II; R = R′ = OH) (1·6 g.), prisms (from acetone–benzene), m. p. 180—192°, $[\alpha]_D$ +45° (in acetone), raised by two crystallisations from acetone to m. p. 192—194°, $[\alpha]_D$ +60° (*c* 1·01 in acetone). In ethanol this product had $[M]_D$ +156° (*c* 0·8) and in 1N-ethanolic potassium hydroxide $[M]_D$ +32° (*c* 0·8).

(b) *From* (+)-α-*campholenic acid.* (i) (+)-α-Campholenic acid, $[\alpha]_D$ +11° (in acetone) (11 g.), oxidised and worked up as in (a) (i), afforded the dihydroxy-lactone (3·4 g.), m. p. 190—192°, $[\alpha]_D$ +30° (in acetone). Repeated crystallisation from acetone raised these constants to m. p. 192—193°, $[\alpha]_D$ +63° (*c* 1·80 in acetone).

(ii) (+)-α-Campholenic acid (920 mg.) was oxidised as in (a) (ii), and the product chromatographed over alumina (grade V), affording dihydro-β-campholenolactone (600 mg.; eluted by benzene), monohydroxy-lactonic material (benzene–ethyl acetate; 2 : 1), and the dihydroxy-lactone (150 mg.; eluted by ethyl acetate). Crystallised twice from acetone, the last substance had m. p. 192—194°, $[\alpha]_D$ +59° (*c* 1·48 in acetone).

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[14] Henbest and Nicholls, *J.*, 1957, 4608.

[15] Brockmann, *Ber.*, 1941, **74**, 73.

Attempts to condense the hydroxy-lactone with (*a*) acetone in presence of hydrogen chloride or anhydrous copper sulphate and sulphuric acid, (*b*) diethyl carbonate or carbonyl chloride in presence of base, and (*c*) benzaldehyde in presence of acid failed, with quantitative recovery of unchanged dihydroxy-lactone.

Attempts to Form the Cyclic Oxalate (II; R + R′ = O•CO•CO•O).—(i) *With oxalyl chloride.* The dihydroxy-lactone (500 mg.) was refluxed with an excess of freshly distilled oxalyl chloride for 10 hr. The half-acid chloride (II; R = O•CO•COCl) obtained by removing unchanged oxalyl chloride *in vacuo* was hydrolysed with water, and the half-acid (II; R = O•CO•CO_2H) characterised as the *methyl ester* obtained with ethereal diazomethane; this formed needles (from acetone–benzene–hexane), m. p. 138—139° (Found: C, 54·55; H, 5·95. $C_{13}H_{18}O_7$ requires C, 54·55; H, 6·35%), $\nu_{max.}$ (in carbon tetrachloride) 3615 (free OH; no bonded OH), 1787, 1805 (shoulder) (γ-lactone), and 1753 (oxalate) cm.$^{-1}$.

The half acid (150 mg.) in dry tetrahydrofuran (10 ml.) was kept with dicyclohexylcarbodi-imide (40 mg.) for 3 days. The product, after removal of solvent, was separated into acidic [75 mg.; unchanged half-acid (infrared)] and neutral (120 mg.) fractions. The latter afforded dicyclohexylurea (insoluble in ether) (mixed m. p. and infrared spectrum) and on chromatography of the remainder (alumina; grade V) only hydroxylic fractions (infrared) but no cyclic oxalate.

The half-acid (70 mg.) and dicyclohexylcarbodi-imide (25 mg.) were kept in dry pyridine (5 ml.) for 16 hr. Dilution with ether and successive extractions with dilute hydrochloric acid and aqueous sodium hydrogen carbonate gave back unchanged acid (62 mg.).

The half-acid chloride (55 mg.) was kept in dry pyridine (7 ml.) for 1 hr. and then refluxed for 1 hr. more. Dilution with ether and working-up in the usual way gave no acidic material. The neutral fraction (40 mg.) was hydroxylic and unsaturated (infrared); chromatography did not reveal the cyclic oxalate.

(+)-*Monocamphorsulphonate* (II; R = $C_{10}H_{15}O_4S$, R′ = OH).—The dihydroxy-lactone, $[\alpha]_D$ +62° (650 mg.), and (+)-camphorsulphonyl chloride (1 mol.) were kept in pyridine for 16 hr. Chromatography of the products, obtained as usual over alumina (grade V), gave (up to 40% ethyl acetate–benzene) the (+)-*monocamphorsulphonate* (400 mg.), followed by unchanged diol (320 mg.). The ester, twice crystallised from ethyl acetate, had m. p. 181—183°, $[\alpha]_D$ +67° (*c* 0·73 in acetone) (Found: C, 58·25; H, 7·25. $C_{20}H_{30}O_7S$ requires C, 57·95; H, 7·3%).

A dihydroxy-lactone of $[\alpha]_D$ +8° gave, after six crystallisations, a (+)-camphorsulphonate, m. p. 181—183°, $[\alpha]_D$ +65° (*c* 1·4 in acetone).

Attempts to hydrolise the (+)-camphorsulphonate by oxalic acid in boiling aqueous dioxan or water were unsuccessful, affording unchanged ester and unsaturated hydroxy-lactone (infrared) respectively.

Monotoluene-p-*sulphonate* (II; R = $C_7H_7O_3S$, R′ = OH).—The *monotoluene*-p-*sulphonate*, obtained in the usual way and crystallised from benzene–light petroleum, had m. p. 110—112°, $\lambda_{max.}$ 226 mμ (ε 11,400) (Found: C, 57·8; H, 6·3. $C_{17}H_{22}O_6S$ requires C, 57·6; H, 6·25%).

Attempts to replace the toluene-*p*-sulphonate by acetate with inversion under a variety of conditions resulted in elimination or recovery of unchanged material.

Monoacetate (II; R = OAc, R′ = OH).—The dihydroxy-lactone (100 mg.) with pyridine and acetic anhydride at 20° afforded the monoacetate, rods (80 mg.) (from benzene), m. p. 80—82°, $[\alpha]_D$ +66° (*c* 1·92 in acetone), $\nu_{max.}$ (in carbon tetrachloride) 3615 (OH), 1784 (γ-lactone), and 1747 (acetate) cm.$^{-1}$ (Found: C, 64·1; H, 7·65. $C_{12}H_{18}O_5,\frac{1}{2}C_6H_6$ requires C, 64·05; H, 7·5%. Found, in material dried at 65°/2 mm.: C, 59·55; H, 7·5. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·5%).

Diacetate (II; R = R′ = OAc).—The diol, when refluxed with acetyl chloride for 2 hr., afforded the *diacetate*, plates (from ethyl acetate–light petroleum), m. p. 105—106°, $\nu_{max.}$ (in carbon tetrachloride) 1790 (γ-lactone) and 1748 (acetate) cm.$^{-1}$ (Found: C, 59·05; H, 6·8. $C_{14}H_{20}O_6$ requires C, 59·15; H, 7·1%).

Hydroxy-ketone (III; R = H).—The diol (150 mg.) in " AnalaR " acetic acid was treated with chromium trioxide (75 mg.) in 5% aqueous acetic acid at 20° for 16 hr., affording the hydroxy-ketone (III), rods (132 mg.) (from chloroform—benzene), m. p. 160—162° (Found: C, 60·85; H, 6·85. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%). A hydroxy-ketone obtained from diol of $[\alpha]_D$ +62° (in acetone) had a positive Cotton curve (*c* 0·28 in $CHCl_3$): (600 mμ) +292°; (589) +340°; (320) +2332°; (300) +1000°. The derived *acetate* obtained with refluxing acetyl chloride separated as needles from ether–hexane and had m. p. 123—125°, $\nu_{max.}$ (in carbon tetrachloride) 1790 (γ-lactone) and 1747 (acetate and cyclopentanone) cm.$^{-1}$ (Found: C, 59·85; H, 6·5. $C_{12}H_{16}O_5$ requires C, 60·0; H, 6·7%).

The ketone (50 mg.) in 0·1N-ethanolic potassium hydroxide (10 ml.), containing freshly distilled benzaldehyde (250 mg.), was kept for 10 min. Extraction of the acidified solution with ether and removal of the aldehyde with aqueous sodium hydrogen sulphite gave, in the usual way, the *benzylidene derivative* as plates (from ethyl acetate–benzene), m. p. 150—151°, $\lambda_{max.}$ 302 mμ (ε 22,600) (Found: C, 71·2; H, 6·4. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·35%).

Reduction of the Ketone (III; R = H) *by Borohydride*.—The ketone (100 mg.) and sodium borohydride (100 mg.) were kept in methanol (10 ml., containing a few drops of water) for 3 days at 20°. The product (95 mg.) obtained with ether from the acidified reaction mixture afforded, on chromatography over alumina (grade V), the dihydroxy-lactone (II; R = R′ = OH) (80 mg.; elution by 1 : 1 benzene–ethyl acetate) and a crystalline compound, m. p. 145° (7 mg.; elution by 1 : 2 benzene–ethyl acetate) which showed no infrared carbonyl absorption and was not investigated further.

When water was used as the solvent, the more polar product was obtained in excess (5 : 2) of the diol.

Changes in the proportion of sodium borohydride and use of potassium borohydride did not afford the epimeric diol lactone.

Catalytic Reduction of the Ketone (III).—The ketone (20 mg.) and Adams catalyst (25 mg.) in ethyl acetate (4 ml.) were shaken in hydrogen until no more was absorbed (3 days; 1·2 ml., 0·58 mol.). Chromatography of the product over alumina (grade V) gave unchanged ketone (14 mg.; eluted by 9 : 1 benzene–ethyl acetate) and the dihydroxy-lactone (II; R = R′ = OH) (4 mg.; eluted by 1 : 1 benzene–ethyl acetate).

Action of Alkali on the Hydroxy-ketone (III).—The ketone (420 mg.) in dry ethanol (5 ml.) containing potassium hydroxide (3 mol.) was kept under nitrogen for ½ hr. at 80°. Potassium carbonate (190 mg.) separated during the reaction. Dilution with water and ether-extraction afforded the *cyclopentenone* (IV; R = OH), affording plates, m. p. 62—63°, from benzene–light petroleum (Found: C, 70·15; H, 8·9. $C_9H_{14}O_2$ requires C, 70·1; H, 9·15%). The *semicarbazone*, prisms from aqueous methanol, had m. p. 216—218° (decomp.), $\lambda_{max.}$ 275 mμ (ε 15,000) (Found: C, 57·0; H, 7·75; N, 19·95. $C_{10}H_{17}N_3O_2$ requires C, 56·85; H, 8·1; N, 19·9%).

Reduction of the Cyclopentenone (IV; R = OH) *with Zinc and Acetic Acid*.—The cyclopentenone (200 mg.) and zinc dust (1·5 g.) in " AnalaR " acetic acid were refluxed for 72 hr. Neutralisation with 4N-sodium hydroxide, saturation with sodium chloride, and ether-extraction furnished the deoxy-ketone (IV; R = H), b. p. 78°/10 mm., n_D^{20} 1·4730, $\lambda_{max.}$ 228 mμ (ε 12,900), $\nu_{max.}$ (film) 1697 (cyclopentenone) and 1615 (conjugated ethylenic linkage) cm.$^{-1}$. The 2,4-*dinitrophenylhydrazone*, orange needles from chloroform–methanol, had m. p. 200—201°, $\lambda_{max.}$ 380 mμ (ε 27,800) (Found: C, 56·9; H, 5·5; N, 17·55. $C_{15}H_{18}N_4O_4$ requires C, 56·6; H, 5·7; N, 17·6%).

Diene Lactone (V).—The dihydroxy-lactone (750 mg.) in pyridine (20 ml.) and phosphorus oxychloride (1 ml.) (both freshly distilled) was refluxed for 2 hr. The product obtained in the usual way was eluted from alumina (grade III) by light petroleum, affording the *diene lactone* (535 mg.), b. p. 77—80°/0·7 mm., n_D^{22} 1·5129 (Found: C, 72·9; H, 7·05. $C_{10}H_{12}O_2$ requires C, 73·15; H, 7·35%).

Dihydro-β-campholenolactone and the Diol (VII).—The diene lactone (16 mg.) in ethyl acetate over platinum oxide absorbed 1·8 mol. of hydrogen in 7 hr. The product (identical by infrared spectrum with authentic dihydro-β-campholenolactone [6]) afforded, on reduction with lithium aluminium hydride, the diol (VII), plates (from benzene), m. p. 142—144°, identical with an authentic specimen [7] in m. p., mixed m. p., and infrared spectrum.

Cyclopentenone (I).—The dihydroxy-lactone (1 g.) was heated with 20% phosphoric acid (20 ml.) in a sealed tube for 6 hr. The neutral fraction of the product afforded the cyclopentenone (I), b. p. 78—80°/12 mm., n_D^{20} 1·4750, $\lambda_{max.}$ 228 mμ (ε 12,800), whose 2,4-*dinitrophenylhydrazone*, orange needles (from chloroform–methanol), had m. p. 202—203° [mixed m. p. with the 2,4-dinitrophenylhydrazone of (IV; R = H) 184—188°], $\lambda_{max.}$ 385 mμ (ε 24,800) (Found: C, 56·45; H, 5·95; N, 17·55. $C_{15}H_{18}N_4O_4$ requires C, 56·6; H, 5·7; N, 17·6%). The semicarbazone, m. p. 176—178°, was identical in m. p., mixed m. p., and infrared spectrum with an authentic specimen.[6]

αββ-*Trimethyl-lævulic Acid Semicarbazone*.—The cyclopentenone (I) in dry methylene chloride (20 ml.) was treated at −70° with ozonised oxygen, until the absorption maximum at

228 mμ had disappeared (½ hr.). Decomposition of the ozonide with water (10 ml.) at 95° and ether-extraction afforded trimethyl-lævulic acid (426 mg.) as a yellow oil, whose *semicarbazone* formed plates, m. p. 175—177°, from aqueous methanol (Found: C, 50·5; H, 8·1; N, 19·4. $C_9H_{17}N_3O_3$ requires C, 50·2; H, 7·95; N, 19·5%).

Trimethylsuccinanil.—The trimethyl-lævulic acid (100 mg.) was added to bromine (350 mg.) and sodium hydroxide (225 mg.) in water (4 ml.). The solution was kept for 10 min., reduced to 1 ml. at the water-pump, and acidified with hydrochloric acid. The crude trimethylsuccinic acid obtained with ether (60 mg.; m. p. 144—154°) was refluxed with aniline (300 mg.) for ½ hr. The product, worked up as usual, afforded from aqueous ethanol needles of *trimethylsuccinanil*, m. p. 131—132° after sublimation (Found: C, 72·2; H, 7·05; N, 6·75. $C_{13}H_{15}NO_2$ requires C, 71·85; H, 6·95; N, 6·45%).

The Hydroxy-lactone (II; R = H, R′ = OH).—Dihydro-β-campholenolactone[6] (1·6 g.) was oxidised by the procedure (a) (i) used for (+)-camphor. Chromatography of the product over alumina (grade V) afforded unchanged dihydro-β-campholenolactone (1·4 g.; eluted by benzene) and the *hydroxy-lactone* [80 mg.; eluted by ethyl acetate–benzene; 1 : 9)], rods (from benzene–light petroleum), m. p. 143—145° (sublimed at 90°/0·5 mm.) (Found: C, 65·2; H, 8·8. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·75%).

The hydroxy-lactone was unchanged when treated with acetic anhydride–pyridine at 20°.

The hydroxy-lactone (250 mg.) was dehydrated with phosphorus oxychloride in pyridine, and the product, dissolved in light petroleum, filtered through alumina, affording the unsaturated *lactone* (XII) (176 mg.), b. p. 88°/0·8 mm., $\lambda_{max.}$ 219 mμ (ε 11,700). (Found: C, 71·75; H, 8·25. $C_{10}H_{14}O_2$ requires C, 72·25; H, 8·5%).

Hydrogenation over platinum oxide in ethyl acetate gave dihydro-β-campholenolactone, which was converted into the diol (VII), identical with material obtained from the diene lactone (V).

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