

THE CRYSTAL STRUCTURE OF FICHELITE, A NATURALLY OCCURRING HYDROCARBON

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ABSTRACT

Fichtelite, $C_{19}H_{34}$, is a saturated hydrocarbon mineral that is monoclinic, space group $P2_1$, with a 10.706(4), b 7.458(2), c 10.824(7) Å, β 105.85(3)°, V 831.4(8) Å³, $Z = 2$. Its structure was determined by direct methods using 1105 observed reflections [$F \geq 3\sigma_F$], with a full-matrix least-squares refinement, producing an R index of 4.6%. The fichtelite molecule contains three nonlinearly fused six-membered carbon rings with an angular methyl, a methyl and an isopropyl group coordinated to the rings in the structure.

Keywords: fichtelite, hydrocarbon, crystal structure, phenanthrene.

SOMMAIRE

La fichtelite, $C_{19}H_{34}$, est un hydrocarbure naturel monoclinique, groupe spatial $P2_1$, avec a 10.706(4), b 7.458(2), c 10.824(7) Å, β 105.85(3)°, V 831.4(8) Å³, $Z = 2$. Sa structure a été déterminée en utilisant 1105 réflexions observées [$F \geq 3\sigma_F$], jusqu'à un résidu R de 4.6% obtenu par méthode de moindres carrés. La molécule de la fichtelite contient trois anneaux de six atomes de carbone chacun, rattachés de façon non linéaire, avec des groupes méthyl, méthyl angulaire et isopropyle coordonnés aux anneaux.

Mots-clés: fichtelite, hydrocarbure, structure cristalline, phénanthrène.

INTRODUCTION

Fichtelite ($C_{19}H_{34}$) was originally discovered in fossilized pine trunks taken from peat beds in the Fichtelgebirge, located in southern Germany (Bromeis 1841); it was subsequently described by Strunz (1962). Acquisition of well-crystallized fichtelite from Sobeslav, Czech Republic, provided the opportunity to solve its crystal structure.

Simonellite and phylloretin (or retene; Simonsen & Barton 1952) are hydrocarbon compounds related to fichtelite. Simonellite is found in lignite beds in Italy ($C_{19}H_{24}$; Foresti & Riva di Sansaverino 1969), and fichtelite, along with phylloretin ($C_{18}H_{18}$; Strunz 1970), occurs in peat beds in the wood of dead conifers. Fichtelite is present as white or yellowish crystals on compact pieces of wood, between annual rings, in cracks and crevices, or along oleoresin ducts (Sterling & Bogert 1939); the material also may be disseminated in the wood, and extraction can yield fichtelite as the major component (Hoering 1967).

The apparent origin of fichtelite from the resin acids (*i.e.*, abietic acid) of living pine trees is supported by its occurrence with retene (a product of dehydrogenation of the resin acids; Burgstahler & Marx 1964). Rosin, the nonvolatile component of

oleoresin, is a mixture of C_{20} , fused-ring monocarboxylic acids in various stages of isomerization; it has the general formula $C_{19}H_{29}COOH$, and is dominated by levopimaric and abietic acids, but also contains other related diterpene acids: neoabietic, d-pimaric, 7-iso-d-pimaric and dehydroabietic acids (Fieser & Fieser 1949). Abietic acid is a main constituent in rosin (although a minor constituent in oleoresin), as well as being one of the important resin acids in living conifers. It is susceptible to numerous chemical transformations, and is sensitive to heat, acid isomerization and autoxidation (Fieser & Fieser 1949). Volatile oils evaporate with progressing age of a deceased plant, and the acidic components are left behind to harden and change through isomerization and processes of oxidation. The process of forming a fossil resin occurs over a timescale of months to thousands of years, to produce different fossil products of the resins (Weaver 1978).

In the diagenesis of fossil wood, varying chemical environments result in different fossil-resin products from resin-acid precursors. A highly reducing environment leads to saturation and decarboxylation of abietic acid to produce fichtelite; sulfur and a dehydrogenating environment alter fichtelite to phylloretin. With increasing age, the extent of decarboxylation

increases, leading to higher concentrations of fossil resins in decaying wood. The association of fichtelite with phylloretin, and its occurrence along oleoresin ducts in the wood, support its origin from abietic-type resin acids. Structural similarity of fichtelite to the terpenes would further support this origin.

Fichtelite has been prepared through a number of synthetic processes: the cyclization of trienols, reduction of abietic acids, decarboxylation of dihydroacids or catalytic dehydrogenation of diene mixtures (Jensen & Johnson 1967, Johnson *et al.* 1968, Taber & Saleh 1980, Burgstahler & Marx 1969).

EXPERIMENTAL.

Sample

The sample, obtained from Forrest Cureton, consists of a piece of compacted, dried-out pine wood with crystals covering an area approximately 5×1 cm. The soft crystals, ranging from 0.5 to 3.0 mm across,

are clear and colorless, with a tabular habit on {001} and showing elongation along [010]. Using powdered crystals in a capillary tube, a range in melting point of $44.2 - 45.0^\circ\text{C}$ was obtained, which compares well with a previously recorded value of $44.8 - 45.1^\circ\text{C}$ (Johnson *et al.* 1968).

Data collection

The powder pattern was recorded using a 114.6-mm Debye-Scherrer camera with iron-filtered $\text{CoK}\alpha$ X-radiation ($\lambda = 1.7902 \text{ \AA}$). No shrinkage or absorption corrections were made, as no back reflections were observed, and α_1 and α_2 could not be resolved. The refined unit-cell values (Table 1) differ from those of Strunz (1962). The current unit-cell is related to the earlier cell by the transformation $(\bar{1}00/010/101)$.

A single crystal ($0.4 \times 0.35 \times 0.1$ mm) was studied on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated $\text{MoK}\alpha$ X-radiation. The unit-cell dimensions were determined by a least-

TABLE 1. POWDER PATTERN FOR FICHELITE

$1/I_0^\circ$	d(obs)	d(calc)	hkl
10	10.533	10.451	001
3	8.635	8.544	101
1	6.585	6.546	101
90	6.100	6.071	011
		6.048	110
20	5.644	5.618	111
100	5.206	5.202	201
		5.168	200
<1	4.941	4.920	111
90	4.292	4.290	112
1	4.140	4.217	201
5	3.710	3.707	212
<1	3.513	3.514	021
		3.507	120
1	3.428	3.417	121
5	3.245	3.240	121
		3.239	113
<1	3.131	3.156	013
		3.128	310
10	3.029	3.030	213
		3.024	220
<1	2.944	2.997	212
		2.848	303
2	2.588	2.588	123
		2.584	400
3	2.460	2.465	014
		2.460	222
3	2.419	2.418	031
		2.417	130
<1	2.280	2.288	314
		2.280	413
1	2.238	2.240	230
2	2.194	2.190	124
2	2.150	2.160	105
		2.148	232
<1	1.966		

*Intensity values were determined visually. Refined cell dimensions are $10.706(4)$, b $7.458(2)$, c $10.824(7)$ \AA and β $105.85(3)^\circ$

TABLE 2. COORDINATES OF C AND H ATOMS IN FICHELITE

Atom	x	y	z	U(iso)
C1	0.2185(8)	0.440(2)	0.6233(8)	0.071(4)
C2	0.2271(8)	0.347(2)	0.7502(8)	0.075(4)
C3	0.3596(8)	0.376(2)	0.8411(8)	0.076(4)
C4	0.3942(7)	0.573(2)	0.8651(7)	0.061(3)
C5	0.3743(6)	0.671(2)	0.7354(6)	0.059(3)
C6	0.4093(8)	0.870(2)	0.7514(7)	0.070(4)
C7	0.4189(7)	0.953(2)	0.6256(7)	0.066(3)
C8	0.2959(6)	0.919(2)	0.5177(6)	0.056(3)
C9	0.2595(6)	0.719(2)	0.5046(6)	0.051(2)
C10	0.2426(6)	0.645(2)	0.6348(6)	0.056(3)
C11	0.1423(8)	0.697(2)	0.3925(8)	0.075(4)
C12	0.1654(8)	0.766(2)	0.2688(7)	0.070(3)
C13	0.1909(6)	0.969(2)	0.2780(6)	0.059(3)
C14	0.3122(7)	-0.005(2)	0.3920(7)	0.061(3)
C15	0.2084(7)	0.038(2)	0.1551(7)	0.072(3)
C16	0.212(1)	0.262(2)	0.172(1)	0.102(5)
C17	0.099(1)	0.016(2)	0.042(2)	0.094(5)
C18	0.3215(8)	0.657(2)	0.9575(8)	0.079(4)
C19	0.1292(7)	0.732(2)	0.6699(9)	0.068(4)
H1	0.269(6)	0.40(1)	0.582(6)	0.08(3)
H2	0.881(5)	-0.080(7)	0.439(4)	0.04(2)
H3	0.797(5)	-0.29(1)	0.268(5)	0.08(2)
H4	0.135(5)	0.416(8)	0.784(5)	0.07(2)
H5	0.574(5)	-0.165(8)	0.200(5)	0.06(2)
H6	0.653(5)	-0.213(9)	0.074(6)	0.08(2)
H7	0.506(5)	1.072(7)	0.106(4)	0.04(2)
H8	0.446(4)	0.615(7)	0.681(4)	0.04(1)
H9	0.486(6)	0.872(9)	0.800(6)	0.07(2)
H10	0.662(5)	0.438(9)	0.205(6)	0.07(2)
H11	0.501(8)	0.39(1)	0.400(7)	0.15(4)
H12	0.522(9)	0.55(1)	0.375(8)	0.16(4)
H13	0.772(4)	0.480(6)	0.460(4)	0.02(1)
H14	0.346(5)	0.613(8)	0.478(5)	0.07(2)
H15	0.969(6)	0.27(1)	0.596(6)	0.12(3)
H16	0.126(4)	0.603(6)	0.375(4)	0.01(1)
H17	0.266(7)	0.68(1)	0.254(6)	0.12(2)
H18	0.894(4)	0.241(7)	0.804(4)	0.02(1)
H19	0.892(4)	0.508(7)	0.704(4)	0.04(1)
H20	0.347(7)	0.11(1)	0.386(7)	0.12(3)
H21	0.392(7)	0.89(1)	0.352(7)	0.13(3)
H22	0.694(5)	0.502(8)	0.857(4)	0.06(2)
H23	0.095(5)	0.929(6)	0.028(5)	0.01(2)
H24	0.144(7)	0.09(1)	0.967(7)	0.14(3)
H25	-0.015(8)	0.04(1)	0.045(6)	0.12(3)
H26	0.228(4)	0.30(5)	0.109(4)	0.03(2)
H27	0.263(5)	0.336(9)	0.226(5)	0.05(2)
H28	0.202(7)	0.62(1)	0.922(7)	0.16(3)
H29	0.334(6)	0.81(1)	0.984(6)	0.09(2)
H30	0.337(5)	0.623(8)	0.026(5)	0.04(2)
H31	0.103(5)	0.689(9)	0.747(5)	0.07(2)
H32	0.048(6)	0.71(1)	0.617(5)	0.08(2)
H33	0.131(7)	0.85(1)	0.695(7)	0.10(3)

TABLE 3. CARBON ATOM: ANISOTROPIC DISPLACEMENT PARAMETERS* ($\times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	84(6)	52(5)	-11(5)	71(6)	14(5)	-4(4)
C2	79(6)	55(6)	85(6)	-7(5)	10(5)	15(4)
C3	93(6)	65(6)	73(6)	15(5)	27(5)	14(5)
C4	56(5)	60(5)	63(5)	7(4)	9(5)	-2(4)
C5	55(4)	65(5)	57(4)	7(4)	15(3)	-3(4)
C6	69(6)	61(6)	70(6)	-20(5)	1(5)	-8(4)
C7	59(5)	64(5)	70(5)	-19(4)	11(4)	-4(4)
C8	53(4)	54(5)	61(5)	-4(4)	18(4)	-6(4)
C9	53(4)	44(4)	55(4)	-3(3)	10(3)	-6(3)
C10	55(4)	40(4)	66(4)	-3(3)	7(3)	3(4)
C11	103(7)	37(5)	73(6)	-23(5)	1(5)	-4(4)
C12	84(6)	61(6)	56(5)	-9(5)	2(4)	-2(4)
C13	51(4)	62(5)	64(5)	4(4)	17(4)	-3(4)
C14	58(5)	65(6)	61(5)	-8(4)	17(4)	0(4)
C15	57(5)	100(7)	57(5)	3(5)	15(4)	14(5)
C16	150(9)	74(6)	72(7)	-43(7)	10(6)	28(6)
C17	117(9)	64(8)	95(7)	13(7)	21(6)	15(6)
C18	99(7)	85(7)	58(6)	10(6)	29(5)	7(5)
C19	46(5)	85(7)	78(5)	4(5)	24(4)	8(5)

* The form of the displacement factor is $\exp[-2\pi^2(U_{11}h^2a^2 +$

$$U_{22}k^2b^2 + U_{33}l^2c^2 + 2U_{12}hka^2b + 2U_{13}hla^2c + 2U_{23}kbl^2c^2].$$

squares fit of 25 automatically centered reflections in the 2θ scan range 6.72 – 20.28° : a $10.706(4)$, b $7.458(2)$, c $10.824(7)$ Å, β $105.85(3)^\circ$. The cell content is $2[C_{19}H_{34}]$ with a cell volume (V) of $831.4(7)$ Å³ and a calculated density of 0.631 g/cm³. Intensities of three reflections were monitored at one-hour intervals and showed a variation of less than 2%. A total of 2351 reflections was collected ($2^\circ < 2\theta < 44^\circ$) with index ranges $-11 \leq h \leq 11$, $0 \leq k \leq 7$, and $-11 \leq l \leq 11$. The data were then corrected for Lorentz, polarization and background effects, and reduced to structure factors: of the 1118 unique reflections measured, 1105 were classed as observed [$F \geq 3\sigma_F$].

TABLE 4. BOND LENGTHS (Å) FOR THE FICHELITE MOLECULE

C1 – C2	1.52(1)	C1 – H1	0.85(7)
C2 – C3	1.51(1)	C2 – H3	1.06(8)
C3 – C4	1.52(2)	C2 – H4	1.25(6)
C4 – C5	1.55(1)	C3 – H5	0.98(6)
C4 – C18	1.56(2)	C3 – H6	1.17(7)
C5 – C6	1.53(2)	C4 – H7	1.03(5)
C5 – C10	1.540(8)	C5 – H8	1.17(5)
C6 – C7	1.52(1)	C5 – H9	0.85(5)
C7 – C8	1.524(9)	C6 – H10	1.13(7)
C8 – C9	1.54(2)	C7 – H11	1.1(1)
C8 – C14	1.53(4)	C7 – H12	0.96(1)
C9 – C10	1.57(1)	C8 – H13	0.94(4)
C9 – C11	1.498(9)	C9 – H14	1.31(5)
C10 – C19	1.51(1)	C11 – H15	1.35(7)
C11 – C12	1.52(2)	C11 – H16	0.74(5)
C12 – C13	1.54(2)	C12 – H17	1.31(8)
C13 – C14	1.541(9)	C12 – H18	0.89(4)
C13 – C15	1.55(1)	C13 – H19	1.00(5)
C15 – C16	1.53(2)	C14 – H20	0.94(8)
C15 – C17	1.48(1)	C14 – H21	1.30(8)
		C15 – H22	1.17(6)
		C16 – H26	0.8(2)
		C16 – H27	0.89(6)
		C17 – H23	0.67(5)
		C17 – H24	1.19(8)
		C17 – H25	1.25(9)
		C18 – H28	1.27(8)
		C18 – H29	1.17(8)
		C18 – H30	0.77(5)
		C19 – H31	1.00(6)
		C19 – H32	0.92(5)
		C19 – H33	0.91(8)

Structure determination and refinement

Crystallographic calculations were done using the Xtal 3.0 software (Hall & Stewart 1990). Full-matrix least-squares refinement converged to an R index of 4.6% for 19 atoms of carbon and 33 of hydrogen with isotropic displacement factors for the hydrogen atoms and anisotropic factors for the carbon atoms. Atomic coordinates and isotropic atomic displacement factors are listed in Table 2, anisotropic atomic displacement factors in Table 3, and bond lengths in Table 4. Bond angles and structure-factor tables are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION

The fundamental molecule in fichtelite (Fig. 1) has a perhydrophenanthrene structure: there are three non-linearly fused, six-membered, saturated carbon rings in chair conformation, with an axial methyl group, an angular methyl group and an isopropyl group attached to the carbon rings. Figure 2 shows the structural similarity of fichtelite to abietic acid, in that both possess a similar phenanthrene structure, along with the attached angular methyl and isopropyl groups. The difference lies in the absence of the carboxylic group in fichtelite. Phylloretin also resembles the basic skeleton of fichtelite, although it lacks the angular methyl group, and its rings are unsaturated. The fichtelite molecule is also structurally similar to that of simonellite (Foresti & Riva di Sanseverino 1969). Simonellite has three non-linearly fused rings with attached isopropyl and two methyl groups; unlike fichtelite, it does not have an angular methyl group, and is partially aromatic in nature.

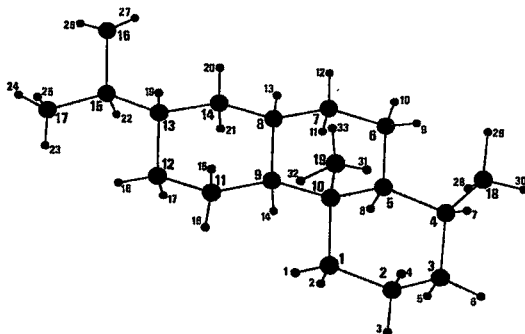


FIG. 1. A general view of the fichtelite molecule showing three fused six-membered carbon rings with attached methyl, angular methyl and isopropyl groups. The large circles represent carbon atoms, and the small circles represent hydrogen atoms.

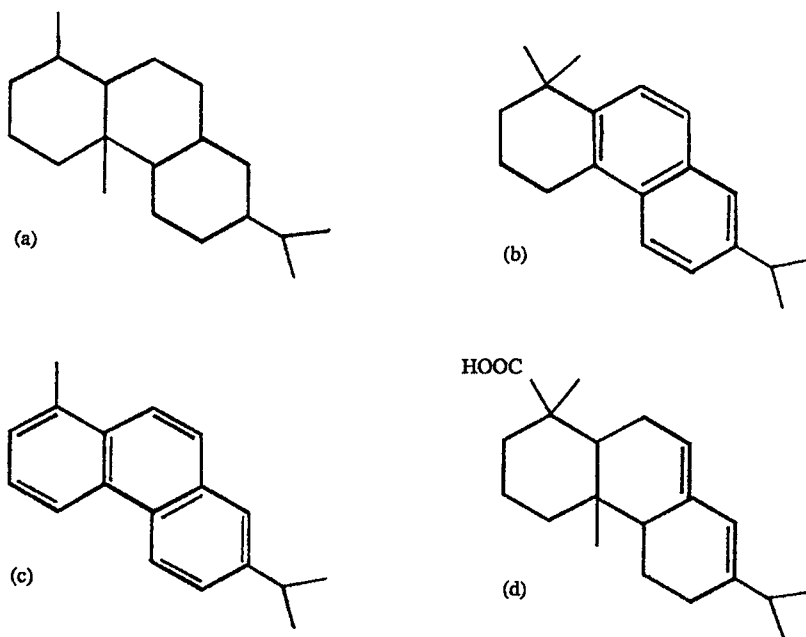


FIG. 2. The structural similarity among (a) fichtelite, (b) simonellite (Foresti & Riva di Sanseverino 1969), (c) phylloretin, and (d) abietic acid (Hoering 1967).

The location of the hydrogen attached to C16 (Fig. 1) in the isopropyl group was not determined. The low steric hindrance (*i.e.*, a low barrier to rotation) of the isopropyl group results in a higher magnitude of thermal motion and increased difficulty in locating the correct positive electron density corresponding to the hydrogen atom. This is apparent in Table 4: C16 has a larger displacement-factor than the other carbon atoms.

A chair conformation is observed in the rings, which is normal for rings of sp^3 -hybridized carbon, in order to minimize angle strain; the chair conformation is associated with an expected 109.5° angle (Banks 1976). All bond angles in the rings agree with the expected value; the angles also are consistent with those in the structure of simonellite (Foresti & Riva di Sanseverino 1969). Minor deviations from ideality are attributable to steric constraints of the structure, which necessitate larger bond-angles. For example, the angle formed by C10–C9–C11 (where C9 is the apex) is the largest at 114.8° . There is a large degree of crowding at this intersection, and the structure must distort to minimize steric interference. As there are no double bonds in the structure, the expected length of C–C bonds is 1.53 Å, and C–H bonds are expected to be

1.09 Å (Ege 1989). Observed bond-distances agree with these values, any deviations being attributable to the conformation of the rings. Shorter C–H bond-lengths are observed for C16 and C17 atoms, which are part of the isopropyl group. The C atoms show larger displacement-factors (related to larger thermal motion), which, in turn, would contribute to shorter bond-lengths. Displacement factors are higher for those atoms not associated with the phenanthrene skeleton. Although they are not part of the isopropyl group, C11 and C19 also show short C–H bond-lengths, whereas the C9–C10 bond is long. In this case, short C–H and long C–C bonds alleviate the overcrowding around both sets of carbon atoms. This is consistent with characteristics of the related structures of simonellite (Foresti & Riva di Sanseverino 1969) and phenanthrene (Trotter 1963).

ACKNOWLEDGEMENTS

We thank Forrest Cureton for supplying the specimen, and Dr. R.D. Heyding for assistance with the powder pattern. This research was supported by an NSERC grant to R.C.P. We also thank an anonymous referee for comments on the original manuscript.

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Received June 17, 1993, revised manuscript accepted May 26, 1994.