Reduction of Vb. (*a*) A solution of Vb (49 mg.) in methanol (3 ml.) was added with stirring to an ice-cooled solution of sodium borohydride (30 mg.) in methanol (2 ml.). The yellow color of the salt Va disappeared immediately. Circular paper chromatograms[4b] (mobile phase, benzene–hexane (1:1); stationary phase, 5 g. of potassium acetate and 25 ml. of acetic acid in 75 ml. of water) of the reaction mixture indicated the presence of two products (potassium iodoplatinate spray reagent),[32] one of which was slower than eburnamonine. The othertr avelled much faster, with the same rate as epieburnamonine, but appeared with a violet rather than the grayish blue color of the latter compound. After brief heating to boiling, the mixture was acidified with acetic acid, diluted with water, basified with ammonium hydroxide, and extracted with chloroform. After drying over potassium carbonate, the extract was concentrated under reduced pressure to give a partly crystalline residue (34 mg.). On paper chromatograms it gave the same two spots as the methanolic reaction mixture. It was believed to be composed of epieburnamonine and the ethyl esters of eburnamoninic and epieburnamoninic acid. This assumption was supported by the infrared spectrum ($CHCl_3$): hydrogen bonded NH 2.88 (m) and 3.00 (m) μ, C=O 5.78 (sh) (s), 5.88 (s), and 6.04 (m).

The mixture was dissolved in 0.1 *M* ethanolic ethoxide (5 ml.) with gentle heating and then left at room temperature for 15 min. On paper chromatography, the solution now gave two spots indistinguishable from those given by eburnamonine and epieburnamonine, respectively. It was acidified with acetic acid and left at room temperature overnight. Basification with ammonium hydroxide and extraction with chloroform gave the crude bases (23 mg.) as an oil, which was chromatographed on alumina (4 g.). Benzene–hexane (1:3) eluted a crystalline material (11.5 mg.) which upon recrystallization from benzene–hexane and aqueous methanol gave pure epieburnamonine (VIII) (9 mg.), m.p. 134.5–136°, m.m.p. 134.5–136.5°; infrared spectra (KBr) identical.

Elution with benzene–hexane (1:1) gave a crystalline fraction (12 mg.) which on recrystallization from benzene–hexane and methanol afforded eburnamonine (XIIIa) (10 mg.), m.p. and m.m.p. 201–202°; infrared spectra (KBr) identical.

(*b*) A mixture of Vb (40 mg.) and 5% palladium–charcoal (20 mg.) in ethanol (3 ml.) was hydrogenated at room temperature and atmospheric pressure until after 14 hr. when the reaction had stopped and the initially yellow color of the starting material had disappeared. Paper chromatograms indicated that the product composition was qualitatively the same as in method a, but with the slow-moving compound in a large excess. The solution was filtered, diluted with water, basified with ammonium hydroxide, and extracted with chloroform. Concentration of the extract gave a partly crystalline residue (28 mg.) which spectral data indicated to be a mixture of the ethyl esters of eburnamoninic and epieburnamoninic acid; ultraviolet spectrum (ethanol), λ_{max} 227 mμ (log ϵ 4.33), 283 (3.73), and 290 (3.67), λ_{min} 247 (3.40) and 288 (3.66); infrared spectrum ($CHCl_3$), NH 2.89 (m) μ, and C=O 5.84 (s).

The ester mixture was treated with sodium ethoxide in ethanol and the product worked up as under method a to give epieburnamonine (VIII) (2 mg.), m.p. and m.m.p. 135–136.5°, and eburnamonine (16 mg.), m.p. and m.m.p. 200–202°; their identities were confirmed by comparison of infrared spectra (KBr).

(32) R. Munier and M. Macheboeuf, *Bull. soc. chim. biol.*, 31, 1144 (1949).

The Total Synthesis of the (±)-Furopelargones

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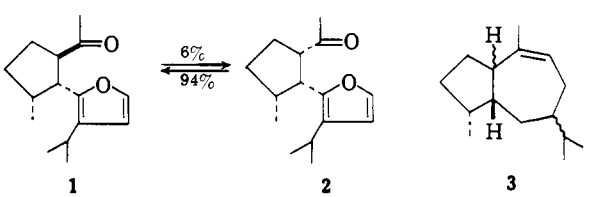
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Massachusetts. *Received November 2, 1964*

Photocitral-A (**9**), *whose configuration was elucidated, served as starting material in the synthesis of the naturally occurring sesquiterpene (?) ketone furopelargone-A* (**1**). *Reformatzky condensation with t-butyl α-bromoisovalerate followed by oxidation yielded a mixture of diastereomeric ketoesters* (**14**). *The latter was alkylated with allyl bromide and the resulting β-ketoester transformed to the dienone* **18** *by pyrolysis. Oxidation with ozone followed by dehydration in acetic acid solution completed the total synthesis of furopelargone-A* (**1**). *The epimeric furopelargone-B* (**2**) *was available by acid- or preferably base-catalyzed equilibration of the A isomer* (**1**).

The high boiling fractions of *Geranium Bourbon Oil*[1] contain the two isomeric furopelargones A and B ($C_{15}H_{22}O$). The structures of these two natural products were elucidated very recently and formulas **1** and **2** also represent their absolute configurations.[2,3] We have verified these structures by a total synthesis which is discussed in this paper.



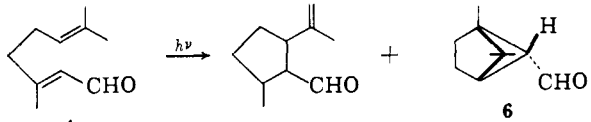
1 **2** **3**

(1) E. Guenther, "The Essential Oils," Vol. IV, D. Van Nostrand and Co., Inc., New York, N. Y., 1952, p. 67.

(2) R. E. Wolff, J. C.-N. Ma, and G. Lukas, *Compt. rend.*, 257, 1784 (1963).

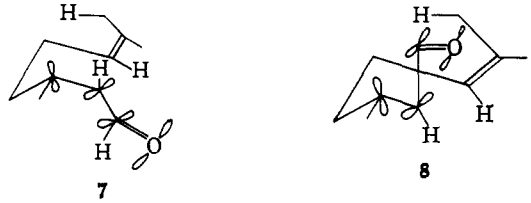
(3) G. Lukas, J. C.-N. Ma, J. A. McCloskey, and R. E. Wolff, *Tetrahedron*, 20, 1789 (1964).

If the formulas **1** and **2** are examined it will be seen that the compounds could originate in nature from the hypothetical bicyclic sesquiterpene (**3**) by oxidative cleavage at the double bond followed by cyclization. It was our plan to use the diketoaldehyde (**19**) as an intermediate and subsequently to convert it to the furopelargones **1** and **2**. For the construction of this monocyclic precursor photocitral-A[4] (**5**) was chosen



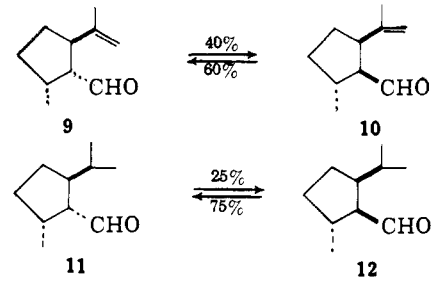
4 **5** **6**

as starting point because we hoped that the isopropenyl group could be converted to a methyl ketone function at a later stage of the synthesis. Cookson[4] had shown that photocitral-A (**5**) can be obtained simply by ultraviolet irradiation of a commercially available mixture of *cis*- and *trans*-citral (**4**) in cyclohexane solution. For the preparation of larger quantities of photocitral-A we found it advantageous to perform the photoisomerization in alcoholic solution and in this manner it was possible to prepare the pure substance routinely in 20% yield. Separation from concomitantly produced photocitral-B (**6**) was accomplished by careful fractional distillation. It is noteworthy that, while three asymmetric centers are created in the photochemical reaction, only one monocyclic product was observed. Only two of the four diastereomers of photocitral-A seem useful in the synthesis of the furopelargones (**1**) and (**2**), and the configuration of the only known isomer had to be ascertained. Mechanistic reasoning previously[4] led to the plausible suggestion that methyl and isopropenyl substituents have a *trans* relationship but the configuration of the formyl group remained unknown. If one makes the purely hypothetical assumption that cyclization occurs within the triplet state of the α,β-unsaturated aldehyde the geometry of the resulting product is dictated by the conformation of one of the two relevant transition states **7** or **8**.[5] Steric crowding clearly is less severe in conformer **7** than in **8**, and photo-



7 **8**

citral-A should have configuration **9**. The following facts seem to support this assignment. Treatment of photocitral-A (**9**) with sodium methoxide in methanol solution resulted in a mixture containing 60% of the original aldehyde (**9**) and 40% of its epimer (**10**). An identical mixture of isomers was produced on equilibration of epiphotocitral-A (**10**). Analogous experiments in the dihydro series[4] furnished mixtures containing 75% of dihydrophotocitral-A (**11**) and 25%



9 **10** **11** **12**

of epidihydrophotocitral-A (**12**). These findings strongly suggest *trans* orientation of the two alkyl groups. The configuration of the formyl group is established if the relative size of substituents does indeed decrease in the order isopropyl > isopropenyl > methyl. Experimental evidence concerning the steric requirements of the two saturated substituents agrees with this assumption.[6,7] Photocitral-A (**9**) consequently is a suitable precursor for furopelargone-A (**1**) and the next phase of the synthesis was concerned with its conversion to the diketoaldehyde (**19**).

Condensation with *t*-butyl α-bromoisovalerate and zinc resulted in smooth conversion to a mixture of hydroxyesters (**13**). Two new asymmetric centers were created in this transformation and the vapor phase chromatogram of the reaction product did in fact reveal four components. The hydroxyesters (**13**) were transformed to the β-ketoesters (**14**) by oxidation with chromium trioxide in acetone solution.[8] Both infrared and ultraviolet spectra suggested that the β-ketoesters (**14**) existed entirely as such and the tautomeric enol forms were not detectable. A molecular model leaves no doubt that the enols represent more crowded structures and this factor might contribute to the higher stability of the ketonic modifications. Although it was not possible to demonstrate the presence of more than one ketoester vapor chromatographically the n.m.r. spectrum was in better agreement with the presence of a mixture of diastereomers. At this point it became of importance to ascertain the configuration at C-1 because the neighboring carbonyl group present in the ketoesters (**14**) could allow inversion at this center. Pyrolysis of the *t*-butyl ester (**14**) at 220° produced a *single* substance whose spectral properties agreed with structure **15**. Epimerization of this ketone (**15**) was accomplished again with sodium methoxide in methanol solution, and at equilibrium the mixture contained approximately 80% of the original ketone (**15**) and 20% of the epiketone **16**. An identical mixture was obtained when the epiketone **16** was subjected to this treatment and it was concluded that both ketoesters (**14**) had retained the desired configuration at C-1. The mixture of β-ketoesters was then allowed to react with sodium hydride in dimethylformamide solution and, when hydrogen evolution had ceased, allyl bromide was added. Although the resulting substitution product appeared homogeneous in vapor phase chromatograms the formation of a single diastereomer is unlikely and the n.m.r. spectrum did support

(4) R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron Letters*, 79 (1962); *Tetrahedron*, **19**, 1995 (1963). We are indebted to Professor R. C. Cookson for sending us a manuscript of the detailed paper prior to its publication.

(5) According to H. L. McMurry, *J. Chem. Phys.*, **9**, 241 (1941), the unpaired electrons in the triplet state of an α,β-unsaturated carbonyl group are located in noninteracting orthogonal orbitals.

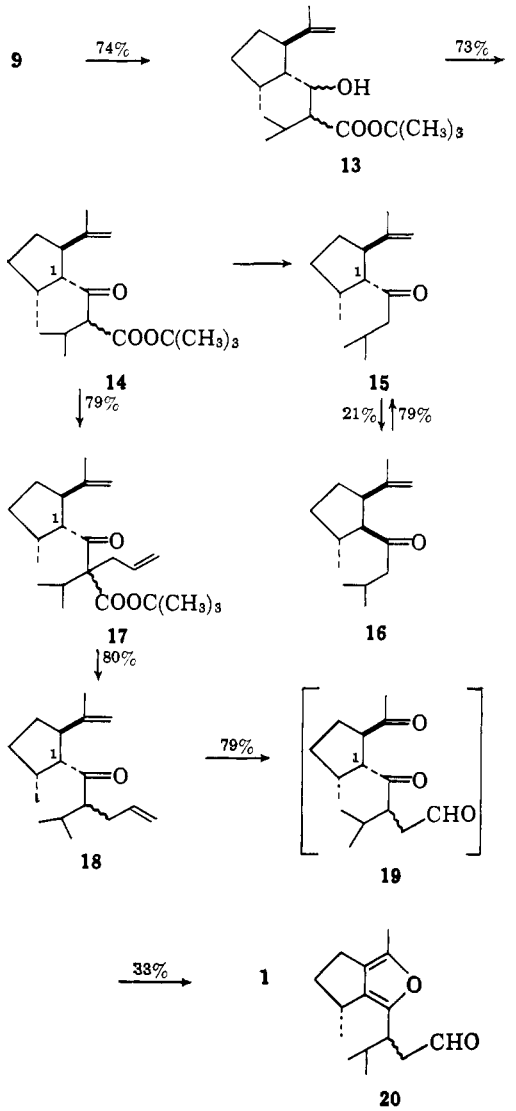
(6) B. J. Armitage, G. W. Kenner, and M. J. T. Robinson, *Tetrahedron*, **20**, 747 (1964); N. L. Allinger, L. A. Freiberg, and S.-E. Hu, *J. Am. Chem. Soc.*, **84**, 2837 (1962).

(7) R. B. Bates, E. J. Eisenbraun, and S. A. McElvain, *ibid.*, **80**, 3413 (1958), have investigated the relative stabilities of the methyl esters of the epimeric 3-methylcyclopentane-1,2-dicarboxylic acids.

(8) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

this contention. It was now necessary to remove the carbo-*t*-butoxy grouping and in planning the synthesis the *t*-butyl ester was chosen because it was expected to undergo facile fragmentation to the ketone (**18**) on heating without migration of double bonds.

Pyrolysis of the β-ketoester **17** was complete within a few minutes at 280° and the resulting product (**18**) was produced in high yield. A vapor phase chromatogram showed a single, but broad peak and the "methyl region" of the n.m.r. spectrum again indicated the presence of a mixture of diastereomers. In an attempt to elucidate the configuration at C-1, the unsaturated ketone **18** was equilibrated as previously



described, but unfortunately the vapor phase chromatogram of the resulting product was indistinguishable from that of the starting material. Treatment with sodium methoxide in deuteriomethanol furnished a sample whose mass spectrum revealed the presence of comparable amounts of mono- and dideuterated ketones. Consequently enolization toward C-1 did occur at least partly and it must be concluded that (a) the two C-1 epimers were not separated in the gas chromatogram or (b) that the equilibrium is very much in favor of the desired isomer **18**. We prefer the latter of these alternatives because the three other pairs of C-1 epimers encountered in this synthesis were all readily separable by vapor phase chromatography.

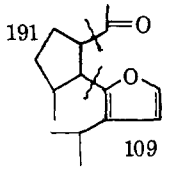
Oxidation of the dienone (**18**) with osmium tetroxide–sodium periodate led to no useful result but ozonization[9] gave the diketoaldehyde **19** which was not isolated in pure form. Dehydration in hot acetic acid containing some acetic anhydride produced a mixture of liquid products which could be separated into individual components by adsorption or gas–liquid chromatography. The major product was indistinguishable from natural furopelargone-A (**1**) in the vapor chromatogram and on thin layer chromatography. Both infrared and nuclear magnetic resonance spectra of the synthetic sample were identical in detail with those of authentic[10] furopelargone-A (**1**). The vapor chromatographic retention time of the minor product corresponded to that of natural furopelargone-B (**2**) and identity was confirmed by comparison of infrared spectra and R_f values in thin layer chromatograms. In agreement with anticipation the highly strained isomer **20** was not observed. This final reaction clearly involved partial equilibration of the two furopelargones (**1** and **2**), and when each isomer was equilibrated separately with sodium methoxide in methanol solution identical mixtures containing approximately 94% furopelargone-A (**1**) and 6% furopelargone-B (**2**) were obtained. It may be argued that the intermediate diketoaldehyde (**19**) in hot acetic acid had ample opportunity to undergo epimerization at both asymmetric centers adjoining carbonyl groups and thus give an isomer of the furopelargones with *trans, trans* configuration. Such a change would involve epimerization at two asymmetric centers. When the dehydration of the diketoaldehyde **19** was performed in deuterioacetic acid a mixture of deuterated furopelargones was obtained, and a mass spectrometric analysis revealed the presence of approximately 7% nondeuterated, 30% mono-, 36% di-, 20% tri-, and 5% tetradeuterated ketones.[11] If isomerization to the *trans,trans* isomer had indeed occurred the resulting furopelargone should have contained a minimum of two deuterium atoms, yet the figures quoted show that 37% of the product had incorporated less than two deuterium atoms. In a separate experiment furopelargone-A (**1**) was heated in deuterioacetic acid at the same temperature for the same length of time. The resulting mixture of isotopically labeled substances contained 25% nondeuterated, 44% mono-, 25% di-, 6% tri-, and 1% tetradeuterated ketone. Consequently, the material obtained by cyclization of the diketoaldehyde **19** had incorporated roughly one deuterium atom more than that prepared by hydrogen–deuterium exchange of furopelargone-A (**1**), and inspection of the fragments *m/e* 109, 110, and 111 (isopropylfuran and deuterated analogs) allowed the location of the extra deuterium atom in the furan ring. This situation can be rationalized if one makes the reasonable assumption that the aldehyde function in the precursor **19** is in rapid and reversible equilibrium with the corresponding sterically unhindered enol. Reconversion to the aldehyde followed by dehydration results in an α-deuterated furan. The mass spectra of the furopelargones (**1** and **2**) contain an important

(9) P. S. Bailey, *Chem. Ber.*, **88**, 795 (1955)

(10) We wish to thank Drs. R. E. Wolff and G. Lukas, Gif-sur-Yvette, France, for samples of natural furopelargones.

(11) We are indebted to Professor K. Biemann, Mr. H. Schnoes, and Dr. S. A. Monti for the mass spectral data.

peak at *m/e* 191 which results from ejection of an acetyl group. This fragment was accompanied by others at *m/e* 192, 193, and 194 in the spectra of the two deuterated ketones under discussion, and intensity measurements showed that 14% of the mixture originating from the diketoaldehyde (**19**) contained *no* label. This finding again demonstrated that the diketoaldehyde (**19**) and furopelargone have identical configurations at the three asymmetric cyclopentane carbon atoms.



mol. wt. = 234

In conclusion it should be mentioned that the furopelargones represent crowded molecules and, although Briegleb molecular models indicate restricted rotation around the bond joining furan and cyclopentane rings, no atropisomers were encountered.

Experimental

Microanalyses were performed by the Midwest Microlab, Inc., Indianapolis, Ind. Infrared spectra were taken in chloroform solution on a Perkin-Elmer Model 237 spectrophotometer. The n.m.r. spectra were measured in deuteriochloroform on a Varian A-60 instrument and chemical shifts are reported in p.p.m. (δ) downfield from an internal tetramethylsilane reference. Boiling points are not corrected. Columns of silicone rubber gum SE-30 and tricyanoethoxypropane (TCEP) were used for vapor phase chromatography. The purity and identity of compounds was determined routinely by thin layer chromatography.

Photocitral-A (**9**). A solution of citral (20 g.) in ethanol (180 ml.) was placed in a water-cooled irradiation vessel. The solution was purged with nitrogen gas and irradiated with a 450-w. Hanovia mercury arc lamp for 20 hr. The solvent was removed *in vacuo* and the residues from 22 batches were combined and distilled. The product distilling between 100 and 108° (10 mm.), 276 g., was fractionated further on a spinning-band column to give 77.3 g. (18%) of photocitral-A (**9**), b.p. 87° (8 mm.); $\nu_{max}^{CHCl_3}$ (cm.$^{-1}$) 3070, 2715, 1720, 1640, and 890; n.m.r. absorptions at δ 4.9 (2 H, multiplet), 1.75 (3 H, multiplet), 1.1 (3 H, doublet, J = 7 c.p.s.), and 9.6 (1 H, doublet, J = 2.5 c.p.s.).

Equilibrium between Photocitral-A (**9**) *and Epiphotocitral-A* (**10**). To a solution of sodium methoxide (100 mg.) in methanol (1 ml.) was added photocitral-A (106 mg.). The mixture was allowed to stand under a blanket of nitrogen for 18 hr. at room temperature. It was then diluted with water, extracted with ether, washed with water, and dried over sodium sulfate. Evaporation of the solvent left a residue (89 mg.) which on vapor phase chromatography (TCEP column) showed two peaks in the ratio 38:62. The peak with the higher retention time corresponded to photocitral-A (**9**). Epiphotocitral-A (**10**) was collected from v.p.c. using the same column and treated again with sodium methoxide solution. A gas chromatogram of the resulting product revealed two components in the ratio 41:59. The retention times were identical with those of epiphotocitral-A (**10**) and photocitral-A (**9**), respectively. The former aldehyde had $\nu_{max}^{CHCl_3}$ (cm.$^{-1}$) 3070, 2720, 1718, 1645, and 905; n.m.r.: δ 1.1 (3 H, doublet, J = 6 c.p.s.); 4.8 (2 H, broad); and 9.5 (1 H, doublet, J = 3 c.p.s.).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.83; H, 10.45.

Equilibrium between Dihydrophotocitral-A (**11**) *and Its Epimer* (**12**). Dihydrophotocitral-A (**11**)[4] was treated with sodium methoxide in methanol solution as described above. A mixture containing 75% of dihydrophotocitral-A (**11**) and 25% of epidihydrophotocitral-A (**12**) was obtained. Treatment of the pure epimer (**12**) under identical conditions gave the same mixture. Epidihydrophotocitral was collected from a gas chromatogram and had n.m.r. absorption at δ 0.82 (3 H, doublet, J = 6.5 c.p.s.); 0.9 (3 H, doublet, J = 6.5 c.p.s.); 1.05 (3 H, doublet, J = 6 c.p.s.); and 9.83 (1 H, doublet, J = 3 c.p.s.).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.82; H, 11.91.

Hydroxyesters **13**. To a suspension of granular zinc[12] (21 g., 0.32 g.-atom) 30 mesh, in dry benzene (400 ml.), was added *t*-butyl α-bromoisovalerate (69 g., 0.29 mole) and photocitral-A (44.3 g., 0.29 mole). The mixture was stirred and allowed to reflux under nitrogen for 4 hr. It was then cooled and decomposed with saturated ammonium chloride solution. The benzene layer was separated and the aqueous solution was extracted twice with ether. All organic layers were combined, washed with water, dried over sodium sulfate, and evaporated. The remaining oil (94 g.) was distilled to yield 66.9 g. (74%) of hydroxyester **13**, b.p. 108–111° (0.2 mm.), $n^{25}D$ 1.4635. Vapor phase chromatography (TCEP column) showed four components and the mixture had $\nu_{max}^{CHCl_3}$ (cm.$^{-1}$) 3510, 1705, 1640, and 890.

Anal. Calcd. for $C_{19}H_{34}O_3$: C, 73.50; H, 11.04. Found: C, 73.27; H, 11.04.

Ketoesters **14**. Hydroxy ester **13** (26.0 g., 0.084 mole) was dissolved in acetone (400 ml.) and the resulting solution was stirred vigorously. A mixture of 8.4 g. (0.084 mole) of chromium trioxide and concentrated sulfuric acid (7.2 ml.) in water (45 ml.) was added over a period of 5 min. at 15–18°. Stirring was continued for 45 min. at room temperature and, after a solution of sodium bicarbonate (25 g.) in water (400 ml.) was added, the acetone was removed *in vacuo* at 30–40°. The mixture was extracted with pentane and the pentane layer was shaken with 2 *N* sodium carbonate and with water, dried over sodium sulfate, and evaporated. Distillation of the residue (24.4 g.) afforded 18.9 g. (73%) of ketoester **14**, b.p. 112–114° (0.2 mm.); $n^{25}D$ 1.4608; $\nu_{max}^{CHCl_3}$ (cm.$^{-1}$) 1725, 1705, 1640, and 895.

Anal. Calcd. for $C_{19}H_{32}O_3$: C, 73.98; H, 10.46. Found: C, 73.75; H, 10.51.

Ketone **15**. A sample of the ketoester **14** (845 mg.) was placed in a distillation flask. After the air in the flask had been displaced by nitrogen the compound was heated to 220–240° for 15 min. The pyrolysate was then distilled and the first fraction, 220 mg., b.p. 80° (bath temperature, 0.2 mm.), consisted of ketone **15**, $\nu_{max}^{CHCl_3}$ (cm.$^{-1}$) 3060, 1705, 1640, and 890; n.m.r. absorp-

(12) The zinc used was previously washed with HCl (2%), water, and finally with acetone. It was then dried at 100° (0.2 mm.).

tions at δ 0.8 (6 H, doublet, J = 6.5 c.p.s.), 0.9 (3 H, doublet, J = 6.5 c.p.s.), 1.66 (3 H, singlet with fine splitting), and 4.6 (2H, broad).

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.89; H, 11.49.

A second fraction (180 mg.), b.p. 100–120°, contained mostly starting material. When treated with sodium methoxide in methanol solution as described above, the ketone (**15**) gave an equilibrium mixture containing 21% of **16** and 79% of **15**. Repetition of this equilibration using the pure epimer **16** gave an identical mixture.

Substituted Ketoester **17**. Ketoester **14** (7.05 g., 0.023 mole) in dry dimethylformamide (5 ml.) was added over a period of 1 hr. to a stirred suspension of sodium hydride (0.82 g., 0.034 mole) in dimethylformamide (30 ml.). The reaction was carried out under nitrogen at room temperature. After hydrogen evolution had ceased (about 2 hr.) allyl bromide (4.06 g., 0.034 mole) was added in the course of 1 hr. and stirring was continued at room temperature for 2 hr. The resulting mixture was poured onto ice and extracted with pentane, and the pentane layer was washed with water, dried over sodium sulfate, and evaporated. Distillation of the remaining oil (8.27 g.) gave 6.28 g. (79%) of ketoester **17**, b.p. 109–112° (0.1 mm.), which contained 9% of starting material (vapor phase chromatography). A pure sample was obtained by chromatography on silicic acid using benzene as eluent. It had $n^{26}D$ 1.4767; $\nu_{max}^{CHCl_3}$ (cm.$^{-1}$) 3060, 1720, 1695, 1640, 985, 925, and 905.

Anal. Calcd. for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41. Found: C, 75.76; H, 10.39.

Ketone **18**. Ketoester **17** (8.88 g.) was placed in a Pyrex round-bottomed flask under nitrogen. The flask was then dipped into an oil bath which was preheated to 280°. Decomposition started within 2 min. and after 15 min. the evolution of gas had essentially ceased. Distillation of the pyrolysis product (6.41 g.) yielded 5.03 g. (79%) of ketone (**18**), b.p. 75–78° (0.1 mm.); $n^{26}D$ 1.4757; $\nu_{max}^{CHCl_3}$ 3080, 1640, 1700, 995, 920, and 900 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.42; H, 11.53.

Deuteration of Ketone **18**. Sodium (130 mg.) was dissolved in deuterioethanol (3 ml.) and ketone **18** (100 mg.) was added. The solution was allowed to stand under nitrogen at room temperature for 18 hr. It was then poured into water and extracted with ether, and the ether layer was washed with water and dried over sodium sulfate. After evaporation, the remaining oil (100 mg.) was distilled to give 72 mg. of deuterated ketone (**18**), b.p. 80° (bath temperature, 0.2 mm.). A mass spectrum suggested the presence of approximately 30% of non-, 40% of mono-, and 30% of dideuterioketones.

Diketoaldehyde **19**. An excess of ozone was passed through a solution of ketone **18** (1.95 g.) in methanol (20 ml.) at −40°. The solution was then added to a cooled mixture of potassium iodide (9 g.) in methanol (18 ml.) and acetic acid (6 ml.). After 20 min. at room temperature, the iodine was reduced with sodium thiosulfate (7 g.) in water (30 ml.) and the methanol was removed at 30° *in vacuo*. The residue was extracted with ether, and the ether layer was washed with 2 *N* sodium carbonate and with water, dried over sodium sulfate, and evaporated. The remaining oil (1.92 g.) was distilled to give 1.56 g. (79%) of ketoaldehyde, b.p. 120° (bath temperature, 0.2 mm.); infrared bands at 2720, 1725, and 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 70.81; H, 9.50.

Furopelargone-A (**1**) *and -B* (**2**). A mixture of the diketoaldehyde **19** (1.56 g.) in glacial acetic acid (16 ml.) and acetic anhydride (1.5 ml.) was allowed to reflux under nitrogen for 2 hr. The dark brown solution was cooled, poured onto ice, and extracted with pentane. The organic layer was washed with 2 *N* sodium carbonate and with water. It then was dried over sodium sulfate and evaporated. The residue (1.49 g.) was distilled to give 981 mg. of a mixture, b.p. 100° (bath temperature, 0.1 mm.), containing approximately 74% of furopelargone-A and 3% of furopelargone-B (vapor phase chromatography). The original mixture was purified by chromatography on 30 g. of silicic acid (Mallinckrodt, 100 mesh). Benzene eluted 485 mg. of pure furopelargone-A (34%), b.p. 100° (bath temperature, 0.1 mm.); $n^{17}D$ 1.4853. The material had the same retention time on v.p.c. (silicone rubber and TCEP column) and the same R_f value on a thin layer plate (silicic acid; solvent: hexane–ethyl acetate 80:20) as natural furopelargone-A. Its infrared and n.m.r. spectra were superimposable on those of the natural product.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.08; H, 9.72.

Treatment of a sample of furopelargone-A (**1**) with sodium methoxide in methanol solution produced a mixture containing 94% of furopelargone-A (**1**) and 6% of furopelargone-B (**2**) (estimated by gas chromatography). Furopelargone-B (**2**) was obtained on v.p.c. collection from the last fraction of the chromatogram described above (elution with benzene–ethyl acetate 80:20). The substance was identical in retention time, R_f, and infrared spectrum with natural furopelargone-B (**2**).

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