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Quinones and Related Compounds in Higher Plants. IX.[1] Absolute Structures of Catalponol and Its Congeners

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The absolute structure (**1a**) of catalponol, a naphthoquinone congener of *Catalpa ovata* (Bignoniaceae), was revised to **1** on the basis of chemical correlation with isocatalponol (**2**), a substance of the same group occurring in *Lippia origanoides* (Verbenaceae). The validity of the absolute structure of **1** thus deduced, and hence those of isocatalponol (**2**) and catalponone (**6**), was verified by single crystal X-ray analysis of the *p*-bromobenzoate of 2-epicatalponol (**9**) derived from **1**.

Keywords——catalponol; isocatalponol; naphthoquinone congeners; absolute structure; X-ray analysis; CD spectra; *Catalpa ovata*; Bignoniaceae; *Lippia origanoides*; Verbenaceae

Catalponol (**1**) is the main constituent of the wood of *Catalpa ovata* G. Don (Bignoniaceae). In 1971, Inouye *et al.*[3] assigned the absolute structure (**1a**) to catalponol by application of the exciton chirality rule to its benzoate. On the other hand, in 1976, Brieskorn *et al.*[4] characterized isocatalponol (**2**) isolated from *Lippia origanoides* H.B.K. (Verbenaceae). The two substances have closely similar structures with reversed relative positions of the hydroxy and carbonyl groups with respect to the prenyl groups, to which opposite absolute configurations have been assigned.

Meanwhile, we have elucidated the biosynthetic pathway of the prenylnaphthoquinone congeners, catalponol (**1**), catalpalactone (**3**) and α-lapachones such as 4,9-dihydroxy-α-lapachone (**4**) as well as dehydro-iso-α-lapachones such as 3-hydroxydehydro-iso-α-lapachone (**5**) occurring in the wood and/or in callus cultures of *Catalpa ovata*.[5] In view of the structural resemblance to cataponol (**1**), isocatalponol (**2**) occurring in a different plant would presumably be biosynthesized through a route similar to that for **1**. Accordingly, it seemed desirable from a biogenetic viewpoint to reexamine whether the configurations of the prenyl groups of these substances are indeed opposite, as presumed, or not.

This problem can be easily solved through comparison of the optical rotations of the dicarbonyl compounds (catalponone and/or its antipode), which could be obtained by Jones oxidation of these substances. Although the optical rotation of catalponol-derived catalponone (**6**) previously assigned as **6a** was known, neither the value of the corresponding oxidation product of isocatalponol (**2**) nor the definite CD spectrum of the latter is available in the literature.

1) Part VIII: H. Inouye, S. Ueda, K. Inoue, and H. Matsumura, *Phytochemistry*, **18**, 1301 (1979).
2) Location: *a) Sakyo-ku, Kyoto 606 Japan*; *b) Fukushima-ku, Osaka 553, Japan.*
3) H. Inouye, T. Okuda, and T. Hayashi, *Tetrahedron Lett.*, **1971**, 3615; T. Shingu, T. Hayashi, and H. Inouye, *ibid.*, **1971**, 3619; H. Inouye, T. Hayashi, and T. Shingu, *Chem. Pharm. Bull.*, **23**, 392 (1975).
4) C.H. Brieskorn and R. Pöhlmann, *Arch. Pharm.*, **309**, 829 (1976).
5) H. Inouye, S. Ueda, K. Inoue, T. Hayashi, and T. Hibi, *Chem. Pharm. Bull.*, **23**, 2523 (1975); K. Inoue, S. Ueda, Y. Shiobara, and H. Inouye, *Phytochemistry*, **16**, 1689 (1977); H. Inouye, S. Ueda, K. Inoue, Y. Shiobara, and I. Wada, *Tetrahedron Lett.*, **1978**, 4551.

This paper deals with the identification of the absolute configuration of the prenyl groups in the two substances, catalponol (**1**) and isocatalponol (**2**), on the basis of the chemical correlation of both compounds and the corroboration of the structure (**1**) thus defined by X-ray analysis of a derivative of the former.

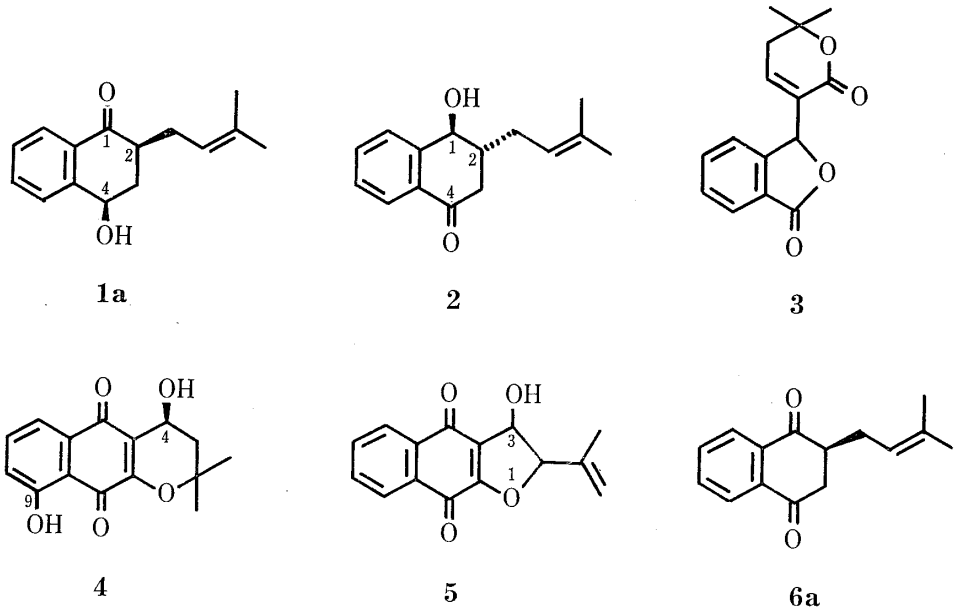
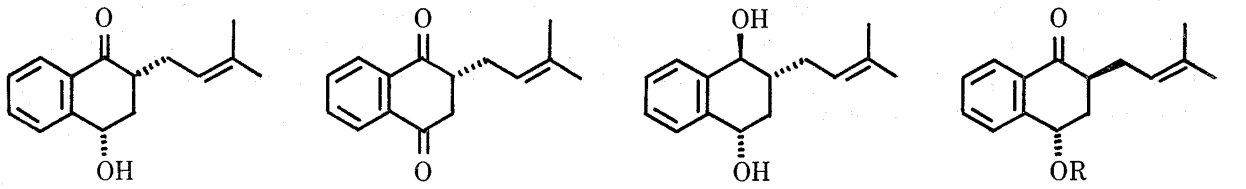


Fig. 1

The conversion of catalponol (**1**) to the substance (**2**) was accomplished in the following way: $NaBH_4$ reduction of catalponol (**1**) in ethanol afforded the diol (**7**) in 57% yield. In the infrared (IR) absorption spectrum, this substance (**7**) showed a hydroxy band at 3320 cm^{-1} but did not show any carbonyl band. In the nuclear magnetic resonance (NMR) spectrum, it showed a new signal at δ 4.40 (br. d, J=7.5 Hz) assignable to the C-1 proton, the J-value of which indicated the *trans* configuration of the two protons at C-1 and C-2. Oxidation of the diol (**7**) in anhydrous benzene with Fétizon's reagent[6] gave, along with a small amount of catalponone, the main product, $C_{15}H_{18}O_2$, mp 80.5—81° as colorless needles in 72% yield. In the IR spectrum, this substance showed absorptions at 3190 (OH), 1670 (α,β conjugated C=O) and 1590 cm^{-1} (C=C), and in the NMR spectrum, it showed signals due to two vinyl methyl groups at δ 1.59 (br. s) and 1.72 (br. s), five protons of a methine and two methylene groups around δ 2.00—3.10, a hydroxy proton at δ 2.86 (br. s, disappeared on addition of D_2O), a proton on a hydroxy-bearing carbon at δ 4.67 (br. d, J=7.0 Hz), an olefinic proton at δ 5.10 (br. t, J=6.5 Hz) and four aromatic protons around δ 7.14—8.10 (m). The conclusion drawn from these data, *i. e.*, that this substance was isocatalponol (**2**) formed by the oxidation of the C-4 hydroxy group of the diol (**7**), was verified by direct comparison including optical rotation with an authentic sample of **2** provided by Prof. Brieskorn.

Though it seems improbable that the inversion of configuration on C-2 would take place during the series of reactions described above, the catalponone obtained from catalponol (**1**) and that from isocatalponol (**2**) isolated from the *Lippia* plant showed the same optical rotation, demostrating the identity of their absolute structures. Accordingly, it was established that catalponol (**1**) and isocatalponol (**2**) have the same steric configuration of the prenyl group. Furthermore, the result of reexamination of the CD data for isocatalponol (**2**) thus obtained

6) M. Fétizon and M. Golfier, *Compt. Rend.*, **267**, 900 (1968); V. Balogh, M. Fétizon, and M. Golfier, *J. Org. Chem.*, **36**, 1339 (1971).



1 **6** **7** **8** : R=COC_6H_4Br-(*p*)
9 : R=H

Fig. 2

was also compatible with the conclusion of Brieskorn *et al.* This implies that the previously proposed absolute structure **1a** for catalponol was erroneous owing to incorrect interpretation of the CD spectrum; it should be revised to **1**, and the structure **6a** for catalponone to **6.**

As the establishment of the absolute structure of catalponol (**1**) thus involves that of the absolute structure of catalponone (**6**),[7] the key intermediate on the biosynthetic route of the series of naphthoquinone congeners in *C. ovata*, we further attempted to confirm the absolute structure of catalponol by X-ray analysis. For this purpose, it was necessary to convert catalponol (**1**), an oily substance, into an appropriate crystalline derivative. After several trials the *p*-bromobenzoate (**8**) of 2-epicatalponol (**9**) obtained by the alkali treatment of **1** through inversion of the prenyl group was subjected to X-ray analysis. A stereoscopic view of the structure determined by the X-ray analysis is shown in Fig. 3. The absolute structure was determined on the basis of the anomalous scattering of the bromine atom. The bond lengths and angles calculated from the atomic parameters in Table I are given in Fig. 4.

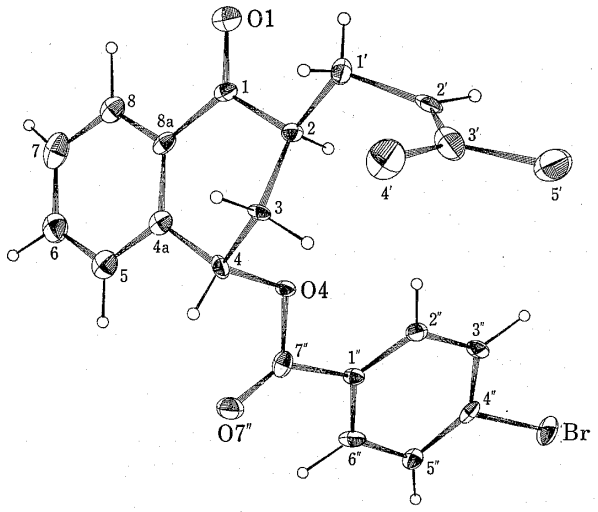


Fig. 3

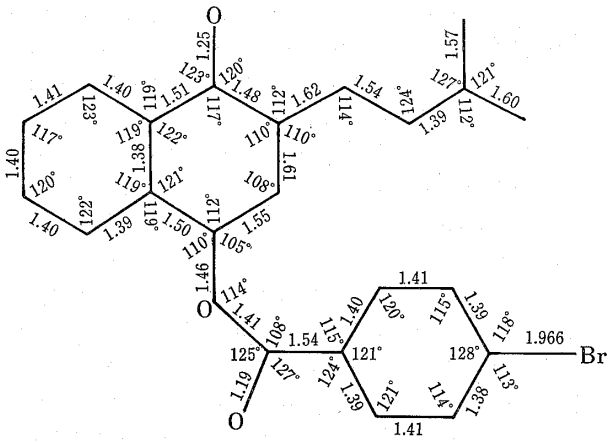


Fig. 4

These results unequivocally demonstrate the absolute structures of catalponol (**1**) and catalponone (**6**) and confirm the absolute configuration of isocatalponol (**2**). Accordingly, it is likely that isocatalponol (**2**) is biosynthesized through the same route as prenylnaphthoquinone congeners of *C. ovata* such as catalponol (**1**) and catalpalactone (**3**). Namely, reduction of the C-4 carbonyl group of catalponone (**6**), the key intermediate leading to these substances, would give rise to catalponol (**1**), while that of the C-1 carbonyl group would give isocatalponol (**2**).

7) Recently, catalponone (**6**) was also found in the wood of *C. ovata*; *cf.* K. Inoue, C.-C. Chen, Y. Shiobara, S. Sakuyama, and H. Inouye, *Yakugaku Zasshi*, **99**, 500 (1979).

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. UV spectra were taken on a Hitachi EPS-3 spectrometer, IR spectra on a Hitachi EPI-S2 spectrometer, NMR spectra on a Varian A-60 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard and mass spectra on a Hitachi RMU 6D spectrometer. Thin-layer chromatography (TLC) and preparative thin-layer chromatography (PLC) were carried out on silica gel 60 GF_{254} (Merck) and PF_{254} (Merck), respectively. Column chromatography was performed on silica gel AR-100 (Mallinckrodt). TLC spots were visualized by exposure to iodine vapor or by irradiation under UV light, and PLC spots by irradiation under UV light. The solvent ratios are expressed by volume. For the X-ray analysis, the atomic scattering factors used in the calculations were taken from "International Tables for X-Ray Crystallography IV." The computation was performed on a FACOM M-190 computer in the Data Processing Center of Kyoto University, using the program system KPAX, which includes the UNICS programs.

$NaBH_4$ Reduction of Catalponol (1)——$NaBH_4$ (410 mg) was added to a solution of **1** (4.84 g) in EtOH (60 ml) and the mixture was stirred at room temperature overnight. After the addition of H_2O (300 ml), the reaction mixture was acidified with 1 N HCl and extracted with $CHCl_3$ (100 ml×3). The extract was washed with H_2O, dried over $MgSO_4$ and concentrated *in vacuo*. The residue (4.50 g) was chromatographed on silica gel (150 g), eluted successively with C_6H_6 (600 ml) and C_6H_6–EtOAc (98: 2) (2 l), and 100 ml fractions were collected. Fractions (Fr.) Nos. 16—23 were combined and concentrated *in vacuo*. Recrystallization of the residue (2.76 g) from C_6H_6 yielded dihydrocatalponol (**7**) as colorless needles, mp 131—132.5°. IR ν_{max}^{Nujol} cm^{-1}: 3320 and 755. NMR δ: 1.67 and 1.74 (each 3H, br.s, $-CH=C(C\underline{H}_3)_2$), 2.40 (2H, br.s, OH, disappeared on treatment with D_2O), 4.40 (1H, d, J=7.5 Hz, C_1–H), 4.70 (1H, dd, J=6.0 and 9.5 Hz, C_4–H), 5.23 (1H, deformed t, J=6.5 Hz, $-CH_2C\underline{H}=C\langle$), 7.17—7.63 (4H, m, 4 arom. protons). *Anal.* Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.41; H, 8.59.

Oxidation of Dihydrocatalponol (7) with Fétizon's Reagent——Substance **7** (2.28 g) was dissolved in anhyd. C_6H_6 (280 ml) under N_2. After the addition of Ag_2CO_3–Celite (22 g) to the solution, the moisture was removed as an azeotrope. The resulting suspension was refluxed for 2 hr with stirring under N_2. After being cooled, the suspension was filtered and the precipitate was washed with hot C_6H_6 (100 ml). The combined filtrate and washings were concentrated *in vacuo* to give a residue (2.30 g), which was subjected to column chromatography on silica gel (70 g). After elution with C_6H_6 (200 ml), the column was further eluted with C_6H_6–EtOAc (97: 3). The combined fractions giving a spot of *Rf* 0.70 on TLC (silica gel, C_6H_6–EtOAc (8: 2)) were concentrated *in vacuo* and the residue (50 mg) was recrystallized from pet. ether to give catalponone (**6**) as colorless needles, mp 78—79°. This substance was identical with an authentic sample (mixed mp, IR and NMR spectra). Combined fractions giving a single spot of *Rf* 0.50 on TLC were concentrated *in vacuo*. The residue (1.63 g) was recrystallized from pet. ether, yielding isocatalponol (**2**) as colorless needles, mp 80.5—81°. $[\alpha]_D^{24}$ +4.77° (c=1.26, MeOH). IR ν_{max}^{Nujol} cm^{-1}: 3190, 1670, 1590, and 770. NMR δ: 1.59 and 1.72 (each 3H, br.s, $-CH=C(C\underline{H}_3)_2$), 2.86 (1H, br.s, OH, disappeared on addition of D_2O), 4.67 (1H, br. d, J=7.0 Hz, C_1–H), 5.16 (1H, deformed t, J=6.5 Hz, $-CH_2-C\underline{H}=C\langle$), 7.14—7.78 (3H, m, $C_{6,7,8}$–H_3), and 7.84—8.10 (1H, m, C_5–H). MS *m/e*: 230 (M^+). CD (c=0.825, MeOH) [θ] (nm): 0 (370), +1290 (347), +2760 (331sh), +3770 (322), 0 (307.5), −9500 (295), −3750 (272), −10000 (254), 0 (238), +4650 (230), and 0 (220). *Anal.* Calcd for $C_{15}H_{18}O_2$: C, 78.25; H, 7.88. Found: C, 78.39; H, 8.01. This substance was identical with an authentic specimen in mixed mp, IR, NMR, and mass spectra.

Jones Oxidation of Isocatalponol (2)——Jones reagent (0.45 ml) was added dropwise to a stirred solution of **2** (208 mg) in Me_2CO (4 ml) under ice cooling. After stirring for a further 30 min, the ice-cooled mixture was mixed with isopropyl alcohol to decompose the excess reagent. The mixture, after addition of H_2O, was extracted with $CHCl_3$ (20 ml×3). The $CHCl_3$ extract was washed successively with saturated aq. $NaHCO_3$ and H_2O, dried over $MgSO_4$ and concentrated *in vacuo*. The residue (198 mg) was chromatographed on silica gel (6 g) with C_6H_6–EtOAc (98: 2) as an eluent, collecting 10 ml fractions. Combined fr. Nos. 2—4 were concentrated *in vacuo* and the residue (154 mg) was recrystallized from pet. ether to give catalponone (**6**) as colorless needles, mp 78—79°, $[\alpha]_D^{24}$ −86.7° (c=3.54, MeOH). IR ν_{max}^{Nujol} cm^{-1}: 1685 and 1595. NMR δ: 1.60 and 1.70 (each 3H, br. s, $-CH=C(C\underline{H}_3)_2$), 5.13 (1H, deformed t, J=7.0 Hz, $-C\underline{H}=C(CH_3)_2$), and 7.63—8.15 (4H, m, 4 arom. protons). *Anal.* Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.99; H, 6.97. This substance was identical with an authentic sample obtained by Jones oxidation of catalponol (**1**) isolated from *C. ovata* on the basis of mixed mp, and comparisons of IR and NMR spectra and $[\alpha]_D$.

Epimerization of Catalponol——The reaction was carried out by a modification of the reported method.[3] 2% NaOH (3 ml) was added dropwise to a stirred solution of **1** (1.12 g) in MeOH (6 ml) at room temperature and the mixture was stirred for a further 5 min. After the addition of saturated aq. NaCl the mixture was extracted with $CHCl_3$ (20 ml×3). The $CHCl_3$ extract was washed with H_2O, dried over $MgSO_4$ and concentrated *in vacuo*. The residue (1.08 g) was chromatographed on silica gel (40 g) using C_6H_6–EtOAc containing an increasing percentage of EtOAc as an eluent. Starting material (533 mg) was recovered from the fractions eluted with C_6H_6–EtOAc (95: 5). Concentration *in vacuo* of the fractions eluted with C_6H_6–EtOAc (93: 7) gave 2-epicatalponol (**8**) as an oily residue (341 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1675, and 1600. NMR δ: 1.62 and 1.70 (each 3H, br. s, $-CH=C(C\underline{H}_3)_2$), 4.96 (1H, t, J=4.0 Hz, C_4–H), 5.15 (1H, deformed t, J=6.5 Hz,

TABLE I. Structure Amplitudes of Bijvoet Pairs

Index	F_{obs}	F_{calc}	Index	F_{obs}	F_{calc}
910	22.4	22.2	$\bar{9}\bar{1}0$	23.3	23.0
220	38.6	32.7	$\bar{2}\bar{2}0$	40.3	34.1
1120	24.0	24.7	$\bar{1}\bar{1}\bar{1}0$	25.8	25.0
520	39.2	38.3	$\bar{5}\bar{2}0$	37.4	37.3
720	37.2	39.4	$\bar{7}\bar{2}0$	38.5	40.0
710	22.4	20.5	$\bar{7}\bar{1}0$	23.2	21.4
330	54.4	55.8	$\bar{3}\bar{3}0$	52.9	55.3
620	34.0	32.6	$\bar{6}\bar{2}0$	35.2	32.5
$\bar{1}\bar{0}21$	23.4	21.7	$10\bar{2}\bar{1}$	20.6	20.5
$\bar{9}31$	8.6	10.3	$9\bar{3}\bar{1}$	8.3	9.7
$\bar{5}21$	35.2	31.6	$5\bar{2}\bar{1}$	35.9	32.1
$\bar{4}21$	37.4	35.6	$4\bar{2}\bar{1}$	38.2	35.9
$\bar{6}11$	44.4	44.1	$6\bar{1}\bar{1}$	42.0	42.3
$\bar{3}21$	43.4	45.7	$3\bar{2}\bar{1}$	42.2	44.7
$\bar{2}21$	22.0	21.4	$2\bar{2}\bar{1}$	20.8	20.2
$\bar{2}11$	29.6	30.2	$2\bar{1}\bar{1}$	28.0	27.8
$\bar{7}12$	10.2	9.7	$7\bar{1}\bar{2}$	10.8	9.7
$\bar{5}12$	43.0	41.0	$5\bar{1}\bar{2}$	44.3	42.5
$\bar{8}12$	21.6	18.6	$8\bar{1}\bar{2}$	23.2	19.0
$\bar{9}12$	33.6	31.8	$9\bar{1}\bar{2}$	32.8	31.5

TABLE II. Atomic Parameters and Their Estimated Standard Deviations

	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	4227(2)	0	2333(2)	4(0)	48(1)	6(0)	−6(1)	−1(0)	−2(1)
C1	9768(15)	1429(50)	8269(21)	3(1)	14(10)	5(2)	1(3)	0(1)	−3(4)
C2	8796(15)	1450(50)	8442(21)	3(1)	13(10)	6(2)	1(3)	0(1)	0(5)
C3	8439(15)	3935(42)	8491(19)	3(1)	7(9)	4(2)	2(3)	0(1)	−1(4)
C4	8513(14)	5042(74)	7294(18)	4(1)	14(9)	5(2)	−4(5)	0(1)	2(6)
C4a	9466(15)	4854(79)	7014(18)	4(1)	21(10)	4(2)	0(5)	0(1)	−4(6)
C5	9767(19)	6410(59)	6277(25)	5(2)	25(13)	9(3)	−1(4)	1(2)	−6(6)
C6	10639(21)	6267(63)	5960(26)	6(2)	35(14)	7(3)	−4(5)	0(2)	0(6)
C7	11251(19)	4605(83)	6432(25)	6(2)	43(17)	10(3)	−5(5)	2(2)	−12(7)
C8	10916(17)	3006(57)	7135(22)	4(1)	29(12)	5(2)	−1(4)	0(1)	−4(5)
C8a	10044(15)	3148(52)	7452(20)	3(1)	23(11)	5(2)	0(3)	0(1)	−4(5)
C1′	8671(14)	169(74)	9648(19)	3(1)	25(11)	5(2)	−3(5)	1(1)	1(7)
C2′	7660(17)	−396(63)	9699(21)	6(1)	12(13)	6(2)	2(4)	1(1)	4(5)
C3′	7122(24)	790(62)	10355(30)	8(2)	26(20)	9(3)	−2(5)	2(2)	2(6)
C4′	6130(20)	−318(96)	10321(27)	6(2)	46(18)	13(3)	3(6)	2(2)	2(9)
C5′	7437(25)	2815(81)	11187(32)	8(2)	43(18)	13(4)	1(6)	3(3)	−7(8)
C1″	6622(15)	3785(48)	4738(19)	3(1)	14(9)	3(2)	1(3)	0(1)	−1(4)
C2″	6172(16)	4794(81)	3694(21)	5(1)	19(12)	7(2)	5(5)	0(1)	1(7)
C3″	5408(15)	3773(50)	2980(20)	3(1)	28(11)	3(2)	−1(3)	0(1)	1(4)
C4″	5217(15)	1667(53)	3340(21)	2(1)	27(12)	6(2)	0(3)	0(1)	−5(5)
C5″	5644(17)	527(51)	4334(22)	5(1)	9(14)	7(2)	2(3)	1(1)	−2(4)
C6″	6360(16)	1706(52)	5053(21)	3(1)	18(11)	6(2)	1(4)	0(1)	0(5)
C7″	7353(15)	5220(74)	5517(19)	3(1)	26(12)	5(2)	−2(5)	0(1)	−4(6)
O1	10303(10)	−53(54)	8729(14)	5(1)	29(7)	8(2)	2(4)	1(1)	1(5)
O4	7859(10)	3862(30)	6399(13)	3(1)	9(6)	4(1)	1(2)	0(1)	0(2)
O7″	7494(13)	7132(37)	5394(16)	6(1)	22(9)	8(2)	1(3)	−1(1)	2(3)

Positional parameters are multiplied by 10^4.
Anisotropic temperature factors are multiplied by 10^3.
Anisotropic temperature factors are in the form
$T=\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hk+2B_{23}kl)\}$.

$-CH_2-C\underline{H}=C\langle$), 7.28—8.04 (m, 4 arom. protons). This substance was identical with an authentic specimen in IR and NMR spectra.

***p*-Bromobenzoylation of 2-Epicatalponol (9)**——*p*-Bromobenzoyl chloride (317.5 mg) was added to a solution of **9** (277 mg) in pyridine (4 ml) and the solution was left to stand for 40 hr at room temperature. After the addition of more *p*-bromobenzoyl chloride (79 mg), it was left for a further 24 hr at room temperature. The reaction mixture was then poured into ice-water and extracted with $CHCl_3$ (20 ml×3). The $CHCl_3$ extract was washed successively with 1 N HCl, saturated $NaHCO_3$ and H_2O, dried over $MgSO_4$ and concentrated *in vacuo*. The residue (548 mg) was subjected to PLC (C_6H_6–EtOAc (75: 25)) and a crystalline residue (431 mg) was obtained from a band around *Rf* 0.61. This substance was recrystallized from Et_2O–pet. ether to yield the *p*-bromobenzoate (**8**) as colorless needles (350 mg), mp 83—84°. IR ν_{max}^{Nujol} cm^{-1}: 1710, 1685, 1590, and 765. NMR δ: 1.63 and 1.68 (each 3H, br. s, $-CH=C(C\underline{H}_3)_2$), 5.14 (1H, deformed t, J=7.0 Hz, $-CH_2C\underline{H}=C\langle$), 6.45 (1H, dd, J=10.5 and 5.0 Hz, C_4–H), 7.25—8.19 (m, 8 arom. protons). CD (c=0.963, MeOH) [θ] (nm): 0 (390), −580 (371), −1020 (356), −570 (342), 0 (336), +280 (332.5), +620 (320), 0 (309.5), −10800 (286), −6150 (270), −7090 (252), 0 (241.5), +24200 (235), 0 (218), 46100 (207), and 0 (202). *Anal.* Calcd for $C_{22}H_{21}BrO_3$: C, 63.96; H, 5.12; Br, 19.29. Found: C, 63.79; H, 5.15; Br, 19.54.

Crystal Data for *p*-Bromobenzoylepicatalponol (8)——The crystal of **8** was monoclinic, space group $p2_1$, with two molecules in a unit cell of dimensions a=14.71(2) Å, b=6.09(1) Å, c=11.44(1) Å and β=100.9(2), V=1024.8 Å^3, D_{calc}=1.352 g/cm^3. The intensity data were collected using a SYNTEX-ADI densitometer from the Weissenberg films. The equi-inclination Weissenberg photographs were taken by rotating the crystals about the *b*- and *c*-axes, using Ni-filtered Cu Kα radiation. The intensity data were corrected for Lorentz and polarization factors, and converged to the structure factors of 983 independent reflections.

Determination of the Absolute Structure of *p*-Bromobenzoylepicatalponol (8)——The absolute structure of compound **8** was solved by the heavy-atom method. The position of the bromine atom was obtained from the Patterson–Harker section at v=0.5. The positional parameters of all the atoms were indicated by the first Fourier map, which had a pseudo mirror symmetry. The structure was refined by the block-diagonal least-squares method. Several cycles of least-squares refinement with the anisotropic thermal parameters for all the atoms gave an *R*-value of 0.098. The hydrogen atoms, whose positions were calculated by assuming a C–H distance of 1.03 Å, were included in the structure factor calculation at the last cycle. The absolute configuration was determined on the basis of the anomalous dispersion term in the atomic scattering factor of the bromine atom. Twenty Bijvoet reflection pairs were selected on the criterion that differences between the observed intensities of the Bijvoet pair were great. The differences of the observed intensities were compared with the differences of the structure amplitudes calculated for the two enantiomorphic structures (Table I). The final atomic parameters and their standard deviations are listed in Table II.

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