Hence, the structures presented here are unique, at least in two points. They are the first examples on the organic ligand sector where face differentiation of a host toward an uncharged molecular guest is definitively shown, and also first- and second-sphere coordination,[15] or cavitate[16] plus clathrate binding[17] of the same guest species within the same crystal, to our knowledge, has not been documented before. Moreover, it should be mentioned that MeCN, just as $MeNO_2$, causes problems with respect to the complexation of 18-crown-6.[4]

For other face differentiations it would be desirable to have more extensive cavities either at face A or B, or at both sides of 1-type hosts. In this respect, we are going to substitute the phenylenes of **1** gradually for naphthylenes, which are more shielding groups.

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Supplementary Material Available: Tables of positional and thermal parameters (Tables I and II), bond distances and bond angles involving non-hydrogen atoms (Tables III and IV), endocyclic torsion angles for the host macrocycle (Table V), and figures with different stereoscopic representations of the host–guest unit (Figures 2 and 3) and of the crystal packing (Figure 4) (10 pages). Ordering information is given on any current masthead page. A list of observed and calculated structure factors is available directly from the author.

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(16) Cram, D. J. *Science (Washington, D.C.)* **1983**, *219*, 1177–1183.
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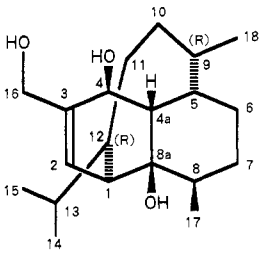
The Structure of Vinigrol, a Novel Diterpenoid with Antihypertensive and Platelet Aggregation-Inhibitory Activities

Summary: The structure of vinigrol (**1**), a novel diterpenoid isolated from a fungus as an antihypertensive and platelet aggregation-inhibiting substance, has been determined by using chemical derivatizations, spectroscopic measurements, and an X-ray crystal analysis.

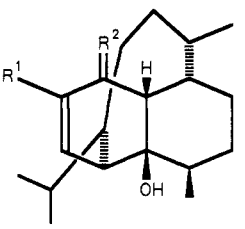
Sir: Vinigrol (**1**) is a novel diterpenoid recently isolated from *Virgaria nigra* as an antihypertensive and platelet aggregation-inhibiting substance.[1a] Herein we report the structure elucidation of this natural product on the basis of chemical and physical evidence and X-ray crystal analysis.

(1) (a) Ando, T.; Tsurumi, Y.; Ohata, N.; Uchida, I.; Yoshida, K.; Okuhara, M. *J. Antibiot.*, in press. (b) Ando, T.; Yoshida, K.; Okuhara, M. *J. Antibiot.*, in press.

Vinigrol (**1**) was isolated as colorless prisms: $C_{20}H_{34}O_3$ (FDMS, m/z 323 ($M^+ + H$). Anal. Calcd for $C_{20}H_{34}O_3$: C, 74.49; H, 10.63. Found: C, 74.20; H, 10.23; mp 108 °C; $[\alpha]_D$ −96.2° (c 1.05, $CHCl_3$). The ^{13}C NMR spectrum ($CDCl_3$) of **1**[2] revealed all the carbon signals which are assignable to a trisubstituted olefin (δ 128.5 (d),[3] 136.5 (s)) and three alcohols (primary, secondary, and tertiary) (δ 67.6 (t),[3] 72.7 (d),[3] 75.5 (s)), the remainder being 15 signals attributable to seven methines (δ 33.1 (d), 34.6 (d), 35.9 (d), 40.3 (d), 44.3 (d), 45.1 (d), 51.3 (d)), four methylenes (δ 27.3 (t), 28.6 (t), 28.9 (t), 29.7 (t)), and four methyls (δ 15.5 (q), 20.6 (q), 21.5 (q), 24.8 (q)).



1



2 $R^1 = CH_2OCOCH_3$; $R^2 = \alpha\text{-}OCOCH_3$; β-H
3 $R^1 = CH_2OH$; $R^2 = O$
4 $R^1 = CHO$; $R^2 = \alpha\text{-}OH$; β-H
5 $R^1 = CHO$; $R^2 = O$
6 $R^1 = CH_2OSi(CH_3)_2C(CH_3)_3$; $R^2 = \alpha\text{-}OH$; β-H
7 $R^1 = CH_2OSi(CH_3)_2C(CH_3)_3$; $R^2 = \alpha\text{-}OCOC_6H_5$; β-H

Acetylation of **1** (Ac_2O/pyridine) gave diacetate **2** (EIMS, m/z 406 (M^+); δ_H 2.10 (s, 3 H), 2.04 (s, 3 H), 4.61 (AB q, J = 12 Hz, 2 H), 5.48 (s, 1 H)).[4] Jones' oxidation of **1** (CrO_3–H_2SO_4/H_2O–acetone) gave ketone **3** as a major product (EIMS, m/z 320 (M^+); δ_H 6.89 (d, J = 6.2 Hz, 1 H), 4.31 (s, 2 H); 54%), together with minor products **4** (EIMS, m/z 320 (M^+); δ_H 9.50 (s, 1 H), 7.01 (d, J = 5.9 Hz, 1 H), 4.63 (s, 1 H); 5%) and **5** (EIMS, m/z 318 (M^+); δ_H 10.16 (s, 1 H), 7.81 (d, J = 6.5 Hz, 1 H); 5%). Since these chemical and spectroscopic methods were found to be impractical for structural determination of this unusual diterpenoid, we decided to submit crystals of **1** or its derivatives to X-ray crystal analysis.

The crystals of **5** were found to be optimum, which formed in the orthorhombic space group $P2_12_12_1$ with a = 18.105 (1) Å, b = 10.355 (1) Å, and c = 9.296 (1) Å; V = 1739.5 (2) Å^3; Z = 4; D_x = 1.22 g cm^{-3}. The structure was determined by the direct method (MULTAN 74) and successive block-diagonal least-squares and Fourier syntheses. Parameters were refined by using anisotropic temperature factors to R = 0.050 for 1644 independent

(2) ^1H NMR ($CDCl_3$) of **1**: δ 5.81 (d, J = 5.6 Hz, 1 H), 4.25 (AB q, J = 12 Hz, 2 H), 4.20 (s, 1 H), 2.32 (d, J = 5.6 Hz, 1 H), 2.23 (d, J = 3.6 Hz, 1 H), 2.12 (m, 1 H), 1.96 (m, 1 H), 1.8–1.5 (m, 5 H), 1.4–1.0 (m, 6 H), 1.0–0.8 (m, 12 H).
(3) The signals at δ 128.5, 67.6, and 72.7 correspond to the proton signals at δ 5.81, 4.25, and 4.20 in the ^1H NMR spectrum of **1** (see ref 2).
(4) ^1H NMR ($CDCl_3$) of **2**: δ 6.14 (d, J = 6 Hz, 1 H), 5.48 (s, 1 H), 4.65 (d, J = 12 Hz, 1 H), 4.57 (d, J = 12 Hz, 1 H), 2.44 (d, J = 6 Hz, 1 H), 2.17 (m, 1 H), 2.10 (s, 3 H), 2.05 (d, J = 3.6 Hz, 1 H), 2.04 (s, 3 H), 2.0–1.85 (m, 3 H), 1.80 (m, 1 H), 1.65 (m, 1 H), 1.53–1.48 (m, 2 H), 1.40 (m, 1 H), 1.35 (m, 1 H), 1.3–1.0 (m, 4 H), 0.99 (d, J = 6.8 Hz, 3 H), 0.98 (d, J = 6.8 Hz, 3 H), 0.95 (d, J = 6.8 Hz, 3 H), 0.94 (d, J = 6.8 Hz, 3 H).

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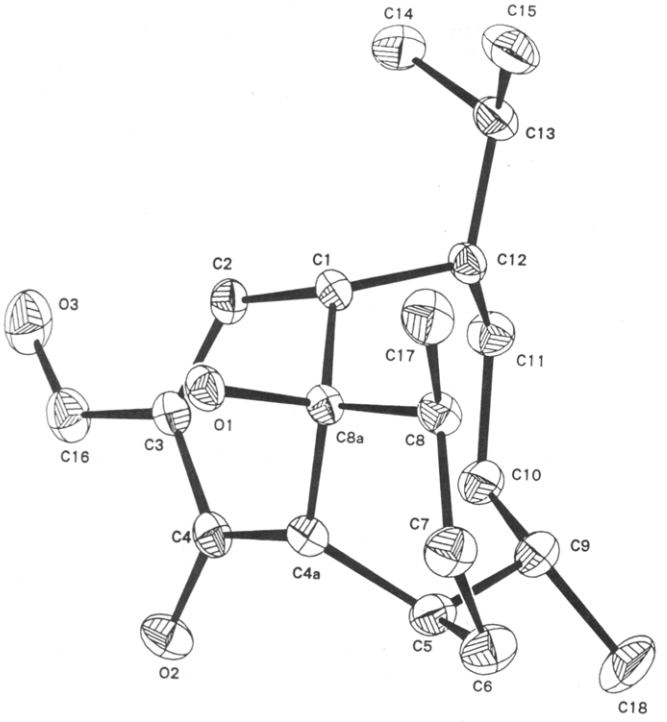

Figure 1. Molecular structure of **5** by an ORTEP drawing.

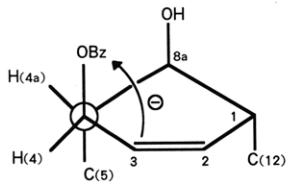

Figure 2. The presumed conformation of benzoate **7**.

reflections. A perspective drawing of the final X-ray model of **5** is given in Figure 1. The structure of the oxidation product was defined to be **5** and hence that of the natural product to be **1** except for the stereochemistry at C-4.

The relative configuration at C-4 of **1** was deduced as follows. In the ^{1}H NMR spectra ($CDCl_3$) of **1** and **2**, 4-Hs (**1**, δ 4.20; **2**, δ 5.48)[2,4] resonated as singlet without coupling to 4a-Hs (**1**, δ 2.23; **2**, 2.05),[2,4] respectively, indicating the dihedral angles of 4-Hs and 4a-Hs in **1** and **2** both to be close to 90°. As shown by a molecular model study (see, e.g., Figure 2), an interpretation was unambiguous as 4-H and 4a-H are in trans configuration. This assignment was further supported by the NOESY spectrum[5] of **2**. The spectrum showed, in addition to NOE's between 4-H and 4a-H and between 4-H and one (δ 4.65) of 16-H_2, that 4-H also brought about NOE's with two other protons at δ 1.89 and 1.22, which were assigned to 5-H and 10-H, respectively.[6] These phenomena are possible only when 4-H and 4a-H are trans and 4a-H and 5-H are cis.

The absolute structure was established by using the CD allylic benzoate method[7] as follows. After protection of the primary alcohol in **1** by silylation (t-Bu(Me)$_2$SiCl/imidazole), the resulting **6** was converted to benzoate **7**[8] (C_6H_5COCl/pyridine/DMAP). The CD spectrum of **7** exhibited a negative Cotton effect ($\Delta\epsilon$ −14.0 at 230 nm (MeOH)), indicating an anticlockwise relationship between the endocyclic double bond and the benzoate chromophore (Figure 2). Consequently, the absolute stereostructure of vinigrol was deduced to be as shown in **1**.

The decahydro-1,5-butanonaphthalene skeleton of vinigrol is unprecedented, and, as far as we are aware, vinigrol is the first example of this structural type. The activity of vinigrol as an antihypertensive and platelet aggregation-inhibiting agent[1b] is also of interest.

Supplementary Material Available: Experimental details and characterization data for **3–5** and details of the X-ray crystal analysis of **5** including tables of fractional coordinates, thermal parameters, interatomic distances, and interatomic angles (8 pages). Ordering information is given on any current masthead page.

(8) FABMS, m/z 563 (M + Na)$^+$; ^{1}H NMR ($CDCl_3$) δ 8.04 (d, J = 8 Hz, 2 H), 7.58 (t, J = 8 Hz, 1 H), 7.46 (t, J = 8 Hz, 2 H), 6.10 (d, J = 6 Hz, 1 H), 5.71 (s, 1 H), 4.21 (s, 2 H), 2.52 (d, J = 6 Hz, 1 H), 2.24–2.17 (m, 2 H), 2.07–1.86 (m, 3 H), 1.70 (m, 1 H), 1.6–1.2 (m, 9 H), 1.04 (d, J = 7 Hz, 6 H), 1.00 (d, J = 7 Hz, 3 H), 0.98 (d, J = 7 Hz, 3 H), 0.90 (s, 9 H), 0.06 (s, 3 H), 0.04 (s, 3 H).

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Catalysis of Diene Polymerization and Diels–Alder Reactions by an Octahedral Tungsten Nitrosyl Lewis Acid. X-ray Crystal Structure of the η^1-Acrolein Complex (*cis*-Me_3P)(*trans*-NO)$(CO)_3$W—O=C(H)C(H)=CH_2

Summary: Cyclopentadiene and isoprene are polymerized by 0.1 mol % $(Me_3P)(CO)_3(NO)W$–$FSbF_5$ (**1**), and catalysis of the Diels–Alder reactions of cyclopentadiene or butadiene with α,β-unsaturated enones is also induced by as little as 0.1 mol % **1**; the X-ray structure of the adduct of **1** and acrolein, the presumed catalytic intermediate, reveals a simple Lewis acid interaction of the tungsten with the acrolein oxygen.

Sir: While catalysis of Diels–Alder reactions by non-transition-metal Lewis acids is well-known,[1] examples of transition-metal catalysis aside from those involving high oxidation state titanium compounds[1b,i] are rare.[2] Recent

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(6) These protons were buried in the signals of δ 2.0–1.85 and 1.3–1.0 (see ref 4). The chemical shifts were determined by measurement of the frequencies showing the largest NOE values by irradiation in the NOE difference spectrum.

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(1) (a) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436–4437. (b) Fray, G. I.; Robinson, R. *Ibid.* **1961**, *83*, 249. (c) Inukai, T.; Kojima, T. *J. Org. Chem.* **1967**, *32*, 872–875. (d) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16–33. (e) Houk, K. N.; Strozier, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4094–4096. (f) Kelly, T. R.; Montury, M. *Tetrahedron Lett.* **1978**, 4311–4314. (g) Fringuelli, F.; Pizzo, F., Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802–2808. (h) Nugent, W. A.; McKinney, R. J.; Harlow, R. L. *Organometallics* **1984**, *3*, 1315–1317. (i) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876–889.

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