

SPECIALIA

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Organic Minerals. Picene and Chrysene as Constituents of the Mineral Curtisite (Idrialite)¹

Curtisite, a yellowish-green mineral consisting of organic material in massive form, was first discovered in association with cinnabar at Skaggs Spring, California². Since that time, curtisite has been shown to be identical with the mineral idrialite^{3,4}, and has also been found in Czechoslovakia⁴ and in the Transcarpathian range^{5,6}. Curtisite occurs in a variety of mineral associations and with varying properties. GRINBERG and SHIMANSKI⁷ divided the mineral into curtisite proper, with a melting point of 272–302°C and curtisitoids, melting at 81–96°C, the latter occurring as orange to brown crystals.

Various compositions have been assigned to native curtisite ($C_{24}H_{18}O^2$, $C_{24}H_{18}^{5,6}$), but its identity has not been established, although STRUNZ and CONTAG⁸ made the suggestion, based upon an X-ray powder diagram of material melting at 319°, that it consisted of picene and other material. We have examined a specimen of curtisite from Skaggs Springs and wish to report the isolation of picene and chrysene, along with evidence that methyl homologs of these are also present.

Isolation of crude constituents. A 14 g specimen of crude curtisite, which consisted of fragments of greyish-brown, soft rock, was ground in a mortar to give a yellow powder containing a few small lumps of non-organic material. The material was boiled with *p*-xylene (175 ml) and decanted to give a brown, fluorescent solution from which yellowish crystals (C-1) separated (3.8 g). The residual insoluble material was boiled with another portion of xylene (75 ml) and the insoluble rocky material (3.9 g) was filtered off. The solution deposited light yellow crystals (C-2, 1.2 g). The combined mother liquors of C-1 and C-2 were evaporated to dryness to give a brown-yellow residue which was washed with ether to yield a yellow solid (C-3, 3.4 g). Addition of methanol to the ether washings gave a light brown solid (C-4, 1.2 g), and the final mother liquor was concentrated to yield a tarry material (C). Small samples of C-1, C-2 and C-3 were recrystallized from benzene and then ethyl acetate to give yellow leaflets melting in the range of about 300–305°, and a final recrystallization of the combined crystalline fractions from xylene gave C-5 (4.5 g) melting at 325–330°.

A specimen of C-5 was successively recrystallized from chloroform (twice), benzene-ethyl acetate and benzene (twice), the melting point rising with each recrystallization, to yield pale ivory colored crystals melting at 351–355°. Analysis: found, C, 94.09; H, 5.76. Calculated for picene, $C_{22}H_{14}$, C, 94.93; H, 5.07.

Picene. A sample of C-5 (0.6 g) was chromatographed on alumina (90 g, 29 × 2.5 cm). Fractions of 100 ml were collected and those fractions yielding solids of similar

melting points were combined. Elution with hexane-benzene (1:1) afforded in fractions 1–4 a colorless solid which was recrystallized from chloroform as colorless crystals (50 mg), m.p. 335–345°. This material on sublimation in vacuo and recrystallization of the sublimate from xylene gave colorless crystals with m.p. 348–354°. The mass spectrum of this substance showed the presence of the 'cracking pattern' of picene, with a base peak at *m/e* 278. It also had peaks at *m/e* 292 (13% of base peak), 306 (4.5%). These differ from the base peak (the molecular ion of picene) by 14 and 28 mass units, and probably represent small amounts of alkyl picenes.

Fractions 5–12 gave a colorless solid which was recrystallized once from chloroform and thrice from xylene to yield colorless leaflets, m.p. 364–365°, which did not depress the melting point of authentic picene (m.p. 366°). The UV-spectrum of this material was identical with that of picene: λ_{max} (in benzene): 286.5 nm (log ϵ 4.95); 304 (4.48); 315 (4.20); 329 (4.31); 357.5 (2.87); and 376 (2.85). The mass spectrum showed a molecular ion peak (the base peak) at *m/e* 278, but it also showed a small peak at 292 (9% of base peak). The mass spectrum was, however, substantially identical with that of authentic picene. Analysis: found, C, 94.82; H, 5.22. Calculated for $C_{22}H_{14}$, C, 94.93; H, 5.07; mol. wt., 278.

Chrysene. The brownish residue from the combined mother liquors and washings (C) was chromatographed on alumina. Elution with hexane furnished a colorless solid in fractions 4–9 which was recrystallized thrice from hexane to give colorless crystals (CH, 20 mg), melting at 224–230°. The UV-spectrum of this material was nearly identical with that of authentic chrysene. The mass spectrum showed that, while it gave the 'cracking pattern' of chrysene, it was a mixture. The base peak appeared at *m/e* 228, but strong peaks appeared at 242 (42% of base peak), 256 (9.5%) and 270 (4.8%), probably

¹ Contribution from the Departments of Chemistry (No. 2078) and Geology, University of California, Los Angeles.

² F. E. WRIGHT and E. T. ALLEN, *Am. Miner.* **75**, 169; *Chem. Abstr.* **24**, 5259 (1930).

³ H. HABERLANDT, *Chem. Erde*, **13**, 212 (1940–41); *Chem. Abstr.* **35**, 3928 (1941).

⁴ K. TUCEK and J. KOURIMSKY, *Rozpr. čsl. Akad. Ved*, **63** (3), 1 (1953); *Chem. Abstr.* **49**, 14590 (1955).

⁵ V. A. FRANK-KAMENETSKII and T. P. MALEEVA, *Dokl. Akad. Nauk. SSSR* **88**, 135 (1953); *Chem. Abstr.* **49**, 11511 (1955).

⁶ I. A. BUD'KU and V. A. FRANK-KAMENETSKII, *Zap. vses. min. Obsch.* **86**, 716 (1957); *Chem. Abstr.* **52**, 7037 (1958).

⁷ I. V. GRINBERG and V. M. SHIMANSKI, *Mineralog. Sb., L'vov* **1954**, No. 8, 95; *Chem. Abstr.* **52**, 15354 (1958).

⁸ H. STRUNZ and B. CONTAG, *Neues Jb. Miner. Mh.* **7**, 19 (1965); *Chem. Abstr.* **62**, 2482 (1965).

due to the presence of alkyl homologs of chrysene. This was substantiated by the proton magnetic resonance spectrum of the material present in the mother liquors from recrystallization of the crude chrysene, which showed signals in the region characteristic of aromatic methyl groups. Analysis of material CH: found, C, 94.50; H, 5.73. Calculated for chrysene, $C_{18}H_{12}$, C, 94.70; H, 5.30; mol. wt., 228.

Rechromatography of CH on alumina gave on elution with hexane-benzene (4:1) a colorless compound which crystallized from hexane as shining, colorless leaflets, m.p. 256–257°, which did not depress the melting point of authentic chrysene (m.p. 257–259°). The mass spectrum of this material was essentially identical with that of authentic chrysene: it showed a molecular ion peak at m/e 228, and the higher peaks, at intervals of 14 mass units, present in the original material (CH), were absent. The UV-spectrum (in 95% ethanol) was identical with that of chrysene: λ_{max} 220 nm ($\log \epsilon$ 4.58); 241 (4.35); 258.5 (4.93); 268 (5.17); 282.5 (4.11); 294 (4.08); 306 (4.11); 320 (4.11); 343 (2.65); 351 (2.20); and 361 (2.71).

Fractions 10–16, also eluted with hexane-benzene, afforded a colorless solid which crystallized from chloroform-hexane as colorless platelets, m.p. 235–250°. Rechromatography of this substance on alumina and elution with hexane-benzene (10:1) gave a colorless solid which, after recrystallization from hexane, had m.p. 250–262°. The mass spectrum showed that it was a complex mixture with a base peak at m/e 256. Although the 'cracking pattern' of chrysene could be discerned, the chrysene M^+ peak at 228 was only 25% of the base peak, and the peak at 242 was 38% of the base peak.

X-ray powder diagrams. The X-ray powder diagrams of the picene and chrysene from the mineral were compared with those of the authentic specimens, and showed complete identity, thus providing further confirmation of their identities.

Discussion. The origins of coronene, the organic constituent of pendletonite⁹, picene and chrysene as massive constituents of these organic minerals, are not known with certainty. MALEEVA¹⁰ has suggested that Transcarpathian curtisite, which is accompanied by bitumens, may be a product of the distillation (sic) of organic substances contained in the sedimentary stratum. Since curtisite is present in veins of probably magmatic origin in sedimentary and metamorphic rocks, it is possible that these stable, polycyclic aromatic hydrocarbons have been derived by pyrolytic transformations of organic matter and deposited, by distillation or from solution, in the formations in which they are now found. It is to be recalled that chrysene and methylated picenes (but not coronene) are among the products formed in the high temperature aromatization of steroidal and triterpenoid compounds. It is worthy of note, however, that the Skaggs Springs deposits are not associated with bituminous or petroleum deposits.

Zusammenfassung. Das massive organische Mineral Curtisite (Idrialite) besteht aus Picen, Chrysen und, wie aus den Massenspektren der rohen Proben zu entnehmen ist, deren Methyl-homologen.

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⁹ J. MURDOCH and T. A. GEISSMAN, *Am. Miner.*, in press.

¹⁰ T. P. MALEEVA, *Mineralog. Sb. L'vov* 8, 85 (1954); *Chem. Abstr.* 52, 989 (1958).

1,2-Methylen-19-nor-17 α -acetoxy-progesteron

Die aufgefundenen starken hormonellen¹, proteinanabol² und antiandrogenen³ Wirkungen in der Reihe der 1,2 α -Methylen-Steroide liessen uns die Synthese des 1,2 α -Methylen-19-nor-17 α -acetoxy-progesterons interessant erscheinen.

Das Fehlen der dirigierenden C_{10} -Methylgruppe lässt eine strukturelle Zuordnung der nach der COREY⁴-Methylenierung von Δ^1 -3-Keto-A/B-cis- bzw. A/B-trans-Steroiden zu erwartenden 1,2-Methylen-Verbindungen in Analogie zu C_{10} -Methyl-Steroiden^{5,6}, nicht ohne weiteres zu.

Deshalb synthetisierten wir sowohl das 1,2 α -Methylen-19-nor-17 α -acetoxy-progesteron als auch das 1,2 β -Methylen-Isomere, um aus deren physikalischen Daten Strukturmerkmale zu finden.

Aus Δ^5 -Pregnen-3 β ,17 α ,19-triol-20-on-17-acetat⁷ (1) entsteht durch Hydrierung (PtO_2 /Methanol) das entsprechende 5 α -Pregnan-Derivat (F. 231–233°C) und daraus durch anschliessende Oppenauer-Oxydation das 5 α -Pregnan-17 α ,19-diol-3,20-dion-17-acetat (2a) (F. 232,5–234,5°C). Nach Acetylierung von (2a) zu (2b) (F. 152–153°C) wird über Bromierung/Bromwasserstoffab-

spaltung die Δ^1 -Doppelbindung zu (3b) (F. 157,5–159°C, UV: ϵ_{230} = 9830) eingeführt.

Die 19-Acetoxy-Gruppe in (3b) wird mit dem alkalischen Dowex-Ionen-Austauscher verseift zum 19-Alkohol, (3a) (F. 263–266°C) dessen Chromsäure/Pyridin-Oxydation den 19-Aldehyd (4) (F. 232–234°C) ergibt. Durch Säurespaltung wird die C_{10} -Formylgruppe eliminiert zu (5b) (F. 181,5–184°C, UV: ϵ_{230} = 11100). Nach alkalischer

¹ R. WIECHERT und F. NEUMANN, *Arzneimittel-Forsch.* 15, 244 (1965).

² F. NEUMANN und R. WIECHERT, *Arzneimittel-Forsch.* 15, 1168 (1965).

³ F. NEUMANN, W. ELGER und R. v. BERSWORT-WALLRABE, *Dt. med. Wschr.* 92, 360 (1967).

⁴ E. J. COREY und M. CHAYKOVSKY, *J. Am. chem. Soc.* 84, 867 (1962).

⁵ H.-G. LEHMANN, *Dt. Bundespatent* 1.183.500 (1962, Schering AG); G. W. KRAKOWER und H. A. VAN DINE, *J. org. Chem.* 31, 3467 (1966).

⁶ R. WIECHERT, O. ENGELFRIED, U. KERB, H. LAURENT, H. MUELLER und G. SCHULZ, *Chem. Ber.* 99, 1118 (1966).

⁷ A. BOWERS, *U.S. Patent* 3.065.228 (1962, Syntex S.A.).