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On Julius Planer's 1861 paper "Notiz über das Cholestearin" in *Annalen der Chemie und Pharmacie**

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Brief review of the literature on the history of thermotropic liquid crystal discovery and the role of the observations reported by Julius Planer in his note published almost 150 years ago.

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In his celebrated article [1], widely known as the first publication on liquid crystals, Friedrich Reinitzer among others gives a proper credit for his finding to the work of Julius Planer [2] published twenty seven years earlier. In particular, Reinitzer wrote: "Thus, Planar reports that cholesteryl chloride displays a violet colour during cooling from the melt which vanishes again upon solidifying. Raymann reports similar observations on the same substance. Lobisch reports that cholesterylamine when melted displays a bluish-violet 'fluorescence' and also mentions the occurrence of the same phenomenon in the case of cholesteryl chloride. I myself observed a similar phenomenon in cholesteryl benzoate, and Latschinoff reports for the silver salt of cholesteric acid, which is formed by oxidation of cholesterol, that it turns steel blue when melted, which fact is probably to be explained in the same way".

The selective reflection in cholesteryl chloride by Planer in 1861 and in cholesteryl benzoate by Reinitzer in 1888 unambiguously proves observation of the cholesteric liquid crystal phase. However, neither Planer nor Reinitzer did not pursue studying liquid crystals further. The research was continued by Otto Lehmann, who realized that this is a new phenomenon and started its systematic study resulting in the paper [3] published in 1889. Many scientists cite only the Reinitzer's article when referring to these pioneering observations. In the modern literature, several textbooks give credit for the observation of liquid crystalline state to Planer, some to both Planer and Reinitzer, whereas some give credit for this important observation to Reinitzer alone. Interestingly, both Reinitzer [1] and Planer [2] papers originally were published in German. However, an English translation of the Reinitzer's article was already republished in 1989, i. e., after hundred years [4]. The goal of this note is to introduce the Planer's 1861 paper to a wider condensed matter community. To show the importance of this paper, in what follows we present the selected citations of the Planer's observations that we were able to locate in modern literature, in particular, in some of the textbooks dedicated to the history of liquid crystals discovery.

To proceed, let us first say a few words on this Planer's 1861 paper [2] (a translation of this paper into English can be found in this issue). From the paper one can learn that Planer is primarily

*Justus Liebigs Annalen der Chemie (often cited as just Liebigs Annalen) was one of the oldest and most historically important chemistry journals worldwide [http:www.nationmaster.com/encyclopedia/Annalen-der-Chemie]. Founded in 1832, it was edited by Justus von Liebig with Friedrich Wohler until Liebig's death in 1873. In 1997 it was merged with a number of other leading national European chemistry journals to continue as the European Journal of Organic Chemistry: History of the journal's name: Annalen der Chemie, 1832–1839; Annalen der Chemie und Pharmacie, 1840–1872; Justus Liebigs Annalen der Chemie und Pharmacie, 1873–1874; Justus Liebigs Annalen der Chemie, 1875–1944 and 1947–1978; Liebigs Annalen der Chemie, 1979–1994; Liebigs Annalen, 1995–1997.

interested in describing the synthesis of cholesteryl chloride. Most of the article is devoted to the details of the compound synthesis and sample preparation (this work, in particular, was important from the viewpoint of assuming that the molecular formula of cholesterol is $C_{27}H_{46}O$ and that of cholesteryl chloride is $C_{27}H_{45}Cl$ [4]). However, Planer also describes the observation of (what we now know as) the liquid crystal state exhibiting selective color reflection in the cholesteric phase. He writes that when slowly crystallized from alcohol/ether, the cholesteryl chloride sample shows long needle-like crystals. These crystals melt at temperature close to the boiling point of water (in good agreement with the current data for the crystal-isotropic phase transition for cholesteryl chloride at approximately (95–98)°C). Upon cooling, the molten (in current terminology this would be "liquid crystalline") substance exhibits a lively violet color when viewed in reflected light and yellow-green color when viewed in transmission light. According to Planer, upon completion of the cooling process, the sample again adopts the crystalline state and the colors vanish.

Interestingly, that besides the already mentioned 1888 paper by Friedrich Reinitzer[1] and its 1989 English translation[4], the chronologically next reference to the Planer's 1861 paper is the 1988/1989 article by Semynozhenko and Lisetski [5]. This article is in Russian and is dedicated to the hundred anniversary of the liquid crystal discovery. At the beginning of this article there is a paragraph that reads[1]: "Against the common tradition one can claim that liquid crystalline state of matter was known at least 27 years earlier [than it has been reported by Reinitzer in 1888 (A.T.)]. In 1861 the journal *Annalen der Chemie und Pharmacie* has published the paper by Prof. Planer from the Lviv University titled "Notiz über das Cholestearin"[2]. In this paper, dedicated to the study of cholesteryl forms there is a phrase: "... long needle-shaped crystals ... melt roughly at the boiling point of water; during the cooling process, the molten substance exhibits a lively violet color in incident light, a yellow-green color in transmitted light; when cooling is complete, it adopts a crystalline consistency again." There is no doubt that using modern terminology, Planer has observed selected reflection from a plane texture of cholesteric liquid crystal."

Further references to the Planer's 1861 paper can be found in textbooks [6–10]. Some of them are:

1) *Nematic and Cholesteric Liquid Crystals: Concepts and Physical Properties Illustrated by Experiments* by Patrick Oswald and Pavel Pieransky, Liquid Crystals Book Series, Vol. 4. Published by CRS Press Taylor & Francis Group. In Part A of this book, *Overview* there is Chapter A1 *Some history*, and on page 12 there is Section 1.3 titled *"Observation of the surprising behavior of cholesteryl esters by Planer and Reinitzer: thermotropic liquid crystals"*. It starts: "Friedel knew that liquid birefringent phases existed not only in solutions, but also in pure bodies. Once more, it is the biologists who set the physicists on the right track. The story begins with cholesterol, a substance extracted from plants. In the 19th century, its chemical structure was still unknown; however, it was classified among alcohols, since one could prepare cholesteryl esters by reaction with fatty acids. The biologist Planer in 1861 and Reinitzer in 1888 noticed its opaqueness and the iridescent colors exhibited by these esters upon melting from the crystalline phase or upon cooling from the isotropic liquid".

2) *Liquid Crystals: Nature's Delicate Phase of Matter* by Peter J. Collings, 2nd Edition, Published by Princeton University Press, 2002, 204 pages. In Chapter 2 of this book, *The story of liquid crystals*, on page 20 there is a paragraph that reads: "The third type of experiment performed in this time period was one with compound synthesized from cholesterol. P. Planer in the city of Lvov (now part of Ukraine), the German chemist W. Lobisch and B. Raymann in Paris all reported that this compound displayed striking colors when cooled. Although it certainly was unusual phenomenon, none of these people had any idea that these colors were coming from the phase of matter other than solid or liquid phase. As will be evident in the next section, these observations were extremely similar to the experiments that forty years later led directly to the discovery of liquid crystals".

3) *Liquid Crystals In Complex Geometries* by G.P. Crawford and S. Zumer. Published by Taylor & Francis Ltd, London. – 1996. In paragraph 8.2. of this book, *Cholesteric liquid*

[1]Translation by author.

crystals, on page 190: "Cholesteric liquid crystals with sufficiently short pitch show selective reflection of circularly polarized light (de Vries, 1951). The discovery of liquid crystals (Planer 1861; Reinitzer, 1888) and one of their first applications were due to this phenomenon".

4) *Chirality in Liquid Crystals* by H.-S. Kitzerow and C. Bahr. Partially Ordered Systems Series. Published by Springer. – 2001. In Preface of this book there is: "Probably even the first observation of liquid crystals by Planer (1861) and Reinitzer (1888) were due to the conspicuous selective reflection of the helical structure that occurs in chiral liquid crystals".

5) *Physical properties of liquid crystals*, Edited by D. Demus, J.W. Goodby, G.W. Gray, H.W. Spiess and V. Vills, Wiley-VCH, 1999. In Chapter I of this book, *Introduction and Historical Development* by G.W. Gray, on page 2 there is a paragraph that reads: "In his article, Reinitzer acknowledges that other workers before him had observed curious color behavior in melts of cholesteryl systems. He mentions that Planer in Russia[2] and Raymann in Paris had noted violet colors reflected from cholesteryl chloride and that Lobish in Germany had observed a bluish-violet fluorescence in the case of cholesteryl amine and cholesteryl chloride".

Summarizing, Planer's observations described in 1861, i. e., an almost 150 years ago, are in good agreement with the currently-known liquid crystalline phase behavior of commercially-available cholesteryl chloride, which exhibits a monotropic cholesteric phase observed upon sample cooling. Certainly, in his article, Planer does not use the modern terminology such as "cholesteric phase", "liquid crystal", and "selective reflection". Moreover, even chemical formula of cholesterol was not known at that time. However, this Planer's 1861 work seems to be the first documented observation of the thermotropic liquid crystal and its phase behavior, and is equally important to the papers of Reinitzer [1] and Lehmann [3].

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[2]Planer used to work at the University in Lviv [called Lemberg in Planer's 1861 paper] that belonged to Austrian Empire at that time. Lviv never was a part of Russia. (A.T.)

До статті 1861 року Юліуса Планера “Замітка про холестерин”, опублікованої у *Annalen der Chemie und Pharmacie*

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Короткий огляд літератури по історії відкриття рідких кристалів та про роль спостережень, занотованих Юліусом Планером у його статті, яка була опублікована майже 150 років тому.

Ключові слова: *історія науки, хлорид холестерилу, монотропна холестерична рідкокристалічна фаза*