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(13) The simplest rationale to explain the failures of these alkylations is the steric hindrance offered by the syn bromo substituent. This would presumably increase O-alkylation, but should also have resulted in endo alkylation, which was not observed. The anti bromo compound corresponding to **8a** or **8b** is not expected to be more useful, since it could be expected[14] to undergo intramolecular alkylation.
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(21) References 1a, c, and d.
(22) References 1b–d.

Celorbicol, Isocelorbicol, and Their Esters: New Sesquiterpenoids from *Celastrus orbiculatus*

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Esters of two new sesquiterpenoid polyalcohols—celorbicol (**1a**) and isocelorbicol (**2a**)—have been isolated from *Celastrus orbiculatus*. Structures of the parent alcohols have been established by x-ray crystallography, and those of the derived esters have been assigned by NMR spectroscopy. These compounds are structurally related to other polyesters and ester alkaloids from the Celastraceae, all of which are based on the dihydroagarofuran ring system.

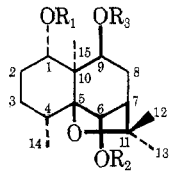
In a previous paper,[1a] we reported the isolation of a series of sesquiterpenoid polyol esters from seeds of *Celastrus orbiculatus* (Celastraceae). In this present paper, we report the complete structural elucidation of the parent alcohols and present evidence for the structures of three of their naturally occurring esters.

The occurrence of sesquiterpenoid esters in the seed oil of *Celastrus paniculatus* was first suggested by Gunde and Hilditch in 1938.[2] Recently, several esters of this sesquiterpenoid group from various celastraceous genera have been characterized, including examples from *Celastrus*,[3,4] *Euonymus*,[5-10] *Maytenus*,[11] and *Catha*.[12,13] The parent alcohols of several of these esters have been characterized, including malkanguniol,[3,4] celapanol,[4] euonyminol,[5] isoeuonyminol,[5] evoninol,[5,7-9] alatol,[5e] maytol,[11] deoxymaytol,[11a] 8-epideoxymaytol,[8] 3,4-dideoxy-7β-hydroxymaytol,[8] and cathol.[12,13] Apparently, all of these alcohols have the same ring system, but they vary in the number, position, and configuration of hydroxyl substituents. This ring system[14] has been considered to be identical with that of β-dihydroagarofuran; however, the widely accepted stereochemistry of β-dihydroagarofuran has been questioned recently.[15] As isolated from their natural sources, the hydroxyl groups of these polyalcohols are acylated with acetic acid and various other carboxylic acids.[3-13] Since certain of these acyl groups contain nitrogen, some of the esters of this series are classed as alkaloids.[4-13]

Isolation of Polyalcohols. After alkaline hydrolysis of *Celastrus orbiculatus* seed oil, a neutral fraction was isolated which provided two isomeric polyalcohols—celorbicol (**1a**) and isocelorbicol (**2a**)[16]—when subjected to preparative TLC. Alcohols **1a** and **2a** are high-melting, crystalline solids with the empirical formula $C_{15}H_{26}O_4$, as shown by high-resolution mass spectra. Their ir spectra showed strong hydroxyl absorptions, but none for carbonyl groups. General features of the NMR and mass spectra of **1a, 2a,** and their various esters (vide infra) led us to infer that **1a** and **2a** are closely related to malkanguniol,[3] and that **1a** is a 1,6,9-trihydroxy derivative of the dihydroagarofuran system.[1a] The complete structure and stereochemistry of **1a** and **2a** were established subsequently by single crystal x-ray crystallography.

X-Ray Crystallographic Analysis. Celorbicol was converted to a mono-*p*-bromobenzoate derivative (**1f**) which was used to elucidate its absolute stereostructure by x-ray diffraction experiments. A computer-generated drawing of the final x-ray model is presented in Figure 1. Table I lists fractional coordinates for **1f**. Figure 1 clearly shows both of the cyclohexane rings in the chair conformation. The hydroxyl at C-1 is equatorial while the one at C-9 is axial. The C-14 and C-15 methyl groups are both axial. The absolute configuration we assign to this structure is the same as that previously reported by Sasaki and Hirata[6,17] for neoevonine. Bond distances and angles agree with generally accepted values and

Scheme I



1a, $R_1 = R_2 = R_3 = H$

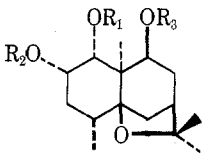
b, $R_1 = C_6H_5C(=O)$; $R_2 = R_3 = Ac$

c, $R_1 = R_2 = C_6H_5C(=O)$; $R_3 = Ac$

d, $R_1 = Ac$; $R_2 = R_3 = H$

e, $R_1 = R_2 = Ac$; $R_3 = H$

f, $R_1 = p$-bromobenzoyl; $R_2 = R_3 = H$



2a, $R_1 = R_2 = R_3 = H$

b, $R_1 = C_6H_5CH{=}CHC(=O)$; $R_2 = R_3 = Ac$

c, $R_1 = Ac$; $R_2 = R_3 = H$

d, $R_1 = R_2 = Ac$; $R_3 = H$

e, $R_1 = p$-bromobenzoyl; $R_2 = R_3 = H$.

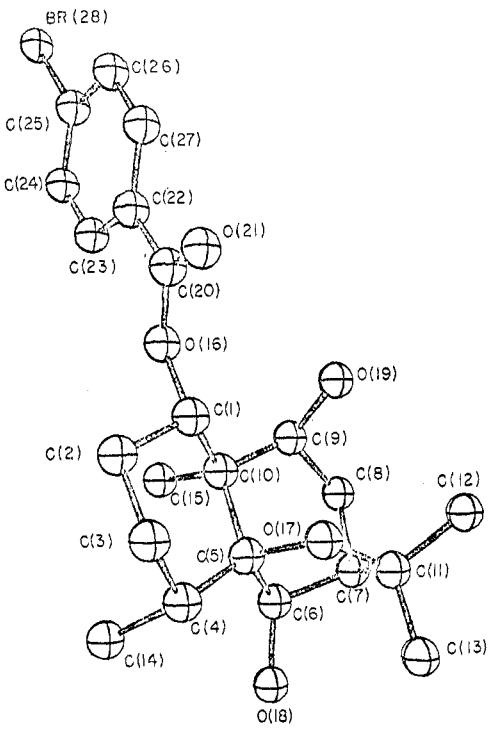


Figure 1. Computer-generated drawing of celorbicol mono-*p*-bromobenzoate (**1f**). Hydrogens are omitted for clarity.

there are no abnormally short intermolecular contacts.[18]

The structure of isocelorbicol was similarly solved by x-ray diffraction. Use of underivatized **2a** proved advantageous, even though its mono-*p*-bromobenzoate (**2e**) was available. A computer-generated drawing of **2a** is given in Figure 2, and Table II gives the final fractional coordinates.[18] The overall molecular conformation of isocelorbicol (**2a**) is identical with that of celorbicol. The hydroxyl groups are located at C-1, C-2, and C-9, and they are equatorial, axial, and axial, respectively. The molecular geometry agrees well with generally accepted values, and there are no abnormally short intermolecular contacts.[18] We have assumed the same absolute configuration for **2a** as we have determined for **1a**.

Table I. Final Fractional Coordinates for the *p*-Bromobenzoate of Celorbicol (1f) [a]

C(1)	1.065 (2)	0.066 (2)	0.2294 (9)
C(2)	1.083 (2)	0.109 (2)	0.118 (1)
C(3)	1.206 (2)	0.205 (2)	0.1368 (9)
C(4)	1.110 (2)	0.285 (2)	0.2009 (9)
C(5)	1.073 (1)	0.241 (2)	0.3109 (9)
C(6)	0.976 (2)	0.314 (2)	0.383 (1)
C(7)	1.068 (1)	0.276 (2)	0.4990 (9)
C(8)	0.964 (2)	0.174 (2)	0.511 (1)
C(9)	0.969 (1)	0.095 (2)	0.420 (1)
C(10)	0.956 (1)	0.135 (2)	0.3002 (9)
C(11)	1.294 (1)	0.264 (2)	0.4902 (9)
C(12)	1.414 (2)	0.191 (2)	0.580 (1)
C(13)	1.405 (2)	0.363 (3)	0.494 (1)
C(14)	0.930 (2)	0.335 (2)	0.119 (1)
C(15)	0.731 (2)	0.148 (2)	0.245 (1)
O(16)	0.944 (1)	−0.029 (2)	0.2128 (7)
O(17)	1.2712 (8)	0.218 (2)	0.3810 (6)
O(18)	1.011 (1)	0.419 (2)	0.3628 (7)
O(19)	1.131 (1)	0.021 (2)	0.4550 (6)
C(20)	1.039 (2)	−0.117 (2)	0.206 (1)
O(21)	1.218 (1)	−0.125 (2)	0.2169 (9)
C(22)	0.892 (1)	−0.201 (2)	0.1801 (9)
C(23)	0.684 (2)	−0.186 (2)	0.1516 (9)
C(24)	0.55 (2)	−0.266 (2)	0.126 (1)
C(25)	0.636 (2)	−0.363 (2)	0.136 (1)
C(26)	0.835 (2)	−0.383 (2)	0.165 (1)
C(27)	0.959 (2)	−0.299 (2)	0.187 (1)
Br(28)	0.4520 (2)	−0.476 (2)	0.1045 (2)
H(1)	1.207[b]	0.054	0.268
H(2A)	0.948	0.124	0.077
H(2B)	1.149	0.056	0.080
H(3A)	1.220	0.229	0.063
H(3B)	1.344	0.185	0.183
H(4)	1.203	0.342	0.226
H(6)	0.828	0.313	0.366
H(7)	1.054	0.316	0.565
H(8A)	0.822	0.188	0.513
H(8B)	1.033	0.143	0.586
H(9)	0.839	0.055	0.412
H(12A)	1.428	0.219	0.657
H(12B)	1.551	0.175	0.566
H(12C)	1.341	0.121	0.580
H(13A)	1.543	0.347	0.478
H(13B)	1.421	0.392	0.571
H(13C)	1.332	0.409	0.436
H(14A)	0.874	0.389	0.157
H(14B)	0.823	0.278	0.095
H(14C)	0.973	0.358	0.050
H(15A)	0.665	0.077	0.239
H(15B)	0.716	0.177	0.170
H(15C)	0.663	0.190	0.294
H(18A)[c]	0.963	0.430	0.299
H(18B)	0.957	0.451	0.404
H(19)	1.129	0.000	0.518
H(23)	0.629	−0.117	0.149
H(24)	0.406	−0.259	0.100
H(26)	0.890	−0.455	0.167
H(27)	1.107	−0.314	0.211

[a] Hydrogen atoms are given the same number as the heavy atom to which they are attached. The estimated standard deviation of the least significant figure is given in parentheses. [b] The hydrogen positions were not varied in refinement. [c] Since this hydrogen appeared twice in the difference map, both positions were included, each with an occupancy factor of one-half.

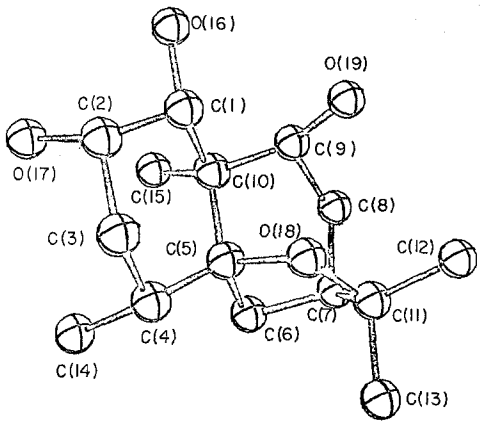


Figure 2. Computer-generated drawing of isocelorbicol (**2a**). Hydrogens are omitted for clarity.

Celoribicol can now be described as a 1α,6β,9β-trihydroxy derivative of β-dihydroagarofuran while isocelorbicol is the corresponding 1α,2α,9β-triol.

Esters of Celorbicol and Isocelorbicol. The most polar fractions from countercurrent distribution of *C. orbiculatus* seed oil contained esters of **1a** and **2a**.[1a] This mixture of esters was resolved into three discrete compounds by preparative TLC; traces of some related esters also were observed. Esters A (**1b**) and C (**1c**), partially characterized previously,[1a] yielded **1a** when subjected to alkaline hydrolysis, and ester B (**2b**) gave **2a** when treated similarly. The nature of the acyl groups of **1b**, **1c**, and **2b** was determined by GLC, mass spectra, and NMR.[1a]

When acetylated under mild conditions, **1a** afforded a monoacetate (**1d**) together with a diacetate (**1e**); monoacetate **2c** and diacetate **2d** were prepared similarly from **2a**. In both cases, one monoacetyl and one diacetyl derivative were the predominant products isolated by preparative TLC, although minor amounts of other isomers were apparent. Similarly, **1a** and **2a** each yielded mainly one mono-*p*-bromobenzoate (**1f** and **2e**) under mild acylating conditions.

NMR Spectra of Celorbicol and Its Esters. From inspection of their NMR spectra (Table III), it is obvious that compounds **1a–f** contain no hydroxymethylene function; no AB quartet corresponding to such a grouping is observed. Celorbicol and its various esters (**1a–f**) show three sets of signals which, within the framework of the dihydroagarofuran ring system, may be attributed to methine protons α to secondary hydroxyl groups. Each of these signals exhibits the expected downfield shift upon acylation of the corresponding hydroxyl group. Decoupling experiments revealed that none of these three methine protons is coupled to another of this group. These observations indicated that none of the hydroxyls has a vicinal relationship, and were consistent with a 1,6,9 arrangement of hydroxyl substituents.

One downfield methine proton appears as a slightly broadened singlet, only weakly coupled ($J < 1$ Hz) to any other proton. The axial proton at C-6 uniquely accommodates this observation with $\phi_{6,7} = 80°$, a dihedral angle corresponding to a value of $J < 1$ Hz.[19] Spectra of related esters from other sources exhibit comparable singlets for the corresponding C-6 protons.[3,4,8]

The axial proton at C-1 appears as a pair of doublets, the X portion of an ABX system, at δ 4.3 (**1a**) or 5.26–5.53 (**1b–f**). These multiplets have couplings appropriate for an axial–axial interaction (J = 10–12 Hz) together with one that is axial–equatorial (J = 4–6 Hz);[20] they are similar to those ascribed to the axial C-1 proton for esters of celapanol.[4] We assign the remaining methine-associated multiplet for **1b** and **1c** to the equatorial proton at C-9; this appears as a doublet of doublets with $J_{ae} = 6$ and $J_{ee} = 1$ Hz due to couplings with methylene protons at C-8 (compare with esters B-1 and B-4 from *Euonymus europaeus*.[8])

Upfield signals (Table III) include proton singlets for angular or geminal methyl groups—C-12, C-13, and C-15—and doublets (J = 7 Hz) for the secondary methyl group, C-14; singlets associated with the various acetyl functions also occur. The H-14 doublets are in accord with corresponding signals for esters of celapanol, as are the singlets generated by H-15.[3,4] In the spectra summarized in Table III (except that of **1e**), signals for C-12 and C-13 protons have the same chemical shift and appear as one six-proton singlet. The coincidence of these two peaks is not generally observed among spectra of related compounds; this overlap may result from a fortuitous balancing of shielding effects from axial oxygen functions at C-6 and C-9.

NMR proton integrals together with mass spectral data indicate that ester A (**1b**) contains two acetate and one benzoate groups, whereas ester C (**1c**) has one acetate and two

Table II. Final Fractional Coordinates for Isocelorbicol (2a) [a]

C(1)	0.3625 (2)	0.4618 (2)	0.3953 (2)
C(2)	0.3876 (2)	0.4697 (2)	0.5614 (2)
C(3)	0.5049 (2)	0.4557 (2)	0.5853 (2)
C(4)	0.5496 (2)	0.3516 (2)	0.5184 (2)
C(5)	0.5178 (1)	0.3395 (1)	0.3527 (2)
C(6)	0.5561 (2)	0.2345 (2)	0.2807 (3)
C(7)	0.5697 (2)	0.2725 (2)	0.1195 (3)
C(8)	0.4591 (2)	0.2894 (2)	0.0549 (3)
C(9)	0.3864 (2)	0.3667 (2)	0.1439 (2)
C(10)	0.3990 (1)	0.3567 (2)	0.3184 (2)
C(11)	0.5318 (2)	0.3763 (2)	0.1448 (2)
C(12)	0.6359 (2)	0.4539 (2)	0.0125 (3)
C(13)	0.7448 (2)	0.3556 (3)	0.1967 (3)
C(14)	0.5288 (2)	0.2524 (2)	0.5174 (3)
C(15)	0.3302 (2)	0.2605 (2)	0.3666 (3)
O(16)	0.2536 (1)	0.4810 (2)	0.3679 (2)
O(17)	0.3263 (1)	0.3940 (1)	0.6444 (2)
O(18)	0.5732 (1)	0.4253 (1)	0.2684 (2)
O(19)	0.3971 (1)	0.4754 (1)	0.0914 (2)
H(1)	0.400 (2)	0.523 (2)	0.350 (3)
H(2)	0.363 (2)	0.544 (2)	0.594 (3)
H(3A)	0.518 (2)	0.459 (2)	0.695 (3)
H(3B)	0.539 (2)	0.519 (2)	0.537 (3)
H(4)	0.631 (2)	0.365 (2)	0.513 (3)
H(6A)	0.504 (2)	0.176 (2)	0.291 (3)
H(6B)	0.624 (2)	0.212 (2)	0.329 (3)
H(7)	0.610 (2)	0.222 (2)	0.056 (3)
H(8A)	0.459 (2)	0.312 (2)	−0.054 (3)
H(8B)	0.425 (2)	0.213 (2)	0.057 (3)
H(9)	0.314 (2)	0.347 (2)	0.120 (3)
H(12A)	0.567 (3)	0.471 (3)	−0.040 (3)
H(12B)	0.673 (4)	0.518 (4)	0.045 (6)
H(12C)	0.682 (3)	0.428 (3)	−0.065 (5)
H(13A)	0.777 (3)	0.419 (4)	0.213 (5)
H(13B)	0.780 (4)	0.319 (4)	0.115 (6)
H(13C)	0.748 (3)	0.305 (3)	0.292 (5)
H(14A)	0.454 (3)	0.239 (3)	0.641 (4)
H(14B)	0.557 (3)	0.181 (3)	0.562 (4)
H(14C)	0.568 (3)	0.261 (3)	0.711 (4)
H(15A)	0.351 (3)	0.227 (3)	0.465 (4)
H(15B)	0.259 (3)	0.283 (3)	0.359 (5)
H(15C)	0.225 (3)	0.203 (3)	0.301 (4)
H(16)	0.216 (3)	0.469 (3)	0.447 (4)
H(17)	0.298 (2)	0.424 (2)	0.715 (4)
H(19)	0.453 (3)	0.504 (2)	0.131 (4)

[a] Hydrogen atoms are given the same number as the heavy atom to which they are attached. The estimated standard deviation of the least significant figure is given in parentheses.

Table III. Proton Chemical Shifts for Celorbicol (1a) and Derived Esters [a]

Protons	1a	1b	1c	1d	1e	1f
H-1	4.3, m	5.43, dd (J = 11, 4)	5.49 dd (J = 12, 4)	5.26, dd (J = 11, 6)	5.28, dd (J = 11, 6)	5.53, dd (J = 10, 5)
H-6	4.3, bs	5.28, bs	5.55, bs	4.34, bs	5.26, bs	4.37, bs
H-9	3.4 dd (?)	4.99, dd (J = 6, 1)	5.04, dd (J = 6, 1)	3.29, dd (J = 6, 1)	3.34, dd (J = 6, 1)	3.34, dd (J = 6, 1)
H-12	1.47, s	1.38, s	1.41, s	1.46, s	1.49, s[b]	1.46, s
H-13					1.35, s[b]	
H-14	1.11, d (J = 7)	0.98, d (J = 7)	1.00, d (J = 7)	1.14, d (J = 7)	0.95, d (J = 7)	1.17, d (J = 7)
H-15	1.04, s	1.30, s	1.36, s	1.13, s	1.16, s	1.28, s
1-O-Acyl		7.2–7.6, m 7.9–8.1, m	7.2–7.7, m 8.0–8.2, m	1.96, s	1.96, s[c]	7.50, 7.82, A_2B_2 system
6-O-Acyl		2.08, s			2.03, s[c]	
9-O-Acyl		1.58, s	1.59, s			

[a] Spectra were determined in $CDCl_3$. Chemical shifts (δ) are expressed in parts per million from tetramethylsilane. Letters following the shifts indicate the number and types of peaks observed before decoupling. [b,c] The assignment of these shifts is uncertain and possibly should be reversed.

Table IV. Proton Chemical Shifts for Isocelorbicol (2a) and Derived Esters [a]

Protons	2a	2b	2c	2d	2e
H-1	4.16, s (?)	5.52, bs	5.28, d (J = 3)	5.36, d (J = 3)	5.56, d (J = 3)
H-2	4.20, m	5.52, bs	4.32, ddd (J = 3, 3, 3)	5.50, ddd (J = 3, 3, 3)	4.47, ddd (J = 3, 3, 3)
H-9	3.2, m	4.73, dd (J = 6, 2)	3.25, m	3.27, m	3.33, m
H-12	1.18, s[b]	1.35, s[c]	1.27, s[d]	1.21, s[e]	1.40, s[f]
H-13	1.46, s[b]	1.38, s[c]	1.45, s[d]	1.45, s[e]	1.43, s[f]
H-14	1.23, d (J = 7)	1.28, d (J = 7)	1.19, d (J = 7)	1.18, d (J = 7)	1.30, d (J = 7)
H-15	1.18, s[b]	1.22, s	1.17, s[d]	1.18, s[e]	1.19, s
1-O-Acyl		6.33, 7.66, AB q (J = 16) 7.2–7.7, m	2.03, s	1.95, s	7.51, 7.87, A_2B_2 system
2-O-Acyl		1.82, s[g]		1.99, s	
9-O-Acyl		2.02, s[g]			

[a] See footnote a, Table III. [b-g] Assignments of these shifts are uncertain and possibly should be interchanged.

benzoate moieties.[1a] By comparing chemical shifts (Table III) for the various sets of three methine protons, the complete structures for esters **1b–f** may be assigned as depicted. Downfield shifts for H-1 signify that the corresponding hydroxyl is acylated in all five esters (**1b–f**); this conclusion is consistent with x-ray crystallographic analysis of **1f**. From similar considerations, the C-6 hydroxyl must be acylated in esters **1b, 1c,** and **1e** but not in **1d** and **1f**. Differences in downfield shifts for H-1 and H-6 indicate that **1c** has benzoate groups attached at both C-1 and C-6 hydroxyl functions, and that **1b** has its single benzoate moiety at C-1. Similarly, the C-9 hydroxyl is not acylated in **1d, 1e,** and **1f**.

Previous workers[4a,5b,11a] have drawn attention to the anomalous upfield shift of signals associated with acetate functions in certain polyalcohol esters of the dihydroagarofuran group. This shift has been attributed to the anisotropic shielding influence ofaromatic rings in neighboring acyl groups. One acetate resonance of **1b** and **1c** (δ 1.59) shows this effect, while other acetate signals recorded in Table I have more typical shifts in the range δ 1.96–2.08. Accordingly, the high-field acetate signals of **1b** and **1c** (δ 1.59) are considered to be generated by an acetoxy group at C-9 where it can be shielded by the benzoate moiety at C-1.

NMR Spectra of Isocelorbicol and Its Esters. The spectra (Table IV) of isocelorbicol and its esters (**2a–e**) indicate the absence of primary hydroxyl functions. As with celorbicol and its esters, there are three sets of signals due to methine protons which are shifted downfield when the adjacent secondary hydroxyl groups are acylated. Two of these resonances are coupled to each other, as revealed by irradiation experiments, but the third is coupled to neither of the other two; a 1,2,9-triol structure is consistent with these results. In the case of **2c,** for example, there was a doublet at δ 5.28 coupled to an apparent quartet at δ 4.32. The quartet collapsed to an apparent triplet when the spectrum was irradiated near δ 5.3, thus signifying three different couplings with adjacent protons, each with approximately the same coupling constant (J = 3 Hz). H-2 is coupled equally with the C-3 protons and also shows an axial–equatorial coupling with H-1; conversely, H-1 appears as a doublet, J = 3 Hz (compare with ddd for C-2 proton in euolalin[5d]). Overlap of signals for H-1 and H-2 obscured the multiplicity of both in the spectra of **2a** and **2b.**

The third methine proton, attached at C-9, appeared as a poorly defined multiplet near δ 3.2 except in the case of **2b,** where it formed a pair of doublets, J_{ae} = 6 and J_{ee} = 2 Hz, due to coupling with C-8 protons.

In contrast to those in the celorbicol series, singlets for C-12 and C-13 protons are well resolved. However, identification of upfield signals (Table IV) associated with methyl groups

of isocelorbicol and its derivatives is not as straightforward as with **1a–f** and assignments of the singlets for C-12, C-13, and C-15 protons are uncertain.

NMR and mass spectral data indicated that ester B contains two acetate and one *trans*-cinnamate groups.[1a] A comparison of the chemical shifts for the C-1 and C-2 methine protons leaves no doubt that the C-1 hydroxyl is acylated in **2b, 2c, 2d,** and **2e,** and that the C-2 hydroxyl likewise is acylated in **2b** and **2d.** From similar considerations, the C-9 hydroxyl must be acylated only in the case of **2b.** H-1 is shifted farther downfield in **2b** than in diacetate **2d,** and is displaced to about the same extent as in **2e** (the mono-*p*-bromobenzoate). From these comparisons, it seems likely that ester B has the structure that we have depicted as **2b.**

Mass Spectra of Celorbicol and Isocelorbicol. In their discussions of the mass spectra of malkanguniol and its esters, both den Hrtog et al.[3a] and Wagner et al.[4b] have stressed the importance of fragments at *m/e* 137 and 124 (or 125) which embrace the original furanoid ring. However, the *m/e* 137 ion is not prominent in the spectra of celapanol derivatives examined by Wagner and co-workers,[4b] nor in the polyalcohols investigated by Budzikiewicz and Römer.[8] In contrast, both the *m/e* 137–138 and 124–125 ions are conspicuous in spectra of **1a** and **2a,** despite the fact that **1a** carries an oxygen substituent at C-6 which must be eliminated. Apparently, the diagnostic value of the *m/e* 137 ion is limited.

Discussion

Celorbicol and isocelorbicol contain four oxygen atoms—fewer than any other of the series of polyalcohols from the Celastraceae. Others contain at least five and as many as ten oxygens. However, mono- and dihydroxy derivatives of dihydroagarofuran have been isolated from *Aquillaria agallocha* wood (family Thymeleaceae).[21] Isocelorbicol is the first of the series found to be acylated with *trans*-cinnamic acid.

ORD curves for **1a** and **2a** were recorded with both chloroform and methanol solutions to provide comparisons with optical rotations reported by den Hertog et al.[3b] and by Wagner et al.[4b] In all cases, values for $[\alpha]_D$ were negative; these results suggest that the sesquiterpenoid ring system of **1a** and **2a** has the same absolute configuration in *C. paniculatus* and *C. orbiculatus.*

Experimental Section

NMR spectra were recorded with a Varian[22] HA-100 instrument, and ir spectra with a Perkin-Elmer Model 137 instrument. Mass spectra were obtained with a Nuclide 12-90G spectrometer. A Beckman DK-2A spectrophotometer was used to measure uv spectra. ORD spectra were recorded with a Cary Model 60 spectropolarimeter. TLC, both preparative and analytical, was carried out on silica gel GF-254 plates (E. Merck, Darmstadt). Components were located under uv light after spraying with ethanolic dichlorofluroescein solution. Melting points were determined with a Fischer-Johns block and are uncorrected.

Isolation of Celorbicol (1a) and Isocelorbicol (2a). Extraction and hydrolysis of *C. orbiculatus* seed oil were described in a previous paper.[1a] A 0.514-g portion of the crude polyalcohol mixture isolated after hydrolysis with methanolic barium hydroxide was subjected to preparative TLC (five 20 × 20 × 0.2 cm plates) with the solvent system chloroform–acetone (3:1); **1a** appeared as a major component at R_f 0.5, and **2a** at R_f 0.3. In addition, three minor bands appeared which were not investigated.

Celorbicol. Elution of the R_f 0.5 bands with chloroform–methanol (3:1) provided 0.205 g of **1a:** mp 222–223 °C after recrystallization from chloroform–acetone; ir ($CHCl_3$) 3598, 3450 (OH), 2940, 1133, 1110, 1009, 965, 900, 855 (broad) cm^{-1}; ORD $[\alpha]^{26}D$ −24, $[\alpha]_{560}$ −27, $[\alpha]_{440}$ −46, $[\alpha]_{400}$ −59, $[\alpha]_{350}$ −83, $[\alpha]_{300}$ −126, $[\alpha]_{270}$ −177, $[\alpha]_{250}$ −236° (*c* 0.47, CH_3OH); $[\alpha]^{26}D$ −27, $[\alpha]_{480}$ −38, $[\alpha]_{400}$ −59, $[\alpha]_{320}$ −100, $[\alpha]_{280}$ −145, $[\alpha]_{260}$ −188° (*c* 0.37, $CHCl_3$); NMR, $CDCl_3$ shifts in Table III; Me_2SO-d_6, δ 0.90 (s, 3 H), 1.00 (d, 3 H, *J* = 7.5 Hz), 1.34 (s, 3 H), 1.41 (s, 3 H), 3.32 (dd, 1 H, *J* = 4, 1 Hz), 3.74 (d, 1 H on hydroxyl, *J* = 4 Hz), 4.0 (m, 3 H), 4.76 (d, 1 H on hydroxyl, *J* = 5 Hz); MS (70 eV) *m/e* (rel intensity) 270 (M^+, 12), 255 (M − CH_3, 100), 159 (50), 149 (35), 138 (36), 125 (34), 109 (38), 97 (23), 95 (25), 85 (28), 83 (29), 69 (27), 57 (22), 55 (35), 43 (61), 41 (24). Found: M^+, 270.182; $C_{15}H_{26}O_4$ requires 270.183.

Isocelorbicol. Elution of the R_f 0.3 band from TLC with chloroform–methanol (3:1) afforded 0.206 g of **2a:** mp 240–241 °C after recrystallization from chloroform–acetone; ir ($CHCl_3$) 3680, 3480 (OH), 2940, 1380, 1361, 1135, 1093, 1063, 1010, 980, 960, 862 (broad) cm^{-1}; ORD $[\alpha]^{26}D$ −8, $[\alpha]_{440}$ −14, $[\alpha]_{360}$ −21, $[\alpha]_{300}$ −25 (minimum), $[\alpha]_{260}$ −16, $[\alpha]_{250}$ −7, $[\alpha]_{245}$ 0, $[\alpha]_{240}$ +12, $[\alpha]_{235}$ +29° (*c* 0.54, MeOH); $[\alpha]^{26}D$ −18, $[\alpha]_{520}$ −22, $[\alpha]_{440}$ −31, $[\alpha]_{360}$ −43, $[\alpha]_{280}$ −69, $[\alpha]_{260}$ −78° (*c* 0.30, $CHCl_3$); NMR, $CDCl_3$ shifts in Table IV; Me_2SO-d_6, δ 1.03 (s, 3 H), 1.06 (s, 3 H), 1.16 (d, 3 H, *J* = 7.5 Hz), 1.41 (s, 3 H), 3.34 (dd, 1 H, *J* = 4,1 Hz), 3.63 (d, 1 H on hydroxyl, *J* = 6 Hz), 3.96 (bm, 4 H); MS (70 eV) *m/e* (rel intensity) 270 (M^+, 28), 255 (M − CH_3, 22), 252 (M − H_2O, 21), 237 (34), 219 (30), 208 (29), 183 (23), 168 (100), 154 (27), 151 (25), 137 (65), 135 (26), 125 (47), 124 (44), 123 (46), 121 (41), 119 (41), 109 (94), 97 (84), 95 (51), 93 (37), 85 (39), 83 (30), 71 (31), 69 (62), 57 (34), 55 (49), 43 (92), 41 (66), 18 (25). Found: M^+, 270.186; $C_{15}H_{26}O_4$ requires 270.183.

X-Ray Analyses. A. Celorbicol *p*-Bromobenzoate (1f). The unit cell of **1f** belonged to the monoclinic space group $P2_1$ with *a* = 6.818 (4), *b* = 13.111 (9), *c* = 12.147 (9) Å, and β = 101.91 (5)°. A calculated and measured density were interpreted to mean two molecules of $C_{22}H_{29}BrO_5$ in the unit cell or one molecule per asymmetric unit. All unique diffraction maxima with $\theta \leq 57°$ were collected using a fully automated four-circle diffractometer and monochromated Cu Kα radiation (1.54178 Å). A total of 1494 reflections were measured and after correction for Lorentz, polarization, and background effects, 1144 were judged observed [$F_o \geq 3\sigma(F_o)$, 77% observed].

Structure solution proceeded routinely. The bromine was located in the Patterson synthesis and careful inspection of the centrosymmetric Br-phased electron density synthesis revealed a plausible starting fragment.[23] The remaining nonhydrogen atoms were located in subsequent electron density syntheses. Hydrogen atoms were located on a difference synthesis after refinement. Full matrix least-squares refinement with nonhydrogen atoms anisotropic, hydrogens isotropic, and with anomalous scattering corrections for Br lowered the conventional discrepancy index to 0.074 for the structure and 0.076 for the enantiomorph.[18,24]

B. Isocelorbicol (2a). Crystals of **2a** are orthorhombic with *a* = 12.770 (1), *b* = 12.374 (3), and *c* = 8.9233 (9) Å and systematic extinctions indicating space groups $P2_12_12_1$. A calculated and measured density indicated one molecule of $C_{15}H_{26}O_4$ per asymmetric unit. Because of the excellent quality of the crystals, all reflections with $\theta \leq 78°$ were collected on a four-circle diffractometer using Cu Kα (1.54178 Å) radiation. After correction for Lorentz, polarization, and background effects, 1535 of the 1628 measured reflections were judged observed (94%).

A starting x-ray model was found by a multiple solution, weighted, tangent formula approach.[25] Refinement with anisotropic nonhydrogen atoms and isotropic hydrogens converged to a final *R* factor of 0.045 for the observed reflections.[18]

Isolation of Ester A (1b), Ester B (2b), and Ester C (1c). The countercurrent fractionation of *C. orbiculatus* seed oil was described in a previous paper.[1a] Material from combined transfers 1461–1469 (0.271 g) was applied to a preparative TLC plate, and was subjected to double development with the solvent system methylene chloride–ethyl ether (95:5); **1c** appeared as major component at R_f 0.65, **1b** at R_f 0.55, and **2b** at R_f 0.37.

Ester A (1b). Elution of the R_f 0.55 band with chloroform–methanol (3:1) yielded 0.116 g of **1b:** mp 179–180 °C after recrystallization from ethyl ether–hexane; ir ($CHCl_3$) 2940, 1730, 1710, 1390, 1375, 1285, 1136, 1107, 1087, 1023, 977, 967, 868 cm^{-1}; NMR, see Table III; MS (70 eV) *m/e* (rel intensity) 458 (M^+, 2) 443 (M − CH_3, 6), 416 (47), 206 (29), 159 (19), 138 (25), 105 (90), 77 (38), 43 (100). Found: M^+, 458.231; $C_{26}H_{34}O_7$ requires 458.230.

Ester B (2b). Elution of the R_f 0.37 band from preparative TLC with chloroform–methanol (3:1) gave 25 mg of **2b,** an amorphous solid which resisted efforts to crystallize it: ir ($CHCl_3$) 2970, 2930, 1740, 1710, 1640, 1450, 1370, 1163, 1135, 1110, 1092, 1070, 1046, 1020, 880 (broad) cm^{-1}; NMR, see Table IV; MS (70 eV) *m/e* (rel intensity) 484 (M^+, 9), 469 (M − CH_3, 2), 353 (79), 233 (30), 131 (100), 105 (23), 103 (24, 43 (56). Found: M^+, 484.246; $C_{28}H_{36}O_7$ requires 484.246.

Ester C (1c). The R_f 0.65 band from preparative TLC was eluted with chloroform–methanol (3:1) to give 23 mg of **1c,** a syrup: ir ($CHCl_3$) 2950, 2930, 1730, 1710, 1450, 1390, 1370, 1105, 1093, 1065, 1021, 980, 892, 875 cm^{-1}; NMR, see Table III; MS (70 eV) *m/e* (rel intensity) 520 (M^+, 11), 505 (M − CH_3, 4), 416 (7), 294 (11), 206 (14), 159 (11), 138 (9), 105 (100), 77 (18), 43 (17). Found: M^+, 520.247; $C_{31}H_{36}O_7$ requires 520.246.

Hydrolysis of Esters A, B, and C. A few milligrams each of **1b, 1c,** and **2a** were hydrolyzed by refluxing for 3 h with 0.2 M methanolic barium hydroxide. Alcohols, isolated by extracting the hydrolysates with chloroform, were examined by analytical TLC [solvent system, chloroform–acetone (75:25)]. The alcohol portion of the hydrolyzates from esters A (**1b**) and C (**1c**) were identical in R_f with **1a,** whereas that from ester B (**2b**) corresponded to **2a.**

Acetylation of Celorbicol (1a). A 0.100-g portion of **1a** was treated overnight at ambient temperature with acetic anhydride–pyridine (2:1). The resulting product was applied to a preparative TLC plate which was developed with chloroform–acetone (95:5). Elution of a band at R_f 0.40 provided a 53% yield of a monoacetate (**1d**), and an R_f 0.60 band gave 29% of a diacetate (**1e**); other minor bands were observed.

Monoacetate **1d** had mp 137–139 °C after recrystallization from chloroform–acetone; ir ($CHCl_3$) 3590, 3460, 2940, 1720, 1377, 1362, 1133, 1113, 1093, 1011, 961, 862 cm^{-1}; NMR, see Table III; MS (70 eV) *m/e* (rel intensity) 312 (M^+, 16), 297 ($M - CH_3$, 18), 252 (38), 243 (33), 237 (52), 219 (30), 210 (23), 206 (36), 194 (32), 191 (38), 177 (31), 176 (64), 159 (70), 155 (46), 140 (38), 138 (75), 137 (57), 125 (91), 109 (96), 97 (63), 95 (37), 85 (36), 83 (72), 72 (43), 69 (39), 55 (39), 43 (100), 41 (39), 28 (49), 18 (83). Found: M^+, 312.194; $C_{17}H_{28}O_5$ requires 312.194.

Diacetate **1e** had mp 154–157 °C after recrystallization from chloroform–hexane; ir ($CHCl_3$) 3590, 3470 (sh), 2940, 1720, 1358, 1135, 1087, 1013, 962, 866 cm^{-1}; NMR, see Table III; MS (70 eV) *m/e* (rel intensity) 354 (M^+, 4), 339 ($M - CH_3$, 3) 252 (21), 234 (23), 176 (51), 159 (27), 138 (32), 137 (21), 125 (21), 124 (12), 109 (27), 43 (100). Found: M^+, 354.204; $C_{19}H_{30}O_6$ requires 354.204.

Acetylation of Isocelorbicol (2a). A 0.100-g portion of **2a** was acetylated as described for **1a,** and the resulting product was similarly fractionated by TLC, except that the developing solvent was chloroform–acetone (90:10). Elution of a band at R_f 0.28 afforded a 72% yield of a monoacetate (**2c**), while an R_f 0.52 band gave 16% of a diacetate (**2d**); minor amounts of other components were noted.

Monoacetate **2c** had mp 176–178 °C after recrystallization from chloroform–hexane; ir ($CHCl_3$) 3570, 2940, 1725, 1360, 1135, 1065, 1013, 987, 957, 863 cm^{-1}; NMR, see Table IV; MS (70 eV) *m/e* (rel intensity) 312 (M^+, 1), 297 ($M - CH_3$, 3), 252 (24), 237 (23), 234 (15), 219 (21), 208 (18), 137 (41), 124 (21), 123 (23), 121 (22), 109 (48), 97 (27), 95 (24), 69 (27), 55 (24), 43 (100), 41 (37), 28 (20). Found: M^+, 312.194; $C_{17}H_{28}O_5$ requires 312.194.

Diacetate **2d** was isolated as a syrup that did not solidify; ir ($CHCl_3$) 3570, 2940, 1725, 1363, 1135, 1110, 1077, 1070, 1015, 978, 967, 855 cm^{-1}; NMR, see Table IV; MS (70 eV) *m/e* (rel intensity) 354 (M^+, 1), 339 ($M - CH_3$, 1), 234 (9), 137 (10), 120 (9), 109 (10), 87 (11), 85 (64), 83 (100), 48 (10), 47 (21), 43 (44), 36 (15). Found: M^+, 354.203; $C_{19}H_{30}O_6$ requires 354.204.

Preparation of Celorbicol *p*-Bromobenzoate (1f). Alcohol **1a** (37 mg) was treated with *p*-bromobenzoyl chloride in pyridine as described by Arora et al.[26] The crude product was applied to a preparative TLC plate which was developed with chloroform–acetone (90:10). Elution of a major component with R_f 0.47 provided 32 mg of **1f:** mp 223–226 °C after recrystallization from chloroform; ir ($CHCl_3$) 3590, 3450 (sh), 2920, 1710, 1585, 1402, 1225, 1100, 1013, 960, 864 cm^{-1}; NMR, see Table III; MS was not recorded because of thermolytic instability of the compound.

Anal. Calcd for $C_{22}H_{29}BrO_5$: c, 58.3; H, 6.5; Br, 17.6. Found: C, 58.1; H, 6.5; Br, 17.9.

Preparation of Isocelorbicol *p*-Bromobenzoate (2e). Alcohol **2a** (50 mg) was treated with *p*-bromobenzoyl chloride in pyridine as described by Arora et al.[26] and the crude product was fractionated by preparative TLC as described for **1f.** Elution of a band at R_f 0.56 yielded 70 mg of **2e:** mp 178–180 °C after recrystallization from ethyl ether–hexane; ir ($CHCl_3$) 3730, 3590, 2940, 1715, 1575, 1470, 1145, 1112, 1105, 1065, 1012, 1000, 990, 957, 863 cm^{-1}; NMR, see Table IV; MS was not recorded because of thermolytic instability of the compound.

Anal. Calcd for $C_{22}H_{29}BrO_5$: C, 58.3; H, 6.5. Found: C, 58.7, H, 6.4.

Registry No.—1a, 59812-41-8; **1b,** 59812-42-9; **1c,** 59812-43-0; **1d,** 59812-44-1; **1e,** 59812-45-2; **1f,** 59812-46-3; **2a,** 59812-47-4; **2b,** 59812-48-5; **2c,** 59812-49-6; **2d,** 59812-50-9; **2e,** 59812-51-0; *p*-bromobenzoyl chloride, 586-75-4.

Supplementary Material Available. A listing of bond distances, bond angles, and observed and calculated structure factors for the *p*-bromobenzoate of celorbicol (**1f**) and for isocelorbicol (**2a**) (16 pages). Ordering information is given on any current masthead page.

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