Germacranolides of *Erlangea cordifolia*. Isolation and Structures of Cordifolia-54, -55, -P2, and -31 by Spectral and *X*-Ray Methods

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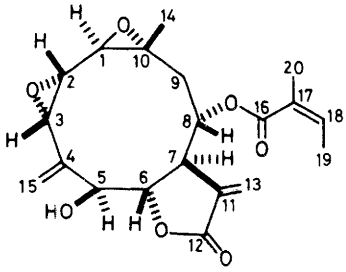
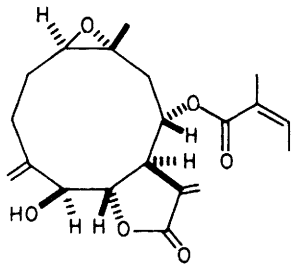
In addition to cordifene (**1**) and cordifene 4β,15-oxide (**5**), four new companion compounds cordifolia-54, -55, -P2, and -31 have been isolated from the insect-antifeedant plant *Erlangea cordifolia*. Cordifolia-54(2) is related to cordifene as the 2,3-dihydrodeoxy derivative, and cordifolia-55(3) is the acetate of a C-2,O-2-seco-cordifene resulting from a formal epoxide reduction. Cordifolia-31 is the methacrylate ester of the same sesquiterpene core as is present in cordifene 4β,15-oxide.

Cordifolia-P2 has ^{1}H and ^{13}C n.m.r. data consistent with structure (**4**) but certain chemical shifts, multiplicities, and coupling constants suggest a conformation markedly different from the five other *Erlangea* structures. This has been confirmed by a single crystal *X*-ray analysis. Cordifolia-P2, in contrast to cordifene and its 4β,15-oxide, has a negative Cotton effect near the n→π* maximum in the c.d. spectrum. This is explained by McPhail's generalisation if all three compounds have the same absolute configuration, since the C(5)–C(6)–C(7)–C(8) torsion angle is significantly <120° (99°) for -P2 but significantly >120° (157°, 159°) for cordifene and its oxide. On the other hand the idealised McPhail relationship between this torsion angle and the C=C–C=O torsion angle of the lactone is incompletely obeyed since the latter is measured as +0.7° in cordifolia-P2.

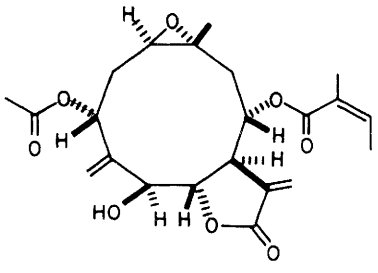
Extractives of the leaves of *Erlangea cordifolia* (S. Moore) (Compositae) have antifeedant properties towards army worm [1] and aphids:[2] they are also of obstetric interest, being used for inducing labour.[3] Recently we have shown by spectroscopic and *X*-ray methods that the structures and stereochemistries of the two major extractives, cordifene and cordifene 4β,15-oxide ('cordifene epoxide'), are (**1**) and (**5**) respectively.[4] The absolute configuration of (**1**) was determined directly as the 5-



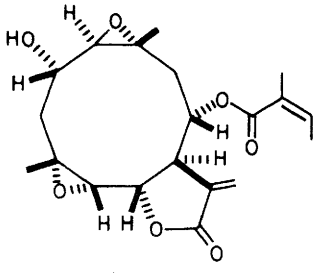
Cordifene (**1**)



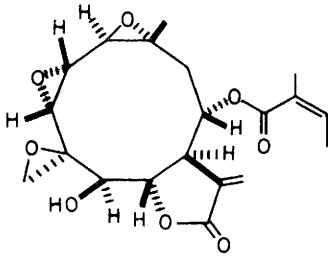
Cordifolia-54 (**2**)



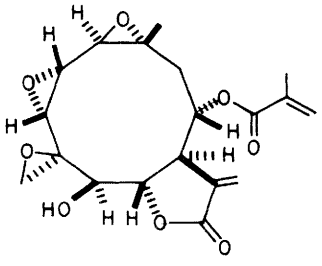
Cordifolia-55 (**3**)



Cordifolia-P2 (**4**)



Cordifene 4β, 15-oxide (**5**)



Cordifolia-31 (**6**)

Table 1. ^{1}H N.m.r. data for *Erlangea cordifolia* extractives[a]

	1-H	2-H	3-H	5-H	6-H	7-H	8-H	9α-H	9β-H
Cordifene (**1**)[g]	2.61 (d)	3.01 (dd)	3.99 (dt)	4.12 (d)	4.39 (d)	2.92 (br d)	5.12 (ddd)	1.35 (br t)	2.58 (dd)
J, Hz	8	4.5, 8	1, 4.5	10	10	10	4, 10, 12	12	4, 12
Cordifolia-54 (**2**)	3.05 (dd)	*ca.* 2.4 (m)[b]	*ca.* 1.5 (m)[b]	3.93 (d)	4.42 (d)	2.99 (d)	5.08 (m)	1.36 (t)	2.59 (dd)
J, Hz	4, 9.5			9	9	9		13	4.13
Cordifolia-55 (**3**)	2.84 (dd)	2.03 (ddd)[b]	5.42 (dd)	4.03(dd)[c]	4.34 (d)	2.94 (d)	5.08 (ddd)	1.35 (dd)	2.62 (dd)
J, Hz	4.5, 9	6, 9, 14	6, 9.5	9	9	9	4, 9, 13	13, 7	4.13
Cordifolia-P2 (**4**)	3.10 (d)	3.77 (ddd)	2.70 (dd)[i]	2.97 (d)	4.60 (dd)	3.26 (dd)	4.71 (dd)	1.83 (m)	2.51 (d)
J, Hz	10	6, 10, 13	6, 13	9.5	8, 9.5	3, 8	3, 10.5		13
Cordifene epoxide (**5**)[g]	2.65 (d)	3.07 (dd)	3.85 (d)	3.24 (d)	4.53 (d)	2.93 (br d)	5.15 (ddd)	1.43 (br t)	2.65 (dd)
J, Hz	8.5	4.5, 8.5	4.5	10	10	10	4, 10, 12	12	4, 12
Cordifolia-31 (**6**)	2.63 (d)	3.07 (dd)	3.84 (d)	3.23 (d)	4.52 (d)	2.96 (d)	5.11 (m)	1.42 (br t)	2.66 (dd)
J, Hz	8.5	4.5, 8.5	4.5, 8.5	10	10	10		12	4, 12

	13-H	13′-H	15-H	15′-H	14-Me	18-H	19-Me	20-Me	OH	MeCO
Cordifene (**1**)[g]	5.69 (d)	6.32 (br s)	5.31 (s)	5.55 (t)	1.59 (s)	6.1 (qq)	1.96 (dq)	1.80 (dq)	*ca.* 3.0 (br s)	
J, Hz	1			1.5		1.5, 7	1.5, 7	*ca.* 1.5		
Cordifolia-54 (**2**)	5.67 (d)	6.30 (s)	←5.36	(br s)[b]→	1.47 (s)	6.09 (m)	1.94 (m)	1.80 (m)	2.71 (d)	
J, Hz	1								1	
Cordifolia-55 (**3**)	5.70 (s)	6.31 (s)	5.60 (s)	5.67 (s)	1.53 (s)	6.04 (m)	1.94 (m)	1.80 (m)	3.35 (br s)	2.09 (s)
J, Hz										
Cordifolia-P2 (**4**)	5.66 (d)	6.33 (d)	←1.54	(s)[d,e]	1.45 (s)[e]	6.18 (m)	1.95 (m)	1.87 (m)	2.70 (obs)	
J, Hz	3	3								
Cordifene epoxide (**5**)[g]	5.68 (d)	6.29 (br s)	3.29 (d)	2.74 (dd)	1.64 (s)	6.11 (qq)	1.93 (dq)	1.80 (m)	3.43 (br s)	
J, Hz	1		5	5, 1				1.88 (t)		
Cordifolia-31 (**6**)	5.70 (s)	6.30 (s)	3.29 (d)	2.74 (d)	1.63 (s)	6.07 (m)[f]				
J, Hz			5	5						

^{1}H Spin-decoupling for cordifolia-54: 1-H⇌2-H→3-H 5-H→6-H 7-H⇌8-H⇌9α-H, 9β-H
^{1}H Spin-decoupling for cordifolia-55: 1-H⇌2a-H, 2β-H⇌3-H 5-H←6-H 7-H⇌8-H⇌9a-H, 9β-H
^{1}H Spin-decoupling for cordifolia-P2: 1-H⇌2-H⇌3α-H, 3β-H 5-H←6-H 7-H⇌8-H→9β-H

[a] Solvent $CDCl_3$. [b] 2-H Signals. [c] Also 2 Hz coupling to OH: disappears with D_2O. [d] Refers to Me (3H). [e] Assignments may be reversed. [f] Also 5.59 (5 line m) (1H), proton *trans* to Me. [g] See ref. 4. [h] Also 2.45 (ddd), *J* 4.5, 9.5 and 14 Hz. [i] Also 1.4 (m).

Table 2. ^{13}C N.m.r. Data for *Erlangea cordifolia* extractives[a]

	1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C
Cordifolene (**1**)[g]	53.3 (d)[b]	55.1 (d)[b]	62.8 (d)	142.0 (s)	81.6 (d)	78.0 (d)	48.7 (d)	69.0 (d)	45.7 (t)	55.9 (s)
Cordifolia-P2 (**4**)	66.7 (d)[c]	66.1 (d)[c]	47.8 (dd)[e]	60.3 (s)[d]	64.4 (d)	79.6 (d)	50.5 (d)	69.3 (d)	43.5 (dd)[e]	57.3 (s)[d]
Cordifene epoxide (**5**)[g]	51.4 (d)	55.5 (d)	61.6 (d)	58.8 (s)	81.0 (d)	78.7 (d)	48.6 (d)	68.9 (d)	45.2 (dd)	56.3 (s)

	11-C	12-C	13-C	14-C	15-C	16-C	17-C	18-C	19-C	20-C
Cordifolia (**1**)[g]	136.2 (s)	168.7 (s)	126.1 (t)	17.9 (q)	117.4 (t)	166.6 (s)	128.3 (s)	139.3 (d)	15.8 (q)	20.4 (q)
Cordifolia-P2 (**4**)	132.6 (s)	168.6 (s)	125.3 (t)	18.3 (q)[f]	19.2 (q)	167.0 (s)	126.4 (s)	141.2 (d)	15.9 (q)	20.2 (q)
Cordifene epoxide (**5**)[g]	136.1 (s)	168.5 (s)	126.0 (t)	17.7 (q)	50.3 (dd)	166.6 (s)	128.2 (s)	139.4 (d)	15.8 (q)	20.3 (q)

[a] Solvent $CDCl_3$. [b–f] Appropriate signals may have reversed assignments. [g] See ref. 4.

bromofuroate using the anomalous dispersion of bromine, and that of (**5**) was related to it by c.d. spectral methods. The structure and conformation of cordifene 4β,15-oxide (**5**) was also confirmed by *X*-ray direct methods so that these two germacranolides form a firm structural and stereochemical foundation for further work. Continued study of the extractives using h.p.l.c. separation methods has now enabled us to isolate four new companion germacranolides which, although present only as minor components, provide useful indicators of late-stage biogenetic relationships among the sesquiterpenes of this plant. The four new compounds are designated cordifolia-54, -55, -P2, and -31.

Cordifolia-54 (**2**), $C_{20}H_{26}O_6$, is related to cordifene (**1**), $C_{20}H_{24}O_7$, as its dihydrodeoxy derivative: it contains one free hydroxy group as indicated by the mass spectrum of the trimethylsilyl ether and the ^{1}H n.m.r. spectrum of the parent. Comparison of ^{1}H n.m.r. data for (**1**) and (**2**) (Table 1) shows that the large segment of the molecules lying between C-4 and C-15, as well as the ester appendages C-16 to C-20, are essentially identical: this is supported by spin-decoupling data. Interest therefore concentrates on the proton signals associated with C-1 to C-3, which differ substantially in the two compounds. The 1-H proton at δ 3.05 in cordifolia-54 is not a doublet as in cordifene, but a double doublet. Irradiation partially collapses a two-proton multiplet at δ 2.4 and irradiation of the latter collapses the double doublet at δ 3.05 as well as a two-proton multiplet at δ 1.5 which represents the 3-H protons. These data lead to structure (**2**).

Cordifolia-55 contains one free hydroxy group (TMS-ether) and the molecular segment between C-4 and C-20 is, from the ^{1}H n.m.r. data, closely similar to the same segments in cordifene and cordifolia-54. The (*Z*)-2-methylbutenoate (angelate) ester is common to all three compounds and in all three there is a 4,15- and an 11,13-vinyl group. Unlike the other two compounds however, cordifolia-55 contains an acetoxymethyl (δ 2.09) and taking this into account its core must be that of a 2-O or a 3-O seco derivative of cordifene. Location of the acetylated hydroxy group follows from the ^{1}H n.m.r. spectrum. The 1-H epoxide hydrogen at δ 2.84 is a double doublet and the presence of a C-2 methylene multiplet (near δ 2.03) was shown by decoupling. Decoupling also confirmed the location (δ 5.42) of the 3-H proton of the carbon bearing the acetoxy substituent. Since the orientation of the 2,3-epoxides in cordifene and cordifene 4β,15-oxide is α and the 2-hydroxy group in cordifolia-P2 is established as α (below), the 3-oxygen of cordifolia-55 is represented as α also.

On a molecular formula basis, cordifolia-P2, $C_{20}H_{26}O_7$, appeared at first sight to be a dihydrocordifene. In the i.r. region both γ-lactone and ester absorptions were present and the presence of an angelate ester residue was readily confirmed by ^{1}H n.m.r. and ^{13}C n.m.r. (Tables 1 and 2). These showed that the customary methylene-γ-lactone was intact and that the sesquiterpene core possessed an extra methyl relative to other members of the *Erlangea* group of natural products. Decoupling established the 1-H, 2-H, 3-H_2 sequence of proton signals and these and the ^{13}C n.m.r. showed a hydroxy group to be present at C-2. The 5-H, 6-H and 7-H, 8-H, 9-H relations were similarly established. A reasonable proposal from the spectral data was that an epoxide now spanned C-4 to C-5, a 15-methyl replacing a 15-methylene. However, the pattern of coupling constants had been disturbed as compared with those for cordifene, its 4β,15-oxide, and cordifolia-54 or -55. This can be seen for example in the couplings of the 7-H and 8-H protons (Table 1): such effects were thought to signal important conformational changes and a single crystal *X*-ray study of cordifolia-P2 was therefore undertaken.

The structure was solved by direct methods using diffractometer data: least-squares refinement converged to R = 5.79% over 823 independent observed reflections and the structure and stereochemistry of the molecule is as presented in (**4**). Figure 1 shows the conformation of the molecule in the crystal and carries the *X*-ray numbering. Bond lengths and angles are listed in Tables 3 and 4 respectively, together with standard deviations. Table 5 shows some selected torsion angles about the 10- and 5-membered rings. In themselves these geometric data seem unexceptional, especially when the larger than average deviations arising from the smallness of the crystal are taken into account. However, when the data are compared with our earlier results for cordifene (**1**) and cordifene 4β,15-oxide (**5**), several very significant differences are revealed.

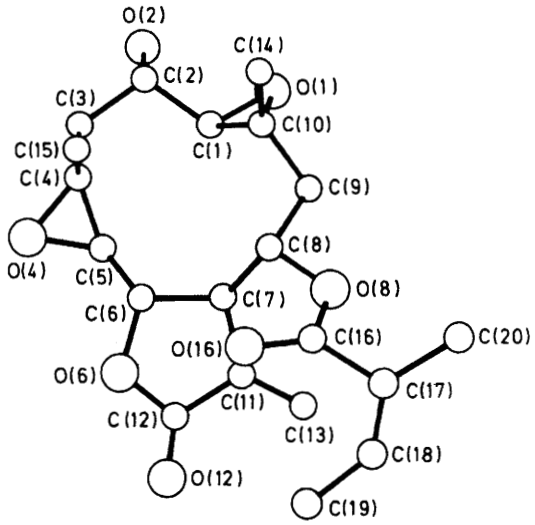


Figure 1. *X*-Ray structure for cordifolia-P2 (**4**).

Despite the relatively small changes in bonding, the conformation of the 10-membered ring in cordifolia-P2 has totally changed relative to cordifene and its epoxide. This is readily seen in the torsion angles of Table 5, as well as by viewing Figure 1 of this paper together with Figures 1 and 2 of our earlier paper.[4] Only in the C(2)–C(1)–C(10)–C(9) region of the ring are the torsion angles at all comparable, the conformation of the remainder of the ring being very different.† While the increase in the C(2)–C(3) bond length, and the decrease in the C(4)–C(5) bond length (as compared with cordifene) would be expected from the absence and presence of epoxide rings respectively, the equally significant increase in the C(1)–C(2) bond length, and decrease in C(5)–C(6), can only be reflected in the conformational change. The large change in ring shape has also modified some bond angles. Most noticeable of these is a significant decrease in the C(5)–C(6)–C(7) angle and an associated increase in the C(5)–C(6)–O(6). Also the neighbouring C(8)–C(7)–C(11) angle is much larger.

This major change in the conformation of the 10-membered ring has a crucial effect on the interpretation of the c.d. spectrum arising from the n→π* transition of the methylene lactone ring near 255 nm. Beecham[7] has shown that in germacranolide methylene lactones a right-handed chirality of the C=C–C=O torsion angle is associated with a positive Cotton effect [see Figure 2 and (7b) for the situation for cordifene]. McPhail has demonstrated that this torsion angle is paired with the endocyclic torsion angle about C(6)–C(7): where this angle Φ_R is $>120°$ (in an idealised case) this leads to a positive Cotton effect, where $<120°$ it is to a negative one.[8] Warning is given

† A referee has pointed out that the conformation taken up by the 1,5-bisepoxide cordifolia P-2 is very like that calculated as the energy minimum for cyclodeca-1,5-diene:[5] the germacranolide 1,5-diene costunolide takes a similar conformation.[6]

Table 3. Cordifolia-P2

Bond lengths (Å)

C(1)–C(2)	1.537(14)	C(8)–C(9)	1.556(15)
C(1)–C(10)	1.460(17)	C(8)–O(8)	1.441(12)
C(1)–O(1)	1.423(12)	C(9)–C(10)	1.509(14)
C(2)–C(3)	1.524(15)	C(10)–C(14)	1.476(16)
C(2)–O(2)	1.414(13)	C(10)–O(1)	1.427(16)
C(3)–C(4)	1.512(22)	C(11)–C(12)	1.485(13)
C(4)–C(5)	1.484(14)	C(11)–C(13)	1.333(12)
C(4)–C(15)	1.469(21)	C(12)–O(6)	1.340(10)
C(4)–O(4)	1.470(12)	C(12)–O(12)	1.194(10)
C(5)–C(6)	1.489(18)	C(16)–C(17)	1.511(18)
C(5)–O(4)	1.445(11)	C(16)–O(8)	1.343(15)
C(6)–C(7)	1.564(12)	C(16)–O(16)	1.240(14)
C(6)–O(6)	1.463(10)	C(17)–C(18)	1.227(17)
C(7)–C(8)	1.559(14)	C(17)–C(20)	1.564(18)
C(7)–C(11)	1.496(12)	C(18)–C(19)	1.450(20)

Table 4. Cordifolia-P2

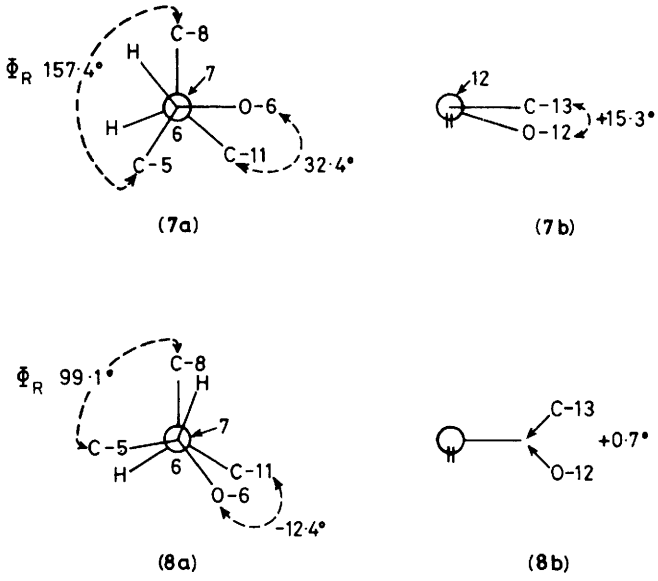
Bond angles (°)

C(2)–C(1)–C(10)	123.8(10)	C(8)–C(9)–C(10)	111.1(8)
C(2)–C(1)–O(1)	114.8(9)	C(1)–C(10)–C(9)	118.9(10)
C(10)–C(1)–O(1)	59.3(7)	C(1)–C(10)–C(14)	124.1(9)
C(1)–C(2)–C(3)	109.1(9)	C(1)–C(10)–O(1)	59.1(8)
C(1)–C(2)–O(2)	110.2(10)	C(9)–C(10)–C(14)	114.4(11)
C(3)–C(2)–O(2)	105.2(11)	C(9)–C(10)–O(1)	113.6(10)
C(2)–C(3)–C(4)	112.1(11)	C(14)–C(10)–O(1)	112.6(9)
C(3)–C(4)–C(5)	114.9(16)	C(7)–C(11)–C(12)	108.1(8)
C(3)–C(4)–C(15)	118.0(9)	C(7)–C(11)–C(13)	130.9(9)
C(3)–C(4)–O(4)	115.5(14)	C(12)–C(11)–C(13)	120.7(9)
C(5)–C(4)–C(15)	123.3(16)	C(11)–C(12)–O(6)	109.5(8)
C(5)–C(4)–O(4)	58.6(6)	C(11)–C(12)–O(12)	128.8(9)
C(15)–C(4)–O(4)	111.5(13)	O(6)–C(12)–O(12)	121.8(9)
C(4)–C(5)–C(6)	122.3(14)	C(17)–C(16)–O(8)	109.3(13)
C(4)–C(5)–O(4)	60.2(6)	C(17)–C(16)–O(16)	129.4(15)
C(6)–C(5)–O(4)	118.1(12)	O(8)–C(16)–O(16)	121.2(12)
C(5)–C(6)–C(7)	109.3(10)	C(16)–C(17)–C(18)	113.8(17)
C(5)–C(6)–O(6)	110.2(9)	C(16)–C(17)–C(20)	116.0(13)
C(7)–C(6)–O(6)	105.1(7)	C(18)–C(17)–C(20)	130.2(17)
C(6)–C(7)–C(8)	113.2(8)	C(17)–C(18)–C(19)	135.3(18)
C(6)–C(7)–C(11)	103.2(7)	C(1)–O(1)–C(10)	61.6(7)
C(8)–C(7)–C(11)	119.2(10)	C(4)–O(4)–C(5)	61.2(6)
C(7)–C(8)–C(9)	111.3(10)	C(6)–O(6)–C(12)	112.6(7)
C(7)–C(8)–O(8)	109.8(8)	C(8)–O(8)–C(16)	116.8(9)
C(9)–C(8)–O(8)	104.5(8)		

Table 5. Cordifolia-P2

Torsion angles (°)

C(10)–C(1)–C(2)–C(3)	−117.1
C(1)–C(2)–C(3)–C(4)	51.1
C(2)–C(3)–C(4)–C(5)	−98.3
C(3)–C(4)–C(5)–C(6)	147.9
C(4)–C(5)–C(6)–C(7)	−102.4
C(5)–C(6)–C(7)–C(8)	99.1
C(6)–C(7)–C(8)–C(9)	−122.3
C(7)–C(8)–C(9)–C(10)	87.8
C(8)–C(9)–C(10)–C(1)	−83.9
C(9)–C(10)–C(1)–C(2)	157.4
O(6)–C(6)–C(7)–C(11)	−12.4
C(6)–C(7)–C(11)–C(12)	10.5
C(7)–C(11)–C(12)–O(6)	−4.7
C(11)–C(12)–O(6)–C(6)	−3.9
O(12)–O(6)–C(6)–C(7)	10.5
O(16)–C(16)–C(17)–C(18)	40.6



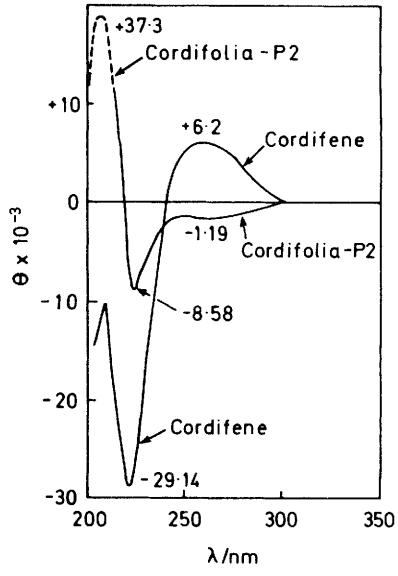


Figure 2. C.d. spectrum of cordifolia-P2 with cordifene for comparison

however that near 120° the Cotton effect will be particularly sensitive to small deviations from ideal geometry and anomalous results will be likely.[8] The situation for cordifene with its Φ_R 157.4° is clear cut [Figure 2 and (7a)]. In the case of cordifolia-P2 the torsion angle Φ_R is only 99.1°, significantly less than McPhail's 120° limit and indeed the compound shows a modest negative n→π* Cotton effect [Figure 2 and (8a)]. Direct measurement of the C=C–C=O torsion angle however gives a value of +0.7°—almost zero within the standard deviation, and the methylene lactone unit is virtually flat. The contribution of the latter might be expected to be near zero to the Cotton effect, though if small energy differences are involved there may be conformational adjustments in solution leading to a small left-handed chirality in the chromophore. However, with a Φ_R angle 99° paired with a chromophore tension angle of near zero it is clear that departures from the ideal McPhail relationship can be considerable. Cordifene and its epoxide have the same absolute configurations[4] and it is thus highly likely, from the discussion above, that cordifolia-P2, despite its negative n→π*

Cotton effect, also belongs to the same absolute configurational series.

The torsion angles in the 5-membered lactone ring (Table 5) are also different from the earlier structures:[4] the ring has been considerably flattened and is now nearly planar with no torsion angle *much larger* than 12°. Crucial torsional angle changes here are responsible for changes in chemical shift, multiplicity, and couplings of the 6-H and 7-H protons of cordifolia-P2 as compared with the other examples listed in Table 1. The large bond angle at C-18 noted earlier in cordifene and its epoxide is again found in cordifolia-P2, and the angelate side chain which differs conformationally as between cordifene and its 4β,15-oxide adopts, as reflected in the C(16)–C(17) torsion angle, yet another conformation in cordifolia-P2. An intramolecular hydrogen bond O(2)–O(12) of length 2.86 Å was noted in the latter structure.

^{1}H N.m.r. data for cordifolia-31, $C_{19}H_{22}O_8$, which differs from cordifene epoxide (**5**), $C_{20}H_{24}O_8$, by having one less CH_2, show that the signals of all the protons belonging to the sesquiterpene element in the two compounds are essentially the same. The difference lies clearly in the ester fragment and ^{1}H n.m.r. data indicate that the angelate ester is replaced by a methacrylate ester: resonances accord well with those for methyl methacrylate. Cordifolia-31 is thus (**6**).

Experimental

Isolation of Cordifolia-31, -54, -55, *and* -P2.—Crude methanol extract of *Erlangea cordifolia*[4] (14.35 g) was separated using a Waters preparative h.p.l.c. instrument (5.7 × 30 cm silica column), eluting with 1% methanol in chloroform. This gave crude cordifene (6.51 g) and crude cordifene 4β,15-oxide (3.55 g). Continued elution with 5% methanol in chloroform then gave a mixture (0.96 g) of more polar compounds.

The crude cordifene oxide fraction was further separated by preparative h.p.l.c. using a C_{18}-reversed phase column, eluting with methanol–water (2:1). Cordifene oxide, cordifene, and mixed fractions containing these were discarded, and attention concentrated on the fraction more polar than either of these compounds. Further h.p.l.c. of the latter using a semi-preparative C_{18} column, eluting with methanol–water (7.5:2.5) finally gave *cordifolia*-31 (15 mg) as needles from methanol which softened near 210 °C forming new spicules melting sharply at 246—247 °C. The trimethylsilylated compound showed only a very weak molecular ion at M^+ 450, but a strong $M^+ - 15$ peak was readily mass-measured (Found: 435.1487. $C_{21}H_{27}O_8Si$ requires M, 435.1499). Unsilylated material gave only weak higher-mass peaks. The R_t of cordifolia-31 on a C_{18} column, eluting with methanol–water (7.5:2.5) at 1 ml/min was 6.1 min. For comparison the R_t of cordifene 4β,15-oxide was 6.6 min, and of cordifene 7.6 min.

The mixture of more polar compounds above (0.96 g) was crystallised to yield cordifene oxide (0.39 g), mixtures of the latter with cordifene, and mother liquors which were separated by semi-preparative h.p.l.c. using silica columns and eluting with ether–light petroleum (b.p. 60—80 °C) (9:1). Repeated runs eventually gave *cordifolia*-54 (8 mg), a white powder with no sharp m.p. Its trimethylsilyl derivative had M^+, 434.2112 ($C_{23}H_{34}O_6Si$ requires M, 434.2102). Also isolated was *cordifolia*-55 (15 mg), m.p. 150—152 °C (although last traces did not disappear until 164 °C). Its trimethylsilyl derivative had M^+, 492.2240 ($C_{25}H_{36}O_8Si$ requires M, 492.2303). R_t-Values on h.p.l.c. using a silica gel column and eluting with ether–light petroleum (b.p. 60—80 °C) (9:1) at 3 ml/min were: cordifolia-54, 7.4 min; cordifolia-55, 7.7 min; cordifene, 6.6 min.

Further chromatography of the polar compounds on silica-G plates (40 × 40 cm, HF 254) eluting with methanol in chloroform (1:20) gave two main mobile products. One of these was present in a small amount (3 mg) and designated cordifolia-P17. It was obtained nearly pure and ^{1}H n.m.r. spectroscopy indicates that it is an angelyl ester closely related to the other *Erlangea* compounds. The major component was further purified on a semi-preparative C_{18} column eluting with methanol–water (7.5:2.5) to give *cordifolia*-P2 (30 mg), m.p. 189—190 °C from methanol. It had M^+, 378.1652 ($C_{20}H_{26}O_7$ requires M, 378.1678), $\nu_{max.}$(KBr) 3 500br, 1 770sh, 1 760, 1 715sh, 1 700, and 1 650 cm^{-1}. In the u.v. range there was only strong end-absorption.

Crystallographic Analysis of Cordifolia-P2 (**4**).—The space group and preliminary cell parameters were determined photographically. For intensity measurement the crystal was

Table 6. Fractional atomic co-ordinates with standard deviations in parentheses. Cordifolia-P2

Atom	*x/a*	*y/b*	*z/c*
C(1)	0.175(2)	0.440 7(7)	0.044 5(5)
C(2)	0.118(2)	0.516 7(8)	−0.008 1(5)
C(3)	0.129(3)	0.615 7(8)	0.024 4(6)
C(4)	0.319(3)	0.632 6(7)	0.059 4(5)
C(5)	0.318(2)	0.616 5(7)	0.133 6(5)
C(6)	0.489(2)	0.580 5(6)	0.170 9(5)
C(7)	0.462(2)	0.471 5(6)	0.186 8(4)
C(8)	0.569(2)	0.404 7(7)	0.136 1(5)
C(9)	0.428(2)	0.334 2(7)	0.100 8(5)
C(10)	0.343(2)	0.378 2(7)	0.037 9(5)
C(11)	0.508(2)	0.465 2(6)	0.260 6(5)
C(12)	0.522(2)	0.564 3(7)	0.287 7(5)
C(13)	0.522(2)	0.389 7(8)	0.301 6(5)
C(14)	0.471(2)	0.377 1(7)	−0.021 5(5)
C(15)	0.495(3)	0.629 2(8)	0.018 2(6)
C(16)	0.860(2)	0.385(1)	0.197 2(5)
C(17)	0.974(2)	0.312(1)	0.236 5(8)
C(18)	1.037(2)	0.342(1)	0.290 5(9)
C(19)	1.024(3)	0.432(1)	0.327 6(6)
C(20)	0.988(2)	0.209 7(7)	0.204 4(7)
O(1)	0.154(2)	0.344 2(5)	0.022 5(4)
O(2)	−0.076(1)	0.505 0(6)	−0.027 1(4)
O(4)	0.323(2)	0.713 2(4)	0.107 3(4)
O(6)	0.503(2)	0.627 2(4)	0.237 0(3)
O(8)	0.701(1)	0.343 6(5)	0.172 3(4)
O(12)	0.546(2)	0.589 6(5)	0.344 8(3)
O(16)	0.892(1)	0.471 8(6)	0.188 6(4)
H(1)	0.1122	0.4802	0.0814
H(2)	0.2105	0.5044	−0.0481
H(3A)	0.0158	0.6211	0.0601
H(3B)	0.0919	0.6680	−0.0107
H(5)	0.2115	0.5806	0.1657
H(6)	0.6125	0.5942	0.1429
H(7)	0.3213	0.4433	0.1819
H(8)	0.6351	0.4489	0.1031
H(9A)	0.4982	0.2715	0.0911
H(9B)	0.3180	0.3171	0.1331
H(13A)	0.5092	0.3206	0.2834
H(13B)	0.5382	0.3957	0.3524
H(14A)	0.4236	0.4092	−0.0633
H(14B)	0.5198	0.3099	−0.0356
H(14C)	0.6068	0.4132	−0.0118
H(15A)	0.6171	0.6401	0.0469
H(15B)	0.5177	0.5631	−0.0046
H(15C)	0.5029	0.6778	−0.0203
H(18)	1.1210	0.2919	0.3198
H(19A)	0.9208	0.4800	0.2817
H(19B)	1.1406	0.4602	0.3583
H(19C)	0.9886	0.4540	0.3767
H(20A)	0.8011	0.2034	0.2139
H(20B)	1.1072	0.1890	0.1560
H(20C)	1.0728	0.1656	0.2439
H(020)	−0.1032	0.4434	−0.0550

then mounted on an Enraf-Nonius CAD4 diffractometer. Accurate lattice parameters were obtained by least-squares refinement of the positions of 25 reflections measured on the diffractometer with θ *ca.* 30°. Intensity data were collected with Cu-K_α radiation using an ω–θ scan for $1° \leqslant \theta \leqslant 66°$. A total of 1 950 independent reflections was measured of which only 823 had $I > 3\sigma(I)$ and were considered observed and used in the subsequent refinement. The data were corrected for Lorentz and polarisation factors, but no absorption corrections were applied. Data reduction and subsequent crystallographic calculations were performed using the CRYSTALS system of programs.

Crystal data. $C_{20}H_{26}O_7$, $M = 378.2$ Orthorhombic, $a = 6.959(2)$, $b = 13.949(3)$, $c = 19.762(3)$ Å, $U = 1\,918.3$ Å^3, $Z = 4$, $D_c = 1.30$ g cm^{-3}, $F(000) = 800$. Space group $P2_12_12_1$ uniquely from systematic absences. Cu-K_α radiation $\lambda = 1.541\,78$ Å, μ(Cu-K_α) = 8.31 cm^{-1}.

Structure solution and refinement. The structure was solved by direct methods using the MULTAN program. More than a dozen different runs of the program with variations of the parameters and the data were required before a solution was obtained. 268 Reflections with $E > 1.25$ were finally used. The E map based on the best set of phases in the final run revealed the positions of 26 of the 27 non-hydrogen atoms among the largest peaks in the map. The remaining atom was readily located in a subsequent difference map. Full-matrix isotropic least-squares refinement of these positions gave a value for R of only 16.6%.

Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms. A difference map next revealed the approximate positions of many of the hydrogen atoms. Geometric considerations were then used to calculate the accurate positions of all the hydrogen atoms whose location could be fixed in this way. The remaining hydrogen atom positions were taken directly from the peaks in the difference map. The hydrogen atoms were then included in the calculations but without refinement. Analysis of the agreement between F_o and F_c suggested the adoption of a weighting scheme based on a Chebyshev polynomial. Refinement finally converged with the largest parameter shift 0.1 σ after 18 cycles of least squares refinement. The final R value at convergence was 5.74% with R_w 0.0663. A final difference map was calculated which showed no peaks or depressions >0.17 e Å^{-3}. Final atomic co-ordinates are listed in Table 6, temperature factors and observed and calculated structure factors are listed as a Supplementary Publication [SUP. No. 23855 (15 pp.)].*

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* For details of the Supplementary Publication scheme, see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.

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