# Conformation and Absolute Stereochemistry of Macrocalyxoformin D (=Longirabdiol)

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**The conformation and the absolute stereochemistry of macrocalyxoformin D (=longirabdiol) was determined based on nuclear magnetic resonance spectroscopy, X-ray crystallographic analysis and circular dichroism spectroscopy.**

**Keywords** macrocalyxoformin D; longirabdiol; 6,7-seco-*ent*-kaurenoid; conformation; absolute stereochemistry; nuclear magnetic resonance; X-ray analysis; circular dichroism; *Rabdosia longituba*

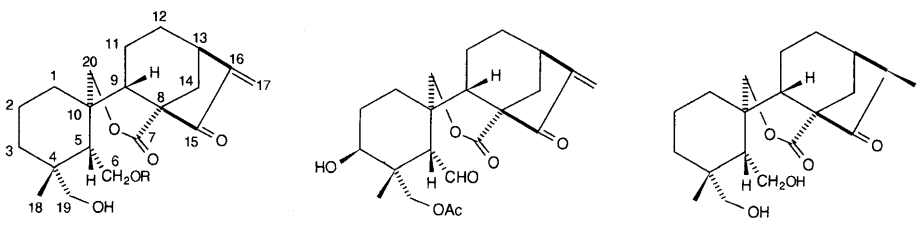
During the course of our systematic investigation of the diterpenoid constituents of *Rabdosia longituba* (MIQ.) (Japanese name: akichouji) (Labiatae),[1] we isolated a diterpene named longirabdiol[2] in the early stage of the study. This compound was finally identified as macrocalyxoformin D (**1**)[3] by means of spectroscopic methods, and has been proposed to have a spiro-seco-kaurene structure or its enantiomer as the basic skeleton. It is known that there are two possible chair conformations for ring A in the *ent*-spiro-seco-kaurene series diterpenoids.[4] However, the conformation of ring A was not discussed in the previous report[3] and the absolute stereochemistry has not been determined yet. Thus, we investigated the stereochemistry of macrocalyxoformin D (**1**) by nuclear magnetic resonance (NMR) spectroscopy, X-ray crystallographic analysis and circular dichroism (CD) spectroscopy. This paper describes the results of these experiments.

The conformation of macrocalyxoformin D (**1**) in $CDCl_3$ solution was examined. The assignments of the proton ($^1H$)- and carbon-13 ($^{13}C$) signals were confirmed by $^1H$–$^1H$-shift correlation spectroscopy ($^1H$-COSY) and ($^1H$–$^{13}C$-shift) correlation spectroscopy ($^1H$–$^{13}C$-COSY). The results are shown in Table I. Some of the $^{13}C$-signal assignments previously reported,[3] especially those for C-5, C-9, C-19 and C-20, were unambiguously reassigned. Based on the assignments of the $^1H$-signals, we performed nuclear Overhauser enhancement (NOE) and $^1H$–$^1H$-nuclear Overhauser enhancement correlation spectroscopy ($^1H$-NOESY) experiments. The results are summarized in Fig. 1. As previously mentioned, there are two possible chair conformations in ring A.[4] One has C-9 equatorial and C-20 axial orientations and the other has C-9 axial and C-20 equatorial orientations. The above mentioned results showed that macrocalyxoformin D (**1**) has a chair conformation having C-9 equatorial and C-20 axial orientations in ring A, the same as that of trichorabdal C (**3**).[5] It is also noteworthy that ring C has a boat conformation as judged from the coupling constants of H-9 (dd, $J=12.5$ and 4.5 Hz).

A single crystal of macrocalyxoformin D 6-*O*-*p*-bromobenzoate (**2**), prepared by treatment of macrocalyxoformin D (**1**) with *p*-bromobenzoyl chloride in methylene chloride in the presence of α-pinene and grown in methanol, was then subjected to an X-ray analysis. The molecular structure of **2** is illustrated in Fig. 2, while bond

TABLE I. Proton- and Carbon-13 NMR Data for Macrocalyxoformin D (**1**)

| | $^1H$ ($CDCl_3$) | $^{13}C$ ($CDCl_3$) |
|---|---|---|
| 1 | | 27.6 |
| 2 | | 18.0 |
| 3 | | 39.4 |
| 4 | | 39.4 |
| 5 | 1.43 (1H, m) | 50.4 |
| 6 | 3.68 (1H, dd, $J=12.5$, 3.5 Hz) | 56.7 |
| | 3.88 (1H, dd, $J=12.5$, 1 Hz) | |
| 7 | | 172.0 |
| 8 | | 57.9 |
| 9 | 2.55 (1H, dd, $J=12.5$, 4.5 Hz) | 44.1 |
| 10 | | 42.8 |
| 11 | | 17.0 |
| 12 | | 29.4 |
| 13 | 3.10 (1H, br dd, $J=9.5$, 4.5 Hz) | 35.1 |
| 14 | 2.15 (1H, d, $J=12$ Hz) | 29.5 |
| | 2.41 (1H, dd, $J=12.5$, 4.5 Hz) | |
| 15 | | 203.0 |
| 16 | | 150.2 |
| 17 | 5.49 (1H, br s) | 118.5 |
| | 6.01 (1H, br s) | |
| 18 | 1.08 (3H, s) | 29.1 |
| 19 | 3.33 (1H, d, $J=11.5$ Hz) | 68.5 |
| | 4.02 (1H, d, $J=11.5$ Hz) | |
| 20 | 4.68 (1H, d, $J=12$ Hz) | 71.4 |
| | 4.92 (1H, d, $J=12$ Hz) | |




1 : R=H
2 : R=CO-C6H4-Br (*p*)

3

4

Chart 1

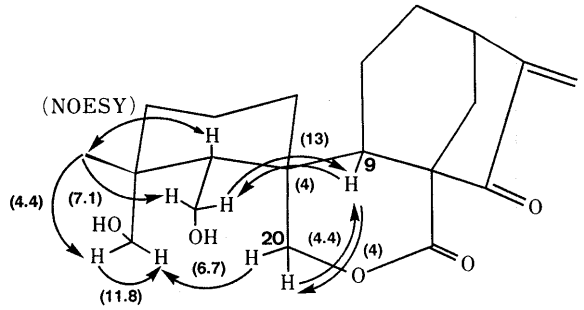



Fig. 1. Summary of NOE and $^1$H-NOESY Experiments
The figures in parentheses show the increments of signal intensity (%).

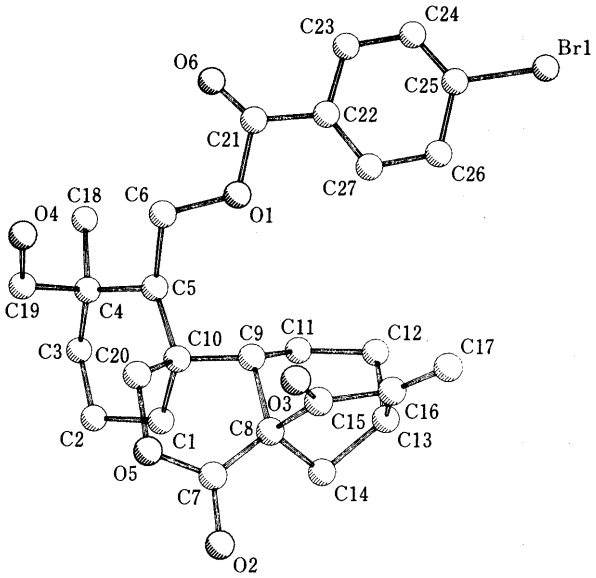



Fig. 2. ORTEP Drawing of Macrocalyxoformin D 6-*O*-*p*-Bromobenzoate (**2**)

TABLE II. Bond Distances (Å) of **2** Involving Non-hydrogen Atoms

| | | | |
|---|---|---|---|
| Br–C(25) | 1.91 | O(1)–C(6) | 1.53 |
| O(1)–C(21) | 1.47 | O(2)–C(7) | 1.25 |
| O(3)–C(15) | 1.24 | O(4)–C(19) | 1.40 |
| O(5)–C(7) | 1.34 | O(5)–C(20) | 1.45 |
| O(6)–C(21) | 1.14 | C(1)–C(2) | 1.57 |
| C(1)–C(10) | 1.60 | C(2)–C(3) | 1.47 |
| C(3)–C(4) | 1.48 | C(4)–C(5) | 1.61 |
| C(4)–C(18) | 1.62 | C(4)–C(19) | 1.64 |
| C(5)–C(6) | 1.52 | C(5)–C(10) | 1.54 |
| C(7)–C(8) | 1.44 | C(8)–C(9) | 1.60 |
| C(8)–C(14) | 1.50 | C(8)–C(15) | 1.57 |
| C(9)–C(10) | 1.53 | C(9)–C(11) | 1.53 |
| C(10)–C(20) | 1.52 | C(11)–C(12) | 1.61 |
| C(12)–C(13) | 1.56 | C(13)–C(14) | 1.57 |
| C(13)–C(16) | 1.51 | C(15)–C(16) | 1.49 |
| C(16)–C(17) | 1.33 | C(21)–C(22) | 1.48 |
| C(22)–C(23) | 1.40 | C(23)–C(27) | 1.37 |
| C(23)–C(24) | 1.40 | C(24)–C(25) | 1.27 |
| C(25)–C(26) | 1.47 | C(26)–C(27) | 1.44 |

S.D. $\pm 0.01 - 0.02$ Å.

distances and angles involving non-hydrogen atoms are given in Tables II and III. The absolute configuration of the molecule was determined by Bijvoet's anomalous dispersion method. Dihydromacrocalyxoformin D (**4**) ob-

TABLE III. Bond Angles (°) of **2** Involving Non-hydrogen Atoms

| | | | |
|---|---|---|---|
| C(6)–O(1)–C(21) | 115.6 | C(20)–O(5)–C(7) | 116.3 |
| C(2)–C(1)–C(10) | 116.0 | C(1)–C(2)–C(3) | 114.4 |
| C(2)–C(3)–C(4) | 115.2 | C(3)–C(4)–C(5) | 115.2 |
| C(3)–C(4)–C(18) | 109.8 | C(3)–C(4)–C(19) | 109.0 |
| C(5)–C(4)–C(18) | 108.5 | C(5)–C(4)–C(19) | 110.2 |
| C(18)–C(4)–C(19) | 103.5 | C(4)–C(5)–C(10) | 117.0 |
| C(4)–C(5)–C(6) | 109.4 | C(10)–C(5)–C(6) | 123.0 |
| C(1)–C(10)–C(5) | 110.0 | C(1)–C(10)–C(9) | 110.7 |
| C(1)–C(10)–C(20) | 108.4 | C(5)–C(10)–C(9) | 112.7 |
| C(5)–C(10)–C(20) | 108.5 | C(9)–C(10)–C(20) | 106.5 |
| C(10)–C(9)–C(8) | 109.7 | C(10)–C(9)–C(11) | 116.8 |
| C(8)–C(9)–C(11) | 107.3 | C(9)–C(8)–C(14) | 111.2 |
| C(9)–C(8)–C(7) | 116.0 | C(9)–C(8)–C(15) | 102.6 |
| C(14)–C(8)–C(7) | 116.7 | C(14)–C(8)–C(15) | 99.0 |
| C(7)–C(8)–C(15) | 108.9 | C(8)–C(14)–C(13) | 102.4 |
| C(14)–C(13)–C(12) | 111.6 | C(14)–C(13)–C(16) | 105.2 |
| C(12)–C(13)–C(16) | 106.9 | C(13)–C(12)–C(11) | 105.3 |
| C(9)–C(11)–C(12) | 115.5 | O(5)–C(20)–C(10) | 112.9 |
| O(5)–C(7)–O(2) | 114.1 | O(5)–C(7)–C(8) | 125.2 |
| O(2)–C(7)–C(8) | 120.7 | O(3)–C(15)–C(8) | 123.1 |
| O(3)–C(15)–C(16) | 125.4 | C(8)–C(15)–C(16) | 111.0 |
| C(13)–C(16)–C(15) | 103.1 | C(13)–C(16)–C(17) | 132.3 |
| C(15)–C(16)–C(17) | 124.3 | O(4)–C(19)–C(4) | 119.0 |
| O(1)–C(6)–C(5) | 107.0 | O(1)–C(21)–O(6) | 117.3 |
| O(1)–C(21)–C(22) | 107.0 | O(6)–C(21)–C(22) | 135.6 |
| C(21)–C(22)–C(23) | 111.7 | C(21)–C(22)–C(27) | 124.6 |
| C(23)–C(22)–C(27) | 123.4 | C(22)–C(23)–C(24) | 116.9 |
| C(23)–C(24)–C(25) | 122.3 | Br–C(25)–C(24) | 123.9 |
| Br–C(25)–C(26) | 112.3 | C(24)–C(25)–C(26) | 123.8 |
| C(25)–C(26)–C(27) | 114.6 | C(22)–C(27)–C(26) | 118.7 |

S.D. $\pm 0.9 - 1.0°$.

TABLE IV. Atomic Coordinates for Non-hydrogen Atoms of **2** with Their e.s.d.'s in Parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Br | 0.8852 (3) | 0.3496 ( 1) | 0.37302 (7) |
| O(1) | 0.913 (1) | 0.1285 ( 6) | 0.6398 (3) |
| O(2) | 1.054 (1) | −0.3048 ( 6) | 0.6112 (4) |
| O(3) | 1.288 (1) | −0.1144 ( 7) | 0.5675 (4) |
| O(4) | 0.996 (1) | 0.0352 ( 6) | 0.8220 (4) |
| O(5) | 1.055 (1) | −0.2067 ( 5) | 0.6837 (3) |
| O(6) | 0.928 (2) | 0.2677 ( 6) | 0.6774 (4) |
| C(1) | 0.683 (2) | −0.1517 ( 9) | 0.6824 (5) |
| C(2) | 0.595 (2) | −0.1555 (11) | 0.7468 (6) |
| C(3) | 0.545 (2) | −0.0668 ( 7) | 0.7717 (6) |
| C(4) | 0.688 (2) | 0.0033 (10) | 0.7681 (5) |
| C(5) | 0.790 (2) | 0.0097 ( 8) | 0.7042 (5) |
| C(6) | 0.912 (2) | 0.0917 (10) | 0.7040 (6) |
| C(7) | 1.028 (2) | −0.2245 ( 8) | 0.6252 (6) |
| C(8) | 0.969 (2) | −0.1602 ( 9) | 0.5811 (5) |
| C(9) | 0.886 (2) | −0.0684 ( 7) | 0.6068 (4) |
| C(10) | 0.841 (2) | −0.0799 ( 7) | 0.6736 (5) |
| C(11) | 0.731 (2) | −0.0411 ( 8) | 0.5651 (6) |
| C(12) | 0.781 (2) | −0.0340 ( 9) | 0.4946 (6) |
| C(13) | 0.887 (2) | −0.1226 ( 9) | 0.4799 (5) |
| C(14) | 0.858 (2) | −0.1962 ( 8) | 0.5298 (5) |
| C(15) | 1.137 (2) | −0.1263 ( 8) | 0.5444 (6) |
| C(16) | 1.085 (2) | −0.0995 ( 8) | 0.4823 (5) |
| C(17) | 1.200 (2) | −0.0704 (11) | 0.4406 (6) |
| C(18) | 0.603 (2) | 0.1013 ( 8) | 0.7835 (5) |
| C(19) | 0.833 (2) | −0.0132 ( 8) | 0.8225 (6) |
| C(20) | 1.009 (2) | −0.1164 ( 8) | 0.7036 (6) |
| C(21) | 0.912 (2) | 0.2271 ( 7) | 0.6344 (5) |
| C(22) | 0.902 (2) | 0.2483 ( 8) | 0.5695 (5) |
| C(23) | 0.894 (2) | 0.3411 ( 9) | 0.5593 (5) |
| C(24) | 0.883 (2) | 0.3693 ( 8) | 0.4995 (6) |
| C(25) | 0.894 (2) | 0.3143 ( 9) | 0.4556 (5) |
| C(26) | 0.910 (2) | 0.2162 ( 8) | 0.4628 (5) |
| C(27) | 0.920 (2) | 0.1859 (10) | 0.5243 (5) |

TABLE V. Determination of Absolute Stereochemistry

| $h$ | $k$ | $l$ | Obs. (+) | ($F_O$) (−) | Calc. (+) | ($F_C$) (−) |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 48.60 > | 34.48 | 37.06 > | 25.45 |
| 1 | 1 | 5 | 77.57 < | 90.67 | 69.15 < | 73.98 |
| 1 | 1 | 8 | 29.43 > | 25.40 | 25.02 > | 19.71 |
| 1 | 1 | 9 | 64.38 > | 54.94 | 59.82 > | 48.11 |
| 1 | 1 | 10 | 68.35 < | 77.74 | 61.24 < | 65.49 |
| 1 | 2 | 1 | 93.53 > | 88.33 | 75.60 > | 69.02 |
| 1 | 2 | 3 | 63.34 < | 74.26 | 55.64 < | 62.31 |
| 1 | 2 | 4 | 47.30 < | 62.49 | 38.81 < | 45.46 |
| 1 | 2 | 5 | 28.71 < | 38.70 | 27.00 < | 31.12 |
| 1 | 3 | 1 | 45.71 < | 56.95 | 46.14 < | 54.08 |
| 1 | 3 | 3 | 61.55 > | 56.58 | 46.64 > | 41.72 |
| 1 | 3 | 8 | 18.34 < | 27.43 | 18.21 < | 25.04 |
| 1 | 4 | 6 | 20.14 < | 29.31 | 24.37 < | 28.59 |
| 1 | 4 | 7 | 9.08 < | 17.15 | 8.43 < | 14.48 |
| 1 | 5 | 2 | 74.34 > | 67.76 | 71.67 > | 64.67 |
| 1 | 5 | 3 | 52.38 < | 65.59 | 45.46 < | 51.77 |
| 1 | 6 | 1 | 57.25 < | 62.88 | 45.51 < | 50.47 |
| 1 | 6 | 5 | 56.90 < | 67.66 | 56.37 < | 61.02 |
| 2 | 2 | 2 | 154.84 > | 148.59 | 106.25 > | 102.32 |
| 2 | 3 | 1 | 50.66 < | 57.99 | 42.78 < | 49.53 |
| 2 | 3 | 4 | 39.54 < | 45.94 | 32.82 < | 37.04 |
| 2 | 3 | 5 | 69.17 < | 77.87 | 57.56 < | 62.18 |
| 3 | 1 | 1 | 29.65 > | 22.34 | 17.92 > | 12.41 |
| 3 | 1 | 2 | 27.09 < | 32.24 | 22.69 < | 28.65 |
| 3 | 1 | 4 | 10.01 < | 15.61 | 13.98 < | 18.85 |
| 3 | 1 | 5 | 42.43 > | 34.29 | 39.46 > | 31.64 |

tained by catalytic hydrogenation of **1** showed a negative Cotton effect ($\Delta\varepsilon_{303}-1.06$) in the CD spectrum,[6] which is consistent with the result obtained by X-ray crystallographic analysis.

## Experimental

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Ultraviolet (UV) and infrared (IR) spectra were taken with a Hitachi 330 spectrophotometer and a Hitachi 215 spectrophotometer, respectively. NMR spectra were recorded with a JEOL JNM FX-200 or a JEOL JNM GSX-400 spectrometer. Chemical shifts are given in $\delta$ values using tetramethylsilane as an internal standard. Optical rotation was determined with a Union Giken PM-201 digital polarimeter and CD spectra were recorded with a JASCO J-600 spectropolarimeter. Mass spectra (MS) were determined with a JEOL JMS D-300 spectrometer. Kieselgel 60 (0.040—0.063 mm, Merck) was used for column chromatography and Kieselgel 60 $F_{254}$ precoated plates (0.25 mm and 0.5 mm, Merck) were used for thin layer and layer chromatographies.

**Isolation of Macrocalyxoformin D (=Longirabdiol) (1)** Dried aerial parts (658 g) of *Rabdosia longituba* collected in Togouchi Town, Hiroshima Pref., Japan were extracted with MeOH (10 l) for 2 weeks at room temperature. The extraction was repeated again in the same manner. The MeOH extract was concentrated *in vacuo* and the residue was dissolved in 90% MeOH (440 ml). After being washed with *n*-hexane (300 ml × 3), the 90% MeOH layer was concentrated *in vacuo*. The residue was suspended in $H_2O$ (400 ml) and the suspension was extracted with EtOAc (300 ml × 3). The EtOAc extract was washed with $H_2O$, dried and evaporated *in vacuo* to give a residue (16.1 g), which was chromatographed on a silica gel (600 g) column with $CHCl_3$–$Me_2CO$ as the eluant, with increasing $Me_2CO$ content. The eluate from 15% $Me_2CO$–$CHCl_3$ (2.993 g) was purified on a silica gel (120 g) column with $Et_2O$ as the eluant and recrystallized from MeOH to give macrocalyxoformin D (=longirabdiol) (**1**) (536 mg) as colorless needles. mp 203—205°, $[\alpha]_D^{22.5}$ +16.5° ($c$=1.21, MeOH), $[\alpha]_D^{22}$ −26.4° ($c$=4.02, $CHCl_3$). UV $\lambda_{max}$ (MeOH): 232 nm ($\varepsilon$ 8580). IR $\nu_{max}$ (KBr): 3200, 1740, 1710, 1640, 1395, 1265, 1235, 1095, 1040, 1030, 995 $cm^{-1}$. $^1H$- and $^{13}C$-NMR (see Table I). *Anal.* Calcd for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 68.77; H, 8.29.

**Macrocalyxoformin D 6-*O*-*p*-Bromobenzoate (2)** α-Pinene (0.2 ml) and *p*-bromobenzoyl chloride (270 mg) were added to a solution of macrocalyxoformin D (=longirabdiol) (**1**) (10.5 mg) in $CH_2Cl_2$ (5 ml), and the mixture was refluxed for 4 h. After cooling down, the mixture was poured into ice water and the resulting precipitates were extracted with $CHCl_3$ (20 ml × 3). The extracts were combined, washed with saturated NaCl aqueous solution, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by column chromatography ($SiO_2$, 45 g, solvent: $CHCl_3$–$Me_2CO$) and layer chromatography (solvent: $CHCl_3$–$Me_2CO$ (19 : 1) developed three times), successively, to give 6-*O*-*p*-bromobenzoyl macrocalyxoformin D (**2**) (8.6 mg). Recrystallization from MeOH gave colorless needles, mp 189—191 °C. IR $\nu_{max}$ ($CHCl_3$): 3550—3400, 1740, 1710, 1640, 1590, 1480, 1400, 1270, 1110, 1100, 1070, 1010 $cm^{-1}$. $^1H$-NMR ($CDCl_3$) $\delta$: 1.21 (3H, s, 18-$H_3$), 1.96 (1H, dd, $J$=7, 2.5 Hz, 5-H), 2.11 (1H, d, $J$=12.5 Hz, 14α-H), 2.43 (2H, m, 9-H, 14β-H), 3.02 (1H, dd, $J$=9.5, 4.5 Hz, 13-H), 3.66 (2H, ABd, $J$=11 Hz, 19-$H_2$), 4.32 (1H, dd, $J$=13, 7 Hz, 6-$H_1$), 4.45 (1H, d, $J$=11.5 Hz, 20-$H_1$), 4.71 (1H, d, $J$=11.5 Hz, 20-$H_1$), 4.80 (1H, dd, $J$=13, 2.5 Hz, 6-$H_1$), 5.42, 5.98 (each 1H, br s, 17-$H_2$), 7.56, 7.77 (each 2H, d, $J$=8.5 Hz, *p*-bromobenzoyl). MS *m/z*: 330.1803 $(M-C_7H_5O_2Br)^+$. Calcd for $C_{20}H_{26}O_4$: 330.1832. FAB-MS *m/z*: 553 and 555 $(M+Na)^+$ (+NaI), 569 and 571 $(M+K)^+$ (+KI). *Anal.* Calcd for $C_{27}H_{31}BrO_6$: C, 61.02; H, 5.88. Found: C, 60.53; H, 5.95.

**X-Ray Analysis of Macrocalyxoformin D *p*-Bromobenzoate (2)** $C_{27}H_{31}BrO_6$, $M$=531.4. Orthorhombic, $a$=7.425 (3), $b$=14.824 (8), $c$=20.216 (22) Å, $Z$=4, $D_x$=1.57 g·$cm^{-3}$, space group $P2_12_12_1$ ($MoK_\alpha$)=20.0 $cm^{-1}$. The cell dimensions and intensities were measured on a Syntex R-3 four-circle diffractometer with graphite-monochromated $MoK_\alpha$ radiation in the $\omega$-scan mode for $2\theta<45°$, and 1238 independent reflections [$I>1.96\lambda(I)$] were used for the structure analysis. The structure was solved by the direct method using MULTAN on a Syntex XTL computer. Refinement by the block-diagonal least-squares method led to a final $R$ value of 0.095. Atomic coordinates for non-hydrogen atoms are given in Table IV. The absolute configuration of the molecule was determined by Bijovet's anomalous-dispersion method based on the observed and calculated structure factors of 26 Friedel pairs (see Table V).

**Dihydromacrocalyxoformin D (4)** Pd–C (5%) (10 mg) was added to a solution of macrocalyxoformin D (**1**) (10.6 mg) in MeOH (5 ml). The mixture was stirred for 1 h at room temperature under an atmosphere of hydrogen. The catalyst was filtered off, and the filtrate was concentrated *in vacuo*. The residue was purified by layer chromatography [solvent: $CHCl_3$–$Me_2CO$ (4 : 1) developed twice] to give the dihydro compound (**4**)[5b] (5.9 mg), which crystallized on addition of MeOH. mp 195—197 °C. IR $\nu_{max}$ ($CHCl_3$): 3370, 1740, 1710, 1260—1190, 1090, 1015 $cm^{-1}$. $^1H$-NMR ($CDCl_3$) $\delta$: 1.08 (3H, s, 18-$H_3$), 1.14 (1H, d, $J$=6.5 Hz, 16-Me), 2.21 (1H, dd, $J$=12.5, 1 Hz, 14α-H), 3.31 (1H, d, $J$=11.5 Hz, 19-$H_1$), 3.69 (1H, dd, $J$=13, 3.5 Hz, 6-$H_1$), 3.88 (1H, dd, $J$=13, 1.5 Hz, 6-$H_1$), 4.00 (1H, d, $J$=11.5 Hz, 19-$H_1$), 4.66 (1H, d, $J$=12 Hz, 20-$H_1$), 4.99 (1H, d, $J$=12 Hz, 20-$H_1$). MS *m/z*: 350.2121 $(M)^+$. Calcd for $C_{20}H_{30}O_5$: 350.2094. CD (MeOH): $\Delta\varepsilon_{303}-1.06$.

## References and Notes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