ON THE TERPENE AND THE SESQUITERPENE OF MITSUBAZERI. PRELIMINARY REPORT.(1)

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Cryptotaenia japonica Hassk (*Umbellifer.*), domestically known as mitsubazeri, grows naturally in forests and in shady places, and is also cultivated in the kitchen-garden as one of the greens. So far as I am aware, the essential oil of this plant does not appear to have been described. The present author began its investigation in the year 1924, and is now obliged to discontinue the work for a short time. Accordingly, the results already obtained, though somewhat imperfect, are published as a preliminary report.

To isolate the essential oil, it was distilled in steam, for when the plant is digested with water, the fragrance becomes stronger. The author thus obtained 128 gr. of an oil from 1125 kilo. of fresh mitsubazeri. On fractionating repeatedly under reduced pressure, the oil separated into two fractions, one boiling at 67–68°/15 mm., and the other, at 142–143°/15 mm. The author proposes to designate the former cryptotaenene, and the latter, mitsubaene.

Whilst cryptotaenene is a terpene having the composition $C_{10}H_{16}$, mitsubaene is a sesquiterpene of the composition $C_{15}H_{24}$. These two hydrocarbons have the odour characteristic of mitsubazeri. The odour of mitsubaene is much more pronounced than that of cryptotaenene.

With the object of obtaining their crystalline derivatives, attempts were

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(1) This communication is the thesis for graduation at the Tohoku Imperial University.

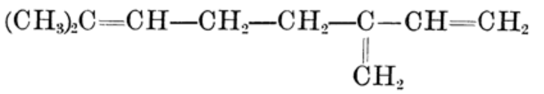
made to prepare bromide, hydrochloride, nitrosite or nitrosate, but without success. The molecular refraction points to the presence of three double bonds in cryptotaenene, together with the formation of triozonide by the action of ozone on the substance. As, however, four atoms of bromine add to one molecule of cryptotaenene, it would appear that it contains a conjugated double bond.

The cryptotaenene triozonide was first decomposed with water, as it was expected that this would throw considerable light on the constitution of cryptotaenene.

The author isolated, as its decomposition products, carbon dioxide, formic acid, acetone, acetone peroxide, succinic acid, and a carbonyl compound which has not yet been determined. Taking into account the fact that α-ketonic acid, RCOCOOH, is oxidised by hydrogen peroxide to a monocarboxylic acid, RCOOH,(1) the constitutional formula of cryptotaenene must be one of the following.

$$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH{=}CH_2 \qquad (I)$$

$$(CH_3)_2C{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \qquad (II)$$



$$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle CH_2}{\|}}{C}{-}CH{=}CH_2 \qquad (III)$$

Formula (III) is identical with that of myrcene.(2) Since cryptotaenene is quite different from myrcene in physical properties, the constitutional formula of cryptotaenene must be either (I) or (II). If this conclusion be correct, oxalic acid should be one of the decomposition products of cryptotaenene triozonide. However, its absence is accounted for by the fact that oxalic acid is decomposed by hydrogen peroxide.(3)

For the further determination of the constitutional formula, cryptotaenene was first partially reduced with hydrogen, using platinum black as the catalyser and then the product was converted into ozonide and decomposed with water. However, the quantity of decomposition products was too small to make it possible to decide between (I) and (II), owing to the small quantity of the starting substance at my disposal.

From the determination of molecular refraction and the results of the addition of bromine, mitsubaene seems to be a sesquiterpene with two double bonds. In the investigation of sesquiterpenes, Ruzicka and his collaborators(4) obtained either cadaline or eudaline by heating a sesquiterpene with sulphur. The author applied this method to mitsubaene and obtained a

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(1) *Rec. Trav. Chim.*, 23 (1904), 169.

(2) T. Brooks, "The Nonbenzenoid Hydrocarbons," p. 182.

(3) Beilstein, "Handbuch der org. Chem.," 4 Auflage, II, p. 508.

(4) *Helv. Chim. Acta.*, 4 (1921), 505; 5 (1922), 345.

liquid, which produced a picrate melting at 90°, identical with the melting point of eudaline picrate. Mitsubaene is thus a sesquiterpene of the eudesmol type. Moreover, the action of ozone on mitsubaene was investigated in order to determine its constitutional formula, and carbon dioxide and formic acid were isolated as the decomposition products of its ozonide.

The further investigation of cryptotaenene and of mitsubaene will be proceeded with as soon as a sufficient supply of the raw material is available.

Experimental.

(1) Three kilo. of fresh mitsubazeri, still edible and about 21 to 24 cm. long, was cut into 3 cm. long and distilled in steam, when the essential oil easily passed over and after 1.5–2 hours the residue had not the characteristic odour of mitsubazeri. The distillate was extracted with ether, and the ethereal solution dried over anhydrous sodium sulphate and evaporated. The quantity of residual oil amounted to 0.21 gr.

(2) Six kilo. of fresh mitsubazeri, not edible and 30 to 75 cm. long were dried for eight days in a shady place and treated in the manner described in (1), when 0.47 gr. of the essential oil was obtained.

From these experiments, it seems that the content of the oil increases with the growth of the plant.

The author obtained 128 gr. of the crude oil from 1125 kilo. of the latter sample by using the second method. On the fractional distillation of the oil under reduced pressure, the following two main fractions were collected :

(a) b.p. 65– 75° under 12–15 mm. ca. 50%
(b) b.p. 135–145° under 12–15 mm. ca. 35%

Cryptotaenene.

On repeating the fractional distillation of fraction (a) under reduced pressure, cryptotaenene was obtained as a colourless mobile oil, b. p. 67–68° under 15 mm., $d_4^{25}=0.8128$, $n_D^{25}=1.47476$, molecular refraction 47.14. $C_{10}H_{16}$, $|\overline{=}_3$ requires 46.98 (Found : C=87.75 ; H=11.78 ; Mol. wt., cryoscopic in benzene. 132, 135. $C_{10}H_{16}$ requires C=88.24 ; H=11.76% ; Mol. wt., 136). Yield : 35 gr.

Determination of the Number of Double Bonds. Addition of Bromine.—An excess of chloroform solution of bromine of known strength was added to a solution of cryptotaenene in the same solvent and, after ten minutes, potassium iodide solution and dilute sulphuric acid were added, and the liberated iodine was titrated with a N/10-sodium thiosulphate solution :

0.1682 absorbed 0.3420 of bromine.

$C_{10}H_{16}$, with two ethylenic linkings, requires 0.3750 of bromine.

Ozonide.—Through a solution of 1 gr. of cryptotaenene in 10 c.c. of chloroform, cooled with a mixture of ice and salt, a current of oxygen containing ca. 5% ozone was passed, at the velocity of 13–14 litres per hour for four hours until no more bromine was absorbed, a current of dry carbon dioxide being passed through it during the operation in order to avoid an explosion. The chloroform was distilled under reduced pressure without the application of heat, when about two grams of ozonide remained behind as a pale yellow oil with a pungent odour. The ozonide was repeatedly purified by dissolving it in a small quantity of ethyl acetate and precipitating with petroleum ether (b.p. 30–60°). The ozonide thus purified was nearly colourless, and was dried over concentrated sulphuric acid in a vacuum desiccator for two days, and then analysed with the following results (Found : C=43.36, 43.66 ; H=5.46, 6.00, $C_{10}H_{16}$, $2O_3$ requires C=42.86 ; H=5.71%).

The Decomposition of the Ozonide. The ozonide obtained from ten grams of cryptotaenene, together with four to five times its weight of water, was put into a flask provided with a reflux condenser, the latter being successively connected with two flasks, the one (A) containing 40 c.c. of cold water and the other (B), 300 c.c. of cold solution of ca. N/5 baryta solution, in order to retain any volatile and gaseous products that might be formed during the decomposition. The flask was carefully warmed over a water-bath, a slow current of hydrogen being passed through the whole apparatus.

On the addition of a solution of p-nitrophenylhydrazine in dilute hydrochloric acid to the contents of the flask (A), a p-nitrophenylhydrazone was obtained, which, after recrystallisation from benzene, melted at 148°, and produced no depression of the melting point on admixture with acetone p-nitrophenylhydrazone, thus leaving no doubt as to its identity with acetone p-nitrophenylhydrazone.

In the flask (B), barium carbonate was precipitated. After filtering off the precipitate, the excess of the baryta in the filtrate was titrated with N/2-sulphuric acid. The quantity of carbon dioxide amounted to 0.5 or 0.55 gr. in two separate experiments.

There was a deposit of a small quantity of a crystalline substance on the lower part of the reflux condenser. After drying this deposit in a desiccator, it melted at 132° and was identified as acetone peroxide by the method of mixed melting point.

The aqueous solution of the decomposition products was distilled in steam, and the distillate (C) and the residue (D) were treated as follows :

The distillate (C) was contaminated with an oily matter with a pleasant odour, which, owing to the lack of available substance, could not be determined. In order to isolate any neutral decomposition products, the distillate, after removing the oil and neutralising it with baryta solution, was again distilled in steam and subjected to fractional distillation, when the following fractions were collected: (1), b.p. below 100°; and (2), b.p. above 100°.

Fraction (1) (b.p. below 100°).—This fraction, on being mixed with a solution of p-nitrophenylhydrazine in hydrochloric acid, precipitated about one gram of a p-nitrophenylhydrazone. The p-nitrophenylhydrazone, after being recrystallised from benzene, melted at 148.5° and was identified as acetone p-nitrophenylhydrazone by the method of mixed melting point and by analysis (Found: $N=21.93$. $C_9H_{11}O_2N_3$ requires $N=21.76\%$).

Fraction (2) (b.p. above 100°).—This fraction was mixed with a solution of p-nitrophenylhydrazine in hydrochloric acid, and allowed to stand for several days, when reddish brown crystals were deposited which are soluble with difficulty in ordinary organic solvents and discoloured at about 250° without melting. The crystals have not been further investigated owing to the small amount of material available.

The barium salt remaining in the distillation flask was evaporated to dryness on the water-bath, and the residue acidified with sulphuric acid (1:3). After filtering off barium sulphate, the filtrate was distilled under ordinary pressure. The fraction distilled at below 105° which showed marked reactions of formic acid, was neutralised with solid lead carbonate, and filtered. After evaporating the filtrate to a small bulk, colourless needles (5 gr.) were obtained, which were recrystallised from hot water and analysed with the following results (Found: $Pb.=69.37$. $(HCOO)_2Pb$ requires $Pb=69.72\%$).

Formic acid was thus established as one of the decomposition products.

Products Non-volatile in a Current of Steam. The residue (D) was first extracted with ether and the ethereal solution (E) and the aqueous residue (F) were treated in the following way:

The ethereal solution (E) was shaken with a solution of sodium bicarbonate, in order to isolate any acidic substances. No neutral or acidic substance was obtained in the pure state from either the etherealor the bicarbonate solution.

The aqueous residue (F) was concentrated to a small bulk and allowed to stand, when crystals (0.8 gr.) and viscid oil (1 gr.) were obtained. The crystals were recrystallised from water with the addition of animal charcoal, when they separated as colourless crystals melting at 183° and were proved to be succinic acid by the method of mixed melting point.

Nothing definite could be isolated from the viscid oil.

Mitsubaene.

On fractionating fraction (b) repeatedly under reduced pressure, mitsubaene was obtained as a faint yellow oil, b.p. 142–143° under 15 mm., $d_4^{25}=0.9175$, $[\alpha]_D^{21.9}=+8.31$, $n_D^{25}=1.50381$, molecular refraction 65.90. $C_{15}H_{24}$, $|^{=}_{2}$ requires 66.13 (Found : C=88.07 ; H=11.83 ; Mol. wt., cryoscopic in benzene, 198, 207. $C_{15}H_{24}$ requires C=88.24 ; H=11.76% ; Mol. wt., 204). Yield : 27 gr.

Thus, mitsubaene has two ethylenic linkings, which result is in agreement with that obtained from the addition of bromine.

Addition of Bromine.—The amount of bromine to be added to mitsubaene was estimated in a manner exactly similar to that employed in the case of cryptotaenene :

0.1062 absorbed 0.1946 of bromine, whereas $C_{15}H_{24}$, with two ethylenic linkings, should require 0.1663 of bromine.

The Action of Sulphur on Mitsubaene. A mixture of 5 gr. of mitsubaene and 2.1 gr. of sulphur was heated to 180–220° in the oil-bath under a reflux condenser. After six hours' heating, the product was distilled under diminished pressure. The distillate was redistilled over metallic sodium under reduced pressure, when 0.5 gr. of oil boiling at 143–147° under 15 mm. passed over, from which a picrate was isolated by adding an alcoholic solution of picric acid. The crude picrate was twice recrystallised from alcohol, when it separated in orange crystals melting at 90°, identical with that of the eudaline picrate.

Ozonide of Mitsubaene. Through mitsubaene dissolved in ten times its volume of dry chloroform, a current of oxygen containing 5% of ozone was passed, until a solution of bromine in chloroform was no longer decolourised, care being taken to avoid the rise of temperature during the ozonisation by cooling it with ice and salt. The chloroform was evaporated under reduced pressure without the application of heat, when a yellow, viscid oil remained behind, which was purified by dissolving it in chloroform and precipitating with petroleum ether. The ozonide thus purified was dried over concentrated sulphuric acid in a vaccum desiccator for two days. As, however, the ozonide decomposed, no decisive results as to the number of double bonds were obtained by analysis.

On decomposing the ozonide by warming it with water, the author isolated carbon dioxide and formic acid.

In conclusion, the author wishes to express his gratitude to Dr. Hiroshi Nomura for his kind guidance during the progress of this investigation.

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