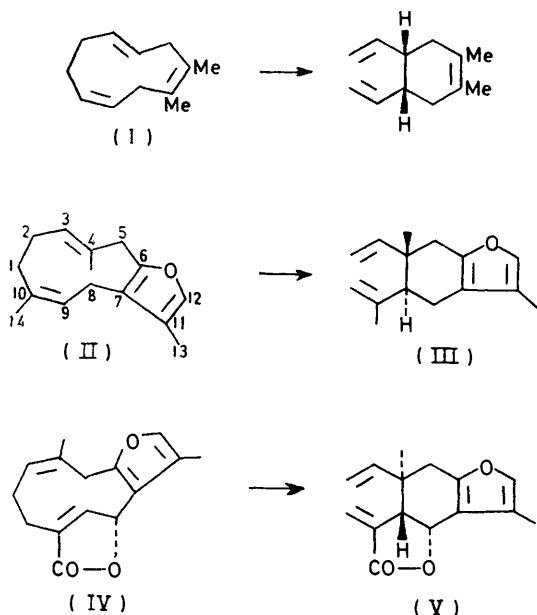


## Cope Rearrangement of Some Germacrane-type Furan Sesquiterpenes. Part V.<sup>1</sup> Preparation and Thermal Rearrangement of Some *cis,trans*-Germacranolides

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The *cis,trans*-germacranolides (3*Z,9E*)-8-acetoxy-6-hydroxygermacra-3,9-dien-12-oic acid  $\gamma$ -lactone (VIIIa) and its deacetoxy-derivative (VIIIb) were synthesized by sensitized photoisomerization of their 3*E,9E*-isomers [dihydrolaurenobiolide (VIIa) and its deacetoxy-derivative (VIIc)]. Cope rearrangements of (VIIIa and b) and the related alcohols (3*Z,9E*)-germacra-3,9-diene-6,8,12-triol (IXa) and (3*Z,9E*)-germacra-3,9-diene-6,12-diol (IXb) established that the presence of a fused five-membered ring at positions 6 and 7 in the *cis,trans*-cyclodecadiene derivatives has an important effect on the rearrangement. The c.d. spectra of these and some reference compounds indicate that the stereochemistry of the Cope-rearrangement products can be deduced from the signs of the c.d. couplet of the cyclodecadiene.

THE *trans,trans*-cyclodeca-1,5-diene system is known to undergo Cope rearrangement to give a *trans*-1,2-divinylcyclohexane, whereas the *cis,trans*-cyclodeca-1,5-diene system gives a *cis*-1,2-divinyl derivative; in particular (1*Z,4Z,8E*)-1,2-dimethylcyclodeca-1,4,8-triene<sup>2</sup> (I) gives a *cis*-1,2-divinylcyclohexane. We have reported<sup>1,3</sup> that the *cis,trans*-cyclodeca-1,5-diene-type furan sesquiterpenes *cis,trans*-furanodiene (II) and neolinderalactone (IV) undergo abnormal Cope rearrangement to give the *trans*-1,2-divinylcyclohexane derivatives isofuranogerma-crene (III) and isolinderalactone (V), respectively, and



that the abnormality is caused not by the methyl groups on the 3,4- and 9,10-double bonds † but by the five-membered nature of the aromatic furan ring. Therefore, we thought it interesting to examine the stereochemistry of Cope rearrangement of some *cis,trans*-germacranolides, in which the furan ring is replaced by a

† For numbering system see formulae (II) and (VI).

<sup>1</sup> Part IV, K. Takeda, I. Horibe, and H. Minato, *J.C.S. Perkin I*, 1973, 2212.

<sup>2</sup> P. Heimbach, *Angew. Chem. Internat. Edn.*, 1964, **3**, 702; W. Brenner, P. Heimbach, and G. Wilke, *Annalen*, 1969, **727**, 194.

<sup>3</sup> K. Takeda, I. Horibe, and H. Minato, *J. Chem. Soc. (C)*, 1970, 2704.

$\gamma$ -lactone ring. We now describe the syntheses and thermal rearrangements of *cis,trans*-germacranolides, and the use of their c.d. spectra in interpreting the effect of the five-membered ring on the Cope rearrangement.

We recently reported the elucidation of the structure of laurenobiolide (VI), isolated from *Laurus nobilis* L., and the Cope rearrangement of dihydrolaurenobiolide (VIIa).<sup>4</sup> As (VIIa) has a  $\gamma$ -lactone ring at positions 6 and 7, geometrical isomerization of (VIIa) would give a *cis,trans*-cyclodecadiene derivative having a  $\gamma$ -lactone ring at the same position as the furan ring in (IV). We therefore examined the sensitized photoisomerization of (VIIa) by a method reported previously.<sup>1</sup>

Upon irradiation in benzene in the presence of acetophenone, dihydrolaurenobiolide (VIIa) was isomerized to compound (VIIIa). To determine the geometry of the two double bonds in (VIIIa), application of the intramolecular nuclear Overhauser effect (n.O.e.)<sup>5</sup> was attempted. However, this was inadequate because in the n.m.r. spectrum of (VIIIa) the vinylic 3- and 9-proton signals mutually overlap in several solvents. In such cases, simultaneous application<sup>6</sup> of n.O.e. and a lanthanide shift reagent<sup>7</sup> is reported to be useful. N.O.e. measurements were therefore performed on a solution of (VIIIa) in [<sup>2</sup>H]chloroform containing 0.18 mol. equiv. of [<sup>2</sup>H<sub>27</sub>]Eu(fod)<sub>3</sub>. Saturation of the 4-Me signal ( $\delta$  1.92) by double irradiation caused a considerable increase (20%) in the 3-H signal ( $\delta$  5.36), while saturation of the 10-Me signal ( $\delta$  2.04) caused no increase in the 9-H signal ( $\delta$  5.76). These results indicated that (VIIIa) should possess a *cis*-3,4- and a *trans*-9,10-double bond.

The Cope rearrangement of (VIIIa) was then investigated, in view of the observation that (VIIa) is readily rearranged to give an equilibrium mixture<sup>4</sup> of starting material (VIIa) and a *trans*-1,2-divinyl derivative (XIa) in a ratio of 3 : 2 on heating at 205°. When (VIIIa) was heated at 175° for 2 h, it remained unchanged. However, when it was heated at 200° for

<sup>4</sup> H. Tada and K. Takeda, *Chem. Comm.*, 1971, 1391.

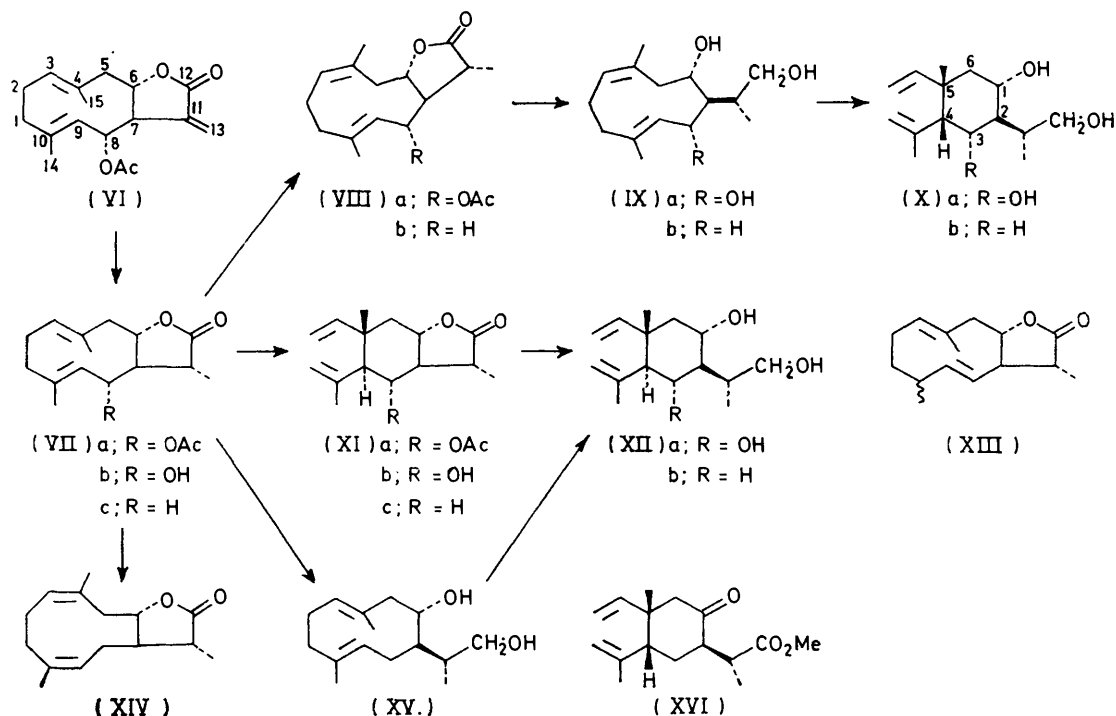
<sup>5</sup> J. A. Noggle and R. E. Schirmer, 'The Nuclear Overhauser Effect; Chemical Applications,' Academic Press, New York, 1971.

<sup>6</sup> K. Tori, I. Horibe, Y. Tamura, and H. Tada, *J.C.S. Chem. Comm.*, 1973, 620.

<sup>7</sup> For a review, see B. C. Mayo, *Chem. Soc. Rev.*, 1973, **2**, 49.

30 min, the acetoxy-group was eliminated. We therefore cleaved the lactone ring in (VIIIa) and subjected the product to the rearrangement. Treatment of (VIIIa) with lithium aluminium hydride gave the corresponding triol (IXa), which readily gave a Cope-rearrangement product (Xa) when heated at 175° for 2 h. To elucidate the stereochemistry of (Xa), the *trans*-1,2-divinylcyclohexane derivative (XIIa) was prepared, by reduction of (XIa) with lithium aluminium hydride. The i.r. and n.m.r. spectra of (Xa) were similar to, but not identical with, those of (XIIa), thus establishing that (Xa) was an isomeric *cis*-1,2-divinylcyclohexane derivative. The n.m.r. spectrum of (Xa) in [2H]chloroform exhibited the 3-H signal ( $\delta$  3.88) as a doublet of doublets, with splittings (11.5 and 6.0 Hz) showing the torsion angles between C(3)-H and C(2)-H

The acetoxy-group in (VIIIa) was eliminated by reduction with lithium in liquid ammonia, followed by oxidation with Collins reagent. The product (VIIIb) showed acceptable i.r. and n.m.r. spectra; however, since the yield was rather poor, the acetoxy-group of dihydrolaurenobiolide (VIIa) was eliminated in the same manner. This yielded the expected (3*E*,9*E*)-6-hydroxygermacra-3,9-dien-12-oic acid  $\gamma$ -lactone (VIIc), along with a double-bond isomer (XIII). The n.m.r. spectrum of (XIII) showed signals of the AB type ( $\delta$  5.00 and 5.83, *J* 15.5 Hz) attributed to two protons on a newly formed *trans*-disubstituted double bond, and no signals due to the acetoxy-group, in agreement with the assigned structure. To obtain the geometrical isomer of (VIIc), sensitized photoisomerization was carried out. Upon irradiation under the same conditions as those used for



and between C(3)-H and C(4)-H to be *ca.* 180 and *ca.* 40°, respectively. Tada and Takeda<sup>4</sup> recently established that the hydrogen atom at C-8 is  $\beta$ -oriented in dihydrolaurenobiolide (VIIa); thus the configuration of the hydrogen atom at C-8 in (VIIIa) or (IXa) is  $\beta$ , and that of the hydrogen at C-3 in (Xa) is also  $\beta$ . The hydrogen atom at C-4 in (Xa) therefore has the  $\beta$ -configuration; thus the angular methyl group at C-5 also has the  $\beta$ -configuration. The above data show that the rearrangement product is a *cis*-elemene derivative (Xa), a normal Cope rearrangement product.

These results suggest that the presence of a  $\gamma$ -lactone ring at positions 6 and 7 has an important effect on the Cope rearrangement of *cis,trans*-cyclodecadiene derivatives. In order to confirm this, we examined the thermal rearrangement of a more simple derivative (VIIIb).

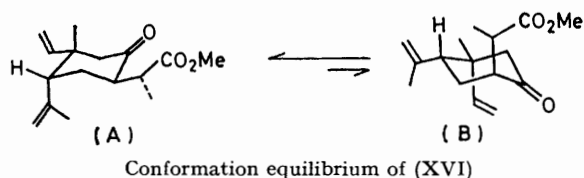
(VIIa), (VIIc) was transformed into two photoisomers, (VIIIb) and (XIV). The former was identical with the *cis,trans*-cyclodecadiene derivative derived from (VIIIa) (mixed m.p. and i.r. spectrum). The other isomer (XIV) was shown to be a geometrical isomer of (VIIc) by n.m.r. (two vinylic protons at  $\delta$  5.03 and  $\delta$  5.25): n.o.e. measurements in [2H<sub>6</sub>]benzene indicated that a vinylic methyl group ( $\delta$  1.55) and a vinylic proton ( $\delta$  5.03) are in a *cis*-relationship (n.o.e. value 20%), as are another vinylic methyl group ( $\delta$  1.68) and vinylic proton ( $\delta$  5.25) (n.o.e. value 19%), thus confirming that compound (XIV) is (3*Z*,9*Z*)-6-hydroxygermacra-3,9-dien-12-oic acid  $\gamma$ -lactone.

The deacetoxy-compounds (VIIc) and (VIIIb) and the corresponding diols (XV) and (IXb) were subjected to the rearrangement to clarify the effect of the  $\gamma$ -lactone ring. The *trans,trans*-diene derivatives (VIIc) and (XV)

underwent Cope rearrangement when heated in a sealed tube, to yield the *trans*-1,2-divinylcyclohexane derivatives (XIc) and (XIIb), respectively. The stereochemistry of both rearrangement products was confirmed by the following reactions.

When the deacetyl derivative (VIIb) of (VIIa) was heated at 220° for 10 min, it gave an alcohol (XIb) whose acetate was identical with the *trans*-1,2-divinylcyclohexane derivative (XIa).<sup>4</sup> Reduction of the mesylate of (XIb) with lithium in liquid ammonia gave a diol (XIIb), which was identical with the rearrangement product of (XV). This diol was also obtained from the other rearrangement product (XIc) by lithium aluminium hydride reduction. These data clearly define the stereochemistry of both Cope products as *trans*-1,2-divinylcyclohexane derivatives (XIc) and (XIIb).

On the other hand, the *cis,trans*-diene derivative (VIIIb) having a  $\gamma$ -lactone ring was converted, on heating at 200° for 30 min, into an oil which was not a Cope rearrangement product. The n.m.r. spectrum of the product showed signals for two vinylic methyl groups at  $\delta$  1.64 and 1.70 and two vinylic protons (at  $\delta$  5.37 and 5.54), indicating that the ten-membered ring still remained. Therefore, this product can be assumed to be a double-bond isomer of (VIIIb). However, (IXb) rearranged readily when heated at 170° in a sealed tube, to give a Cope product (Xb), whose i.r. and n.m.r. spectra corresponded to, but were not identical with, those for (XIIb); thus we assumed that (Xb) was a *cis*-1,2-divinylcyclohexane derivative. The stereochemistry of (Xb) was deduced as follows. Oxidation of (Xb) with Jones reagent gave an oxo-carboxylic acid, which was converted into an oxo-ester (XVI). The c.d. spectrum of (XVI) showed weak negative and positive effects at 270 and 305 nm, respectively. The observed sign and magnitude were compatible with those expected from the octant rule for two possible conformational isomers (A) and (B) for (XVI). The result was supported by the variable-temperature c.d. spectra. Thus the stereochemistry of the Cope product (Xb) was confirmed.

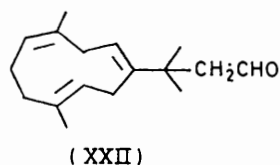
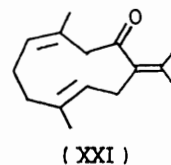
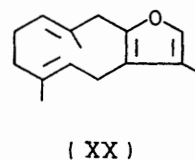
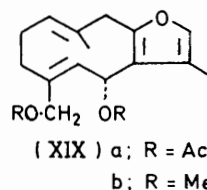
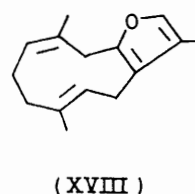
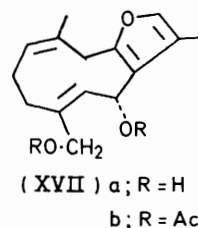


We thus showed that the *cis,trans*-derivatives (VIIIa) and (VIIIb), which have a  $\gamma$ -lactone ring at positions 6 and 7, did not undergo Cope rearrangement, whereas the *cis,trans*-alcohols (IXa) and (IXb), in which the lactone ring had been reductively cleaved, underwent normal Cope rearrangement in the same way as (I), giving a *cis*-1,2-divinylcyclohexane derivative. These results led us to conclude that the presence of a  $\gamma$ -

<sup>8</sup> K. Takeda, I. Horibe, and H. Minato, *J. Chem. Soc. (C)*, 1970, 1142.

lactone ring has an important effect on the Cope rearrangement of *cis,trans*-cyclodecadiene derivatives. We therefore decided to examine the rearrangement of (3*Z*,9*E*)-6,12-epoxygermacra-3,6,9,11-tetraene (XVIII) for direct comparison of the effect of the furan ring with that of the  $\gamma$ -lactone ring.

When the diacetate (XVIIb) of (XVIIa)<sup>3</sup> derived from (IV) was reduced with lithium in liquid ammonia, it gave the *cis,trans*-furanodiene (XVIII), the structure of which was confirmed by the observation of a considerable n.o.e. (ca. 20%) between the 4-Me signal ( $\delta$  1.53) and 3-H signal ( $\delta$  5.01), but not between the



10-Me signal ( $\delta$  1.68) and the 9-H signal ( $\delta$  5.15). Similar reduction of the diacetate (XIXa)<sup>8</sup> gave the *trans,trans*-furanodiene, identified as the natural isofuranodiene (XX) reported by Rucker *et al.*<sup>9</sup>

The isofuranodiene (XX) easily underwent Cope rearrangement when heated at 160° for 1 h in a sealed tube, to give isofuranogermacrene (III) in quantitative yield, whereas the *cis,trans*-furanodiene (XVIII) remained unchanged under the same conditions. However, when heated at 200° for 30 min, (XVIII) gave an abnormal Cope-rearrangement product which was found to be identical with isofuranogermacrene (III) by g.l.c.-mass spectrometry. This result agreed well with those for (II) and (IV). Since we have previously reported<sup>1</sup> that the two compounds (XXI) and (XXII) which correspond to the furan-cleavage product of (XIII) undergo normal Cope rearrangement to yield *cis*-1,2-divinylcyclohexane derivatives, the above observations reveal that the abnormal rearrangement of (XVIII) probably is caused by the presence of a five-membered furan ring. This result is compatible with those for (VIIIa and b) which have a  $\gamma$ -lactone ring, and

<sup>9</sup> G. Rucker, G. A. de Assis Brasil e Silva, and L. Bauer, *Phytochemistry*, 1971, 10, 221.

leads us to attribute the abnormal rearrangement of the *cis,trans*-cyclodeca-1,5-diene-type furan sesquiterpenes (II) and (IV) to the five-membered nature of the furan ring.

In an attempt to understand the effects of the five-membered ring, we examined the c.d. spectra of various cyclodeca-1,5-diene derivatives.

The Cope rearrangement of cyclodeca-1,5-diene derivatives is known to proceed through a transition state having a four-centre, chair-like geometry. Hence, if the ground-state conformation of the ten-membered ring is geometrically closely related to that of the transition state, Cope rearrangement would readily occur. In such a ground-state conformation, because the two nonconjugated double bonds are in close proximity, their  $\pi$ - $\pi^*$  transitions may interact with each other. It would therefore be expected that the c.d. spectra of cyclodecadienes would show a c.d. couplet near 200 nm, mainly due to exciton splitting.<sup>10</sup> The Table summarizes the results of our c.d. measurements.

C.d. data of some cyclodeca-1,5-diene derivatives

Compound	$\lambda$ /nm ( $\Delta\epsilon$ )	Solvent <sup>a</sup>
<i>trans,trans</i> -Cyclodecadienes		
(VIIa)	216 (+33.8)      200 (-10.9) <sup>b</sup>	EtOH
(VIIb)	215 (+30.6)      198 (-10.3) <sup>b</sup>	EtOH
(XV)	232.5 (+1.03)    217 (-7.97)	EtOH
	197 (+2.93) <sup>b</sup>	
(XIXb) <sup>8</sup>	215 (+10.6)      205 (-9.09) <sup>b</sup>	EPA
(XXIII) <sup>8</sup>	212 (+5.06)      194 (-28.3)	EtOH
(XXIV) <sup>12</sup>	221.5 (+28.2)    205 (-8.24) <sup>b</sup>	EtOH
(XXV) <sup>c</sup>	217.5 (+20.3)    194 (-12.7)	EtOH
(XXVIa) <sup>13</sup>	224 (-24.7)      201.5 (+29.0)	Iso-octane
(XXVIIb) <sup>13</sup>	225 (-27.5)      200 (+41.3)	MeOH
(XXVII) <sup>14</sup>	231 (-9.39)      208 (+12.6)	Iso-octane
<i>cis,trans</i> -Cyclodecadienes		
(VIIIa)	203.5 (-27.1)	EtOH
(VIIIb)	204 (-20.0)	EtOH
(IXa)	206 (-35.5)      190 (+20.0) <sup>b</sup>	EtOH
(IXb)	206.5 (-30.6)    191 (+14.5) <sup>b</sup>	EtOH
(XVIIa) <sup>3</sup>	210 (-14.3)	EtOH

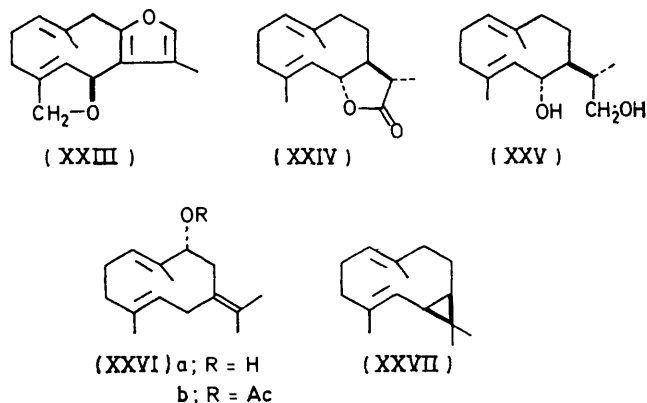
<sup>a</sup> EPA: ether-isopentane-ethyl alcohol, 5:5:2. <sup>b</sup> Not a maximum, lowest recorded value. <sup>c</sup> G. H. Kulkarni, G. R. Kelkar, and S. C. Bhattacharyya, *Tetrahedron*, 1964, **20**, 1303.

The characteristic c.d. couplet, similar to that reported by Suchý *et al.*,<sup>11</sup> was observed for most of the *trans,trans*-cyclodecadienes, whether there was a five-membered ring or not, indicating that the double bonds in the ten-membered ring are close together. Similar results were also obtained for the *cis,trans*-cyclodecadienes (IXa), (IXb), and (XXVIII), but not for (VIIIa), (VIIIb), and (XVIIa), which have a five-membered ring at positions 6 and 7. These results correspond well with those for the Cope rearrangement. Since the magnitudes of the c.d. couplet reflect the chirality,<sup>10</sup> and in particular the

distance between the two double bonds, the results obtained for (VIIIa), (VIIIb), and (XVIIa) revealed that these compounds adopt ground-state conformations in which the double bonds are considerably separated from one another by introduction of the five-membered ring.

From these results, we conclude that introduction of the five-membered ring at positions 6 and 7 of *cis,trans*-cyclodecadienes influences the stereostructure of the ten-membered ring related to the transition state of the Cope rearrangement.

Moreover, it was found that the *trans,trans*-cyclodecadienes (XXIII)<sup>8</sup> and (XXIV),<sup>12</sup> which give normal elemene-type products, exhibited the c.d. couplet with positive first and negative second Cotton effects, whereas (XXVI)<sup>13</sup> and (XXVII),<sup>14</sup> which give antipodal elemene-type products, showed a similar c.d. couplet with opposite signs. These observations show that the signs of the c.d. couplet enable us to deduce the stereochemistry of the Cope-rearrangement products. In fact, the stereochemistry of rearrangement products obtained from (VIIa), (VIIb), and (XV) agreed with that expected from the signs of their c.d. couplets.



On the other hand, the *cis,trans*-cyclodecadienes (IXa) and (IXb), giving normal *cis*-elemene-type products, exhibited similar c.d. couplets with opposite signs to those of (XXIII) and (XXIV). This result seems to indicate that the prediction for *trans,trans*-systems could also be applied to *cis,trans*-cyclodecadiene derivatives, but with opposite signs.

Furthermore, these relationships between the c.d. spectra of cyclodecadienes and the stereochemistry of their Cope-rearrangement products could more readily be explained by considering the conformation of the starting ten-membered ring in which the two double bonds have a crossed orientation, in the light of our previous proposal<sup>15</sup> that the stereochemistry of the

<sup>13</sup> J. Endo, T. Ogino, and M. Nagasawa, *Yakugaku Zasshi*, 1972, **92**, 874; I. Horibe, K. Tori, K. Takeda, and T. Ogino, *Tetrahedron Letters*, 1973, 735.

<sup>14</sup> K. Nishimura, N. Shinoda, and Y. Hirose, *Tetrahedron Letters*, 1969, 3097; K. Takeda, I. Horibe, and H. Minato, *Chem. Comm.*, 1971, 308; K. Nishimura, I. Horibe, and K. Tori, *Tetrahedron*, 1973, **29**, 271.

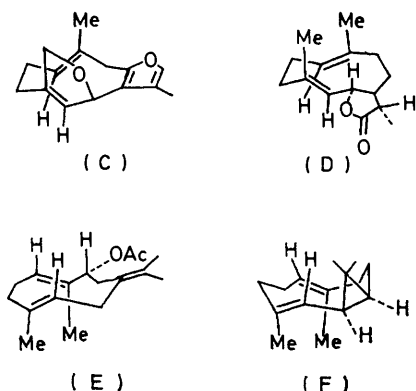
<sup>15</sup> K. Takeda, K. Tori, I. Horibe, M. Ohtsuru, and H. Minato, *J. Chem. Soc. (C)*, 1970, 2697.

<sup>10</sup> A. S. Davydov, 'Theory of Molecular Exciton,' trans. M. Kasha and M. Oppenheimer, jun., McGraw-Hill, New York, 1962; W. Hug and G. Wagnière, *Tetrahedron*, 1972, **28**, 1241; N. Harada and K. Nakanishi, *Accounts Chem. Res.*, 1972, **5**, 257.

<sup>11</sup> M. Suchý, L. Dolejš, V. Herout, F. Šorm, G. Sznatzke, and J. Himmelreich, *Coll. Czech. Chem. Comm.*, 1969, **34**, 229.

<sup>12</sup> T. C. Jain and J. E. McCloskey, *Tetrahedron Letters*, 1969, 4525.

Cope-rearrangement products is controlled by the ten membered ring conformation. Recently, we have reported that the *trans,trans*-cyclodecadienes (XXIII),



Molecular conformations of (XXIII), (XXIV), (XXVib), and (XXVII)

(XXIV), (XXVib), and (XXVII) adopt the conformations (C),<sup>15</sup> (D),<sup>6</sup> (E),<sup>13</sup> and (F),<sup>14</sup> respectively. However, the c.d. spectra for these compounds showed opposite signs to those expected from application of the exciton theory to their conformation. Further work on this discrepancy is in progress.

#### EXPERIMENTAL

Unless otherwise stated, n.m.r. spectra were taken for solutions in deuteriochloroform with Varian A-60A and HA-100 spectrometers; i.r. spectra were taken for solutions in chloroform; and optical rotations for solutions in ethanol. M.p.s were measured with a Kofler hot-stage apparatus. N.O.e. experiments were performed with a Varian HA-100 spectrometer using *ca.* 5% (w/v) degassed solutions in the frequency-swept and internal tetramethylsilane-locked mode. The integrated intensities of a signal were measured more than four times with and without irradiation at another frequency. C.d. spectra were measured with a JASCO model ORD/UV/CD-6 spectropolarimeter. Concentrations and path lengths were chosen such that optical densities were less than 2. C.d. data are recorded in the form  $\lambda/\text{nm}$  ( $\Delta\epsilon$ ).

**Sensitized Photoisomerization of Dihydrolaurenobiolide (VIIa).**—A solution of (VIIa) (400 mg) and acetophenone (0.8 g) in benzene (40 ml) was irradiated with a 100 W high-pressure mercury-vapour lamp through Pyrex for 2 h under nitrogen. The solvent was evaporated off and the residue was chromatographed on alumina (14 g) to give (3*Z*,9*E*)-8-acetoxy-6-hydroxygermacra-3,9-dien-12-*oic*  $\gamma$ -lactone (VIIIa) (275 mg) as needles, m.p. 103–104° (from light petroleum-ether),  $[\alpha]_D^{25.5} -81.9^\circ$  ( $\pm 1.5^\circ$ ) (*c* 0.535),  $\nu_{\text{max}}$  1771, 1735, 1670, 1243, 1170, 1067, 1018, 996, 960, and 860  $\text{cm}^{-1}$ ,  $\delta$  1.31 (3H, d, *J* 7.0 Hz, 11-Me), 1.73 (3H, d, *J* 1.5 Hz, 10-Me), 1.77br (3H, s, 4-Me), 2.07 (3H, s, Ac), 3.68 (1H, m, 6-H), 5.13 (1H, dm, *J* 10.0 Hz, 9-H), 5.25 (1H, dd, *J* 9.3 and 7.0 Hz, 3-H), and 5.53 (1H, t, *J* 10.0 Hz, 8-H) (Found: C, 69.9; H, 7.95.  $\text{C}_{17}\text{H}_{24}\text{O}_4$  requires C, 69.85; H, 8.25%).

**Action of Heat on the Lactone (VIIIa).**—Compound (VIIIa) (30 mg) was heated at 200° in a sealed tube for 30 min. The product was separated by preparative t.l.c.

on silica gel [benzene-ethyl acetate (9:1)] into starting material (VIIIa) (16 mg),  $R_F$  0.26, and an oil (4 mg),  $R_F$  0.46, assumed to be derived by elimination of the acetoxy-group since acetoxy-absorption was not observed in the i.r. spectrum.

**Reduction of the Lactone (VIIIa) with Lithium Aluminium Hydride.**—A solution of (VIIIa) (164 mg) in dry ether (3 ml) and dry tetrahydrofuran (3 ml) was reduced with lithium aluminium hydride (50 mg) at room temperature for 3 h. The product was recrystallized from ether-light petroleum to give (3*Z*,9*E*)-germacra-3,9-diene-6,8,12-triol (IXa) (135 mg) as prisms, m.p. 142–143°,  $[\alpha]_D^{23} -89.5^\circ$  ( $\pm 2.6^\circ$ ) (*c* 0.493),  $\nu_{\text{max}}$  3600, 3363, 1675, 1081, 1020, 1004, 995, 970, and 935  $\text{cm}^{-1}$  (Found: C, 70.9; H, 10.55.  $\text{C}_{15}\text{H}_{26}\text{O}_3$  requires C, 70.85; H, 10.3%).

**Cope Rearrangement of the Triol (IXa).**—Compound (IXa) (125 mg) was heated at 175° for 2 h in a sealed tube. The product was chromatographed on alumina (4 g) to give the starting material (IXa) (70 mg), and *t*-2-(2-hydroxy-1-methylethyl)-*c*-4-isopropenyl-5-methyl-*c*-5-vinylcyclohexane-*r*-1,*c*-3-diol (Xa) (36 mg), an oil, (*M* - 18)<sup>+</sup> 236,  $[\alpha]_D^{23.5} 31.0^\circ$  ( $\pm 0.7^\circ$ ) (*c* 1.032),  $\nu_{\text{max}}$  3608, 3390, 3085, 1641, 1108, 1020, and 915  $\text{cm}^{-1}$ ,  $\delta$  1.01 (Me), 1.08 (Me), 1.79 (Me), 2.40 (1H, d, *J* 6.0 Hz, 4-H), 3.63 (2H), 3.68 (1H, ddd, *J* 11.0, 11.0, and 5.5 Hz), 1-H), 3.88 (1H, dd, *J* 11.5 and 6.0 Hz, 3-H), and 4.81–5.06 (4H) and 5.85 (1H) (vinyl and isopropenyl groups).

**Reduction of the Lactone (XIa) with Lithium Aluminium Hydride.**—A solution of (XIa) (36 mg) in dry ether (3 ml) and dry tetrahydrofuran (2 ml) was reduced with lithium aluminium hydride (12 mg) at room temperature for 1 h. The product was recrystallized from ether to give *t*-2-(2-hydroxy-1-methylethyl)-*t*-4-isopropenyl-5-methyl-*c*-5-vinylcyclohexane-*r*-1,*c*-3-diol (XIIa) (22 mg) as prisms, m.p. 128–130°,  $[\alpha]_D^{23.5} 18.7^\circ$  ( $\pm 1.8^\circ$ ) (*c* 0.326),  $\nu_{\text{max}}$  3560, 3393, 3083, 1643, 1023, 956, 919, and 909  $\text{cm}^{-1}$ ,  $\delta$  1.00 (Me), 1.05 (Me), 1.78 (Me), 3.33–4.00 (4H), and 4.70–5.17 (4H) and 5.78 (1H) (vinyl and isopropenyl groups) (Found: C, 70.95; H, 10.25.  $\text{C}_{15}\text{H}_{26}\text{O}_3$  requires C, 70.85; H, 10.3%).

**Conversion of Compound (VIIIa) into the Deacetoxy-derivative (VIIIb).**—A solution of (VIIIa) (100 mg) in dry tetrahydrofuran (2 ml) and dry ether (4 ml) was added dropwise to a stirred solution of lithium (200 mg) in liquid ammonia (25 ml) at -60 to -70°. After 1 h ammonium chloride (2.5 g) was added in portions, and the ammonia was allowed to evaporate. The residue was diluted with water and extracted with ether. The product (91 mg) was chromatographed on silica gel (2.0 g) to give a diol (12 mg). This was dissolved in dichloromethane (1 ml) and oxidized with Collins reagent [from chromium trioxide (80 mg) and dry pyridine (0.15 ml) in dichloromethane (3 ml)]. After 10 min the liquid was decanted and the organic layer was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated, leaving a crystalline residue. This was crystallized from light petroleum to give (3*Z*,9*E*)-6-hydroxygermacra-3,9-dien-12-*oic* acid  $\gamma$ -lactone (VIIIb) (8.2 mg) as needles, m.p. 89.5–90°,  $[\alpha]_D^{24} -43.8^\circ$  ( $\pm 1.2^\circ$ ) (*c* 0.521),  $\nu_{\text{max}}$  1767, 1176, 1164, 1137, 1010, and 985  $\text{cm}^{-1}$ ,  $\delta$  1.26 (3H, d, *J* 6.5 Hz, 11-Me), 1.62 (3H, d, *J* 1.1 Hz, vinylic Me), 1.78 (3H, d, *J* 1.2 Hz, vinylic Me), 3.87 (1H, dt, *J* 8.6 and 3.7 Hz, 6-H), and 4.98–5.40 (2H, m, 3- and 9-H) (Found: C, 76.6; H, 9.3.  $\text{C}_{15}\text{H}_{22}\text{O}_2$  requires C, 76.9; H, 9.45%).

**Conversion of Dihydrolaurenobiolide (VIIa) into the Deacetoxy-derivative (VIIc).**—A solution of (VIIa) (2.4 g) in dry tetrahydrofuran (20 ml) and dry ether (20 ml) was

added dropwise to a stirred solution of lithium (2.4 g) in liquid ammonia (200 ml) at  $-60$  to  $-70^\circ$ . After 1 h ammonium chloride (18 g) was added, and the product was worked up as for compound (VIIIa). The material (2.3 g) was chromatographed on alumina (23 g) to give a diol mixture (1.40 g), which was dissolved in dichloromethane (20 ml) and oxidized with Collins reagent [from chromium trioxide (3.96 g) and dry pyridine (6.8 ml) in dichloromethane (100 ml)]. After 10 min the liquid was decanted and the organic layer was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated, leaving a crystalline residue (1.39 g). This was separated by 10% silver nitrate-alumina (60 g) chromatography into (3E,9E)-6-hydroxygermacra-3,9-dien-12-*oic acid*  $\gamma$ -lactone (VIIc) (477 mg), prisms, m.p.  $132.5$ – $133^\circ$  (from light petroleum-ether),  $[\alpha]_D^{23.5}$   $135.3^\circ$  ( $\pm 2.1^\circ$ ) ( $c$  0.522),  $\nu_{\text{max}}$  1767, 1668, 1178, 1135, 1046, 988, and  $936\text{ cm}^{-1}$ ,  $\delta$  1.29 (3H, d,  $J$  6.8 Hz, 11-Me), 1.55br (6H, s, 4- and 10-Me), 4.17br (1H, dd,  $J$  11.0 and 8.0 Hz, 6-H), 4.54 (1H, vinylic H), and 4.93 (1H, vinylic H) (Found: C, 77.0; H, 9.2.  $\text{C}_{15}\text{H}_{22}\text{O}_2$  requires C, 76.9; H, 9.45%); and (3E,8E)-6-hydroxygermacra-3,8-dien-12-*oic acid*  $\gamma$ -lactone (XIII) (568 mg), needles, m.p.  $145$ – $146^\circ$  (from light petroleum-ether),  $[\alpha]_D^{23.5}$   $-185.6^\circ$  ( $\pm 2.5^\circ$ ) ( $c$  0.540),  $\nu_{\text{max}}$  1770, 1667, 1179, 1164, 1116, 1051, 1033, and  $997\text{ cm}^{-1}$ , c.d.  $[\lambda/\text{nm} (\Delta\epsilon)]$  (EtOH) 268 (0), 232 ( $-31.2$ ), 200 (0), and 195 ( $+6.97$ ); (EPA) at  $24^\circ$ : 262 (0) and 233 ( $-30.2$ ); at  $-68^\circ$ : 262 (0) and 233 ( $-34.5$ ); at  $-190^\circ$ : 261 (0) and 233 ( $-37.9$ ),  $\delta$  1.08 (3H, d,  $J$  7.0 Hz, 10-Me), 1.17 (3H, d,  $J$  6.7 Hz, 11-Me), 1.63br (3H, s, 4-Me), 3.96 (1H, ddd,  $J$  9.3, 9.0, and 5.6 Hz, 6-H), 5.00 (1H, dd,  $J$  15.5 and 9.0 Hz, 8-H), 5.22 (1H, dm,  $J$  10.5 Hz, 3-H), and 5.83 (1H, dd,  $J$  15.5 and 3.0 Hz, 9-H) (Found: C, 76.8; H, 9.5.  $\text{C}_{15}\text{H}_{22}\text{O}_2$  requires C, 76.9; H, 9.45%).

**Sensitized Photoisomerization of Compound (VIIc).**—A solution of (VIIc) (300 mg) and acetophenone (400 mg) in benzene (30 ml) was irradiated for 1 h with a 100 W high-pressure mercury-vapour lamp under nitrogen. The solvent was evaporated off and the residue was chromatographed on 10% silver nitrate-alumina (16 g). The fraction eluted with benzene-ethyl acetate (9:1 to 4:1) was further purified by preparative t.l.c. on silica gel to give (3Z,9Z)-6-hydroxygermacra-3,9-dien-12-*oic acid*  $\gamma$ -lactone (XIV) (93 mg), an oil,  $[\alpha]_D^{24}$   $3.9^\circ$  ( $\pm 0.8^\circ$ ) ( $c$  0.517),  $\nu_{\text{max}}$  1770, 1171, 998, 979, 905, and  $854\text{ cm}^{-1}$ ,  $\delta$  1.24 (3H, d,  $J$  6.6 Hz, 11-Me), 1.72 (3H, d,  $J$  1.1 Hz, 10-Me), 1.76 (3H, d,  $J$  1.2 Hz, 4-Me), 4.16 (1H, ddd,  $J$  9.7, 4.8, and 4.8 Hz, 6-H), 5.32br (1H, t,  $J$  8.6 Hz, 9-H), and 5.46br (1H, t,  $J$  6.3 Hz, 3-H).

The fraction eluted with benzene-ethyl acetate (1:1) was recrystallized from light petroleum to give the *cis,trans*-germacranolide as needles, m.p.  $89.5$ – $90^\circ$ , identical with compound (VIIb) derived from (VIIIa) (mixed m.p. and i.r. spectrum).

**Cope Rearrangement of Compound (VIIc).**—Compound (VIIc) (74 mg) was heated at  $220^\circ$  for 10 min in a sealed tube. The product was separated by preparative t.l.c. into 5-isopropenyl-3,6-dimethyl-6-vinylperhydrobenzofuran-2-one (XIc) (19 mg), as prisms, m.p.  $89$ – $90^\circ$  (from light petroleum),  $[\alpha]_D^{24}$   $-8.3^\circ$  ( $\pm 0.5^\circ$ ) ( $c$  1.032),  $\nu_{\text{max}}$  1772, 1641, 1184, 1162, 1121, 1088, 1003, 917, and  $900\text{ cm}^{-1}$ , c.d.  $[\lambda/\text{nm} (\Delta\epsilon)]$  (EtOH) 246 (0), 217 ( $-1.85$ ), and 202 (0),  $\delta$  1.10 (Me), 1.22 (Me), 1.73 (Me), 4.02 (1H), 4.65 (1H) and 4.89 (1H) (isopropenyl group), and 4.92 (1H), 5.00 (1H), and 5.88 (1H) (vinyl group) (Found: C, 76.9; H, 9.45.  $\text{C}_{15}\text{H}_{22}\text{O}_2$  requires C, 76.9; H, 9.45%), and starting material (VIIc) (50 mg).

**Reduction of the Lactone (XIc) with Lithium Aluminium Hydride.**—A solution of (XIc) (15 mg) in dry ether (3 ml) was reduced with lithium aluminium hydride (15 mg) at room temperature for 1 h. The product was recrystallized from ether-light petroleum to give t-2-(2-hydroxy-1-methyl-ethyl)-t-4-isopropenyl-5-methyl-c-5-vinylcyclohexan-r-1-ol (XIIb) (10 mg), as prisms, m.p.  $128$ – $130^\circ$ ,  $[\alpha]_D^{24}$   $18.0^\circ$  ( $\pm 3.3^\circ$ ) ( $c$  0.178),  $\nu_{\text{max}}$  3593, 3406, 1640, 1023, 975, 912, and  $893\text{ cm}^{-1}$ ,  $\delta$  0.92 (Me), 1.00 (Me), 1.70 (Me), 3.57 (2H), 3.72 (1H, 1-H), 4.60 (1H) and 4.83 (1H) (isopropenyl group), and 4.75–5.07 (2H) and 5.83 (1H) (vinyl group) (Found: C, 75.65; H, 11.15.  $\text{C}_{15}\text{H}_{26}\text{O}_2$  requires C, 75.6; H, 11.0%).

**Reduction of the Lactone (VIIc) with Lithium Aluminium Hydride.**—A solution of (VIIc) (30 mg) in dry tetrahydrofuran (2 ml) and dry ether (3 ml) was reduced with lithium aluminium hydride (20 mg) at room temperature for 3 h. The product was recrystallized from ether-light petroleum to give (3E,9E)-germacra-3,9-diene-6,12-diol (XV) (23 mg) as prisms, m.p.  $113$ – $114^\circ$ ,  $[\alpha]_D^{23.5}$   $-1.6^\circ$  ( $\pm 1.3^\circ$ ) ( $c$  0.322),  $\nu_{\text{max}}$  3620, 3385, 1065, 1027, 1011, and  $858\text{ cm}^{-1}$  (Found: C, 75.8; H, 10.95.  $\text{C}_{15}\text{H}_{26}\text{O}_2$  requires C, 75.6; H, 11.0%).

**Cope Rearrangement of the Diol (XV).**—Compound (XV) (10 mg) was heated at  $150^\circ$  in a sealed tube for 1 h. The product was purified by preparative t.l.c. and recrystallized from ether-light petroleum to yield a Cope rearrangement product (6 mg) as prisms, m.p.  $127$ – $129^\circ$ , identical with (XIIb) derived from the lactone (XIc) (mixed m.p. and i.r. spectrum).

**Conversion of Dihydrolaurenobiolide (VIIa) into the Lactone (XIb).**—To a stirred solution of (VIIa) (300 mg) in methanol was added 2N-potassium hydroxide (2.5 ml), and the mixture was stirred for 1 h at room temperature. Ammonium chloride (500 mg) was then added, and methanol was removed under reduced pressure. The residue was acidified with 2N-hydrochloric acid (1 ml) and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate and water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated, giving oily (3E,9E)-6,8-dihydroxygermacra-3,9-dien-12-*oic acid* 12,6-lactone (VIIb) (257 mg),  $\nu_{\text{max}}$  3595, 3475, 1762, 1666, 1179, 1158, 1044, 1006, and  $966\text{ cm}^{-1}$ .

This was heated at  $220^\circ$  in a sealed tube for 10 min to give 4-hydroxy-5-isopropenyl-3,6-dimethyl-6-vinylperhydrobenzofuran-2-one (XIb) and starting material (VIIb) in the ratio ca. 2:3. This mixture was chromatographed on silica gel (5 g) to give (XIb) (77 mg) as an oil,  $\nu_{\text{max}}$  3578, 1778, 1643, 1103, 1031, 1001, 973, 915, and  $906\text{ cm}^{-1}$ ,  $\delta$  1.10 (Me), 1.37 (Me), 1.80 (Me), 3.92 (1H), 4.06 (1H), 4.80 (1H) and 5.18 (1H) (isopropenyl group), and 4.90–5.12 (2H) and 5.85 (1H) (vinyl group); and (VIIb) (114 mg).

Compound (XIb) (23 mg) was acetylated with acetic anhydride (0.1 ml) and dry pyridine (0.4 ml), and the product was crystallized from ether-light petroleum to give an acetate (12 mg) as needles, m.p.  $138$ – $140^\circ$ ,  $\nu_{\text{max}}$  3085, 1775, 1731, 1648, and  $903\text{ cm}^{-1}$ , identical with (XIa) derived from Cope rearrangement of dihydrolaurenobiolide (VIIa) (i.r. and n.m.r. spectra and mixed m.p.).

**Conversion of the Lactone (XIb) into the Diol (XIIa).**—A solution of methanesulphonyl chloride (0.1 ml) in dichloromethane (1 ml) was added to a solution of (XIb) (65 mg) and triethylamine (0.2 ml) in dichloromethane (3 ml) with stirring in an ice-bath. After 30 min the mixture was poured into ice-cooled 2N-sulphuric acid and extracted with dichloromethane. The extract was washed with aqueous sodium hydrogen carbonate and water, dried

( $\text{Na}_2\text{SO}_4$ ), and evaporated, leaving an oily methanesulphonate (79 mg). This was dissolved in dry ether (2 ml) and added to a stirred solution of lithium (100 mg) in liquid ammonia (10 ml) at  $-60$  to  $-70^\circ$ . After 1 h ammonium chloride (0.5 g) was added, and the ammonia was allowed to evaporate. The residue was diluted with water and extracted with ether; the extract afforded an oily residue (30 mg) which was purified by preparative t.l.c. to yield a diol (6 mg), m.p.  $128-130^\circ$  (from light petroleum-ether), identical with the diol (XIIb) derived from the lactone (XIc) (mixed m.p. and i.r. spectrum).

**Thermal Rearrangement of Compound (VIIIb).**—Compound (VIIIb) (27 mg) was heated at  $220^\circ$  in a sealed tube for 30 min. The product was separated by preparative t.l.c. on silica gel [benzene-ethyl acetate (9:1)] into starting material (VIIIb) (10 mg),  $R_F$  0.43, and an isomer (13.4 mg), an oil,  $R_F$  0.37,  $[\alpha]_D^{24}$   $160.6^\circ$  ( $\pm 5.0^\circ$ ) ( $c$  0.241),  $\nu_{\text{max}}$  1768, 1171, 1056, 1011, 972, 911, and 866  $\text{cm}^{-1}$ , c.d.  $[\lambda/\text{nm} (\Delta\epsilon)]$  (EtOH) 250 (0), 233 ( $-0.22$ ), 228.5 (0), 211 ( $+3.82$ ), and 205 ( $+3.39$ ),  $\delta$  1.13 (3H, d,  $J$  6.5 Hz, 11-Me), 1.64 (Me), 1.70 (Me), 4.33 (1H, dt,  $J$  8.2 and 3.5 Hz, 6-H), 5.37br (1H, t,  $J$  6.0 Hz), and 5.54br (1H, t,  $J$  6.5 Hz).

**Reduction of the Lactone (VIIIb) with Lithium Aluminium Hydride.**—A solution of (VIIIb) (20 mg) in dry tetrahydrofuran (1 ml) and dry ether (2 ml) was reduced with lithium aluminium hydride (10 mg) at room temperature for 2 h. The product was recrystallized from ether to give (3Z,9E)-germacra-3,9-diene-6,12-diol (IXb) (16 mg) as prisms, m.p.  $145-145.5^\circ$ ,  $[\alpha]_D^{23.5}$   $-22.4^\circ$  ( $\pm 2.8^\circ$ ) ( $c$  0.223),  $\nu_{\text{max}}$  3620, 3426, 1044, 1019, and 1001  $\text{cm}^{-1}$  (Found: C, 75.65; H, 11.15.  $\text{C}_{15}\text{H}_{26}\text{O}_2$  requires C, 75.6; H, 11.0%).

**Cope Rearrangement of the Diol (IXb).**—Compound (IXb) (50 mg) was heated at  $170^\circ$  for 4 h in a sealed tube. The product was purified by preparative t.l.c. on silica gel [benzene-ethyl acetate (1:1)], and recrystallized from light petroleum-ether to give t-2-(2-hydroxy-1-methylethyl)-c-4-isopropenyl-5-methyl-c-5-vinylcyclohexan-r-1-ol (Xb) (26.5 mg) as prisms, m.p.  $79-80.5^\circ$ ,  $[\alpha]_D^{24}$   $70.6^\circ$  ( $\pm 6.2^\circ$ ) ( $c$  0.180),  $\nu_{\text{max}}$  3613, 3413, 1639, 1604, 1026, 918, and 896  $\text{cm}^{-1}$ ,  $\delta$  0.90 (Me), 1.10 (Me), 1.73 (Me), 3.60 (2H), 3.78 (1H, 1-H), 4.80 (2H, isopropenyl group), and 4.77-5.10 (2H) and 6.03 (1H) (vinyl group) (Found: C, 75.65; H, 10.75.  $\text{C}_{15}\text{H}_{26}\text{O}_2$  requires C, 75.6; H, 11.0%).

**Conversion of the Diol (Xb) into the Oxo-ester (XVI).**—A solution of (Xb) (18 mg) in acetone (1.5 ml) was treated with Jones reagent [from chromium trioxide (60 mg) and conc. sulphuric acid (0.2 ml) in water (1 ml)]. Next day the mixture was diluted with water and extracted with ether. Evaporation of the extract gave an oily acid (10 mg) which was dissolved in ether (2 ml) and then esterified with diazomethane-ether to yield an oil. This oil was purified by preparative t.l.c. on silica gel to give methyl 2-(5-isopropenyl-4-methyl-2-oxo-4-vinylcyclohexyl)propionate (XVI) (1.8 mg) as an oil, c.d.  $[\lambda/\text{nm} (\Delta\epsilon)]$  (EtOH) 346 (0), 305 ( $+0.41$ ), 287 (0), 270 ( $-0.48$ ), and 241.5 (0); at  $-68^\circ$ : 345 (0), 305 ( $+0.44$ ), 289 (0), 270 ( $-0.59$ ), and 239 (0).

**Conversion of the Diol (XVIIa) into the cis,trans-Furanodiene (XVIII).**—Compound (XVIIa) (50 mg) was acetylated with acetic anhydride (0.2 ml) and pyridine (0.8 ml) and purified by preparative t.l.c. to yield (3Z,9E)-8,14-diacetoxy-6,12-epoxygermacra-3,6,9,11-tetraene (XVIIb) (43 mg) as an oil,  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1736, 1621, 1235, 1016, and 953  $\text{cm}^{-1}$ .

This oil was dissolved in dry ether (5 ml) and added to a stirred solution of lithium (100 mg) in liquid ammonia (15 ml) at  $-60$  to  $-70^\circ$ . After 1 h ammonium chloride (0.5 g) was added in portions with stirring at the same temperature. Ammonia was allowed to evaporate, and the residue was extracted with ether. The extract was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated leaving an oil (30 mg). This was purified by preparative t.l.c. to give (3Z,9E)-6,12-epoxygermacra-3,6,9,11-tetraene (XVIII) (18 mg), an oil,  $M^+$  216,  $\nu_{\text{max}}$  (film) 1669, 1624, 1138, 1102, 1089, 891, 872, 855, 835, 751, and 739  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.53 (3H, d,  $J$  1.4 Hz, 4-Me), 1.68 (3H, d,  $J$  1.2 Hz, 10-Me), 1.88 (3H, d,  $J$  1.2 Hz, 11-Me), 5.01br (1H, t,  $J$  9.0 Hz, 3-H), 5.15 (1H, m, 9-H), and 6.91 (1H, q,  $J$  1.2 Hz, 12-H).

**Reduction of the Diacetate (XIXa).**—A solution of (XIXa) (105 mg) in dry ether (5 ml) was reduced with lithium (100 mg) in liquid ammonia (15 ml) as described above. The product (72 mg) was chromatographed on alumina (3 g) and the fraction eluted with light petroleum was recrystallized from ethanol to give the isofuranodiene (XX) (47 mg), prisms, m.p.  $66.5-67.5^\circ$ ,  $\nu_{\text{max}}$  (Nujol) 1669, 1555, 1132, 1080, 1025, 989, 900, 890, 850, 782, 762, and 758  $\text{cm}^{-1}$ , identical with an authentic sample [i.r. (KBr) and n.m.r. spectra, and mixed m.p.].

**Cope Rearrangement of the Isofuranodiene (XX).**—(i) When compound (XX) was heated at  $130^\circ$  in a sealed tube for 30 min, it gave a mixture of isofuranogermacrene (III) and starting material in the ratio ca. 1:1.

(ii) Compound (XX) (20 mg) was heated at  $160^\circ$  in a sealed tube for 1 h. The product was purified by preparative t.l.c. on silica gel [n-hexane-benzene (4:1)] to give isofuranogermacrene (III) (18 mg) as an oil,  $R_F$  0.40, identical with an authentic sample (i.r., n.m.r., and mass spectra).

**Thermal Rearrangement of the cis,trans-Furanodiene (XVIII).**—Compound (XVIII) (5 mg) was heated at  $200^\circ$  in a sealed tube for 30 min. The products showed two peaks,  $t_R$  3.2 and 6.6 min, ratio ca. 1:2, on g.l.c. (5% PEG-6000;  $130^\circ$ ;  $\text{N}_2$  50 ml  $\text{min}^{-1}$ ) and two spots,  $R_F$  0.54 and 0.33, on t.l.c. [10%  $\text{AgNO}_3$ -silica gel (benzene)]. This oil was separated by preparative t.l.c. on 10%  $\text{AgNO}_3$ -silica gel into isofuranogermacrene (III) (1.2 mg),  $t_R$  3.2 min,  $R_F$  0.33, identical with an authentic sample (t.l.c., g.l.c., and mass spectrum), and starting material (XVIII) (3.2 mg),  $t_R$  6.6 min,  $R_F$  0.54.

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