Mineralogical Magazine, February 2015, Vol. 79(1), pp. 59–70

Refikite from Krásno, Czech Republic: a crystal- and molecular-structure study

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[*Received 10 April 2014; Accepted 3 July 2014; Associate Editor: S. J. Mills*]

ABSTRACT

The crystal structure of the organic mineral refikite has been determined. The mineral was found in joints in bark and wood from pine trees in the 'V Borkách' peat deposit near the town of Krásno, Slavkovský les Mountains, western Bohemia, Czech Republic. It forms white to light-yellow polycrystalline crusts or randomly intergrown, transparent, colourless, very thin, acicular crystals up to 0.2−0.5 mm long. Sometimes, colourless-to-white elongated prismatic crystals up to 1−1.5 mm in size were encountered. The mineral is soft (Mohs hardness ~1) and very brittle, with an uneven fracture. No visible cleavage was discerned. Crystals have a greasy-to-glassy lustre; fine crystal aggregates have a pearly lustre. Refikite, empirical formula $C_{20}H_{34}O_2$ or $C_{19}H_{33}COOH$, is a derivative of abietic acid. It is orthorhombic, space group $P2_12_12$, with a = 22.6520(7), b = 10.3328(3), c = 7.6711(2) Å, V = 1795.49(9) Å^3, Z = 4. Refikite comprises two closely related compounds based on perhydrophenanthrene. The major component has two axial methyl groups, one terminal carboxylic group and one terminal propan-2-yl (isopropyl) group joined to the three fused rings in the same fashion as in abietic acid. However, the fused ring system is fully reduced (contains single bonds only). In the minor component, the terminal propan-2-yl group is replaced by a propen-2-yl (methylvinyl) group. The crystal structure is stabilized by strong O···H−O hydrogen bonds. High-resolution mass spectroscopy (HRMS) confirmed a molecular mass of 306 and the formula $C_{20}H_{34}O_2$. Hydrogen-1 and carbon-13 nuclear magnetic resonance (NMR) spectroscopy showed the presence of four methyl groups in the major component; infrared (IR), Raman and NMR spectra are consistent with the structure. The HRMS, IR and Raman spectroscopy methods confirmed the presence of a minor component containing the propen-2-yl group replacing the propan-2-yl group. This is also reflected in a shortened C15−C17 single bond metric of 1.468(6) Å shown by single-crystal X-ray analysis. The trivial name of the major component of refikite is tetrahydroabietic acid or abietan-18-oic acid. This work represents the first proof of the existence of abietic acid derivatives as naturally occurring species.

KEYWORDS: refikite, 1,4a-dimethyl-7-propan-2-yl-tetradecahydrophenanthrene-1-carboxylic acid, abietic-type resin acids, crystal structure, single-crystal X-ray diffraction, infrared spectroscopy, Raman spectroscopy, NMR, high-resolution mass spectroscopy.

Introduction

REFIKTE is a rare member of a small group of natural oxygen-containing hydrocarbons, along with acetamide, kladnoite, uricite, guanine, hoelite and flagstaffite. From a chemical point of

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DOI: 10.1180/minmag.2015.079.1.06

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https://doi.org/10.1180/minmag.2015.079.1.06 Published online by Cambridge University Press

view these minerals can be classified as an amide, purine, quinone, alcohol or abietic-acid minerals (Echigo and Kimata, 2010; Hazen *et al*., 2013).

Refikite was first described by La Cava in 1852 (Dana, 1892; Hintze, 1933) from Montório al Vomano, Teramo Province, Abruzzo, Italy, where it occurred in lignite as very soft, brittle, transparent, amorphous masses, also, rarely, as radially-acicular or thin-foliated aggregates. It was named after the Turkish journalist Refik Bay (?–1865) (Anthony *et al*., 2003). This occurrence in Italy was later mentioned in the papers of Leymerie (1857, 1859) and Legrand des Cloiseaux (1874). A second occurrence of refikite was described by Strunz and Contag (1965) from "fossil" roots of spruce in pits associated with peat mining at Kolbermoor, Rosenheim, Bayern, Germany. Strunz and Contag (1965) reported the powder X-ray diffraction pattern (7 lines), and assigned the non-centrosymmetric space group $P2_12_12$ (from Weissenberg photographs), with unit-cell parameters $a = 10.43$, $b = 22.35$, $c = 7.98$ Å. On the basis of the IR spectrum (not included in their paper) they identified refikite as δ13-dihydro-d-pimaric acid ($C_{20}H_{32}O_2$).

A recent discovery of well-formed refikite crystals at a third locality: the 'V Borkách' peat deposit, Czech Republic, made it possible to acquire new data for this unusual organic mineral phase and to revise its crystal structure and molecular composition on the basis of the data obtained directly from the natural material.

Local geology

In 2002, refikite was found by one of us (J.T.) in joints in the bark and wood of pine trees in the 'V Borkách' peat deposit, located on a plateau under Špičák hill, ~2 km to the west of Krásno, Slavkovský les Mountains, western Bohemia, Czech Republic (50º06′31″N, 12º45′38″E). The area belongs to the Saxothurigian zone of the Bohemian Massif. The basement consists of biotitic migmatitic orthogneiss (the so-called 'Slavkov orthogneiss'). A Li-topaz-albite granite of the Čistá type (younger intrusive complex of the Karlovy Vary granite massif) penetrates the area from the north (Fiala, 1968).

The 'V Borkách' peak deposit at an altitude of 770–780 m asl is the most important upland bog of the Slavkovský les Mountains. The maximum thickness of the peat is 7 m and its estimated age is ~6000 y. According to Tesař (2007) the organic matter consists mostly of cellulose and hemi-cellulose (45 vol.%) and humic-acid substances (25 vol.%), where the so-called 'undegradable residue' forms 17 vol.% (lignin, humic substances, etc.). The peat is classified on the basis of its composition as a moss-eriophorum-wood type. More than 80% of the humic acids present are in a dissociated form and – due to the absence of the inorganic substances – the humic acids in particular are responsible for a relatively low pH value. In the basement of the peat horizon virtually intact root systems of trees are abundant.

From 1978 to 1999 intensive, large-scale peat mining for agricultural and balneological purposes was carried out. The deposit was mined by cutting dry layers. When the samples of humified wood with refikite were collected, the surface had practically no vegetation. At the end of the mining activities a gradual return of wetland plants associated with scattered occurrences of *eriophorum* and *carex* and, in drier places, heather, can be observed (Fig. 1). At present the 'V Borkách' locality is important on a European scale as a Special Area of Conservation (SAC), "Krásenské rašeliniště" (Krásno peatery). The upland bog is surrounded by forest biotopes interrupted by open peat laggs and wetland meadows. The total area of the SAC is ~152 ha and the peatery itself represents about one-third of the area (Krása, 2013).

Chemical and physical properties

Refikite was found in thin joints in bark and, rarely, in the wood close to the bark of the pine



FIG. 1. A view of the 'V Borkách' peat deposit after the cessation of mining activities showing a gradual return of wetland-plant associations (*Calluna vulgaris*). Photo: Vylita, 2007.

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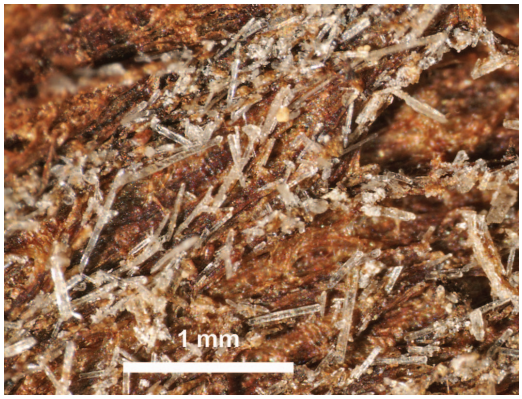


FIG. 2. Randomly intergrown, tiny, transparent, colourless and very thin acicular crystals of refikite on pine-tree bark. Field of view: 3 mm; photo: J. Sejkora.

tree *Pinus rotundata* Link. It forms white to light-yellow polycrystalline crusts up to several square centimetres in size. More rarely it was found as randomly intergrown, transparent, colourless, very thin, acicular crystals up to 0.2–0.5 mm long (Fig. 2). Sometimes, colourless-to-white elongated prismatic crystals up to 1–1.5 mm in size (Fig. 3) were encountered. The mineral is soft (Mohs hardness ~1) and very brittle, with an uneven fracture. No visible cleavage was discerned. Crystals have a greasy-to-glassy lustre; fine crystal aggregates have a pearly lustre. No fluorescence was observed under shortwave or longwave UV radiation. Refikite from Krásno is insoluble in water, which probably helped its preservation in the aqueous environment of the deposit. The melting point of refikite was measured as 179–183°C.

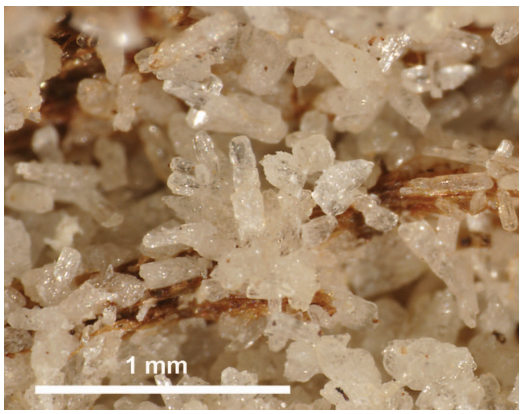


FIG. 3. Colourless-to-white, elongated, prismatic crystals of refikite on pine-tree bark. Field of view: 2 mm; photo: J. Sejkora.

The sample of refikite was analysed by negative electrospray ionization (ESI–), HRMS (negative ion mode, target mass resolution of R = 30,000 at *m/z* 400, H-ESI temperature 250ºC). In the mass spectrum the $[M - H]^-$ ion 305.2483 Da was observed (relative abundance 100%). The calculated elemental composition of the $[M - H]^-$ ion was found to be $C_{20}H_{33}O_2$; the difference between the measured and theoretical mass was 2.4 ppm. The result corresponds with the structure of refikite with the molecular mass of 306 Da. The ESI– spectrum also showed a weak peak of the $[M - H]^-$ ion at 303.2322 Da (relative abundance 5.5%) with a calculated elemental composition of $C_{20}H_{31}O_2$, showing a minor component with the propen-2-yl group which was also confirmed by NMR and single-crystal X-ray analysis. Hydrogen-1 and carbon-13 NMR at 500 MHz using a Bruker 500 Avance III spectrometer with a sample dissolved in CD_3OD shows explicitly that the fundamental molecule in refikite contains four CH_3 groups (Fig. 4). Two equivalent methyls of the propan-2-yl group can be found as a doublet at 0.88 ppm. The remaining two methyls are singlets at 0.91 ppm (C20) and 1.18 ppm (C19). The integral intensities are in the ratio of 2:1:1 (the signal at 1.18 ppm overlaps with some other signals and, therefore, its intensity is slightly larger). The ^{13}C spectrum confirmed the structure determined from single-crystal X-ray diffraction.

Molecular structure

The refikite sample was analysed by Fourier transform infrared spectroscopy using a Nicolet 6700 spectrophotometer (number of scans = 64, resolution = 4 cm^{-1}, apodization Happ-Genzel, ATR correction, spectroscopic range = 4000–400 cm^{-1}). As the IR spectrum of refikite, or its synthetic analogue, has not been published to date, the full measured spectrum is presented in Fig. 5, including probable assignments for the most significant bands observed. The spectrum in the range 1348–1397 cm^{-1} was used to distinguish two different situations on the terminal carbon atom C15 (Fig. 6). In this region, deformation vibrations of the C–H bonds in the geminal CH_3 groups (umbrella vibration) split into a doublet as a result of asymmetric and symmetric modes. To interpret this region, a theoretical spectrum of an amorphous analogue of refikite

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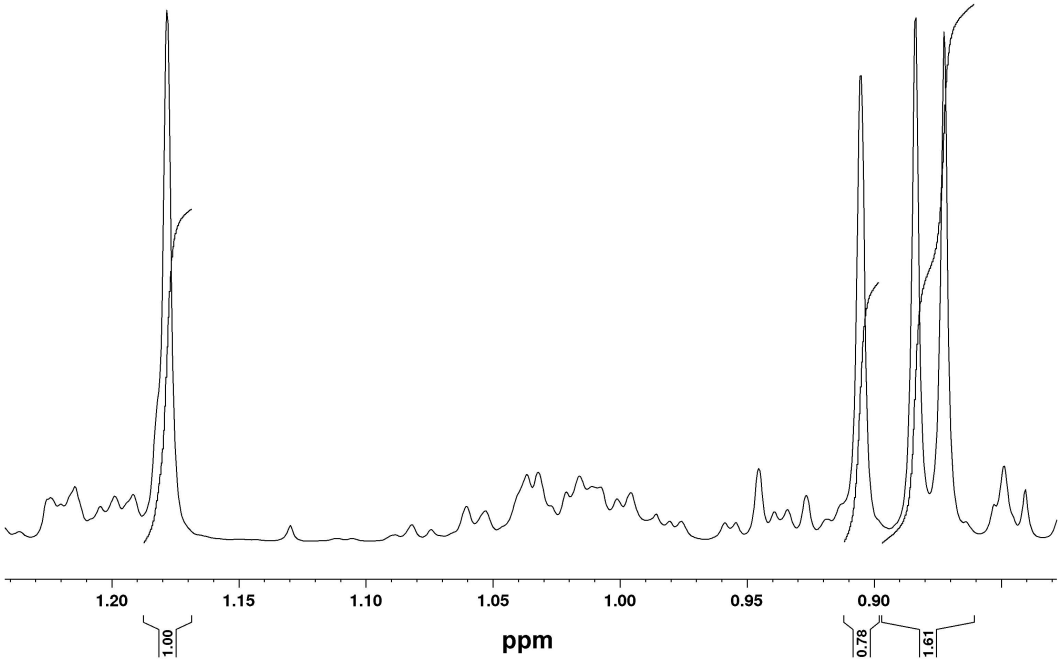


FIG. 4. Sections of the ^{1}H NMR spectrum showing signals for four methyl groups, together with integral intensities indicated below the horizontal axis.

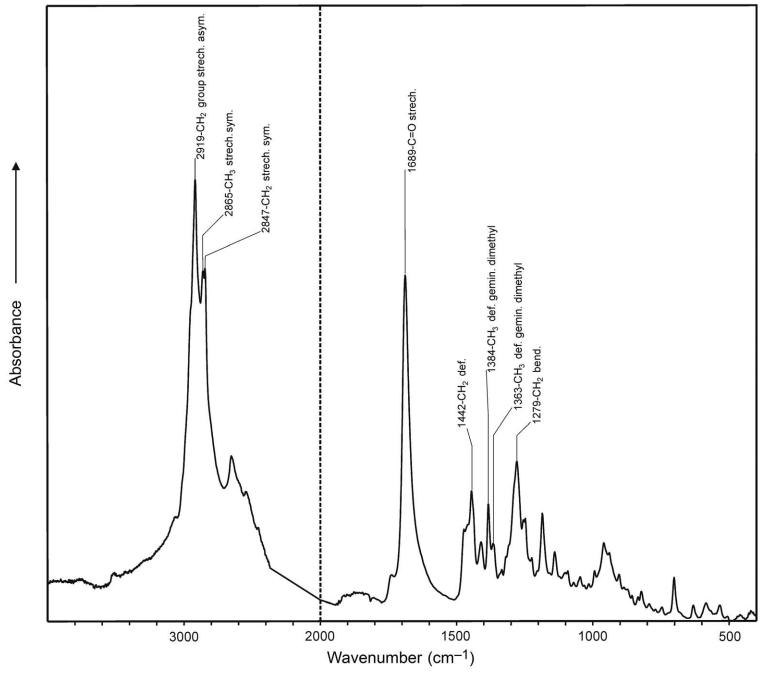


FIG. 5. IR spectrum of refikite from Krásno.

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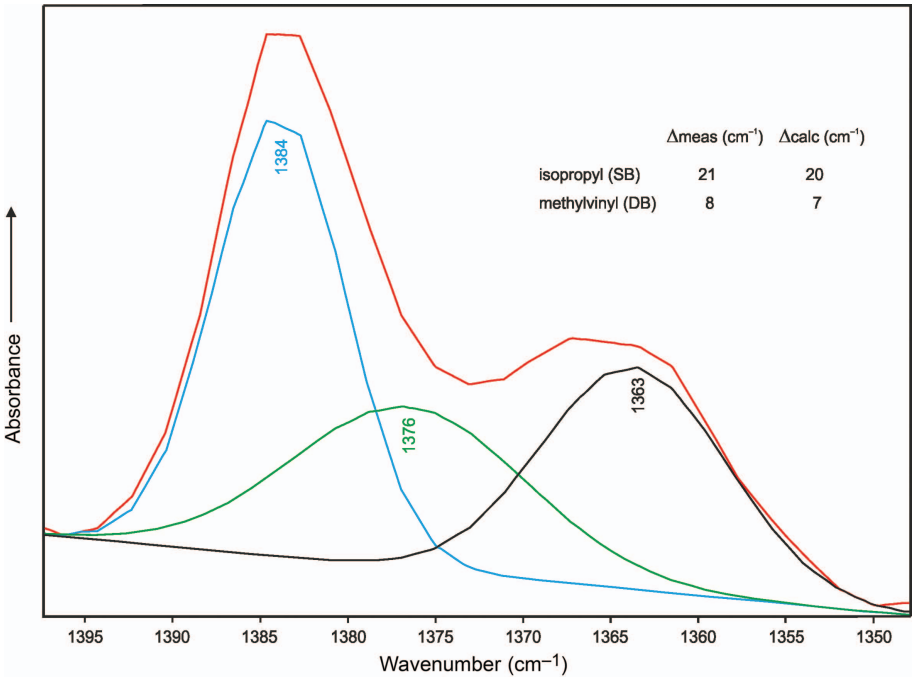


FIG. 6. Deconvolution of the IR spectrum of refikite from Krásno in the range 1348–1397 cm^{-1}.

was calculated using the software *GAUSSIAN* 5.0 (Dennington *et al*., 2009).

Due to a noticeable shift in wavelengths between the theoretical spectrum (amorphous phase) and the measured one (the crystalline phase), a direct comparison of the two spectra is not really possible. However, the difference (labelled Δ) between wavelengths of doublet components can be used to differentiate between them. The prevailing configuration with the terminal propan-2-yl group (i.e. geminal dimethyl) is marked SB (single bond) and has $\Delta_{calc.}$ = 20 cm^{-1}. The minor component with a double bond between C15 and C17 atoms, i.e. methyl-vinyl substitution on the C15 atom (propen-2-yl group) is marked as DB (double bond) and has $\Delta_{calc.}$ = 7 cm^{-1}. In the experimental spectrum of refikite (Fig. 6) a pronounced doublet with peaks at 1384 and 1363 cm^{-1} ($\Delta_{meas.}$ = 21 cm^{-1}) was observed, corresponding to the prevailing SB form. As the molecule in refikite contains other methyl groups on C4 and C10, the intensity of the band at 1384 cm^{-1} is greater than that of the band at 1363 cm^{-1}. The doublet corresponding to the minor DB molecule is not separated in the real pattern. However, it is seen as a shoulder at 1376 cm^{-1} ($\Delta_{meas.}$ = 8 cm^{-1}), revealed after deconvolution of the spectrum.

The Raman spectrum of refikite was obtained using a Nicolet DXR Raman Microscope (532 nm, grating = 900 lines mm^{-1}, aperture = 25 μm pinhole, resolution = 2 cm^{-1}, exposure time = 60 s, number of exposures = 40, range = 50–3416 cm^{-1}). As neither the Raman spectrum of refikite nor its synthetic analogue have been published to date, the full measured spectrum is presented in Fig. 7, including probable assignments of the most significant bands observed. The Raman spectrum shows a small but distinctive peak at 3013 cm^{-1} corresponding to the valence vibration of the C–H bond in the propen-2-yl group on C15 (DB molecule). This peak is non-existent in the calculated pattern of the SB molecule. This confirms that, along with a major constituent with a terminal propan-2-yl group, refikite also contains a minor constituent with a propen-2-yl substituent on the C15 atom.

X-ray diffraction study and the crystal structure of refikite

Original powder X-ray diffraction data for refikite from Kolbermoor at 293 K (PDF 00-028-200) reported by Strunz and Contag (1965), contained seven diffraction lines. New powder diffraction

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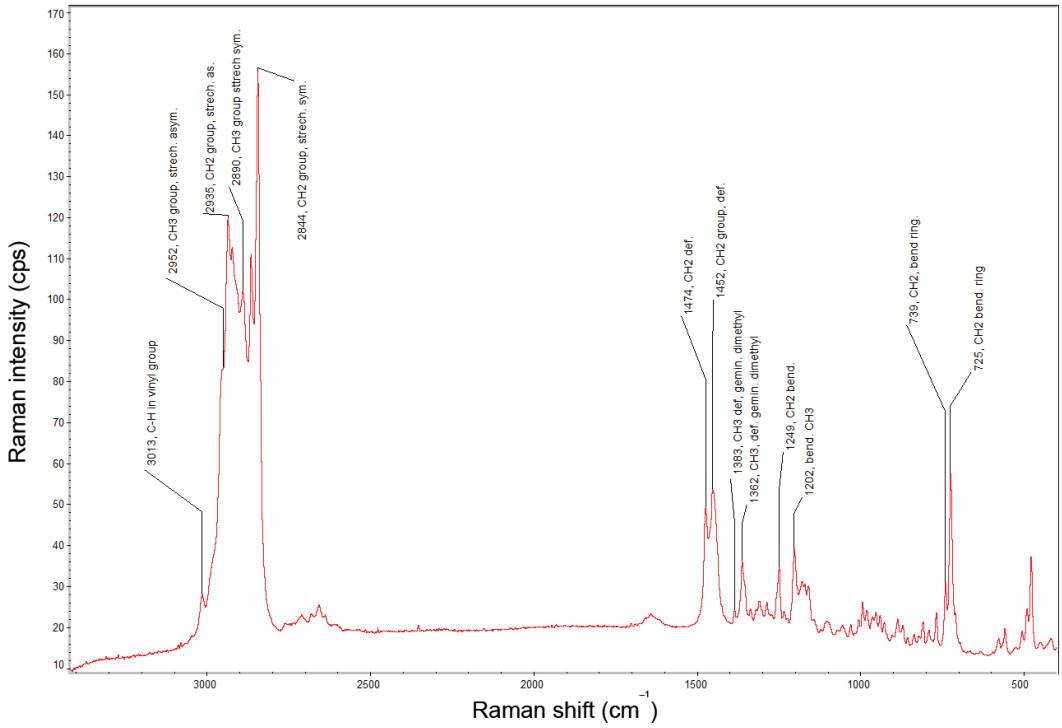


FIG. 7. The Raman spectrum of refikite from Krásno; the band at 3013 cm^{-1} corresponding to the C−H vibration in the propen-2-yl (vinyl) group (DB) is evident.

data for refikite from 'V Borkách' at 293 K with nineteen diffraction peaks were published by Pažout and Sejkora (2012), with a = 22.55(2), b = 10.469(6), c = 7.930(9) Å, V = 1871.82 Å^3, Z = 4, space group $P2_12_12$. The single-crystal data have smaller unit-cell parameters and volume (difference of 76 Å^3; 4%) because the measurements were taken at 120 K while the powder pattern was obtained at room temperature.

Single-crystal X-ray experiments were performed with a four-circle Oxford Diffraction Gemini CCD diffractometer, with graphite-monochromated Cu$K\alpha$ radiation (λ = 1.5418 Å). The crystal structure was solved by the charge-flipping method using the program *Superflip* (Palatinus and Chapuis, 2007) and refined with the *Jana2006* program package (Petříček *et al.*, 2006) by full-matrix least-squares on F. The molecular structure plots were prepared using *ORTEP III* (Farrugia *et al.*, 1997) and supra-molecular interactions were viewed in *Mercury* (Macrae *et al.*, 2008). Crystallographic data and details of the data collection and structure refinement are listed in Table 1, final atom coordinates are given in Table 2 and displacement parameters in Table 3. Selected bond distances and angles are listed in Table 4. In the first step, all hydrogens on carbons were positioned geometrically and refined using a riding model, with C−H = 0.96 Å and U_{iso}(H) = 1.2U_{eq}(C). In the final stages of refinement, the restrictions were removed and all H atoms were refined isotropically without constraints with the exception of H atoms on the three carbons of the terminal propan-2-yl group (C15, C16 and C17). The position of the H atom of the hydroxyl group was found in a difference Fourier map and refined isotropically without constraints.

The crystal structure of the mineral refikite consists of discrete $C_{20}H_{34}O_2$ molecules, space group $P2_12_12$, with one formula unit in the asymmetric unit (Figs 8, 10). The fundamental molecule in refikite has a perhydrophenanthrene structure. This is formed by three fused six-membered cyclohexane rings (hydrophenanthrene) with two methyl groups, one propan-2-yl (or isopropyl) group and one carboxyl group attached to the rings. The three fused rings (ring A – the ring with the carboxyl group, ring B – the

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TABLE 1. Summary of data collection and refinement parameters for refikite.

Crystal data	
Structural formula	$C_{20}H_{34}O_2$
Crystal system	Orthorhombic
Space group	$P2_12_12$ (Nr.18)
a (Å)	22.6520(7)
b (Å)	10.3328(3)
c (Å)	7.6711(2)
V (Å^3)	1795.49(9)
Z	4
Molecular weight (Da)	306.5
Density (calc.) (g/cm^3)	1.1334
F(000)	680
Crystal size (mm)	$0.26 \times 0.18 \times 0.13$
Crystal colour	White
Data collection	
Temperature (K)	120
Diffractometer	Oxford Diffraction Sapphire
Radiation	Cu$K\alpha$ 40 kV, 30 mA
Detector–sample distance (mm)	65
Number of frames	880
Measurement time (s/frame)	90
R_{int}	0.0236
Measured reflections	9043
Unique reflections	2856
Observed reflections ($I > 3\sigma(I)$)	2479
θ_{min} / θ_{max}	3.9/ 66.69
Range of h, k, l	h(min) = −25, h(max) = 25 k(min) = −11, k(max) = 11 l(min) = −8, l(max) = 7
Refinement	
Refinement on	F
R, wR (observed reflections)	0.0540/0.0628
R, wR (all reflections)	0.0625/0.0637
Gof (observed reflections)	3.18
Gof (all reflections)	2.97
No. of least-squares parameters	307
No. of constraints	28
Largest difference peak/hole (e.Å^{-3})	0.35/ −0.23

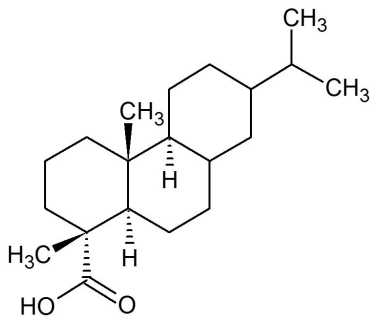


FIG. 8. The structural formula of refikite.

central ring, ring C – the ring with the propan-2-yl group) contain single bonds only and adopt the chair conformation.

The structure is similar to that of fichtelite, $C_{19}H_{34}$ (Mace and Peterson, 1995; Cambridge Structural Database (CSD) ref code ZAVGUY, www.ccdc.cam.ac.uk), the difference being the presence of a carboxyl group at C4 in refikite instead of hydrogen in fichtelite. The structure is similar to, but not isostructural with the following three abietic acid structures in the CSD database: levopimaric acid ($C_{20}H_{30}O_2$; CSD ref code LEVPIM10; Kahle, 1972), the difference being

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TABLE 2. Atomic coordinates and equivalent isotropic displacement parameters for refikite.

	x	*y*	*z*	U_{iso}
C1	0.21159(14)	0.6574(3)	1.1128(4)	0.0394(10)
C2	0.15520(15)	0.6297(3)	1.2127(5)	0.0446(11)
C3	0.10756(16)	0.7278(3)	1.1749(4)	0.0433(11)
C4	0.09270(12)	0.7366(3)	0.9781(4)	0.0387(10)
C5	0.15096(12)	0.7608(3)	0.8759(4)	0.0361(9)
C6	0.14111(13)	0.7810(3)	0.6808(4)	0.0384(10)
C7	0.19761(14)	0.8287(3)	0.5938(4)	0.0416(11)
C8	0.25042(13)	0.7409(3)	0.6295(4)	0.0415(10)
C9	0.25838(13)	0.7224(3)	0.8255(4)	0.0369(10)
C10	0.20235(13)	0.6641(3)	0.9131(4)	0.0358(9)
C11	0.31529(14)	0.6500(4)	0.8674(5)	0.0481(12)
C12	0.36834(16)	0.7090(4)	0.7774(5)	0.0521(13)
C13	0.36029(15)	0.7133(4)	0.5812(5)	0.0580(13)
C14	0.30548(15)	0.7928(4)	0.5427(5)	0.0456(12)
C15	0.41371(15)	0.7501(4)	0.4767(5)	0.0717(15)
C16	0.46331(19)	0.6478(6)	0.4935(8)	0.109(2)
C17	0.43708(19)	0.8776(5)	0.5252(6)	0.0883(19)
C18	0.05218(13)	0.8532(3)	0.9610(4)	0.0395(10)
C19	0.05740(16)	0.6174(3)	0.9215(5)	0.0464(12)
C20	0.19080(17)	0.5261(3)	0.8432(5)	0.0438(11)
O21	−0.00111(10)	0.8426(2)	0.9543(3)	0.0603(9)
O22	0.07803(10)	0.9661(2)	0.9565(4)	0.0627(10)
H1C1	0.2295(11)	0.739(3)	1.158(4)	0.036(7)
H2C1	0.2426(12)	0.585(3)	1.147(4)	0.047(8)
H1C2	0.1369(13)	0.547(3)	1.173(4)	0.052(9)
H2C2	0.1635(12)	0.630(3)	1.343(4)	0.043(8)
H1C3	0.0764(19)	0.712(4)	1.238(5)	0.081(13)
H2C3	0.1258(12)	0.811(3)	1.231(4)	0.046(9)
H1C5	0.1684(10)	0.843(3)	0.920(4)	0.026(6)
H1C6	0.1074(11)	0.840(2)	0.659(3)	0.024(6)
H2C6	0.1306(13)	0.707(3)	0.632(4)	0.047(10)
H1C7	0.1893(13)	0.839(3)	0.462(4)	0.047(9)
H2C7	0.2087(13)	0.920(3)	0.649(4)	0.049(8)
H1C8	0.2412(15)	0.646(4)	0.573(5)	0.076(11)
H1C9	0.2652(11)	0.811(3)	0.876(4)	0.031(7)
H1C11	0.3142(15)	0.554(4)	0.839(5)	0.070(11)
H2C11	0.3197(13)	0.644(3)	0.996(4)	0.047(9)
H1C12	0.4061(15)	0.655(3)	0.805(5)	0.072(11)
H2C12	0.3783(11)	0.796(3)	0.818(4)	0.034(8)
H1C13	0.3686(9)	0.609(2)	0.504(3)	0.019(6)
H1C14	0.3133(12)	0.882(3)	0.570(4)	0.039(8)
H2C14	0.3026(12)	0.801(3)	0.420(4)	0.036(8)
H1C15	0.4008	0.7539	0.3577	0.086009
H1C16	0.4461	0.5632	0.5031	0.131054
H2C16	0.4881	0.6511	0.3921	0.131054
H3C16	0.4865	0.6656	0.5955	0.131054
H1C17	0.4584	0.8707	0.633	0.106
H2C17	0.4631	0.908	0.4354	0.106
H3C17	0.405	0.9374	0.5391	0.106
H1C19	0.0793(13)	0.536(3)	0.960(4)	0.047(8)
H2C19	0.0532(14)	0.616(3)	0.798(5)	0.067(12)
H3C19	0.0193(16)	0.613(4)	0.979(5)	0.068(11)
H1C20	0.1686(13)	0.530(3)	0.718(5)	0.054(9)
H2C20	0.1690(14)	0.469(4)	0.920(5)	0.065(11)
H3C20	0.2273(13)	0.480(3)	0.836(4)	0.044(8)

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TABLE 3. Anisotropic displacement parameters for refikite (Å).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0540(18)	0.0335(16)	0.0307(18)	0.0042(14)	−0.0097(15)	−0.0003(14)
C2	0.059(2)	0.0444(19)	0.0302(19)	−0.0037(15)	0.0021(16)	0.0020(15)
C3	0.0514(19)	0.0425(18)	0.036(2)	−0.0073(15)	0.0017(16)	−0.0046(15)
C4	0.0417(15)	0.0329(15)	0.0414(19)	−0.0050(12)	−0.0015(13)	−0.0035(14)
C5	0.0452(16)	0.0300(15)	0.0331(18)	−0.0052(13)	−0.0075(13)	−0.0043(13)
C6	0.0461(18)	0.0355(16)	0.0336(18)	−0.0027(15)	−0.0102(14)	−0.0033(15)
C7	0.0515(18)	0.0418(18)	0.0316(18)	−0.0014(13)	−0.0104(15)	0.0015(14)
C8	0.0482(17)	0.0472(18)	0.0290(19)	−0.0027(15)	−0.0049(14)	0.0061(14)
C9	0.0494(17)	0.0350(16)	0.0262(17)	0.0039(13)	−0.0063(14)	−0.0023(13)
C10	0.0485(17)	0.0322(15)	0.0269(15)	−0.0022(12)	−0.0050(14)	−0.0013(13)
C11	0.0493(18)	0.059(2)	0.036(2)	0.0091(16)	−0.0023(16)	0.0061(17)
C12	0.054(2)	0.062(2)	0.041(2)	0.0144(17)	−0.0064(17)	0.0047(18)
C13	0.0519(19)	0.083(3)	0.039(2)	0.0133(18)	0.0070(16)	0.004(2)
C14	0.0521(19)	0.057(2)	0.028(2)	0.0002(15)	−0.0096(15)	0.0043(16)
C15	0.060(2)	0.092(3)	0.063(3)	−0.005(2)	0.0028(19)	0.003(2)
C16	0.078(3)	0.143(5)	0.107(4)	0.018(3)	0.020(3)	−0.012(4)
C17	0.084(3)	0.105(3)	0.076(3)	0.014(3)	0.026(3)	0.015(3)
C18	0.0451(18)	0.0410(16)	0.0323(18)	−0.0089(13)	0.0023(14)	−0.0058(15)
C19	0.053(2)	0.0385(18)	0.048(2)	−0.0098(15)	−0.0056(18)	−0.0048(16)
C20	0.060(2)	0.0325(16)	0.039(2)	0.0031(16)	−0.0013(18)	−0.0024(15)
O21	0.0425(13)	0.0451(12)	0.093(2)	−0.0057(10)	0.0106(13)	0.0050(13)
O22	0.0442(13)	0.0323(12)	0.112(2)	−0.0028(11)	−0.0101(14)	−0.0133(13)

that its C ring has two double bonds; 7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,-5,6,7,8,9,10,10a-dodeca-hydrophenanthrene-1-carboxylic acid, ($C_{20}H_{32}O_2$; CSD refcode PUGQAK; Rao *et al*., 2009), the difference being that the C8−C9 (between ring B and C) is a double bond; 7,13-abietadien-18-oic acid ($C_{20}H_{30}O_2$; CSD refcode YAWMOY10; Okada and Takekuma, 1994), the difference being that the B and C rings have one double bond each. All three are non-centrosymmetric and dimeric units linked by strong hydrogen bonds are present in all three. They differ from refikite by having two molecules in the asymmetric unit.

The described configuration, *R* on C4, *R* on C10, *S* on C9, *S* on C8 and *R* on C5, was eventually confirmed crystallographically, although the determination of the absolute configuration of this non-centrosymmetric structure is not straightforward due to the absence of any atom heavier than oxygen. Normally, the absolute configuration is determined by computing the Flack parameter (Flack, 1983), achieved by introducing an inversion twin in the

TABLE 4. Selected bond lengths (Å) and angles (º).

C1−C2	1.517(5)	C2−C3	1.508(5)	C3−C4	1.549(5)
C4−C5	1.555(4)	C5−C6	1.528(4)	C5−C10	1.560(4)
C6−C7	1.526(4)	C7−C8	1.526(4)	C8−C9	1.526(4)
C9−C10	1.558(4)	C9−C11	1.525(4)	C11−C12	1.514(5)
C12−C13	1.517(5)	C13−C14	1.518(5)	C8−C14	1.512(4)
C13−C15	1.500(5)	C15−C16	1.548(7)	C15−C17	1.468(6)
C4−C19	1.531(4)	C10−C20	1.545(4)	C4−C18	1.521(4)
C18−O21	1.213(4)	C18−O22	1.305(4)	O22−H1O22	0.78(4)
C13−C15−C17	112.5(4)	C13−C15−C16	111.6(4)	C17−C15−C16	109.3(3)
O21−C18−O22	121.7(3)	C5−C4−C19	115.4(3)	C9−C10−C20	110.2(2)

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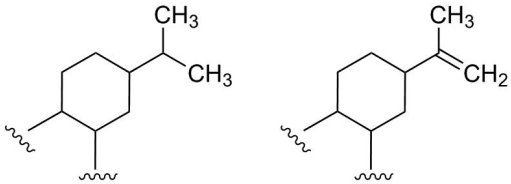


FIG. 9. The terminal propan-2-yl group (left) and the terminal propen-2-yl group (right).

structure and refining the twin volume fractions. If the volume fraction of the inversion twin (the inverted structure) is close to 0, the original structure (before introducing the inversion twin) is indeed the correct absolute configuration. If it is close to 1, then the inverted structure is the correct absolute configuration. The determination of the absolute configuration was undertaken using two parallel methods: (1) use of intensity quotients in terms of sums and differences of Friedel pairs calculated by the program *XNPP* (Parsons *et al*., 2013) produced the calculated Flack parameter 0.02(12) confirming the structure presented (Fig. 8) is the correct absolute configuration; (2) analysis of Bijvoet pairs using the program *Platon* (Spek, 2003) calculated the value of Hooft y (Hooft *et al*., 2008) to be −0.08(13), confirming the same result.

All bond lengths and angles in refikite are within expected ranges and are similar to those in fichtelite (Mace and Peterson, 1995). The only exception is a shortened C15−C17 bond of 1.468(6) Å, too short for a single bond and too long for a double bond. This is interpreted as the result of averaging of both types of bonds over a number of unit cells. It suggests that the crystal contains two types of molecules; the predominant molecule has a terminal propan-2-yl (isopropyl) group and the minor molecule has a terminal 1-propen-2-yl (methylvinyl) group in place of the propan-2-yl group (Fig. 9).

The dihedral angle between the mean plane of ring A and the carboxyl group in refikite is 71.8(3)º. Molecules in refikite form dimers bonded by a strong O···H−O hydrogen bond. These dimers are fundamental building units in the structure of refikite, similar to the structure of levopimaric acid (Karle, 1972). The dimer assumes an S-shaped conformation (Fig. 10). The dihedral angle between the two molecules forming a dimer is 8.17º (between planes of the carboxyl group), similar to LEVPIM10 where this angle is 2.72º (Karle, 1972). The dihedral angle between planes of perhydrophenanthrene in the two molecules forming a dimer is 48.8º.

Two different orientations of the dimers towards the (001) plane are shown in Fig. 10.

Dimers form two types of parallel alternating layers perpendicular to *c* and parallel to (001). One layer is formed by dimers with the H-bond pair in cell corners and the other layer is formed by dimers with H-bond pair at ½,½,0 − in both cases the plane of the H-bond pair is perpendicular to *c*. When viewed down *c*, molecules of the dimer with H-bond pairs in the corners have the A ring under the plane O21–O22–O21^{i}–O22^{i} and

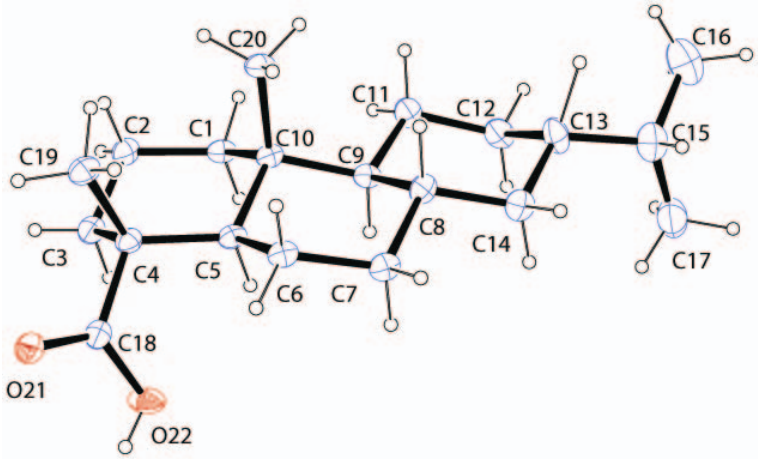


FIG. 10. The molecular structure (using *ORTEP*) of refikite showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius.

https://doi.org/10.1180/minmag.2015.079.1.06 Published online by Cambridge University Press

molecules of the dimer with H-bond pairs at ½,½,0 have the A ring above the O21–O22–O21^{i}–O22^{i} plane. A chessboard arrangement of dimers in two adjacent parallel layers perpendicular to the *c* axis is shown in Fig. 11.

The crystal structure is held together by a pair of two strong H bonds with the carbonyl oxygen, O22, of one molecule being an acceptor and the hydroxyl oxygen, O21, of the adjacent molecule acting as the donor. The H bond thus links carboxyl groups of two neighbouring molecules, the two sequences of the pair being O21^{i}···H1O22–O22 and O21···H1O22^{i}–O22^{i} [symmetry code (i) is $-x$, $2-y$, z]. The distances are O21···H1O22 = 1.86(4), O22–H1O22 = 0.78(4) and O21···O22 = 2.635(3) Å and the O21···H1O22–O22 angle is 174(4)º. The plane in which the pair of the bonds lies is parallel to (001), the twofold axis being in the centre of the pair of hydrogen bonds. The plane of the pair of hydrogen bonds that forms the dimer is defined by the four oxygen atoms of the pair O21, O22, O21^{i}, O22^{i}. Weaker C···H–O interactions were not considered to form hydrogen bonds.

According to this present study, the major chemical component of refikite has the trivial name tetrahydroabietic acid or abiet-13(15)-an-18-oic acid and the systematic name 1,4a-dimethyl-7-propan-2-yl-tetradecahydrophenanthrene-1-carboxylic acid. It belongs to the class of abietic-type resin acids. The systematic name differs from that given by Strunz and Contag (1965) and was established on the basis of the single-crystal structure of the mineral.

Conclusions

The crystal structures of abietic-acid resin minerals have not been known to date. This article presents the first crystal structure of an abietic-acid resin mineral, that of refikite. The structure was confirmed by a multi-method approach employing IR and Raman spectroscopy, HRMS and NMR spectroscopy. The existence of two different molecules in refikite has been revealed: a predominant molecule with a terminal propan-2-yl group and a minor molecule containing a terminal propen-2-yl group in its place. These data provide important information about mineral phases that can form during the peating of plants and coalification processes.

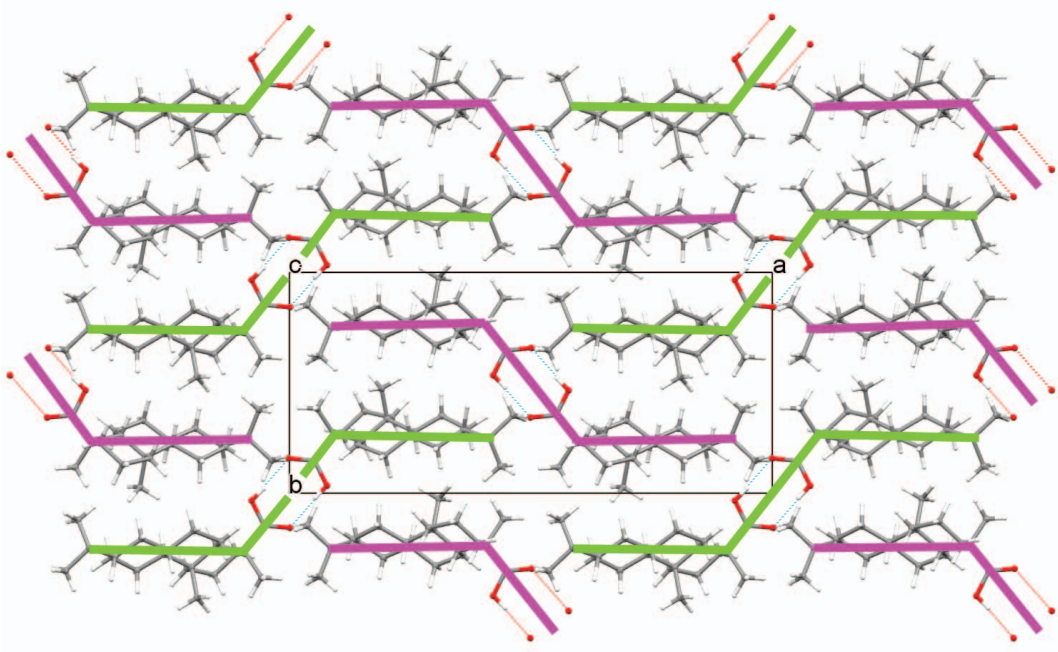


FIG. 11. General arrangement of the dimers forming hydrogen bonds in the structure of refikite, showing two orientations of the dimers and the chessboard arrangement (viewed down the *c* axis).

https://doi.org/10.1180/minmag.2015.079.1.06 Published online by Cambridge University Press

Acknowledgements

This work was supported financially by the Grant Agency of the Czech Republic (P106/12/1276) for RP and JM, project DKRVO 2013/02 and 2014/02 (National Museum 00023272) of the Ministry of Culture of the Czech Republic for JS and by the Project Praemium Academiae of ASCR for MD. The authors thank Miroslava Novotná for the IR and Raman spectroscopy, Josef Chudoba for the HRMS, Richard Hrabal for the NMR and Otakar Šida (National Museum, Prague), Tomáš Vylita (Karlovy Vary) and Petr Krása (Karlovy Vary) for helpful information about the locality. Thanks also to Simon Parsons and Jan Fabry for consultations on the absolute configuration. The editorial care of Pete Williams and Peter Leverett is greatly appreciated.

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