CCLXXX. REACTIONS OF TERPENES WITH ANTIMONY TRICHLORIDE.

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ANTIMONY trichloride in chloroform solution yields colour reactions with fish-liver oils and fish-liver oil concentrates [Carr and Price, 1926], with carotenoid pigments [Moore, 1929; Euler *et al.* 1928], with certain sterols and their derivatives [Karrer, 1928; Wokes, 1928; Heilbron and Spring, 1930; Seel, 1931], and with certain five-membered monoheterocyclic compounds [Levine and Richman, 1933].

Unsaturation and the terpene groupings are common chemical factors in carotenoid pigments, in vitamin A and in sterols occurring in the plant and animal organism, according to Karrer *et al.* [1929; 1930; 1931] and to Heilbron, Morton and Webster [1932]. Norris and Church [1930] have studied the antimony trichloride reaction with relation to some thirty-four essential oils. They reported that these oils yield various shades of yellow, brown and red. Wormwood oil, however, gave a green colour, etheral oil a purple and cedar wood oil an intense permanent blue, which has an absorption band with a maximum at $580 m\mu$. Corbet *et al.* [1933] reported several terpenes as interfering substances in the antimony trichloride test for vitamin A in cod-liver oil.

We have studied the antimony trichloride reaction among compounds of the terpene group. The reagent used was that of Carr and Price. Antimony trichloride, washed three times in chloroform (U.S.P.) containing 1 % alcohol, was dried in the desiccator. A solution of this product was made by adding 30 g. to 100 cc. of chloroform. The clear solution was decanted and used as the reagent. The terpenes were made up to 20 % solutions or mixtures in chloroform. Three to four drops of the chloroform mixture were added to 2 cc. of the antimony trichloride reagent. The reaction mixture containing terpene and reagent we have designated as Reaction mixture A.

We have also adopted a procedure in which three to four drops of the terpene in chloroform are added to 0.5 cc. of acetic anhydride before final admixture with antimony trichloride solution. The acetic anhydride prevents the formation of precipitates in the reaction mixture. It also acts as a catalytic agent, inducing a more vigorous reaction and a more intense display of colour changes. The reaction mixture containing acetic anhydride we have designated as Reaction mixture B. The results are given in Table I.

The reaction is usually characterised by a succession of colour changes. In many cases the final colour is purple. Citral in the presence of acetic anhydride changes from dark yellow to brown, to wine, to purple and finally to dark blue. Ionone is a terpene which may be obtained by the oxidation of carotene and of vitamin A [Karrer *et al.*, 1929; 1930; 1931]. This unsaturated terpene gives with antimony trichloride an amber colour changing to wine, and finally on long

Table I. *Reaction of terpenes with antimony trichloride.*

Compound	Chemical nature	Reaction mixture	Results
<i>Camphane group</i>			
1. Borneol	Saturated compound; 1 secondary alcohol group	A	Colourless, slight pink overnight
		B	Colourless; no change
2. <i>d</i> -Camphor	Saturated compound; 1 ketone group	A	Light pink to rose
		B	Colourless, to amber with pink tint
3. <i>d</i> -Camphor	"	A	No colour after 24 hours
		B	No colour after 24 hours
4-7. <i>d</i> -Camphoric acid <i>d</i> -Camphoric anhydride <i>d</i> -Camphorsulphonic acid	"	A	No colour after 24 hours
		B	No colour after 24 hours
8. Fenchyl alcohol	Saturated compound; 1 secondary alcohol group	A	Deep lemon turning cloudy green, finally white precipitate and light brown fluid
		B	Colourless, changing quickly to deep lemon-yellow, brownish yellow, purple and to wine colour with brown tinge
9. Pinene	Unsaturated compound; 1 double bond	A	Creamy, chalky precipitate, to orange precipitate and brown wine-coloured liquid
		B	Colourless, then brown-purple colour, finally light brown
<i>Menthane group</i>			
10. <i>p</i> -Menthane	Saturated hydrocarbon	A	Slightly cloudy, light pink, to salmon colour, gray precipitate
		B	Colourless, to light lemon, light amber and finally light red-brown
11. Cinzole (eucalyptol)	Saturated hydrocarbon; 1 bridge oxygen	A	Cloudy with pink tint. On standing precipitate forms, supernatant liquid orange with purple tint then to purple-brown
		B	Colourless to pink, purple-pink, rose-purple to purple
12. <i>l</i> -Menthone	Saturated compound; 1 ketone group	A	Colourless; cloudy faint pink after 24 hours
		B	Pale straw, to very light tan after 24 hours
13. <i>l</i> -Menthol	Saturated compound; 1 secondary alcohol group	A	No colour
		B	No colour
14. Thujone	Saturated compound; 1 ketone group	A	Slightly cloudy, to light pink, yellow pink, to brown with pink tinge
		B	Slight amber, dark amber, brown
15. Terpene hydrate	Saturated compound; 2 tertiary alcohol groups	A	Cloudy, light orange with pink tinge, overnight light brown with pink tint
		B	Colourless, to pink, overnight to mahogany-brown with pink tint
16. Terpineol	Unsaturated compound; 1 double bond and 1 tertiary alcohol group	A	Light liquid, then pinkish precipitate and orange-yellow liquid, which becomes purple-brown, finally brown with slight green tinge
		B	Colourless, to lemon colour, light pinkish brown, reddish brown
17. Limonene	Unsaturated compound; 2 double bonds	A	Creamy suspension, to brick colour; white precipitate with a brown liquid, which finally changes to purplish
		B	Greenish lemon, to mahogany-brown and finally to purplish brown
18. Carvone	Unsaturated compound; 2 double bonds and 1 ketone group	A	Lemon yellow changing to rose
		B	Lemon yellow changing to red-brown
19. Ionone	Unsaturated compound; 2 double bonds and 1 ketone group	A	Amber to wine, overnight to purple
		B	Amber to greenish amber, mahogany-brown to reddish purple

Table I (*cont.*).

Compound	Chemical nature	Reaction mixture	Results
<i>Olefine group</i>			
20. Citronellal	Unsaturated compound; 1 double bond and 1 aldehyde group	A	White flaky precipitate, to orange, to pink supernatant red-brown fluid
		B	Amber, purple amber, brownish purple to wine colour
21. Citronellol	Unsaturated compound; 1 double bond and 1 primary group	A	Yellowish suspension, cloudy brown, to brown, to orange, to red-brown
		B	Amber, purple amber, brownish purple to wine colour
22. Isoprene	Unsaturated hydrocarbon; 2 double bonds	A	Yellow at once, changing to orange and then to cherry-red liquid with brown precipitate
		B	No colour formation within first half hour, then yellow to orange, to deep red, to brown
23. Geraniol	Unsaturated compound; 2 double bonds and 1 primary alcohol group	A	Creamy coloured suspension, to orange, brown-orange, mahogany-brown
		B	Lemon, changing instantaneously to faint pink, then pink-purple, to purplish brown
24. Geranial (citral)	Unsaturated compound; 2 double bonds and 1 aldehyde group	A	Dark yellow precipitate, dark brown liquid
		B	Dark yellow, brown brick precipitate, mahogany-brown liquid changing to purple tint
25. Geranyl acetate	„	A	Golden yellow, brownish brick precipitate and mahogany-brown liquid to purple tint
		B	Greenish lemon, light green, light gray-brown with purple tint
26. Linalool	Unsaturated compound; 2 double bonds and 1 tertiary alcohol group	A	Light orange suspension, light pink, yellow-pink, brown with pink tinge
		B	Lemon, turning instantaneously to light purple-brown, purple mahogany-brown, to distinct purple-brown

standing to purple. In the presence of acetic anhydride the initial colour is amber, which changes to greenish amber, mahogany-brown and finally to reddish purple. Vogel and Stohl [1933] converted β -ionone by cyclisation with sulphuric acid into an orange-yellow powder, which gave with antimony trichloride in chloroform solution a permanent and very intense blue colour with a maximum absorption spectrum at $510m\mu$ and a large band beginning at $430m\mu$.

The following compounds yield no colour reactions: *dl*-camphor, *d*-camphoric acid, *d*-camphoric anhydride, *d*-camphorsulphonic acid and *l*-menthol. The following react very slowly and very slightly: *d*-camphor, borneol and *l*-menthone.

The terpenes that react most vigorously are the unsaturated ones and the higher the degree of unsaturation, the greater the reactivity of the compound. The presence of an aldehyde, alcohol or ketone group induces greater reactivity in the unsaturated compound. The camphane group is the least reactive and the olefine group the most reactive.

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