monly invoked for mercury(II) cleavage reactions.[5,7-11,15] Significantly, however, this pathway is entirely consistent with the reported stereochemical outcome of such scission at the pseudotetrahedral, chiral iron center in (η^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe(CO)[$P(C_6H_5)_3$]CH_3.[14] Moreover, a similar mechanism was proposed by McDonald and Basolo[25] for reactions of $Mo(CO)_4$(L-L) (L-L = bipy and phen) with HgX_2 (X = Cl or Br). We believe that such a pathway for eliminative cleavage reactions merits very serious consideration whenever the metal is susceptible to attack by Lewis acids.[26]

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(22) Other mechanisms consistent with the observed second-order dependence on $HgCl_2$ may be proposed as well. For example, formation of the ion pair $HgCl^+HgCl_3^-$ according to the equation

$$2HgCl_2 \rightleftharpoons HgCl^+HgCl_3^-$$

and subsequent reaction of it with η^5-$C_5H_5Fe(CO)_2R$ likewise yields third-order kinetics. We find by osmometry that $HgCl_2$ is monomeric and shows no evidence of association at higher concentrations in THF in the range of 0.027–0.13 *M*. It is also a nonelectrolyte at 0.1–0.002 *M* concentrations. Thus $HgCl^+HgCl_3^-$, if formed at all, exists in very low concentrations and would be required to exhibit a much higher reactivity than $HgCl_2$ toward η^5-$C_5H_5Fe(CO)_2R$ for this mechanism to be credible. Studies *in aqueous media* on the cleavage of η^5-$C_5H_5Fe(CO)_2CH_2C_5H_4NH^+$ by $HgCl_n^{m}$ indicate that $HgCl^+$ is 7000 times as reactive as $HgCl_2$ (ref 11c); however, no data are available for THF solutions.
(23) By considering the k' path only, one obtains

$$-\frac{d[Fe-R]}{dt} = \frac{k'K_1[Fe-R][HgCl_2]}{1 + K_1[HgCl_2]}$$

which simplifies to

$$-\frac{d[Fe-R]}{dt} = k'K_1[Fe-R][HgCl_2]$$

when $K_1[HgCl_2] \ll 1$. Other mechanisms may be proposed which are also consistent with this observed rate expression.
(24) For example, SO_2 insertion into the Fe–R bonds of η^5-$C_5H_5Fe(CO)_2R$ follows the order R = $CH_3 \gg C(CH_3)_3$; see S. E. Jacobson and A. Wojcicki, *J. Am. Chem. Soc.*, **95**, 6962 (1973).
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cis-Sativenediol, a Plant Growth Promotor, Produced by Fungi

Sir:

In our search for a biologically active substance among fungal metabolites, we have found that two pathogenic fungi, i.e., *Cochliobolus setariae* IFO 6635 and *Helminthosporium sativum*,[1] produced a new compound active for promoting elongation of rice seedlings. The active compound designated as *cis*-sativenediol was isolated from both fungal mycelia and culture filtrates with several related metabolites including its trans isomer. This communication describes the structure elucidation of *cis*- and *trans*-sativenediol (**1** and **2**) and the biological activity of all metabolites isolated from these fungi, emphasizing that the cis diol (**1**) is a new plant growth promotor with gibberellin-like activity. It is interesting that pathogenic fungi containing growth inhibitory substances for host plants produce also a plant growth-promoting substance as well.

The both fungi were cultured by shaking on malt–dextrose medium. The fraction containing *cis*- and *trans*-sativenediol was easily isolated by a column chromatography (silicic acid; elution with 3% ethyl acetate in *n*-hexane) of ethyl acetate extracts of the culture broth. Owing to difficulty of the clear separation of these diols from each other, this mixture was treated with 2,2-dimethoxypropane and *p*-TsOH. Pure *trans*-sativenediol and an acetonide of the cis diol were isolated from the reaction mixture, and the latter compound was subsequently hydrolyzed liberating *cis*-sativenediol in pure form (yields: **1**, 20 and 19 mg, and **2**, 6 and 11 mg, respectively, from 10 l. of the culture broth of *C. setariae* and *H. sativum*).

cis-Sativenediol (**1**) [oil; $C_{15}H_{24}O_2$; *m/e* 236 (M^+); $[\alpha]^{25}D$ −119° (*c* 0.94, $CHCl_3$)] has the following partial structures: an isopropyl [NMR ($CDCl_3$) two 3 H doublets at δ 0.89 and 0.95, J = 7 Hz], a tertiary methyl (3 H singlet at δ 1.08), an exocyclic methylene (two 1 H doublets at δ 4.66 and 4.98), and two vicinal hydroxyl groups [ir (CCl_4) 3670 and 3360 cm^{-1}; NMR two 1 H doublets at δ 3.68 and 4.08, J = 6 Hz], which were decoupled to each other in double resonance experiments and shifted downfield (δ 4.72 and 5.05, respectively) upon acetylation (Ac_2O and pyridine) into the diacetate [*m/e* 320 (M^+); two CH_3COO at δ 2.05]. These data are indicative of **1** being a dihydroxy derivative of sativene,[2] a tricyclic sesquiterpene produced by *H. sativum*, although sativene itself was not isolated from our strain of this fungus. This assumption was unequivocally confirmed by subjecting **1** to oxidation ($NaIO_4$ in MeOH–H_2O) followed by acetal formation (EtOH and *p*-TsOH). The product (**4**) ($[\alpha]^{25}D$ −60° (*c* 0.32, $CHCl_3$)) showed the NMR spectrum completely in agreement with that of the diethyl acetal of prehelminthosporal (**3**) reported by de Mayo.[3] The negative optical rotation of **4**, almost the same as the −68° reported,[3] established that **1** has the same

absolute stereochemistry as that of sativene.[2,4] A cis relation between the vicinal glycols was shown from (a) an easy formation of the acetonide **5** [*m/e* 276 (M^+); NMR two singlet methyls of the isopropylidene group at δ 1.28 and 1.46] and (b) the facile cleavage of **1** upon periodate oxidation. The absolute stereochemistry was determined by nuclear overhauser (NOE) experiments; that is, irradiation of **5** at the resonance frequency of the tertiary methyl at δ 1.04 produced an increase of 10% in the one (δ 4.38) of two doublet methines, indicating that both protons should approximate spatially, thus with the conclusion that the cis diol is placed in the exo direction of the bicyclo[2.2.1] system of the molecule.

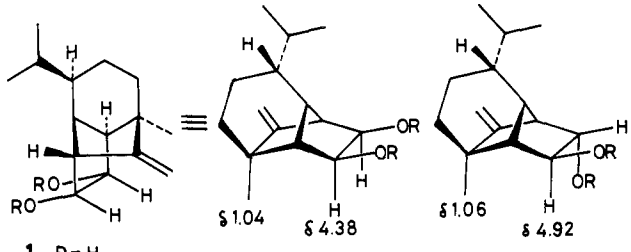
trans-Sativenediol (**2**) [colorless needles; mp 176°; $C_{15}H_{24}O_2$; *m/e* 218 ($M^+ - H_2O$); $[\alpha]^{27}D$ −3.4° (*c* 1.4, $CHCl_3$)] showed the partial structures quite similar to those of the cis diol (**1**), i.e., an isopropyl [NMR ($CDCl_3$) two 3 H doublets at δ 0.95 and 1.05, J = 6.5 Hz], a tertiary methyl (3 H singlet at δ 1.00), an exocyclic methylene (two 1 H singlets at δ 4.75 and 5.05), and two vicinal secondary hydroxyl groups (two 1 H of a slightly splitting broad singlet at δ 3.68 and 4.45, J = <2 Hz), which were decoupled to each other in double resonance experiments and shifted downfield (δ 4.70 and 4.92, respectively) upon acetylation into the diacetate **6** [oil; *m/e* 320 (M^+); two CH_3COO at δ 1.99 and 2.07]. The only difference of **2** from **1** was observed on stereochemical features of the hydroxyl function; that is, their trans relation was shown from (a) a small coupling constant (<2 Hz)[5] between the methine protons on the vicinal hydroxyl-bearing carbons and (b) a severe resistance of **2** against periodate oxidation. Its absolute stereochemistry was determined by applying exciton chirality method[6] to the benzoate derivative of **2** [uv (EtOH) λ_{max} 230 nm (ϵ 23,000)] which showed the positive CD Cotton effect ($[\theta]_{236}$ +15,200), thus with the conclusion that two benzoxyl groups should be directed in clockwise twist. This conclusion was ascertained by NOE experiments; that is, an increase of 12% in the one (δ 4.92) of two methine protons was observed upon irradiation of the diacetate **6** at the resonance frequency of the tertiary methyl at δ 1.06.

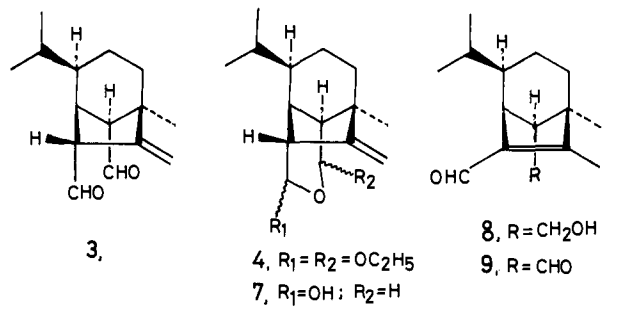
Additionally, three related metabolites, i.e., prehelminthosporol (**7**),[3,7] helminthosporol (**8**),[8] and helminthosporal (**9**),[9] were isolated from the both fungi. Among them, the latter two compounds (**8** and **9**) have been known as growth promoting and inhibitory substances, respectively, for plants. All compounds we have isolated from the fungi and prehelminthosporal (**9**), obtained as an oxidation product of **1**,[10] were subjected to bioassay on rice seedlings. The results are shown in Table I. Quite interestingly, the cis diol promoted markedly the elongation, although the activity is not so strong as that of gibberellic acid, whereas the trans diol was slightly suppressive. Prehelminthosporal (**3**) caused severe damage on the plants, suggesting that **3** is the major toxic principle of these pathogenic fungi. Briggs presented a hypothesis[11] on helminthosporol (**8**) from its structural similarity to gibberellic acid that the true effective structure of **8** in plants might be a prehelminthosporol-type compound with an exocyclic methylene group produced by migration of the double bond of **8**. The present data do not support the hypothesis, because **7** itself showed only the weak activity. That *cis*-sativenediol is active in plants by itself and not by being converted into helminthosporol is reasonably speculated from (a) the stronger activity (more than ten times) of **1** than that of **7** and (b) the fact that none of the possible biogenetic intermediates, **3**, **7**, and **9**, showed appreciable activity. An interesting problem that remains is the determination of the detailed biosynthetic sequence of all metabolites, especially whether the precursor of **3** (or **7**) is **1** or **2**.

Table I. Activities of *cis*-Sativenediol and Related Metabolites on Rice Seedlings (*Oryza sativa* L. cv. Norin 29)[a]

	Concn, μg/ml		
	3	30	300
cis-Sativenediol (1)	177	276	210
trans-Sativenediol (2)	92	85	84
Prehelminthosporal (3)	60	64	10
Prehelminthosporol (7)	108	105	124
Helminthosporol (8)	103	141	237
Helminthosporal (9)	130	104	105
Gibberellic acid (GA_3)	295		
Control, 100%			

[a] Activities were expressed as percentages of promoting or inhibiting elongation of the second leaf sheath, compared to that of control plants (100%), whose mean growth for 9 days incubation was 1.86 cm.





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References and Notes

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