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EICOSYL ALCOHOL: AN ORGANIC CONSTITUENT OF CALCITE  
FROM DEUTSCH-ALTENBURG, AUSTRIA

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ABSTRACT

Analysis of red-tinted calcite from Deutsch-Altenburg, Austria, probably of Miocene age, failed to confirm the existence of a metal porphyrin compound as reported by H.

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Haberlandt (1944). The visible coloration was found to be due to a finely dispersed mixture of hydrated ferric oxides. Further analysis has identified the ultraviolet fluorescent constituent as being eicosyl alcohol. Aromatic and nitrogenous compounds were found to be absent in the sample tested. Recent investigations by various authors into the mechanisms of porphyrin synthesis reactions suggest strongly that many of the porphyrins previously reported are artifacts created during the extraction procedure.

#### INTRODUCTION

The existence of iron and gallium porphyrins as the fluorescent and pigment constituent of red-tinted calcites from two Austrian localities was reported by H. Haberlandt (1944). Attempts by several investigators to synthesize gallium porphyrins since that date have yielded poor to negative results. On this basis a re-investigation of the original material was deemed appropriate. The results are herein reported.

#### EXPERIMENTAL

Examination of a sample from the type locality of Deutsch-Altenburg, Austria<sup>1</sup> confirmed the existence of a long wave fluorescent property. Extraction by various non-acidified organic solvents (chloroform, methanol) of a very finely powdered sample yielded in each case a waxy white solid. Benzene and hexane as extraction solvents yielded under the same conditions no measurable product. The melting point of the waxy solid after complete removal of solvents under vacuum was 65.5–66.0°C. The total yield was 2.8 mg (0.007%) from an initial sample of 40 grams. The powder calcite residue remaining after extraction by chloroform and methanol ceased to exhibit a fluorescent property. Extraction with benzene or hexane did not alter the fluorescence of the sample.

Using procedures of Lucas (1930) and Feigl (1955) the waxy product was determined to be a primary alcohol. The use of NMR confirmed the presence of only aliphatic (CH<sub>2</sub>, CH<sub>3</sub>) protons. Failure to observe a hydroxyl (OH) proton signal was attributed to two factors: low total sample (2.8 mg) and unfavorable hydroxyl to aliphatic proton ratio (1:41). Both UV and IR spectrums confirm the identification of the waxy solid as an aliphatic primary alcohol. There was a complete absence of a Soret pattern, typical of porphyrin compounds in the near UV portion of the visible spectrum. The IR spectrum was obtained using a method known as Multiple Internal Reflection Spectroscopy.

Analysis using TLC (thin layer chromatography) of the residues produced by extraction with acidified and non-acidified organic solvents confirmed the existence of only a single detectable organic species. However, the acid procedure of extraction yields initially the acid ester of the alcohol. Saponification of the ester yields a product identical to that produced by nonacid procedures. Use of a procedure of F. Feigl (1958) failed to detect the presence of a nitrogenous compound. Solvents used in the extraction and identification procedures were purified and/or analyzed to insure complete absence of a residue.

Both a 4-nitrobenzoate (Vogel, 1957) and an acetate ester (Wild, 1958) derivative were prepared to fully characterize the alcohol product. On examination after recrystallization and removal of solvents and unreacted reagents, the 4-nitrobenzoate derivative was found

<sup>1</sup> The calcite examined is noted as occurring as crystals with zonal coloring from cavities in the limestone strata near the thermal springs at Deutsch-Altenburg on the Danube River in Lower Austria. Other calcites of a similar type (porphyrin containing) are found in alpine crevices (in limestone) on the Knorren, Hohe Tauern, Austria: the material from the latter locality was not available for study.

to have a melting point of 69.0°C;<sup>1</sup> The acetate ester a melting point of 39.8°C.<sup>2</sup> Analysis by TLC of the derivatives again confirmed the existence of a single organic species. Matching of the data obtained with that in the literature provides a near perfect match for eicosyl alcohol<sup>3</sup> (1-icosanol, arachidic alcohol).

The red pigment was not extractible by organic solvents. Dissolution of a sample in acetic acid yielded a colored solution. The resultant solution was vacuum dried and redissolved in 6 N hydrochloric acid. Using the procedures of Collins (1959) and F. Feigl (1931 and 1958) the pigment was confirmed as being a ferric iron compound (probably a hydrated oxide) in low concentrations. Analysis for gallium (Onishi, 1955) yielded negative results. As well as can be determined, the sole metallic cation present (other than calcium or magnesium) was ferric iron.

#### HISTORICAL NOTES

Geographically, Deutsch-Altenburg was situated on the south bank of the Danube River midway between the towns of Petronell and Hainburg near the Austria-Czechoslovakia border. The area has been known since Roman times for its thermal springs.<sup>1</sup> The earliest published study on the springs was by Formickin (1634), followed by those of Managettam (1758) and Crantz (1777). From this same period came a translation of an undated (probably Roman) Latin manuscript describing the medicinal qualities of the thermal springs (*translation* by Dietmann and Lehr, 1734).<sup>2</sup> As can be seen, the town's existence from earliest times was dependent economically on income derived from the spas. Sometime between the 1890's and 1910, this income declined and the town was subsequently abandoned.<sup>3</sup> The last study to be done on the springs and the geology of the immediate area seems to be that of Burgerstein (1882).<sup>4</sup>

#### DISCUSSION

Geologically, Deutsch-Altenburg is within a series of marine limestones and brackish sedimentary rocks of Lower and Middle Miocene age (Vetters, 1933; Schaffer, 1951). However, this formation is on the trailing edges of an "Alpine Juraform" consisting of Jurassic calcareous rocks identical in most respects to those of the High Calcareous Alpine nappes to the north.<sup>1</sup> Within the area are also brackish sedimentary rocks of Upper Miocene age as well as a small outcropping of Paleozoic rocks.

<sup>1</sup> For eicosyl alcohol, literature value (m.p. = 69.4°C).

<sup>2</sup> For eicosyl acetate, literature value (m.p. = 40.0°C).

<sup>3</sup> Empirical formula C<sub>20</sub>H<sub>41</sub>OH.

<sup>1</sup> During Roman times, the area was the site of the town of Carnuntum.

<sup>2</sup> See also Bastler (1844).

<sup>3</sup> Recent maps (past 1920) fail to note the locality.

<sup>4</sup> Article describes in detail contemporary history and layout of the town and the location of the various thermal springs. Analysis of the mineral salt content of the springs' waters, as well as a seasonal record of the water temperature (of thermal springs) included. In addition a tabulation of the fossil species identified in the limestone strata of the locality is presented.

<sup>1</sup> Within the same general area, to the east, the beginning edges of formations (limestones) associated with the Carpathian Mountains begin their emergence.

In association with calcite, the occurrence of finely crystallized specimens of gypsum, sulfur, aragonite, and iron pyrite have been noted in an early mineralogical treatise (Sigmund, 1909). The calcite examined was probably collected from a vein in a small limestone quarrying operation<sup>1</sup> on a hill identified as Pfaffenberg (327 meters) immediately behind the town (see Burgerstein, 1882, 110). However, there is no direct evidence of the specimen being from this locale. The exact origin must therefore be considered lost.

The deposition of the calcite probably coincided with similar occurrences in the Alpine veins (clefths) of Switzerland. The deposition process, however, occurred well after the period of Alpine deformation. According to Weibel (1966) the depositional process occurred in Pleistocene times. The constituents of Alpine vein minerals are generally considered to have been derived from the surrounding rocks (Parker, 1954, Niggli, 1940), Miocene in this case. The alcohol may have a similar origin; if so, it has survived 20–25 million years.

Regardless of the analytical procedure employed, the presence of a porphyrin compound could not be verified. The constituents identified account accurately for the physical properties observed. In recent years, detailed kinetic and synthetic studies have been undertaken on the mechanism of porphyrin synthesis. In particular, a paper by A. Adler (1968) indicates the strong possibility that reported porphyrins in minerals are artifacts created by acid extraction of the sample. This work reinforces the earlier work by Hodgson (1967) on the abiogenesis of porphyrins under mild conditions. The conditions wherein pyrrole-pyrrole derivatives can easily be synthesized to porphyrin compounds are akin to those encountered in the reported acidic extraction procedures used.

The general method of extracting porphyrin compounds from rock samples is essentially that of Treibs (1934a). Minor modifications of this technique have been utilized by Groenning (1953), and Dunning and Carlton (1956). Under these conditions of extraction, it is possible to form porphyrin artifacts (if suitable precursors are present) of the *m*, *s*-tetraphenyl type. No naturally occurring porphyrins of proven biological origins have been found of this type. In view of results obtained, reinvestigation of porphyrins reported as mineral components should be attempted using nonacidic extraction procedures.

The majority of naturally occurring metal porphyrines have iron as the metal. There have been reported isolations of copper, (Nicholas,

<sup>1</sup> Quarrying of limestone is noted as an industry for the general area. The material quarried is from a formation identified as "Miocene Leitha Limestone".

1951), manganese-(Borg, 1958), nickel- and vanadium<sup>1</sup> (Treibs, 1934b) containing porphyrines. The most recent was the isolation and identification of the fluorescent constituents of pearls as being a zinc haematoporphyrin. In addition detailed studies on the occurrence of porphyrins<sup>2</sup> in bitumens, oils and shales have been done by Fisher (1937, 1940) and Dhéré (1934).

A distinguishing feature of artificially produced porphyrins is an absorption peak in the Soret region at 420 nm. In addition, *m,s*-tetraphenyl porphyrins share common peaks at 500, 535, 565, and 620 nm with natural porphyrins. On comparing Haberlandt's data with the general literature, we must confirm that the material examined by him was a gallium haematoporphyrin.<sup>1</sup> Whether the material was of natural origin or artificial can never be decided. It is interesting to note that a member of the research group supplied a synthetic gallium haematoporphyrin for the comparative and identification studies.<sup>2</sup> The synthesis was never published.<sup>3</sup> On this basis, the evidence is that Haberlandt's porphyrin (if not artificial) was a rare event, probably occurring as a single small local inclusion in the calcite. An extensive study of the mineral quincite by J. Goni<sup>4</sup> to determine or confirm the presence of a porphyrin also noted by Haberlandt, yielded negative results.

The case for eicosyl alcohol as a genuine mineral product is, however, on solid ground. Eicosyl alcohol has been found to be naturally occurring in the present era in various animal oils (Toyama, 1938) in natural plantation rubber extracts, (Heilbron, 1941) and in numerous algae and diatoms.

Studies on montan wax (derived from lignites) by Pschorr and Pfaff (1920) yielded several related saturated compounds; ceryl ( $C_{26}H_{54}O$ ) and myricyl ( $C_{30}H_{62}O$ ) alcohols. These alcohols have also been proven to be present in contemporary plants by Deuel (1951). Similar waxes composed of saturated alcohols have been shown to be present in oils,

<sup>1</sup> Vandaium and nickel porphyrins have been theorized as being formed from respiratory pigments of plants and animals by metal exchange (Blumer, 1950; Dyemenkova and Kurbatskaya, 1955)

<sup>2</sup> First studies on porphyrin compounds were initiated and published by Hoppe-Seyler (1871).

<sup>3</sup> A comprehensive review on haematoporphyrin and porphyrins has been published by Falk (1964).

<sup>4</sup> Most of Haberlandt's associates were members of the H. Fischer school which pioneered synthetic preparation of porphyrin compounds.

<sup>5</sup> The reaction needed to produce only a few milligrams for the studies done by Haberlandt.

<sup>6</sup> *Private communication.* Research performed at Dept. Laboratories, Bureau Recherches Geologiques et Minières, Orleans, France.

shales and peats of England (Cawley, 1948), Finland (Sundgren, 1949), Ireland (Reilly, 1940) and Russia (Roginskaya, 1936; Kuznetsov, 1938). The existence of eicosyl alcohol, therefore, as a "fossil" chemical in view of the *long term* stability of saturated, long-chained alcohols in general, can be expected.

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REFINEMENT OF THE CRYSTAL STRUCTURE OF A  
CHROME PYROPE GARNET: AN INCLUSION  
IN NATURAL DIAMOND

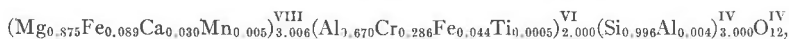
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ABSTRACT

The crystal structure of a chrome pyrope garnet,  $a = 11.526(1) \text{ \AA}$ ,



has been refined to  $R = 0.038$  using 3-dimensional data. The Si–O bond length is  $1.639(1) \text{ \AA}$  and the  $\text{M}^{\text{VI}}\text{–O}$  bond is  $1.905(1) \text{ \AA}$ . The structural data are similar to those of synthetic pyrope (Gibbs and Smith, 1965).

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