American Mineralogist, Volume 83, pages 1340–1346, 1998

Hartite from Bílina

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ABSTRACT

In the Bílina Mine (Czech Republic), a very chemically pure material corresponding to hartite was found as a product of distillation into the pelosiderite nodule during coalification of a lignite seam in the Miocene or later. The amount of the material available allowed characterizing this natural mineral equivalent of the hydrocarbon (+)-phyllocladane [16α(H)-phyllocladane] thoroughly.

Elementary analysis of hartite from Bílina gave C = 87.45 wt% and H = 12.55 wt%, which corresponds to the formula $C_{20}H_{34}$. The IR spectrum demonstrated the presence of gem-dimethyl groups (doublet $\delta_s CH_3$ at 1369 and 1383 cm^{-1}). Other bands indicated the presence of methyl and methylene groups. NMR studies showed that the hydrocarbon (hartite) molecule contains four CH_3 groups, nine CH_2 groups, four CH groups, and three quaternary carbon atoms. The sample exhibits a well-defined melting point between 71 and 71.5 °C. Measurements of optical rotation gave $[\alpha]_D = +24.2°$ ($CHCl_3$, $c = 0.7$). Lattice parameters from single-crystal study measured at 293(2) K were a = 11.407 (1), b = 20.952 (2), c = 7.4060 (8) Å, α = 93.941 (9)°, β = 100.750 (8)°, and γ = 80.499 (9)°. The crystal system is triclinic with space group *P*l, Z = 4, V = 1713.8 (3) $Å^3$. Densities are D_m = 1.04 g/cm^3 and D_x = 1.064 g/cm^3, respectively. Isotopic composition of C in hartite from Bílina gave $\delta^{13}C_{(PDB)} = -24.4(1)$ ‰, a common value for coal and organic sedimentary material derived from higher plants.

INTRODUCTION

Most of the data characterizing hartite, so far, was obtained from products of lignite extraction using organic solvents and repeated crystallization. Colorless tabular crystals were usually obtained by dissolving lignite, purification, repeated crystallization, and a slow gradual evaporation of the solvent. These crystals were identified as bombiccite, hartite, or simply phyllocladane in numerous previous studies (Pellizzer 1955a, 1955b; Serantoni et al. 1978; Alexander et al. 1987; Vávra 1993).

White, waxy lustrous, coarse crystalline to lamellar aggregates and coatings of hartite were identified in a pelosiderite at the base of an Early Miocene lignite seam in the Bílina Mines of the North Bohemian lignite Basin (Czech Republic). The mineral was also found in the form of whitish coatings and thin crystalline crusts in fractures of fossil coalified and silicified tree trunks in the roof of the lignite seam of the same mine.

Purification using chemical methods as previously required was not needed. Except for morphological data published earlier (see below), this is the first time that physical, chemical, and structural data were simultaneously obtained from genuine natural hartite.

HISTORY OF HARTITE INVESTIGATION

The mineral hartite was originally described by Haidinger (1841) from lignite in a coal seam of Carpathian age (Middle Miocene) at Oberhart near Gloggnitz, Lower Austria. Type material of hartite is kept at the Krahuletz Museum, A-3730 Eggenburg, Krahuletzplatz 1, Lower Austria, in the mineralogical collection of ‘‘Niederösterreichisches Landesmuseum.’’ Hartite was later identified in a woody substance of lignite from Rosenthal near Köflach in Lower Austria by Kenngott (1856) who also gave its density (1.036–1.060 g/cm^3) and hardness (1 on the scale of Mohs). Tiny, well-preserved, triclinic crystals of hartite in lignite from Oberdorf near Voitsberg in Styria (Austria) were described by Rumpf (1869 and 1870) who also provided morphological data and crystal drawings. Machatschki (1924), using goniometric measurements, established the axial ratio $a:b:c$ = 1.8237:1:0.6568 and angles α = 100°26′, β = 93°44′, and γ = 80°34′.

More recently hartite also has been described from Göriach near Turnau in Austria (Sigmund 1918) and from Terni, Montevaso, and Castelnuovo di Valdarno in the Florence area, Italy (Bombicci 1869; Ciusa and Galizzi 1921).

Hofmannite and branchite, described by Boeris (1921), and iosene identified by Soltys (1929), are identical with

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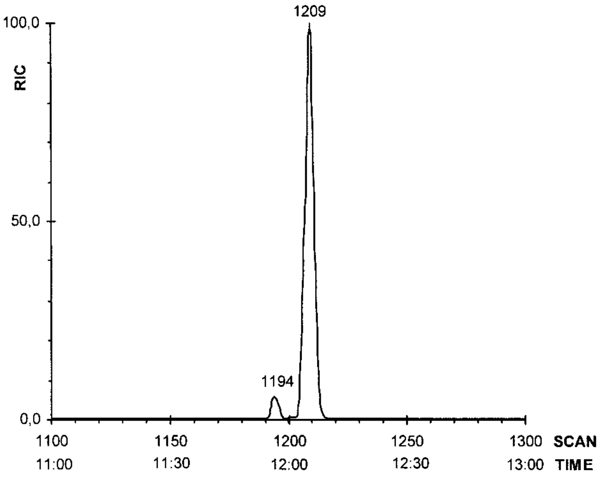

FIGURE 1. Gas chromatogram of original hartite crystals indicating high chemical purity of the material studied. The smaller peak at scan 1194 corresponds to an admixture that is 4.31% of the total weight amount.

hartite. Crystallographic study by the X-ray powder method (Pellizzer, 1955a) and using single-crystals (Pellizzer 1955b) showed that bombiccite is identical to hartite. Briggs (1937) identified iosene as α-dihydrophyllocladane. This identification was confirmed by Vávra (1996) who states that some specimens of lignite may contain compounds close to phyllocladane (isophyllocladene, 16β (H)-phyllocladane, and 16α(H)-phyllocladane) and also products of their diagenesis (dehydroabietane and simonellite). We consider some genus of Taxodiaceae as a possible botanical source for compounds of the phyllocladane series.

Hey (1962), Streibl and Herout (1969), and Vávra (1993) based on published data give the following names as synonyms for hartite: iosene (also josene), bombiccite, hofmannite, branchite, rhetenite, and krantzile (perhaps correctly krantzite). These names thus became redundant (cf. Strunz 1978).

The phyllocladane (tetracyclic diterpane) is a common constituent of resins and some tissues in conifers (Hanson 1968). It was also identified in fossil resins (Grimalt et al. 1988). The compound was extracted from Czech and Slovak (Streibl et al. 1972; Kristín et al. 1976), German (Hollerbach 1980), Italian (Serantoni et al. 1978; Menchi et al. 1995; Corazza et al. 1994; Staccioli et al. 1993), Hungarian (Alexander et al. 1987; Hetenyi and Sajgo 1990; Brukner-Wein and Sajgo 1990), Australian (Noble et al. 1985a), Nigerian (Disnar and Harouna 1994), and Russian lignites (Vorob'eva et al. 1987), and from Chinese coal (Hou et al. 1992; Sheng et al. 1992). This hydrocarbon also occurs in crude oil (Weston et al. 1989; Noble et al. 1986; George 1992; Dzou and Hughes 1993), in liquid fuels (Strachan et al. 1989), and in sediments (Noble et al. 1985b; Grimalt et al. 1990). The content of terpenic hydrocarbons varies widely in different coals due to variations in their origin (Lu and Kaplan 1992).

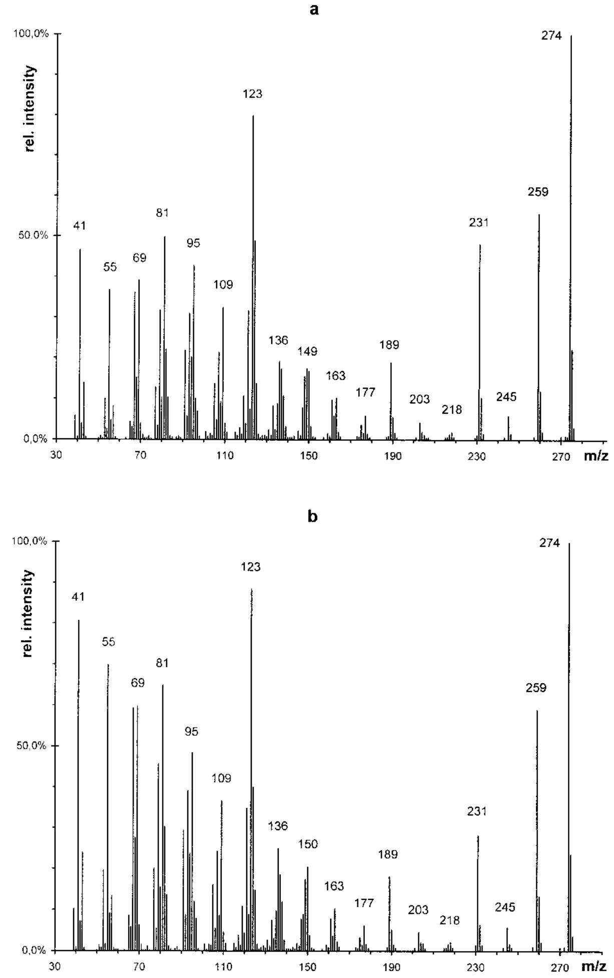

FIGURE 2. Mass spectra of (**a**) the smaller peak at scan 1194 [probably (−)-phyllocladane] and (**b**) the major component, i.e., (+)-phyllocladane.

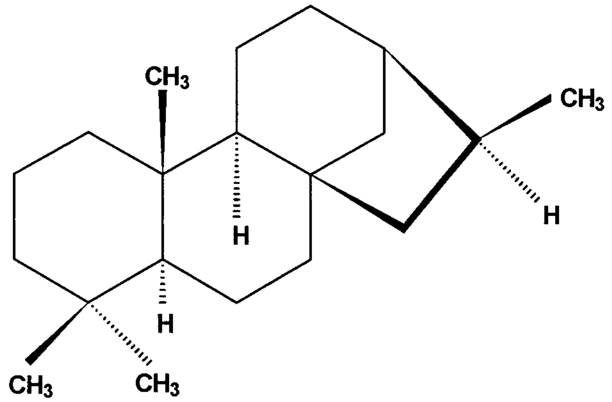

FIGURE 3. Stereochemical structure of (+)-phyllocladane, i.e., the basic unit of hartite. Thick lines are under the plane; dotted lines are below the plane.

TABLE 1. X-ray powder diffraction data of hartite from the pelosiderite nodule, Bílina

hkl	d_{obs}	d_{calc}	I_{rel}
010	20.75	20.71	2.1
020	10.38	10.35	33.7
$1\bar{2}0$	7.02	7.04	4.8
$01\bar{1}$	6.96	6.98	3.4
$11\bar{1}$	6.59	6.59	33.1
$1\bar{1}\bar{1}$	6.11	6.11	18.1
$12\bar{1}$	5.96	5.96	8.4
021	5.85	5.85	1.5
101	5.58	5.64	16.8
200	5.54	5.51	100.0
$1\bar{1}1$	5.38	5.39	9.0
220	5.17	5.19	6.7
040		5.18	
$\bar{2}10$	5.12	5.14	5.8
$13\bar{1}$		5.13	
$03\bar{1}$		5.13	
121	5.06	5.04	3.1
140	4.996	4.976	0.0
$21\bar{1}$	4.896	4.878	2.1
$\bar{2}20$	4.597	4.588	2.0
$\bar{1}31$	4.499	4.510	1.0
$1\bar{4}0$	4.430	4.439	3.3
041	4.134	4.139	7.5
240	4.073	4.084	3.8
$2\bar{1}1$	3.928	3.924	4.4
$24\bar{1}$	3.850	3.849	10.9
$1\bar{4}1$	3.737	3.737	10.4
$2\bar{4}0$	3.524	3.521	6.5
160	3.446	3.441	12.9
$1\bar{4}\bar{2}$	2.870	2.869	8.7

Unit-cell parameters

a, Å	11.34(1)
b, Å	20.99(2)
c, Å	7.43(1)
α, °	94.11(1)
β, °	100.87(2)
γ, °	80.92(1)
V, Å³	1715.1(4)

TABLE 2. Crystallographic data for hartite

mw		274.47
crystal system		triclinic
space group		*P*1 (No.1)
a, Å		11.407(1)
b, Å		20.952(2)
c, Å		7.4060(8)
α, °		93.941(9)
β, °		100.750(8)
γ, °		80.499(9)
V, Å³		1713.8(3)
Z		4
ρ_{calc}, g/cm³		1.064
μ(Mo*K*α), mm⁻¹		0.059
temperature, K		293(2)
crystal size, mm³		0.14 × 0.28 × 0.46
scan limits (θ), °		$0 \leq 24$
data collected:	*h*	−13;12
	k	−23;23
	l	0;8
No. of reflections collected		5369
No. of reflections unique		5369
No. of reflections observed		4093 [$F_o \geq 4\sigma(F_o)$]
standard reflections		3 after every 1 h
variation in standards, %		2
R_F, %*		4.12
R_{wF}, %†		10.47
GooF‡		1.012
Δ/σ(max)		−0.001
Δ(ρ), e/Å³		−0.12; 0.15

* $R_F = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

† $R_{wF} = \{\Sigma[w(F_o^2 - F_c^2)^2]\Sigma[w(F_o^2)^2]\}^{0.5}$. $w = [\sigma^2(F_o^2) + w_1P^2 + w_2P]^{-1}$; $P = [\max(F_o^2) + 2F_c^2]/3$. $w_1(w_2) = 0.0645(0.218)$.

‡ GooF = $[\Sigma(w|F_o|^2 - |F_c|^2)^2/(N_o - N_v)]^{0.5}$.

DESCRIPTION OF SAMPLES AND LOCAL GEOLOGY

In 1992, the organic mineral hartite was found in a crack in a single nodule of pelosiderite at the base of 30 m thick lignite seam. The nodule was discovered during excavations at the bottom of the Bílina open pit mine of the North Bohemian Mines Co. in the North Bohemian lignite Basin. The nodule was found 160 m below the original surface (the coal seam and overlying sediments). The locality lies at the site of the former village Liptice, northwest of the town of Bílina. The lignite seam of Early Miocene age (Holešice Member, Most Formation; Malkovský 1985; Hurník and Pešek 1997) is composed mostly of huminite and is coalified into ortho- to metatypes.

The basal part of the seam often contains large loaf-like and disk-like pelosiderite nodules, which are about 2 m in diameter and maximally 1 m high. The interior of these nodules shows pelosiderite septarian fractures, which are occasionally filled with water.

Septaria cracks in nodules are coated with tiny crystals of yellow to brown-gray siderite. Yellowish crystals of whewellite occur rarely.

Hartite was found in one nodule only being 1.5 m in diameter and about 1 m high. The mineral occurred in a water-bearing fracture in the form of discontinuous white to gray-white waxy lustrous coarse crystalline coatings and cleavable, partly translucent lamellae. Crystals of hartite from Bílina are similar to those reported by Rumpf (1869) from Austria. The polycrystalline, lamellar aggregates reach a maximum thickness of 3 mm and are always fretted and corroded. This material was examined in detail.

The second specimen of hartite was found at the Bílina Mine in 1995. This mineral forms whitish to clear colorless coatings and thin crystalline crusts on fractures in coalified and silicified fossil tree trunks, particularly in their root systems. Roots were found to be completely sideritized and limonitized. The mineral in fractures of silicified tree trunks forms coatings, blobs, or crystalline aggregates in quartz cavities. Tree trunks are believed to belong to the genus *Taxodium*. They occur in sandy-clayey sediments in the roof of the coal seam about 60 m from the original surface at the former village Jenišův Újezd, west of Bílina (Bouška and Dvořák 1997).

The samples of hartite studied are deposited in the mineral collection of the Geological Department of the Bílina Mines, North Bohemian Mines Co., Chomutov, in the mineral collection of the National Museum at Prague (specimen numbers P1N 84597 and P1N 84598), and in the Mineral Museum of the Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Prague (specimen no. 21287).

TABLE 3. Atomic coordinates and equivalent isotropic displacement parameters for hartite

	x	*y*	*z*	U_{eq}
C(011)	0.4901(3)	0.0532(2)	0.2159(5)	61(1)
C(021)	0.4947(5)	0.0192(2)	0.3944(7)	86(1)
C(031)	0.4165(5)	0.0560(2)	0.5235(6)	86(1)
C(041)	0.4500(4)	0.1232(2)	0.5745(5)	71(1)
C(051)	0.4412(3)	0.1641(2)	0.4057(4)	50(1)
C(061)	0.5040(3)	0.2245(2)	0.4698(4)	51(1)
C(071)	0.4461(4)	0.2699(2)	0.6122(5)	71(1)
C(081)	0.5068(4)	0.3291(2)	0.6693(6)	82(1)
C(091)	0.5349(4)	0.3609(2)	0.5063(6)	73(1)
C(101)	0.6133(3)	0.3112(2)	0.4044(6)	71(1)
C(111)	0.5263(3)	0.2655(2)	0.3155(5)	51(1)
C(121)	0.5792(3)	0.2218(2)	0.1673(5)	59(1)
C(131)	0.5147(3)	0.1642(2)	0.1042(5)	54(1)
C(141)	0.5141(3)	0.1237(2)	0.2677(5)	48(1)
C(151)	0.5926(4)	0.0170(2)	0.1208(7)	89(1)
C(161)	0.3706(4)	0.0486(2)	0.0852(6)	74(1)
C(171)	0.3067(3)	0.1830(2)	0.3242(5)	58(1)
C(181)	0.4263(3)	0.3791(2)	0.3523(6)	68(1)
C(191)	0.3113(4)	0.4146(2)	0.4130(7)	88(1)
C(201)	0.4137(3)	0.3146(2)	0.2400(5)	57(1)
C(012)	−0.0831(3)	0.1120(2)	0.7996(6)	67(1)
C(022)	−0.1049(4)	0.0916(2)	0.5947(6)	78(1)
C(032)	−0.0193(4)	0.1135(2)	0.4880(6)	79(1)
C(042)	−0.0249(4)	0.1870(2)	0.5042(5)	65(1)
C(052)	−0.0008(3)	0.2137(2)	0.7041(4)	49(1)
C(062)	−0.0413(3)	0.2885(2)	0.7020(5)	56(1)
C(072)	−0.0257(4)	0.3247(2)	0.5909(5)	71(1)
C(082)	−0.0161(5)	0.3982(2)	0.5937(7)	92(2)
C(092)	−0.0324(4)	0.4259(2)	0.7849(7)	90(2)
C(102)	−0.1196(4)	0.3917(2)	0.8545(7)	90(2)
C(112)	−0.0477(3)	0.3237(2)	0.8925(5)	64(1)
C(122)	−0.1091(4)	0.2873(2)	1.0089(6)	79(1)
C(132)	−0.0664(4)	0.2156(2)	1.0116(5)	75(1)
C(142)	−0.0819(3)	0.1854(2)	0.8150(5)	58(1)
C(152)	−0.1892(4)	0.0966(3)	0.8811(7)	99(2)
C(162)	0.0321(4)	0.0711(2)	0.9007(7)	90(2)
C(172)	0.1349(3)	0.1957(2)	0.7777(5)	59(1)
C(182)	0.0802(4)	0.4111(2)	0.9331(6)	76(1)
C(192)	0.1984(4)	0.4220(2)	0.8847(7)	85(1)
C(202)	0.0759(3)	0.3418(2)	0.9877(5)	64(1)
C(013)	−0.0089(3)	0.6160(2)	0.4404(5)	55(1)
C(023)	−0.0123(4)	0.5798(2)	0.2525(6)	72(1)
C(033)	0.0706(5)	0.6003(2)	0.1379(6)	82(1)
C(043)	0.0415(4)	0.6729(2)	0.1065(6)	75(1)
C(053)	0.0479(3)	0.7147(2)	0.2869(4)	48(1)
C(063)	−0.0124(3)	0.7853(2)	0.2382(5)	52(1)
C(073)	0.0503(5)	0.8178(2)	0.1109(6)	78(1)
C(083)	−0.0073(5)	0.8881(2)	0.0707(7)	91(1)
C(093)	−0.0380(4)	0.9273(2)	0.2439(6)	77(1)
C(103)	−0.1202(4)	0.8931(2)	0.3265(7)	77(1)
C(113)	−0.0357(3)	0.8325(2)	0.4035(5)	53(1)
C(123)	−0.0946(4)	0.8005(2)	0.5347(6)	67(1)
C(133)	−0.0334(4)	0.7326(2)	0.5837(5)	62(1)
C(143)	−0.0300(3)	0.6897(2)	0.4089(5)	47(1)
C(153)	−0.1133(4)	0.5992(2)	0.5215(7)	81(1)
C(163)	0.1075(4)	0.5916(2)	0.5701(7)	81(1)
C(173)	0.1812(3)	0.7103(2)	0.3781(6)	67(1)
C(183)	0.0671(4)	0.9280(2)	0.4019(7)	77(1)
C(193)	0.1844(5)	0.9425(3)	0.3603(9)	107(2)
C(203)	0.0766(3)	0.8627(2)	0.4948(5)	63(1)
C(014)	0.5269(4)	0.8153(2)	−0.2583(5)	64(1)
C(024)	0.4258(4)	0.8576(2)	−0.1764(6)	72(1)
C(034)	0.4163(5)	0.8403(2)	0.0154(7)	83(1)
C(044)	0.4006(4)	0.7692(2)	0.0164(6)	74(1)
C(054)	0.5024(3)	0.7216(2)	−0.0514(5)	50(1)
C(064)	0.4623(3)	0.6533(2)	−0.0824(5)	54(1)
C(074)	0.4434(4)	0.6240(2)	0.0924(6)	74(1)
C(084)	0.4062(4)	0.5566(2)	0.0592(8)	91(2)
C(094)	0.4801(4)	0.5127(2)	−0.0645(7)	79(1)
C(104)	0.4675(4)	0.5454(2)	−0.2440(7)	79(1)
C(114)	0.5390(3)	0.6019(2)	−0.1891(5)	54(1)
C(124)	0.5649(4)	0.6299(2)	−0.3599(5)	72(1)
C(134)	0.6084(4)	0.6950(2)	−0.3236(5)	66(1)
C(144)	0.5156(3)	0.7433(2)	−0.2425(5)	53(1)
C(154)	0.6507(4)	0.8338(2)	−0.1652(7)	87(1)
C(164)	0.5082(5)	0.8308(2)	−0.4636(6)	97(2)
C(174)	0.6180(4)	0.7213(2)	0.0919(5)	66(1)
C(184)	0.6167(3)	0.5049(2)	−0.0008(6)	69(1)
C(194)	0.6655(5)	0.4897(2)	0.2008(7)	96(2)
C(204)	0.6522(3)	0.5666(2)	−0.0649(5)	61(1)

Note: xyz are in Å^2 × 1000. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

CHEMICAL AND PHYSICAL PROPERTIES OF HARTITE FROM BÍLINA AND ITS MOLECULAR STRUCTURE

Waxy, white crystals of hartite from Bílina burn completely without any incombustible residue. The mineral has revealed a well-defined melting point between 71 and 71.5 °C measured using a Kofler microscope heating stage (Type PHMK, VEB Analytik Dresden, Germany). This indicates the high chemical purity of the material, which was also demonstrated by gas chromatography (see below). Melting points of hartite so far published are as follows: 72° for pure material (Kenngott 1856); for extracted α-phyllocladane 73.5 °C, 74–74.5 °C, 73 °C (Beilstein 1930, 1937, 1938); 73–74 °C (Briggs et al. 1965); 73.4 °C (Streibl and Herout 1969). The mineral melts to give a clear colorless and odorless liquid. Density measured on a fragment of cleavable crystal gave D_m = 1.04 g/cm^3, density calculated from single-crystal data is D_x = 1.064 g/cm^3.

Hartite crystals from Bílina are insoluble in water, which probably helped their preservation in the aqueous environment of the fractures in the nodule. They are soluble in non-polar to medium polar solvents (e.g., petroleum ether, hexane, benzene, and $CHCl_3$). The mineral belongs to solubility group I (inert substances). Organic elementary analysis on material from the pelosiderite nodule from Bílina (C = 87.45 wt%, H = 12.55 wt%) give the formula $C_{20}H_{34}$. The composition analyzed is close to the theoretical values (C = 87.51 wt%, H = 12.49 wt%) and consistent with previous analytical studies of hartite by Kenngott (1856), Rumpf (1870), and Hatler (1885).

Mass spectrometry (MS) studies at high resolution using JEOL MS D300 proved that the material is a hydrocarbon with molecular weight equal to 274 and elementary composition $C_{20}H_{34}$. Combined GC-MS analysis (GC Varian 3400, capillary column DB5, column temperature program 1.0 min at 80 °C, then rate 15 °C/min to 280 °C, injector temperature 250 °C; detection MS Incos 50, Finnigan) showed the sample to be of high purity containing only about 4 wt% of admixture (Fig. 1). Fragmentation pattern of the admixture mass spectrum showed the same lines as the major compound differing only in the intensities (Figs. 2a and 2b), which indicates that the admixed material is very probably a stereoisomer (−)-phyllocladane [16β(H)-phyllocladane], in agreement with the anal-

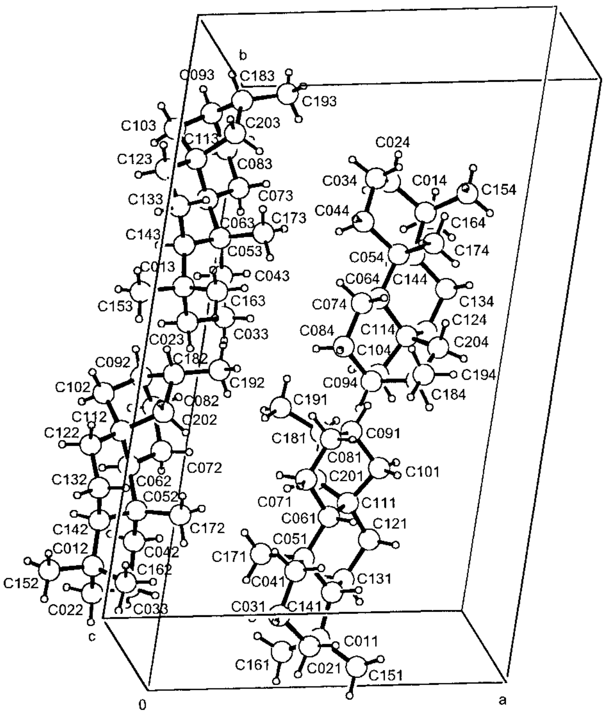

FIGURE 4. View of the unit cell of hartite with atom labeling. Note four symmetrically independent molecules similar to each other.

yses published previously for phyllocladane from lignite extracts (Alexander et al. 1987; Vávra 1996).

The infrared spectrum was collected using Perkin-Elmer, Model 684. Material was measured as a thin layer on Irtran acquired after evaporation of its CH_3Cl solution. The spectrum corresponds to a hydrocarbon containing gem-dimethyl groups [doublet $\delta_s(CH_3)$ at 1369 and 1383 cm^{-1}]. Other bands indicate only the presence of methyl [$\delta_{as}(CH_3)$ at 1477 cm^{-1}, $\nu_s(CH_3)$ at 2864 cm^{-1} and $\nu_{as}(CH_3)$ at 2960 cm^{-1}] and methylene [scissor $\delta(CH_2)$ at 1454 cm^{-1}, $\nu_s(CH_2)$ at 2846 cm^{-1} and $\nu_{as}(CH_2)$ at 2922 cm^{-1}].

Measurements of optical rotation (ETL-NPL Automatic Polarimeter, Type 143A, Bendix Ericsson) gave $[\alpha]_D = +24.2°$ ($CHCl_3$, $c = 0.7$). This value is similar to data on optical rotation for (+)-phyllocladane extracts from lignite published by Beilstein (1964) [+22.98 ($CHCl_3$, $c = 1.5$) (1937), +23.3° (A, $c = 1$) (1937), and +23.9° ($CHCl_3$, $c = 5$) (1938)].

Nuclear magnetic resonance spectroscopy of (^1H and ^{13}C) at 400 MHz using spectrometer Varian VXR-400 and sample dissolved in $CHCl_3$ explicitly shows that the hartite contains four CH_3 groups, nine CH_2 groups, four CH groups, and three quaternary carbon atoms. The structure of hartite from Bílina is identical with the earlier described hydrocarbon (+)-phyllocladane or also 5α, 9α, 10β-kaurane, often called (+)-α-dihydrophyllocladene or 16α(H)-phyllocladane or simply α-phyllocladane (Fig. 3).

TABLE 4. Selected bond lengths (in angstroms) for hartite for the four molecules

Species	1	2	3	4
C(01)-C(02)	1.533(6)	1.534(6)	1.536(6)	1.527(5)
C(01)-C(14)	1.556(5)	1.537(6)	1.549(5)	1.550(5)
C(01)-C(15)	1.542(6)	1.536(6)	1.529(6)	1.550(6)
C(01)-C(16)	1.531(5)	1.539(6)	1.522(5)	1.544(6)
C(02)-C(03)	1.514(7)	1.508(6)	1.511(6)	1.517(6)
C(03)-C(04)	1.525(6)	1.527(6)	1.526(6)	1.530(6)
C(04)-C(05)	1.543(5)	1.538(5)	1.543(5)	1.538(5)
C(05)-C(17)	1.537(5)	1.535(5)	1.534(5)	1.530(5)
C(05)-C(14)	1.555(5)	1.553(5)	1.549(5)	1.556(5)
C(05)-C(06)	1.559(5)	1.560(5)	1.562(5)	1.563(5)
C(06)-C(07)	1.539(5)	1.533(6)	1.537(5)	1.534(6)
C(06)-C(01)	1.557(5)	1.554(5)	1.554(5)	1.543(5)
C(07)-C(08)	1.516(6)	1.534(6)	1.535(6)	1.532(6)
C(08)-C(09)	1.526(7)	1.526(7)	1.540(7)	1.520(6)
C(09)-C(10)	1.513(6)	1.499(7)	1.505(6)	1.509(7)
C(09)-C(18)	1.536(6)	1.530(6)	1.513(6)	1.527(6)
C(10)-C(11)	1.522(5)	1.539(6)	1.536(5)	1.537(5)
C(11)-C(12)	1.527(5)	1.518(6)	1.524(5)	1.527(6)
C(11)-C(20)	1.548(5)	1.549(5)	1.545(5)	1.548(5)
C(12)-C(13)	1.517(5)	1.502(7)	1.513(5)	1.516(6)
C(13)-C(14)	1.527(5)	1.538(5)	1.528(5)	1.519(5)
C(18)-C(19)	1.526(6)	1.513(6)	1.510(6)	1.529(7)
C(18)-C(20)	1.550(5)	1.544(6)	1.552(6)	1.546(6)

X-RAY DIFFRACTION STUDY AND CRYSTAL STRUCTURE OF HARTITE

Two samples of hartite from Bílina were used for X-ray powder diffraction study. One was the whitish remarkably cleavable, lamellar to scaly coarse crystalline aggregate from the inner wall of the pelosiderite nodule. The other sample was white to yellow-gray thin crystalline crusts taken from fractures in silicified fossil wood. The well-developed cleavage required preparation of several specimens to find one with a small amount of preferred orientation. Both samples yielded almost identical powder data. The sample from the pelosiderite nodule provided a larger amount of material and was therefore selected for further studies.

Powder specimens (in a flat specimen holder) were examined using a horizontal powder diffractometer HZG4/TuR M62 (Freiberger Präzisionsmechanik) with Bragg-Brentano (θ/2θ) configuration using nickel-filtered Cu*K* radiation and a gas proportional counter. The detection circle of the goniometer had $r = 250$ mm. Step scanning was employed with step size 0.02 °2θ and exposure of 15 s per step. Lanthanum hexaboride was used as an external standard.

The data acquired were processed by the powder diffraction software ZDS (Version 6.01, Ondruš 1995). Line profiles were fitted using the Pearson VII function, and the powder diffraction pattern was indexed with the aid of a theoretical powder pattern calculated by the programs Lazy Pulverix (Yvon et al. 1977) and DBWS3 (Wiles et al. 1990) from the structure data of Serantoni et al. (1978) and ours (see later). The unit-cell dimensions were refined using the program ZDS. Powder data for hartite from Bílina are summarized in Table 1.

The studied phase was unambiguously identified as hartite, the mineral equivalent of (+)-phyllocladane,

$C_{20}H_{34}$ (JCPDS card 30-1702 and/or JCPDS card 30-2002). The lattice parameters obtained from powder data differ slightly from single-crystal data below and in Serantoni et al. (1978). This difference apparently reflects a very limited number of observed diffraction maxima in hartite powder patterns, which are moreover located in low diffraction angle region.

For the single-crystal X-ray measurement, a fragment of hartite of irregular shape was mounted on a glass fiber and measured using a four-circle diffractometer CAD4-MACHIII (Enraf-Nonius) with Mo$K\alpha$ radiation. The crystallographic data are summarized in Table 2. The crystal structure was established by direct methods (SHELXS86, Sheldrick 1990) and refined by a full matrix least squares procedure based on F^2 (SHELXL93, Sheldrick 1993). Hydrogen atoms were placed in geometrical position and fixed during refinement. The final difference map provided no peaks of chemical significance. Scattering factors were those employed in the SHELX programs. The final atomic coordinates are given in Table 3, with atom numbering shown in Figure 4.

The conformation and the intramolecular distances of four symmetrically independent molecules are similar to each other with regard to standard deviations (Table 4). All structural parameters are more or less close to those given by Serantoni et al. (1978) for ‘‘bombiccite’’ extracted from lignite of Castelnuovo di Valdarno and purified by repeated crystallization using benzene as a solvent. We obtained considerably lower *R*-factors on natural material compared to a study of extract by Serantoni et al. (1978).

ISOTOPIC COMPOSITION OF CARBON

Hartite from the pelosiderite nodule from Bílina open pit mine was studied in the Isotopic Laboratory of the Czech Geological Survey at Prague. Two different methods were applied: (1) oxidation in O and inert gas (He) stream at 1050 °C followed by chromatographic separation of CO_2 and on-line measurement by mass spectrometer (Conflo model), and (2) oxidation in oxygen stream at 950 °C and separation of CO_2 through chilling and on-line measurement in the same instrument. Both procedures gave the same results (within measuring error) corresponding to $\delta^{13}C_{(PDB)} = -24.4 \pm 0.1‰$. The isotopic composition is typical of coal and sedimentary organic material of plant origin (Hoefs 1973).

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Manuscript received November 5, 1997
Manuscript accepted May 28, 1998
Paper handled by Anastasia Chopelas