the addition product dissolved in alcohol and this solution evaporated to remove the alcohol. After this treatment a thick syrup was obtained. This was then dissolved in a little acetic acid and water added when we obtained 2.5 g. of a slightly gummy product, but well crystallized in the form of needles. The substance showed little tendency to crystallize from the ordinary solvents. It was finally obtained pure by dissolving in ether and then precipitating by dilution with petroleum ether. In this manner the acid was finally freed from gum and obtained in a colorless condition. It melted at 178–179° as observed by Einhorn and Grabfield.[1] Analysis (Kjeldahl):

Calc. for $C_{10}H_9O_5NBr_2$: N, 3.65; found: N, 3.71.

NEW HAVEN, CONN.

ON THE BLUE HYDROCARBON OCCURRING IN SOME ESSENTIAL OILS.

[PRELIMINARY NOTE.]

BY ALFRED E. SHERNDAL.

Received November 7, 1914.

Scattered through the literature of the essential oils are frequent descriptions of blue fractions obtained in the distillation of various oils, the most intensely colored sections distilling between the temperatures, 275° and 300°, or higher. A few oils, such as those of chamomile, wormwood, and cubebs, are notable for their blue or green color before fractionation.

In a few instances where intensely colored fractions have been obtained, the investigators have thought themselves in the possession of a pure substance.[2] In most cases however, they have recognized that the color is due to the presence of some colored substance other than the bodies making up the bulk of the oil, and the usually accepted view has been, that this is an oxygenated substance related to the sesquiterpene alcohols.[3]

Semmler[4] has summarized the literature covering these oils, and remarks that there are two views possible in regard to the blue fractions: either the greater part is colorless, and appears colored owing to the presence of a small amount of an intensely blue substance, or the sections boiling between 275° and 300°, are actually composed principally of a blue compound. That the latter is not the case, however, is evident from a survey of the literature, since the only purification method resorted to is a fractionation out of oils which contain large amounts of sesquiterpenes and sesquiterpene alcohols, with boiling points also ranging from 250°

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[1] *Loc. cit.*

[2] Piesse, "Art of Perfumery," 1879, p. 57.

[3] Bartelt, "Die Terpene und Campherarten," 1908, p. 4.

[4] *Die Aetherischen Öle*, 3, p. 260.

to 300°. For the same reason no importance can be assigned to the various analyses of the blue fractions.

Blue products have also been obtained in the laboratory by various reactions, usually from oils composed principally of sesquiterpenes and sesquiterpene alcohols. In such cases, there seems always to have taken place a dehydration and subsequent oxidation of a sesquiterpene alcohol, or a direct oxidation of a sesquiterpene. For example, Wallach and Tuttle,[1] by the action of phosphoric anhydride, or zinc chloride on guaiol, the alcohol of guaiac-wood oil, obtained a blue sesquiterpene. They considered the color to be due to the presence of a small amount of an oxidation product. On the other hand, Gadamer and Amenomija[2] obtained a guaiene without blue color, by dehydrating guaiol with potassium acid sulfate.

An interesting observation was made by Hentschel and Wislicenus[3] who found, on rectifying the products of the dry distillation of calcium adipate, that the fraction boiling between 135° and 145° at 30 mm., had a blue color resembling that of Roman chamomile.

Semmler and Jakubowicz[4] obtained blue oils by heating the gurjunene sesquiterpenes in autoclaves filled with air or oxygen.

As far as the writer knows, no connection has as yet been assumed between the blue oils, and the striking color reactions which have frequently been observed when oils consisting largely of sesquiterpenes or sesquiterpene alcohols are treated in dilute solutions with mineral acids. An experiment seems, however, to indicate that such a connection may exist. If oil of gurjun balsam be dissolved in acetic anhydride, and a small amount of sulfuric acid added, the mixture becomes intensely blue, and on diluting with water and distilling the oil in a current of steam, a deep blue distillate is obtained.

Very many oils containing sesquiterpenes and related compounds, give strong color reactions when dissolved in acetic anhydride containing a trace of sulfuric acid. Of the oils examined in this laboratory, those of gurjun, amyris, and guaiac-wood give strong blue or violet colors under these conditions; santal and cedar-wood, none. This test may be used to advantage to detect adulterants in some oils, such as santal.

As to the nature of this blue constituent, nothing whatever has so far been definitely ascertained, for the reason that, as already indicated, it has not been isolated in a state of even approximate purity. A remarkable fact is that a substance with such intense color should possess a comparatively low boiling point, indicating a simple molecule. Semmler[5] suggests the possibility of a bimolecular structure, closely related to

[1] *Ann.*, **279**, 397 (1894).

[2] *Archiv. der pharm.*, **241**, 33 (1903).

[3] *Ann.*, **275**, 312 (1893).

[4] *Ber.*, **47**, 2252–9 (1914).

[5] *Aetherischen Öle*, **3**, p. 266.

the sesquiterpenes, which on distillation dissociates, and on condensing, again forms a bimolecular compound, with a group similar to that in indigo: $>C : C<$. As a rule, however, the assumption has been made that the blue substance is an oxygenated compound of alcoholic nature.

The following work describes the isolation of this body in a state of purity, as shown by the analysis and reactions. As a pure substance, its remarkable properties become even more striking than before. The analysis shows it to be a highly unsaturated hydrocarbon, but the peculiar grouping of atoms to which it owes its unique properties is more difficult to speculate upon than ever.

The property which was utilized to isolate the substance, and which has heretofore not been noted, is its solubility in mineral acids of certain strengths. The method of preparation was as follows:

Fifty grams of a very blue fraction, freshly steam distilled, were shaken with 10 g. of 63% sulfuric acid, and the mixture allowed to settle over night. The acid layer was then drawn off, diluted with water, and extracted with petroleum benzine until no more blue color was taken up. The benzine solution, dark blue in color, was then shaken out with 85% phosphoric acid until no longer blue, the dark red acid solution drawn off, diluted with water, and extracted with ether. The residue from the evaporation of the ether amounted to 0.141 g., or 0.28%. This, redissolved in 50 g. of a pale yellow oil, gave a mixture with about the same tint as the original, showing that there was no appreciable loss in the preparation.

Larger quantities, isolated in this way, were further purified by distillation with steam, and finally *in vacuo*. The substance thus obtained was a slightly viscid liquid, intensely blue in thin layers, black in quantity, with a weak phenolic odor, suggesting thymol, especially when warm.

Subst., 0.2118 and 0.2294 g. gave CO_2 0.7054 and 0.7587 g.; H_2O, 0.1478 and 0.1903 g.; calc. for $C_{15}H_{18}$: $C = 90.84$; $H = 9.15$; found: $C = 90.83$ and 90.20; $H = 9.23$ and 9.28.

The molecular weight determination was made by Dr. Earl F. Farnau, of New University, by the cryoscopic method, using benzene as solvent. Found: 187.2 and 193.4 (av., 190.3); calc. for $C_{15}H_{12}$: 1.98.

The compound is, then, a hydrocarbon, having most probably the formula $C_{15}H_{18}$, and for it the writer would preserve the name "azulene," proposed in 1863 by Piesse,[1] one of the earliest investigators, for the blue fraction which he obtained from oil of worm-wood.

The specific gravity at 25° is 0.9738, when freshly steam-distilled. Exposed to light and air, it is gradually converted into a brown resin. Distilled at atmospheric pressure, the boiling point rises from 295° to 300°, leaving a tarry residue, soluble in ether with a brown color. At about 25 mm. azulene distils from 185° to 195°, leaving a brown residue of about 5%. Since the product had been previously distilled with steam, this

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[1] *Compt. rend.*, 57, 1016 (1864).

shows that it cannot be distilled without change under these conditions. When evaporated on the water-bath in an open dish, a brown resin, amounting to 10%, or more, remains.

Azulene is readily soluble in most organic solvents. In 95% alcohol it is miscible in all proportions; in more dilute alcohol the solubility is much less, but even 50% alcohol takes up enough to be tinted, a decided blue.

Its solubility in strong inorganic acids, which makes its isolation possible, is especially remarkable. In 60 to 65% sulfuric acid, azulene dissolves to a clear yellow, strongly fluorescent solution; on dilution with water, it is thrown out again as a blue oil, apparently unchanged. It also dissolves in 50% sulfuric acid, but less readily. The solution in phosphoric acid is remarkable for its fluorescence; reddish yellow by transmitted light, intense apple green by reflected light. These acid solutions can be extracted with benzine without removing any azulene, and by repeating several times, a product can be obtained, free from sesquiterpenes or alcohols.

Azulene is strongly resistent to the action of even strong sulfuric acid. When heated with two parts of 94% acid for fifteen hours on the water-bath, a dark brown solution results, which, on diluting with water, again yields the blue oil. Strong formic acid dissolves it with a green color, but in acetic acid the color remains unchanged, as in the neutral solvents. On mixing dry ether solutions of azulene and hydrochloric acid, no change in color was observed.

Nitric acid in acetic acid solution produces yellow amorphous substances, not further examined.

The oxidation of azulene with permanganate has so far yielded only lower fatty acids.

It is not attacked by sodium in hot alcohol, nor does heating with strong alkali affect the color.

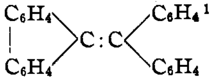
By the action of acetic anhydride and sulfuric acid, a substance was obtained, evidently a sulfonic derivative, which was soluble in water. On adding sodium carbonate in excess a sodium salt separated out, which was recrystallized from hot water. The water solution of the salt is colored violet, and changes to a light green on acidifying. If then shaken with ether, the latter becomes violet, and this color is again taken out by shaking with alkali.

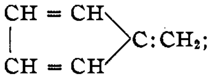
The sodium salt, on heating, gives off blue fumes which condense to a blue oil; at the same time sulfur dioxide is liberated.

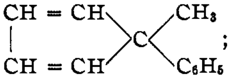
On standing three months in a corked bottle, a preparation of the sodium salt had decomposed into a mixture of oil and resin.

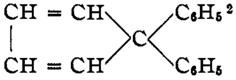
The water solution gives blue precipitates with barium and calcium solutions, and is decolorized by bromine water.

It appears established that azulene is closely related to the sesquiterpenes. From no other class of compounds have hydrocarbons been obtained which show such intense color. Colored hydrocarbons which have so far been prepared, are characterized by complex structure or a dense arrangement of the atoms, the intensity of the color increasing with the size of the molecule; for example:




1. Yellow.


2. Red liquid.



3. Deep red solid.

Rubicen, a red hydrocarbon, $C_{26}H_{14}$, m. p. 306°.[3]

It is obvious that in azulene we have an entirely different and unique chemical compound. We hope, in a subsequent communication, to collect further data on this interesting substance.

The writer wishes here to acknowledge his indebtedness to Dr. Francis D. Dodge for helpful suggestions as well as for aid in obtaining material used in connection with the above work.

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[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXIX. GEOMETRICAL ISOMERISM IN THE HYDANTOIN SERIES.

BY TREAT B. JOHNSON AND SIDNEY E. HADLEY.

Received November 19, 1914.

In order that geometrical isomerism may be shown in an unsaturated carbon compound, two fundamental conditions must be fulfilled: first, that the molecule contains a double bond between two of its carbon atoms, and second, that the two radicals linked to each of these two carbon atoms must be different. Theoretically, the accepted structural formula of an *aldehyde-hydantoin* condensation product (I) fulfills both these conditions and consequently a hydantoin of this type might be expected to occur in *cis-* and *trans-*modifications. The constitutions of such isomeric forms might be expressed by the two graphic Formulas II and III, respectively. Several unsaturated compounds of this type (I) have been prepared in this laboratory, but hitherto we have not detected the occurrence of more than one modification. In this paper we will now discuss the first case of this type of isomerism so far observed in the hydantoin series.

[1] Graebe, *Ber.*, 26, 2334 (1892); 25, 3146 (1891).

[2] Thiele, *Ber.*, 33, 668, 851, 3395 (1900); *Ibid.*, 36, 842 (1903); *Ann.*, 319, 226 (1901).

[3] Pummerer, *Ber.*, 45, 294 (1912).