

CCCCXII.—*The Constituents of Oil of Supa. A New Natural Source of Copaene.*

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OIL of supa from the tree *Sindora Wallichii*, Benth, which is widely distributed over the Philippine Islands, has been examined by Clover (*Philippine J. Sci.*, 1906, **1**, 191), who found it to contain an unknown crystalline hydrocarbon and a mixture of sesquiterpenes from which a good yield of cadinene dihydrochloride was obtained.

We have now made a more complete examination of the oil, for a sample of which we are much indebted to Mr. Walter L. Brooke, Bureau of Science, Manila. The crystalline solid, which is present to the extent of a few units %, is triacontane, $C_{30}H_{62}$. From one of the fractions of the oil we have obtained a second *compound*, m. p. 172—178°; this appears to be another substance of high molecular weight, but the quantity of it so far available has not permitted a more complete examination of its properties.

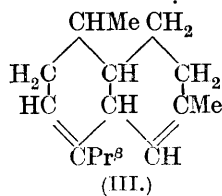
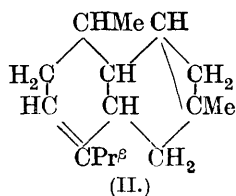
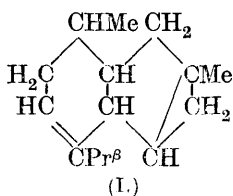
The volatile portion of the oil does not contain cadinene to any large extent, but the dihydrochloride which is obtained in good yield on treating certain fractions with hydrogen chloride is derived from a *tricyclic* sesquiterpene whose structure is evidently closely related to that of cadinene but whose physical properties differ considerably from those of pure regenerated cadinene. Deussen (*Arch. Pharm.*, 1900, **238**, 149; 1902, **240**, 288) has shown that the naturally occurring sesquiterpene in West Indian sandalwood oil which yields cadinene dihydrochloride differs in optical properties from the regenerated product. More important, however, is the work of Semmler and Stenzel (*Ber.*, 1914, **47**, 2558) on African copaiba, from which they isolated a new tricyclic sesquiterpene, *copaene*, which gave a 30% yield of cadinene dihydrochloride. The

principal fraction which we have obtained from supa oil is almost identical in its physical properties with Semmler's copaene and differs markedly from pure cadinene, as the following table shows :

	B. p./ 10 mm.	d_4^{15-20} .	n_D^{15-20} .	$[R_L]_D$.	$[\alpha]_{5461}^{18}$.
Principal fraction from supa oil	115—117°	0.9074	1.4944	65.4	-15.98°
Copaene	119—120	0.9077	1.4894	65.0	-13.35
Cadinene	130—134	0.9189	1.5097	66.4	(for D line) -125

Supa oil therefore appears to offer a new and more convenient source of copaene than African copaiba, from which the separation of the copaene is complicated by the presence of other sesquiterpenes.

The relationship of copaene to cadinene was further established by Ruzicka's dehydrogenation method. When the former compound was heated with sulphur, complete dehydrogenation occurred, and a good yield of cadalene was isolated. In view of this result, and also since copaene is readily transformed into cadinene by the action of acids, it is evident that copaene contains the dicyclic cadinene structure (III), and that the third ring must take the form of an easily ruptured bridge, probably of the sabinene type. Hence Semmler's provisional formula for copaene (I) requires revision, and (II) more probably represents the structure of this sesquiterpene.



EXPERIMENTAL.

Distillation of Supa Oil.—The oil consisted of a pale yellow, mobile liquid containing leaflets of a colourless solid, and possessed a faint but characteristic odour. After a number of fractional distillations under reduced pressure, the following fractions were isolated: (a) a colourless, mobile liquid, b. p. 115—117°/10 mm., constituting about 50% of the original sample; (b) a smaller fraction, b. p. 120—130°/10 mm., which after several distillations still boiled over a range of 10° and appeared to be a mixture; (c) a very small portion, b. p. 130—140°/10 mm. No distillate was obtained above 140°. The residue (d) when cold consisted of a brown, semi-solid mass which, however, was not resinous.

Conversion of the Copaene Fraction into Cadinene and Cadalene.—The fraction (a) after several distillations remained unaltered in

b. p. and had the physical properties recorded above ($[R_L]_D$ found, 65.4; calc. for a tricyclic sesquiterpene, 64.4; the large exaltation is consistent with the type of structure postulated by Semmler) (Found : C, 87.8; H, 11.6. $C_{15}H_{24}$ requires C, 88.2; H, 11.8%).

A solution of the fraction (a) (20 g.) in glacial acetic acid (60 g.), when gradually treated at 0° with hydrogen chloride, became greenish-blue and finally red. After saturation the solution was kept for 24 hours at 0°; the crystals then formed, after purification, melted at 118°, alone or mixed with cadinene dihydrochloride (yield, 35% of fraction a).

For comparison of this yield with that obtained from other ethereal oils, an examination was made of samples of oil of cubebes and of maracaibo copaiba. The chief sesquiterpene fraction from oil of cubebes had b. p. 130—140°/10 mm. and consisted principally of cadinene, but a small fraction was obtained, b. p. 110—120°/10 mm. This on similar treatment with hydrogen chloride yielded only 2—4% of cadinene dihydrochloride. The lowest-boiling portion of maracaibo copaiba had properties somewhat similar to those of copaene, but upon treatment with hydrogen chloride a mixture of the dihydrochlorides of cadinene and caryophyllene was obtained.

The copaene fraction (a) (9 g.) was heated with sulphur (4.5 g.) at 200—250° for 1½ hours. Hydrogen sulphide was evolved freely at the latter temperature. The product was freed from sulphur by distillation over sodium under reduced pressure, and yielded an oil, b. p. 130—160°/12 mm., which was identified as cadalene by means of its picrate, m. p. and mixed m. p. 114—115°.

The Higher-boiling and the Solid Constituents of Supa Oil.—The fraction (b), b. p. 120—130°/10 mm., was a mixture. In a solution in a large excess of acetone, a fine, white precipitate formed, which became flocculent upon agitation; it could not be satisfactorily purified by crystallisation, but was obtained in a relatively pure condition as an amorphous, white powder by repeated dissolution in anhydrous ether and precipitation by an excess of acetone; m. p. 172—178° (Found : C, 86.9; H, 10.2%).

The residue (d) was dissolved in ether, and an excess of ethyl alcohol added. The white solid that separated was difficult to free from adhering oil by crystallisation from acetone, and more than ten crystallisations were necessary before the pure substance was obtained as fine flakes with a nacreous lustre, m. p. 63—64°. The compound is readily soluble in ether and in hot alcohol and acetone, but only very slightly soluble in benzene (Found : C, 84.8; H, 14.5; *M*, in camphor, 429, 420, 421, 443. $C_{30}H_{62}$ requires C, 85.3; H, 14.7%; *M*, 422).

After removal of the solid paraffin in the manner described, the viscous liquid residue gave, on vacuum distillation, a small quantity of a viscous, slightly yellow liquid, b. p. 145—155°/10 mm., d_4^{18} 0.9484, in which the presence of a sesquiterpene alcohol is indicated (Found : C, 84.3; H, 11.5%).

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