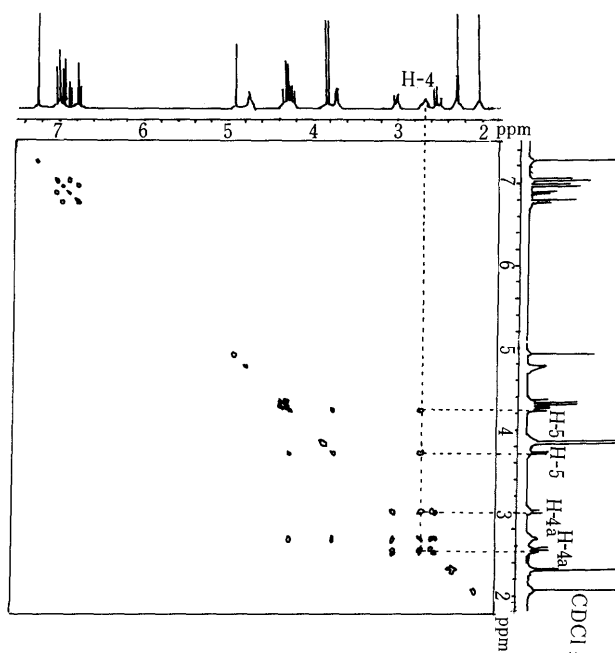


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Keywords *Berchemia racemosa*; Rhamnaceae; tetrahydrofuranoid lignan; (–)-berchemol; (–)-secoisolariciresinol; X-ray analysis; CD spectrum; 2D-NMR

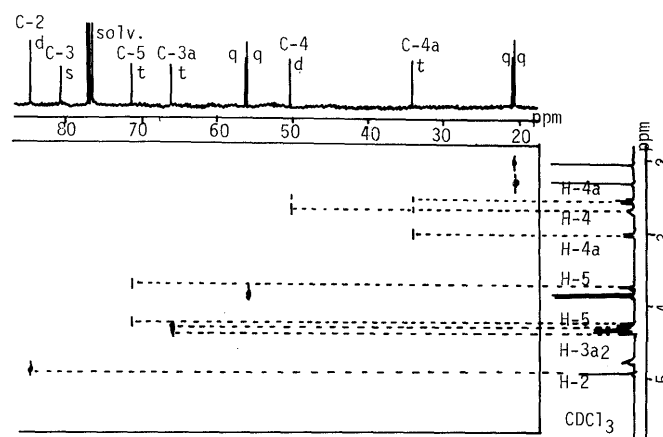
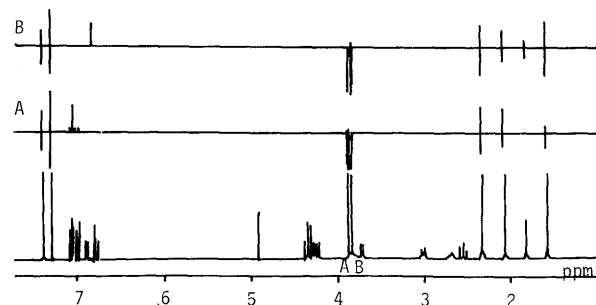
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Fig. 1. ^1H - ^1H COSY Spectrum of the Triacetate (**1a**)TABLE II. ^{13}C -NMR Chemical Shifts (—)-Berchemol (**1**) and Its Derivatives (**1a**—**1c**), ppm from TMS in CDCl_3 (100 MHz)

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. ^1H - ^{13}C COSY Spectrum of the Triacetate (**1a**)Fig. 3. ^1H -NMR (Normal and NOE Difference) Spectra of the Triacetate (**1a**) a

with those of (—)-massonirecinol.⁶⁾ The two dimensional ^1H - ^{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 ^1H - and ^{13}C -NMR spectra of **1**, in comparison with that of olivil,⁶⁾ suggest the presence of a tetrahydrofuran ring.

The ^1H -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 dimethyl-ether (**1b**), $[\alpha]_D -8.3^\circ$, $\text{C}_{22}\text{H}_{28}\text{O}_7$. 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**),

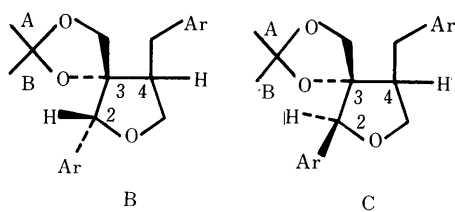
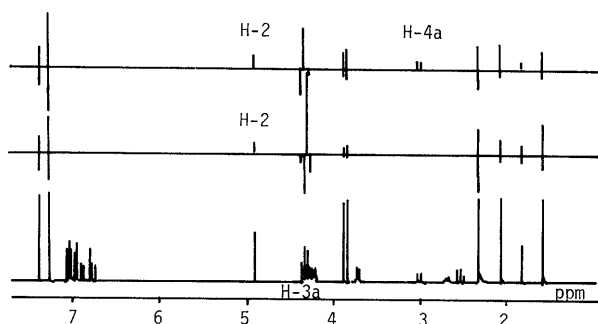
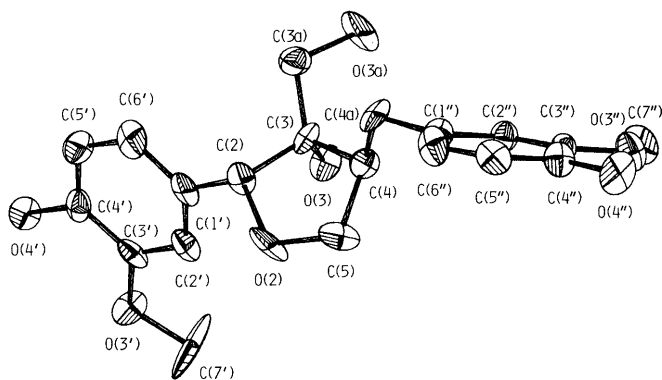


Chart 2

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. ¹H-NMR (Normal and NOE Difference) Spectra of the Triacetate (**1a**) bFig. 5. ORTEP Drawing of (-)-Berchemol (**1**)

was established as **1** (Chart 1), which is the same as that proposed incorrectly by Freudenberg and Weinges⁸) 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 acetone (**1c**), C₂₃H₂₈O₇. If the relation between the 3a-hydroxymethyl 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

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{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

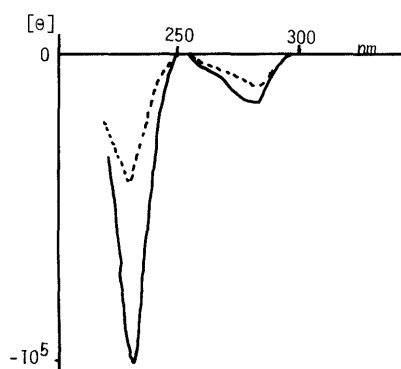
O(2)—C(2)	1.434 (10)	O(2)—C(5)	1.428 (11)
O(3)—C(3)	1.458 (10)	O(3a)—C(3a)	1.433 (10)
O(3')—C(3')	1.368 (10)	O(3'')—C(3'')	1.411 (15)
O(4')—C(4')	1.380 (10)	O(3'')—C(3'')	1.367 (10)
O(3'')—C(7'')	1.429 (11)	O(4'')—C(4'')	1.355 (11)
C(2)—C(3)	1.525 (11)	C(2)—C(1')	1.507 (11)
C(3)—C(4)	1.554 (11)	C(3)—C(3a)	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)		

difference should be 0.09 ppm (Chart 2). In the ¹H-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-hydroxymethyl 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 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'')	121.5 (7)
C(2'')–C(3'')–C(4'')	120.6 (8)	O(4'')–C(4'')–C(3'')	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, $[\alpha]_D -2.9^\circ$, $C_{25}H_{32}O_7$, 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**), $[\alpha]_D -6.7^\circ$, $C_{28}H_{34}O_{10}$. On treatment with sodium methoxide, **2a** afforded compound **2**, mp 113–114 °C, $[\alpha]_D -25.7^\circ$,

$C_{20}H_{26}O_6$. 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. ¹H- and ¹³C-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 60F₂₅₄ plates (Merck) and detection was carried out by UV irradiation and by spraying 10% H₂SO₄ 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 SiO₂ with benzene–EtOAc and CHCl₃–MeOH, and on Sephadex LH-20 with benzene–EtOAc–MeOH–H₂O (40:40:8:1). The fraction showing a TLC spot at *R*_f 0.50 (CHCl₃–MeOH (5:1)) was acetylated with Ac₂O (1 ml) in pyridine (1 ml). After usual work-up, the crude product was chromatographed on SiO₂ 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. $[\alpha]_D^{21} +8.7^\circ$ ($c=1.5$, CHCl₃). IR $\nu_{\max}^{CHCl_3}$ cm^{–1}: 3570, 1770, 1745, 1603, 1508, 1200. MS *m/z* (%): 502 (*M*⁺, 7), 137 (100). High MS *m/z*: Calcd for C₂₆H₃₀O₁₀, 502.1839. Found: 502.1852. ¹H-NMR: Table I. ¹³C-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 SiO₂ with CHCl₃–acetone (5:2) to afford **1**, colorless needles (from MeOH) (29 mg), mp 188–189 °C, $[\alpha]_D^{20} -7.9^\circ$ ($c=0.3$, MeOH). UV $\lambda_{\max}^{MeOH}$ nm (log ε): 231 (4.1), 281 (3.7). IR $\nu_{\max}^{KBr}$ cm^{–1}: 3530, 3485, 3380, 1617, 1520. MS *m/z* (%): 376 (*M*⁺, 17), 137 (100). High MS *m/z*: Calcd for C₂₀H₂₄O₇, 376.1510. Found: 376.1513. ¹H-NMR: Table I. ¹³C-NMR: Table II. CD ($c=2.60 \times 10^{-3}$, MeOH): $[\theta]_{283} -8450$, $[\theta]_{229} -38400$. Cf. (–)-Olivil ($c=2.57 \times 10^{-3}$, MeOH) $[\theta]_{282} -15600$, $[\theta]_{231} -101000$.

Methylation of 1 Compound **1** (72 mg) in MeOH (2 ml) was methylated with ethereal CH₂N₂. After work-up as usual, the product was chromatographed on SiO₂ with CHCl₃–acetone (5:1) to give the dimethyl ether (**1b**) (14 mg). An oil. $[\alpha]_D^{24} -8.3^\circ$ ($c=0.8$, CHCl₃). IR $\nu_{\max}^{CHCl_3}$ cm^{–1}: 3680, 3550. MS *m/z*: 404 (*M*⁺, 16), 151 (100). High MS *m/z*: Calcd for C₂₂H₂₈O₇, 404.1835, C₉H₁₁O₂, 151.0758. Found: 404.1843; 151.0758. ¹H-NMR (CDCl₃) δ: 3.87, 3.88, 3.89, 3.90 (each 3H, s, 4 × OCH₃). ¹³C-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 SiO₂ with CHCl₃–acetone (5:1) to give **1c** (14 mg). An oil. MS *m/z* (%): 416 (*M*⁺, 21), 137 (100). High MS *m/z*: Calcd for C₂₃H₂₈O₇, 416.1836. Found: 416.1837. ¹H-NMR (CDCl₃) δ: 0.77, 1.38 (each 3H, s, CH₃). ¹³C-NMR: Table II.

Methylation of 1c Compound **1c** (13 mg) in MeOH (2 ml) was methylated with ethereal CH₂N₂. After work-up as usual, the crude product was chromatographed on SiO₂ with benzene–EtOAc (5:1) to give the acetonide dimethyl ether (**1d**) (11 mg). Colorless needles (from EtOH). mp 152–153 °C. $[\alpha]_D^{21} -2.9^\circ$ ($c=0.4$, CHCl₃). IR $\nu_{\max}^{CHCl_3}$ cm^{–1}: 1610, 1593, 1510, 1385, 1375. MS *m/z* (%): 444 (*M*⁺, 21), 151 (100). High MS *m/z*: Calcd for C₂₅H₃₂O₇, 444.2147. Found: 444.2142. ¹H-NMR (CDCl₃) δ: 0.77, 1.38 (each 3H, s, CH₃), 3.87 (12H, s, 4 × OCH₃).

X-Ray Structure Analysis of (–)-Berchemol (1) Crystals of **1** were grown from EtOH as colorless prisms. Crystal data: C₂₀H₂₄O₇;

$M_r = 376.41$; orthorhombic; $P2_12_12_1$; $a = 12.631$ (10), $b = 20.386$ (22), $c = 7.024$ (15) Å; $V = 1808.6$ (4.5) Å³; $Z = 4$; $D_c = 1.383$ 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 diffractometer using CuK_α radiation monochromated by means of a graphite plate. A total of 1269 reflections 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 80¹¹⁾ 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. $[\alpha]_D^{25} -6.7^\circ$ ($c = 0.8$, CHCl_3). IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 1770, 1745, 1605, 1510, 1220. MS m/z (%): 530 (M^+ , 3). High MS m/z : Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_{10}$, 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 $113\text{--}114^\circ\text{C}$. $[\alpha]_D^{21} -25.7^\circ$ ($c = 0.6$, MeOH). (Lit. mp $112\text{--}114^\circ\text{C}$, $[\alpha]_D^{25} -32^\circ$).

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References and Notes

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