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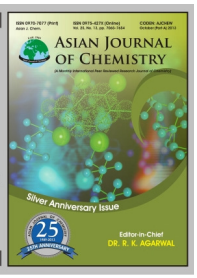

Synthesis and Crystal Structure of Chiral (1R,5R)-3-Arylidenopinones

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Three (1R,5R)-(-)3-arylideneopinones (**2a**, **2b** and **2c**) were first synthesized and characterized by IR, MS, NMR, elemental analysis and single-crystal X-ray diffraction method. The structure indicates that the compound **2a** belongs to orthorhombic, space group $P2_12_12_1$ with a = 1.0378 (5) nm, b = 1.1156 (6) nm, c = 1.2775 (7) nm, β = 90º. V = 1.4791 (13) nm^3, Z = 4, ρ = 1.223 g cm^{-3}, μ = 0.083 mm^{-1}, F (000) = 584 and final R_1 = 0.0327, wR2 = 0.0876. The compound **2b** belongs to trigonal, space group $P3_2$ with a = 0.93024(12) nm, b = 0.93024(12) nm, c = 1.3215(4) nm, β = 90.0º. V = 0.9903(3) nm^3, Z = 3, ρ = 1.219 g cm^{-3}, μ = 0.079 mm^{-1}, F(000) = 390 and final R_1 = 0.0350, wR2 = 0.0912. The compound **2c** belongs to monoclinic, space group $P2_1$ with a = 1.20252 (15) nm, b = 0.99228(12) nm, c = 2.3905(3) nm, β = 92.769(2)º. V = 2.8491(6) nm^3, Z = 8, ρ = 1.216 g cm^{-3}, μ = 0.254 mm^{-1}, F(000) = 1104 and final R_1 =0.0440, wR2 = 0.1069.

Key Words: (1S,5S)-(-)-β-pinene, (1R,5S)-(+)-nopinone, (1R,5R)-(-)-3-arylideneno-pinones, Crystal structure, Synthesis.

INTRODUCTION

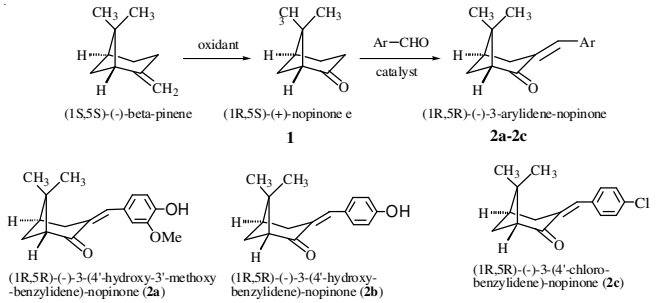
It is a well-known fact that an over exposure to solar ultraviolet radiation is harmful to human health, the major acute effects on normal human skin comprise sunburn cells, tanning, premature skin aging and an increased risk for skin cancers[1-3]. The steady increase in the incidence of melanoma, non-melanoma cutaneous neoplasia and preneoplasic disorders has contributed to the demand for more effective protection from the sun[4-6].

Terpenoid derivatives, such as benzylidene camphor, *p*-methylbenzylidene camphor, benzylidene camphor sulfonic acid, are widely used as UV filters in cosmetics because of their stable storage, no irritation to skin, no photosensitization, low toxicity, good stability and chemical inertness and low absorption to skin[7,8]. However, natural camphor is expensive and the synthesized camphor exist several disadvantages including a long process of synthesis routes and severe environmental pollution. The crystal structure of such compounds are interesting and have seldom been reported. Herein, we report the synthesis and structural characterization of a chiral (1R, 5R)-3-arylidenopinones (**2a-2c**) which had good ultraviolet absorption characteristics by using a low cost and abundant renewable resource β-pinene as the raw material.

EXPERIMENTAL

NMR spectra were recorded in $CDCl_3$ solution on a Bruker AV 400 spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C, respectively. The chemical shifts were expressed in ppm (δ scale) relative to the reference compound tetramethylsilane (TMS). Electronic impact (EI) gas chromatography-mass spectrometry (GC-MS) was conducted on an Agilent 6890 N GC coupled to an Agilent Technologies 5973 inert mass selective detector using a 30 m × 0.25 mm i.d., 0.25 μm file thickness HP-5MS capillary column (Agilent Technologies, Wilmington, DE) with helium as carrier gas (36 cm/s, 80 ºC for 2 min and then programmed to 280 ºC at 15 ºC/min and held for 20 min). A 70 eV electron beam was employed for sample ionization. GC analyses were performed on an Agilent 6890 GC equipped with a flame ionization detector (FID) using a 30 m × 0.32 mm i.d., 0.25 μm file thickness HP-5 capillary column with nitrogen as carrier gas (38 cm/s, 80 ºC for 2 min and then programmed to 280 ºC at 10 ºC/min and held for 20 min) in the split mode and the split ratio was 50:1. Fourier-transform infrared (FT-IR) spectra of samples were recorded from potassium bromide disks prepared with each crystalline sample on a Nicolet 380 FT-IR spectrophotometer in the scan range of 4000-400 cm^{-1}. Melting points and specific rotation were measured using X-6 microscopic melting point apparatus and Shanghai Spoif W22-2S automatic polarimeter. The raw material β-pinene with a purity of 98.1 % (GC) and $[\alpha]_D^{25}$ -21.1º (c = 1.0, $CHCl_3$) was purchased from Deqing Forest Chemical Plant of China. Flash column chromatography was carried out on silica gel 60 (230-400 mesh). All reactions were performed

under a nitrogen atmosphere with magnetic stirring and the syntheses of 3-arylidenenopinones from β-pinene were shown in **Scheme-I**.



Scheme-I

Synthesis

(+)-Nopinone (1): Nopinone was prepared by β-pinene oxidation using acidic potassium permanganate. A 500 mL dried three-necked flask equipped with a thermometer, condenser and stirrer was charged with acetone 100 mL, 2 mol/L H_2SO_4 15 mL and β-pinene 50 g and cooled with ice bath to about 15 ºC. 87 g of $KMnO_4$ fully crashed was added in portions within 1~1.5 h. The ice bath was removed after complete addition of $KMnO_4$ and the reaction was kept at room temperature for another 5-6 h. The reaction was monitored by GC until the peak of β-pinene was disappeared. The resulting mixture was filted with a sand-core funnel to remove the solid MnO_2 and was washed with acetone (2 × 40 mL). The filtrate was concentrated by a rotor evaporator to recover acetone and the bottom residue was diluted with 100 mL of hexane. The diluted residue was washed with saturated brine to neutral and the organic layer was dried over Na_2SO_4 and then was distilled to collect the fraction at 100~102 ºC/266 kPa, a colourless oily liquid with a yield over 83.9 %, purity 95.04 % (GC), specific rotation $[\alpha]_D^{25}$ + 27.3º (c = 1.0, $CHCl_3$).

(1R, 5R)-(-)-3-(4-hydroxy-3-methoxybenzylidene) nopinone (2a): A 100 mL dried flask fitted with a agitator, thermometer and condensor was charged with (+)-nopinone (1.38 g, 0.01 mol), vanillin (1.824 g, 0.012 mol) and 3 g of powderd potassium *tert*-butoxide in 30 mL of toluene under a nitrogen atmosphere and the resulting mixture was refluxed for 10~12 h until the main product reached 70~75 % and the byproduct was controlled within 10~15 % (monitored with GC) and then 15 mL of water was added. The mixture was separated into two layers and the organic layer was washed with water and brine to neutrality, dried over Na_2SO_4 and concentrated to afford the yellow crude product, which was purified by recrystallization in mixed solvent containing 10 mL of acetone and 0.5 mL of ethanol for several days at room temperature to afford 1.044 g (3.84 mmol, 38.4 % isolated yield, purity 95.3 %) of compound **2a** as a colourless transparent crystal, m.p. 173.5-174.2 ºC, [α] -44.7º (c = 0.32, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.929-1.379 (d, 6H, -CH_3), 1.500-1.520 (d, 1H, -CH_2), 2.368-2.379 (m, 1H, -CH_2), 2.609-2.633 (m, 1H, -CH), 2.681-2.704 (t, 1H, -CH), 2.951-2.972 (s, 2H, -CH_2), 7.644-7.653 (s, 1H, C=CH-C), 3.921 (s, 3H,-OCH_3), 6.056 (s, 1H, -OH), 6,955-6.972 (d, 1H, CH), 7.095-7.099 (s, 1H, CH), 7.189-7.209 (d, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.58, 26.18, 27.56, 30.95, 39.49, 55.82, 55.91, 113.61, 114.66, 124.84, 128.29, 130.16, 135.90, 203.58; FT-IR (KBr, ν_{max}, cm^{-1}): 3238 ν(O-H), 2966-2901 ν(C-H), 1674 ν(C=O), 1593-1440 (C_6H_3-, $\nu_{as\ C=C}$), 1307-1130 ν(O-CH_3), 856-619 τ(C-H); EI-MS *m/z* (%): 272 (M^+, 100), 257 (19), 229 (18), 203 (30), 162 (26), 137 (24), 115 (21), 91 (20), 83 (16), 55 (33), 41 (19).

(1R,5R)-(-)-3-(4-hydroxybenzylidene) nopinone (2b): A 100 mL dried flask equippedd with a agitator, thermometer and condensor was charged with (+)-nopinone (1.380 g, 0.01 mol), *p*-hydroxybenzaldehyde (1.83 g, 0.015 mol) and 3.0 g of powderd potassium *tert*-butoxide in 30 mL of *tert*-butanol under a nitrogen atmosphere and the resulting mixture was refluxed for 7~8 h until the conversion ratio of nopinone reached over 95 % (monitored with GC) and then 10 mL of water was added. The mixture was extracted with ethyl acetate (3 × 10 mL) and the combined organic layers were washed with water and saturated brine to neutrality, dried over Na_2SO_4 and concentrated to afford the yellow crude product, which was purified by recrystallization in 10 mL of acetone for 3 days at room temperature to provide 1.88 g (7.76 mmol, 77.6 % isolated yield, purity of 97.4 %) of compound **2b** as a colourless transparent crystal, m.p. 199.6-200.6 ºC, $[\alpha]_D^{25}$ -56.3º (c = 0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.929-1.378 (d, 6H, -CH_3), 1.496-1.531 (d, 1H, -CH_2), 2.374-2.384 (m, 1H, -CH_2), 2.587-2.641 (m, 1H, -CH), 2.661-2.730 (t, 1H, -CH), 2.948-2.956 (s, 2H -CH_2), 7.690 (s, 1H, C=CH-C), 6.908(m, 1H, -OH), 7.312-7.601 (m, 2H, CH), 7.573-7.601 (d, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.63, 26.19, 27.59, 29.69, 31.00, 39.47, 55.86, 115.78, 128.14, 129.84, 132.96, 136.23, 157.17, 204.92; FT-IR (KBr, ν_{max}, cm^{-1}): 3378 ν(O-H), 2962-2911 ν(C-H), 1669 ν(C=O), 1607~1469 (C_6H_4-, $\nu_{as\ C=C}$), 987-647 (C_6H_4-, τ_{C-H}); EI-MS *m/z* (%): 242 (M^+, 100), 227 (M^+-15, 31), 199 (227-C_2H_4, 42), 186 (22), 171 (47), 132 (56), 107 (54), 83 (35), 55 (53), 41(34).

(1R, 5R)-(-)-3-(4-chlorobenzyliene) nopinone (2c): A 100 mL dried flask fitted with a agitator, thermometer and condensor was charged with (+)-nopinone (1.38 g, 0.01 mol), *p*-chlorobenzaldehyde (1.68 g, 0.012 mol) and 3 g of powderd sodium mehoxide in 30 mL of tertiary butanol under a nitrogen atmosphere and the resulting mixture was refluxed for 5-8 h until the conversion ratio of nopinone reached 100 % and 15 mL of water was added and then extracted with ethyl acetate for three times (3 × 15 mL). The combined organic layer was washed with water and brine to neutrality, dried over Na_2SO_4 and concentrated to afford the deep yellow crude product, which was purified by recrystallization in mixed solvent containing 10 mL of acetone and 0.5 mL of ethanol for several days at room temperature to afford 2.223 g (8.55 mmol, 85.5 % isolated yield, purity 97.8 %) of compound **2c** as a colourless transparent crystal, m.p. 109.7-110.7 ºC, $[\alpha]_D^{25}$ -22.88º (c = 0.31, CCl_3). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.921-1.381 (d, 6H, -CH_3), 1.484-1.505 (d, 1H, -CH_2), 2.356-2.374 (m, 1H, -CH_2), 2.618-2.651 (m, 1H, -CH), 2.694-2.717 (t, 1H, -CH), 2.930-2.941 (t, 2H, -CH_2), 7.636-7.645 (t, 1H, C=CH-C), 7.362-7.384 (t, 2H, CH), 7.499-7.516 (t, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.55, 26.12, 27.36, 30.78, 39.29, 40.82, 55.78, 128.73, 131.78, 133.10, 134.10, 134.18, 134.74, 202.91; FT-IR (KBr, ν_{max}, cm^{-1}): 2984-2874 ν(C-H), 1686

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT RESULTS FOR **2a-2c**

Compound	**2a**	**2b**	**2c**
Empirical formula	$C_{17}H_{20}O_3$	$C_{16}H_{18}O_2$	$C_{16}H_{17}OCl$
Formular weight	272.33	242.30	260.75
Temperature [K]	296(2)	296(2) K	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Trigonal	Monoclinic
space group	$P2_12_12_1$	$P3_2$	$P2_1$
Unit cell dimension			
a(Å)	10.378(5)	9.3024(12)	12.0252(15)
b(Å)	11.156(6)	9.3024(12)	9.9228(12)
c(Å)	12.775(7)	13.215(4)	23.905(3)
β(º)	90	90	92.769(2)
Volume [Å^3]	1479.1(13)	990.3(3)	2849.1(6)
z	4	3	8
ρ (calc)(g/cm^3)	1.223	1.219	1.216
Absorption Coefficient	0.083	0.079	0.254
F(000)	584	390	1104
Crystal size (mm)	0.20 × 0.20 × 0.10	0.15 × 0.15 × 0.10	0.20 × 0.15 × 0.10
Limiting indices	-12 <= h <= 12	-11 <= h <= 11	-14 <= h <= 13
	-13 <= k <= 12	-11 <= k <= 11	-11 <= k <= 12
	-15 <= l <= 15	-16 <= l <= 15	-29 <= l <= 29
Reflections collected/ unique	10742/2825 [R(int) = 0.0312]	7385/1288 [R(int) = 0.0254]	21132/9917 [R(int) = 0.0273]
Max. and min. transmission	0.984 and 0.992	0.988 and 0.992	0.955 and 0.975
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2825/0/182	1288/1/167	9917/1/649
Goodness-of-fit on F^2	1.013	1.094	1.026
Final R indices [I > 2 σ (I)]	R1 = 0.0327, wR2 = 0.0876	R1 = 0.0350, wR2 = 0.0912	R1 = 0.0440, wR2 = 0.1069
R indices (all data)	R1 = 0.0365, wR2 = 0.0906	R1 = 0.0359, wR2 = 0.0918	R1 = 0.0718, wR2 = 0.1178
Absolute structure parameter	0.2 (10)	0.2(15)	-0.03(5)

ν(C=O), 1686-1407 (C_6H_4-, $\nu_{as\ C=C}$), 979-686 (C_6H_4-, τ_{C-H}); EI-MS *m/z* (%): 260 (M$^+$, 97), 245 (54), 217 (54), 204 (21), 189 (39), 165 (31), 150 (48), 141 (47), 125 (48), 115 (100), 83 (78), 55 (89).

Crystal structure determination: Crystallographic data of **2a-2c** were collected at 292 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized MoK$_\alpha$ radiation (λ = 0.071073 nm). An empirical absorption correction was applied. The structures were solved by the direct method and refined using the SHELXL-97 software[9]. All nonhydrogen atoms were refined by full-matrix least-squares method on F^2 with anisotropy thermal parameters, while all hydrogen atoms were refined in calculated positions, assigned isotropic thermal parameters and allowed to ride their parent atoms. Crystallographic data and structure refinement results are summarized in Table-1.

RESULTS AND DISCUSSION

The compounds **2a-2c** are light yellow crystals and stable in air at room temperature. The ^{1}H NMR, MS and elemental analysis for these three compounds are all in good agreement with the assumed structure. In order to obtain a definitive structural proof of the 3-arylideneopinones and stereochemical information, the single crystal X-ray diffraction study was undertaken.

The compound **2a** crystallizes in the orthorhombic space group $P2_12_12_1$. The molecular structure of the compound **2a** is shown in Fig. 1, which displays the **E** conformataion with respect to the C=C double bond mainly due to the intramolecular repulsive interaction between O3 and H6A. The absolute

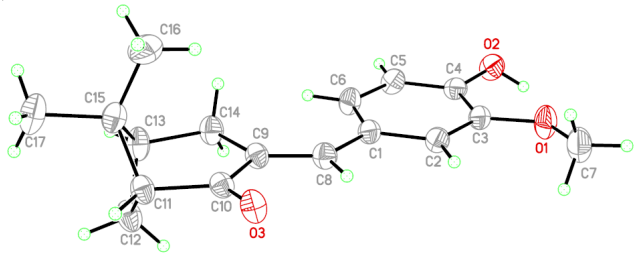


Fig. 1. Molecular structure of the compound **2a**

configuration of C11 and C13 was established as R. The selected bond lengths and bond angles are listed in Table-2. The C-C bond lengths within the phenyl ring are normal in the range from 0.1380(2) to 0.1409(2) nm with normal angles close to 120º with the exception of the the angle (C2-C1-C6, 117.61(13). The cyclohexanone ring in the bicyclic ring system adopts a flattened half chair conformation that is constrained by the dimethyl substituted cyclobutane ring. The dihedral angle between the plane consisting of C9-C10-C11-C13-C14 and the phenyl ring is 5.04 (0.10)º, which indicates the two planes are nearly coplanar. In addition, the aromatic ring bonded to the C8 is coplanar around the C8-C9 bond with a torsion angle C6-C1-C8-C9 of 2.6 (3)º, which suggests a conjugation with the remaining part of the system of C8-C9-C10-O2. The bond length of C8-C9 and C10-O3 are 0.1348(2) and 0.12248(17) nm respectively which indicates a doule-bond character, but they are slight longer than that of lack conjugation of the double bond[10]. However, the C1-C8 (0.1463(2) is shorter than the normal C-C single bond, suggesting a big conjugation system exists in the double bond and phenyl ring and the electronic transfer occurs from the aromatic ring the

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º) FOR THE COMPOUND **2a**

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
C1-C2	1.409(2)	C9-C10	1.501(2)	C13-C15	1.566(2)
C2-C3	1.385(2)	C9-C14	1.522(2)	C15-C17	1.542(2)
C3-C4	1.402(2)	C10-C11	1.505(2)	O1-C3	1.3708(19)
C4-C5	1.380(2)	C11-C12	1.558(2)	O1-C7	1.426(2)
C5-C6	1.389(2)	C11-C15	1.565(2)	O2-C4	1.3621(18)
C1-C6	1.401(2)	C12-C13	1.527(3)	O3-C10	1.2248(17)
C1-C8	1.463(2)	C13-C14	1.528(2)	–	–
C8-C9	1.348(2)	C15-C16	1.520(3)	–	–
Angle	(º)	Angle	(º)	Angle	(º)
C3-C2-C1	121.69(14)	O2-C4-C5	118.57(14)	C14-C13-C15	111.09(13)
C2-C3-C4	119.62(14)	O1-C3-C2	125.92(14)	C9-C14-C13	111.53(13)
C5-C4-C3	119.22(13)	C3-O1-C7	117.89(13)	C10-C9-C14	116.07(13)
C4-C5-C6	121.34(15)	O3-C10-C9	124.09(13)	C17-C15-C11	110.86(15)
C5-C6-C1	120.51(15)	C8-C9-C10	117.42(13)	C11-C15-C13	85.05(12)
C6-C1-C2	117.61(13)	C9-C10-C11	115.14(12)	C16-C15-C17	109.00(16)
C6-C1-C8	125.35(13)	C10-C11-C12	107.25(12)	C16-C15-C13	119.20(16)
C2-C1-C8	116.99(13)	C10-C11-C15	109.66(12)	C9-C14-C13	111.53(13)
C9-C8-C1	132.17(14)	C14-C13-C12	109.33(15)	C17-C15-C13	112.33(15)

O=C-C=C system. The other bond lengths and angels for the bicyclic ring fragments are consistent with those previously reported values[10]. A srong O-H···O intermolecular hydrogen-bond interaction is observed in the molecule structure, which forms an infinite one dimension zigzag chain structure (Table-3, Fig. 2).

The compound **2b** crystallizes in the orthorhombic space group P32. The molecular structure of the compound **2b** is shown in Fig. 3. The selected bond lengths and bond angles are listed in Table-4. Bond lengths and angles observed in **2b**

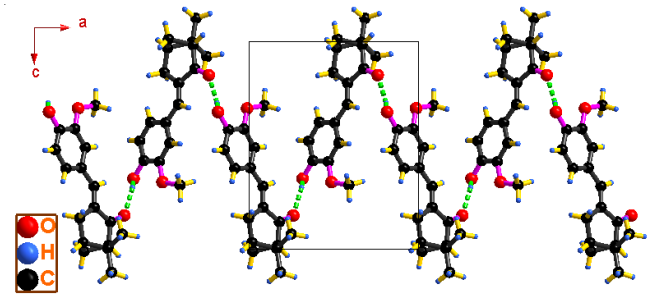


Fig. 2. Molecular one-dimensional chain hydrogen-bond structure of the compound **2a**

TABLE-3
HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (º) FOR THE COMPOUND **2a**

D-H···A	d(D-H)	D(H···A)	D(D···A)	∠DHA
O2-H2A···O3^{i}	0.82	1.95	2.7189(19)	155.1

Symmetry codes: (i) x + 1/2, -y-1/2, -z-2

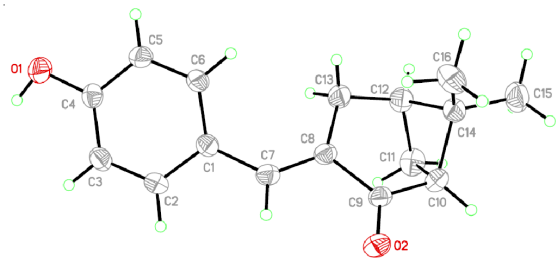


Fig. 3. Molecular structure of the compound **2b**

are in normal ranges and similar to the corresponding values in **2a**. However, the phenyl ring is oriented with the respect to the plane consisting of C8-C9-C10-C12-C3 at a dihedral angle of 42.94(0.07)º. In addition, a torsion angle of C6-C1-C7-C8

TABLE-4
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º) FOR THE COMPOUND **2b**

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
C1 C2	1.399(3)	C7-C8	1.342(3)	C11-C12	1.533(4)
C2-C3	1.370(3)	O1-C4	1.361(3)	C12-C14	1.563(3)
C3-C4	1.390(3)	O2-C9	1.230(3)	C13-C12	1.522(3)
C4-C5	1.388(3)	C8-C9	1.494(3)	C8-C13	1.515(3)
C5-C6	1.374(3)	C9-C10	1.495(3)	C16-C14	1.510(4)
C1-C6	1.400(3)	C10-C11	1.551(3)	C14-C15	1.538(4)
C7-C1	1.459(3)	C10-C14	1.568(3)	–	–
Angle	(º)	Angle	(º)	Angle	(º)
C3-C2-C1	121.9(2)	C7-C8-C9	117.41(18)	C8-C13-C12	111.30(18)
C2-C3-C4	120.2(2)	C8-C9-C10	115.44(17)	C9-C8-C13	115.78(18)
C5-C4-C3	119.0(2)	C9-C10-C11	106.91(19)	C16-C14-C10	118.0(2)
C6-C5-C4	120.5(2)	C9-C10-C14	110.16(19)	C16-C14-C12	119.2(2)
C5-C6-C1	121.45(19)	C13-C12-C11	110.0(2)	C15-C14-C10	111.2(2)
C2-C1-C6	116.9(2)	C13-C12-C14	110.92(19)	C16-C14-C15	109.8(2)
C8-C7-C1	129.19(19)	C12-C14-C10	85.11(18)	O2-C9-C8	121.6(2)
O1-C4-C3	123.0(2)	C11-C12-C14	87.94(19)	–	–

TABLE-6
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR THE COMPOUND **2c**

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
C1-C2	1.395(4)	C7-C8	1.338(4)	C12-C14	1.512(4)
C2-C3	1.372(4)	C8-C9	1.495(4)	C13-C15	1.548(5)
C3-C4	1.362(4)	C9-C10	1.484(4)	C13-C16	1.521(5)
C4-C5	1.361(4)	C10-C11	1.551(5)	C8-C14	1.526(4)
C5-C6	1.374(4)	C10-C13	1.554(4)	O1-C9	1.209(3)
C1-C6	1.385(4)	C11-C12	1.523(4)	O2-C30	1.217(3)
C7-C1	1.460(4)	C13-C12	1.549(5)	O3-C46	1.213(3)
Cl1-C4	1.740(3)	Cl2-C20	1.743(3)	O4-C57	1.218(3)
Cl3-C36	1.740(3)	Cl4-C52	1.736(3)	C17-C18	1.394(4)
C18-C19	1.380(4)	C20-C19	1.374(4)	C20-C21	1.371(4)
C22-C21	1.374(4)	C22-C17	1.389(4)	C23-C17	1.461(4)
C23-C24	1.344(4)	C24-C25	1.514(4)	C26-C25	1.517(3)
C26-C27	1.532(4)	C28-C27	1.544(4)	C26-C29	1.548(4)
C28-C29	1.554(4)	C30-C28	1.485(4)	C29-C32	1.532(4)
C29-C31	1.524(5)	C24-C30	1.503(4)	C39-C40	1.340(3)
C56-C55	1.344(3)	–	–	–	–
Angle	(°)	Angle	(°)	Angle	(°)
C1-C2-C3	121.3(3)	C8-C7-C1	130.3(3)	C16-C13-C15	110.1(3)
C2-C3-C4	119.9(3)	C7-C8-C9	118.1(2)	C15-C13-C10	115.9(3)
C3-C4-C5	120.5(3)	C10-C9-C8	115.2(3)	C16-C13-C12	112.7(4)
C4-C5-C6	119.9(3)	C9-C10-C11	107.3(3)	C12-C14-C8	110.7(2)
C5-C6-C1	121.5(3)	C9-C10-C13	110.6(2)	C9-C8-C14	115.9(2)
C6-C1-C2	116.9(3)	C12-C11-C10	86.5(3)	O1-C9-C8	122.9(3)
C6-C1-C7	124.4(3)	C12-C13-C10	85.5(2)	C3-C4-Cl1	119.9(3)
O2-C30-C24	123.1(3)	C19-C20-Cl2	119.2(3)	O3-C46-C40	123.1(2)
C35-C36-Cl3	119.9(2)	O4-C57-C56	123.5(2)	C51-C52-Cl4	120.0(2)

is -31.92(1)°. All these parameters indicate that there is lack of conjugation in the system of C7-C8-C9-O2. However, there is also a strong intermolecular O-H···O hydrogen bond (Table-5) between the carbonyl and hydroxy groups which link the molecules into a two-dimesional network, in which they may be effective in the stabilization of the structure.

TABLE-5
HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (°) FOR THE COMPOUND **2b**

D-H···A	d(D-H)	D(H···A)	D(D···A)	∠DHA
O1-H1A···O2^{i}	0.88(5)	1.91(5)	2.775(2)	169(4)

Symmetry code: (i) –x + y + 1/2, -x + 1, z-2/3

The compound **2c** crystallizes in the orthorhombic space group $P2_1$. The molecular structure of the compound **2c** is shown in Fig. 4. There are four crystallographically independent molecules in the asymmetric unit different from **2a** and **2b**. The selected bond lengths and bond angles are listed in Table-6. The C-Cl bond distances are in the range of 1.736(3)-1.743(3) Å. There are lack of inetermolecular hydrogen and π-π stacking interactions, the molecular strucuture is is stablilized by van der Waals forces.

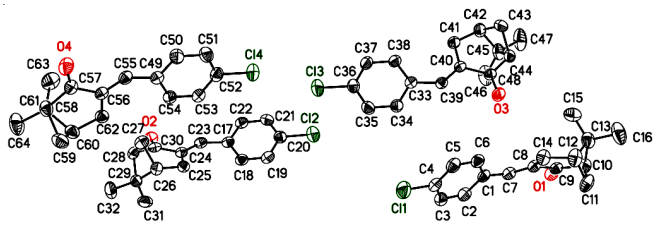


Fig. 4. Molecular structure of the compound **2c** (hydrogen atoms were omitted for clarity)

Conclusion

Three (1R, 5R)-(-)3-arylideneopinone derivatives (**2a**, **2b** and **2c**) were successfully synthesized and characterized by single-crystal X-ray diffraction method. These compounds crystallize on three different space group belongs $P2_12_12_1$, P32 and P21 respectively. There is also a strong intermolecular O–H···O hydrogen bond between the carbonyl and hydroxy groups in **2a** and **2b**, but there are lack of inetermolecular hydrogen in **2c**.

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