XXXV.—*Studies of the Terpenes and allied compounds. The nature of Turpentine oils, including that obtained from Pinus Khasyana.*

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AMONG the compounds which attracted my attention when I began to study terpenes and allied compounds, now many years ago, was the crystalline substance of the formula $C_{10}H_{18}O_2$, briefly described by Sobrero, in 1851 (*Compt. rend.*, **33**, 66; *Annalen*, **80**, 106), obtained by exposing oil of turpentine together with moist oxygen to sunlight—a substance which was rendered none the less interesting by Sobrero's statement that, when boiled with dilute sulphuric acid, it was converted into a volatile product having a strong odour resembling that of camphor as well as that of turpentine.

It was to be supposed that Sobrero had worked with French oil of turpentine, and therefore this was first submitted to air-oxidation in sunlight; the results obtained were in complete accordance with the account given by Sobrero. On substituting American for French turpentine, a substance was obtained identical with that resulting from the oxidation of the French hydrocarbon, except in its optical characters.

These results led me to study the behaviour of oils from various sources containing $C_{10}H_{18}$ hydrocarbons, in the hope that information might be gained which would serve to elucidate the complex problem presented by the existence of an apparently infinite variety of essential oils.

It was soon ascertained that a clear atmosphere and a bright, high sun—conditions which are always exceptional in London—were requisite for the formation of the crystals. It has rarely happened that crystals began to form until late in May, and each exposure has usually lasted from two to three months. Necessarily, therefore, the information has been acquired at a slow rate. The earlier experiments were carried on at the London Institution, Finsbury Circus, on the roof—a particularly unsuitable locality. But very little progress was made during the subsequent years in which the arrangement of the laboratory and the organisation of the teaching, first at the Finsbury Technical College, and very shortly afterwards at the Central Institution, claimed my attention. During the past three summers, the experiments have been regularly resumed at the Central Institution, and it has been possible, chiefly owing to the important assistance which one of my students, Mr. Pope, has rendered me in submitting the products to crystallographic examination, to collate the scattered results.

The conclusions arrived at are, I venture to think, of some importance, and justify the hope formed at an early period of the enquiry, that a comparative study of the air-oxidation products from various oils would not be without interest.

The following passage from the second edition of my *Introduction to the Study of Organic Chemistry* (London: Longmans, Green, & Co.), published in 1880, is here quoted as an indication of the views which guided me in the enquiry, and which are justified in the present note:—

“The hydrocarbons of the formula $C_{10}H_{16}$, derived from plants, may be divided into two classes, viz., (1) those boiling at about 156° , which are conveniently termed *terpenes*, as they are the chief constituents of ordinary turpentine oils; and (2) those boiling at about 176 – 178° , which may be termed *citrenes*, as they are the chief constituents of the oils derived from the various species of *Citrus*. The terpenes and citrenes are all capable of rotating the plane of polarisation of light, but no two plants furnish terpenes or citrenes of identical rotatory power, and often different parts of the same plant yield different products; the different terpenes appear, however, to agree in all other physical properties, and also in their chemical properties; and the same is true of the different citrenes. It is probable that the number of isomerides of the formula $C_{10}H_{16}$ is very much smaller than has been supposed, and that the differences observed in the rotatory powers of the hydrocarbons from various sources are due to their being mixtures in varying proportions of two or more isomerides” (p. 106).

In a paper read before the Society of Chemical Industry, in 1882 (their Journal, p. 478), detailing the results of the examination of a very large number of samples, representing many thousand barrels of different kinds of commercial turpentine, after calling attention to the almost absolute uniformity of the French oil and the wide variation which was noticeable on comparing the rotatory powers of different samples of the American oil, I stated that I had been led to think it not unlikely that the low dextrorotatory power of American turpentine is due “to the presence of a lævorotatory turpentine; this would serve to explain the difference in optical character of products from different localities.” That this is actually the case I have no longer any doubt. The crystalline product from French turpentine is all but uniform; that from American turpentine is but rarely so: the earlier crystallisations usually consist of a substance which may be said to be the image of that from the French oil, but although the crystals in later fractions may exhibit the same melting point as those separated at an early stage, the rotatory power of the fraction as a whole is lower. The explanation of the difference was discovered

in the course of the examination of a very beautiful turpentine oil from British Burmah, the produce of *Pinus Khasyana*, which came into my possession in 1881, through the kind assistance of Mr. Thiselton Dyer, the Director of the Royal Gardens, Kew. This oil is in every respect, so far as I have been able to ascertain, the counterpart of French turpentine, but its optical image, and if it could be obtained in quantity would form a most valuable article of commerce; a description of its derivatives will form the subject of a later communication. The air-oxidation product of the Khasyana terpene is the image of that from French turpentine and identical with that obtained from American oil, the difference in the Burmese and American oils being that the former, like the French oil, affords a more nearly uniform product.

When the two varieties of equal opposite rotatory power of the oxidation product are mixed, an inactive substance is obtained of much lower melting point, and it is this substance which is present in considerable quantity in the product from American oil along with the dextrorotatory active form. The melting point observed in the case of the later fractions of the product from American turpentine is a matter of accident, for if the crystal used in the determination be not specially selected from the mass, it may be either the active or the inactive substance.

As the relation of the crystalline oxidation product to the parent hydrocarbon cannot yet be determined, and as it is not improbable that, as in other cases, a molecular change has attended its formation, and that it is not a simple derivative of the hydrocarbon, I would suggest that in giving it a name (as one or both of its oxygen atoms possess alcoholic functions), to recognise its discovery by Sobrero, it be termed *sobrerol*.

The numerous observations which I have made lead me to think that *sobrerol* is only obtainable from the terpenes proper; and that, according as an oil yields either dextro- or lævo-*sobrerol*, or a mixture of either modification with the inactive form, it is to be regarded as containing one or other of the corresponding terpenes, or, as in the case of American turpentine, a mixture of the two. In other words, *that there are but two terpenes*, viz., those represented by the essential components of the French and Burmese oils.

Bearing in mind that we are indebted to Berthelot for the first systematic study of the varieties of turpentine oil, and that he proposed the name *terebenthene* for the characteristic hydrocarbon of such oils, as a matter of justice, it would appear but right to retain this name, terming the two optically different varieties *dextroterebenthene* and *lævoterebenthene*.

So long as we are unaware of the structure of the terebenthenes, it

is impossible to pronounce an opinion on theoretical grounds as to the possibility or otherwise of a distinct inactive modification; the argument from analogy alone makes the existence of such an intra-compensated modification conceivable, however.

The oil which Sobrero obtained by distilling the crystalline oxidation product with acid has proved to be identical with the isomeride of camphor, which Wallach and Otto obtained by the interaction of turpentine and nitrous acid (*Annalen*, **253**, 249), which they have named *pinol*. Being a strict adherent to the view that the *ol* termination should be reserved for hydroxy-derivatives exhibiting alcoholic functions, as the compound does not appear to be of this class, I have ventured to suggest (*Proc.*, 1890, 99) that it should be named *sobrerone*, to indicate its relationship to *sobrerol*. Having succeeded in reconverting "pinol" into the crystalline oxidation product, $C_{10}H_{18}O_2$, Wallach (*Annalen*, **259**, 313) proposes to name the latter *pinol hydrate*; unfortunately this name also appears to me to be inappropriate, for the reason that it is desirable to restrict the term hydrate, as far as possible, to compounds containing so-called water of crystallisation.

The "sobrerone" obtained from the two active modifications of *sobrerol* is optically inactive, and when reconverted into *sobrerol* by Wallach's method, yields the inactive form of the latter.

It is to be mentioned that the proportion of crystalline oxidation product obtained is relatively very small, the greater part of the turpentine being converted into the well known non-volatile viscid oil. Much better results would be obtained, I imagine, if the oxidation were effected under the influence of a tropical sun. As it appeared possible that the viscid oil might contain some *sobrerol*, it was digested with dilute sulphuric acid and steam-distilled; a considerable amount of volatile oil was obtained, but hitherto all attempts to separate "sobrerone" from this have failed. Notwithstanding that the greater part of the hydrocarbon is converted into products other than *sobrerol*, as dextro- and lævo-terebenthene are apparently oxidisable at the same rate under similar conditions, it is to be supposed that when a mixture is oxidised the crystalline product will regularly betray its origin, unless, indeed, pressure have a perceptible influence on the rate of oxidation. On oxidising American turpentine fractionally, that is to say, if, when the oxidation has gone on for some time, the crystals are collected and the unoxidised oil is separated by steam-distilling and re-exposed to oxidation, &c., a series of products are obtained, the first of which has a higher dextro-rotatory power than subsequent fractions. This is exactly what should happen if dextroterebenthene be the chief constituent of American turpentine.

It appears not unlikely that sobrerol may occur naturally ; I have, however, only on one occasion met with evidence of its presence. In the course of the investigation of so-called terebene which Professor Tilden and I carried out several years ago, I had occasion to distil a large quantity of American turpentine which I had received in a wooden barrel. The most volatile portion was collected separately, and put away in a blue Winchester quart, in a dark cellar ; after a time, the sides and bottom of the bottle were found to be encrusted with crystals, which were collected and recrystallised from alcohol. Only a very few grams of the crystals were thus obtained from 10 gallons of turpentine. This substance has proved to be *inactive* sobrerol, chiefly mixed with some dextrosobrerol.