A New Lignan, (−)-Berchemol, from *Berchemia racemosa*

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A new tetrahydrofuranoid lignan, named (−)-berchemol (1), mp 188—189 °C, $[\alpha]_D$ −7.9°, $C_{20}H_{24}O_7$, was isolated together with a known lignan, (−)-secoisolariciresinol, from the stems of *Berchemia racemosa* SIEB. *et* ZUCC. (Rhamnaceae). The relative stereostructure of 1 was elucidated on the basis of chemical evidence, and spectroscopic and X-ray analysis. The absolute configuration of 1 was determined by comparison of its circular dichroism spectrum with that of (−)-olivil. (−)-Berchemol was determined to be (2*R*,3*S*,4*S*)-2,4-bis(4-hydroxy-3-methoxyphenyl)-3-hydroxy-3-hydroxymethyltetrahydrofuran.

Keywords *Berchemia racemosa*; Rhamnaceae; tetrahydrofuranoid lignan; (−)-berchemol; (−)-secoisolariciresinol; X-ray analysis; CD spectrum; 2D-NMR

The roots and stems of *Berchemia* spp. are used as a herbal medicine for cholelithiasis and hepatitis in China and Japan. In a previous paper,[1] we reported the isolation of two phenol compounds, a 3(2*H*)-benzofuranone, carpusin, and a diglucoside of naphtho-γ-pyrone, rubrofusarin 6-β-gentiobioside, from the stems of *Berchemia racemosa* SIEB. *et* ZUCC. (Rhamnaceae) (Japanese name: kumayanagi). As components of the stems, some phenol compounds, 2,6-dimethoxybenzoquinone,[2] lignans[3] and monoterpene glycosides[4] were isolated and the structures were elucidated by Yamasaki *et al.*, and some flavonoids[5] were reported by Kikuchi and Sugiyama. This paper describes the isolation of a new tetrahydrofuranoid lignan, named (−)-berchemol (**1**), and a known lignan, (−)-secoisolariciresinol, and the elucidation of their structures on the basis of chemical and spectroscopic evidence, and X-ray analysis. The extraction and separation were carried out as described in the experimental section.

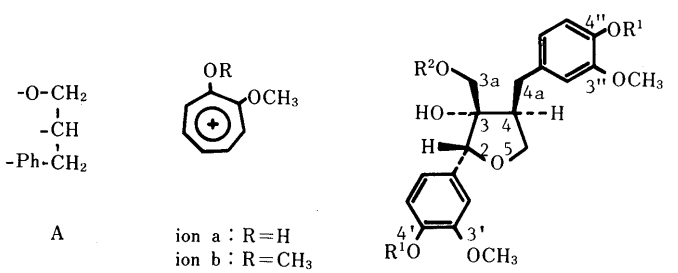
(−)-Berchemol (**1**) was isolated as a triacetate (**1a**), $[\alpha]_D$ +8.7°, $C_{26}H_{30}O_{10}$ from the acetone extract of *B. racemosa*. On treatment with sodium methoxide, **1a** afforded **1**, mp 188—189 °C, $[\alpha]_D$ −7.9°, $C_{20}H_{24}O_7$. The proton nuclear magnetic resonance (^{1}H-NMR) and the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of **1a** indicated that no skeletal rearrangement had occurred during acetylation. The ultraviolet absorption (UV) spectrum of **1** showed maxima at 231 and 281 nm due to aromatic rings.

The ^{1}H-NMR spectrum of **1** showed the presence of eight protons apart from six aromatic protons on two trisubstituted benzene rings (ABX systems) and two aryl methoxyl groups. The eight proton signals appeared as a singlet due to an oxybenzylic proton at δ 4.86 ppm, a pair of doublets of an AB system due to an oxygen-bearing methylene group at δ 3.64 and 3.89 ppm, a multiplet due to a methine group at δ 2.60 ppm, a pair of double doublets due to a benzylic methylene group at δ 2.44 and 3.07 ppm and another pair of double doublets due to an oxygen-bearing methylene group at δ 3.72 and 4.17 ppm (Table I). Two dimensional ^{1}H–^{1}H correlation spectroscopy (^{1}H–^{1}H COSY) of the triacetate (**1a**) showed a clear group of correlations (Fig. 1). The multiplet due to a methine group (H-4) at δ 2.70 ppm, which appeared at δ 2.60 ppm in the ^{1}H-NMR of **1**, correlated with two pairs of double doublets due to two methylene groups at δ 2.54, 3.02 and 3.72, 4.24 ppm (2H-4a, and 2H-5). Thus, the presence of the partial structure A was shown (Chart 1).

The ^{1}H-NMR spectrum of the acetate (**1a**) showed the signals of one aliphatic and two aromatic acetoxyl groups. A pair of downfield-shifted doublets (2H, δ 4.29 and 4.35) in **1a** was attributed to an acetoxymethylene group, and therefore, (−)-berchemol (**1**) was found to have a primary hydroxy group. Furthermore, no decoupling was detected among three pairs of doublets due to three methylene groups. In the ^{1}H–^{1}H COSY of **1a**, a doublet at δ 4.29 ppm correlated only with a doublet at δ 4.35 ppm. This implied that this methylene group and the oxybenzylic proton were isolated by oxygen or fully substituted carbon atoms.

TABLE I. ^{1}H-NMR Chemical Shifts of (−)-Berchemol (**1**) and the Triacetate (**1a**) δ ppm from TMS in $CDCl_3$ (*J*/Hz in Parentheses)

Proton No.	1	1a
H-2	4.86 s	4.91 s
H-4	2.60 m	2.70 m
H-5	3.72 dd (8.7, 4.9)	3.72 dd (8.8, 5.4)
	4.17 dd (8.7, 6.4)	4.24 dd (8.8, 6.6)
H-3a	3.64 d (11.5)	4.29 d (11.7)
	3.89 d (11.5)	4.35 d (11.7)
H-4a	2.44 dd (12.9, 12.5)	2.54 dd (13.2, 12.2)
	3.07 dd (12.9, 4.2)	3.02 dd (13.2, 3.9)
H-2′	6.90 d (1.7)	7.01 d (1.7)
H-5′	6.92 d (8.1)	7.04 d (7.9)
H-6′	6.79 dd (8.1, 1.7)	6.88 dd (7.9, 1.7)
H-2″	6.70 d (1.7)	6.79 d (1.7)
H-5″	6.85 d (6.1)	6.97 d (7.9)
H-6″	6.69 dd (6.1, 1.7)	6.76 dd (7.9, 1.7)
OCH_3	3.88	3.83
OCH_3	3.90	3.85
OAc		2.31
OAc		2.31
OAc		2.05



A

ion a : R=H
ion b : R=CH_3

1 : R^1, R^2=H
1a : R^1, R^2=$COCH_3$
1b : R^1=CH_3, R^2=H

Chart 1

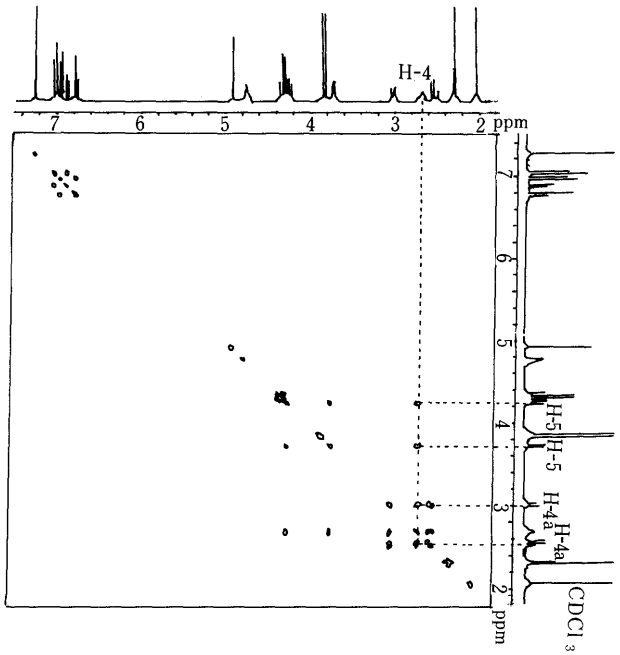


Fig. 1. ^{1}H–^{1}H COSY Spectrum of the Triacetate (**1a**)

TABLE II. ^{13}C-NMR Chemical Shifts (−)-Berchemol (**1**) and Its Derivatives (**1a**—**1c**), ppm from TMS in $CDCl_3$ (100 MHz)

Carbon No.	1	1a	1b	1c
C-2	84.4	84.9	84.4	85.0
C-3	82.3	80.8	82.4	89.7
C-4	50.1	50.5	50.1	50.1
C-5	71.3	71.6	71.5	71.4
C-3a	64.3	66.1	64.4	66.7
C-4a	34.2	34.3	34.2	35.0
C-1′	128.8	138.3	132.4	131.3
C-2′	109.7	111.7	110.5	111.2
C-3′[a]	146.6	151.4	149.4	146.6
C-4′[b]	145.8	140.0	149.3	145.5
C-5′	114.4	122.8	111.6	113.5
C-6′	120.1	119.7	119.5	121.0
C-1″	131.6	135.8	132.4	129.5
C-2″	111.3	113.0	111.4	111.3
C-3″[a]	146.8	151.3	149.2	146.1
C-4″[b]	144.2	138.5	147.8	144.2
C-5″	114.5	123.0	112.2	114.5
C-6″	121.5	120.9	120.9	120.3
OCH_3	55.9	56.0	56.0	56.0
OCH_3	56.1	56.1	56.1	56.1
OCH_3			56.0	
OCH_3			56.0	
OAc		20.7		
OAc		20.7		
OAc		20.8		
OAc		169.0		
OAc		169.2		
OAc		170.8		
-O-C-O-				111.0
CH_3				27.0
CH_3				25.2

a, b) Assignments marked in each column may be reversed.

The ^{13}C-NMR spectrum of **1** showed that, in addition to twelve aromatic and two methoxyl carbons, there were six carbon atoms, *i.e.*, three methylene carbons, two methine carbons and a quaternary carbon (Table II). The assignments of the carbon signals of **1** were made by comparison

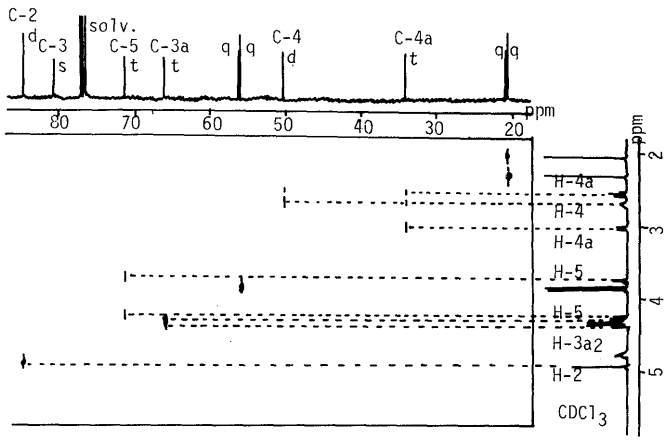


Fig. 2. ^{1}H–^{13}C COSY Spectrum of the Triacetate (**1a**)

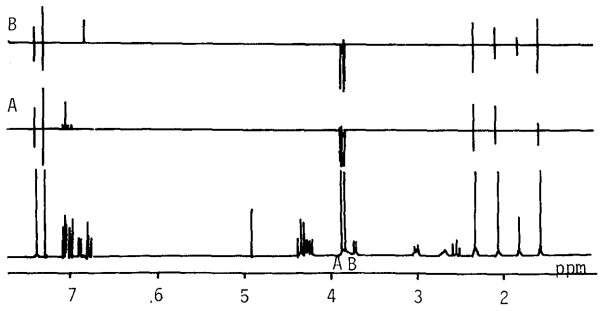


Fig. 3. ^{1}H-NMR (Normal and NOE Difference) Spectra of the Triacetate (**1a**) a

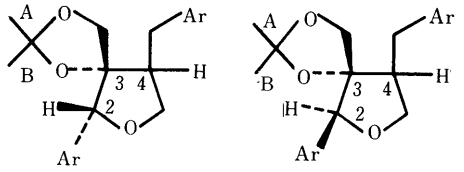
with those of (−)-massonirecinol.[6] The two dimensional ^{1}H–^{13}C COSY of **1a** also supported these assignments (Fig. 2). Based on the unsaturation number (nine) in the molecular formula it was considered that **1** has another ring besides the two phenyl rings in its structure. The ^{1}H- and ^{13}C-NMR spectra of **1**, in comparison with that of olivil,[6] suggest the presence of a tetrahydrofuran ring.

The ^{1}H-NMR spectrum of **1** showed four singlets (lost on addition of D_2O) due to the four hydroxyl groups. The infrared (IR) spectrum of the triacetate (**1a**) showed the presence of a hydroxyl group (3570 cm^{-1}). The fact that **1** gave **1a** under the usual acetylation conditions revealed the presence of a hindered alcohol group in **1**. These data and the presence of the partial structure A suggested that a tertiary hydroxyl group is located at C-3 in **1**.

On methylation with diazomethane, **1** gave a dimethylether (**1b**), $[\alpha]_D$ −8.3°, $C_{22}H_{28}O_7$. The mass spectra (MS) of **1** and **1b** showed as their base peak ions *m/z* 137 and 151, respectively, assigned to the ions a and b,[7] arising *via* benzylic A (Chart 1).

The positions of the two phenolic hydroxyl groups and two methoxyl groups of **1** were assigned with the aid of a nuclear Overhauser effects (NOEs) experiment on **1a**. When the methoxyl protons at δ 3.83 and 3.85 ppm were irradiated, NOEs were observed on aromatic protons at δ 6.79 and 7.01 ppm (X and X′ of two ABX and ABX′ systems), respectively. The observed difference NOE spectra are shown in Fig. 3. It was confirmed that the phenolic hydroxyl groups were located at C-4′ and C-4″, and the methoxyl groups were at C-3′ and C-3″.

Accordingly, the plane structure of (−)-berchemol (**1**),



B C

Chart 2

TABLE III. Shielding Shifts Calculated by the Use of McConnell's Equation

B				C			
	CH_3 Angle (°)	Distance (Å)	$\Delta\delta$		CH_3 Angle (°)	Distance (Å)	$\Delta\delta$
A	20	3.8	0.90	A	40	5.6	0.13
B	30	5.4	0.24	B	47	6.6	0.04
A—B			0.66	A—B			0.09

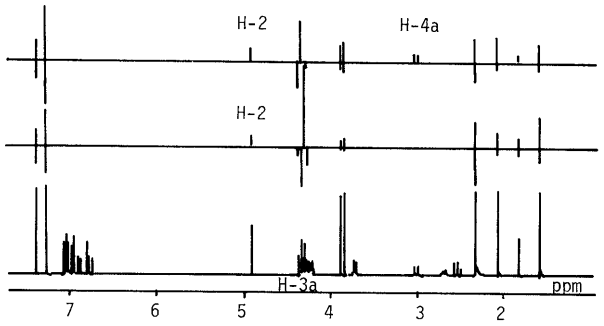


Fig. 4. ^{1}H-NMR (Normal and NOE Difference) Spectra of the Triacetate (**1a**) b

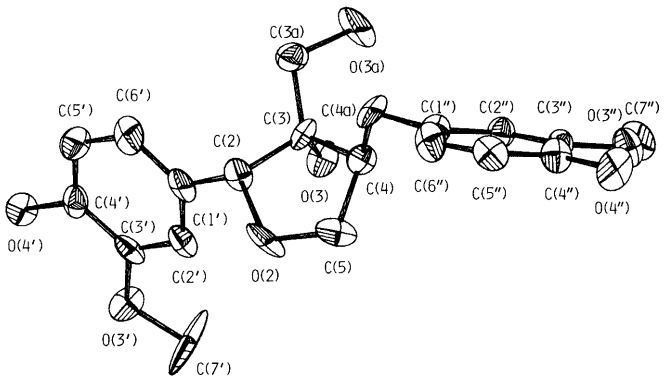


Fig. 5. ORTEP Drawing of (−)-Berchemol (**1**)

was established as **1** (Chart 1), which is the same as that proposed incorrectly by Freudenberg and Weinges[8] for (−)-olivil.

For the determination of the relative stereochemistry of (−)-berchemol (**1**), the nuclear magnetic shielding shifts were measured. (−)-Berchemol (**1**) was treated with acetone and *p*-toluenesulfonic acid to give an acetonide (**1c**), $C_{23}H_{28}O_7$. If the relation between the 3a-hydroxylmethyl group and the aromatic ring at C-2 in **1c** is *trans* (partial structure B), the difference of chemical shifts due to the methyl groups should be 0.66 ppm on the basis of the shielding shifts calculated by the use of McConnell's equation.[9] If the relation is *cis* (partial structure C), the difference should be 0.09 ppm (Chart 2). In the ^{1}H-NMR spectrum, the singlets due to the two C-methyl groups were observed at δ 0.77 and 1.38 ppm, and the difference of the chemical shifts between them is 0.61 ppm. Hence, the relationship between the 3a-hydroxylmethyl group and H-2 was found to be *cis* in the plane of the tetrahydrofuran ring (Table III).

The stereochemistry of **1a** has been studied by measuring the NOE difference spectrum. The observed NOE difference spectra are shown in Fig. 4. Irradiation at the resonances due to H-3a$_A$ (δ 4.29 ppm) produced NOEs for H-2 (4.91 ppm) and H-4a$_A$ (3.02 ppm). Irradiation at the H-3a$_B$ (4.35 ppm) resonance produced NOE for H-2. Therefore, it was considered that H-2, 2H-3a and H-4a$_A$ are sterically in close proximity. Thus, the relative stereostructure of **1** was determined to be as shown in Chart 1.

TABLE IV. Final Atomic Parameters for Non-hydrogen Atoms and Equivalent Thermal Parameters, with Estimated Standard Deviations in Parentheses, of (−)-Berchemol (**1**)

Atom	x	y	z	B_{eq} (Å^2)
O(2)	1.3081 (5)	0.9327 (3)	0.4839 (8)	4.3
O(3)	1.3962 (4)	0.8242 (2)	0.2636 (8)	2.9
O(3a)	1.4517 (5)	0.8633 (3)	−0.0953 (9)	4.5
O(3')	1.0973 (4)	0.7309 (3)	0.6511 (8)	3.1
O(4')	0.9427 (4)	0.7242 (2)	0.3903 (8)	3.1
O(3'')	1.8556 (4)	1.0219 (2)	0.2470 (9)	3.4
O(4'')	1.8349 (4)	1.1482 (2)	0.3057 (9)	4.2
C(2)	1.2693 (6)	0.9118 (4)	0.302 (1)	2.8
C(3)	1.3680 (5)	0.8894 (3)	0.195 (1)	2.4
C(4)	1.4545 (6)	0.9375 (3)	0.268 (1)	2.6
C(5)	1.4140 (7)	0.9565 (4)	0.466 (1)	4.0
C(3a)	1.3533 (6)	0.8857 (4)	−0.017 (1)	3.1
C(4a)	1.4716 (6)	0.9969 (4)	0.136 (1)	3.0
C(1')	1.1839 (6)	0.8610 (3)	0.329 (1)	2.6
C(2')	1.1835 (6)	0.8196 (4)	0.482 (1)	3.0
C(3')	1.1034 (6)	0.7745 (4)	0.504 (1)	2.7
C(4')	1.0235 (6)	0.7692 (4)	0.371 (1)	2.7
C(5')	1.0250 (6)	0.8099 (4)	0.212 (1)	3.1
C(6')	1.1058 (6)	0.8564 (4)	0.192 (1)	3.3
C(7')	1.1891 (8)	0.7174 (6)	0.759 (2)	7.9
C(1'')	1.5662 (6)	1.0374 (3)	0.190 (1)	2.7
C(2'')	1.6550 (6)	1.0085 (3)	0.201 (1)	2.5
C(3'')	1.7539 (6)	1.0446 (3)	0.236 (1)	2.4
C(4'')	1.7471 (6)	1.1125 (3)	0.266 (1)	2.9
C(5'')	1.6489 (6)	1.1419 (3)	0.257 (1)	3.2
C(6'')	1.5588 (6)	1.1051 (4)	0.223 (1)	3.6
C(7'')	1.8697 (7)	0.9526 (4)	0.229 (1)	3.7

TABLE V. Bond Lengths (Å) for (−)-Berchemol (**1**) with Estimated Standard Deviations in Parentheses

O(2)–C(2)	1.434 (10)	O(2)–C(5)	1.428 (11)
O(3)–C(3)	1.458 (10)	O(3a)–C(3a)	1.433 (10)
O(3')–C(3')	1.368 (10)	O(3')–C(7')	1.411 (15)
O(4')–C(4')	1.380 (10)	O(3'')–C(3'')	1.367 (10)
O(3'')–C(7'')	1.429 (11)	O(4'')–C(4'')	1.355 (11)
C(2)–C(3)	1.525 (11)	C(2)–C(1')	1.507 (11)
C(3)–C(4)	1.554 (11)	C(3)–C(3a)	1.506 (11)
C(4)–C(5)	1.533 (12)	C(4)–C(4a)	1.538 (11)
C(4a)–C(1'')	1.500 (11)	C(1')–C(2')	1.365 (11)
C(1')–C(6')	1.381 (12)	C(2')–C(3')	1.376 (11)
C(3')–C(4')	1.378 (11)	C(4')–C(5')	1.392 (12)
C(5')–C(6')	1.400 (13)	C(1'')–C(2'')	1.382 (11)
C(1'')–C(6'')	1.404 (12)	C(2'')–C(3'')	1.365 (11)
C(3'')–C(4'')	1.402 (12)	C(4'')–C(5'')	1.380 (12)
C(5'')–C(6'')	1.383 (13)		

TABLE VI. Bond Angles (°) for (−)-Berchemol (**1**) with Estimated Deviations in Parentheses

C(2)–O(2)–C(5)	110.0 (6)	C(3′)–O(3′)–C(7′)	119.0 (8)
C(3″)–O(3″)–C(7″)	116.5 (7)	O(2)–C(2)–C(3)	104.3 (6)
O(2)–C(2)–C(1′)	109.5 (7)	C(3)–C(2)–C(1′)	116.3 (7)
O(3)–C(3)–C(2)	108.1 (6)	O(3)–C(3)–C(4)	107.2 (6)
O(3)–C(3)–C(3a)	108.1 (6)	C(2)–C(3)–C(4)	103.0 (6)
C(2)–C(3)–C(3a)	113.6 (7)	C(3a)–C(3)–C(4)	116.4 (7)
C(3)–C(4)–C(5)	102.8 (6)	C(3)–C(4)–C(4a)	113.5 (6)
C(4a)–C(4)–C(5)	113.2 (7)	O(2)–C(5)–C(4)	107.9 (7)
O(3a)–C(3a)–C(3)	106.7 (6)	C(4)–C(4a)–C(1′)	113.2 (7)
C(2)–C(1′)–C(2′)	121.9 (7)	C(2)–C(1′)–C(6′)	117.9 (7)
C(2′)–C(1′)–C(6′)	120.2 (8)	C(1′)–C(2′)–C(3′)	120.1 (8)
O(3′)–C(3′)–C(2′)	124.1 (7)	O(3′)–C(3′)–C(4′)	114.9 (7)
C(2′)–C(3′)–C(4′)	121.1 (7)	O(4′)–C(4′)–C(3′)	121.7 (7)
O(4′)–C(4′)–C(5′)	119.1 (7)	C(3′)–C(4′)–C(5′)	119.2 (7)
C(4′)–C(5′)–C(6′)	119.4 (8)	C(1′)–C(6′)–C(5′)	120.0 (8)
C(2″)–C(1″)–C(6″)	118.1 (8)	C(2″)–C(1″)–C(4a)	119.9 (8)
C(6″)–C(1″)–C(4a)	122.0 (7)	C(1″)–C(2″)–C(3″)	121.5 (7)
O(3″)–C(3″)–C(2″)	126.9 (7)	O(3″)–C(3″)–C(4″)	112.5 (7)
C(2″)–C(3″)–C(4″)	120.6 (8)	O(4″)–C(4″)–(C3″)	120.8 (8)
O(4″)–C(4″)–C(5″)	120.8 (8)	C(3″)–C(4″)–C(5″)	118.5 (8)
C(4″)–C(5″)–C(6″)	120.8 (8)	C(1″)–C(6″)–C(5″)	120.5 (8)

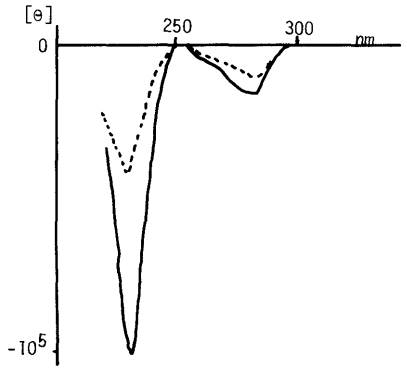


Fig. 6. CD Curves of (−)-Berchemol (**1**) and (−)-Olivil
------, (−)-berchemol; ——, (−)-olivil.

Methylation of **1c** with diazomethane gave an acetonide dimethyl ether (**1d**), mp 152—153 °C, $[\alpha]_D$ −2.9°, $C_{25}H_{32}O_7$, which was shown to be O-isopropylidenedihydrogmelinol-II, on the basis of the physical and spectroscopic data.[10]

The relative structure of (−)-berchemol (**1**) proposed on the basis of the chemical and spectroscopic analysis was confirmed by X-ray analysis. The structure was solved by the direct method using MULTAN 80.[11] The ORTEP drawing of the structure of (−)-berchemol (**1**) is shown in Fig. 5. Final atomic parameters, bond lengths and bond angles are listed in Tables IV, V and VI, respectively.

The absolute configuration of **1** was elucidated by comparison of its circular dichroism (CD) spectrum with that of (−)-olivil.[12] Both showed negative Cotton effects (229, 285 and 231, 282 nm). The similarity between the two CD spectra defined the configuration of (−)-berchemol as being the same as that of (−)-olivil (Fig. 6).

Thus (−)-berchemol (**1**) was concluded to be (2*R*,3*S*,4*S*)-2,4-bis(4-hydroxy-3-methoxyphenyl)-3-hydroxy-3-hydroxymethyltetrahydrofuran (Chart 1).

Compound **2** was isolated as a tetraacetate (**2a**), $[\alpha]_D$ −6.7°, $C_{28}H_{34}O_{10}$. On treatment with sodium methoxide, **2a** afforded compound **2**, mp 113—114 °C, $[\alpha]_D$ −25.7°, $C_{20}H_{26}O_6$. Compound **2** was assigned as (−)-secoisolariciresinol on the basis of literature data. (−)-Secoisolariciresinol-*O*-β-D-glucopyranoside has been isolated from *B. racemosa* by Yamasaki *et al.*,[3] and (−)-secoisolariciresinol has been reported as a component of many plants, such as *Araucaria angustifolia*[13] and *Xanthoxylum ailanthoides*.[14]

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-181 automatic polarimeter in a 1 dm tube. UV spectra were recorded with a Shimadzu UV-250 spectrometer. IR spectra were recorded with a Hitachi 260-10 spectrometer. MS were measured on a JEOL JMS D-300 spectrometer. CD spectra were recorded on a JASCO J-500 C spectropolarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded with JEOL JNM FX-100, GX-270 and GX-400 spectrometers with tetramethylsilane (TMS) as an internal standard. Chemical shifts are recorded in δ ppm, and signals are described as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Column chromatography was performed on Kieselgel 60 (Merck, 70—230 mesh) and Sephadex LH-20 (Pharmacia Fine Chemicals). Thin layer chromatography (TLC) was carried out with precoated Kieselgel 60F_{254} plates (Merck) and detection was carried out by UV irradiation and by spraying 10% H_2SO_4 followed by heating.

Isolation The dried stems (3 kg) of *Berchemia racemosa* were extracted with hexane, acetone and MeOH (each 6 l × 3) under reflux, successively. Each fraction was concentrated *in vacuo* to afford the hexane extract (9 g), acetone extract (23 g), and MeOH extract (139 g). The acetone extract was chromatographed repeatedly on SiO_2 with benzene–EtOAc and $CHCl_3$–MeOH, and on Sephadex LH-20 with benzene–EtOAc–MeOH–H_2O (40 : 40 : 8 : 1). The fraction showing a TLC spot at *Rf* 0.50 ($CHCl_3$–MeOH (5 : 1)) was acetylated with Ac_2O (1 ml) in pyridine (1 ml). After usual work-up, the crude product was chromatographed on SiO_2 with benzene–EtOAc (10 : 1—1 : 1) to afford a triacetate (**1a**) (55 mg) and a tetraacetate (**2a**) (50 mg).

The Triacetate (1a) A white powder. $[\alpha]_D^{21}$ +8.7° (*c* = 1.5, $CHCl_3$). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3570, 1770, 1745, 1603, 1508, 1200. MS *m/z* (%): 502 (M^+, 7), 137 (100). High MS *m/z*: Calcd for $C_{26}H_{30}O_{10}$, 502.1839. Found: 502.1852. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

(−)-Berchemol (1) A mixture of **1a** (55 mg) in absolute MeOH (4 ml) and 0.5% NaOMe–MeOH (4 ml) was left at room temperature for 2 h. After usual work-up, the crude product was chromatographed on SiO_2 with $CHCl_3$–acetone (5 : 2) to afford **1**, colorless needles (from MeOH) (29 mg), mp 188—189 °C, $[\alpha]_D^{20}$ −7.9° (*c* = 0.3, MeOH). UV λ_{max}^{MeOH} nm (log ε): 231 (4.1), 281 (3.7). IR ν_{max}^{KBr} cm^{-1}: 3530, 3485, 3380, 1617, 1520. MS *m/z* (%): 376 (M^+, 17), 137 (100). High MS *m/z*: Calcd for $C_{20}H_{24}O_7$, 376.1510. Found: 376.1513. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II. CD (*c* = 2.60 × 10^{-3}, MeOH); $[\theta]_{283}$ −8450, $[\theta]_{229}$ −38400. *Cf.* (−)-Olivil (*c* = 2.57 × 10^{-3}, MeOH) $[\theta]_{282}$ −15600, $[\theta]_{231}$ −101000.

Methylation of 1 Compound **1** (72 mg) in MeOH (2 ml) was methylated with ethereal CH_2N_2. After work-up as usual, the product was chromatographed on SiO_2 with $CHCl_3$–acetone (5 : 1) to give the dimethyl ether (**1b**) (14 mg). An oil. $[\alpha]_D^{24}$ −8.3° (*c* = 0.8, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3680, 3550. MS *m/z*: 404 (M^+, 16), 151 (100). High MS *m/z*: Calcd for $C_{22}H_{28}O_7$, 404.1835, $C_9H_{11}O_2$, 151.0758. Found: 404.1843; 151.0758. ^{1}H-NMR ($CDCl_3$) δ: 3.87, 3.88, 3.89, 3.90 (each 3H, s, 4 × OCH_3). ^{13}C-NMR: Table II.

The Acetonide (1c) Compound **1** (16 mg) in acetone (4 ml) was treated with *p*-toluenesulfonic acid (10 mg) at room temperature for 24 h. After usual work-up, the product was chromatographed on SiO_2 with $CHCl_3$–acetone (5 : 1) to give **1c** (14 mg). An oil. MS *m/z* (%): 416 (M^+, 21), 137 (100). High MS *m/z*: Calcd for $C_{23}H_{28}O_7$, 416.1836. Found: 416.1837. ^{1}H-NMR ($CDCl_3$) δ: 0.77, 1.38 (each 3H, s, CH_3). ^{13}C-NMR: Table II.

Methylation of 1c Compound **1c** (13 mg) in MeOH (2 ml) was methylated with ethereal CH_2N_2. After work-up as usual, the crude product was chromatographed on SiO_2 with benzene–EtOAc (5 : 1) to give the acetonide dimethyl ether (**1d**) (11 mg). Colorless needles (from EtOH). mp 152—153 °C. $[\alpha]_D^{21}$ −2.9° (*c* = 0.4. $CHCl_3$). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1610, 1593, 1510, 1385, 1375. MS *m/z* (%): 444 (M^+, 21), 151 (100). High MS *m/z*: Calcd for $C_{25}H_{32}O_7$, 444.2147. Found: 444.2142. ^{1}H-NMR ($CDCl_3$) δ: 0.77, 1.38 (each 3H, s, CH_3), 3.87 (12H, s, 4 × OCH_3).

X-Ray Structure Analysis of (−)-Berchemol (1) Crystals of **1** were grown from EtOH as colorless prisms. Crystal data: $C_{20}H_{24}O_7$;

$M_r = 376.41$; orthorhombic; $P2_12_12_1$; $a = 12.631$ (10), $b = 20.386$ (22), $c = 7.024$ (15) Å; $V = 1808.6$ (4.5) Å^3; $Z = 4$; $D_c = 1.383\,g\,cm^{-3}$; $F(000) = 800$. The diffraction intensities were collected from a (−)-berchemol crystal with dimensions of $0.7 \times 0.25 \times 0.1$ mm on a Rigaku AFC-5 FOS four-circle difractometer using CuK_α radiation monochromated by means of a graphite plate. A total of 1269 refractions were measured within a 2θ range of 100° as above the $3\sigma(F)$ level.

Determination of the Structure The structure was solved by the direct method using MULTAN 80[11] and refined by the block-matrix least-squares method. In the final refinement, anisotropic thermal parameters were used for non-hydrogen atoms. The contribution of the three hydroxyl hydrogen atoms was ignored. The final R factor was 0.064.

Tetraacetate (2a) An oil. $[\alpha]_D^{25}$ −6.7° ($c = 0.8$, $CHCl_3$). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770, 1745, 1605, 1510, 1220. MS m/z (%): 530 (M^+, 3). High MS m/z: Calcd for $C_{28}H_{34}O_{10}$, 530.2152. Found: 530.2159.

Compound 2 Compound **2a** was treated in the same way as described for **1** to give **2**. Colorless needles (from *n*-hexane–EtOAc–MeOH). mp 113—114 °C. $[\alpha]_D^{21}$ −25.7° ($c = 0.6$, MeOH). (Lit. mp 112—114 °C, $[\alpha]_D^{25}$ −32°).

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